

Research Advance in the Use of Catalysts for Sludge Pyrolysis

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Abstract. In recent years, the discharge amount of all kinds of sewage is increasingly increased, and therefore the handling problem of sewage sludge, an inevitable product of sewage treatment, has drawn more and more attention. As a new type of sludge treatment technology, the production technology of bio-oil from sewage sludge by means of sludge pyrolysis becomes quite popular. Currently the existing researches on this technique mainly focus on the impact of some influencing factors such as catalyst, heating temperature, heating rate, retention time on the products of sludge pyrolysis and their distribution. In this paper, the catalysts used in the experiments of sludge pyrolysis and the related research results in recent decades with regard to the factor of catalyst for the production of bio-oil from sewage sludge are summarized and concluded.

1 Introduction

Sludge is the inevitable product of municipal sewage treatment. The yield of sewage sludge significantly increases with the increase of sewage discharge, and it is extremely urgent to study about the technology for sludge treatment and disposal. As a new type of sewage sludge treatment solution, the production technology of bio-oil from sewage sludge by means of sludge pyrolysis can produce widespread environmental and economic benefits.

The production technology of bio-oil from sewage sludge by means of sludge pyrolysis began to develop in other countries since the mid-1980s, its fundamental principle is: under the oxygen-deficient or oxygen-free condition, solid sludge can be decomposed into three kinds of products including oil (including water), incondensable gas and carbon when it is heated to a definite temperature (low temperature 600°C; high temperature 600°C~1000°C)[1].

Sludge pyrolysis involves various complicated physical and chemical reactions, and moreover, there are many factors which can have an impact on the products of sludge pyrolysis and their distribution, such as catalyst, heating temperature, heating rate and retention time, among which the influencing factor of catalyst is one of the hottest topics to be researched at present. In recent years, the catalysts used in various experiments of sludge pyrolysis can be categorized into a variety of types including sludge carbon residue, metal, molecular sieve and other. In this paper, these catalysts and the related research results are summarized and concluded.

2. Sludge carbon residue

In the late 1980s and early 1990s, there are some researches about the use of sludge carbon residue as a catalyst, but the studies are much less in-depth; and in recent years, Chinese scholar Zhang Ya [4] et al has conducted an in-depth study on the use of single sludge carbon residue as a catalyst, and moreover, he also researches about the catalytic effect of modified carbon residue on sludge pyrolysis by making sludge carbon residue loaded with metal elements.

2.1 An in-depth study on the use of single sludge carbon residue as a catalyst

H.W. Campbell [2] et al once have emphatically analyzed the catalytic reaction process between volatile organic content and solid carbon residue in the fragmentation process of organic matter and pointed out that there is an interphase catalytic reaction between the organic vapor escaping from sludge and carbon residue. E. Churin [3] once have also mentioned that the carbon from the pyrolytic reaction have a significant impact in catalyzing pyrolytic oil to be transformed into linear hydrocarbon and reducing the viscosity of pyrolytic oil, but at that time it is only a speculation that the substance with an effect of catalysis has something to do with the heavy metal existing in the carbon in the form of a salt.

Zhang Ya [4] et al used sludge carbon residue as a catalyst for sludge pyrolysis and the results show that: for sludge pyrolysis, the addition of carbon residue is helpful to remove volatiles, and the yield of organic phase decrease with the addition of carbon residue; the content of oxygenated chemicals in organic phase significantly decreases with the increase of carbon residue, the content of alkanes and alkenes increases from 18% in the condition of sludge only to 39% in the condition of 200% adding proportion, which indicates that the addition of carbon residue has a good effect on hydrodeoxygenation of organic phase, this can significantly improve the quality of oil; and moreover, the addition of carbon residue is also helpful to remove the chlorine-bearing compound and monocyclic aromatic hydrocarbon from organic phase while the content of polycyclic aromatic hydrocarbons increases.

2.2 Research on modified sludge carbon residue loaded with other elements as a catalyst

Zhang Ya [4] et al then modified the carbon residue by making it loaded with the metal elements such as Al, Fe, Ni and Cu and studied the catalytic effect of such modified carbon residue on sludge pyrolysis. The results show that the content of alkanes and alkenes in the organic phase of pyrolytic oil increases significantly after

the carbon residue is modified while the content of oxygenated chemicals decreases significantly as well. In other words, all the four kinds of modified catalysts are conducive to the decrease of viscosity of organic phase and the increase of calorific value. And meanwhile, it is found that Fe/SSC and Ni/SSC have a significant impact on decreasing the content of nitrogen in organic phase; the content of aromatic compounds slightly increases in the organic phase obtained with the use of modified carbon residue catalyst.

3. Metal catalysts

Metal catalysts can be divided into two groups including K and Na, Fe and Al. In this century, several researchers in China have conducted an in-depth study on sludge pyrolysis with the use of single Na_2CO_3 as a catalyst, including the researches on the optimum volume of catalyst, the best pyrolysis time and the best pyrolysis temperature as well as the analysis on the yield and quality of pyrolysis products, etc.; in addition, there are also some comparative experiments that many metallic compounds (mainly including K-containing compounds and Na-containing compounds) are respectively used as a catalyst, the indexes for contrastive analysis based on the results of experiments mainly include the rate of pyrolytic reaction, the conversion ratio of pyrolysis, the yield of liquid, coke and pyrolysis gas, the content of various elements such as aliphatic hydrocarbon, oxygenated chemicals, aromatic compounds and so on in organic phase. Furthermore, there are also researches about the use of Fe and Al metallic compound as a catalyst.

3.1 K-containing and Na-containing compounds catalysts

3.1.1 Multiple researches on the use of single Na_2CO_3 as a catalyst

He Limin [5] used Na_2CO_3 as a catalyst for the production of bio-oil from sewage sludge by means of sludge pyrolysis in the process of refinery sewage treatment. The results show that the yield of oil increases with the increase of temperature, and the oil yield is over 54% when the temperature reaches up to 300°C . Subsequently, Xing Yingjie [6] conducted an in-depth study and found that the optimum volume of Na_2CO_3 as a catalyst is 4g per 100g sludge.

Yu Jianliang[7] also used Na_2CO_3 as a catalyst for catalytic low-temperature thermolysis of dewatered sludge based on the experiments by He Limin [5] and Xing Yingjie[6] and analyzed that the best reaction temperature is about 270°C within the scope of controlled conditions and the best reaction time is 75min, the optimum volume of Na_2CO_3 as a catalyst is 4g per 100g sludge. The oil yield can reach up to 18.4% under the best condition of three single factors mentioned above.

Du Yu [8] et al conducted the process of low-temperature pyrolysis for municipal sewage sludge under the catalyst-free condition and under the condition of compound carbonate used as a catalyst. The results show

that after the addition of compound carbonate as a catalyst, the required temperature for maximum oil yield decreases from 450°C to 400°C , and the maximum oil yield increases from 34.53% to 38.71%, the calorific value of pyrolytic oil increases from 30.43MJ/kg to 33.61MJ/kg. From this it can be seen that the use of catalyst can improve the oil yield and quality of bio-oil from pyrolysis of sludge; and meanwhile, the rate of carbon production is significantly reduced comprehensively.

3.1.2 Contrastive research on various K-containing and Na-containing compounds as the catalyst

Shie [9] et al studied about the catalysis of K-containing compounds such as KCl, KOH and K_2CO_3 as well as the Na-containing compounds including NaCl, NaOH and Na_2CO_3 on sludge pyrolysis and concluded that the liquid yield increased by the use of catalyst is in the order of $\text{KCl} > \text{Na}_2\text{CO}_3 > \text{NaCl} > \text{catalyst-free} > \text{NaOH} > \text{K}_2\text{CO}_3 > \text{KOH}$ when the temperature is $377\sim 437^\circ\text{C}$. The rate of conversion is the highest when K_2CO_3 is added as a catalyst for pyrolysis, reaching up to 88.52%; while the rate of conversion is 83.66% under the catalyst-free condition. This indicates that the use of catalyst can improve the liquid yield and the conversion rate of pyrolysis. In the meanwhile, the addition of catalyst increases the reaction rate of pyrolysis and reduces the yield of coke accordingly.

Ning Fangyong[10] added four kinds of catalysts including KCl, Na_2CO_3 , Fe_2O_3 and residue respectively and found that the sludge pyrolysis process moved towards the low temperature area at varying degrees, and the addition of KCl makes the sludge pyrolysis process moved towards the low temperature area most, followed by Fe_2O_3 , residue and Na_2CO_3 .

After the addition of catalyst, the temperature significantly decreases when the biggest weight loss ratio of sludge occurs, indicating that the use of catalyst can prompt sludge experience the pyrolytic reaction ahead of time; and moreover, the half-peak breadth of reaction increases so that the organic ingredients in sludge can be decomposed to the greatest extent, the thermo-chemical conversion effect of the organic ingredients in sludge can be improved at varying degrees.

Li Guiju [11] investigated the catalytic effect of three sodium salts including Na_2CO_3 , Na_2SO_4 and NaCl as well as the amount of catalyst used for the production of bio-oil from tannery sludge. The results show that the addition of these three sodium salts respectively makes the sludge pyrolysis process moved towards the low temperature area, the rank of their catalytic effect from better to less is Na_2CO_3 , Na_2SO_4 and NaCl. And meanwhile, the analysis results show that the optimum dosage of sodium salt as a catalyst is 2% of the total amount of sludge on a sodium basis; the oil yield can reach up to 41.01% when the optimum dosage of sodium salt is applied and the direct liquefaction method of thermo chemistry is used.

Sun Yu [11] et al studied the catalytic effect of high alumina bauxite particle and its loaded KCl, Na_2SO_4 or

K₂SO₄ on the production of bio-oil from municipal sludge. The results show that the yield of pyrolytic oil decreases significantly and the yield of carbon residue and gas increases after the addition of high alumina bauxite as a catalyst; the content of aliphatic hydrocarbon and oxygenated chemicals decreases in organic phase while the content of aromatic compounds increases.

Compared with high alumina bauxite unloaded with KCl, the reduction value of the yield of pyrolytic oil is relatively smaller when high alumina bauxite loaded with KCl is used as catalyst, the increment in the yield of carbon residue is reduced while the yield of gas does not increase but instead decrease; the proportions of aliphatic hydrocarbon and oxygenated chemicals slightly increase, while the content of aromatic compounds slightly decreases. And moreover, according to an in-depth study on the use of high alumina bauxite loaded with KCl, its catalytic effect can be enhanced by increasing the temperature for the catalytic reaction and increase the height of bed of material.

From the yield of products, the catalytic effect of high alumina bauxite loaded with Na₂SO₄ or K₂SO₄ on the catalytic pyrolysis process of sludge is similar with that of high alumina bauxite loaded with KCl; but from the perspective of constituents in organic phase, the constituents of pyrolytic oil changes not obviously when high alumina bauxite loaded with KCl is used as a catalyst by comparison with the use of high alumina bauxite loaded with Na₂SO₄ or K₂SO₄.

3.2 Fe-containing and Al-containing compounds

Shie [13] et al used some cheap and harmless Al-containing compounds such as Al, Al₂O₃ and AlCl₃ and Fe-containing compounds such as Fe, Fe₂O₃, FeSO₄ · 7H₂O, Fe₂C₁₃, and Fe₂(SO₄)₃ · 7H₂O as the catalysts for the production of bio-oil from sewage sludge. The results show that the catalytic activity of Fe₂(SO₄)₃ · nH₂O is the greatest among all of the catalysts mentioned above.

4. Molecular sieve based catalysts

In recent years, the molecular sieve based catalysts used in China mainly include HZSM-5 and its derivative molecular sieve based catalysts as well as 5A molecular sieve and so on; the molecular sieve of zeolite has also been used as a catalyst to research sludge pyrolysis in foreign countries.

Zhang Li [19] selected five kinds of catalysts including HZSM-5, CaHZSM-5, ZnHZSM-5, 5A molecular sieve and kaolin to carry out the catalytic experiment of sludge pyrolysis under the same experiment condition, and the results show that the higher the silica-alumina ratio is, the higher the yield of oil produced from the catalytic experiment of sludge pyrolysis will be; the yield of coke is the greatest when 5A molecular sieve is used as a catalyst, reaching up to 30.4%, while coke yield is the smallest with the use of kaolin, that is 12.5%. From the two aspects of oil yield and coke yield, HZSM-5(50) is the best catalyst. And

then a regeneration experiment is conducted for the catalyst of HZSM-5(50), the results show that the yield of oil does not change significantly for the former three times before catalyst regeneration while it decreases significantly since the fourth time of catalyst regeneration.

Canadian researchers Kim [15] et al studied the impact of different additive amounts of zeolite on sludge pyrolysis. The results show that when the additive amount of zeolite is greater than 0.2g per 1g dry sludge, the yield of coke decreases with the increase of catalytic amount, while yield of goudron does not change significantly. It can be seen that the addition of catalyst is helpful for solid coke to be transformed into gas so as to accelerate it to produce more pyrolysis gas, but its impact on goudron is not very significant.

5. Conclusion

The catalysts used in various studies about sludge pyrolysis can be approximately categorized into a variety of types including sludge carbon residue, metal, molecular sieve and other at present.

The relevant researches about the use of sludge carbon residue as a catalyst are mainly conducted in foreign countries during the late 1980s and early 1990s, but the studies are much less in-depth and it is still the beginning process of exploration; but in recent years, many scholars in China have conducted further researches by not only deeply analyzing the catalyst of single sludge carbon residue but also the catalytic effect of modified carbon residue on sludge pyrolysis by making sludge carbon residue loaded with metal elements.

Metal catalysts can be divided into two groups including K and Na, Fe and Al. For K and Na catalysts, many researchers in China have conducted in-depth studies about the catalytic effect of single Na₂CO₃ on sludge pyrolysis; and in addition, there are also some comparative experiments to study the use of various metallic compounds including K-containing and Na-containing compounds. Besides, there are also some related studies on the use of Fe-containing and Al-containing compounds as the catalysts for sludge pyrolysis.

For molecular sieve based catalysts, the experiments with the use of HZSM-5 and its derivative molecular sieve based catalysts as well as 5A molecular sieve are conducted in China during recent years; there are also researches on the use of zeolite catalyst for sludge pyrolysis.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 41501514), Colleges and universities in Hebei province science and technology research key project (zh201283), Science and technology project of Hebei Province (13273617), Annual Students Research Fund of Northeast University at Qinhuangdao.

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