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# The impact of nano-additives on the properties of sludge microwave pyrolysis products

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## ABSTRACT

The annual output of refinery waste sludge is huge in our country, and the resource disposal of sludge has become a difficult problem that needs to be overcome. In order to increase the content of renewable gas and light oil after pyrolysis of oil sludge at the bottom of refinery tank, nano-CuO and nano-γ-$Al_2O_3$ with good wave-absorbing property and good catalytic property were selected to study the effect of additive load on the characteristics of pyrolysis reaction products by experimental research and analysis. The results show that the highest oil and gas yields can be obtained when the nano-CuO content is 10%. When nano-γ-$Al_2O_3$ was loaded at 15%, the pyrolysis oil and pyrolysis gas yield reached the peak. Moreover, the light component of pyrolysis oil can be improved, and the proportion of gasoline and diesel ($C_4 \sim C_{12}$, $C_{13} \sim C_{18}$) is 75.422%. $H_2$ volume content reaches the highest at 15% load.

**Keywords:** oily sludge; microwave pyrolysis; microwave absorbent.

## 1. INTRODUCTION

In the current era of social progress, the paramount concern of environmental preservation has garnered escalating global attention. Thus, the task of safeguarding the existing ecological system and utilizing available technologies to address environmental pollution and resource recycling has become a major challenge for all countries [1]. Although oil, a non-renewable energy source, plays a critical role in accelerating economic development and is a vital component of our daily lives, it generates solid waste during extraction, transportation, and refining, which contains a complex composition of numerous toxic substances known as oily sludge. China's annual production of oily sludge is more than 5 million tons [2], and laws and regulations have been established to govern the disposal of oily sludge [3].

Several methods for disposing of oily sludge are available, such as solvent extraction, surfactant, freeze-thaw, and mechanical separation methods [4]. However, each of these methods has its drawbacks. For instance, the solvent extraction method has high solvent loss, easy to cause secondary pollution, requires more processing equipment, too many processing processes, more complex processing technology, and high investment cost. Chemical surfactants can be toxic and pose a threat to the environment, while biological surfactants are costly and challenging to obtain. Similarly, the freeze-thaw method exhibits low efficiency and consumes a considerable amount of energy during the freezing process. Moreover, the mechanical separation method is costly to acquire and maintain, besides generating noise pollution, which necessitates noise reduction processing. The treatment effect is affected by the sludge source, the tempering process of demulsifier and surfactant not only increases the cost of treatment, but also brings environmental pollution problems.

In contrast, the pyrolysis method emerges as a promising technology. Pyrolysis is a versatile process with applications spanning various industries, including refining and petrochemicals for breaking down crude oil, biomass energy for converting organic materials into carbon, biofuels, and biochar, waste management for transforming organic waste into energy and valuable chemicals, plastic recycling for re-manufacturing plastic products, material synthesis for producing advanced materials, environmental pollution control by treating hazardous waste, e-waste management for resource recovery, and food processing to enhance flavor and preserve nutrition.

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In summary, pyrolysis methods serve as a versatile tool across diverse industries, fostering improved efficiency and environmental stewardship in resource utilization, energy production, waste handling, and material development. Notably, microwave heating has found a significant role in pyrolysis applications. This innovative approach offers distinct advantages over conventional techniques, such as enhanced heat and mass transfer, uniform heating, effortless temperature control, streamlined pyrolysis processes, and remarkable gains in energy efficiency. Its potential is particularly promising when dealing with organic matter and chemical raw materials. By harnessing high-frequency electromagnetic waves, microwave heating rapidly generates heat within materials, resulting in significantly accelerated drying rates compared to conventional methods. As microwave technology continues to advance across industries. It can also treat oily sludge efficiently and rapidly. This method not only allows for the recovery of valuable resources and energy but also exhibits stronger potential for industrial applications [5].

The pyrolysis technique involves heating the oily sludge to a fixed high temperature (400°C~800°C) without oxygen, resulting in the organic matter becoming unstable and cracking to produce solid-liquid-gas three-phase products. The organic molecules precipitate into small carbon molecules, while organic hydrocarbons are continuously decomposed and recombined for recovery of organic matter through condensation. The residual products and bio-oil after pyrolysis are reusable energy resources. Although most pyrolysis processes rely on conventional heat conduction, heat convection, or heat radiation, these traditional heating methods often encounter challenges such as heat loss, heat transfer resistance, and secondary reactions due to prolonged heating. Thus, due to its unique selectivity and heating uniformity, microwave pyrolysis has become a popular option among scholars [6]. The principle of microwave pyrolysis is to penetrate solid particles and aggregates within the particles using microwave radiation to accelerate the heating speed of the sample and achieve rapid pyrolysis [7]. When contrasting with traditional pyrolysis methods, microwave pyrolysis stands out by generating heat from the inside to the outer surface [8]. This unique characteristic leads to a higher central temperature of the material during microwave heating compared to its surrounding material [8]. Microwave heating offers numerous advantages over traditional electric heating, such as low thermal resistance, rapid response, swift heating speed, heightened efficiency, safety, harmlessness, cleanliness, and ease of control [9].

Currently, extensive research is being conducted on the microwave direct pyrolysis of oily sludge to recover bio-oil, syngas, and other valuable products. MANGESH *et al*. [10–13] have studied how pyrolysis oil from waste plastics can be converted into a usable clean fuel by adding catalysts, thereby purifying the environment. LIU *et al*. [14] investigated the influence of temperature and power on the distribution and characteristics of microwave pyrolysis products of oily sludge. They found that the optimal conditions for oil yield recovery were a temperature of 550°C and a power of 800W. The study also analyzed the gas characteristics of the pyrolysis products. However, there is limited research on the pyrolysis of oily sludge under microwave radiation with an appropriate catalyst.

In a study by PRASHANTH *et al*. [15], the use of an activated carbon carrier as a catalyst for recovering hydrocarbons from sludge through microwave-assisted pyrolysis was investigated. The researchers demonstrated that oily sludge can yield liquid fuel and petrochemical products through microwave pyrolysis. To further improve product yield, it is worth exploring the potential benefits of catalyst regulation, particularly when comparing microwave pyrolysis of biomass and other solid wastes.

Nano-metal oxides offer a promising avenue as catalysts that are not only readily accessible but also highly efficient. They play a crucial role in diminishing the energy outlay, curtailing time demands, and trimming expenses linked with microwave pyrolysis [16, 17]. Against this backdrop, this study embarks on an exploration of the influence wielded by nano-CuO and nano-$\gamma$-$Al_2O_3$ additives. These additives are introduced with the aim of elucidating their impact on product yield, as well as oil and gas composition, subsequent to the microwave pyrolysis of oily sludge. Hence, this experimental study delves into the impact of nano-additives on the attributes of microwave-induced pyrolysis products derived from oily sludge. The primary objective is to investigate how the inclusion of nano-CuO and nano-$\gamma$-$Al_2O_3$ as additives influences the yield of products, as well as the oil and gas content following the microwave pyrolysis of oily sludge. Furthermore, special attention is dedicated to examining how variations in the additive loading levels affect the properties of the resultant pyrolysis products.

## 2. MATERIALS AND METHODS

### 2.1. Materials

The oily sludge used in this experiment was sourced from the crude oil storage tanks situated in Daqing Oilfield, Heilongjiang Province, China. A comprehensive composition analysis of the oil-bearing mud is presented in Table 1.

**Table 1:** Composition analysis of oily sludge.

| ELEMENT COMPOSITION (wt%) | | | | | PHYSICAL COMPOSITION | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | N | S | Moisture content (wt%) | Oil length (wt%) | Calorific value (MJ/Kg) | Ash content (wt%) |
| 36.42 | 15.79 | 23.09 | 8.3 | 1.16 | 38.5 | 23.03 | 33.57 | 15.24 |

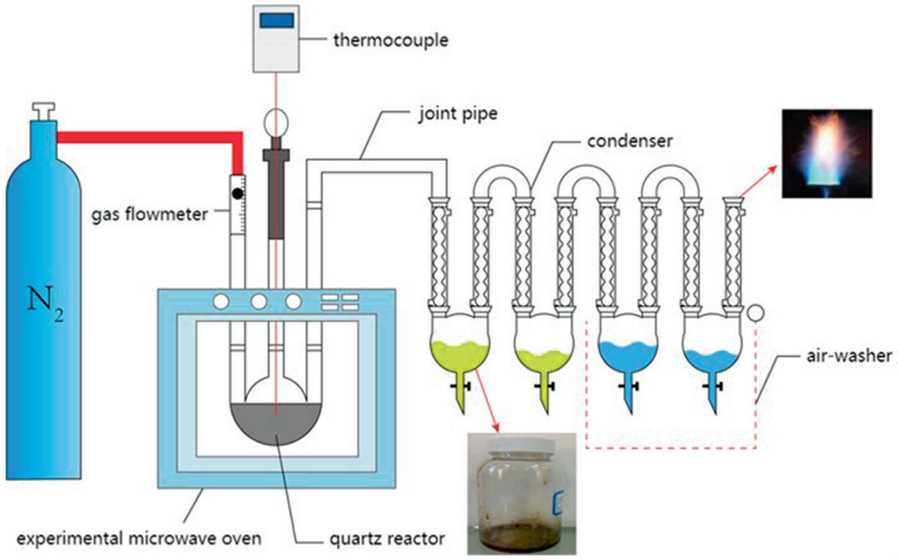


**Figure 1:** Schematic diagram of experimental equipment for microwave pyrolysis.

To investigate the impact of catalysts on oil and gas production, two nano-metal oxide catalysts were carefully selected for this experiment. These catalysts, namely nano-CuO and nano-γ-$Al_2O_3$, were acquired from Nanjing Hongdenami Materials Co., LTD. The nano-γ-$Al_2O_3$ catalyst possesses an average particle size ranging from 150nm to 500nm, while other nano-metal oxides exhibit an average particle size falling within the range of 20nm to 40nm. It is essential to highlight that all the catalysts employed in this study are in a powdery form, with a purity level of 99%.

### 2.2. Design of microwave pyrolysis system for sludge

In Figure 1, you can observe the schematic diagram of the ingeniously designed microwave pyrolysis and recovery system for light oil and combustible gas. This comprehensive system comprises various essential components, including a microwave oven, a built-in quartz reactor, a high-precision thermocouple, a condensing bottle, a washing bottle, a collecting bag, and an $N_2$ bottle [18].

The experimental microwave oven, manufactured by Henan Keer Microwave Innovation Technology Co., LTD., has an impressive power range of 0 to 2200W and operates at a frequency of 2450 ± 50Hz. The furnace cavity is equipped with a 30mm aperture strategically placed above and on the left side of the center end. A U-shaped glass tube is inserted into the furnace cavity, connecting it to the internal quartz reactor for achieving efficient internal heating and external atmosphere condensation. To collect the condensed pyrolytic oil, transparent PET bottles are utilized, while Dalian Delin Company's air collection bags are employed for gathering the pyrolysis gas.

Ensuring utmost safety, the system guarantees microwave leakage levels below 5mW/cm$^2$, in compliance with international standards. To establish an inert atmosphere for the experiment, a nitrogen cylinder is connected to the left side, efficiently purging the air from the quartz reactor beforehand.

In addition, a high-precision thermocouple is affixed to the outer wall of the quartz reactor, enabling real-time measurement of the material temperature within the quartz reaction vessel during pyrolysis. The microwave oven is further equipped with a PLC system, which automatically adjusts the temperature and power settings, with the real-time measured temperature conveniently displayed through the PLC system screen.

### 2.3. Experimental process

Before commencing the experiment, the right end of the microwave oven underwent a 5-minute nitrogen purging at a flow rate of 200 mL/min, creating an inert atmosphere within the oven. The 200g sample of oily sludge was accurately weighed using an electronic balance and then carefully placed into the quartz reactor located inside the microwave oven cavity. To achieve uniform heating of the sludge, microwave pyrolysis was employed.

The catalyst load was systematically set at 5%, 10%, and 15% of the mass of the oily sludge. Ensuring thorough mixing of the oily sludge and catalyst, the sludge sample was preheated to 50°C to reduce viscosity. Subsequently, a precisely measured quantity of catalyst was added to the sludge in the crucible and vigorously stirred until an even mixture was achieved. With the furnace door securely closed, the microwave power was set to 2000W, and an air collecting bag was connected at the device's end. The microwave oven was then activated to initiate the experiment.

Throughout the experiment, meticulous temperature readings were diligently recorded at 2-minute intervals, commencing from 0 minutes and continuing until the pyrolysis process was concluded. After the high-temperature oil and gas generated during the microwave pyrolysis process condensed, the resulting pyrolysis oil was collected in a condensing bottle, while the non-condensing gas was directed through a gas washing device and gathered in the air collection bag (replaced every 3 minutes).

Upon the conclusion of the reaction, the microwave oven door was opened to dissipate heat, allowing the residue in the reactor to cool to room temperature. To ensure the accuracy of the data, each experiment was meticulously repeated 3 times.

### 2.4. Analytical method

The detection of non-condensable gases was carried out using a gas chromatograph (Agilent, Model 8890) equipped with FID and TCD detectors. During the test, the air sample collected in the bag was connected to the instrument inlet and quantitatively fed into a tube. Subsequently, the air sample was automatically processed through the six-way valve and analyzed on the machine based on the predefined program settings. The instrument parameters were set with a shunt ratio of 20:1. The programmed temperature rise included an initial temperature hold of 60°C for 1 minute, followed by a ramp of 20°C/min up to 80°C, and finally, a ramp of 30°C/min up to 180°C for TCD1 and TCD2 detectors. The FID detector operated at a constant temperature of 300°C.

To detect pyrolytic oil, an appropriate sample amount was first taken and dissolved in dichloromethane, followed by a 20-fold dilution. Ultrasonic extraction was then performed using a dedicated machine for testing. The analysis was carried out employing the highly reliable Agilent gas chromatography-mass spectrometry (GC-MS) with the advanced Agilent 19091S-433 model. The GC-MS system was equipped with an HP-5 fused silicon capillary column, measuring 30m × 250μm × 0.25μm, ensuring precise separation of components. A sample size of 1μL was utilized, and helium was used as the carrier gas at a flow rate of 1.0 ml/min, ensuring smooth and efficient chromatographic performance. The initial temperature of the gas chromatography was set at 50°C, which was gradually increased to 100°C after 3 minutes at a rate of 10°C/min. Subsequently, it was further raised to 280°C at a rate of 15°C/min for 4 minutes and finally reached 320°C at a rate of 30°C/min. The mass spectrometer settings included electron shock mode with an electron energy of 70ev, filament current of 34μA, doubling voltage of 2117 V, and a complete scan. The identification of compounds was accomplished by meticulously comparing the data with the comprehensive NIST mass spectrometry library, ensuring accurate and reliable results. Moreover, the relative contents of the samples were determined using area normalization, providing a quantitative assessment of each component's concentration.

## 3. RESULT AND DISCUSSION

### 3.1. Effect of additive loading on pyrolysis gas composition

#### 3.1.1. Effect of nano-CuO additive loading on pyrolysis gas composition

Figure 2 illustrates the changes in volume percentage of $CO_2$, $H_2$, $CH_4$, CO, and $C_xH_y$ emitted from waste sludge under different loads of nano-CuO during microwave pyrolysis. As depicted in the figure, $CO_2$ exhibits an increasing trend, while CO shows a decreasing trend, with noticeable changes observed for both components. The minimum volume content of CO at a 15% load is measured at 8.735%, whereas the maximum volume content of $CO_2$ at the same load reaches 50.673%. This trend can be attributed to the increased oxygen content resulting from the interaction between nano-CuO, waste sludge, and the load.

The formation of $CO_2$ primarily stems from the fracture of carbonyl and carboxyl functional groups within the waste sludge at lower temperatures [19], hence explaining the rise in volume content of $CO_2$ with increasing nano-CuO load.

Furthermore, the volumes of $H_2$, $CH_4$, and $C_xH_y$ exhibit a turning point at a 10% load, reaching their highest peaks when loaded with 10% nanometer CuO. Notably, the volume content of $CH_4$ and $H_2$ decreases with an increased loading of nano-CuO. This phenomenon indicates that the loading of CuO at 10% nm7 promotes a series of reactions such as methane reforming (as shown in Formula 1) and organic cracking (as shown in Formula 2), thereby facilitating the generation of clean gas $H_2$ and fuel gas $CH_4$.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (1)$$

$$organics + H_2O \rightarrow CO + H_2 \quad (2)$$

**3.1.2. Effect of nano-γ-$Al_2O_3$ additive loading on pyrolysis gas composition**

Figure 3 illustrates the volume fraction changes of gas components $CH_4$, $H_2$, CO, $CO_2$, and other gases ($C_xH_y$) with varying loads of nano-γ-$Al_2O_3$. The y-axis represents the volume fraction of different gases in the pyrolysis gas.

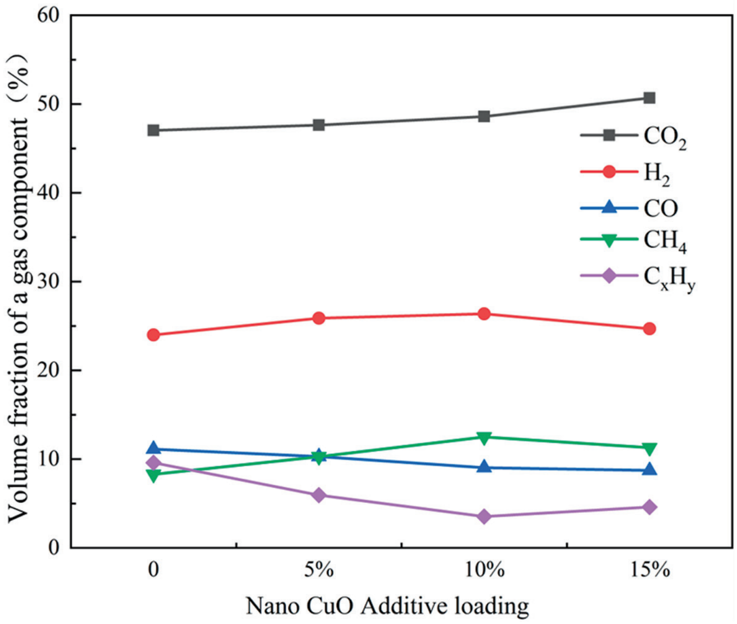


**Figure 2:** Effect of nano-CuO loading on gas components.

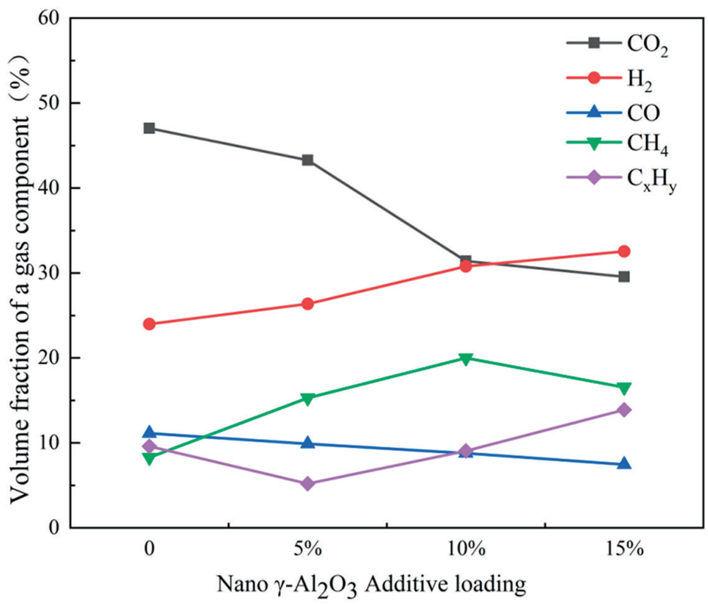


**Figure 3:** Effect of nano-γ-$Al_2O_3$ loading on gas components.

As observed in the figure, $CO_2$ and $H_2$ exhibit relatively high-volume contents. Upon the addition of additives, the volume content of $H_2$ increases with an increasing load of nano-γ-$Al_2O_3$, peaking at a 15% load. These results indicate that the addition of additives significantly promotes the production of $H_2$ through primary water-gas reactions during microwave sludge pyrolysis. Specifically, adding a 15% load of nano-γ-$Al_2O_3$ has the potential to synthesize a fuel gas rich in $H_2$.

Conversely, the volume content of $CO_2$ decreases as the load of nano-γ-$Al_2O_3$ increases, with the smallest proportion observed at a 15% load. This suggests that nano-γ-$Al_2O_3$ exhibits strong adsorption capacity at this additive load, effectively absorbing a significant amount of $CO_2$ generated during the pyrolysis of oxygen compounds and organic matter.

On the other hand, the other gas components show minimal changes under the catalysis of nano-γ-$Al_2O_3$. As the additive load increases, the volume content of $CH_4$ exhibits an interesting pattern. Initially, it rises and reaches its peak at a 10% additive load. However, beyond this point, it starts to decrease gradually. The overall volume content of CO shows a slight downward trend, albeit not particularly pronounced.

This phenomenon may be attributed to the fact that a portion of the CO present in the pyrolysis gas originates from the reduction reaction of $CO_2$ and C. As the volume content of $CO_2$ decreases due to an increased additive load, the rate of escape from the quartz reactor after gas generation accelerates. Consequently, the involvement of $CO_2$ in reduction reactions decreases, resulting in a slight decline in the volume content of CO with increasing additive load.

## 3.2. EFFECT OF ADDITIVE LOADING ON PYROLYSIS OIL COMPONENTS

### 3.2.1. Effect of nano-CuO loading on pyrolysis oil components

After conducting the GC-MS test, the carbon number distribution in the pyrolysis oil phase was analyzed for different amounts of nano-CuO.

Figure 4 provides a direct representation of the composition changes in the pyrolysis oil with varying loads of nano-CuO. It can be observed that the content of light components ($C_4$ to $C_{12}$) initially increases and then slightly decreases. The maximum content of light components, reaching 21.617%, is observed at a 10% additive load. This phenomenon can be attributed to the presence of Cu, a metal element, in nano-CuO. During microwave pyrolysis, as the additive load and concentration increase, Cu ions on the active sites react extensively with oxygen (O), sulfur (S), and other substances present in the waste sludge. This reaction promotes the cracking of C-C bonds, leading to the production of more light oil components. The optimal reaction conditions are achieved at a 10% additive load, resulting in the peak content of light components.

The medium components ($C_{13}$ to $C_{18}$) also show a slight increase with increasing additive load. As the additive load increases, the heavy components, such as asphaltenes, present in the sludge undergo deep cracking

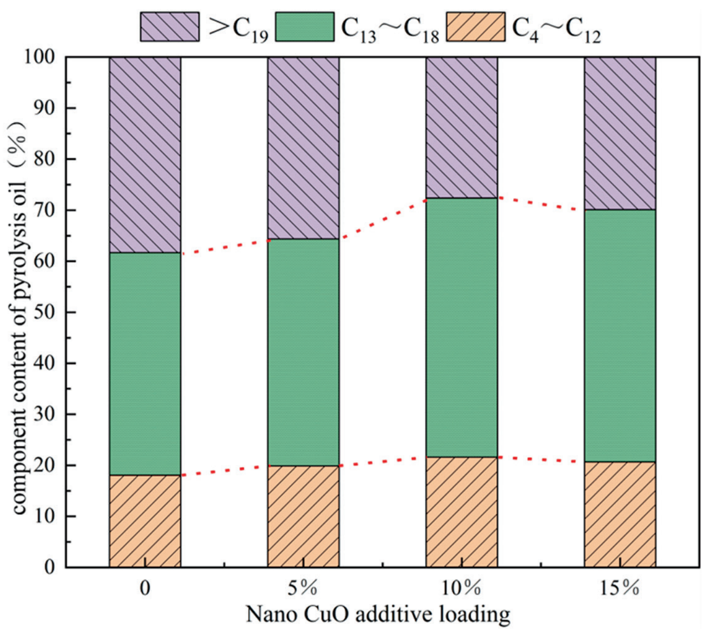


**Figure 4:** Effect of nano-CuO loading on carbon number distribution of pyrolysis oil.

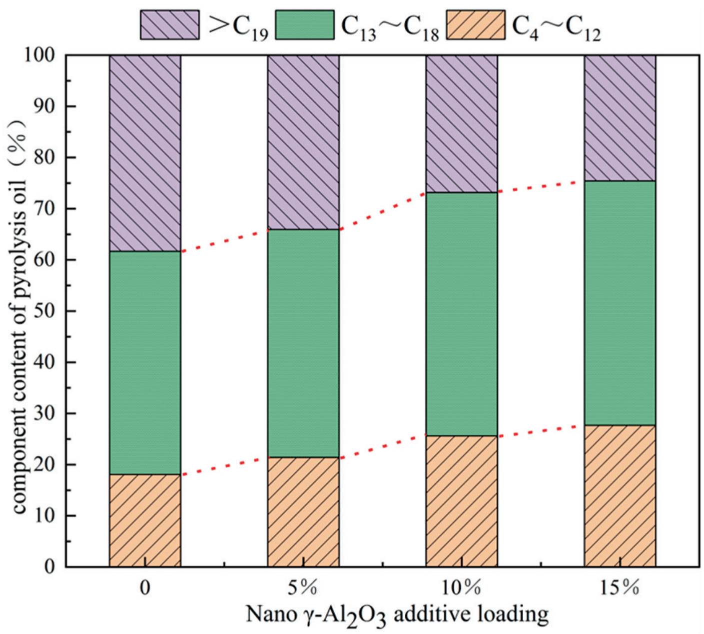


**Figure 5:** Effect of nano-γ-$Al_2O_3$ loading on carbon number distribution of pyrolysis oil.

and transformation into medium components. The maximum value of medium components, reaching 50.751%, is observed at a 10% load, followed by a slight decrease with further increase in the additive load.

The distribution of heavy components (> $C_{19}$) in the pyrolysis oil shows an initial decrease followed by a slight increase as the additive load increases. From the carbon number distribution analysis of the pyrolysis oil, it can be concluded that the catalytic cracking effect is most effective at a 10% additive load of nano-CuO. This particular load significantly improves the conversion rate of light oil and enhances the quality of the pyrolysis oil.

#### 3.2.2. Effect of nano-γ-$Al_2O_3$ loading on pyrolysis oil components

Figure 5 illustrates the influence of nano-γ-$Al_2O_3$ loading on the components of pyrolysis oil. In contrast to nano-CuO, the addition of nano-γ-$Al_2O_3$ leads to a gradual increase in the content of light components ($C_4$ to $C_{12}$) and medium components ($C_{13}$ to $C_{18}$), while the overall content of heavy components (> $C_{19}$) decreases.

With an increasing load of nano-γ-$Al_2O_3$, both the pyrolysis of heavy components into medium components and the pyrolysis of medium components into light components occur simultaneously. As the additive load rises, the pyrolysis process reaches an equilibrium state, resulting in a continuous decrease in the content of heavy components, while the content of medium and light components consistently increases.

As shown in the figure, the content of medium components surpasses that of light components. This phenomenon is attributed to the fact that at lower additive loads, the heavy components in the waste sludge gradually crack into medium components with increasing temperatures. As the additive load further increases, more medium components are generated through cracking reactions.

In summary, without the addition of nano-γ-$Al_2O_3$, the contents of $C_4$ to $C_{12}$, $C_{13}$ to $C_{18}$, and > $C_{19}$ components are measured at 18.073%, 43.62%, and 38.307%, respectively. Comparing these values with a 15% load of nano-γ-$Al_2O_3$, there is an increase of 9.616% for light components, an increase of 4.113% for medium components, and a decrease of 13.729% for heavy components. These results emphasize the significant influence of nano-γ-$Al_2O_3$ loading on the components of pyrolysis oil. The optimal catalytic effect is achieved at a 15% loading, enhancing the production of light components and consequently improving the quality of the pyrolysis oil.

### 3.3. Effect of additive load on pyrolysis product yield

#### 3.3.1. Effect of nano-CuO loading on the yield of pyrolysis products

The findings from Figure 6 reveal the distribution of gas, liquid, and solid residue yields during the pyrolysis of waste sludge with varying nano-CuO loads. As the nano-CuO load increases from 0% to 10%, the gas yield steadily rises, reaching its peak at 30.6% with a 10% load. However, the gas yield shows a slight decrease to 28.6% when the load is further increased to 15%.

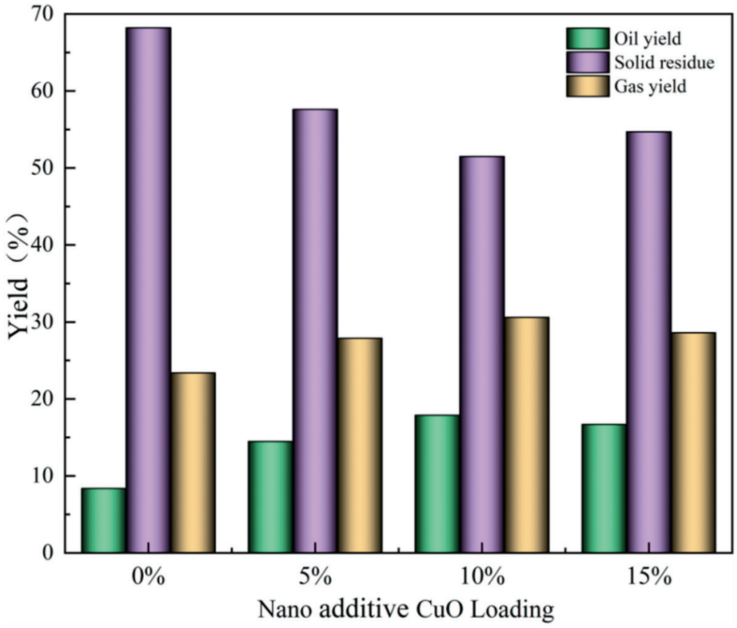


**Figure 6:** Effect of nano-CuO loading on pyrolysis product yield.

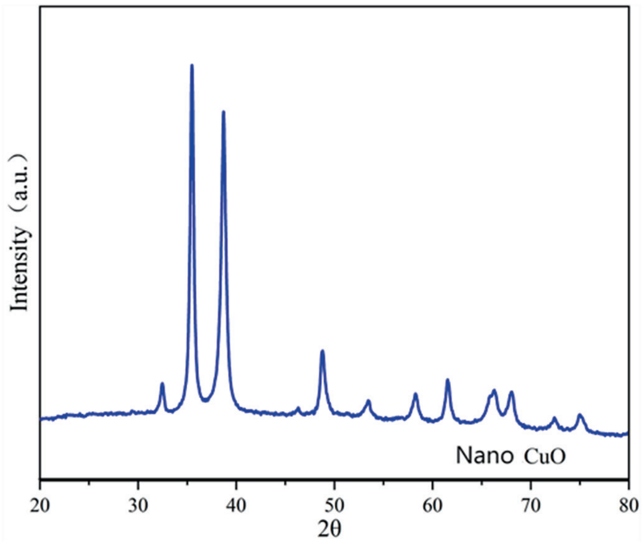


**Figure 7:** XRD pattern of nano-CuO before pyrolysis.

To further understand the influence of the nano-CuO load on the pyrolysis gas yield, XRD testing was conducted on the nano-CuO additive, as shown in Figure 7. The XRD spectrum reveals that only a single phase of CuO was detected before the pyrolysis reaction, indicating that only CuO participates in the pyrolysis process. During pyrolysis, CuO plays a dominant role. Water molecules in the sludge volatilize and condense into water during this process. Simultaneously, CuO loses electrons and forms Cu ions. These Cu ions exhibit a strong affinity towards the volatilized water molecules, causing the escape of small water molecules. As the concentration of Cu ions increases, more and more of the small water molecules escape, resulting in peak gas yield at 10% additive loading. However, as the concentration of Cu ions continues to increase, the water molecules reach a saturation point where they no longer escape as small molecules. Consequently, the gas yield slightly decreases under a 15% additive load.

In contrast, the solid residue yield decreases from 68.2% to 51.5% within the 0–10% nano-CuO load range and then increases to 54.7% when the load is increased from 10% to 15%. The pyrolysis oil yield exhibits an increase from 8.4% to 17.9% within the 0-10% nano-CuO load range, followed by a decrease to 16.7% from a 10% to 15% load.

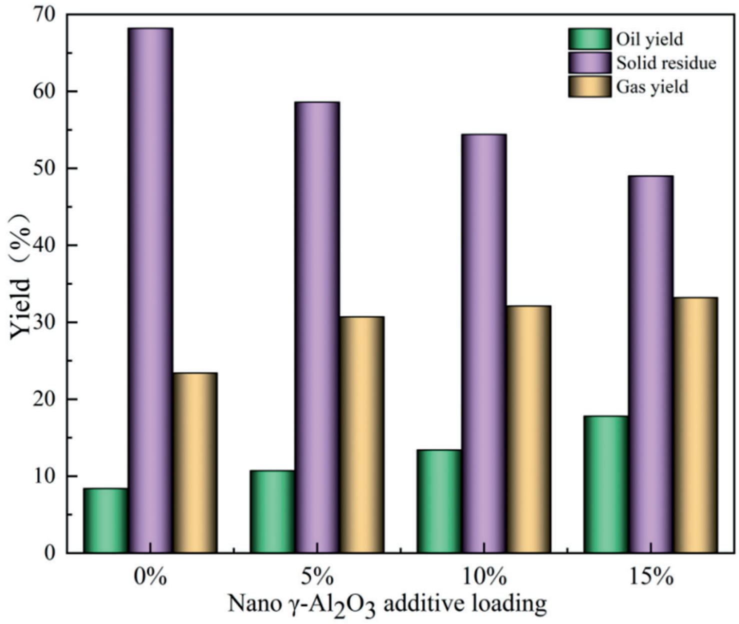


**Figure 8:** Effect of nano-γ-$Al_2O_3$ loading on pyrolysis yield.

Overall, the highest pyrolysis oil yield and lowest solid residue yield are achieved with a 10% nano-CuO load for waste sludge assisted pyrolysis. A very small amount of nano-CuO does not provide sufficient heat for co-pyrolysis with the sludge, resulting in lower gas and oil production compared to a 10% load at 5% nano-CuO load. Conversely, adding a large amount of nano-CuO may lead to increased coking and a higher yield of solid residue due to the rapid heating rate of microwaves. Excessive catalyst loading can also inhibit the pyrolysis process. Therefore, a 10% nano-CuO load is considered the optimal additive load. When using a single additive for microwave pyrolysis of waste sludge, a 10% nano-CuO load can achieve the highest yield of gas and oil production.

#### 3.3.2. Effect of nano-γ-$Al_2O_3$ loading on pyrolysis product yield

In Figure 8, an informative depiction of the gas, liquid, and solid residue yields distribution is presented, illustrating the varying outcomes observed during the pyrolysis of waste oil sludge under different nano-γ-$Al_2O_3$ loads. As the nano-γ-$Al_2O_3$ load increased from 0% to 15%, there was a significant rise in the pyrolysis gas yield, increasing from 23.4% to 33.2%. This result indicates that the addition of nano-γ-$Al_2O_3$ promotes the cracking of macromolecular compounds into non-condensing gases and smaller molecules [20].

It is essential to note that the quantitative analysis of gases with carbon numbers greater than 3 was not feasible due to limitations of the GC analyzer. Consequently, the inclusion of nano-γ-$Al_2O_3$ additives may generate a certain amount of $C_4$ and $C_2$~$C_3$ small molecule gases, contributing to the substantial variation in additive load (0% to 15%) and gas yield (23.4% to 33.2%).

Additionally, XRD characterization of the nano-γ-$Al_2O_3$ structure is depicted in Figure 9. The figure reveals the presence of AlO(OH), $Al(OH)_3$, and $Al_2O_3$ as hydrated alumina and complex forms prior to the pyrolysis reaction. Hydrated alumina, which is an amphoteric oxide, decomposes at 190°C during pyrolysis, releasing $Al_2O_3$ and water molecules. Water molecules have excellent wave absorption properties, facilitating the microwave pyrolysis reaction of sludge, accelerating the reaction process, and promoting the hydration reaction of hydrated alumina. The hydration reaction results in the production of anion AlO-, which can combine with other nano-metal oxide cations, enhancing the complete cracking of nano-metal oxide, improving catalytic effectiveness, and speeding up the reaction process.

Concerning the yield of pyrolysis oil, there was a substantial increase from 8.4% to 17.8% as the nano-γ-$Al_2O_3$ load increased from 0% to 15%. In contrast to nano-CuO, which exhibited an oil production peak at a 10% load, the oil yield with nano-γ-$Al_2O_3$ continued to rise without reaching a plateau. This behavior can be attributed to the unique crystal structure of nano-γ-$Al_2O_3$. To gain insight into the grain sizes of nano-γ-$Al_2O_3$ and nano-CuO, the Scherer formula was employed, and the results are presented in Table 2. Smaller grain sizes indicate better plasticity of the nano-metal oxide itself, potentially leading to an enhanced catalytic effect with increasing load. As a result, when investigating the influence of nano-γ-$Al_2O_3$ load on the pyrolysis product

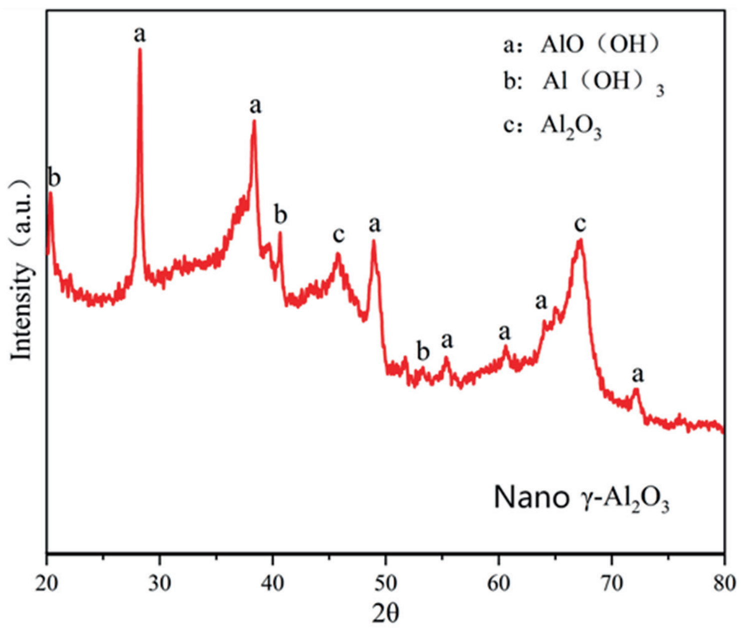


**Figure 9:** XRD patterns of nano-γ-$Al_2O_3$ nanoparticles before pyrolysis.

**Table 2:** Comparison of grain size between nano-CuO and nano-γ-$Al_2O_3$.

| Grain (angstrom) | 151(2) | 33(1) | 153(32) | 177(29) |
|---|---|---|---|---|
| Phase name | AlO(OH) | $Al(OH)_3$ | $Al_2O_3$ | CuO |

yield of oily sludge, both pyrolysis oil and pyrolysis gas yields experienced significant increases, reaching their respective peaks.

## 4. CONCLUSIONS

Through an in-depth analysis of pyrolysis product characteristics, this study delves into the impact of compound additives on the sludge at the bottom of refinery tanks during microwave pyrolysis, leading to the following conclusions:

(1) The additive load has a notable influence on the yield and characteristics of the three-phase products. The most favorable results in terms of oil and gas yield and the lowest solid residue yield are achieved with a 10% nano-CuO additive load. On the other hand, increasing the nano-γ-$Al_2O_3$ loading substantially boosts the yields of both pyrolysis oil and pyrolysis gas.

(2) Pyrolysis oil and gas yields reach their peak at a 15% load. The catalytic cracking effect of nano-CuO is optimal at a 10% additive load, improving the conversion rate of light oil. Nano-γ-$Al_2O_3$ exhibits the best catalytic effect at a 15% load, increasing the light components of the pyrolysis oil. The proportion of gasoline and diesel ($C_4$~$C_{12}$, $C_{13}$~$C_{18}$) reaches 75.422%, enhancing the quality of the pyrolysis oil.

(3) For nano-CuO additives, the highest peaks of $H_2$ and $CH_4$ occur at a 10% nano-CuO additive load, reaching 26.375% and 12.49%, respectively. The volume content of CO decreases with increasing load, reaching its minimum value of 8.735% at a 15% load. For nano-γ-$Al_2O_3$ additives, the volume content of $H_2$ increases with increasing nano-γ-$Al_2O_3$ loading, reaching its highest value at a 15% load. The volume content of $CH_4$ initially increases and then decreases with increasing additive load, peaking at a 10% load. The volume content of CO slightly decreases with increasing additive load.

(4) Overall, the proper selection of additive loads and compound additives can significantly impact the yield and characteristics of pyrolysis products, providing opportunities to optimize the conversion rate of light oil and improve the quality of the pyrolysis oil.

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