

Original Research

Thermal Decomposition Properties of Industrial Oily Sludge under Different Atmospheres

Shaobiao Zhang^{1,2}, Huichun Jiang³, Dayong Xu^{3*}, Lili Yang², Shufeng Xi³

¹Harbin Institute of Technology, Harbin, 150090, China

²Southern University of Science and Technology, Shenzhen, 518055, China

³Shenzhen Urban Public Safety and Technology Institute, Shenzhen, 518046, China

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Abstract

The environmentally friendly degradation of and energy recovery from oily sludge is a common concern in both research and industry. In this study, industrial oily sludge was collected after wastewater treatment by oil storage corporations. First, the physical and chemical properties of the samples were observed. Then, samples were analyzed using thermogravimetry-gas chromatography-mass spectrometry under air atmosphere and under nitrogen atmosphere. The characteristics of the residue after thermal decomposition were determined through Fourier-transform infrared spectroscopy, scanning electron microscopy, and energy dispersive spectrometry. The results revealed that the thermal degradation of oily sludge is divided into three steps under nitrogen atmosphere but four steps under air atmosphere. Moreover, thermal decomposition was mainly exothermic under nitrogen atmosphere but endothermic under air atmosphere. The mass loss of oily sludge was greater under air atmosphere. The final residue was 26.6% under an air atmosphere, which was lower than the 35.8% observed under nitrogen atmosphere. The gaseous products of oily sludge included gaseous fuels under nitrogen atmosphere but were only combustion products under air atmosphere. In both atmospheres, the solid products remaining in the residue were the metallic elements Fe, Al, Mg, Na, and Ca, which can be reused in desulfurization applications.

Keywords: oily sludge, energy recovery, waste treatment, thermal decomposition process, gaseous products

Introduction

Main text paragraph. Oil plays an indispensable role in global energy infrastructure [1]. Most cities establish large-scale oil storage tank farms to meet the rapidly growing demand for oil [2]. During the storage and transportation of oil, hazardous waste

is inevitably produced [3]. Oily sludge is a common solid waste product of oil storage tank farms that is produced both by deposition in tanks and as a byproduct of wastewater treatment [4]. According to a survey, an oil storage corporation might produce dozens of tons of oily sludge every year. Because oily sludge can contain polycyclic aromatics, heavy metals, and even radioactive material, it is a potential threat to human health and environmental safety [5].

*e-mail: xudy@szsti.org

Although oily sludge is a dangerous form of pollution, it is also a potentially recyclable energy source [6, 7]. Usually, oily sludge has high amounts of hydrocarbons and heavy metals, which can be recycled and reused [8,9]. Therefore, worldwide research into degradation treatments of and resource recovery from oily sludge has been extensive [10]. Research is ongoing into the critical problem of developing a safe, green, efficient, and economic method of degrading oily sludge.

Present degradation and recovery methods for oily sludge include centrifugal separation [11], solvent extraction [12], stabilization and solidification [13], biodegradation [14], and thermal decomposition [15]. These methods describe feasible treatments for oily sludge, but research into their mechanisms is insufficient. Among these methods, thermal decomposition primarily realizes the degradation and recovery of oily sludge by using combustion and pyrolysis [16, 17]. Chen et al. [18] investigated N/S/Cl pollutants during the pyrolysis and combustion of oily sludge by using thermogravimetry (TG)-mass spectrometry and pyrolysis-gas chromatography-mass spectrometry. Petrovsky et al. [19] briefly introduced the pyrolysis method of treating oily sludge and described the mechanism of thermal destruction of hydrocarbons in oily sludge. Tang et al. [20] used a newly developed industrial-scale reactor to analyze the pyrolysis of oily sludge and to characterize the composition of products from pyrolysis at temperatures between 450 and 600°C. Liu et al. [21] evaluated the thermal characteristics and kinetics of oily sludge, litchi peels, and their blends by using TG experiments under air atmosphere, revealing that blending inhibits devolatilization and promotes char oxidation. In contrast to combustion, when oily sludge is pyrolyzed under nitrogen atmosphere, hydrocarbons can be released and recycled. Some researchers have attempted to maximize resource recovery through the copyrolysis of oily sludge with additives such as rice husk, walnut shell, sawdust, apricot shell, and polyolefin [22-24]. Therefore, in the pursuit of maximizing resource recovery from oily sludge treatment, pyrolysis and copyrolysis offer an opportunity for technological advancement.

The aim of this study was to evaluate the effects of atmosphere on the degradation of sludge and recovery of hydrocarbons during the thermal decomposition of oil sludge. First, a TG analysis of oily sludge was performed under nitrogen atmosphere and air atmosphere. Then, a TG-Fourier-transform infrared (TG-FTIR) spectrometer was used to track the gases produced

during thermal decomposition in real time. Finally, a Fourier-transform-infrared-(FTIR) spectrometer, a scanning electron microscope (SEM), and an energy dispersive spectrometer (EDS) were used to characterize the composition and microstructure of the solid residue after thermal decomposition. In summary, this study analyzed the thermal decomposition of oily sludge over a large temperature range with a focus on degradation and resource recovery capacities under nitrogen and air atmospheres.

Material and Methods

Samples

Oily sludge was obtained from a large oil storage corporation in Dapeng County, Shenzhen City, Guangdong Province, China. The sludge was produced during wastewater treatment. The oily sludge was a dark viscous slurry without particulates. The initial composition of the sample was determined by proximate and ultimate analysis. Table 1 lists exactly the contents of moisture (M), volatile matter (V), fixed carbon (FC), ash (A), and organic elements (C, H, O, N, and S).

Because of its high moisture content, the sample was dehydrated at 80.0°C for 2.0 h in a vacuum drying oven (DZF-6050, Shanghai Jing Hong Laboratory Instrument Co, Ltd., Shanghai, China).

Experiments

Proximate and Ultimate Analysis

The moisture (M), volatile matter (V), fixed carbon (FC), and ash (A) content were determined using a muffle furnace according to the Chinese standard for the proximate analysis of coal (GB/T 212-2008). The content of organic elements (C, H, O, N, and S) was characterized using an elemental analyzer (Vario EL Cube, Elementar Analysensysteme GmbH, Langensfeld, Germany).

TG

The thermal decomposition processes of the oily sludge were performed using TG (TGA/DSC 3+, Mettler Toledo, Zurich, Switzerland). A 10.0±0.2-mg sample was spread uniformly in a 100 µL alumina crucible. The mass of the sample was measured as it was heated from 25.0 to 1000.0°C at 5.0°C·min⁻¹.

Table 1. Results of proximate and ultimate analysis of oily sludge.

Material	Proximate analysis /wt%				Ultimate analysis /wt%				
	M	V	A	FC	C	H	O	N	S
Oily sludge	34.90	13.92	8.25	77.83	2.41	6.36	44.46	0.30	0.16

In both the air and nitrogen atmosphere experiments, gas was injected at a flow rate of 50.0 mL·min⁻¹.

TG-FTIR

The TG-FTIR system comprises a TG (TGA 2, Mettler Toledo, Zurich, Switzerland) coupled with an FTIR (Tensor II, Bruker Corporation, MA, USA) through a pipe and flow cell. TG-FTIR experiments were performed at a heating rate of 5.0°C·min⁻¹ under nitrogen and air atmospheres. The real-time infrared spectra data were collected from 4000 to 400 cm⁻¹.

FTIR, SEM, and EDS

The FTIR (Vertex 80, Bruker Corporation, MA, USA) was used to analyze the functional groups of the thermal decomposition products of the oily sludge. The infrared spectra data were collected from 4000 to 400 cm⁻¹.

The SEM (Zeiss Sigma 300, Carl Zeiss, Jena, Germany) and EDS (XFlash 6, Bruker Corporation, Massachusetts, USA) were used to analyze the microstructure and composition of the char. The sample was coated with a thin layer of gold by using a sputter coater.

Results and Discussion

Thermal Decomposition Process Analysis

The TG, derivative TG (DTG), and normalized heat flow curves of oily sludge at a heating rate of 5.0°C·min⁻¹ under air and nitrogen atmospheres are compared in Figs 1-3, respectively. The critical thermodynamic parameters of onset decomposition temperature (T_0), peak decomposition temperature (T_p), inflection point temperature (T_{ip}), end decomposition temperature (T_{ed}), and residual mass (r) at different reaction stages are listed in Table 2. In both air and nitrogen atmospheres, oily sludge lost mass at the beginning of TG experiments. As the temperature increased, the thermal decomposition of oily sludge had distinct characteristics under nitrogen and air atmospheres.

When the oily sludge was heated under air atmosphere, the thermal decomposition process could be divided into four stages. The first stage occurred between 51.0 and 205.0°C, and the mass loss was approximately 14.8%. The second stage occurred between 205.0 and 454.0°C, and the mass loss was approximately 37.0%. The third stage occurred between 454.0 and 586.0°C, and the mass loss was approximately 21.6%. After reaching 586.0°C, the mass of sample remained largely unchanged, leaving a residual of 26.6% of the original mass. When the oily sludge was heated under nitrogen atmosphere, the initial thermal decomposition process was similar to that under air atmosphere. By contrast, the mass of the sample heated

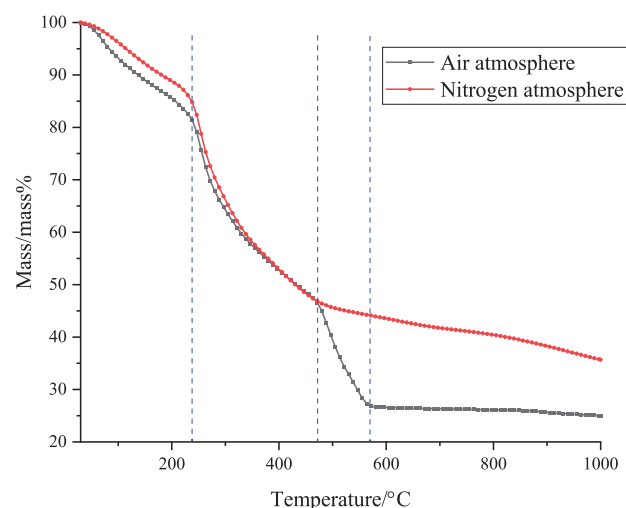


Fig. 1. TG curves of oily sludge under air and nitrogen atmospheres.

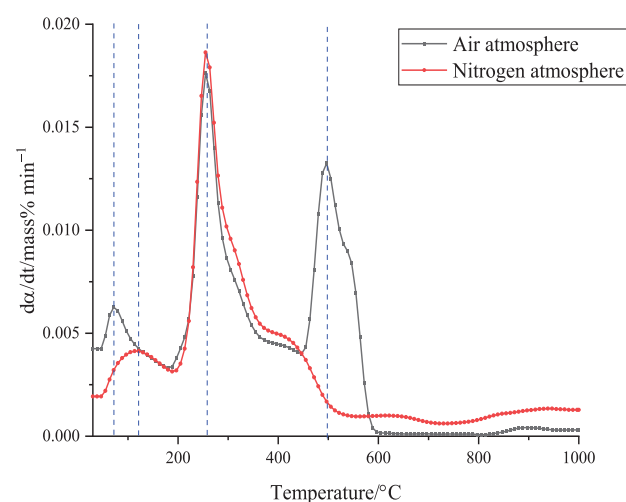


Fig. 2. DTG curves of oily sludge under air and nitrogen atmospheres.

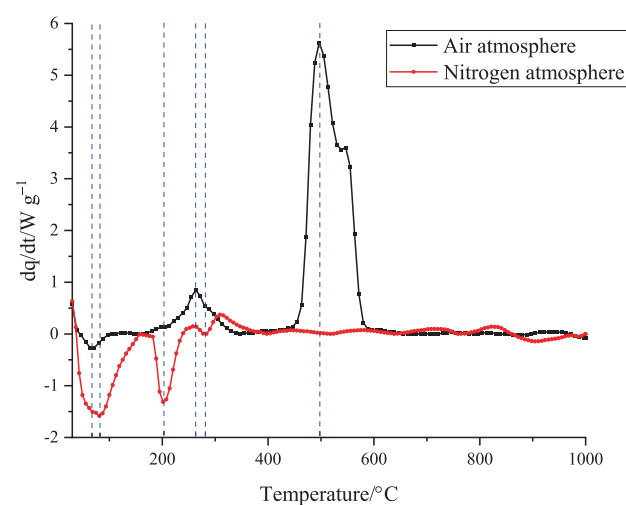


Fig. 3. Normalized heat flow of the thermal decomposition reaction of oily sludge under air and nitrogen atmospheres.

Table 2. Relevant thermodynamic parameters of oily sludge under air and nitrogen atmospheres.

Atmosphere	Stage	T_0 /°C	T_p /°C	T_{ip} /°C	T_{ed} /°C	r /mass%
Air	Stage 1	51.0	73.0	205.0	–	85.2
	Stage 2	–	258.0	454.0	–	48.2
	Stage 3	–	496.0	–	586.0	26.6
Nitrogen	Stage 1	50.0	121.0	204.0	–	88.5
	Stage 2	–	255.0	–	–	35.8

under nitrogen atmosphere continued to decrease as the temperature increased to 1000.0°C. However, the mass loss rate of the sample under nitrogen atmosphere rapidly decreased after 450.0°C. The final residue of sample under nitrogen atmosphere was 35.8% of the original mass. As can be seen in Fig. 3, regarding the heat released in the two conditions, the samples mainly produced endothermic peaks under air atmosphere but produced exothermic peaks under nitrogen atmosphere. Two exothermic peaks were detected when the sample was heated under nitrogen atmosphere. When the sample was heated under air atmosphere, one exothermic and two endothermic peaks were detected. The maximum endothermic peak occurred between 454.0 and 586.0°C.

Gas Products Analysis

The three-dimensional FTIR spectra of gas products of oily sludge under nitrogen and air are presented in Figs 4 and 5. The FTIR spectral intensity along the time axis corresponds to the thermal decomposition process as found by TG analysis [25]. According to

the thermal decomposition properties of samples, the FTIR spectra at peak temperatures under two conditions are extracted. Fig. 6 shows the FTIR spectra of gas products at 74.0, 253.0, 261.0, 497.0, and 810.0°C under air atmosphere. CO_2 and H_2O were the main gas products when the oily sludge was heated under air atmosphere. This result is consistent with hydrocarbon combustion. Fig. 7 shows the FTIR spectra of gas products at 119.0, 254.0, 259.0, and 947.0°C under nitrogen atmosphere. In comparison to Fig. 6, more functional groups are observed in Fig. 7. In particular, at 259.0°C, HCOO^- at 1180 cm^{-1} , $-\text{CH}_3$ at 1370 cm^{-1} , $-\text{CH}_2-$ at 2982 cm^{-1} , and $-\text{OH}$ at 3590 cm^{-1} are observed. These observations suggest that oily sludge can produce fuel gases when pyrolyzed under nitrogen atmosphere. Moreover, pyrolysis at the peak thermal decomposition temperature of 259.0°C achieves the maximum yield.

Solid Products Analysis

To analyze the components of solid products after thermal decomposition under different atmospheres,

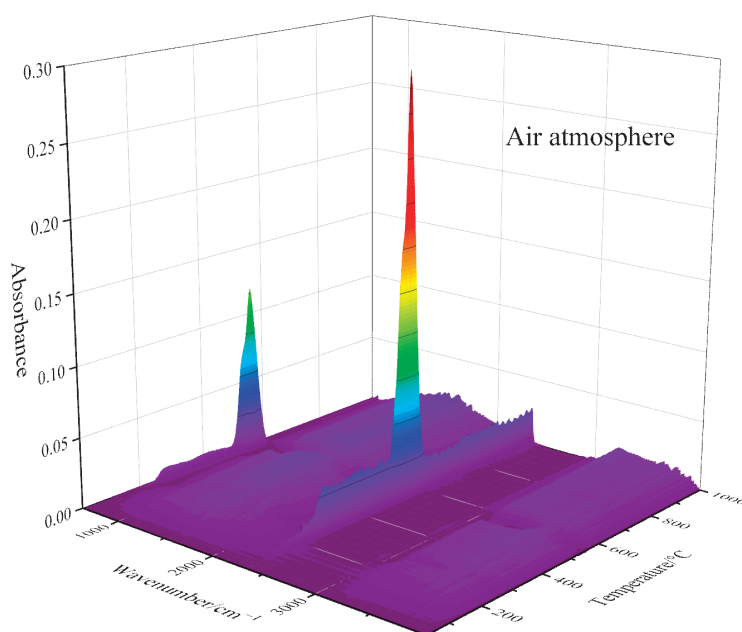


Fig. 4. Three-dimensional infrared spectra of oily sludge under air atmosphere.

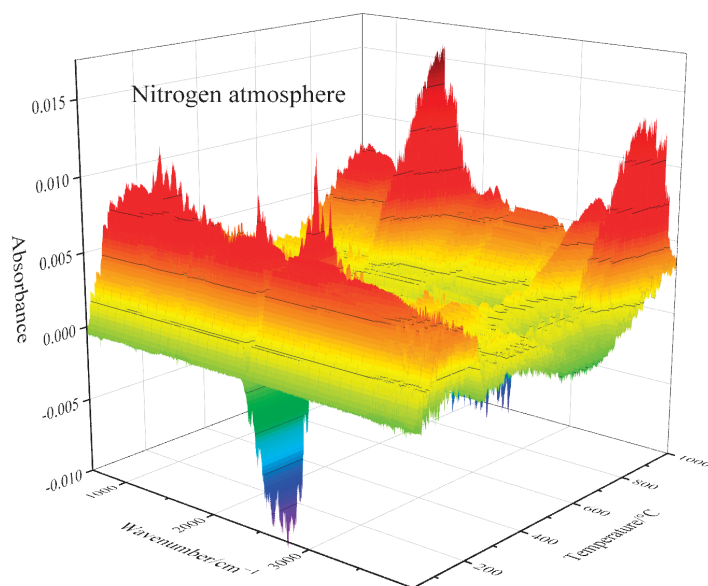


Fig. 5. Three-dimensional infrared spectra of oily sludge under nitrogen atmosphere.

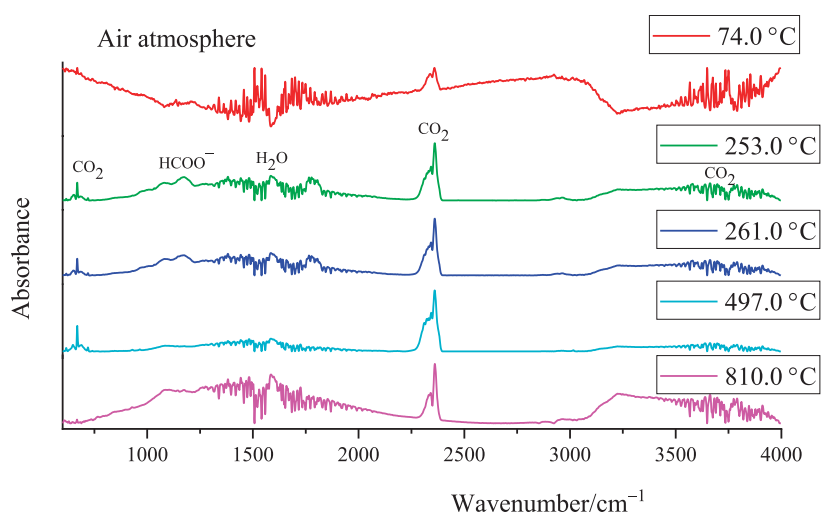


Fig. 6. Infrared spectra of oily sludge at peak temperature under air atmosphere.

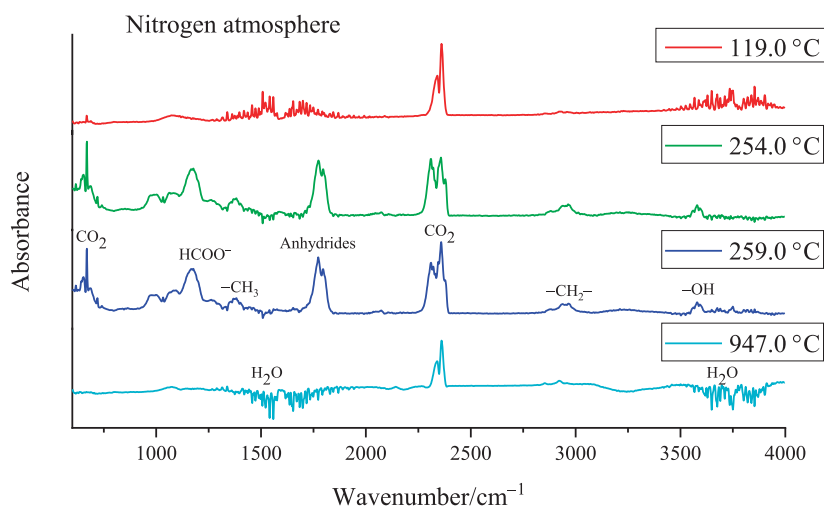


Fig. 7. Infrared spectra of oily sludge at peak temperature under nitrogen atmosphere.

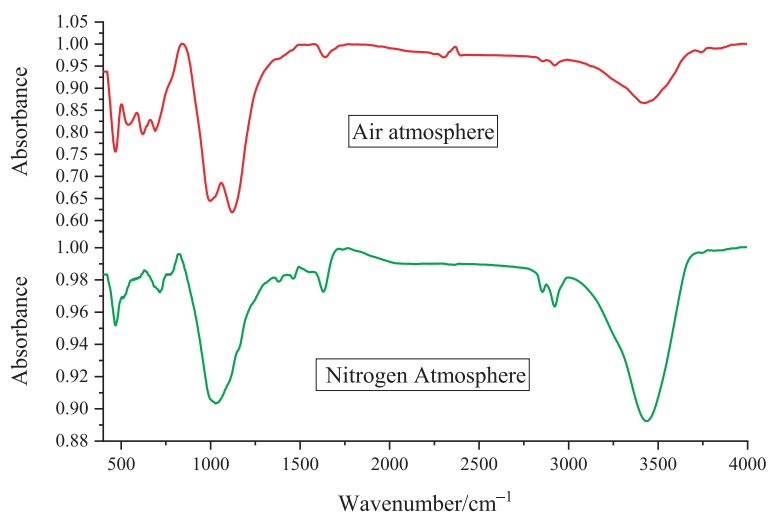


Fig. 8. Infrared spectra of oily sludge residue chars under air and nitrogen atmospheres.

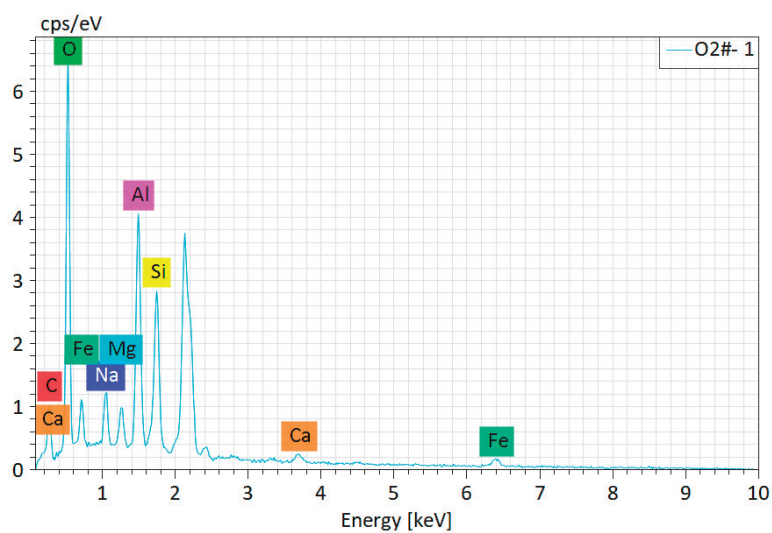


Fig. 9. Energy spectra of oily sludge residue chars under air atmosphere.

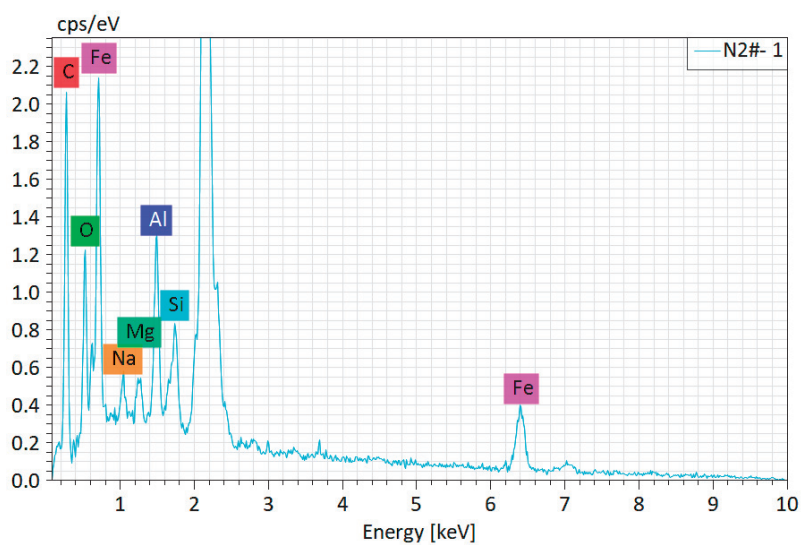


Fig. 10. Energy spectra of oily sludge residue chars under nitrogen atmosphere.

Table 3. Normalized mass fractions of oily sludge residue chars under air and nitrogen atmospheres.

Spectrum		Carbon / wt%	Oxygen / wt%	Sodium / wt%	Magnesium /wt%	Aluminium /wt%	Silicon / wt%	Calcium / wt%	Iron /wt%
Air	#1	10.33	37.82	4.18	2.51	15.27	16.04	2.40	11.44
	#2	5.43	34.14	1.67	2.67	6.80	11.02	20.00	18.27
	Mean	7.88	35.98	2.93	2.59	11.03	13.53	11.20	14.85
	Sigma	3.46	2.60	1.78	0.11	5.99	3.55	12.45	4.83
	Sigma Mean	2.45	1.84	1.26	0.08	4.24	2.51	8.80	3.42
Nitrogen	#1	22.74	6.78	1.98	1.82	6.89	5.56	0.00	54.24
	#2	30.72	12.18	2.25	1.80	7.69	8.26	17.24	19.87
	Mean	26.73	9.48	2.12	1.81	7.29	6.91	17.24	37.05
	Sigma	5.64	3.82	0.20	0.02	0.57	1.91	0.00	24.31
	Sigma Mean	3.99	2.70	0.14	0.01	0.40	1.35	0.00	17.19

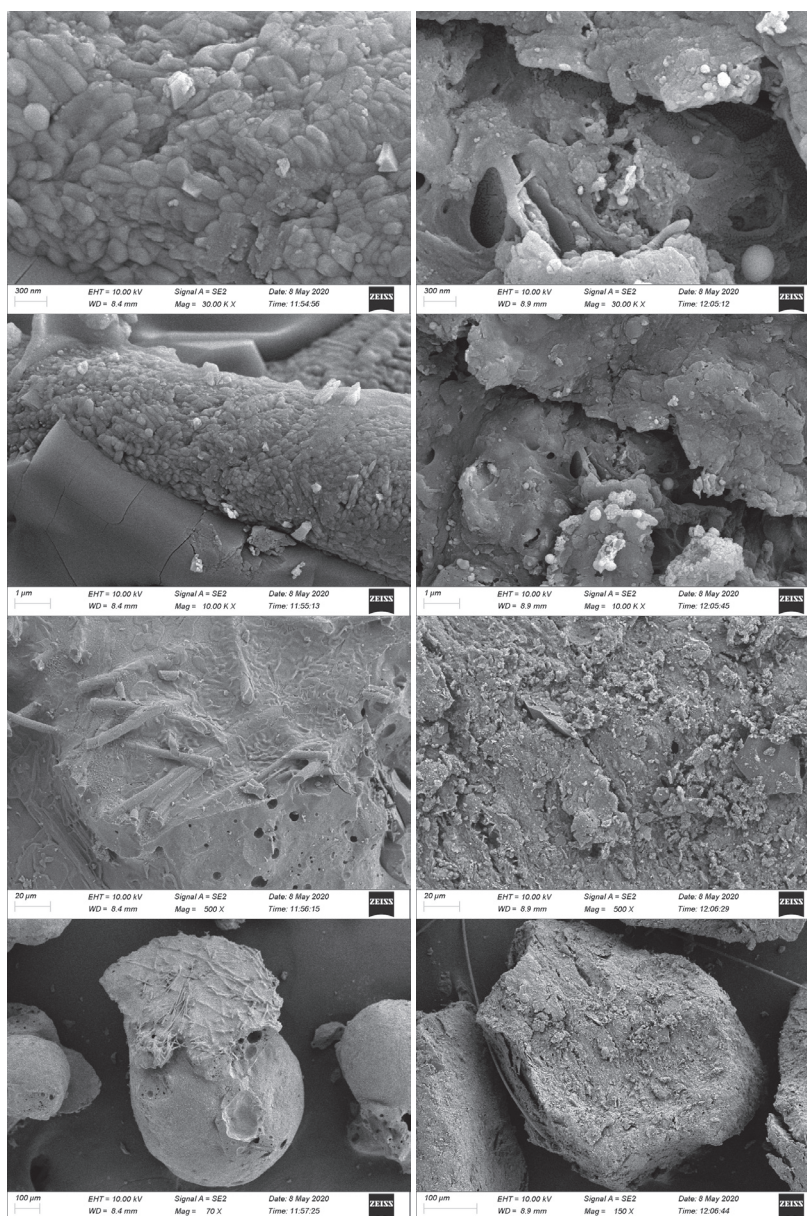


Fig. 11. SEM photographs of oily sludge residual chars under air (left side) and nitrogen (right side) atmospheres.

the microcharacterization technologies of FTIR, SEM, and EDS were separately applied in this study. First, Fig. 8 shows that the FTIR spectra of solid products of oily sludge under two atmospheres are similar. It means that the influence of air and nitrogen on the solid products of oily sludge is negligible. Then, EDS was used to quantitatively analyze the microcomponents of solid products. The Energy spectra of solid products under air and nitrogen atmospheres were drawn in Fig. 9 and Fig. 10, respectively. The Corresponding quantitative data were listed in Table 3. The EDS results show that the metallic elements were also detected in the thermal residues, including Fe, Al, Mg, Na, and Ca. In a word, the thermal decomposition of oily sludge can produce usable metals in both air and nitrogen atmosphere. Finally, the microstructures of solid products were observed using SEM and compared in Fig. 11. SEM results revealed that the residue had a porous structure and that the solid particles were more loosely arranged for samples heated under nitrogen atmosphere compared with those heated under air atmosphere. These characterized microscopic components and structures can guide the reuse of solid products of oily sludge. For example, Fe and Al can be used as active constituents of flue gas desulfurizer [26, 27]. Similarly, Mg, Ca, and Na can be used to improve the alkalinity of adsorbing materials.

Conclusions

This experimental comparative study demonstrated the effects of atmosphere on the thermal decomposition processes and products of oily sludge. First, oily sludge thermally degraded more thoroughly under air atmosphere than nitrogen atmosphere. The final thermal residue was 26.6% under air atmosphere and 35.8% under nitrogen atmosphere. Oily sludge thermally degraded exothermically under nitrogen atmosphere, and the maximum exothermic peak occurred between 454.0 and 586.0°C. Oily sludge produced fuel gases under nitrogen atmosphere but only combustion gases under air atmosphere. Comparing the microresults between the air and nitrogen atmospheres, the effects of atmosphere are smaller on the thermal residues than on the gaseous products. The thermal residues of oily sludge can be reused as a critical component of desulfurization materials. These results provide basic and essential data regarding effective treatment of and resource recovery from oily sludge.

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Conflict of Interest

The authors declare no conflict of interest.

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