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Review

Recent Progress in Sludge Co-Pyrolysis Technology

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Abstract: With the development of society and industry, the treatment and disposal of sludge have become a challenge for environmental protection. Co-pyrolysis is considered a sustainable technology to optimize the pyrolysis process and improve the quality and performance of pyrolysis products. Researchers have investigated the sludge co-pyrolysis process of sludge with other wastes, such as biomass, coal, and domestic waste, in laboratories. Co-pyrolysis technology has reduced pyrolysis energy consumption and improved the range and quality of pyrolysis product applications. In this paper, the various types of sludge and the factors influencing co-pyrolysis technology have been classified and summarized. Simultaneously, some reported studies have been conducted to investigate the co-pyrolysis characteristics of sludge with other wastes, such as biomass, coal, and domestic waste. In addition, the research on and development of sludge co-pyrolysis are expected to provide theoretical support for the development of sludge co-pyrolysis technology. However, the technological maturity of sludge pyrolysis and co-pyrolysis is far and needs further study to achieve industrial applications.

Keywords: sludge; additives; co-pyrolysis; collaborative processing

Citation: Han, L.; Li, J.; Qu, C.; Shao, Z.; Yu, T.; Yang, B. Recent Progress in Sludge Co-Pyrolysis Technology. *Sustainability* **2022**, *14*, 7574. https://doi.org/10.3390/su14137574

Academic Editors: Lixiang Zhou and Guanyu Zheng

Received: 14 May 2022
Accepted: 17 June 2022
Published: 21 June 2022

1. Introduction

With the rapid development of the energy industry, great challenges in treating all types of sludge (oil sludge, paper sludge, municipal sludge, etc.) have emerged [1]. It has been predicted that the total growth rate of various types of sludge in China will increase by approximately 10% per year [2]. Thus, the development of sludge treatment technology worldwide has drastically increased. Currently, the main methods used in sludge treatment include incineration, land cultivation, and thermochemical conversion. Although they have certain applications, they still have their own limitations, and it is difficult to meet the requirements of various countries for sludge treatment and disposal. Among these methods, pyrolysis is considered a promising method for sludge valorization owing to the associated low heavy metal content, volume minimization, zero-waste conversion, and high-value product recovery [3]. In addition, compared with incineration, fewer sulfur oxides and a lower heavy metal content are produced in residues during sludge pyrolysis, and the by-products, such as pyrolysis oil, pyrolysis residues, and combustible gas, have reutilization value [4].

At present, pyrolysis technology has effectively reduced the volume of sludge and eliminated some pollutants in the sludge treatment process. In addition, the residue derived from the pyrolysis of sludge can be used in the fields of adsorbents, catalysts, and soil remediation agents [5–7]. However, sludge pyrolysis still faces serious disadvantages such as high energy consumption, high ash content, and low added value of products, owing to the influence of the sludge source and characteristics. Therefore, in recent years, scholars have attempted to optimize the pyrolysis process and the distribution of pyrolysis products by studying the synergistic effect of sludge and some solid waste [8,9].

This review presents an overview of recent advances in the co-pyrolysis of sludge and biomass, coal, and domestic waste from the perspective of engineering applications. Additionally, this review introduces not only recent research results pertaining to the factors influencing co-pyrolysis, but also the various types of sludge. Future research directions are further suggested for commercially feasible sludge co-pyrolysis processes.

2. Types and Characteristics of Sludge

There are many ways to classify sludge. It can be classified as organic, inorganic, or hydrophobic sludge according to its composition and the characteristics produced during sewage treatment. Based on the different stages of treatment, sludges are categorized as raw, thickened, and dried sludge, among other types. Further, according to one source, it can be divided into municipal, oily, papermaking, printing, and dyeing sludge, among others. However, they are usually treated according to the source of the sludge. In sludge treatment, the different sources of sludge and their basic characteristics are shown in Table 1.

Table 1. The source and characteristics of sludge.

The Kinds of Sludge		The Source of Sludge	The Main Component	The Characteristics	References
Domestic sludge	Water supply plant sludge	Wastewater treatment plants.	Al, Fe and other trace elements are higher in sludge. The main mineral composition is Muscovite and kaolin.	High cleanliness, not suitable for agricultural soil due to the addition of flocculants, the content of heavy metals exceeds the standard.	[10–12]
	Municipal Sludge	Municipal facilities such as municipal sewage works.	High moisture content, rich in N, P, K and ash content.	Stable source composition.	[13–15]
Industrial sludge	Oily sludge	The process of exploitation and refining in the petroleum industry.	Because of different sources, the water content, heavy metals and polycyclic aromatic hydrocarbon content are high.	The composition is complex, the oil content varies greatly, the stability is high, and the treatment is difficult.	[16–18]
	Papermaking sludge	The treatment process of wastewater produced. during ash removal in a paper mill.	High water content, small residue content, the organic matter is mainly cellulose, the heavy metal content is low.	Cellulose is abundant and can be developed as a renewable fuel.	[19–21]
	Printing and dyeing sludge	Printing and dyeing wastewater treatment process.	High moisture content, heavy metals, organic compounds and other complex components.	Organic compounds are complex with heavy metal content and heavy pollution.	[22–24]
	Electroplating sludge	Electroplating wastewater treatment process.	High moisture content, residue content, Zn, Cr and other heavy metals content.	Low nutrient element and agricultural value; The composition is complex and the heavy metal is unstable, so the crystallinity of the phase is small.	[25–28]
	Metallurgical sludge	Iron and steel production process, metallurgical industry production process.	Fe, FeO, SiO_2, CaO content are high, iron sludge high carbon content, heavy metal content.	Corrosive and chemically toxic.	[29,30]

It can be seen from Table 1 that the main composition and characteristics of sludge from different sources are relatively obvious. Therefore, the classification of sludge by source is helpful for researchers to further clarify the reasons for potential synergy between sludge and different additive co-pyrolysis.

3. Sludge Co-Pyrolysis Technology

Pyrolysis, one of the main technologies for sludge treatment, has the advantages of thorough treatment, volume minimization, and the recovery of high-value products [31]. However, sludge pyrolysis is often associated with problems such as high volatility and low ash content, as well as poor application performance of pyrolysis residues. Therefore, researchers have carried out investigations into sludge co-pyrolysis technologies with biomass and other additives in recent years. Generally, sludge, biomass, and solid waste are different in chemical and physical properties, such as ash content, volatile matter, and oxygen content, which can result in synergetic interactions during co-pyrolysis [32]. The use of the synergistic effect with the co-pyrolysis of sludge and additives can solve the shortcomings of sludge pyrolysis and realize associated resource utilization.

3.1. Co-Pyrolysis of Sludge and Biomass

Biomass comprises an organism formed through photosynthesis. The use of clean, renewable biomass energy has always been a hot topic for researchers [33,34]. Therefore, in recent years, researchers have studied the multi-phase products (gas, pyrolysis oil, biochar) of the co-pyrolysis of sludge and biomass and found that it not only solves the problem of sludge and biomass resource utilization, but can also improve the quality of multi-phase products and the prospects of product reuse [35–37].

3.1.1. Effect of Sludge and Biomass Co-Pyrolysis on the Performance of Biochar

Hua has obtained a heavy-metal adsorbent with a rich pore structure and more mineral particles from the co-pyrolysis of municipal sludge and banana peel [38]. Hong found that an increase in the pyrolysis temperature results in an increase in ash content and the specific surface area of the residue in the co-pyrolysis of dehydrated sludge and water hyacinth, and the adsorption capacity of Cr^{3+} reached 44.96 mg g^{-1} [39]. Wang obtained potential soil amendment products with higher carbon storage capacity in the soil from the co-pyrolysis of sewage sludge and cotton straw in terms of higher carbon content and lower H/C and N/C values [40]. In addition, because the residue has a high cation exchange capacity, it can enhance the nutrient supply and nutrient retention capacity in the degraded soil, and thus, it has high economic and environmental value. Xu et al. [41] used bamboo scraps as an additive to pyrolyze sewage sludge at 700 °C and found that the residue yield, pH value, ash content, specific surface area, and residue aromatization degree increased significantly, whereas H/C remained relatively low. At the same time, with the increases in bamboo chip proportions, the potential ecological risk factor of heavy metals in the residue drops below 40. Heavy metals are also reduced to a low risk level, indicating that the addition of bamboo chips is beneficial to improve the quality of the residue.

These studies of the co-pyrolysis of sludge and biomass can greatly improve the problems of low carbon content and underdeveloped pore structure in the residue with the pyrolysis of sludge. Therefore, the co-pyrolysis of sludge and biomass into biochars represents a promising strategy for waste disposal and resource reuse [42].

3.1.2. Effect of Co-Pyrolysis of Sludge and Biomass on Gas and Liquid Phases

The co-pyrolysis of sludge and biomass will not only change the properties of the biochar but also improve the quality of gas–liquid products [43,44]. Many researchers have evaluated the co-pyrolysis of sludge and biomass to enhance the properties of the gas and liquid phases and reduce activation energy during pyrolysis [45,46]. For example, Li found that the addition of peanut shells in the pyrolysis of municipal sludge can decrease the ammonia nitrogen content of the liquid phase product to 1369.00 mg/L, and the water phase product is one of wood vinegar [47]. Wan found an increase in the H_2 yield of combustible gas with an increase in the pyrolysis temperature during the co-pyrolysis of domestic sludge and pine wood chips [48]. Wang also observed that the addition of pine wood chips to the pyrolysis of domestic sludge can decrease the pyrolysis activation energy by approximately 117 kJ/mol [49]. Li studied the reaction kinetics and product distribution characteristics of the co-pyrolysis process from the co-pyrolysis of municipal domestic sludge and vinegar grains in a fixed-bed reactor and revealed that the presence of grains not only increases the H_2 and CO yield and the distribution of phenols and esters in the bio-oil, but also reduces the final temperature of the pyrolysis reaction [50]. Lin used rice husk as an additive to co-pyrolyze oily sludge and found that it not only increased the concentration of chain hydrocarbons in the pyrolysis oil but also reduced the content of oxygenated compounds by 46–93%, with the production of more H_2, CO, and C_1–C_2 hydrocarbons [51].

Taken together, the synergetic effect between sludge and biomass provides a variety of potential application prospects for the residue after pyrolysis (Table 2), but it will also help to optimize the gas- and liquid-phase products of sludge pyrolysis (Table 3). Therefore, the findings of the co-pyrolysis between sludge and biomass might provide an alternative way to utilize sludge and biomass.

Table 2. The effect of co-pyrolysis of sludge and biomass on the residue.

Sludge and Biomass Species	The Characteristics of Residues from Co-Pyrolysis	The Application Prospect	References
Municipal sludge and banana peels	The pore structure is developed, abundant in surface mineral particles, and the pore structure is mostly mesoporous	Heavy metal adsorbents	[38]
Sewage sludge and water hyacinth	The specific surface area is large, the pore structure is rich and orderly, the leaching toxicity is low, and the tubular and pore structure is obvious	Biochar materials for energy production and environmental remediation	[39]
Sewage sludge and cotton straw	High cation exchange capacity, high carbon content and low H/C and N/C ratios	Soil nutrients, heavy metal fixators	[40]
Sewage sludge and bamboo chips	low H/C ratio, high pH value, ash content, and high specific surface area and degree of aromatization	Heavy metal fixator for sludge	[41]

Table 3. The effect of co-pyrolysis of sludge and biomass on the gas-liquid products.

Sludge and Biomass Species	Characteristics of Gas and Liquid Phase Products	The Application Prospect	References
Municipal sludge and peanut shells	The water phase product is alkaline, the quality of tar is high	Pesticide additives, antibacterial agents, plant growth regulator	[47]
Domestic sludge and pine sawdust	Higher gas-phase yield, calorific value and H_2 content in combustible gas	Heating power generation and other fuel agents	[48,49]
Urban living sludge and vinegar grains	The product quality of pyrolysis oil and the content of phenols and esters in pyrolysis oil is high, the composition tends to be single	High calorific value green fuel	[50]
Oily sludge and rice husks	The content of saturated oil and aromatics is increased, and the heavy fraction is reduced, H_2S emission is inhibited, H_2, CO and C_1–C_2 hydrocarbon yield is increased	Catalyst, fuel agent	[51]

3.2. Co-Pyrolysis of Sludge and Coal

China has abundant coal reserves, and coal is an important primary energy source. Some high-rank coals, such as anthracite, have been exploited in large quantities, but low-rank coals, such as lignite, long-flame coal, and bituminous coal, have the disadvantages of low calorific value and high moisture content [52]. Therefore, if improperly handled, they are likely to cause secondary pollution in the environment. Studies have found that coal and sludge have a synergistic catalytic effect on the co-pyrolysis process. On one hand, the synergetic effect can improve sludge pyrolysis characteristics during the co-pyrolysis of sludge and coal, and achieve the effective utilization of solid waste. On the other hand, sulfur contaminant emissions can also be controlled.

For example, Li found that the addition of bituminous coal to the pyrolysis of dried sludge can reduce the pyrolysis temperature at the peak of gas production by 100 °C compared to that with the pyrolysis of sludge alone, effectively decrease the activation energy, and increase the yield of H_2 by 50% [53]. Chang obtained two independent pyrolysis zones of the co-pyrolysis process from the co-pyrolysis of low metamorphic coal and municipal sludge, and the results showed that the pyrolysis of sludge occurred mainly below 450 °C, whereas higher temperatures were mainly associated with the pyrolysis of coal [54]. However, owing to the synergetic effect, the activation energy for the co-pyrolysis of sludge and coal is less than that of the pyrolysis of sludge and coal separately. The concentration of small-molecule combustible gases, such as H_2 and CO, in mixed pyrolysis accounts for more than 85% of the total gas phase yield, and the calorific value can reach 32.05 MJ/Nm^3. Moreover, the iodine value can reach 277 mg/g. These properties make pyrolysis residues promising as fuels and for adsorbent applications. Chen found that the synergetic effect between domestic sludge and Shenmu coal results in the comprehensive release characteristic index of volatile matter being increased by 1.86 times, but the activation energy was determined to be only 75% of the pyrolysis of sludge [55]. In addition, he revealed that co-pyrolysis has stable devolatilization and low reaction activation energy and also observed an increase in the yield of CH_4 and H_2 but a decrease in the emission of CO_2 and nitrogen-containing gas yield [56]. Zhao et al. [57] also observed a significant inhibitory effect on the release of H_2S and SO_2 yield during the co-pyrolysis of Zhundong coal and domestic sludge, and when the mass ratio of Zhundong coal to sludge was 1:1, the inhibitory effect of sulfur pollutants was best.

The co-pyrolysis of coal and sludge can reduce the activation energy of the pyrolysis reaction, improving the utilization rate of coal and sludge and reducing the emission of sulfur pollutants [58,59]. In this context, the co-pyrolysis of sludge and coal could be a feasible approach to achieve the sustainable development and resource utilization of sludge.

3.3. Co-Pyrolysis of Sludge and Domestic Waste

With the growth of social and urban living standards, a large amount of domestic waste is produced. Domestic waste refers to the solid waste generated in daily life, and its presence is a huge threat to the living environment. The harmless treatment of domestic waste is an important topic for ecological development [60]. As sludge and domestic waste share many usable resources, co-pyrolysis technology can be used to reuse sludge and domestic waste resources.

Fang studied the co-pyrolysis of combustible solid waste and paper mill sludge and found that when the blending mass ratio is 10%, oxygen-containing substances increase by 20.11% [61]; further, when the blending mass ratio is 50%, it can promote sulfur and nitrogen fixation and minimize pollutant emissions. In addition, upon assessing the thermal characteristics and kinetics of the co-pyrolysis of municipal solid waste and paper mill sludge by TG-GC/MS, the activation energy of the solution was found to be only 95.70 kJ/mol, with further increases in the yields of gas–liquid products [62]. Hu et al. used KOH-activated wind turbine blade waste (WTBW) as an additive for co-pyrolysis with sewage sludge and found that with an increase in WTBW, the specific surface area and micropore content of the pyrolysis residue were increased, whereas the apparent activation energy decreased by 20.4 kJ/mol [63].

Therefore, using domestic waste as an additive for sludge pyrolysis not only promotes the pyrolysis of sludge but also helps to deal with the pollution problems caused by domestic waste [64,65]. This research deserves to be extended in the future.

3.4. Research on the Co-Pyrolysis of Sludge and other Additives

Beyond the additives discussed previously herein, some special substances are also used for co-pyrolysis with sludge. For example, Liu prepared magnetic biochar based on the co-pyrolysis of sewage sludge with nano-zero-valent iron and used it to remove Cr^{6+} in wastewater [66]; they found that the removal rate of Cr^{6+} was good, and the adsorption amount could reach 11.56 mg g^{-1}. Milato used polyolefins as additives to co-pyrolyze oily sludge in a fixed-bed reactor at 450 °C [67]. They found that different products were produced due to the presence of polyolefins in the pyrolysis of oily sludge. At the same time, due to the synergistic effect of tertiary carbon in polyolefin and oily sludge, the pyrolysis process was optimized, and the content of heavy hydrocarbons ($\geq C_{25}$) was found to increase. Liu [68] found that the immobilization effect on heavy-metal biochar via co-pyrolysis with sewage sludge and calcium sulfate resulted in a proper pyrolysis temperature, and the residence time was found to promote the formation of crystals and spherical or elliptical particles in biochar, with more mesoporous and macroporous structures. This is beneficial for the immobilization of heavy metals such as Cr, Pb, Cu, Ni, and Zn.

Overall, based on the characteristics of sludge and the additives, sludge co-pyrolysis technology could increase the application of co-pyrolysis residues (such as adsorbents, catalysts, soil nutrients, pesticide additives, antibacterial agents, etc.). Therefore, it is suggested future research focus on the co-pyrolysis of sludge with more large-scale additives, which have a greater synergistic effect with sludge, to further improve the potential value of sludge co-pyrolysis products.

4. Factors Influencing the Co-Pyrolysis of Sludge

Studying the influencing factors of sludge co-pyrolysis technology contributes to the maximization of the synergistic effect between sludge and additives and is helpful in obtaining high-quality pyrolysis products. Current research focuses primarily on the influence of the mixing ratio, co-pyrolysis temperature, co-pyrolysis time, and catalysts on sludge co-pyrolysis technology.

4.1. Mass Blending Ratio

The mixing ratio is an important factor affecting the co-pyrolysis process of sludge. An assessment of the mixing of sludge and additives in different proportions demonstrated that they could not only affect the synergistic effect of co-pyrolysis between sludge and additives but might also improve the catalytic efficiency of the catalyst added during the co-pyrolysis process [69]. For example, Wan revealed that the distribution of gas, liquid, and solid three-phase products at different mixing ratios of wood chips and domestic sludge during co-pyrolysis resulted in a mixing ratio of sludge quality from 0% to 60%, and the yield of gas-phase products decreased significantly, but the yield of the solid phase increased by 19.9% [48]. Cheng pyrolyzed the dehydrated sludge with pine sawdust, litter, fallen leaves, and other biomass in different mass ratios. Studying the calorific value of gas and the carbon conversion rate [70], it was found that when m(sludge):m(pine sawdust) = 1:1, the calorific value of combustible gas is higher, and the carbon conversion rate is greater than 70%, ensuring a high fuel gas heating value and carbon conversion rate. Fang found that different mass mixing ratios between paper sludge and municipal solid waste resulted in a reduction in the initial temperature and activation energy of the catalytic pyrolysis of metal oxides, and with an increase in the mixing ratio of papermaking sludge, the degree of reduction in the initial temperature by the catalyst changed as follows: ZnO > MgO >

Al_2O_3 to Al_2O_3 > MgO > ZnO [71]. Gao studied the distribution of co-pyrolysis products of fly ash and oily sludge, which was evaluated by TG analysis, and found that when *m*(fly ash):*m*(oily sludge) = 1:1, the oil and combustible gas yields were increased by 13.85% and 2.24% [72].

4.2. Co-Pyrolysis Temperature

Pyrolysis temperature is another important factor affecting the co-pyrolysis process of sludge. Wang revealed three stages of co-pyrolysis in the co-pyrolysis of sewage sludge with sawdust as an additive as follows [73]: (1) at 40~180 °C, moisture and other volatile components evaporate and precipitate, which is the dry degassing stage of pyrolysis; (2) 190~520 °C is the light-weight analysis phase, and due to the synergetic effects between sewage sludge and wood chips, the weight loss rate of co-pyrolysis is 7.0% higher than that of sludge; (3) 615~715 °C is the coke formation and carbonization stage of co-pyrolysis, and, at this stage, a small amount of organic material, inorganic salts, and coke undergo deep pyrolysis. Wang studied the DTG curve of the co-pyrolysis of sewage sludge and rice husk at different temperatures (Figure 1) and found that there are four stages [74]: (1) the evaporation of water mainly occurs at 30~150 °C, which is the water vaporization stage of pyrolysis. (2) The pyrolysis of hemicellulose, cellulose, polysaccharides, carboxylate and protein mainly occurs at 150~600 °C, which is the stage of light component volatilization. At this stage, as the mixing ratio of rice husk quality increases, the decomposition of volatiles is promoted. Moreover, there is a shoulder peak between the weight loss peaks, indicating that there is an overlap in the decomposition process of volatiles and carbon due to the synergistic effect of co-pyrolysis. (3) The carbonization of lignin and remaining hydrocarbons mainly occurs at 600~700 °C, which is the carbonization stage of pyrolysis. (4) The decomposition of minerals mainly occurs at 700~1000 °C, which is the mineral decomposition stage of pyrolysis.

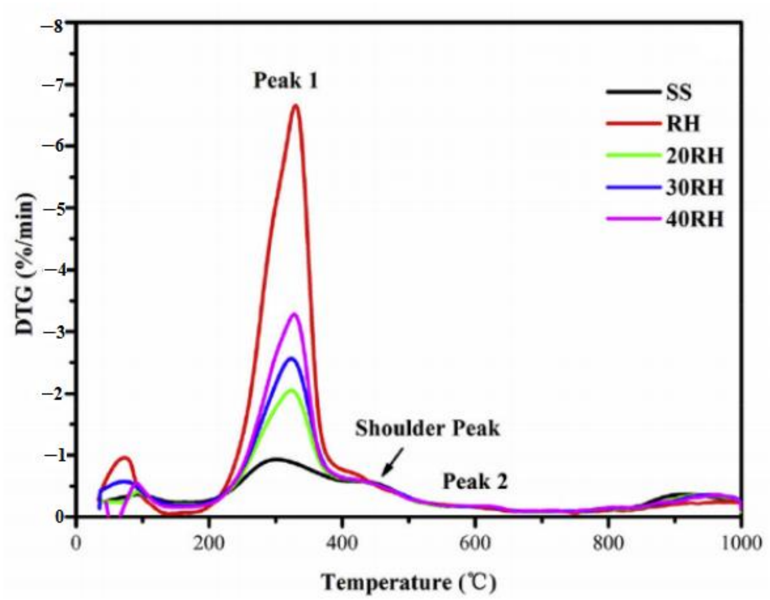

Figure 1. DTG curves of co-pyrolysis of sewage sludge (SS) and rice husk (RH) at different temperatures [74]. Reproduced with permission from [Teng Wang], [Journal of Cleaner Production]; published by [Elsevier], (2020).

4.3. Co-Pyrolysis Time

Different co-pyrolysis times will lead to different degrees of pyrolysis. A suitable co-pyrolysis time will make up for the lack of pyrolysis carbonization or light component volatilization time, thereby optimizing the quality and performance of co-pyrolysis products [75]. Wang also explored the effect of biochar prepared under different co-pyrolysis times on the iodine value during the co-pyrolysis of sludge and straw and found that with the extension of the co-pyrolysis time, the iodine value continued to increase [76]. After 120 min, since the pyrolysis residue had been fully carbonized, its pore structure remained unchanged and the iodine value also tended to stabilize. Wang prepared biochar via the co-pyrolysis of sewage sludge and cotton stalks and found that the extension of the co-pyrolysis time resulted in an increase in the surface alkalinity of the biochar, ash content, and the specific surface area of biochar, but if the pyrolysis time was too long, the specific surface area of the biochar would be reduced [77]. In addition, the results of heavy metal risk assessment show that extending the pyrolysis time reduces the potential environmental risks of heavy metals in the biochar.

4.4. Catalyst

During the co-pyrolysis of sludge, large-scale applications might be affected by high pyrolysis temperatures and high energy consumption. Therefore, because the catalyst functions by reducing the pyrolysis temperature, reaction time, and pyrolysis energy consumption and improving pyrolysis efficiency, it is widely used in the pyrolysis process. Qiu studied the co-pyrolysis of sewage sludge and rice husk, using the pyrolysis residue of rice husk as a catalyst, and found that the calorific value of pyrolysis oil increased from 25.75 MJ/kg to 34.67 MJ/kg, the O_2 content decreased from 31.1 wt.% to 8.81 wt.%, and the pH increased from 4.06 to 5.48, which effectively proved the optimization of the pyrolysis process with the catalyst [78]. Fang used the catalysts MgO, Al_2O_3, and ZnO to study the co-pyrolysis of paper sludge and municipal solid waste under an N_2 atmosphere and found that they could effectively reduce the activation energy of the co-pyrolysis, and the catalytic effect was as follows: MgO > Al_2O_3 > ZnO [62]. (Figure 2).

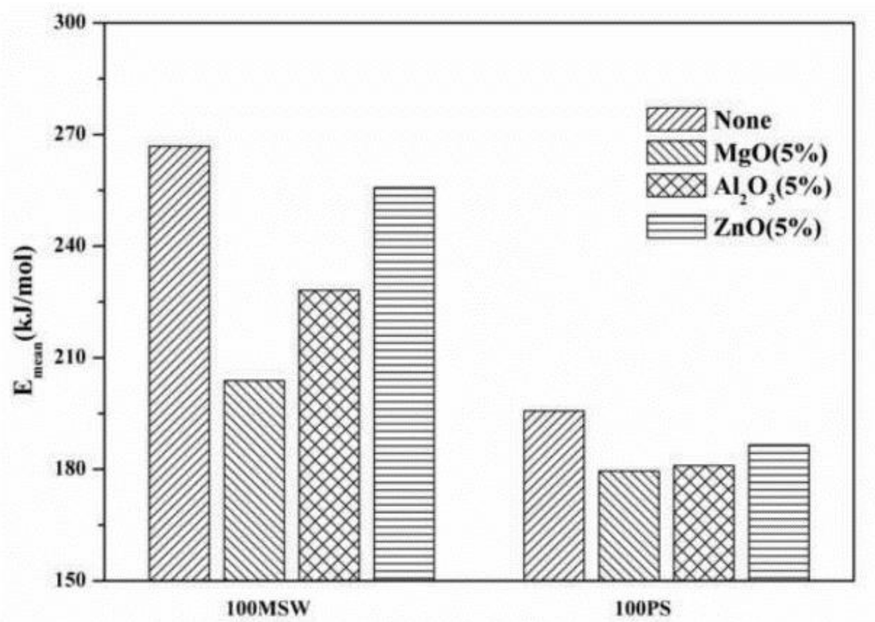

Figure 2. Effect of catalysts on activation energy of municipal solid waste and paper sludge [62]. Reproduced with permission from [Shiwen Fang], [Applied Thermal Engineering]; published by [Elsevier], (2017).

5. Conclusions

Although sludge pyrolysis and co-pyrolysis technology has produced undisputable advances, due to the complex source of sludge components, insufficient pyrolysis, and high energy consumption, there is still a long road to industrial applications. However, exploring the sludge co-pyrolysis technology of sludge and additives will provide us with innovative ideas and directions. By combining the characteristics of various sludges, it is believed that hotspots with broad application prospects should be the following: (1) in-depth understanding of the pyrolysis mechanism between the co-pyrolysis of sludge and different additives, explicitly studying the reasons for the underlying synergy to further improve co-pyrolysis efficiency. (2) Conducting research on the co-pyrolysis of sludge and more kinds of cheap and easily available substances and studying more influencing factors of sludge products, such as fast pyrolysis and slow pyrolysis so as to better optimize the synergistic effect of sludge co-pyrolysis technology. (3) Using different sludges to study the issues related to industrial applications, such as plant configuration, running time, feeding system, etc., to achieve the goal of "waste recycling".

Author Contributions: Conceptualization, J.L.; methodology, L.H.; validation, C.Q.; formal analysis, L.H.; investigation, T.Y. and B.Y.; resources, C.Q.; data curation, Z.S.; writing—original draft preparation, L.H.; writing—review and editing, J.L. and L.H.; visualization, T.Y. and B.Y.; supervision, C.Q.; project administration, J.L.; funding acquisition, C.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science of China (21808182, 51974245), Key Research and Development Program of Shaanxi Province (2022SF-045, 2022GY-128), Key Laboratory Scientific Research Project of Shaanxi Provincial Department of Education (18JS088), and Science and Technology Plan Project of Xi'an (2020KJRC0097, 2020KJRC0098).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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