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Review

Transformation and Mitigation of Tar and Related Secondary Pollutants during Sewage Sludge Pyrolysis

Qingyuan Lin, Yongxiao Liu, Yimeng Jiao, Pengzhao Lv *, Yanbo Liu, Wei Zuo, Yu Tian and Jun Zhang *

State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), School of Environment, Harbin Institute of Technology, Harbin 150090, China; linqingyuan6814@163.com (Q.L.); 23s136538@stu.hit.edu.cn (Y.L.); 23b329011@stu.hit.edu.cn (Y.J.); 23B929088@stu.hit.edu.cn (Y.L.); zuoweistar@163.com (W.Z.); hit_tianyu@163.com (Y.T.)

* Correspondence: lvpengzhao1014@126.com (P.L.); hitsunyboy@126.com (J.Z.); Tel./Fax: +86-0451-8628-3077 (J.Z.)

Abstract: Sewage sludge has long been perceived as the bottleneck of wastewater treatment plants in China, restraining the healthy development of sewage treatment for decades. In recent years, pyrolysis as a promising multifunctional platform has attracted increasing interest for converting sludge into valuable resources. However, the generation and presence of pyrolysis tar, one of the key by-products during sludge pyrolysis, limit the wide application of pyrolysis product resources. The efficient and selective conversion of tar is complicated by the inherent complexity of sludge and various pollutants (e.g., N-, S-, and Cl-containing organic pollutants, heavy metals) in pyrolysis products, which may either migrate into tar or be released into the environment, complicating the in-depth treatment of tar and posing environmental risks. This review systematically examines the transformation and migration of tar and related secondary pollutants during sludge pyrolysis in order to optimize the pyrolysis process for resource recovery. We provide an overview of the research progress on tar generation, transformation, and secondary pollutants during pyrolysis; discuss potential control strategies for pollution abatement; and highlight the importance of understanding tar transformation during pyrolysis. Additionally, we offer insights into future development trends and research hotpots in this field. This review aims to deliver valuable information on the mechanism of tar formation, the conversion pathways of secondary pollutants, and corresponding control strategies, thus guiding the design and optimization of sludge pyrolysis processes to achieve higher efficiency and selectivity, with minimal environmental pollution.

Keywords: sewage sludge pyrolysis; transformation; mitigation; tar and secondary pollutants; co-pyrolysis

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1. Introduction

Energy shortages and environmental damage are considered issues of growing concern for sustainable development [1]. China has suggested a two-stage carbon emission reduction target, the "double-carbon strategic goal", in response to this situation, in which it is expected that carbon dioxide emissions will peak in 2030 and that carbon neutrality will be achieved by 2060. Sewage treatment contributes approximately 1–2% of the total greenhouse gas emissions in the world [2]. Recently, the sewage treatment industry in China has lowered its carbon emissions mainly by using low-energy magnetic levitation fans, precise aeration systems, and wastewater reuse systems and reducing additional carbon sources [3]. Therefore, controlling carbon emissions from sewage treatment is an effective way to meet China's goal of carbon neutrality. Sewage sludge (SS), as the main byproduct of the sewage treatment process, is definitely generated in sewage treatment plants [4–6]. The annual production of dewatered SS in China was between 72 million and 75 million tons from 2014 to 2020, according to data from the Ministry of Ecology and Environment of China, as shown in Figure 1. It is estimated that the sludge yield will reach

90 million tons in 2025, with a growth rate of 8–10% [7]. However, the effective treatment rate of SS is only about 30%, greatly limiting the healthy development of sewage treatment. Furthermore, improper SS treatment can cause serious environmental pollution, especially secondary pollution of soil and water, subsequently entering the food chain. In recent years, with the continuous improvement in SS discharge standards, the cost of SS treatment has accounted for the vast majority of the total cost of water treatment [8]. Due to this circumstance, people are beginning to rethink traditional SS treatment processes for more sustainable SS management [9].

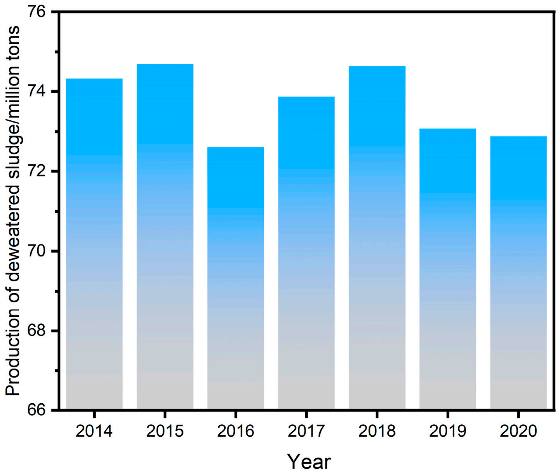

Figure 1. Annual production of dewatered SS in China from 2014 to 2020.

In China, the traditional treatment of SS is mainly landfilling, anaerobic digestion, incineration, agricultural purpose, and construction material production [10], which are limited in their development due to high pollution and non-recyclability [11]. Due to the huge SS output in China and the scarcity of land resources, the large-scale promotion of sanitary landfills is unrealistic [12], and due to the lack of system management systems, SS has become the main source of pollution in many areas near landfills [13]. Although most SS is still landfilled in EU countries, regulations have been put forward that aim at minimizing landfills, and France banned SS landfills in 2002 [14].

Compared with landfills, incineration has grown significantly in China as the most thorough SS treatment method, but its high cost and tendency to cause secondary pollution such as dioxins and fly ash during combustion limit its further development [15,16]. To ensure the sustainability of SS treatment and management, it is necessary to evaluate each process in terms of both the advantages and disadvantages (Table 1). Traditional disposal methods have their own limitations and cause secondary pollution of the environment. To comply with improved SS disposal standards, more environmentally friendly and efficient SS disposal methods need to be developed [17].

Table 1. Advantages and disadvantages of SS treatment technologies [18–22].

SS Treatment Technology	Description	Advantages	Disadvantages
Agricultural purposes	Stabilized SS could be used as a fertilizer.	N, P, and K can provide high-value fertilizer; organic matter can serve as an effective soil conditioner.	The direct disposal of SS in farmland can be a source of risks for both human health and the environment.
Construction material production	SS could be used as building materials.	Reduced land occupation and the consumption of resources; recycling of resources.	There are strict requirements for the pre-processing of SS.

Table 1. *Cont.*

SS Treatment Technology	Description	Advantages	Disadvantages
Landfilling	Landfilling is the conventional way of treating, storing and disposing of SS.	Well-known process for disposal of SS due to mature technology; extensive experience; Simple operation management; economic energy saving; low investment, fast results; generates 50–60% of CH_4 under anaerobic conditions.	The high moisture and volatile solids contents of the SS complicates the process; the CH_4 could be generated along with CO_2 (30–40%) and many harmful pollutants, such as H_2S, NH_3, and volatile organic compounds; additional environmental challenges include limited land resources and strict anti-leakage requirements.
Incineration	Operating temperature: 800–900 °C; O_2/air atmosphere; atmospheric pressure; suitable for dry SS.	High Waste volume reduction (up to 70%); recovery of fuel (similar to the sub-grade coal); overall CO_2 reduction; effectively kill the pathogen; solve the problem of stains and smell.	High cost; Source of noxious emissions of furans, dioxins, HF, C_xH_y, HCl, SO_2, N_2O, and NO_X; strict emission standards; require additional fuel.
Gasification	Operating temperature: >700 °C; gasifying agent (steam/CO_2, etc.) needed; atmospheric pressure; suitable for dry to semidry SS.	High-grade burnable gas.	High-energy consumption; low resulting gas quality; low gasification efficiency.
Anaerobic digestion	Anaerobic digestion is one of the most well-known conventional processes for the stabilization of organic SS, and it is now considered an essential part of modern wastewater treatment due to its economical and environmentally friendly aspects.	Sustainable technology for SS management; production of biogas for heat and power generation or conversion into transport fuel or renewable natural gas; reduce 35% -50% of volatile solids in SS; reduce the amount of SS dry solids; reduce subsequent SS treatment costs.	Sticky reaction conditions; need for additional energy input; low treatment yield, low product recovery; high greenhouse gas production; small fraction of CH_4 produced; limited reduction of volatile solids; long reaction time (over 20 days), high environmental conditions and long initial debugging of the microbial bacteria; high moisture content of the SS after anaerobic and digestion.
Pyrolysis	Operating temperature: 400–600 °C; inert atmosphere; atmospheric pressure or high pressure; suitable for dry SS.	Production of bio-oil, biogas, or biochar; optimization of the conversion and maximization of the most desired product yield and properties.	High costs for the pre-drying process.

The SS pyrolysis process has received increasing attention worldwide due to its lower SO_X, $NO_{X,}$ and greenhouse gas emissions and lower mobility of heavy metals than combustion. It is also considered as an effective way to realize resource utilization, reductions, and the harmlessness of SS [23]. Developing clean SS pyrolysis technology, converting waste SS into biomass energy, and recycling organic resources and energy in SS will become the new directions of industrial development in the future. Consequently, pyrolysis can produce diverse attractive value-added products, such as tar, biogas, and biochar [24,25]. The properties and components of products may change as the pyrolysis conditions change [26].

In addition, the bibliometric analysis by using “sludge pyrolysis” as the keyword is conducted in the “Web of Science” database. Figure 2a shows that since the first article was published in 1976, a total of 7008 articles had been published by February 2023, reaching the highest number of publications in 2022 and showing an overall increasing trend year by year. Through the VOS analysis of clustering network visualization (Figure 2b) and co-occurrence density visualization (Figure 2c) of SS pyrolysis, the popular keywords studied in recent years are “biochar”, “production”, “co-pyrolysis”, “gas”, “kinetic”, “model”, etc., while “bio-oil” or “tar” are less frequently found, indicating that more research focusing on “bio-oil” or “tar” is needed in the future. Early studies mainly focus on mesophilic flash pyrolysis to maximize the tar yields [27,28]. In addition to temperature, there are many conditions, such as heating method, residence time, and SS properties, which would affect the yield of final products [14]. Although the introduction of SS pyrolysis has been conducted in published reviews, there is little systematic and overall introduction of the effects of pyrolytic sludge on tar components, the key role of tar transformation into secondary pollutants, together with the contaminant control strategies. This review aims to evaluate pyrolysis technology as a promising clean, energy-efficient pollutant treatment option for SS treatment. Furthermore, we anticipate that this review will provide valuable information for optimizing SS pyrolysis platforms to achieve high efficiency and low pollution and stimulate research efforts to reduce SS pyrolysis pollution.

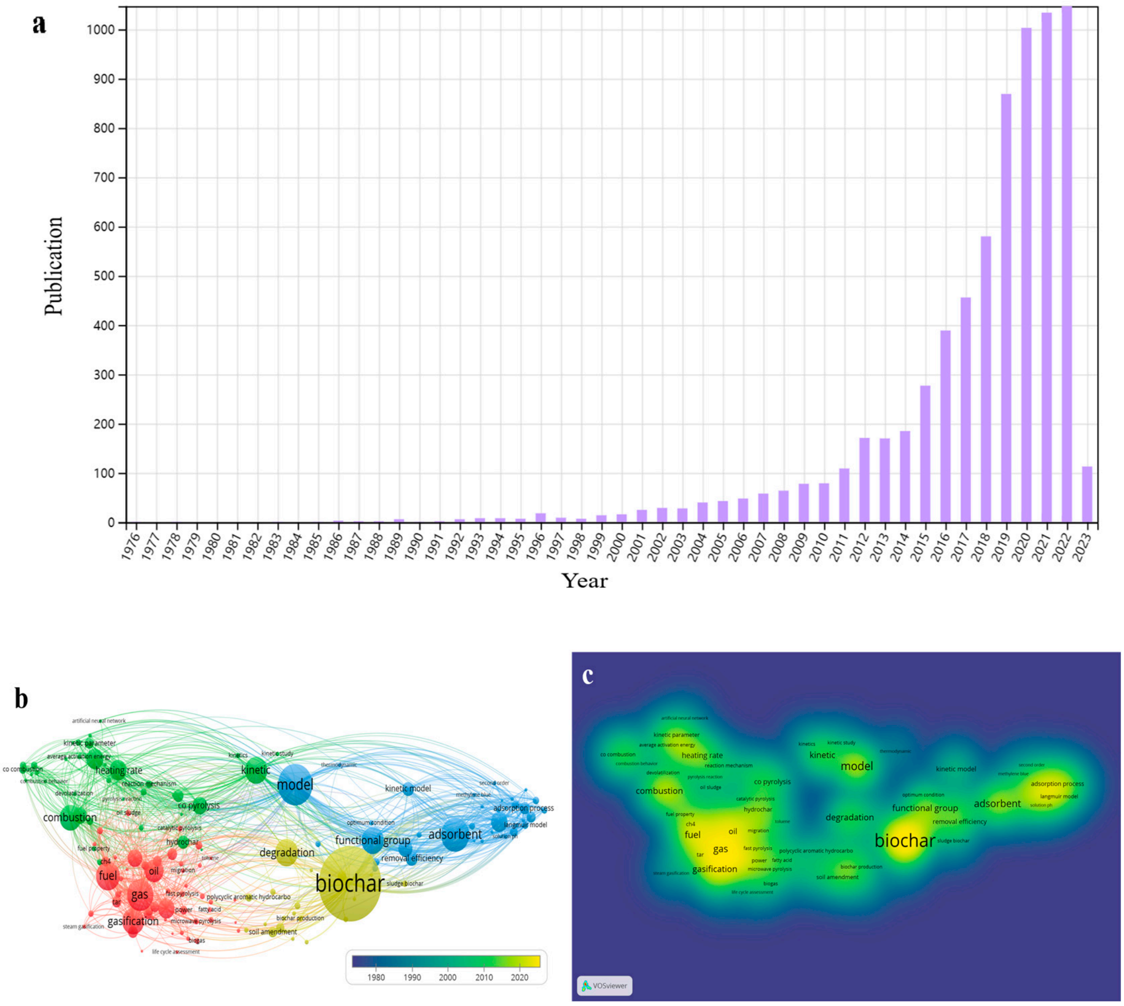

Figure 2. (**a**) Number of articles related to SS pyrolysis; (**b**) net visualization; (**c**) density visualization.

2. Insight into the Generation and Characteristics of Tar from SS

The calorific value of the dry base of SS is usually in the range of 12 to 20 MJ·kg^{-1}, similar to that of low-rank coal, paper, wood, and black liquor [29]. Thus, tar (also known as bio-oil or pyrolytic oil) produced from SS pyrolysis at relatively low temperatures (400–700 °C) contains a large amount of C and H elements, resulting in a high calorific value depending on the water content of tar [30].

2.1. Influence of SS Composition on Pyrolysis Tar

Tar composition is mainly derived from the diverse and complex characteristics of SS, including organic matter, water content, elemental composition, and ash content [31], which further affects the distribution and composition of pyrolysis tars. Organic matter in SS mainly consists of proteins (24–42%), carbohydrates (7–18%), and lipids (1–14%). Li et al. [32] studied the relationship between the composition of SS and its combustion performance and found that combustion performance was different with different components of

SS organic matter; protein was the main component of volatile matter, and SS combustion performance was significantly affected by protein concentration. It can be concluded that the tar composition is significantly affected by SS characteristics and pyrolysis processes. Here, we summarized the main components in tar from the pyrolysis of SS, as shown in Table 2.

Table 2. Major components in tar from pyrolysis of SS.

Components	**Proportion of Peak Area of Relative Contents (%)** [a]						
	[24] [b]	**[33]**	**[4]**	**[34]**	**[35]**	**[36]**	**[37]**
Alcohols	2.08	4.65	0	2.54	6.02	7.40	3.25
Aldehydes	0.19	1.74	-	0.07	-		-
Aliphatic hydrocarbons	0.23	21.93	5.86	-	3.08	12.26	13.57
Amides	3.42	1.20	9.93	-	-	3.83	-
Amines	1.09	-	-	-	-	-	-
Aromatic hydrocarbons	0.33	2.46	9.21	1.81	-	8.50	9.38
Acids	5.53	3.15	20.13		8.45	25.76	-
Ethers	1.20	-	-	1.65	-	-	-
Esters	0.72	0.88	9.18	-	-	1.37	48.59
Furans	3.24	1.66	-	-	-	-	-
Ketones	6.85	11.72	6.40	2.00	7.25	-	-
Nitriles	2.37	8.18	5.47	-	-	14.89	-
Phenols	17.82	15.28	7.00	1.48	0	1.40	6.95
Pyrroles	3.82	4.04	-	-	27.99	-	-
Saccharides	2.66	-	-	-	-	-	-
Halo hydrocarbon	-	-	20.44	-	-	-	-
Guaiacol	-	-	-	0.45	-	-	-

Notes: [a] expressed in the proportion of peak area (%) in GC-MS result except stated otherwise; [b] expressed in wt%; - not mentioned.

It can be found that the tar yield of most of the SS increases with the proportion of organic matter in SS, and most of the liquid compounds in tar are derived from the devolatilization of SS [38]. However, too high a pyrolysis temperature is not conducive to the output of tar, and the production of PAHs increases significantly when the temperature is higher than 625 °C, indicating that high temperature produces toxic tars rich in polycyclic aromatic hydrocarbons (PAHs) [39]. Compared with the higher tar yield of SS from WWTPs, some industrial SS samples, such as paper SS, leather and textile SS, high-ash SS, and milk processing SS, show lower tar yields [40], mainly due to their complex components, promoting the deoxygenation and aromatization reactions of heteroatom tars to form PAHs by self-pyrolysis, resulting in a decrease in tar quality. Therefore, pyrolytic tar of SS still faces serious shortcomings, such as high energy consumption, being low value-added, and the formation of toxic substances, due to the influence of SS sources and components.

2.2. *Comparison of Pyrolysis Tar between Conventional and Microwave Pyrolysis*

Different heating methods have a certain influence on the yield and composition of tar [41]. Conventional pyrolysis (CP) mainly refers to the method of transferring energy from the outside to the SS surface by means of electricity or fuel combustion. In the last decade, the CP technology of SS has mainly developed into the slow pyrolysis process [42], fast pyrolysis process [43,44], and flash pyrolysis process [45]. Future studies on CP of SS should focus on thermogravimetric analysis [46], metal oxide catalysts [47], characteristics of biochar [48], tar components [49], and biogas components [50]. Researchers have found that more tar can be produced at moderate temperatures and shorter residence times [51]. During the CP process, heat is first transferred to the surface of SS, and the local temperature increases, which first causes moisture evaporation in the drying stage (DS), and then the pyrolysis volatiles are gradually released at the primary pyrolysis stage (PPS). Primary volatiles are mainly produced by thermal cracking of chemical bonds of proteins, carbohydrates, lipids, and other organic compounds in SS. However, it is noted that CP of SS generally suffers from some key challenges, including low energy efficiency, high reactor complexity, poor product quality, and so on [52].

Microwave-assisted pyrolysis of SS (MP) has received increasing attention since 1999 due to the advantages of short processing times, low energy requirements, efficient heat transfer, and selective heating [53]. The energy transfer of MP is achieved by dipole rotation and ion conduction into heat inside the particles, which has the advantages of a fast temperature rise, uniform temperature distribution, and energy saving compared to the CP process. A comparison of CP and MP is shown in Figure 3 [54,55].

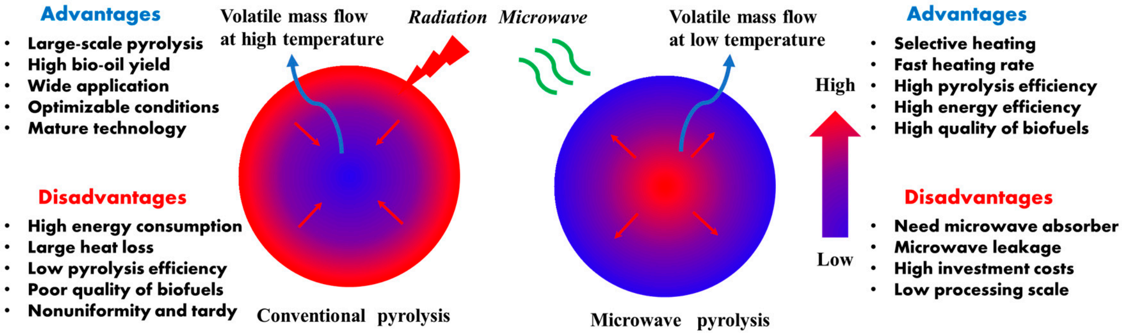

Figure 3. Comparison of conventional pyrolysis and microwave pyrolysis.

Due to the selective heating of the MP process, the effect of MP on chemical bonds in SS is very different [56]. Recent studies have found that MP can reduce the activation energy of H_2 and CO by 23% and 36%, respectively [57], thereby increasing the release of H_2 and CO, which can reduce the side reaction and promote the transfer of oxygen-containing functional groups to the liquid tar. A further increase in temperature can promote the cyclization and condensation of tar and the thermal decomposition of ester groups [58]. Other studies have shown that under the condition of MP, a higher H/C ratio indicates that more hydrogen atoms are directly converted into tar rather than released into biogases, due to the side reaction of hydrogen transfer during pyrolysis. There are more aromatic compounds in tar during MP, indicating that microwave can promote hydrogen transfer reaction at higher temperature in tar recovery [41]. From the point of view of energy saving, product quality, and efficiency, MP is considered a better method than CP because of its unique heating mechanism. Therefore, cooperation between different disciplines should be strengthened to promote the commercialization and development of this promising technology [59].

2.3. Characteristics of Tar Components from SS Pyrolysis

The tar produced by SS pyrolysis is a complex, dark-brown, smelly, and sticky compound in composition and includes organic compounds (hydrocarbons, heteroatomic compounds, ketones), minerals, and water (initial water evaporation of SS, dewatering reaction and fragmentation of high molecular weight oxygenated compounds) [24,60]. Some studies calculate the yield of tar including water and organic matter, while others quantify the yield of the water phase and organic phase, respectively [27,61]. Generally, the liquid product is divided into at least two layers, with the ratio of the aqueous phase to the organic phase being approximately 65:35 (v%), depending on the distribution of SS components, process conditions, and liquid recovery methods [29]. The density and viscosity of pyrolytic tar at 20 °C are in a range of about 940–1250 kg·m^{-3} and 17 cSt, respectively. And, because of the high moisture content, the heat value of the water phase is lower than 20 MJ·m^3, while the heat value of the organic phase is as high as 30–45 MJ·m^3, respectively [30,62]. The water phase mainly contains polar compounds, including ammonia, acetonitrile, carboxylic acid, methanol, trace monomeric, and oligomeric saccharides, and other polar organic compounds, while the organic phase is usually composed of aliphatic and aromatic hydrocarbons, phenols, carboxylic acids, aliphatic esters, and nitrogen heterocyclic compounds [63,64]. The overall calorific value of pyrolytic tar is in the range of 20–30 MJ·m^3 due to differences in tar composition. The pH of the tar is slightly alkaline (7.9–10.1), because of the high nitrogen content in the SS [65]. The differences in polarity and density of many of the constituents are conducive to phase separation in SS pyrolysis tar. Each phase has different physical and chemical properties, and induced phase separation can improve the physical and chemical properties of tar.

The complexity (difficult to separate), corrosivity, and instability of tar compounds (susceptible to ageing and degradation, low-molecular-weight oxygen-containing compounds will undergo re-polymerization, condensation, etherification and esterification even at room temperature, leading to thermal instability and ageing of tar) and density with a low oxygen rate limit the direct application of tar [66]. Moreover, S and N compounds in tar, such as mercaptan, amide, and pyrrole, may emit potentially harmful gases such as SO_2 and NO_X during combustion [67]. Like other biomass pyrolytic tar, pyrolytic tar of SS has a large amount of water and free oxygen content [68]. The high water content significantly reduces the calorific value and limits its applicability as fuel, while contents with high oxygen rates make fuel upgrading challenging [69].

3. Key Role of Tar in the Transformation of Secondary Pollutants during Pyrolysis

Tar can be classified into five classes of compounds, including aliphatic, heterocyclic, light aromatic, light polyaromatic hydrocarbons, and heavy polyaromatic hydrocarbons. It is reported that the various abundant components of pyrolytic tar play important roles in the release of secondary pollutants during pyrolysis. Wang et al. [70] and Zhang et al. [71] reported that the pyrolysis of high nitrogen contents in oil sludge contributes to either NO_X or N_2O. Gao et al. [72] investigated the potential ecological risk index of pyrolysis chars containing a high concentration of heavy metals. Zhang et al. [73] investigated the behavior of sulfur during pyrolysis of waste tires and found that the sulfur-containing compounds in pyrolysis char are mainly composed of non-volatile sulfur, sulfur, and trace amounts of organic sulfides. Gao et al. [74] found that chlorine mainly remained in char (42.36%) in the form of inorganic Cl, while 35.03% and 22.61% of chlorine migrated into gas and tar, respectively. Based on the previous studies, the most reported secondary pollutants, such as N, S, Cl, and heavy metals (HMs), have been significantly investigated in recent years due to their toxic and harmful impacts on ecology and the environment.

3.1. Tar in the Transformation of Nitrogen-Containing Pollutants

The N content of SS (2.4–9.0 wt%) is higher than those of most conventional fuels, such as coal (<1.0 wt%) and biomass (0.1–4.0 wt%), of which 50–80% is converted to nitrogenous gas [75]. Moreover, the main nitrogen-containing substances in SS are in the form of protein–N, while pyridine–N and pyrrole–N are the main nitrogen-containing substances in coal [76,77]. The nitrogen compounds in SS may be more active than those in higher-rank coals and may even be less stable than those in lower-rank coals [78].

Previous researchers have conducted many studies focusing on the migration behavior of tar–N. Recently, Yan et al. [79] investigated the conversion of N-containing species in the pyrolysis of biomass. Liu et al. [80] studied the source of HNCO generation during coal tar pyrolysis. And Tian et al. [81] investigated the nitrogen conversions during microwave pyrolysis of sewage sludge. The main tar–N compounds were 1-cyanonaphthalene and 2-cyanonaphthalene, 5, 6-benzoquinoline, carbazole, quinoline, thiocyanic acid, 1H-indol-3-lyest, 9-cyanophenanthrene and acenaphtho (1, 2-B) pyridine. In SS pyrolysis, the light PAHs, such as cyano-aromatic compounds and N–heteroaromatic compounds, make up the majority of tar–N compounds. In addition, nitrogen-containing chemicals (amides, pyrroles) have been found in the tar formed by SS pyrolysis, which might lead to NO_X emissions during combustion [67]. It is found that the thermal cracking of proteins in SS produced three important intermediate compounds, including amino–N, heterocyclic–N, and nitrile–N compounds. Meanwhile, the deamination of amino–N compounds in the range of 300 to 500 °C mainly leads to the formation of NH_3. The hydrogenation and polymerization of amine–N from tar contribute to the formation of nitrile–N and heterocyclic–N compounds, respectively, which further thermally crack into hazardous HCN between 500 and 800 °C. Thus, HCN and NH_3 emissions can be reduced by controlling the production of three intermediates at temperatures of 500–800 °C [81]. In addition, research on the pyrolysis of soybean protein also found that the decomposition of three intermediate compounds contributed more than 97% of the total (HCN and NH_3) production. The N–migration paths of the SS and protein model compounds are shown in Figure 4 (a) and (b), respectively [81,82]. A detailed summary of the types of compounds to which N migrates is shown in Figure 4c [83].

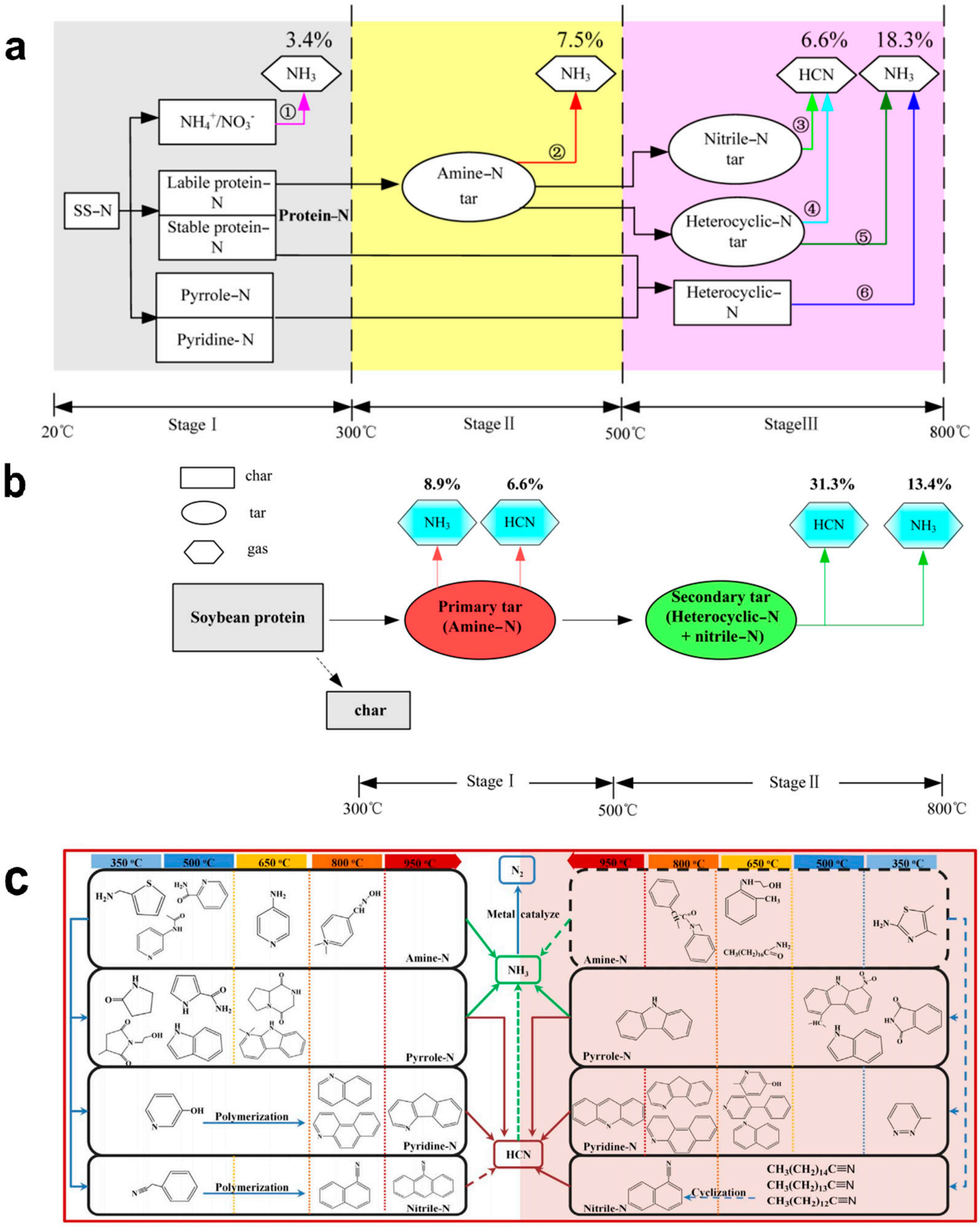

Figure 4. N migration of SS (**a**), soybean protein (**b**) and tar–N (**c**) during the pyrolysis [81–83].

During the pyrolysis of SS, a part of the nitrogen is released in the form of N–tar compounds. In addition to N–tar compounds, approximately 50–80% of the total nitrogen is released as nitrogenous gases, including NH_3, N_2, HCN, and nitrogen oxides. However, it is worth noting that the large amounts of harmful nitrogenous gas mainly containing NH_3 and HCN may be converted into NOx, contributing to the severe photochemical smog and acid rain pollution. It is also reported that the cyano–N and heterocyclic–N compounds are identified as the major nitrogenated compounds in the tars during the pyrolysis of SS, which may also pose hazards to the environment and threats to human health [67,84].

Studies have shown that, although SS pyrolysis is different from SS combustion, there are still a number of nitrogen oxidation and nitrogen hydrogenation substances produced when the SS is heated in isolation from air. In the gas phase, approximately 0.2–0.6% of N in the SS would be converted into NO due to the presence of nitrite. A large amount of HCN is produced in the form of volatile components at 500 °C, and a maximum of 40% of the SS–N is converted into HCN at 800 °C [85]. NH_3, as another important nitrogenous gas in SS pyrolysis, will pollute the atmosphere and environment. The formation of NH_3 in the gas phase will be promoted by nitrogen-containing heterocyclic aromatic compounds in the tar in a temperature range of 200–600 °C [86]. At temperatures above 500 °C, the nitrogen-containing heterocyclic rings in tar are hydrogenated to form NH_3 by the action of H free radicals [87].

The N migration from the char phase into the tar and gas phase has also been reported. It is believed that the N content in the char phase gradually decreases with increasing temperature, and the content of char–N decreases from 50% to 20% when the pyrolysis temperature increases from 500 to 800 °C [88]. The content of protein–N in char decreased continuously and transformed into high-thermal-stability pyridine–N, pyrrole–N, and quaternary graphic–N in tar, which could account for more than 90% of gaseous N production [89]. Although many studies have been carried out on N-functional groups in biochar, there are still many gaps to be filled. Firstly, there are various analytical methods for analyzing the composition and content of N-functional groups. However, due to technical limitations and the interactions between pyrolysis substances, there may be deviations or even errors in the determination of some nitrogen-containing species, such as pyrrolic–N and pyridine–N, which may not be accurately distinguished using the existing technologies. Furthermore, the development of in situ detection technology for Char–N compounds is also worthy of attention.

3.2. Tar in the Transformation of Sulfur-Containing Pollutants

Sulfur contents in SS are higher than 1 wt%, which is primarily constituted by S-containing biomolecular structures (e.g., amino acids with S-containing side chains), inorganic sulfides, and insoluble sulfates [90]. H_2S and various S-containing compounds (e.g., thiols, organic sulfides, and thiophene-S) are identified as the major sulfur species in the gas and tar phase during SS pyrolysis [91]. The relationship between the behavior of S-containing compounds in tar and H_2S formation has been extensively studied to search for the transformation pathway. Xu et al. [92] studied the migration mechanism of sulfur elements during SS pyrolysis and found that the content of H_2S gradually increased in a range of 400 to 600 °C, which was mainly formed from methionine at low temperature. A large amount of sulfur-containing heterocyclic compounds was found in the tar, which were generated from sulfur-containing amino acids. With an increase in pyrolysis temperature, the heterocyclic compounds were further decomposed to produce H_2S. Meanwhile, the aliphatic sulfur and aromatic sulfur compounds were identified as the two main organic sulfur sources for the release of sulfur-containing gases [93], while the presence of sulfonic acid and thiophene in tar had no significant effect on the release of sulfur-containing gases. Huang et al. [90] studied the migration of S during SS pyrolysis (250–750 °C) and found that aliphatic-S and sulfonates degraded preferentially at low temperatures (below 350 °C), contributing to the volatilization of S from the solid phase. The sulfates were thermochemically reduced and aromatized above 450 °C, contributing to the formation of metal sulfides (up to 27%) and thiophene (up to 70%).

The sulfur distribution and evolution of sulfur-containing compounds in char, tar, and gas fractions during the CP (conventional pyrolysis) and MP (microwave pyrolysis) process have been investigated in detail previously. Three similar H_2S migration pathways were found during microwave pyrolysis and conventional pyrolysis. However, the secondary decomposition of thiophene-S compounds only occurs during CP above 700 °C. Comparing the contribution of MP and CP to H_2S, the significant increase in H_2S production of CP was mainly due to the decomposition of aromatic-S (10.4% increase) and thiophen-S compounds (11.3% increase). A further study on the mechanism of inhibiting H_2S formation by microwave pyrolysis confirmed that the special heating characteristics and relatively short residence time of microwave pyrolysis promoted the retention of H_2S on CaO and inhibited the secondary cracking of thiophen-S compounds at high temperature. The S migration in the char, tar, and gas products from the microwave pyrolysis and conventional pyrolysis is shown in Figure 5 [91].

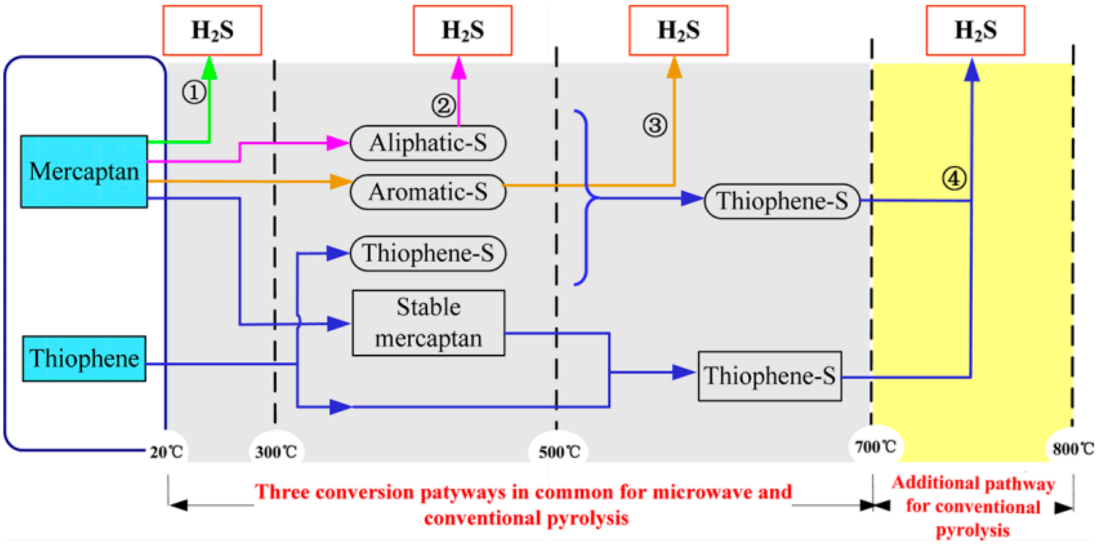

Figure 5. S migration in the char, tar, and gas products from microwave pyrolysis and conventional pyrolysis [91].

3.3. Tar in the Transformation of Chlorine-Containing Pollutants

The conversion characteristics of chlorine-containing contaminants in tar are usually neglected in SS pyrolysis. Some oily sludges (OSs) contain high levels of chlorine-containing compounds, with the chlorine originating mainly from the crude oil itself and chemicals added during the extraction and refining process [94,95]. The main source of chlorine in raw SS includes inorganic chlorides such as sodium chloride (NaCl) and calcium chloride ($CaCl_2$) and organochlorine compounds such as chlorobenzene [96]. The addition of NaCl and KCl can also inhibit the release of CH_3Cl [97]. The Cl in OS can be distributed 78.59–73.14 wt% into the solid residues after pyrolysis, and increasing the pyrolysis temperature contributed to the migration of Cl from the solid phase to the tar and gas phase [98,99]. Lin et al. [100] also found that NaCl can retain 99% of total Cl in char, while polyvinyl chloride (PVC) releases about 33% of Cl into the gas, and multiple organic chlorine-containing compounds were detected in pyrolysis tar, mainly CH_2Cl_2 and $C_6H_4Cl_2$. Some studies have summarized the migration for Cl release during the pyrolysis of biomass, as shown in Figure 6 [101], and found that the release of Cl was greatly influenced by the inorganic substances in the biomass, especially the alkali metal or alkaline earth metal (such as K, Ca, and Mg) compounds. Similar to S, Cl release in pyrolysis also comes from inorganic and organic Cl species available in biomass. Tar-associated Cl or HCl released at low temperatures can be recaptured by biochar through secondary reactions with available metals.

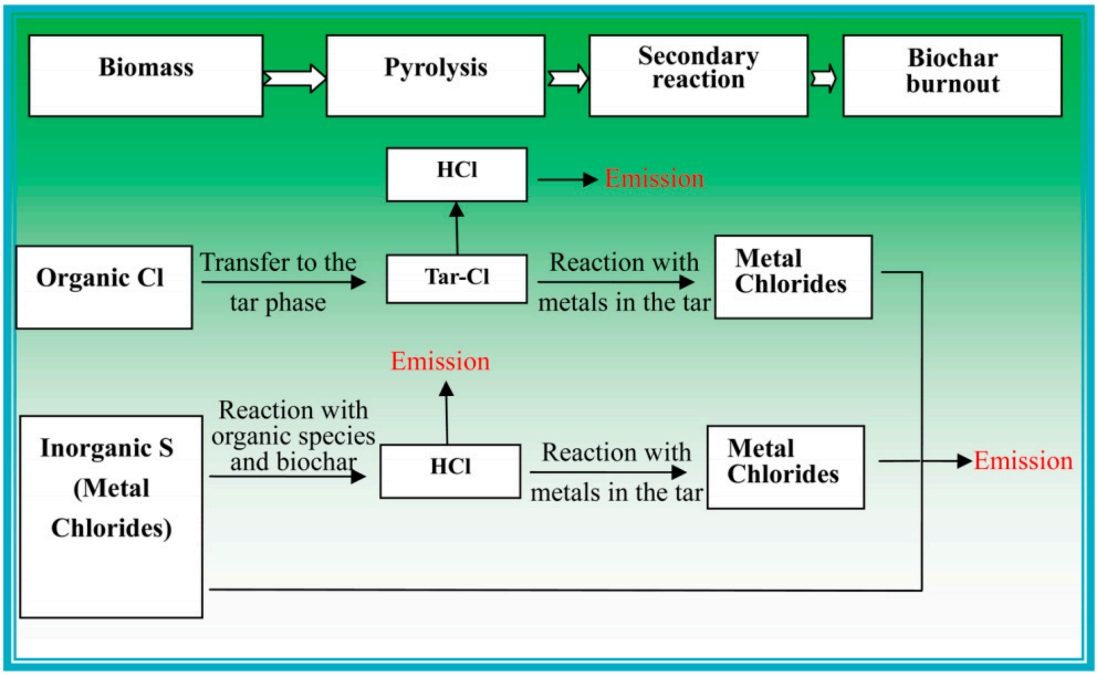

Figure 6. Migration of Cl in biomass pyrolysis [101].

During higher-temperatures phases, more Cl elements are generated by OS pyrolysis, and the possibility of dioxin formation will further increase. During the pyrolytic conversion of SS with a high chlorine content, Cl^- is easily converted to acid chloride or alkali chloride in the gas phase via evaporation. It is generally believed that Cl is most commonly coupled with potassium and sodium to form alkali chlorides, which exhibit considerable volatility through the evaporation into the gas phase above 600 °C, and this is the primary route for chlorine release [102].

It is noted that few studies focused on the release and transformation of chlorine-containing pollutants during the pyrolysis of SS, including OS [103]. The evolution of Cl covers the whole process of sludge pyrolysis, where the rapid release of HCl was in the 200 °C to 600 °C stage and the slow evaporation of KCl was in the >600 °C stage. The release of CH_3Cl was below 500 °C, which could be effectively suppressed by increasing the heating rate from 10 $°C \cdot min^{-1}$ to 500 $°C \cdot min^{-1}$ [104].

3.4. Tar in the Transformation of Heavy Metal Pollutants

The distribution and transformation of heavy metals (HMs) during SS pyrolysis are quite important, as they will affect the environmental adaptability of pyrolysis products and recycling. Zn, Cu, Ni, Pb, Cr, Cd, As, Mn, and Hg are the most reported metals during SS pyrolysis [105], among which Cu and Zn are the main HMs in SS due to their extensive uses such as in water pipes and zinc-plating materials. Since the normal pyrolysis temperature of SS is lower than the boiling point of most HMs, this contributes to 80% HMs remaining in the char after SS pyrolysis [106].

To better explain the migration process in tar, the metals can be divided into four parts: exchangeable and acid-soluble part (F1), reducible part (F2), oxidizable part (F3), and residual part (F4) [107]. Cu, Zn, Pb, Cr, Mn, and Ni are detected mostly in F1 and F2 fractions in the pyrolysis chars ranging from 400 °C to 600 °C [108]. Nevertheless, biochar exhibits lower leaching properties of HMs than that of incineration residues or hydro char from hydrothermal treatment [29,109,110]. The immobilization of HMs in char is called HM immobilization, in which HMs in SS are transformed from weak binding forms (F1 and F2) to more stable forms (F3 and F4) during pyrolysis [108]. The improvement in pyrolysis conditions can make the form of heavy metals more stable, thus greatly reducing the ecological risk of SS biochar to the environment.

Kistler et al. [111] found that Cd volatilizes significantly at 600 °C (98% when the temperature reaches 750 °C) during SS pyrolysis. This is because HMs with lower boiling points become metallic vapor and escape at higher pyrolysis temperatures. When the pyrolysis temperature is higher than 600 °C, the rank of thermal volatilities of HMs is Cu < Cr < Ni < Mn < Pb < As < Zn < Cd ≈ Hg [112]. The migration patterns of HMs are mainly determined by their boiling points and corresponding chemical forms, so HMs with lower relative boiling points (such as Pb, Zn, and Cd) are more likely to be removed from the pyrolysis process than metals with higher boiling points (such as Ni, Cr, and Cu) [113]. Therefore, the pyrolysis process is considered to be an effective method for the treatment of SS-containing HMs at relatively low temperatures.

It is worth noting that previous research on the migration of HMs in SS pyrolysis mainly focuses on the char fraction, but the distribution of HMs in tar during pyrolysis has received little attention in previous studies. Yuan et al. [114] conducted a risk assessment of HMs in SS pyrolysis tar and found that at high pyrolysis temperatures (>850 °C), Zn and Cd in tar have high risks, while at low pyrolysis temperatures, Cd, Zn, and Ni are the main pollutants. In addition, the mechanism of HM migration in IS pyrolysis is shown in Figure 7. Therefore, in the future, to evaluate the safety of SS pyrolysis, the study of heavy metals in the tar and gas phases will become a meaningful research work.

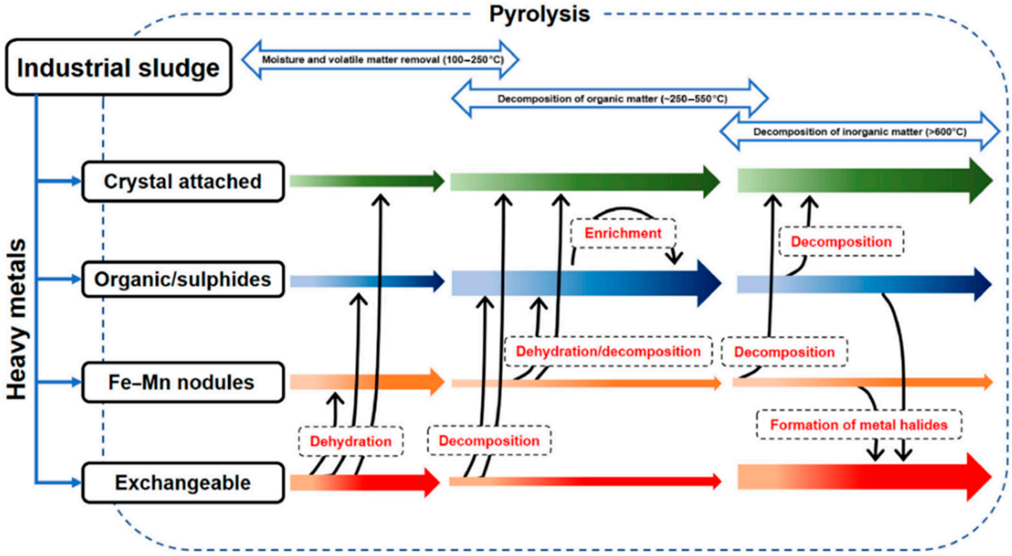

Figure 7. The mechanism of HM migration in IS pyrolysis [115].

4. Contaminant Mitigation Strategy in SS Pyrolysis

From the above section, it can be concluded that tar plays an important role in the migration and transformation of N, S, Cl, and HM-related secondary pollutants during SS pyrolysis. On this basis, it is necessary to search for effective measures to prevent the generation and discharge of these pollutants.

The pretreatment process prior to SS pyrolysis has been found to have a significant impact on the control of pollutants, in particular the reduction of nitrogen, sulfur, and chlorine pollutants. The most reported strategies include torrefaction pretreatment, hydrothermal pretreatment (HTP), alkali treatment, acid treatment, oxidant treatment, biological treatment, co-pyrolysis, etc. [116,117]. In the following section, the control of pollutant elements in terms of N/S/Cl as well as HMs and tar during treatment processes will be discussed.

4.1. Nitrogen, Sulfur, and Chlorine Contaminants' Control Strategy in SS Pyrolysis

In recent years, studies have shown that torrefaction can enhance the grindability, energy density, and calorific value of SS. It is also suggested that the roasting process has the advantage of the devolatilization, polycondensation, and carbonization of biodegradable organic matter in SS into non-biodegradable substances with stable aromatic and heterocyclic structures, where about 30% of N and 50% of sulfur in SS can be removed via torrefaction pretreatment [18]. This results in a significant reduction in the emissions of NO_X and SO_X precursors, such as NH_3, HCNO, H_2S, COS, CS_2 methyl mercaptan, pyrrole, and indole [18]. However, the majority of the existing literature primarily focuses on the effect of the drying degree on the physicochemical properties of SS [118,119]. The structural changes in carbonized sewage sludge and the resulting pyrolysis behavior, especially the formation of NO_X and SO_X precursors and corresponding control strategy of pyrolysis pollutants, have not been discussed in depth.

It is found that SS pretreatment through a combination of initial HPT and high-temperature pyrolysis influences the formation pathways related to NO_X precursors in different pyrolysis stages, thereby significantly reducing their total yield (66-95%), and the effect on NH_3–N is greater than that on HCN–N. Specifically, denitrification during hydrothermal pretreatment is one reason for weakening the source of NO_X precursors in the primary pyrolysis stage, while nitrogen function stabilization during hydrothermal pretreatment is another reason for suppressing the formation of NO_X precursors in the secondary reaction stage. Zhao et al. [120] found that HTP can efficiently convert organic Cl to inorganic Cl, thus reducing the possibility of clogging, corrosion, and dioxin formation during the combustion of high-Cl-content biowaste. However, at present, hydrothermal pretreatment coupled with pyrolysis mainly focuses on the control of N pollution, and the control of pollutants like S and Cl needs further in-depth research to evaluate its application in sludge pyrolysis.

Alkali treatment primarily adjusts the acid–base balance of SS by adding alkaline substances, such as NaOH or KOH, which can promote the degradation and oxidation of organic matter, thereby increasing the efficiency of pyrolysis reactions. At lower temperatures (i.e., 250 °C), alkali can facilitate the conversion of unstable organic aliphatic and aromatic sulfurs to more stable sulfoxides and sulfonic acids. The alkali can also immobilize inorganic sulfides and sulfates in the char. Moreover, the use of strong alkali exhibits a more pronounced reduction effect on sulfur-containing gases, possibly due to the generation of more ·OH through organic sulfur conversion. In addition, alkali treatment also has a certain influence on the pyrolysis of OS. Chen et al. [121] found that the washing treatment with surfactants and alkali can remove a significant proportion of organic components from the sludge, thereby reducing the generation of pollutants.

Oxidation treatment involves increasing the oxygen concentration by adding oxidants, such as K_2FeO_4 or $KMnO_4$, to the sludge. This accelerates the oxidation reaction of organic matter and promotes their decomposition and degradation. Simultaneously, the oxidant helps to remove certain organic pollutants and odorous substances in the sludge. K_2FeO_4 as a sludge conditioner has been shown to reduce the activation energy required for SS pyrolysis, making SS more susceptible to thermal decomposition, resulting in the production of volatiles. Specifically, K_2FeO_4 facilitates the release of C/H/O gases while suppressing the release of N/S/Cl noxious gases from the SS [122]. In addition, combined oxidation processes, such as Fenton peroxidation and CaO regulation, have been proposed to control the release of pollutants [123]. This combined regulation inhibits the conversion of amine–N/pyridine–N, pyrrole–N, and nitrile–N to HCN, thereby increasing their yields in char. The formation of the $Ca_2Fe_2O_5$ complex facilitates the decomposition of these intermediates, thereby enhancing the conversion of sludge–N and NO_X precursors (such as tar–N, NH_3, and HCN) to N_2, thereby effectively controlling pollutant emissions. The content of calcium acetate and sodium acetate in nitrogenous gas emissions is significantly reduced due to the production of acetone when acetate is heated, and acetone readily reacts with NH_3 to form binary clusters or amines. The above studies suggest that the addition of acetate is an important strategy to mitigate NH_3 emissions during SS pyrolysis.

Furthermore, co-pyrolysis is considered as a sustainable technology to optimize the pyrolysis process and improve the quality and performance of pyrolysis products. With the addition of Ca/Fe/Si/Al substances, the pyrolysis behavior of SS and the thermal conversion of nitrogen-containing substances are significantly affected. CaO facilitates the transfer of nitrogen into the gas/tar phases in the form of NH_3 and heterocycle–N at relatively lower temperatures (350–450 °C). In contrast, polyferric salts (PFA) inhibit the devolatilization of mono–heterocyclic–N and enhance the thermal stability of heterocyclic–N compounds, resulting in an increase in the nitrogen content in the char while reducing the release of NH_3 and HCN. However, the effect of silica-aluminates (SIA) on the pyrolysis behavior of PR was less significant compared to that of CaO and PFA. The acid centers on the SIA attacking the C-C or C-O bonds in the char matrix, promoting the transfer of aromatics and phenolics to the tar phase, which reduced the stability of the carbon–nitrogen bond, further leading to a slight increase in the release of nitrogen-containing gases and volatiles [124], while the residual iron compounds in ferrous SS stabilize char–N in a more stable form of pyridine–N and pyrrole–N (e.g., pyrrole–N appears at 900 °C). This stabilization process inhibits the secondary cracking of amine–N compounds in tar–N [125].

CaO is considered as an additive with high sulfur retention capacity for sulfur-containing pollutants. At temperatures below 350 °C, the addition of CaO can inhibit the decomposition of aliphatic sulfur-containing compounds and promote the formation of aromatized aliphatic sulfur-containing compounds, thereby controlling the emission of harmful S-containing gases. Li et al. [47] found that with an increase in the OS pyrolysis temperature, solid minerals, such as CaO, MgO, Fe_2O_3, Al_2O_3, etc., tend to inhibit the N, S, and Cl pollutant emissions at the dehydration and devolatilization stages (<358 °C). However, in the thermal cracking and secondary reaction stages (>358 °C), these minerals facilitate the release of pollutants. The co-pyrolysis of municipal domestic waste and paper SS adding additive (MgO) also confirmed that the addition of MgO resulted in a decrease in the mass of tar and a decrease in pollutant emissions (CO, SO_2, NO, and HCl). These results demonstrate the remarkable role of metal oxides and alkaline minerals in the control of SS pollutant precursors, offering meaningful insight for the mitigation of pollutants during energy utilization.

4.2. Heavy Metals Control Strategy in SS Pyrolysis

As described in the previous section, some of the strategies for N-, S-, and Cl-containing pollutant control can also contribute to heavy metal removal in the SS treatment process. Hydrothermal pretreatment (HTP) of SS has been shown to transform SS into a homogeneous, carbon-rich solid product (hydro char) with a low alkali metal content and low contaminant content [120]. During the pyrolysis of dead leaves of fan palm (a plant species common in Southern China) with HTP, it is found that HTP can effectively remove most alkaline earth metals/alkali metals and destroy the chemical structure of fan palm significantly, increasing the hydrocarbon content of pyrolysis tar [126].

Biological pretreatment is proven as an effective way to mitigate the HM transformation during SS pyrolysis. Previous studies have found that adding *Ochrobactrum* in pretreatment can inhibit the volatilization of Cr and Cu during SS pyrolysis, especially in the case of high-concentration Cu [127]. This study is of great significance for the subsequent acceleration of HM fixation in SS, and its mechanism still needs to be further investigated.

Moreover, more and more attention has been paid to the in situ control of contaminants during the pyrolysis of SS in recent years. People tried adding organic and inorganic chlorination reagents (PVC, NaCl, $MgCl_2$, $CaCl_2$) to control HMs in situ during SS pyrolysis and found that the removal of Zn, Mn, Cu, and Pb can efficiently reach above 86%. However, it should be noted that the operating costs and levels of secondary chlorine contaminants such as Cl_2 and HCl will increase significantly to corrode equipment and pollute the environment [128]. The addition of metal-loaded PVC microplastics to SS had a positive effect on the immobilization of HMs during the pyrolysis process, which can reduce the bioavailable yields of Cd, Cr, Ni, and Zn in biochar [129]. In addition, the phosphorus content of biomass can also greatly alter the behavior of HMs. Similar findings have been reported in subsequent studies. It is confirmed that phosphorus can be combined with HMs (Cu, Zn, Ni, etc.). Xiong et al. [130] verified the effect of phosphorus and revealed the relationship between orthophosphate content and HM migration during pyrolysis. It may be due to the degradation of organic groups during the co-pyrolysis process, and organophosphates are transformed into orthophosphates and inorganic phosphates by precipitation or adsorption of HMs. Furthermore, the number of functional groups increased as the proportion of biomass increased. Among them, functional groups such as carboxyl, hydroxyl, and phenolic hydroxyl are easy to complex with HMs, affecting the migration of HMs, and the addition of biomass also indirectly reduces the concentration of HMs [48]. Studying the co-pyrolysis of different SS (electroplating SS and sewage SS), it has been found that HMs can combine with inorganic mineral components to form stable crystalline compounds (CuCl, Cu_2NiSnS_4, $NiSi_2$ and ZnS). Meanwhile, it can also react with functional groups (Si-O-Si, -OH) on the surface of biochar and aromatic groups generated by the decomposition of organic matter through complexation reactions, where the combination with π electrons promotes the immobilization of HMs [131]. Therefore, the co-pyrolysis of different types of sludge also provides a new idea for HM immobilization during sludge treatment. Co-pyrolysis has broad potential for improving product quality and immobilizing HMs, as it may enable the use of additives to overcome the mismatch between SS properties and pyrolysis.

4.3. Tar Pollutants Control Strategy in SS Pyrolysis

The changes in tar constituents during SS pyrolysis are clearly related to the hydrothermal pretreatment. It is found that the ketone and acid content of tar decreases, while the levoglucosan content is much higher than that of the original tar without HTP, which will help to improve the thermal stability and calorific value of tar and extract levoglucosan from tar. Furthermore, Jiang et al. [132] found that the HTP can decompose oxygen-containing functional groups and remove some water-soluble inorganic substances in oil shale, thereby reducing the formation of gas and water during pyrolysis. The tar obtained by further pyrolysis has a higher H/C ratio, which is conducive to increasing the production of shale oil. However, the effect of HTP on the control of pollutants in sludge pyrolysis and the characterization of treated SS pyrolysis derivatives has barely been reported in the literature. There are still relatively few studies on the regulation mechanism of HTP and SS pyrolysis on the contaminant control strategy [133].

HTP also leads to an increase in the proportion of stable heterocyclic–N in char, which further controls nitrogen oxide emissions. Liu et al. [134] investigated the effect of HTP on SS and found that the properties of SS during HTP are improved, including better thermal stability, reduced nitrogen content, and enhanced aromaticity, which may affect the subsequent pyrolysis. After HTP, the composition of tar showed obvious changes. The contents of unwanted O/N-containing compounds, especially acids and amides, are significantly reduced, while the yields of aliphatic and aromatic hydrocarbons increased by 10% and 23%, respectively. Additionally, many studies have been devoted to improving the quality of tar and reducing pollutant emissions by combining HTP with the pyrolysis of various biomass or low-rank coals.

Chemical methods also play a very important role in controlling tar quality. Acid treatment can promote the hydrolysis and decomposition of organic matter and reduce the catalytic activity of inorganic compounds by either washing out the metals or passivating metals from interacting with organic components [135,136], further affecting the contaminant distribution of the pyrolysis process. It is reported that acid pretreatment of SS in pyrolysis can improve the quality of tar and enhance the adsorption performance of biochar [137,138]. Other studies have found that a higher acid concentration and lower treatment temperature can achieve a better deashing effect [139]. However, the internal effects of acid pretreatment on catalytic pyrolysis of SS are limited, and the associated corrosion problem as well as the need for additional chemicals for neutralization are also special challenges for strong acid desalination.

From the above sections, the strategies for controlling different contaminants in SS pyrolysis are summarized, which indicates that the research focus of SS pyrolysis technology in recent years has begun to evolve towards co-pyrolysis with other biomass, which can make the SS pyrolysis process more efficient, environmentally friendly, and economical. It can be seen that the co-pyrolysis technology has great potential in the pyrolysis and immobilization of HMs in SS, but there are few studies focusing on the control of other pollutants. Due to the complexity and variability of SS itself and the unclear pyrolysis mechanism, its industrial application still has a long way to go. However, previous research on sludge pyrolysis pretreatment were not investigated systematically, and there is no uniform standard for the pretreatment process. Therefore, in future research on the pretreatment process of SS pyrolysis, the development of a new pretreatment process and method and the study of its pollutant control mechanism will become the focus.

Based on the above analysis, future research in the field of tar pollutant mitigation should include the following aspects: (1) in-depth study of the impact of HPT on the release of S, Cl, and even HMs during the subsequent pyrolysis of SS; (2) in-depth understanding of the pyrolysis mechanism of co-pyrolysis of SS and various additives, clearly study the reasons for their potential synergy and pollutant control mechanism, and further improve the efficiency of co-pyrolysis; (3) investigation of co-pyrolysis processes of SS and more types of biomass substances and explore the synergistic mechanism of SS co-pyrolysis.

5. Conclusions and Future Perspectives

This study addresses the critical issues of tar generation and transformation during SS pyrolysis, with a particular focus on the formation and mitigation of secondary pollutants. The findings of this study are aimed at developing effective strategies to improve the pyrolysis tar quality and to minimize the risk of secondary pollution during pyrolysis.

Sewage sludge is increasingly considered as a recoverable carbon-rich resource that can be used as a raw material for the production of various chemicals, biofuels, and solid biochar from a renewable carbon supply through pyrolysis. However, the complexity of sludge composition and the generation of hazardous secondary contaminants pose significant challenges such as the low quality of the pyrolysis product. Therefore, to maximize the benefits of SS pyrolysis, it is crucial to enhance the pyrolysis efficiency, conversion selectivity, and control of pyrolysis pollutants. Understanding the distribution, transformation, and release of various constituents and pollutants during SS pyrolysis is critical. Despite numerous studies, gaps remain in transforming biomass and compounds into target products efficiently and selectively and in controlling and regulating the pyrolysis process.

Future research should focus on the development of in situ analytical or online detection techniques, such as TG-FTIR-MS, Py-GC-MS coupling techniques, and other advanced techniques such as solid-state ^{13}C NMR spectroscopy and synchrotron-based X-ray adsorption spectroscopy, which could provide a practical way to better understand the mechanism and behavior of complicated sludge pyrolysis products. Additionally, future research should also focus on the novel, efficient, and sustainable pyrolysis catalysts, optimization of pyrolysis process parameters, etc., to convert C, N, H, O, and S elements in sludge into target products (such as tar) and avoid unnecessary by-products (such as N-, S-, Cl-containing gases and other organic pollutants). The catalyst design should focus on specific reaction mechanisms and the stability of catalyst under different pyrolysis conditions. Multifunctional pyrolysis catalysts with tunable pore sizes and structures can improve various catalytic processes, such as hydrodeoxygenation, hydrogenation, hydrogen transfer, steam reforming, and water gas conversion reactions. Reducing tar formation and improving tar quality through effective catalyst design will further improve the economic viability of pyrolysis products.

Finally, the large-scale production and economic competitiveness of pyrolysis tar compared to fossil fuels remain a challenge [140]. Future research should aim to lower production costs, improve products quality, and reduce secondary pollution to make it competitive with petroleum fuels. Fluidized bed reactors, known for their efficiency and economic viability, should be considered for large-scale sludge pyrolysis.

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