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Effect of nano-metal oxides types on oil sludge during microwave pyrolysis

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ABSTRACT

In this paper, based on the analysis of oil sludge composition and environmental hazards, the microwave catalytic pyrolysis of oil sludge for recovering combustible gas and chain hydrocarbon light oil disposal process, is proposed to perform the recycling of oil sludge and reduce the risk of environmental pollution. In order to improve the yield of combustible gas and light oil in oil sludge pyrolysis, the impact of adding four catalysts (nano-CuO, nano-NiO, nano-MgO, and nano-γ-Al_2O_3) on the heating characteristics of oil sludge and the composition and quality of products during microwave pyrolysis, were experimentally studied and analyzed. The results show that the catalyst can increase the heating rate of sludge and the yield of pyrolysis oil and gas. The increasing order of heating is: nano-CuO > nano-γ-Al_2O_3 > nano-MgO > nano-NiO > blank group. Compared with the blank group, the content of combustible gas (H_2 + CH_4 + CO) increases by 18.824wt% (MgO), 4.511wt% (CuO), 9.28wt% (NiO), and 16.164wt% (γ-Al_2O_3), respectively. It can be deduced that nano-metal oxide catalysts, especially γ-Al_2O_3, can promote the decomposition of oil sludge, improve the content of low carbon straight chain hydrocarbons and alcohols, and improve the quality of pyrolysis oil products.

Keywords: Oily sludge; Microwave pyrolysis; Nano-metal oxides; Wave absorbent.

1. INTRODUCTION

The petroleum industry produces much oily sludge in crude oil extraction, transportation, storage, and refining. The oily sludge has a very complex composition, mostly accompanied by a pungent odor. In fact, waste oil sludge contains hydrocarbons, which volatilizes in the high temperature mechanism to produce a pungent odor, heavy metal elements, and pathogenic bacteria and microorganisms [1]. If arbitrarily disposed, it is not only a waste of resources but also damages the ecosystem. It is known that the oil content of oily sludge is usually between 10% and 50%, and the sludge contains many hydrocarbons that can be reused as fuel and chemicals [2]. Therefore, the treatment and recovery of oily sludge are of great significance [3].

The resource disposal methods of oily sludge mainly include the solvent extraction, surfactant, freeze-thaw, and mechanical separation methods [4–7]. The solvent extraction method has high solvent loss and secondary pollution. In the surfactant method, the chemical surfactant contains toxicity that will cause harm to the environment. In addition, the biosurfactant cannot be easily obtained and has a high cost. The freeze-thaw method has low efficiency and high energy consumption in the freezing process. In the mechanical separation method, the cost of the equipment procurement and maintenance is high, and it will cause noise pollution. Therefore, a noise reduction treatment is required. Compared with these technologies, the pyrolysis process is one of the most valuable technologies for industrial applications. Its main principle is that in an inert atmosphere, the oily sludge heating to 400–800°C results in the organic thermal cracking or hot shrinkage reaction, can condensate oil products of low molecular weight and small molecules of non-condensable gas product, and get a solid coke. These products may have a higher value than the original oily sludge [6]. However, the endothermic reaction of traditional pyrolysis should provide a large amount of external heat, which results in a high operating cost [6]. Moreover, the water content of oily sludge is relatively high, and the dehydration treatment before pyrolysis will further increase the total cost, which limits the development and application of the pyrolysis technology for oily sludge.

The microwave pyrolysis of oil sludge can absorb the microwave using water in it, and rapidly heating it to a higher temperature from the inside [8]. It can also crack heavy hydrocarbons into small molecular compounds,

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which is considered as the most promising pyrolysis technology [9]. Therefore, adding absorbent materials with high dielectric constant to promote high-temperature pyrolysis of oil sludge, has become crucial. GOMEZ *et al*. [10] used iron oxide as a microwave absorbing material, which can release 5% water and volatile matter after heating for only 5 min under the action of a microwave (1000 W, 2450 MHz). MENÉNDEZ *et al*. [11] added solid particles containing carbon to the oil sludge as wave-absorbing material, and heated it to 1000°C by microwave to obtain gas products rich in CO and H_2, as well as oil products having low PAH content. While studying the absorbing materials, it is deduced that metal oxides, as absorbing materials, can absorb the radiation energy of microwave and have catalytic activity, which can reduce the pyrolysis temperature of sludge and allows to obtain the products of oil and gas with good quality at a relatively low unit temperature.

Compared with the traditional catalysts, nano-metal oxides have smaller diameter particles, higher specific surface area, and higher recovery. In addition, they are often used in biocatalysis. MADHUVILAKKU *et al*. [12] used nano-metal oxide (TiO_2) as catalyst to produce biodiesel from waste olive oil. They reached a conversion rate as high as 91.2%. KUMAR *et al*. [13] prepared Ni-supported Zn/CaO mixed oxide catalyst using wet impregnation method to promote the transesterification reaction of waste cottonseed oil and improve the conversion rate of diesel oil. JIANG *et al*. [14] used magnetic nanoparticle oxide as a catalyst for the pyrolysis of oil sludge. They demonstrated that when the mass concentration of $ZnFe_2O_4$ nanoparticles increases, the contents of H_2, CH_4, and C_2H_6 in gas phase pyrolysis products increase. It can be concluded that nano-metal oxides can effectively improve the content of clean gas and the conversion rate of diesel oil. Therefore, this study aims to explore the wave absorption and catalytic performance of different nano-metal oxides as microwave absorbers and catalysts, and analyze the impacts of nano-metal oxides on the improvement of the quality and conversion of pyrolysis products in the process of microwave pyrolysis of sludge by GC-MS.

2. MATERIALS AND METHODS

2.1. Materials

The oily sludge used in this experiment was sampled from the crude oil tank in Daqing Oilfield, Heilongjiang Province, China. Table 1 shows the composition analysis of this oily sludge. Figure 1 is the static diagram of waste sludge.

Table 1: Composition analysis of the oily sludge used in the experiment.

ELEMENTAL COMPOSITION (wt%)					PHYSICAL COMPOSITION			
C	H	O	N	S	MOISTURE CONTENT (wt%)	OIL CONTENT (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

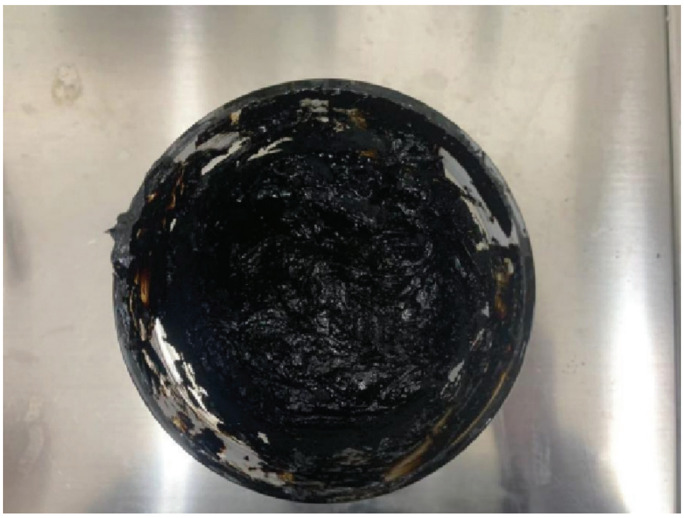

Figure 1: Static appearance of oily sludge.

In order to study the influence of the catalyst on oil and gas production, nano-CuO, nano-NiO, nano-MgO, and nano-γ-Al_2O_3 were used as nano metal oxide catalyst. They were all purchased from Nanjing Hongde Nanomaterials Co, Ltd. Nano-γ-Al_2O_3 has an average particle size in the range of 150–500 nm, while the average particle size of the other nano metal oxides is in the range of 20–40 nm. Note that nano-γ-Al_2O_3 has a powder appearance (purity of 99%).

2.2. Design of microwave pyrolysis system for oil sludge

Figure 2 shows the schematic diagram of the microwave pyrolysis experimental device. The system consists of a microwave oven, built-in quartz reactor, high-precision thermocouple, condensing bottle, gas washing bottle, air collector bag, and N_2 bottle. The used experimental microwave oven (Henan Keer Microwave Innovation Technology Co., Ltd.) has a power of 0-2200 W and a frequency of 2450 ± 50 MHz, and its 30 mm aperture is opened above and on the left side of the center in the furnace cavity. The special U-shaped glass tube is inserted into the furnace cavity and connected with the quartz reactor five to perform internal heating and external atmosphere condensation. The condensed pyrolysis oil is collected by PET transparent plastic bottle, and the pyrolysis gas is collected by the gas collecting bag produced by Dalian Delin Company [15]. The microwave leakage level is less than 5 mW/cm^2, which is in line with international standards. The left side is connected with nitrogen bottle, which purges the air in the quartz reactor before the experiment, and retains the inert atmosphere. The outer wall of the quartz reactor is connected with a high-precision thermocouple, which is used to measure the material temperature in the quartz reaction flask in real-time during pyrolysis. Microwave ovens equipped with a PLC system can automatically adjust the temperature and power, and the real-time measured temperature can be displayed on the PLC system screen.

2.3. Experimental process

Before the experiment, the whole microwave heating device was purged with nitrogen gas from the right end of the microwave oven at a flow rate of 200 mL/min, and the purging time was 5 min to keep the inert atmosphere inside. The oily sludge used in each group had 200 g, which was weighed by an electronic balance and then put into the quartz reactor in the inner cavity of the microwave oven. The added catalyst load was 10% of the weight of oily sludge [15]. In order to evenly mix the oily sludge and catalyst, the oily sludge sample was first heated to 50°C to reduce the viscosity, and then a quantitative catalyst was added in the crucible and stirred. Afterwards,

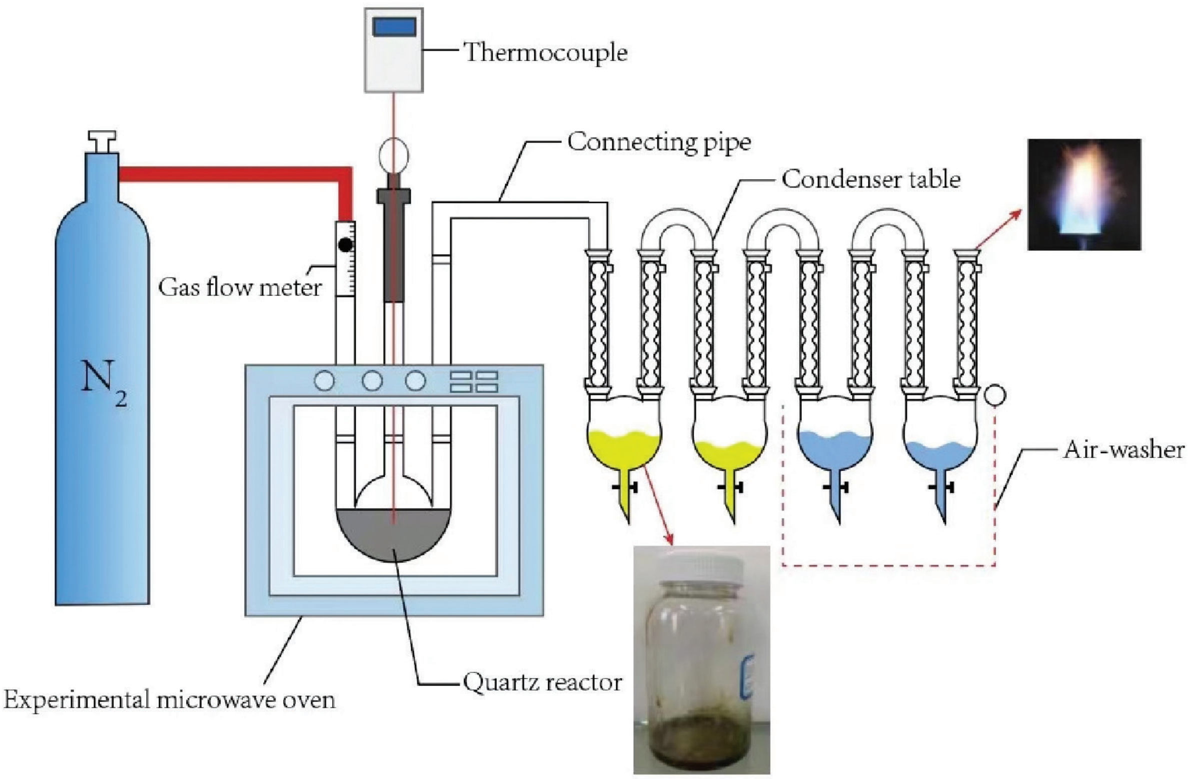

Figure 2: Schematic diagram of the microwave pyrolysis experimental device.

the furnace door was closed, the microwave power was set to 2000 W, and the air collector bag was connected at the end of the device's outlet. The microwave oven was then run. During the experiment, the temperature was recorded every 2 min, starting from 0 min until the pyrolysis was completed. The condensing pipe condensed the high-temperature oil and gas generated in the process of microwave pyrolysis. The pyrolytic oil was collected by the condensing bottle, while the non-condensing gas was washed by the gas washing device and then collected in the air collection bag. The collecting bag was replaced every 3 min, collecting at 350°C and end collection at 400°C. After the reaction, the microwave oven door was opened for heat dissipation, and the residue in the reaction kettle was removed for weighing when it cooled to room temperature. Each experiment was repeated three times to ensure a high data accuracy.

2.4. Pyrolysis products and analytical methods

2.4.1. Composition of the pyrolysis products

Figure 3 shows the composition of the products produced by microwave pyrolysis of oil sludge. After microwave pyrolysis of oil sludge, the products include pyrolysis oil, pyrolysis gas, and solid residue carbon. The main components of the pyrolysis gas are H_2, CO, CH_4, CO_2, C_2-C_4 short-chain alkanes, and alkenes. Hydrocarbons, alcohols, lipids, and aromatic compounds are mainly pyrolysis oil components. The oil group can be separated into diesel, gasoline, and fuel oil by distillation.

2.4.2. Analysis method

Non-condensing gases were detected through a gas chromatograph (Agilent, model 8890) equipped with FID and TCD detectors. A Supelo CarboxenTM 1010 carbon molecular sieve (30 m × 0.53 mm) column were used. Helium was used as carrier gas for the determination of CO, CO_2 and CH_4. During testing, the sample air bag was connected with the instrument sample inlet, filled with the loop, automatically injected through the six-way valve, and tested on the machine according to the program. The instrument parameter shunt ratio was adjusted to 20:1. The program temperature was 60°C. After 1 min, 20°C/min was set until 80°C, and 30°C/min was set until 180°C temperature. TCD1 had a temperature of 250°C, while the temperature of TCD2.FID was 300°C.

During the detection of pyrolysis oil, a proper amount of samples was first considered, and the methylene chloride was dissolved and diluted 20 times. After ultrasonic extraction, the samples were tested on the machine. The agilent gas chromatography-mass spectrometry instrument (GC-MS, Agilent 19091S-433), equipped with HP-5 fused silicon capillary column (30 m × 250 μm × 0.25 μm), was used. The sample size was 1 μl. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min, and the GC was set to 50°C. After 3 min, the samples were heated to 100°C at 10°C/min, then to 280°C at 15°C/min, and finally to 320°C at 30°C/min. The mass spectrometer conditions were: electron shock, electron energy of 70 eV, filament current of 34 μA, doubling voltage of 2117 V, and complete scan. The compounds were identified by comparison with data from the NIST mass spectrometry library, and the relative contents of the samples were calculated by area normalization.

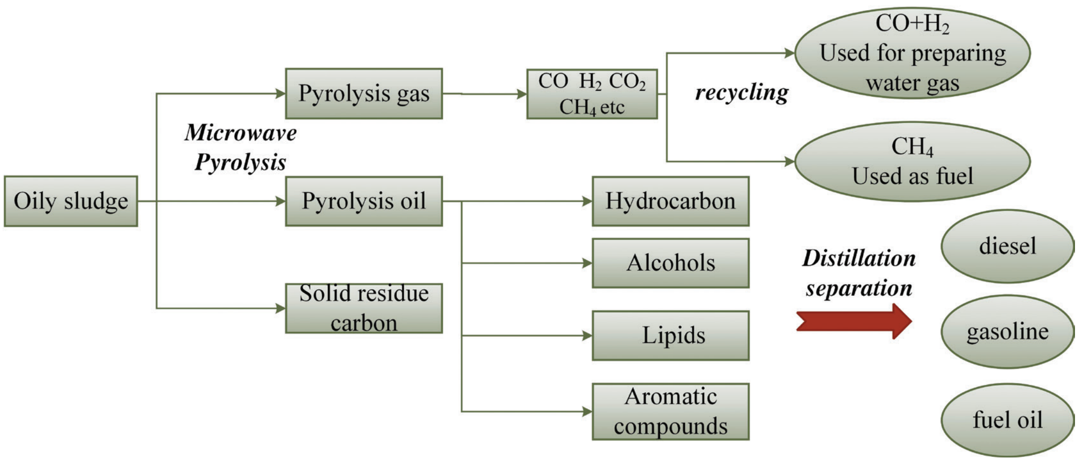

Figure 3: Microwave pyrolysis process of oily sludge.

3. RESULTS

3.1. Mechanism of microwave catalytic pyrolysis

The pyrolysis of sludge after heating in the microwave oven is divided into two parts: the pyrolysis reaction section and the catalytic pyrolysis reaction section. During microwave pyrolysis, the pyrolysis reaction of oily sludge first occurs with the increase of the internal temperature, as shown in Figure 4. The internal chain hydrocarbons form alkenes through dehydrogenation and cleavage (breaking the C-C bond and C-H bond), accompanied with the release of CH_4, H_2, and light hydrocarbon gases [16]. Similarly, oxygen-containing compounds form alkenes by deoxygenation, accompanied with the release of CO and CO_2. The olefins, formed in the microwave heating to high temperature (≥500°C) dehydrogenation polymerization, generate aromatic hydrocarbons. This reaction section is thermal cracking. The aromatic hydrocarbons generated by thermal cracking, and the aromatic hydrocarbons contained in the oily sludge itself, will be adsorbed on the surface of nano-metal oxides, while part will be degraded by steam reforming reaction to form clean gases such as H_2. The other part will continue to crack to form light hydrocarbons, and some polycyclic aromatic hydrocarbons will adsorb on the surface of nano-metal oxides for dehydrogenation polymerization, which results in the catalyst deactivation.

3.2. Heating process

Figure 5 shows the real-time temperature curve of microwave pyrolysis of oily sludge after adding five catalysts, including nanometer CuO, nanometer NiO, nanometer MgO, and nanometer γ-Al_2O_3, at a microwave power of 2000 W. It can be seen that the warming trend of oily sludge in the blank group and the catalyst group is generally consistent, and both increase with the extension of the pyrolysis time [16]. The heating process during sludge pyrolysis can be divided into five stages. (1) Rapid heating: in the first 10 min, the temperature rapidly increases from room temperature to 100°C. (2) 100–150°C is the stage of moisture drying in oily sludge. (3) 150–500°C is the stage of hydrocarbon volatilization in oily sludge. (4) 500–600°C is the stage of pyrolysis of oily sludge. (5) 600–800°C is the stage of carbonization of oily sludge.

The rapid temperature increase in the first stage is due to the evaporation of water in oily sludge and the absorption of internal microwaves. As the permittivity of water is almost 80 F/m, it is a polar substance which induces a dielectric polarization effect while absorbing the microwave. This results in internal friction and release in the form of more heat energy, rapidly heating up to 100°C [17]. At 100°C, it is observed that water droplets are constantly precipitated below the condensing tube, accompanied by a large amount of vapor evaporation, as shown in Figure 6. After all the water evaporated, the temperature increases to 150°C and then starts to volatilize hydrocarbons in the oil sludge. Light hydrocarbon components in the oil sludge significantly volatilize with the temperature increase. At 280–350°C, a large amount of smoke precipitate from the end of the condensate pipe. When the hydrocarbons in the oil sludge are volatilized, the oil sludge enters the pyrolysis stage, and the heavy oil components in the oil sludge start to continuously crack into light hydrocarbons and

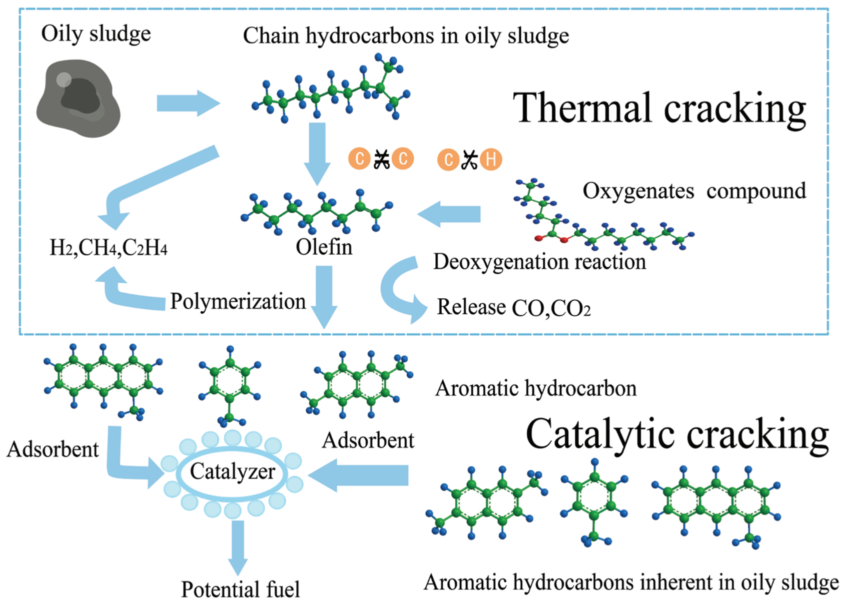

Figure 4: Mechanisms of microwave pyrolysis.

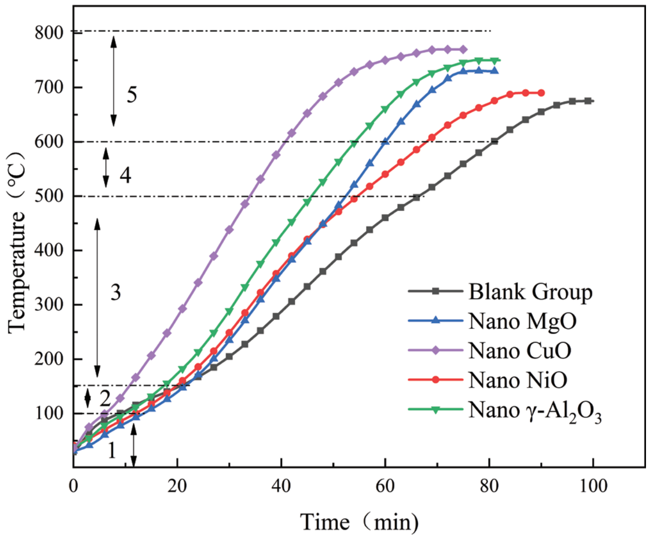

Figure 5: The heating curve of sludge during microwave pyrolysis.

Figure 6: Real-time temperature phenomena during microwave pyrolysis of sludge.

small molecular compounds. At 500°C, the reaction is severe, and a large amount of smoke is generated at the tail of the condensing tube, which may contain H_2S, NO, and other harmful gases. When the temperature reaches 600°C, the reaction becomes gradually stable, and the flue gas basically dissipates. It then enters the final stage of sludge pyrolysis - carbonization, and the carbonization reaches almost 750°C to maintain the temperature equilibrium, and stabilizes.

It can be seen from Figure 5 that the heating rate and final pyrolysis temperature change with respect to the catalyst type, and the order of the final pyrolysis temperature from high to low is: nanometer CuO >

nanometer γ-Al_2O_3 > nanometer MgO > nanometer NiO > blank group. It can also be seen that nano-CuO has good wave absorption. However, its high temperature pyrolysis, which will form a large number of defects in its crystal structure. This is conducive to the adsorption of materials and improvement of the absorption efficiency. The other nano-metal oxides used as microwave absorbers, can effectively shorten the pyrolysis time and increase the final temperature and heating rate of pyrolysis.

3.3. Influence of the nano metal oxide type on the yield of pyrolysis products

Figure 7 shows the influence of different nano-metal oxides on the distribution of pyrolysis gas, pyrolysis oil, and solid residue of oily sludge. The results show that the type of microwave absorbent has a significant effect on the products after microwave pyrolysis of oily sludge. Compared with the blank group, the addition of nano-MgO gas in the process of microwave pyrolysis of oily sludge significantly increases the gas yield, reaching its highest value of 41.2% under high temperature pyrolysis, which is increased by 17.8% compared with the blank group. The increase of gas yield is closely related to the decrease of solid residue yield. After adding CuO nanoparticles, the yield of pyrolysis oil becomes 30.6%, which is 9.5% higher than that of the blank group. The gas production from high to low is: nano-MgO > nano-γ-Al_2O_3 > nano-CuO > nano-NiO > blank group. The oil production from high to low is: nanometer CuO > nanometer γ-Al_2O_3 > nanometer NiO > blank group > nanometer MgO.

All the obtained results showed that using nanometer metal oxide as a microwave absorbent, in addition to nanoscale MgO style, the pyrolysis oil production rate is less than the blank group. In addition, the rest of the group of pyrolysis oil and pyrolysis gas production rate is improved. However, the gas rate is significantly increased with the nanoscale MgO style group. This is due to the fact that after joining nanoscale MgO style to promote the oil into the next phase of evaporation, secondary cracking or thermal decomposition occurs. Compared with other catalysts, nano-metal oxides can absorb more microwave energy and convert it into heat energy [13], which improves the pyrolysis temperature and heating rate. The rapid pyrolysis of oily sludge also contributes to the production of oil fractions.

3.4. Gas composition

Figure 8 shows the change of composition of non condensable gas produced by microwave pyrolysis of oily sludge after adding different nano metal oxides as catalysts. It can be seen that CO_2, H_2, CO, and CH_4 are the main gas components of the pyrolysis gas [18]. The content of CO_2 and H_2 is high, and that of light hydrocarbons (C_xH_y) is low. Compared with the blank group, after adding different types of nano metal oxides, the total content of combustible gas (H_2 + CH_4 + CO) is increased, as shown in Figure 9. This demonstrates that nano metal oxides play an important role in microwave catalytic cracking of oily sludge.

3.4.1. Catalytic cracking of oily sludge on nano-MgO

After adding nano MgO, the content of H_2 significantly increased and became 8.28wt% higher than that of the blank group. The water content of oily sludge was high, and the water molecule itself can also participate in the

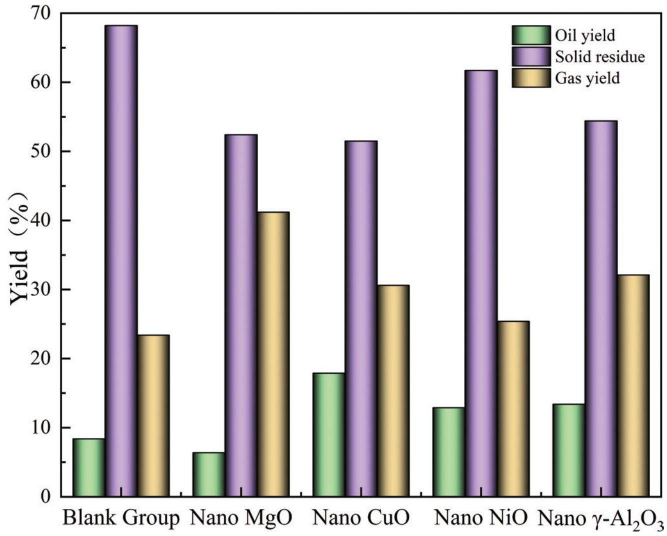

Figure 7: Product distribution after microwave pyrolysis of oily sludge under different catalysts.

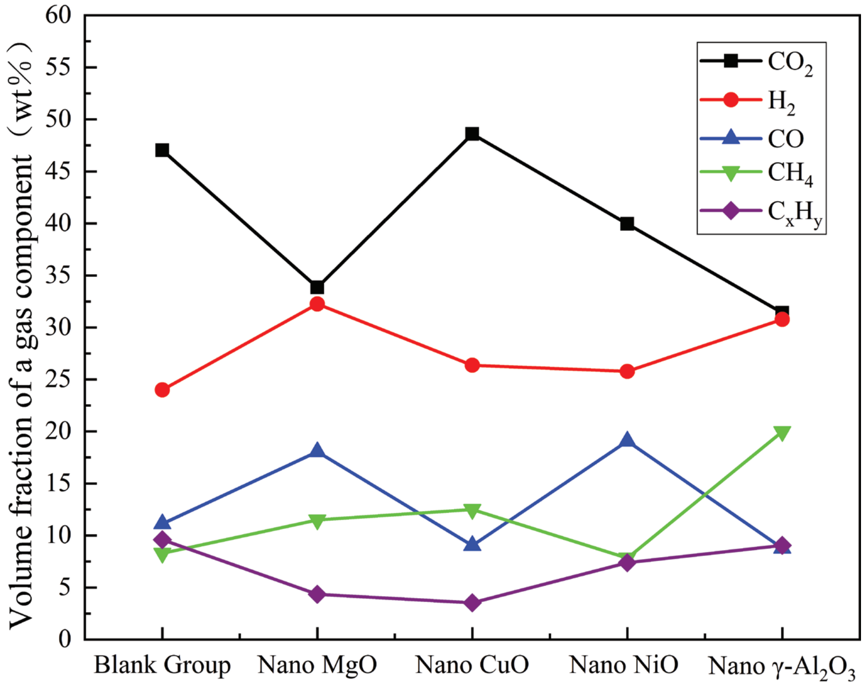

Figure 8: Impact of different nano-metal oxides on the gas composition.

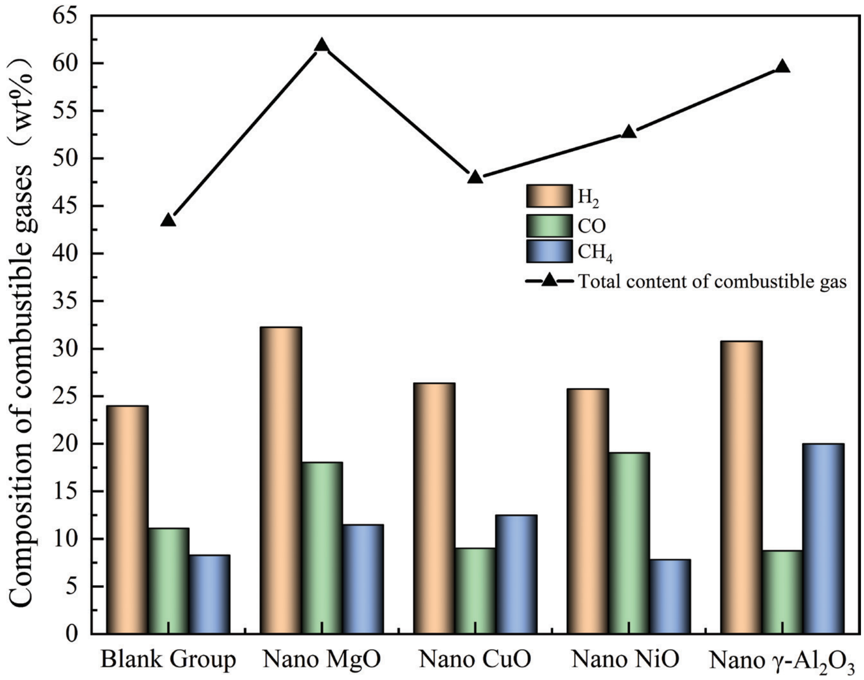

Figure 9: Content of combustible gas components in pyrolysis oil.

reaction in the cracking process. Therefore, the catalytic cracking of oily sludge on nano MgO can be considered as the water gas reaction and steam reforming reaction of hydrocarbons. The pre-pyrolysis nano-MgO was characterized by X-ray diffractometer (XRD) as shown in Figure 10 , and the scanning angle was 2θ: 20°~80°, two-phase MgO and Mg $(OH)_3$ were detected in nano-MgO and Mg $(OH)_3$ was detected in non-used nano-MgO, indicating that MgO is easy to absorb water deterioration during storage, Mg $(OH)_3$ was formed, and the formed Mg $(OH)_3$ trapped and absorbed the CO_2 in the gas products during the pyrolysis reaction, resulting in the decrease of CO_2 content in the pyrolysis gas after adding nano-MgO. A sharp diffraction peak is observed at about 2θ = 42 of the MgO phase. The results show that the MgO phase plays a dominant role in the pyrolysis reaction. The addition of nano MgO promotes the steam reforming and water gas reaction of light hydrocarbons,

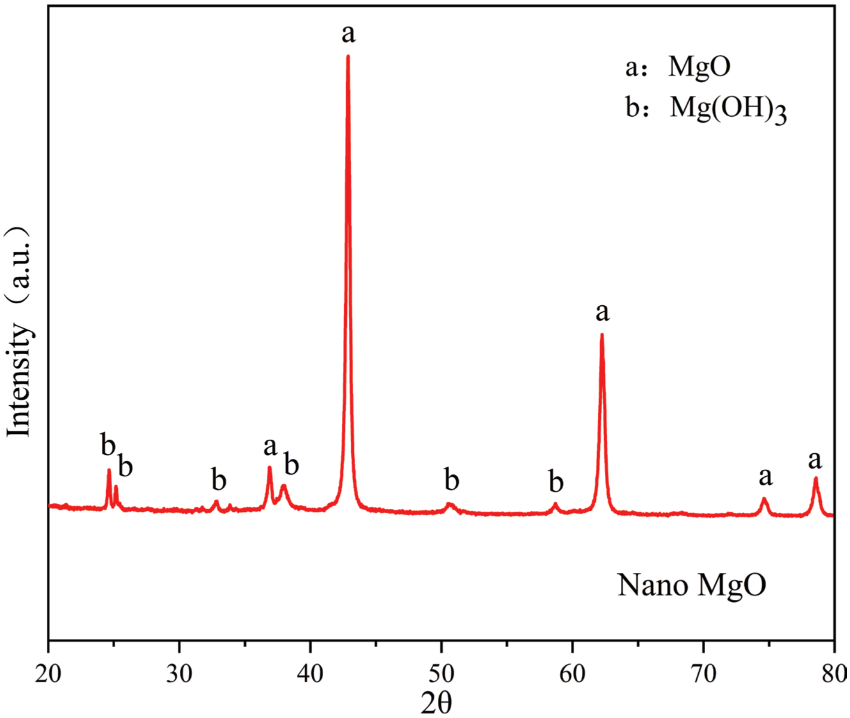

Figure 10: XRD spectrum of nano MgO before pyrolysis reaction.

as shown in Equations (1) and (2). Therefore, the content of CO and H_2 has increased after the addition of nano MgO. However, the CO_2 content has decreased. As shown in Equation (3), nano MgO has an adsorption capacity. Compared with conventional MgO, it has a higher density of basic sites on the surface. In addition, it has a higher adsorption capacity for CO_2, and can capture the generated CO_2. Therefore, the CO_2 content decreased [19], which solves the problem of greenhouse gas emission after pyrolysis of oily sludge.

$$C_xH_y + xH_2O \rightarrow xCO + \left(\frac{x+y}{2}\right) H_2 \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

$$MgO + CO_2 \rightarrow MgCO_3 \tag{3}$$

3.4.2. Catalytic cracking of oily sludge on nano-NiO

The addition of nano-NiO resulted in higher gas yield, and the combustible gas accounted for more than 50% of the total gas produced by microwave pyrolysis of oil sludge. Compared with the blank group, the contents of H_2 and CO increased, while those of CO_2 and CH_4 decreased. Nano-NiO contributed to the cracking of light hydrocarbon organic matter and promoted CO_2 reforming (Equation (4)) and steam reforming (Equation (1)) [20]. Moreover, the nano-NiO had a high thermal conductivity, and can dissipate microwave energy through joule heating effect.The pre-pyrolysis nano-NiO was characterized by XRD, as shown in Figure 11. From the Figure 11, it can be seen that nano-NiO only has a single phase of NiO, and does not have characteristic peaks of other oxides, the characteristic derivative peaks of NiO were detected at $2\theta = 38.24°$, 44.56°, 64.35°, 76.87°, 79.52°. The obtained results show that the content of CH_4 decreased and that of CO increased after the addition of nano-NiO for microwave catalytic pyrolysis, which indicates that nano-NiO had a good catalytic activity for CO_2 reforming and steam reforming. During the catalytic process, nano NiO is reduced to elemental Ni by reducing gases such as H_2 and CO [21]. The element Ni is then used as the main catalytic active site for tar cracking and plays a major role in tar decomposition. It is worth noting that the addition of nano NiO leads to higher yields of CO and H_2. Syngas is mainly composed of CO and H_2, which has high calorific value and is widely used in various industrial fields. In industry, this method can be considered to produce combustible gas, for example, water gas is mainly composed of H_2 and CO, because the unique characteristics of microwave heating, the introduction of NiO as a catalyst during the pyrolysis of sludge to produce water gas, clean gases such as H_2 and CO can be purified by gas membrane separation. The gas membrane separation also depends on the effect

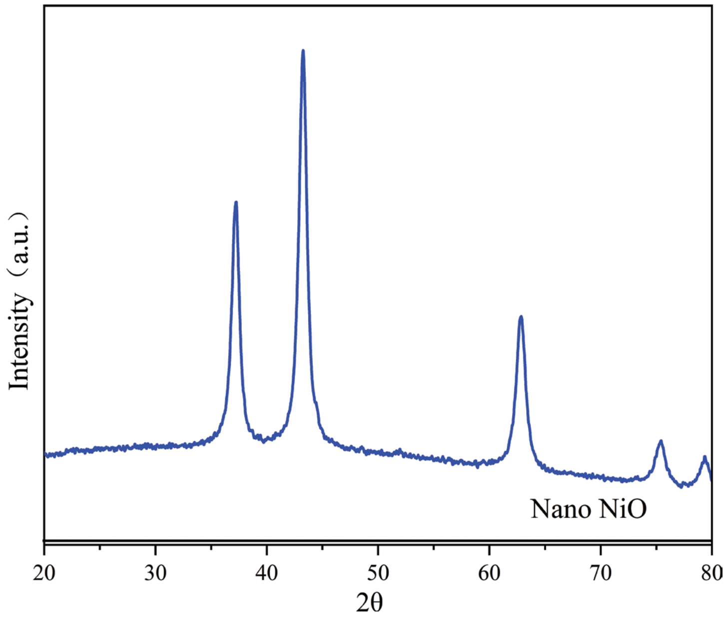

Figure 11: XRD spectrum of nano NiO before pyrolysis reaction.

of pressure difference and the selective permeability of the membrane. The permeation rate of different gases in the gas mixture in the separation membrane is very different, thus, the separation of different components of the mixed gas can be realized. The separation membranes used are mainly asymmetric membranes and polymer composite membranes with high permeation flux and high mechanical strength. The separation of CO and H_2 in gas mixture can be accomplished quickly by using the difference of selectivity and permeability of different gas molecules in polymer membrane. In the process of gas membrane separation technology, the high concentration gas mixture containing various gas components enters the membrane separation component after pretreatment. Because of the different penetration rate of the membrane, the gas with faster penetration rate quickly reaches the other side of the membrane, while the gas with slower penetration rate is trapped, thus achieving the goal of gas separation. Polymer membranes have strong selectivity and different gas permeation rates. If this method is used to extract and separate CO and H_2 from mixed pyrolysis gas to prepare water gas, it has advantages such as low investment, low energy consumption, and simple operation, creating good economic and social benefits. Compared with traditional methods for producing water gas, it not only meets environmental requirements, but also reduces costs and process conditions. It has important practical significance for efficient and clean conversion and utilization of waste oil sludge.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{4}$$

3.4.3. Catalytic cracking of oily sludge on CuO and γ-Al_2O_3 nanoparticles

The contents of H_2 and CH_4 are increased after the addition of nano-CuO and γ-Al_2O_3. It can be deduced from the heating curve in Figure 5, that nano-CuO and γ-Al_2O_3 have good absorbing property. As shown in Figure 12, CuO and γ-Al_2O_3 both have a porous structure. In addition, their appropriate porosity can provide channels for microwave incident materials, which is conducive to improving the impedance matching between the absorber and electromagnetic wave. The impedance matching is crucial for increasing the microwave absorption performance, and it can reach higher temperature in a short time. Due to the fact that the C-C bond can easily break and the C-H bond is difficult to break at low temperature, nano CuO and γ-Al_2O_3 are added to absorb microwave, which rapidly increases the reaction temperature, accelerates the C-H bond fracture, and promotes the dehydrogenation reaction [22], thus increasing the H_2 content. Such nano-metal oxides with good absorbability can promote the hydrocarbon in the catalytic cracking of sludge, the aliphatic chain break and secondary cracking reaction. They can also lead to the increase of the content of the small molecule hydrocarbon CH_4. Moreover, the high temperature also promotes the cracking of hydrocarbons, and therefore the CH_4 content is increased after the addition of these two catalysts. However, it is important to mention that the reduction of CO content after the addition of nano-CuO is due to the REDOX reaction of nano-CuO in the presence of CO at high temperature, precipitating copper powder, as shown in Equation (5). This is also confirmed that the nanometer CuO and γ-Al_2O_3 have good catalytic activity on cracking tar component in oil sludge at high temperature.

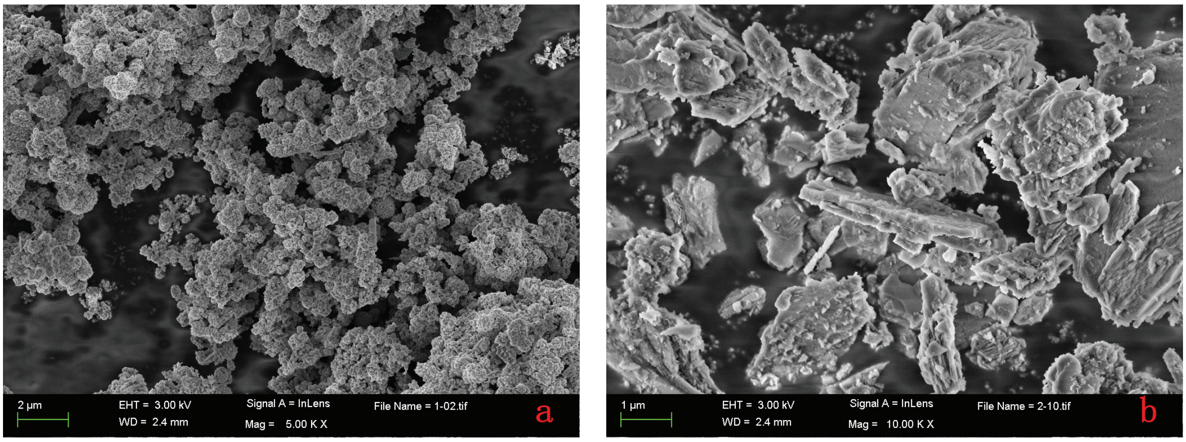

Figure 12: Nano CuO and Nano γ-Al_2O_3 SEM characterization.

3.5. Oil composition

3.5.1. Impact of nano-metal oxides on the pyrolysis oil composition

In this paper, the component content of pyrolysis oil was detected by GC-MS. The component content results are shown in Figure 13. The main components of pyrolysis oil are alkanes, alkenes, aromatic hydrocarbons, in addition to a small amount of aliphatic compounds, cycloalkanes, and cycloalkenes, which can be divided into light components and heavy components. The light weight group was C_4-C_{12} and C_{13}-C_{18}, and the heavy weight group was greater than C_{19}. It can be seen from Figure 8 that after the addition of nano-MgO, nano-CuO, and γ-Al_2O_3, the heavy component content of pyrolytic oil significantly decreased, while the light component content increased. Compared with the blank group, the light components increased by 8.254%, 10.675%, and 11.473%, respectively. This is due to the fact that nano-metal oxides can reduce the degree of polycondensation of aromatic rings [23] and increase the light components in pyrolysis oil. Compared with the blank group, the content of light components of nano-γ-Al_2O_3 increased the most. Nano-γ-Al_2O_3 was more acidic and can share more acidic sites. These acidic sites can effectively reduce the Ea required for frequency band opening. Therefore, more light components were generated. Based on the molecular composition of nano-metal oxides, the particle size of nano-γ-Al_2O_3 used in this study was 150–500 nm, which is larger than other nano-metal oxides. Studies have shown that the thermal conductivity increases with the increase of the nano-size. Therefore, the thermal conductivity of nano-γ-Al_2O_3 increases faster, the catalytic effect is satisfactory, and the heavy oil component in the oil sludge is rapidly cracked. More light components are then generated. However, it is important to mention that after adding nano NiO, the pyrolysis oil increased instead of heavy metals, and the light component was reduced. According to the study on the help of NiO for aromatic hydrocarbon to be converted to aliphatic hydrocarbons [23], under a certain temperature, adding nano NiO can make C-H bond rupture, increase the rate of low carbon number of aromatic hydrocarbon cracking, and reduce the light component. From the perspective of cracking effect, after the addition of nano-oxide, the content of straight-chain hydrocarbon with low carbon number increases, while that of straight-chain hydrocarbon with high carbon number decreases. This demonstrates that nano-metal oxide has a significant promoting effect on the cracking of heavy oil, and the higher the content of straight-chain hydrocarbon, the better the quality of pyrolysis oil [24]. Furthermore, it is proved that adding nano-metal oxides, such as nano-MgO, nano-CuO, and nano-γ-Al_2O_3, can improve the content of light components of pyrolysis oil and optimize its quality.

3.5.2. Impact of nano-metal oxides on the content of alcohols in pyrolysis oil

After the addition of nano-metal oxide catalyst, the components in the pyrolysis oil were semi-quantitatively analyzed according to the chromatographic peak area after GC-MS detection [25], and the obtained peak area content was the relative component content in the oil pyrolysis oil. Through this analysis, the content of each component in the pyrolysis oil was determined. Shown in Figure 14, the main components of alcohols in the pyrolysis oil include 1-22-docoediol, 19-alkanol, 1-16-alkanol, and stearol. It was deduced that the total content of alcohols in the pyrolysis oil was increased after the addition of nano-metal, and the maximum content of alcohols in nano-MgO was 10.723%. However, the stearol content decreased. Stearol alcohol belongs to microtoxic substances, which will cause minor damage to human skin and mucous membrane, as well as water pollution. The addition of nano-metal oxides promoted the transesterification of stearol and lipids in the pyrolysis

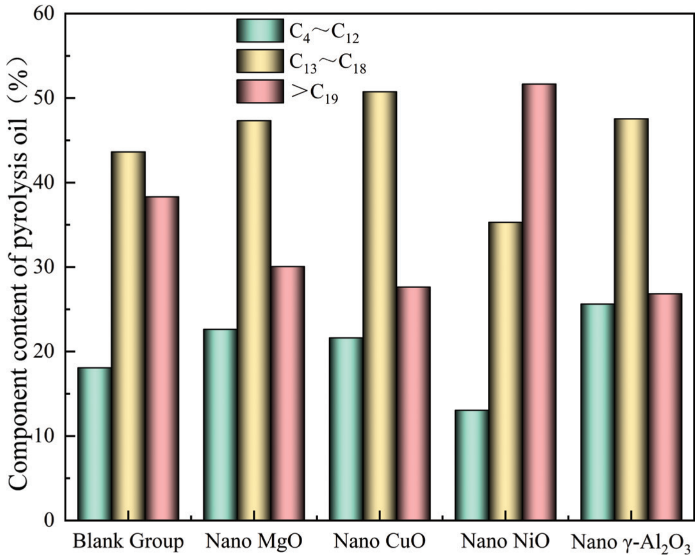

Figure 13: Carbon number distribution of pyrolysis oil after adding different nano metal oxides.

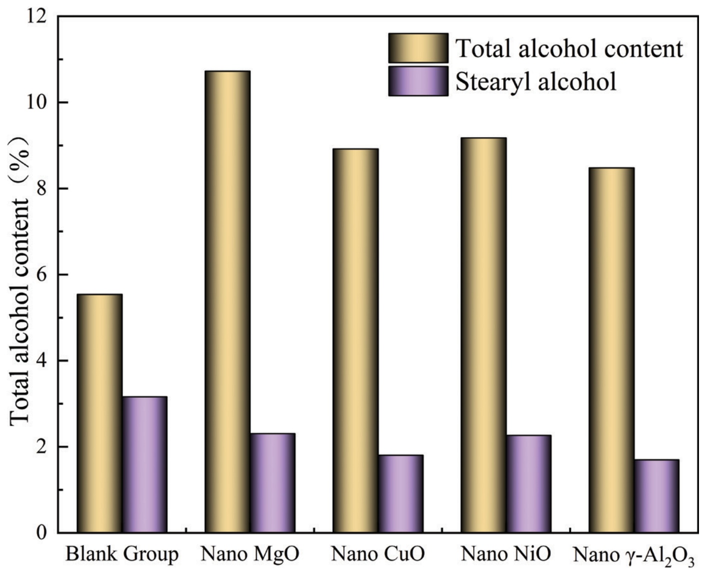

Figure 14: Impact of adding different nano-metal oxides on the content of alcohols in pyrolysis oil.

oil, reduced the stearol content to a small extent, and reduced the harmful substances in the pyrolysis oil. Except the stearol that was decreased, the contents of the other alcohols in the pyrolysis oil were increased. These alcohols can further optimize the quality of oil, such as 1–16-alkanol used in the production of surfactants, as well as lubricants. 19-alkanol can be used as a solid skin moisturizer to help disperse pigment. Therefore, nano-metal oxides can be used as catalysts to increase the total content of alcohols and reduce the content of stearol, which is beneficial for the optimization of the pyrolysis oil quality.

4. CONCLUSION

By analyzing the characteristics of pyrolysis products, this study proved the feasibility of the addition of nano metal oxides to oily sludge in order to induce microwave pyrolysis, and further studied the impact of nano metal oxides on the oil sludge at the tank bottom of microwave pyrolysis refinery plant. The following conclusions were drawn:

(i) Nanometer metal oxides affect the heating process and product distribution. The heating rate and final temperature of oil sludge during microwave pyrolysis were increased. From the perspective of wave absorbing property, nano CuO has good wave absorbing property, which increases the final pyrolysis temperature to 770°C and shortens the pyrolysis time to 67 min. The oil and gas yields were improved by adding nano metal oxides.

(ii) In terms of the catalytic effect, the content of H_2 significantly increased after the addition of nano MgO, which indicates that MgO promoted the steam reforming of light hydrocarbons and water gas reaction. The addition of nano NiO leads to higher yields of CO and H_2. The nickel-based catalyst has higher decomposition activity, which is conducive to the cracking of light hydrocarbon organics. Moreover, when adding nano CuO and γ-Al_2O_3, the content of H_2 and CH_4 increased. It is suggested that nano CuO and γ-Al_2O_3 should be compounded in proportion to prepare composite catalyst, in order to further increase the combustible gas content.

(iii) For pyrolysis oil components, when adding nano metal oxides, such as nano MgO, nano CuO, and nano γ- Al_2O_3, the content of light components (C_4-C_{12} and C_{13}-C_{18}) increases, and that of heavy components (greater than C_{19}) decreases. This shows that the nano metal oxides can effectively promote the decomposition of asphaltene in sludge, generate more straight chain hydrocarbons and alcohols having a low carbon number, and improve the pyrolysis oil quality.

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