Research Progress of Sludge Pyrolysis Catalysts

Lei Han¹, Faguo Chong², Zhiqiang Guo², Chao Wang², Zhibin Wu², Tao Yu¹, Chengtun Qu¹,*

¹College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Shaanxi Oil and Gas Pollution Control and Reservoir Protection Key Laboratory, Xi'an 710065, China
²Xi'an Changqing Science and Technology Engineering Co. LTD, China

* Corresponding author email: Wangshuangct@yeah.net

Abstract. Sludge treatment has become one of the most important challenges in environmental protection. With the improvement of sludge treatment standards, the environmentally-friendly and efficient pyrolysis technology developed has a good development prospect. The addition of catalyst is one of the important conditions affecting sludge pyrolysis. This paper introduces the influence of different kinds of catalysts on pyrolysis, and summarizes their advantages and disadvantages.

1. Introduction
With the rapid economic development, the output of sludge has also increased substantially. The environmental pollution caused by sludge has become increasingly prominent, which has caused great safety hazards, environmental pressures and economic burdens [1]. It is predicted that according to the effective sewage treatment rate, the sludge output in 2020 will reach 120 million tons [2]. The treatment of sludge in my country has become one of the most significant challenges in environmental protection [3]. The traditional final disposal methods of sludge are mainly incineration, composting, and land cultivation. The incineration method is more thorough, but the facility investment is large and the treatment cost is high. The incineration of organic matter may produce dioxin and other highly toxic substances, which may cause secondary pollution to the environment. Composting has low processing cost, but requires a large area, long processing time, and heavy metals will accumulate in plants and pollute the soil. Although the land cultivation method has low cost and large processing capacity, it requires a large area of land and the degradation process is slow. It is not suitable for use in areas with long winters. It is time-consuming and secondary pollution caused by VOCs may pollute groundwater [4]. The traditional methods have their own limitations. Therefore, with the improvement of sludge treatment standards, the environmentally friendly and efficient pyrolysis technology developed to achieve the goal of sludge treatment reduction, stabilization, harmlessness, and recycling has attracted widespread attention [5]. In addition to the traditional pyrolysis process, many new sludge pyrolysis processes have emerged, such as microwave pyrolysis process and supercritical pyrolysis process [6-7]. The so-called sludge pyrolysis is the chemical process of heating the sludge under anaerobic or anaerobic conditions to transform it into gaseous, liquid and solid products [3]. So far, the mechanism of pyrolysis is not very clear. Taking the pyrolysis of oily sludge as an example, it is generally believed that the pyrolysis process goes through the following stages: (1) Drying and degassing stage (50-180°C), during which moisture And other volatile components evaporate; (2) light oil volatilization stage (180-
370℃), when the pyrolysis reaction of oil sludge begins; (3) heavy oil thermal decomposition stage (370-500℃) The crude oil generally starts to crack at around 370 °C, and the condensation reaction also accelerates; (4) this coking stage (500-600 °C) and mineral decomposition stage (> 600 °C)[8]. In the pyrolysis process, in addition to the characteristics of the pyrolysis sludge itself, the pyrolysis conditions have a greater impact on the pyrolysis products, and the addition of catalyst is one of the most important conditions affecting the pyrolysis process.

This study reviews the types of catalysts in the process of sludge pyrolysis technology, and compares their advantages and disadvantages, in order to provide a reference for the optimization and improvement of catalysts for sludge pyrolysis technology in my country.

2. Sludge pyrolysis catalyst

| Classification       | Catalyst                                                                 |
|---------------------|--------------------------------------------------------------------------|
| Pyrolysis residue   | Residue from pyrolysis of sludge itself                                  |
| Metal oxide         | Fe₂O₃, Al₂O₃, CaO, MgO, CuO, Fe₃O₄, ZnO, Al₂O₃, TiO₂, etc.               |
| Salt                | NaCl, Na₂CO₃, Na₂SO₄, KCl, MgCl, CaCl₂, ZnCl₂, CaCO₃, etc.               |
| Natural minerals    | Dolomite, activated clay, high alumina bauxite, kaolin, etc.            |
| Solid Waste         | Coal gangue, iron tailings, fly ash, red mud, etc.                      |
| Others              | Molecular sieve, biomass, homemade pyrolysis catalyst, etc.             |

These catalysts can promote the pyrolysis of sludge to a certain extent, but due to the specificity of their action, they have different effects on the oil and residue after pyrolysis. For example, the pyrolysis residue needs to be pretreated before use, and the efficiency is not high; the catalytic effect of metal oxides mostly occurs at medium and high temperature (>600°C); the salt catalysts are mainly potassium and sodium salts, which are affected by sodium and potassium salts. The limitation of types is difficult to apply to oily sludge with complex composition and diverse sources; natural minerals and solid wastes also have the problem of insufficient efficiency as catalysts. Therefore, the above five types of sludge pyrolysis catalysts were compared and analyzed.

2.1. Sludge pyrolysis residue catalyst

Currently, there are many types of sludge pyrolysis catalysts. Most researchers are dedicated to developing and synthesizing new sludge pyrolysis catalysts to improve pyrolysis efficiency, but they have not considered the cost of the catalyst and the possibility of large-scale application. Therefore, the use of pyrolysis residue as a catalyst for sludge pyrolysis has certain advantages.

The pyrolysis residue of sludge is rich in carbon and a small amount of metal elements. The rich carbon element in the residue gives it a loose porous structure, forming a pore structure dominated by mesopores and supplemented by micropores. Using the good specific surface area and chemical inertness of the sludge pyrolysis residue as a catalyst for the pyrolysis process not only has a good effect, but also achieves the concept of waste treatment, which is more conducive to the research of pyrolysis technology resource utilization [8]. Gao Minjie et al [9]. Analyzed the pyrolysis residue produced by the pyrolysis of sludge and found that the residue has a richer specific surface area and a microstructure of large and mesopores. Using pyrolysis residue as a pyrolysis catalytic material is not only beneficial the recycling of sludge pyrolysis saves treatment costs and reflects the superiority of pyrolysis residue as a catalyst. Zheng Yongjie et al. [10] compared the pyrolysis residue with copper oxide and iron oxide catalysts, and found that the use of pyrolysis residue as a catalyst for pyrolysis of municipal sludge yielded higher oil yield and the best cracking effect. Liu Longmao et al. [11] studied the pyrolysis of pyrolysis residues at different pyrolysis temperatures and found that the yield of pyrolysis oil increased by 4.5% compared with no catalyst. Zhang Ya et al. [12] studied the effect of pyrolysis residue on the catalytic pyrolysis of municipal sludge, and found that adding the residue is more conducive to the hydrideoxygenation of the organic phase and the removal of chlorine-containing compounds. Chen Li et al. [13] used the pyrolysis residue as a catalyst for pyrolysis of sludge and found that the pore structure
of the pyrolysis residue was more developed than that of pure sludge, which made it have the potential for development and application as an adsorbent. Liu Wenwen et al. [14] found that the ash surface of the sludge is not smooth, and its morphology is irregular pore structure, and there are irregular pores between particles. This morphology and structure feature provides an effective transmission for the pyrolysis process. The quality space can be used as a catalyst carrier. Therefore, CuO-loaded pyrolysis residue is used as a catalyst for sludge pyrolysis. The results show that the copper oxide-loaded sludge pyrolysis residue not only greatly reduces the temperature of pyrolysis, but also has an oil yield of up to 27.72%.

To sum up, because the pyrolysis residue not only contains heavy metal elements remaining after pyrolysis of sludge, but also has irregular pores between particles and a large specific surface area, which makes the residue have greater catalytic activity. In addition, the main component of the pyrolysis residue is carbon, so that it can be used as a catalyst support body, and its catalytic performance can be enhanced by modifying or modifying it.

2.2. Metal oxide catalyst

In recent years, the use of metal oxides as sludge pyrolysis catalysts has been extensively studied. Zhihang Huang et al. [15] studied the Fe2O3 catalytic pyrolysis process in a fixed-bed reactor at 400-600°C and found that when Fe2O3 equal to 5% was added to the dry sludge, the gas yield increased by 2.93%. The yield of hydrolysis oil increased by 6.2%, while the yield of pyrolysis residue decreased by 9.13%. At the same time, it was found that Fe2O3 is beneficial to promote the formation of CO and H2 and inhibit the formation of CH4. Zheng Yongjie et al. [10] studied CuO, Fe3O4 and pyrolysis residues to catalyze the extraction of organic matter from municipal sludge. Through orthogonal experiments, they found that the highest oil yields after pyrolysis of Fe3O4 and CuO were 23.42% and 22.54%, respectively. Chen Li et al. [13] used CaO as a catalyst, and compared with no catalyst, the H2 yield increased by 80%. The addition of CaO was beneficial to the increase of CO and H2 yields. Shiwen Fang et al. [16] used MgO, ZnO, Al2O3 as catalysts for the co-pyrolysis of municipal solid waste and papermaking sludge, and found that both can reduce the initial pyrolysis temperature and activation energy of the samples, and the effect is MgO>Al2O3>ZnO.

In addition, pyrolysis oil contains a large number of macromolecular aromatic compounds, such as polycyclic aromatic hydrocarbons (PAH), which causes pyrolysis oil to be considered environmentally unfriendly [17]. Yanjun Hu et al. [18] used CaO, Na2CO3 and Fe2O3 as the catalyst for pyrolysis of sludge. It is found that it can effectively inhibit the formation of polycyclic aromatic hydrocarbons (PAHs) in pyrolysis oil and reduce the toxic equivalent (TEQ) of PAHs. When Jingai Shao et al. [19] studied the pyrolysis of sewage sludge by metal oxides, they found that the presence of Fe2O3 and ZnO inhibited the decomposition of organic matter in sludge samples, and the solid phase yield increased. And Al2O3 and TiO2 are beneficial to reduce the pyrolysis time.

Sun et al. [20] used self-made composite alumina (complex material formed from alumina particles with a diameter of 0.3-0.5 mm in a biomass fluidized bed at about 850°C) as a catalyst for sludge pyrolysis and found the presence of composite alumina can enhance secondary cracking. In addition, the effect of composite alumina on the decomposition of fatty acids and the formation of aromatic compounds is similar to temperature. This means that the reaction temperature can be reduced by introducing composite alumina (CA), which has a positive effect on reducing energy consumption. Zhu Guangguang et al. [21] studied the catalytic pyrolysis reaction by thermogravimetric analysis and found that the catalyst not only reduced the initial and final temperature of pyrolysis, but also peaked in the high temperature section, indicating that CaO and Na2CO3 as catalysts can promote pyrolysis in the high temperature section the reaction proceeded and the reaction time was shortened. Rui Ma, et al. [22] studied the effect of catalysts on the conversion of organic matter and biofuel production during microwave pyrolysis of sludge, and found that adding CaO and Fe2O3 to the microwave pyrolysis system can improve the yield and quality of biogas and bio-oil.
To sum up, due to the difference of metal oxides, there is a big gap in catalytic effect and performance, and its catalytic effect generally occurs in the medium and high temperature area (>600 °C), which consumes a lot of energy and requires further research by scholars.

2.3. Salt catalyst

Hu et al. [18] proved that adding appropriate salt catalysts is beneficial to control the formation of polycyclic aromatic hydrocarbons (PAHs). The catalytic pyrolysis of 20% KCl and 20% Na2CO3 significantly inhibited the formation of PAHs. The results are consistent with previous studies (Pawlak-Kruczek et al., 2018) [23], indicating that the addition of salt during pyrolysis prevents the production of more aromatic compounds. When PAHs are classified by the number of rings, the influence of catalyst loading on the formation of PAHs is as follows: When KCl is used as the catalyst, the maximum concentration of low-ring PAHs is observed at 10% loading, and the middle ring and the concentration of high-ring PAHs is the largest. But under a load of 20%, the concentration of all PAHs is at the lowest level. Therefore, the catalyst loading is one of the factors that affect the degree of the pyrolysis reaction. The right amount of catalyst can help to completely pyrolyze the heavier molecules into light hydrocarbons and chemically convert polycyclic aromatic hydrocarbons into other molecules. The use of KCl and Na2CO3 can increase the output of pyrolysis oil. And in inhibiting the generation of PAHs in pyrolysis oil and reducing TEQ, loading 20% Na2CO3 in sludge proved to be the most effective. Eilhann E. Kwon et al. [24] showed that CaCO3 can not only increase the production of carbon monoxide, but also reduce the content of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge pyrolysis products. CO2 derived from CaCO3 enhances the thermal cracking of volatile organic carbon generated during the pyrolysis of sewage sludge, and provides additional sources of C and O, which will increase the production of CO above 650 °C. In addition, by adding CaCO3 in the pyrolysis of sewage sludge, more solid products can be converted into gaseous and liquid products. Studies have shown that CaCO3 can be used as a cheap source of CO2, improve the thermal efficiency of the pyrolysis process, and reduce the release of harmful chemicals (PAHs) in by-products in municipal and industrial processes. Therefore, the use of CaCO3 as an additive in pyrolysis raw materials can improve the thermal efficiency of the pyrolysis process and has environmental benefits. Liu Wenwen et al. [14] used CuCO3 and CuCl2 as the catalyst for pyrolysis of sludge. The results show that it has a good catalytic effect on low-temperature catalytic pyrolysis of sludge, which can reduce the temperature of sludge pyrolysis and reduce the energy consumption of pyrolysis.

In summary, the current salt catalysts have a superior effect on the pyrolysis of sludge. The current impact of sodium, potassium, and calcium salts on pyrolysis is mainly to improve the quality and yield of pyrolysis oil and reduce the pyrolysis temperature. However, other salt compounds (copper salts, etc.) have little effect on the composition of oil products.

2.4. Natural mineral catalyst

Wang Feifei et al. [25] used 5% and 10% HCl to modify activated clay for pyrolysis of sludge. The analysis found that the yield of pyrolysis oil was greatly improved, and the pyrolysis time was also reduced. From the analysis of pyrolysis oil components, it can be seen that catalytic pyrolysis increases the recovery rate of C6-C15, and the quality of pyrolysis oil is also improved. Sun Yu [26] used a fixed-bed catalytic pyrolysis device to study the catalytic pyrolysis of municipal sludge by high alumina bauxite particles and typical components of the loaded biomass ash, and analyzed the product yield and the organic phase of pyrolysis oil and found that high alumina Alumina promotes the secondary cracking of pyrolysis gas, making oxygen-containing organics more prone to decarboxylation, decarbonylation reaction to generate aliphatic hydrocarbons, and further cyclization and aromatization to produce more aromatic compounds. Under the condition of high alumina bauxite as a catalyst, the oxygen-containing compounds in the organic phase of the pyrolysis oil decreased by 5.10% and the aromatic compounds increased by 9.74%, indicating that the high alumina bauxite has a catalytic deoxidation effect on the pyrolysis gas. And for the high bauxite supported by KCl, increasing the temperature and the height of the material layer can enhance the catalytic effect, not only inhibits the aromatization reaction at high
temperatures, but also increases the amount of hydrocarbons in the pyrolysis due to the presence of potassium ions. Content. Hu Haijie et al. [27] used cheap and easily available kaolin as a catalyst for the pyrolysis of oily sludge, and loaded active metals on the kaolin. Through the analysis of the effect of sludge pyrolysis, they found the recovery rate and oil yield of pyrolysis oil. All have a certain catalytic ability but the effect is not obvious, and the catalytic performance is greatly improved after the active titanium metal is loaded. The recovery rate of pyrolysis oil has increased by 4.58%. At the same time, the gas-liquid components in the pyrolysis products are analyzed and found that the oil produced by pyrolysis is mainly C_{16}-C_{20}. After adding the catalyst, the heavy oil component is significantly reduced, and the light component content increases. At the same time, with the pyrolysis time the content of CH_{4} produced by prolonged pyrolysis gradually decreases, while the content of CO_{2} increases. Zhu Guangquan et al. [21] found through studying the pyrolysis of sludge that when pyrolysis alone, the effect of the catalyst on the activation energy of sludge pyrolysis is in the order of mixed>dolomite>CaO>Na_{2}CO_{3}. It proves that the catalytic performance of dolomite to sludge is relatively good.

Although natural minerals have a certain catalytic ability for pyrolysis of sludge, they have the problem of low catalytic efficiency. A series of treatments such as acidification and loading are often required to increase their catalytic ability and increase the cost of pyrolysis.

2.5. Solid waste catalyst

Research has found that coal gangue, iron tailings, fly ash and other mining solid wastes used as catalysts for sludge pyrolysis can not only increase the sludge pyrolysis gas-liquid yield, but also improve the sludge reduction effect. In addition, solid waste is used as sludge pyrolysis catalyst, and the quality of gas-liquid products is also better [28].

Some scholars have studied the catalytic mechanism of red mud (RM), the polluting waste slag discharged from the extraction of alumina in the aluminum industry, on the pyrolysis of sewage sludge. By using the discrete distributed activation energy model (DAEM), the three main components (Fe_{2}O_{3}, Al_{2}O_{3}, SiO_{2}) in red mud (RM) have been used to clarify the influence of the pyrolysis of organic matter in sewage sludge [29]. The simulation results show that in RM the Fe_{2}O_{3} and Al_{2}O_{3} promoted the pyrolysis of organic matter in the high temperature stage. The pyrolysis experiment of the original sludge with different additives at 600, 700, 800 and 900 C showed that the red mud (RM) can reduce the main the final temperature of the decomposition stage and shorten the decomposition time. Compared with the original sludge, red mud (RM) reduced the average activation energy of pyrolysis by 20.09 kJ mol^{-1} respectively. The Fe_{2}O_{3} and Al_{2}O_{3} in red mud (RM) can increase the production of H_{2} by catalyzing the cracking of C—C and C—H bonds in the tar reforming reaction. Fe_{2}O_{3}, as a transition metal, can form unstable intermediates with pyrolysis products. This leads to changes in the distribution of electrons outside the C atom and reduces the binding energy of the decomposition of the C—C bond to release more gas. This improves the gas yield. In addition, the coke produced from the pyrolysis of sewage sludge containing red mud (RM) is magnetic and has a variety of potential applications.

2.6. Other catalysts

With the development of sludge pyrolysis catalysts, scholars have found that the use of molecular sieves, biomass and other different types of catalysts also have obvious effects on sludge pyrolysis. Gu Bo [30] successfully combined the catalytic performance of the metal and the molecular sieve itself through the Ni and Co metal-loaded HZSM-5 molecular sieve (see Figure 1-1), and the metal was well dispersed on the inner and outer surfaces of the molecular sieve. The study found that Ni and Co metal-supported HZSM-5 molecular sieves can significantly promote the formation of aromatics. The Ni-supported HAMS-5 catalyst greatly increases the total carbon yield of light aromatics, which is slightly stronger than that of the Co-supported HAMS-5 catalyst, so that the pyrolysis oil has the best upgrading performance. At the same time, the introduction of metals enhances the transfer of nitrogen in the sludge to solids and gases. Due to the presence of Ni and Co metals, nitrogen is transferred to NH_{3}, and NH_{3}
can be used as a raw material for the production of nitrogen fertilizers. It is of great significance to the resource utilization of sludge.

Figure 1. TEM images of HASM-5, 0.5Ni-HZ and 0.5Co-HZ [32].

3. Characteristics of sludge pyrolysis catalyst

Through the analysis and research of the above-mentioned different types of catalysts, the advantages and disadvantages of the five types of catalysts such as pyrolysis residues, metal oxides, salts, solid waste, and natural minerals are summarized.

| Catalyst type          | Advantage                                                                 | Disadvantage                                                                 |
|------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Pyrolysis residue      | Wide sources, developed pore structure, and large specific surface area are beneficial to the subsequent preparation of supported catalysts to enhance catalytic performance | All need to be dried and then ground into particles of a certain size, which increases energy consumption, makes the pyrolysis process more complicated, and is not conducive to the removal of PAHs. |
| Metal oxide            | Good catalytic effect, extensive research, some metal oxides can also reduce the formation of polycyclic aromatic hydrocarbons and improve the product quality of pyrolysis oil | The cost is high, and it mostly occurs in the medium and high temperature zone, which is not conducive to reducing the energy consumption of pyrolysis. |
| Salt compounds         | The effect is remarkable, the price is relatively low, and the quality and yield of pyrolysis oil are significantly improved. | It is found that there are fewer salts that have a catalytic effect on the pyrolysis of sludge, and the catalytic effect is limited by the type of salt. |
| Solid Waste            | Wide range of sources, improved gas-liquid yield and quality, and product specificity | Poor catalytic performance, often need to load other substances to enhance the catalytic effect, making the process complicated and increasing the cost of pyrolysis. |
| Natural minerals       | Low cost, has a certain catalytic effect on solid-liquid yield             | The catalytic performance is poor, and a series of treatments such as acidification and loading are often required to increase its catalytic ability, increase the cost of pyrolysis, and make the process complicated. |

4. Conclusion

Currently, although the research on catalysts in sludge pyrolysis technology is very extensive, due to the specificity of the sludge itself and the influence of the catalyst, the pyrolysis treatment still has problems such as high energy consumption, high cost, and complex process. Therefore, in order to realize the industrial application of pyrolysis technology, the sludge pyrolysis catalyst should be further studied. Combining the advantages and disadvantages of various catalysts, the author believes that the future promising research is: (1) The pyrolysis residue has good physical and chemical properties, and the
preparation of supported catalysts on the residue as a carrier is beneficial to solve the current problems of poor catalytic effect. Is conducive to the industrial development of pyrolysis technology. (2) For metal oxides, in-depth research should be conducted on substances that are effective in pyrolysis catalysis in the medium and low temperature regions to reduce energy loss during pyrolysis. (3) Salt compounds should start research on other salts other than sodium salt and potassium salt to get rid of the influence of salt types on the catalytic effect. (4) The focus of research on solid waste and natural minerals is to increase the prediction of such substances. Treatment means to achieve the purpose of increasing the catalytic performance. It is believed that with the deepening of research, the pyrolysis technology will show its environmentally friendly and efficient treatment capacity, and realize the resource treatment of sludge in my country.

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