Microwave pyrolysis of sludge: a review
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Abstract
As an environmentally friendly energy recovery technology, microwave pyrolysis has huge development potential in sludge resource treatment. This paper comprehensively reviews the progress of microwave pyrolysis of sludge, focusing on the mechanisms and development status of microwave pyrolysis equipment. The effects of pyrolysis temperature, heating rate, microwave absorbers, sludge properties and catalysts on microwave pyrolysis efficiency and its products are also discussed. Finally, the differentiation compared with conventional pyrolysis is summarized. It is suggested that target products can be controlled directionally by changing the pyrolysis conditions and exploring the harmful products produced in the microwave pyrolysis process. Future research directions are proposed to help the subsequent extensive application of microwave pyrolysis technology in sludge treatment.

Keywords: Microwave pyrolysis, Sludge, Pyrolysis products, Pyrolysis process, The influencing factors, Harmful products

1 Introduction
In recent decades, the amount of excess sludge discharge and oily sludge production is increasing along with the expansion of the sewage treatment industry and petrochemical industry, reaching annual outputs of 90 and 3 Mt respectively [1, 2]. Wastewater sludge contains a large number of pathogenic bacteria, trace metal elements and polycyclic aromatic hydrocarbons (PAHs), and other toxic pollutants. Besides those mentioned above, oily sludge also contains radioactive materials [3]. Sludge is highly perishable, and toxic substances limit the beneficial applications of sludge, increasing the cost of sludge treatment, which has significant environmental and health hazards. Moreover, sludge contains a high amount of organic matter, which can be treated with adequate technologies to reduce pollution and use as renewable energy [4, 5].

The common treatment technologies mainly include dewatered sludge to landfill, biological treatments and heat treatments but these technologies still have some drawbacks. For instance, solidified sludge for landfilling requires land occupation and has serious hazards to the ecological environment [6]. Biological treatments mainly use microbes and plants for remediation or use sludge composting to prepare soil amendments, such as sludge compost, anaerobic digestion, which is simple to operate and have great potential for success, but takes time and is sensitive to temperature, and also has many other factors affecting efficiency and is difficult to control [6]. Heat treatments have certain advantages for energy recovery and reducing sludge volume, including incineration, gasification, liquefaction, and pyrolysis. The first three terms can kill pathogens completely and recycle the calorific value, but other resources are not fully used. It also discharges toxic substances with environmental and health hazards, even giving rise to the problem of energy consumption. In contrast, pyrolysis is economically effective and does not generate secondary pollution, which plays an important role in solid waste reduction and energy recovery [7].

Pyrolysis is a process in which the materials are heated in an oxygen-free atmosphere, with the volatilization, dehydration, dehydrogenation and decarboxylation of organic components first, followed by the pyrolysis or catalytic pyrolysis of heavy compounds or coke which can produce pyrolysis residue (bio-char), pyrolysis oil (bio-oil) and pyrolysis gas (syngas). Pyrolysis is divided into conventional pyrolysis (CP) and microwave pyrolysis (MWP) according to heating methods [7]. The pyrolysis temperature of CP is high, which expends a
considerable amount of heat and the operation is complicated, leading to a problem of secondary energy consumption. Compared to CP, MWP has a lower pyrolysis temperature and a high energy resource utilization rate [5]. High-quality pyrolysis products can be obtained in MWP which are widely used to recover and utilize biomass and other organic wastes.

In this paper, the research progress of sludge MWP is reviewed for the pyrolysis mechanisms, the differentiation between MWP and CP, and the development status of MWP equipment. Then, the effects of the pyrolysis temperature, heating rate, microwave absorbers, sludge properties and catalysts on MWP efficiency and characterization of products are discussed. Moreover, the harmful products in MWP are analyzed. Through the review of recent literature, the understanding of MWP sludge process is deepened, and the reasonable selection of pyrolysis process parameters and treatment of harmful substances is expected to realize the recovery of directional products in MWP. Finally, the potential research directions of MWP sludge in the future are put forward to provide help for the application of MWP in sludge treatment.

2 Methods
2.1 Microwave pyrolysis mechanisms
Microwaves are high-frequency electromagnetic waves with frequencies of 300 MHz–300 GHz. 2450 MHz is one of the most commonly used frequencies in industry. The distribution of temperature and heat transfer direction of conventional electric heating and microwave heating is shown in Fig. 1 [8]. As shown in Fig. 1, conventional electric heating firstly heats the surface of materials and then the heat is transferred towards the interior of materials, whereas microwave heating starts from the interior and then transfers heat to the surface of materials.

In CP, a thick carbonization layer is formed on the surface of sludge, which is not conducive to heat transfer, resulting in high surface temperature and low internal temperature of the sludge [9]. The heat transfer and mass transfer of pyrolysis products are in opposite directions, combined with moisture content and high viscosity, it leads to high local temperature and low efficiency of pyrolysis. Contrarily, a gradually decreasing temperature gradient is formed from the inside of the materials to the outside surface in microwave heating. The released volatile matter diffuses from the inside to the external surface in the same transfer direction. Typically, the efficiency of converting electromagnetic energy to heat energy can be as high as 80–85% through the control of microwave power and effective microwave absorption of materials. Thus, compared with CP, MWP can more effectively promote the heat transfer and mass transfer of volatile products.

The interaction between microwave energy and matter can be divided into absorption, transmission, and reflection. Therefore, materials are divided into the following three types [10]:

1. Microwave absorbers: microwaves can be absorbed by these materials, leading to rapid heating of the medium.
2. Microwave-transparent materials: microwaves can pass through these materials without any loss.
3. Microwave-reflective materials, where microwaves cannot penetrate and are reflected with no or only a tiny coupling of energy.

2.2 Microwave pyrolysis equipment
2.2.1 Main equipment
At present, the industrial application of MWP technology has not been realized due to strict safety
requirements. The development and design of MWP equipment on an industrial scale has become an urgent problem that needs to be solved [11]. MWP equipment is similar to CP equipment, as shown in Fig. 2 [12], mainly including a device for carrier gas, materials conveying, microwave, temperature detection, oil/gas separation and gas collection. Among these, the most critical part is the microwave device, which consists of two main parts: the microwave generator (magnetron) and the microwave reaction chamber. The magnetron is controlled by an electronic temperature controller that turns the magnetron on and off instantaneously and controls the heating process according to the immediacy of microwave heating. The reactor is placed in the microwave reaction chamber, where materials absorb the microwave radiation and turn it into heat.

### 2.2.2 Measurement system

Measuring the various parameters accurately in the MWP process can help to analyze and optimize the operation process of MWP [13]. Temperature is an essential parameter in MWP, and the development history of high-precision temperature measurement systems is relatively long. Previously, thermocouples and infrared optical pyrometers were mainly used to measure pyrolysis temperature. Dominguez et al. [14] measured the internal temperature of biomass by using a thermocouple, and calibrated temperature with an optical pyrometer in MWP, and found that the temperature measured by the optical pyrometer represents the average pyrolysis temperature of materials as the process reaches steady-state. However, the traditional thermocouple and optical pyrometers are inconvenient to use due to the lack of automatic control. Thus, Chen [15] and Lam et al. [16] connected thermocouples to personal computers through data acquisition systems, realizing the real-time measurement of temperature. Later, Chaouki et al. [13] compared and analyzed the traditional thermocouple and optical pyrometer during the measurement process, and found differentiation between the measured temperature and the temperature of materials, which might be related to the interference between electromagnetic field and thermocouple. Therefore, in terms of improvement measures, reducing the interference between electromagnetic field and thermocouple can help to improve the accuracy of temperature measurements for one hand, trying to make the thermocouple able to measure the overall temperature of materials, which could also eliminate the temperature measurement errors.

Farag and Chaouki [17] used an air-thermometer in MWP to measure the overall temperature of materials with an uneven temperature gradient. Compared to the traditional measurement methods, the air-thermometer can reduce measurement errors and provide more accurate thermodynamic parameters for kinetic analysis of the pyrolysis process.

In addition to temperature, the weight change of materials is also an important parameter for heat and mass transfer in the kinetics analysis of MWP. The initial microwave thermo-gravimetric-analyzer (MW-TGA) was built by Farag and Chaouki [17]. The system can real-time monitor the weight of materials at different reaction stages. Farag et al. [18] further improved the MW-TGA system by connecting the reactor outlet with a product manifold, which can online measure the weight loss and the average temperature of materials at
the same time. Moreover, this system can also separate products at different times and temperatures.

2.2.3 Stirring device in microwave pyrolysis equipment
The absorbers are carbonized on the sludge surface in the MWP process due to the selectivity of microwave heating, resulting in the dielectric loss of sludge. The carbonization zone along with the temperature increases forms high-temperature hot spots instantaneously [19]. Therefore, fully mixing of microwave absorbers and materials can improve the uniformity of microwave absorption and temperature field [13]. Besides that, it is necessary to optimize the design of stirring devices in MWP equipment to improve the uniformity of materials in absorbing effective microwave radiation.

When the materials are composed of tiny particles, a modal agitator is used in the irradiation chamber to enhance the uniform distribution of microwaves emitted by the magnetron. The modal agitator is located near the outlet of the microwave generator in the exposed area. Using multi-metal blade rotation form, it can effectively enhance the uniform distribution of effective microwave radiation [13].

2.2.4 The controversies of MWP equipment
MWP is an optimized pyrolysis technology based on CP to some extent, which improves pyrolysis efficiency, but there are still some controversies about the MWP process. From the perspective of energy consumption, CP can use industrial waste heat to meet the requirements and consume low-quality energy, while MWP can only use high-quality electrical energy, resulting in high-quality energy consumption. For the temperature measuring system, since the temperature measuring requirements of MWP are higher than those of CP, it is necessary to further develop new thermometers suitable for MWP [13]. Currently, optimizing thermometers focuses on two aspects: one is optimizing size to improve the accuracy and to reduce the response time of thermometers. The other is to develop materials for manufacturing thermometers minimize the effects of microwave radiation. For the design of microwave reactors, the use of reflective materials such as metals should be avoided because the presence of metals can generate electric arcs which may damage microwave equipment. Moreover, more innovations are needed in MWP devices besides the mode stirrer to improve the uniform distribution of microwaves in the materials [13].

3 Discussion
3.1 Influencing factors of MWP
3.1.1 MWP temperature
The yield and composition of gas, liquid and solid products in MWP are closely related to the operating temperature. Solid-phase products are mainly produced at low temperature and low heating rate, whereas gas-phase products are easily produced at high temperature and have a long residence time, while liquid-phase products are easily produced at high temperature and have short residence time [16]. This is correlated with the breaking of different bonds at different temperatures. The C-H alkyl and C=O carbonyl groups are cleavable below 600 °C, but the aromatics are cleaved and reformed again at high temperatures [20]. As a result, the yield of liquid-phase products composed of aromatic hydrocarbons and aliphatic hydrocarbons can decrease, while the yield of gas-phase products can increase. In addition, there is a complex kinetic and thermodynamic coupling during the pyrolysis process. A high final pyrolysis temperature can change the phase equilibrium and increase evaporation, decreasing the residence time of pyrolysis oil to secondary reaction and the pyrolysis oil is rapidly gasified. Then liquefied into a liquid phase after leaving the high-temperature zone [21]. Therefore, the temperature is one of the most critical factors of MWP.

Temperature also has an important influence on the distribution of products. Zhang et al. [12] analyzed the distribution of MWP products and transformation of nitrogen in coke, tar and gas products at different temperatures, and showed that the temperature plays an important role in transforming nitrogen in coke, tar and gas products. The yield of biogas fraction produced at temperatures above 500 °C is higher than 10%, while the yield of tar is lower than 15%. Most volatiles are escaped in the range of 300–500 °C, and when the temperature is above 800 °C, the production of coke, tar and gas tends to stabilize. As reported by Lin et al. [22], pyrolysis oil obtained from MWP is mainly formed between 200 and 400 °C, increasing pyrolysis temperature and prolonging residence time did not improve the yield of the liquid phase significantly.

To improve the yield and quality of pyrolysis products, the temperature can be optimized and appropriate catalysts can be added to promote the formation or fracture of some functional groups. Lam et al. [23] used an activated carbon particle bed under inert conditions for the MWP of waste oil and found the optimal pyrolysis temperature to be 600 °C. At this temperature, the liquid phase products are mainly composed of light alkanes and aromatic hydrocarbons, and the recovery is nearly 75%, while the recovery of gas phase and solid phase products is the lowest. Xie et al. [20] studied the influence of temperature on the yield and composition of pyrolytic oil and found that the proportion of aliphatic group and aromatic hydrocarbon in the product is the highest at the temperature of the highest pyrolysis oil yield, while the proportion of oxygen and nitrogen compounds is the lowest.
Lin et al. [24] pyrolyzed the petrochemical industrial sludge with high moisture content by using a multi-mode microwave oven at 400–800 °C. Sludge has two pyrolysis peaks at 325–498 and 548–898 K in the entire process, and pyrolysis oil is composed mainly of aromatic hydrocarbons, with the carbon atom range of C9–C14 and calorific value range of 36.4–38.5 MJ kg\(^{-1}\). In a word, the target products with higher yields can be obtained by adjusting the pyrolysis temperature to realize the recycling of resources and reduce pollution.

### 3.1.2 Heating strategy

The heating strategy is also one of the essential parameters in MWP which can be divided into slow pyrolysis, fast pyrolysis, and flash pyrolysis [8]. Slow pyrolysis is characterized by the heating rate < 1 K s\(^{-1}\), temperature range of 550–950 K, and residence time of 450–550 s. Fast pyrolysis is characterized by the heating rate of 10–200 K s\(^{-1}\), temperature range of 850–1250 K, and residence time of 0.5–10 s. Flash pyrolysis has a heating rate > 1000 K s\(^{-1}\), temperature range of 1050–1300 K and residence time < 0.5 s [25]. Different heating strategies lead to different pyrolysis products, the main products of slow pyrolysis are pyrolysis residues, and faster heating rate is favorable for the generation of liquid and gas fractions.

The pyrolysis of organic matter in sludge only starts after water evaporates in CP, which counteracts the combined effect of pyrolysis and steam distillation, resulting in the slow rise of temperature and the extension of low-temperature pyrolysis time. However, the interaction between water evaporation and organic matter pyrolysis runs through the entire MWP process, which significantly increases the heating rate and is beneficial to increase the yield, quality, and heat value of pyrolysis oil [22]. Wan et al. [26] treated the waste shipping oil by using MWP technology, and 66 wt% pyrolysis oil, 24 wt% pyrolysis gas, and 10 wt% pyrolysis residues were obtained at a fast heating rate (40 °C min\(^{-1}\)) and temperature of 600°C. The pyrolysis oil is mainly composed of C9–C30 hydrocarbons, and the calorimetric value and energy recovery of oily sludge are significantly improved.

Although MWP can reach the same or higher temperature than CP in a short time, there are also some bottlenecks. Firstly, the heating rate control is difficult due to the influence of microwave power. Secondly, a fast heating rate can lead to the problems, such as condensation difficulty, which limits the industrial application of the technology. However, the development prospects of MWP sludge are very bright with the development of related research and MWP equipment.

### 3.1.3 Microwave absorbers

The dielectric loss of microwave absorbers becomes the only heat source when water evaporation is completed. Thus, microwave absorbers can improve the entire temperature in MWP, deepening the degree of sludge pyrolysis. However, most of the organic components in sludge are not microwave absorbers, meaning that the sludge cannot be directly heated to the temperature required for pyrolysis. Therefore, mixing sludge with microwave absorbers can rapidly achieve the desired pyrolysis temperature. The common microwave absorbers include graphite, SiC, activated carbon, carbon fiber, pyrolysis residues, and biomass char. The selection of microwave absorbers should follow the following principles: low economic costs; no pollution to the products; and no toxic substances produced [27].

Graphite and carbon as microwave absorbers can increase the yield of syngas (H\(_2\) + CO). Dominguez et al. [28] conducted related experimental analysis. Using carbon as an absorber can increase the yield of syngas by 66%, while using graphite as an absorber can significantly increase the hydrocarbon content of gas products. Regarding the energy absorption efficiency of SiC, pyrolysis residues and graphite as microwave absorbers, the energy recovery efficiency of SiC is higher than that of graphite and pyrolysis residues [29]. Although SiC can better achieve sludge reduction and resource recovery, but the cost of SiC is high, and the harmful gas and dust pollution emitted by SiC residues into the environment cannot be ignored. According to economic analysis, mixing original sludge with its pyrolysis residues can reach a high temperature of pyrolysis, which could reduce the volume of sludge by more than 80% and can obtain alkaline porous carbonaceous residues, combustible gases and liquids, which provide a good choice for reducing resource consumption [29].

The methane conversion rates of adding pyrolysis residues and activated carbon under different pyrolysis conditions are different. Activated carbon has a larger specific surface area in CP, which has better catalytic activity than pyrolysis residues. Under the conditions of MWP, the methane conversion rate of pyrolysis residues as absorbers is significantly higher than that of activated carbon. The solid residues produced melted beads after pyrolysis due to the “microwave plasma” generated in MWP, which causes Si/Al and other materials in the residues to melt, and then pass through the metal-microwave interaction to promote pyrolysis [30].

The amount of absorbers can influence the MWP process. The basic characteristics of the formation rate of liquid/gas phase products remain unchanged, but the recovery rate of pyrolysis oil firstly increases and then decreases. As the amount of absorbers increases, the heating rate of oily sludge and the yield of products
and dehydrogenate, resulting in a higher H₂ yield [32]. The heat of the heating process cannot satisfy the complete pyrolysis when the amount of GAC is too small. And excessive addition can cause serious coking, both of which lead to a decline in yield and quality of pyrolysis oil.

For now, the co-pyrolysis of sludge and another biomass has become the current research focus [31]. Blending several biomass feedstocks can deepen the co-pyrolysis reaction, increasing the calorific value of pyrolysis products, and reducing the content of inorganic and toxic substances, which has an extensive application prospect. Although related literature confirmed that pyrolysis residues and other microwave absorbers join pyrolysis, but until now, it is still unclear how they can absorb microwave energy and need to further deepen the pyrolysis mechanisms.

3.1.4 Sludge properties

The sludge properties are key factors affecting the dielectric properties of sludge, such as moisture content, oil content and particle size, which are crucial to the entire pyrolysis process [5, 27]. Therefore, it is necessary to discuss the different properties of sludge.

3.1.4.1 Moisture content

The moisture in sludge is an excellent absorber, the rapid changes in the electric field of microwave radiation cause the dipole to rotate, leading to its dielectric loss factor increasing with the increase of microwave frequency. The moisture content of most of the sludge is as high as 80%, which significantly affects the dielectric property of sludge and the penetration depth of microwaves, thereby increasing the pyrolysis efficiency [27].

Moisture is beneficial to the formation of gas-phase products and has a certain effect on oil composition, reducing the yield of coke. The high-frequency electromagnetic energy of microwave radiation directly acts on chemical bonds, which are more likely to vibrate, break and dehydrogenate, resulting in a higher H₂ yield [32].

Moisture contributes to the generation of hydrogen and produces a steam-rich atmosphere at high pyrolysis temperatures, which intensifies the endothermic reaction with the pyrolysis steam [7], leading to the reaction between water vapor and methane increasing with the increase of moisture content, and more CH₄ is converted into CO and H₂.

For energy analysis, Capodaglio et al. [33] used the monomodal microwave oven to pyrolysis wastewater sludge, and evaluated the energy by comparing the recovery rate of pyrolysis oil, indicating that the recoverable energy in pyrolysis oil is greater than the energy consumed in the actual pyrolysis process. As there is no process standardization for MWP at present, Table 1 summarizes the product yields of MWP sludge under different moisture content and operating conditions in different literature. The recovery rate of pyrolysis oil under different processes is determined, which is helpful to analyze the energy balance in the pyrolysis process.

Compared with CP technology, MWP technology can integrate drying, dehydration, and pyrolysis with a higher heating rate and shorter sludge pyrolysis time for sludge with high moisture content. However, the excessively high moisture content may lead to the mixing of water fractions in pyrolysis oil, reducing the quality of pyrolysis oil [8].

3.1.4.2 Oil content

Oily sludge has highly toxic and carcinogenic effects and is very dangerous with a high recovery value and oil content of 10–50% [2]. However, oil is non-polar and negatively affects the uniform heating of the sludge in MWP. The high oil content leads to the slow heating rate of sludge and increases energy consumption. Therefore, microwave absorbers should be added to improve the efficiency of MWP and reduce energy consumption, and its pyrolysis products have better quality and higher value [16]. Chen [15] used MWP to treat sludge from crude oil storage tanks with GAC, and mass fractions of carbon and hydrogen in pyrolysis oil are 67.6–72.1 and 10.4–14.2% respectively. The calorific value of pyrolysis oil is approximately 33.2–36.8 MJ kg⁻¹, which can be used as boiler fuel or raw materials for gasoline and diesel oil production.

Liu et al. [37] conducted MWP of oily sludge and obtained pyrolysis yields of 9.3 wt% (syngas), 85.9 wt% (pyrolysis oil) and 4.7 wt% (biochar). For the energy input and output, the yield of total chemical energy recovery is 80% and the yield of energy loss is 20%. For large-scale MWP, energy efficiency can be improved. Through the above yield of energy recovery and products, Table 2 summarizes the pyrolysis products obtained by MWP of sludge with different oil content for energy analysis under different pyrolysis conditions. Due to the differences in sludge composition, MWP equipment and pyrolysis operating conditions, the composition and yield of pyrolysis products are different, and some pyrolysis efficiency indices are expressed as oil removal efficiency. In conclusion, it can be seen from Table 2 that a part of the yield of pyrolysis oil is relatively high, which fully indicates that MWP of sludge with high oil content is technically feasible. However, despite its broad application prospects, there are still few studies on the application of MWP technology in the treatment of oily sludge, and the recovery and utilization of pyrolysis oil require safety testing.

3.1.4.3 Sludge particle size

The sludge particle size is also an important factor in the pyrolysis process, which can affect the intensity and distribution of the
microwave field, thus affecting the microwave absorption efficiency of sludge [27].

The effects of sludge particle size on MWP are mainly as follows: (1) the heating rate of sludge particles and the volatile precipitation rate; (2) the heat and mass transfer rate; and (3) the contact area between the gas/solid phase and the catalysis between the gas/solid phases [14]. Basically, the specific surface area of sludge increases with the decrease of sludge particle size, which promotes the catalysis of the solid phase and increases the gaseous phase products [14]. At present, there are few pieces of research on the effects of sludge particle size in MWP and its mechanisms of action, and it is urgent to carry out relevant research.

### 3.1.5 Catalysts

Apart from the above factors, adding an appropriate amount of catalyst in MWP could effectively reduce the activation energy of pyrolysis reaction and the temperature required by the reaction, which provides a
possibility for MWP technology in the application of sludge recycling [35]. Adding catalysts to the pyrolysis process could improve the yield and quality of pyrolysis gas, and directional production can be realized. However, the residence time of pyrolysis steam through the catalyst increases, which easily leads to the pyrolysis and carbonization of volatile compounds, thus reducing the yield of pyrolysis oil. For pyrolysis residues, using the catalysts can improve the yield of pyrolysis residues [20].

The commonly used catalysts are mainly zeolite catalysts (ZSM-5, HZSM-5) and metal oxide catalysts (CaO, Fe$_2$O$_3$), etc. The yield of pyrolysis oil is reduced by using ZSM-5 as a catalyst in the MWP of sludge. Due to the high selectivity of ZSM-5 to aromatics, the quality of pyrolysis oil is improved [34]. As reported by Xie et al. [20], HZSM-5 catalyst has high stability in the process of microwave-assisted pyrolysis of sludge, and report the effects of pyrolysis temperature and catalyst ratio on the product distribution and composition of pyrolysis oil. When CaO and Fe$_2$O$_3$ as catalysts, CaO is conducive to acquiring pyrolysis gas in the MWP process, while Fe$_2$O$_3$ is better for pyrolysis oil. Moreover, the catalyst is affected by pyrolysis temperature in the MWP. The quality of pyrolysis oil catalyzed by CaO has the best quality at 800 °C, and CaO can directionally catalyze the production of large amounts of H$_2$. However, Fe$_2$O$_3$ catalyzes the production of large amounts of CH$_4$ at 900 °C [35].

Due to the rapid rise of temperature and short pyrolysis process of materials during the MWP, the deactivation of catalysts caused by sintering and coking at high pyrolysis temperature may occur. Therefore, the

| Sludge source | Composition | Pyrolysis conditions/ carrier gas | Pyrolysis temperature (°C) | Catalyst/ microwave absorbers | Pyrolysis carbon yield (wt%) | Pyrolysis oil yield (wt%) | Pyrolysis gas yield (wt%) | Ref. |
|---------------|-------------|---------------------------------|-----------------------------|-------------------------------|-----------------------------|----------------------------|---------------------------|------|
| Oily sludge in the crude oil storage tank of a petroleum refinery plant | Moisture: 28.67 wt%; Sludge combustibles: 68.85 wt%; Ash: 2.48 wt%; Oil: 45.21 wt%; | N$_2$; 890$^b$ | | | 32.3–8.3–14.9$^d$ | 56.3–77.5–68.6$^d$ | 11.4–Not reported–16.5$^d$ | [15] |
| Waste automotive engine oil in an MG-ZT diesel car | Containing the harmful substances such as soot and PAHs, as well as additive impurities such as chlorinated paraffins and polychlorinated biphenyls. | N$_2$; 400 | | Particulate carbon | 67 | 8 | 25 | [16] |
| Oily sludge in Shengli Oil Field | Moisture$: 5.88$ wt%; TPH$: 95300 mg kg$^{-1}$; C$: 10.54$ wt%; N$: 0.14 wt%; H$: 1.58$ wt%; S$: 0.20$ wt%; | 300 | Multimode-microwave oven; N$_2$; | | | | | [19] |
| Waste shipping oil in the diesel engine of fishing boats | Containing metal particles, soot and other scum, and high concentrations of potentially hazardous compounds (such as PAHs, metals and soot) | 1 kW microwave oven; N$_2$; | 400 | 20 wt% Activated carbon | 59 | 20 | 21 | [26] |
| Oily sewage generated during crude oil extraction on the Bohai Sea oil production platform, China. | Moisture$: 31.03$ wt%; Volatile: 65.86 wt%; Ash: 1.67 wt%; | 500 | Monomodal microwave oven; N$_2$; | | | | | [37] |
| Soil contaminated with heavy furnace oil (HFO Grade IV) | Moisture$: 4.9$ wt%; TPH$: 40–110 g kg$^{-1}$; pH: 6.83; | Domestic microwave oven; He; | | | 2.5 wt% Spent graphite | 41.3$^a$ | | [38] |

$^a$Dry base
$^b$Maximum quantity
$^c$Optimal amount
$^d$Process temperature value or addition amount. Indicating the temperature range of the pyrolysis process or the added amount, and corresponds to the range of the pyrolysis product yield
$^e$Oil removal efficiency
$^f$Oil recovery efficiency
$^g$Total Petroleum Hydrocarbon
3.2 Harmful products during MWP of sludge

Compared with CP, MWP sludge produces less harmful substances, but there are still harmful components produced, which impact the environment. Therefore, this section will analyze the harmful products produced in the process of sludge treatment by MWP technology.

3.2.1 Harmful gas products

The content of organic components in sludge residues gradually decreases with the increase of MWP temperature, such as C, H, O and N. These elements generate H₂, CH₄ and CO and some oily products containing nitrogen or oxygen [29]. CO₂ generated by MWP can be self-volatilized with sludge residues, which leads to the concentrations of CO₂ and CH₄ in MWP gas products to 50 and 70% lower than that in CP gas products, respectively [39]. For the following reasons, except for electromagnetic energy acting on chemical bonds, the higher the temperature of MWP is, the more it is conducive to the water/gas conversion reaction and the cracking of long-chain alkanes. The presence of water vapor promotes the steam reforming reaction of volatile substances and the partial gasification of solid carbon-containing substances, leading to increased CO production with the increase of temperature [40]. Meanwhile, methane reforming is caused by the heterogeneous reaction between solid residues and volatile substances assisted by microwave, which can explain the decrease of CO₂ and CH₄ content and the increase of H₂ and CO production in the gas obtained from MWP [32]. MWP process dramatically reduces the production of H₂S at the same time [14, 15]. Figure 3 shows the production pathway of H₂S in MWP and CP processes. The first three pathways exist in both pyrolysis, while the fourth pathway only exists in CP. It can be seen from Fig. 3 that the production pathway of H₂S in the pyrolysis process is as follows [41]:

1. The unstable mercaptan structure in sludge decomposes to H₂S when the temperature is lower than 300 °C. (2) The unstable aliphatic-S compounds in tar decompose to H₂S at 300–500 °C. (3) Aromatic-S compounds in tar decompose to H₂S at 500–800 °C. (4) The stable thiophene-S compounds decompose to H₂S at 700–800 °C in CP.

The decomposition of aromatic-S and thiophen-S compounds resulted in a significant increase in the yield of H₂S in CP. However, CaO in coke is promoted to react with H₂S due to its unique heating characteristics and short residence time in MWP, and secondary cracking of thiophen-S compounds is inhibited, significantly reducing the generation of H₂S [41]. The higher pyrolysis temperature of MWP also promotes the conversion of sulfur into inorganic sulfur with higher stability in pyrolysis carbon. Moreover, microwave reduces the specific surface area of biochar, which is also conducive to solidifying the sulfur elements in sludge [29].

![Fig. 3 Sulfur transformations in the pyrolysis processes [41]](image-url)
In conclusion, MWP technology reduces the emission of carbon dioxide and hydrogen sulfide, increases the calorific value of pyrolysis gas, and reduces the harm to the environment.

### 3.2.2 PAHs

PAHs have anti-biodegradability and carcinogenicity, while liquid phase products produced by CP sludge contain a large number of PAHs, which are mainly formed by the following two ways [32, 42, 43]:

1. **Diels-Alder reaction** for the formation of PAHs. While alkanes generate olefins and dienes under dehydrogenation reactions, and cyclization and subsequent aromatization generate aromatic compounds during pyrolysis to form PAHs, Microwaves can enhance the Diels-Alder reaction to cyclize single alkenes and conjugated dienes (including their derivatives) at higher temperatures to form more cyclohexene and its derivatives [32, 42]. Its mechanisms are shown in the Fig. 4. (2) In secondary pyrolysis reaction, light aromatic hydrocarbons are condensed with acetylene to form a small amount of PAHs in the gas phase.

2. **Cracking** and **dehydrogenation** in MWP can reduce high molecular weight PAHs and improve synthesis gas quality, resulting in a lower PAH content in gas-phase products. In terms of the types of PAHs contained in solid residues, Lin et al. [44] measured about 26 PAHs in MWP residues, including 16 PAHs and 10 nitro-PAHs. When the pyrolysis temperature is 800 °C, 2–3 rings of naphthalene, phenanthrene and anthracene are the main PAHs, whose content has been significantly reduced. The content of 5–6 rings of benzo(a) pyrene, indeno (1,2,3-cd) pyrene and dibenzo(a,h) anthracene is the lowest. As reported by Xu et al. [45], the residues hardly contain over 4-

![Fig. 4 Diels–Alder reaction for the formation of polycyclic aromatic hydrocarbons [42]](image-url)
rings PAHs after high-temperature pyrolysis. MWP can produce less PAHs than CP by selecting appropriate pyrolysis parameters to reduce the risk of toxicity.

3.2.3 Heavy metal ions in solid and liquid phases
MWP residues have significant immobilization effects on heavy metal ions, significantly reducing the number of dissolved heavy metals. The mechanisms of immobilization of heavy metals are that the carbon obtained from MWP has small pores by selecting appropriate pyrolysis temperature, and can make residues appear glassy and improve the fixation efficiency of heavy metals, which reduces the leaching capacity of organic matter and heavy metals.

In the pyrolysis process, the mechanisms of metal migration are as follows [1]: weak acid extraction of metal state due to dehydration consolidation function decomposition, gradually transformed into oxidation state or state residue. As the pyrolysis temperature rises, vitreous residual lattices damage and speed up the release of heavy metals, leading to cut down the content of the heavy metal residue state. Meanwhile, some of the organic matter escapes under the high-temperature and heavy metal residue state is released into the environment, part of the particle adsorption, the rest reacts to form a reducible state. Thus, a highly alkali environment is formed in MWP, resulting in the formation of a large number of particles containing metal elements on the surface, which contributes to the stability of heavy metals [1, 46]. A schematic diagram of metal migration in the pyrolysis process is shown in Fig. 5.

In addition, after pyrolysis of sludge at high temperatures, some vitrification pyrolysis residues can be obtained. Figure 6 shows the SEM diagram of the residues obtained after CP and MWP of sludge. It can be seen that different from the porous texture of the residues generated by CP, the solid residues of MWP are glassy, and the heavy metals remaining in the residues can be embedded in the glassy residues tightly [39].

For liquid-phase products, Lam et al. [23] performed oily sludge in MWP and found that the content of heavy metal ions in pyrolysis oil is significantly reduced, the Cd and Cr decreased by 46 and 32% respectively, and the total content of Cu, Ni, Pb, Zn and Fe decreased by 93–97%. There are three possible reasons for the decrease of heavy metal ion content in the pyrolysis oil obtained by MWP technology [13]:

1. Microwaves produce local hot spots, which weaken the bonding force between metal and four different nitrogen atom rings in the porphyrin ring, and promote the release of metal ions from the pyrolysis oil to solid residues.
2. In pyrolysis oil, heavy metal ions exist in the form of polar salts, significantly enhancing heavy metal removal ability.
3. The difference in dielectric properties and magnetic properties of the absorbers improves the selectivity of removing heavy metal ions from the pyrolysis oil and the yield of the pyrolysis oil is not affected.

In conclusion, the content of heavy metals in pyrolysis oil is effectively reduced after the treatment of sludge by MWP, which indicates that the microwave radiation and the addition of absorbers have essential effects on the solidification of heavy metals in pyrolysis residues. However, more details such as the interaction of complex components and the immobilization of free heavy metal ions in the MWP process have not been clarified, and the treatment mode of pyrolytic carbon after heavy metal enrichment and the migration behavior of heavy metals in pyrolysis gas products also need to be further studied.

3.3 Summaries of MWP
3.3.1 Differentiation between CP and MWP
At present, the MWP industry has broad prospects. In general, due to the unique method of microwave.
heating, there are many differences in the heating mode of materials, process equipment, influencing factors of the pyrolysis process and pyrolysis products. The organic components of raw materials absorb microwave energy in MWP, which destroys the branches and part of the main skeleton of organic macromolecules to form free radical carbon chains. These small molecular fragments recombine to form condensable products, such as aromatics, aliphatic hydrocarbons, and some non-condensable products. These products escape from pyrolysis residues in the form of volatile compounds and are discharged from the pyrolysis system via carrier gas [47]. The high efficiency of microwave heating can inhibit the secondary reaction in the solid phase and improve the quality of pyrolysis oil and pyrolysis gas. This section also sorts out the differentiation between CP and MWP, as shown in Table 3.

### 3.3.2 Products recyclability of MWP

In the form of microwave heating, the controllability and immediacy of the MWP temperature are conducive to the fixation of the enriched metals in the carbon-containing matrix, thus reducing the possibility of release into the food chain in the soil [48]. Biochar can be used as the microwave absorber for product recycling to participating in in-situ pyrolysis. Moreover, it also has been shown to have a variety of uses, such as solid fuels, soil conditioner and flue gas purification applications, construction materials or contaminated site remediation. The obtained pyrolytic oil can replace some fossil fuels, and be used to produce energy and chemicals, or be used as a substitute for asphalt [5]. However, the assessment of risk characteristics of pyrolysis oil must be carried out systematically for safety use [49]. Microwaves can promote heterogeneous catalytic reactions by

| Table 3 | The differentiation between conventional pyrolysis and microwave pyrolysis |
|---------|--------------------------------------------------------------------------------|
| **Differentiation** | **Conventional pyrolysis (CP)** | **Microwave pyrolysis (MWP)** | **Ref.** |
| Heating mode | Conventional heat source heating | Microwave heating | [7, 8] |
| Energy conversion | Chemical energy, electrical energy, etc., into heat energy | Electromagnetic energy into heat energy | [10] |
| Heating path | Superficial heating via conduction, convection, and radiation | In-core volumetric and uniform heating at molecular level | [8] |
| Heating characteristics | Nonuniformity, tardy | Selectivity, immediacy, uniformity, high efficiency | [9, 19, 27] |
| Pyrolysis process | Slower, longer time | Faster, shorter time | [8, 16] |
| Main influencing factors | Pyrolysis temperature, heating rate, catalyst | Pyrolysis temperature, heating rate, microwave absorbers, sludge properties | [12, 21, 23, 24] |
| Pyrolytic products | Pyrolysis residues, pyrolysis oil, pyrolysis gas | Pyrolysis residues, pyrolysis oil, pyrolysis gas, the quality of pyrolysis oil/gas is better | [26] |
| Harmful products | Relatively more, strong carcinogenic character | Relatively few, little carcinogenic character | [32, 39, 41–43] |
| Energy output rate | Relatively low utilization rate | Relatively high utilization rate | [37] |
interacting with biochar to generate microplasmas and hot spots, which helps to increase the content of syngas in biogas to replace biogas [47].

4 Conclusions
The research on microwave pyrolysis sludge mainly focuses on the differentiation between MWP and CP and optimizing the microwave pyrolysis process, while there are relatively few studies on the mechanisms of microwave pyrolysis, energy conversion, heat and mass transfer, and other issues. Although the pyrolysis conditions (pyrolysis temperature, heating strategy, microwave absorbers, sludge properties, catalysts etc.) can achieve the directional control of the pyrolysis target products, due to the complex composition of sludge, the influencing mechanisms and regulation mechanisms of various pyrolysis factors have not been clearly defined, and there are also disputes on the input of high-grade electric energy for microwave pyrolysis. At present, there are two trends in the development direction of microwave pyrolysis sludge: one is the safety assessment of microwave pyrolysis products to improve the recycling of sludge disposal; the other is the energy analysis of microwave pyrolysis technology to achieve the purpose of reducing energy consumption and saving resources. Therefore, subsequent studies on microwave pyrolysis sludge can be carried out from the following aspects:

(1) The mechanisms of microwave absorbers and the in-situ participation of pyrolysis residues in the pyrolysis process. (2) The content and migration of heavy metals in pyrolysis oil and pyrolysis gas to enhance the safety of oil and gas products. (3) The kinetic equation of microwave pyrolysis sludge should be established to solve the energy efficiency ratio under different operating conditions to provide basic data for the process optimization of microwave pyrolysis sludge. (4) The preparation of microwave absorbing catalysts with good wave absorbing performances and high catalytic activities. (5) The design of large microwave pyrolysis reactors and the application of microwave pyrolysis sludge processes.

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Declarations

Competing interests
The authors declare they have no competing interests. And all authors declare no financial and personal relationships with other people or organizations that can inappropriately influence this manuscript, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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