

Research Status on Co-pyrolysis of Municipal Sludge and Biomass

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Abstract: Municipal sludge is a by-product in the sewage treatment process, and its main properties include high moisture content, containing organic toxic substances, large specific surface area and porosity, and easy to produce irritating gases. Biomass is a renewable energy source, including wood, straw, rice husks, sawdust, etc. This article mainly takes garden waste as an example. The co-pyrolysis of municipal sludge and garden waste is of practical significance for the reduction and resource utilization of both. This article summarizes the development and application of co-pyrolysis of municipal sludge and garden waste.

Keywords: Municipal sludge; garden waste; co-pyrolysis.

1. Introduction

With the continuous advancement of urbanization in China, the amount of urban sewage treatment is increasing year by year, and the output of municipal sludge is also increasing year by year. According to statistics, China's urban wet sludge with 80% moisture content has exceeded 60 million tons per day.

In addition to a large amount of moisture, municipal sludge also contains a large number of refractory toxic components, such as organic matter, heavy metals, salts, and harmful components such as pathogenic microorganisms and parasite eggs. If not properly treated, it will cause secondary pollution and endanger the ecological environment and human health. Therefore, it is also very difficult to resource it. The resource utilization of municipal sludge is also necessary.

Judging from the current status of urban sludge resource treatment in China, China's traditional sludge treatment and disposal technologies mainly include sanitary landfill, sludge composting, sludge incineration, and land use, but traditional technologies have certain limitations.

Among them, pyrolysis, as a very efficient sludge treatment and resource recovery method, has received widespread attention.

Co-pyrolysis refers to the process of thermally decomposing municipal sludge and biomass at a certain temperature under anaerobic or oxygen-deficient conditions to produce gaseous, liquid, and solid products. During the co-pyrolysis process, the organic matter in municipal sludge and biomass undergoes thermal decomposition, generating small molecule gases and volatile organic compounds, which further decompose and reform at high temperatures to form combustible gases and liquid products. However, municipal sludge has the characteristics of high ash content and low energy density, resulting in problems such as low conversion efficiency, poor product quality, and unstable reactor operation in its separate pyrolysis process, which restricts the application and promotion of pyrolysis technology in the field of municipal sludge treatment. Some researchers have improved the pyrolysis effect of materials by adding sawdust, peanut shells, etc. to municipal sludge. For example, after adding 40% sawdust, the pyrolysis temperature of the material can be reduced; after adding 25% pine sawdust to the sludge, the activation energy in the pyrolysis process can be reduced from 39.589 kJ/mol to 7.059 kJ/mol, and the initial heating temperature can be reduced. This is because the metal elements such as K and Ca in pine sawdust have a certain catalytic effect. In particular, K in pine sawdust can react with Si in sludge to produce potassium silicate, increase reaction activity and catalyze the secondary cracking of sludge. These interactions make the mixture more likely to react at low temperatures, resulting in a lower initial decomposition temperature; Lin also found that there is a synergistic effect between oil palm solid waste and paper sludge during

co-pyrolysis. This is due to the hydrogenation effect caused by the catalysis of minerals in the sludge; Wang Zhongke found that in the co-pyrolysis of sludge and peanut shells, the pyrolysis gas increased by more than 20% and the calorific value increased from 6.7 MJ/m³ to 11.46 MJ/m³ after adding 80% peanut shells. This is because the addition of peanut shells can promote the breaking of hydrogen bonds in macromolecules to generate hydrogen; in the co-pyrolysis experiment of sludge and rice straw, it was found that there is a synergistic effect in the product yield during the co-pyrolysis process, and the experimental value of volatile product yield is higher than the theoretical value. The addition of rice straw promotes the formation of volatile products.

Biomass is a renewable energy source, including wood, straw, rice husks, sawdust, etc. The co-pyrolysis of municipal sludge and biomass can achieve the synergistic disposal of the two, improve resource utilization, and reduce processing costs. At the same time, the biochar produced during the co-pyrolysis process can be used in soil improvement, adsorbents, and other fields, with high economic value. And there is also a huge amount of garden waste in China. The whole country produces about 40 million tons of garden waste every year, and the main treatment methods are landfill or traditional composting methods, which occupy a large amount of land, resulting in a serious waste of land resources. Garden waste has the characteristics of high organic matter content and large output. If not properly treated, it will not only cause waste of organic matter resources, but also cause waste of land resources.

Therefore, this study intends to add garden waste to municipal sludge to improve the material properties of municipal sludge, so that municipal sludge can be better treated and better utilized.

2. Municipal sludge and garden waste treatment and disposal technologies

At present, China's sludge treatment and disposal is mainly through sanitary landfill, sludge composting, sludge incineration and land use, and the treatment methods for garden waste are mostly aerobic composting, making biofuels and organic mulch.

(1) Traditional disposal methods of municipal sludge

Sanitary landfill: Sanitary landfill was once widely used as a sludge treatment method at home and abroad in the early days. It has received certain attention due to its strong adaptability, simple treatment methods, large amount of sludge that can be treated, and low landfill costs. However, the shortcomings of landfilling are also very obvious. When the amount of sludge is very large, landfilling will consume a lot of land resources, and there are very high requirements for the location. Moreover, if it is not properly disposed of, causing leachate to seep, it will seriously pollute the soil environment and groundwater resources, causing irreversible damage. In addition, landfill gas will also be generated during the landfill process, which will cause greenhouse effects and explosion risks. Therefore, landfill technology is gradually being replaced by other disposal methods.

Sludge composting: Sludge composting refers to the process of using microorganisms to convert the organic matter in sludge into humus rich in nutrients and carry out composting under aerobic and well-ventilated conditions, so that sludge can be reduced and detoxified to a certain extent. However, heavy metals and odors in the composting process are difficult to control and the area occupied is large. In addition, the new standards issued by the Ministry of Agriculture and Rural Affairs clearly stipulate that sludge compost products cannot be used for agricultural purposes, which further limits the application market of sludge humus.

Sludge incineration: Municipal sludge contains a large amount of organic matter and pathogens. Incineration can effectively kill the pathogens and convert the organic matter into stable inorganic matter. Moreover, after incineration, the volume of sludge can be reduced by more than 60%, which is currently recognized as one of the effective ways to reduce sludge. Due to the high moisture content of sludge, direct incineration will consume a huge amount of energy, so the sludge is usually incinerated after drying. Sludge incineration is generally divided into total dry incineration and semi-dry incineration. However, the disadvantages of sludge incineration are also very obvious.

After sludge is incinerated, a large amount of waste gas will be produced, in addition to conventional CO₂, SO₂, and NO₂, it will also generate toxic and harmful substances such as dioxins and polycyclic aromatic hydrocarbons. In addition, sludge incineration also has problems such as high processing costs, high investment costs, and difficult post-maintenance. Therefore, sludge incineration is not the optimal sludge treatment and disposal method.

Land use: Land use is a method of treating sludge by spreading and deep ploughing after harmless and stable treatment. Sludge is rich in nutrients and minerals required by plants and can be used as a soil conditioner to improve soil structure, soil fertility and plant growth. Sludge land use is mostly used in soil remediation, woodland improvement, landscaping and agricultural soil improvement. However, municipal sludge contains high concentrations of pathogens, organic pollutants and heavy metals, which will cause harm to the soil and plants. Therefore, the sludge must be scientifically and reasonably treated before land use can be considered.

(2) Traditional disposal methods of garden waste

In China, the annual output of garden waste is very large. If not treated in time, it will cause harm to the environment and lead to a waste of resources. At present, the main treatment methods in China include aerobic composting, making biofuels and organic mulch, but these treatment technologies have certain limitations.

Aerobic composting: Aerobic composting is a process of composting garden waste using aerobic microorganisms under the condition of sufficient oxygen supply. The garden waste is placed in a suitable environment such as C/N, moisture content, temperature, oxygen content, and structure, and the organic matter in the material is decomposed by aerobic bacteria to achieve mature material and finally obtain organic fertilizer. Aerobic fermentation first causes easily decomposed simple green plants to decompose rapidly, releasing a large amount of heat, continuously increasing the temperature of the green waste pile. Above 50°C, it can kill pathogenic bacteria to the greatest extent. When the temperature drops below 50°C, actinomycetes multiply rapidly, causing the un-decomposed complex green plants in the high-temperature stage to continue to decompose and transform, forming humus. Humus is a loose dark brown substance that is rich in nutrients required for plant growth and is beneficial to plant growth. However, due to the different moisture contents of the mixed components of garden waste, the C/N ratio is relatively high, and it contains a large amount of lignin. When using aerobic fermentation technology, a certain amount of auxiliary materials are needed to adjust the moisture content and carbon-nitrogen ratio, and compared with other organic perishable wastes, garden waste takes longer to mature and occupies more land resources, which limits the development of aerobic composting technology.

Making biofuels: The combustible component content in garden waste is high and the calorific value is high. Using landfill or direct incineration is not appropriate, which is a waste of the potential value of high calorific value components. Through the steps of "crushing - sorting - molding", garden waste can be processed into the required shape of solid fuel. Biofuel technology can not only achieve the control of secondary pollution in the system and solidified fuel, but also has the advantage of lower secondary pollution compared to landfill and direct incineration, and can achieve the goal of energyization and comprehensive utilization of garden waste. At the same time, it can also solve the problems of garden waste occupying land resources and polluting the environment, and can also alleviate the shortage of new fuel resources in China, and achieve the goals of sustainable development and energy conservation and emission reduction. After being made into biofuels, garden waste can reduce its volume and is convenient for transportation, which helps to reduce carbon emissions and reduce the greenhouse effect. However, making biofuels requires heat energy consumption, and when the moisture content of the raw materials is high, it will affect the pyrolysis effect, the investment is large, and the process is complicated.

Organic mulch: Garden organic mulch mainly crushes garden waste, dyes it as needed, and then covers it on the exposed ground of municipal road flower beds, under tree pools of shrubs and trees, and bare ground to improve the soil and ground coverage. Garden organic mulch can not only protect the soil and improve the ecology, but also play a decorative role and beautify the

environment, thereby realizing the recycling of garden waste. The main functions of garden organic mulch on the soil include moisture retention, heat preservation, weed suppression, increased nutrition, dust retention, and color enhancement. The use of mulch can keep the moisture in the soil, reduce transpiration, and have a good water-saving effect; laying to a certain thickness can effectively reduce the germination of weeds; the use of mulch improves the water absorption and permeability of the soil, preventing soil erosion; the surface of organic mulch is rough, which can reduce the ground wind speed and absorb dust; the aesthetic effect is good and the maintenance cost is low. But the production cost of organic mulch is high and the price of the finished product is high.

In addition, China lacks awareness of the resource utilization of garden waste, lags behind in technology, has a single type of resource products, and limited application scope, which will all hinder the treatment of garden waste in China. Exploring harmless treatment and resource utilization methods for urban garden waste is of great significance for saving natural resources, preventing environmental pollution, and realizing the development of ecological economy.

3. Development of co-pyrolysis technology for municipal sludge and garden waste

(1) Development of pyrolysis technology

Pyrolysis refers to the process of thermally cracking organic substances in the feedstock into solid, gaseous, and liquid phases under anaerobic or oxygen-deficient conditions. Pyrolysis is a relatively advanced heat treatment technology, and its products have certain energy values. Therefore, pyrolysis is an effective resource recovery technology.

In 1939, Shibata in France first mentioned sludge pyrolysis in a patent and described in detail the process flow of treating sludge by pyrolysis. Since then, scholars from various countries have begun to study pyrolysis technology.

Bayer et al. first proposed a process for preparing bio-oil from sludge at low temperatures in the 1980s. Campbell et al. conducted low-temperature pyrolysis research on sludge and conducted a feasibility analysis of sludge pyrolysis in combination with practical applications.

In the 1990s, the sludge pyrolysis process "Enersludge" emerged, and the first commercial sludge pyrolysis refinery was built in Australia. Stammabach et al. also confirmed that zeolite promotes the generation of sludge pyrolysis gas and pyrolysis oil.

In recent years, scholars at home and abroad have also conducted more and more research on sludge pyrolysis, and many factors in the sludge pyrolysis process may also lead to changes in products. Ji Aimin et al. found that an increase in temperature leads to an increase in gaseous products. Domínguez. A et al. The research shows that the hydrogen content in the sludge pyrolysis and the total amount of gaseous products increase with the increase of moisture content. This is because the moisture in the sludge provides a steam atmosphere during the pyrolysis process, and pyrolysis products such as tar, small molecule hydrocarbons, and various gaseous products are prone to reforming reactions and steam gasification in the steam atmosphere, resulting in an increase in hydrogen content. Chang Fengmin's research found that different catalysts have an impact on volatile products.

It can be seen that more and more Chinese scholars are also conducting research and analysis on sludge pyrolysis.

(2) Factors affecting co-pyrolysis

During the co-pyrolysis process, parameters such as pyrolysis temperature, heating rate, feedstock particle size, residence time, and reactor type will all affect the properties and distribution of sludge pyrolysis products. Among them, pyrolysis temperature, heating rate, and pyrolysis time are the most prominent factors.

The influence of pyrolysis temperature: In the pyrolysis process, temperature has a significant impact on the composition and properties of the products. The pyrolysis process can be divided into

several different stages: first, the evaporation of moisture in the feedstock; then, the organic matter in the feedstock undergoes cracking and releases volatile substances under heating conditions, resulting in the generation of bio-oil; finally, the increase in temperature promotes the endothermic reaction, resulting in the secondary cracking of bio-oil to produce more gaseous products.

The influence of heating rate: The heating rate determines the rate at which volatile matter is separated from the char, which is one of the key parameters affecting the sludge pyrolysis process. Generally, in the sludge pyrolysis process, a higher heating rate is beneficial to the generation of gas-liquid products, but the char yield will be reduced.

The influence of pyrolysis time: Pyrolysis time is also an important factor affecting sludge pyrolysis. At present, scholars mainly explore the influence of pyrolysis time on the reaction from two aspects: char carbonization time and volatile matter residence time. During the pyrolysis process, the cracking of sludge organic matter, the aromatization of sludge solid products, and the enrichment of heavy metals and their morphological changes all require a certain amount of time to complete.

4. Application of co-pyrolysis technology for municipal sludge and garden waste

(1) Application of biochar

Biochar has a large porosity and specific surface area, strong adsorption, antioxidant and anti-biological decomposition capabilities, and can be used as:

Soil improvement: Biochar can increase the organic matter content in the soil, improve soil structure, improve soil water retention and fertility, promote plant growth and stress resistance, and reduce the use of chemical fertilizers and pesticides.

Fertilizer slow-release agent: Biochar can be used as a slow-release agent for fertilizers, slowly releasing nutrients, improving fertilizer utilization efficiency, and reducing nutrient loss.

Carbon sequestration and emission reduction: Biochar can convert unstable organic carbon in biomass into stable biochar, thereby achieving carbon sequestration in the soil and achieving the goal of carbon sequestration and emission reduction.

Energy production: Biochar can be converted into biomass fuels such as biomass pellets, biomass gas, and biomass liquid fuel through pyrolysis, etc., and used for heating, power generation, and industrial production.

Other fields: Biochar can also be applied in water treatment, air purification, food processing, medicine, etc.

(2) Application of pyrolysis oil

Pyrolysis oil is a liquid product obtained by converting organic matter into liquid through pyrolysis technology, and has a wide range of application prospects, including:

Direct use as fuel: Pyrolysis oil has a low viscosity, high calorific value, high light fraction content and relatively low heavy fraction content, and can be directly used as fuel.

Application of light fractions: By adding a certain proportion of light fractions to naphtha for mixed refining, the octane number of gasoline products can be increased, or raw materials with higher industrial value, such as BTX (benzene, toluene, xylene), can be extracted.

Application of medium fractions: Pyrolysis oil has a high aromatic content and can be used to produce aromatic feedstocks. It can be used as a rubber extender in rubber production, which can increase the elasticity of rubber and reduce the internal friction between rubber molecules, thereby facilitating mixing and improving the flexibility of rubber.

Application of heavy fractions: Pyrolysis oil has the characteristics of low wax content and high aromatic, gum, and asphalt content in the heavy fraction, and can be used as a raw material for the production of road asphalt.

In addition, pyrolysis oil can also be used to produce other chemicals, such as solvents and lubricants. With the continuous progress of technology and the expansion of application fields, the application prospects of pyrolysis oil will be even broader.

(3) Application of pyrolysis gas

Pyrolysis gas is a gaseous product generated during the pyrolysis of sludge, and has the following applications:

5. Conclusion

As an important part of urban waste treatment, more and more environmental protection practitioners are recycling municipal sludge, and the principle of "reduction, harmlessness, and recycling" should be adopted as the treatment and disposal principle. Although the new process of treating sludge is limited by the environment, cost, and operating conditions, managers should maximize the residual value of sludge to provide more help for human life and achieve the goal of a win-win situation between the economy and the environment.

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