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Review

Air-Polluting Emissions from Pyrolysis Plants: A Systematic Mapping

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Abstract: There is a growing interest in the use of pyrolysis plants for the conversion of solid waste into useful products (e.g., oil, gas, and char) and the analysis of air-polluting emissions associated with such a process is an emerging research field. This study applied a systematic mapping approach to collating, describing, and cataloging available evidence related to the type and level of air pollutants emitted from pyrolysis plants, the factors affecting emissions, and available mitigation strategies that can be adopted to reduce air pollution. The scientific literature indexed in Scopus and Google Scholar, as well as available industry reports, was interrogated to document the evidence. A database comprising 63 studies was synthesized and cataloged from which 25 air pollutants from pyrolysis plants were considered, including volatile organic compounds and persistent organic pollutants. Air pollutant levels varied depending on the scale of the pyrolysis plants, their operating conditions, and the feedstock used. Various technologies, such as wet scrubbers, electrostatic precipitators, and baghouse filters, are available and have been utilized to reduce emissions and comply with the existing EU regulations for waste incineration (2010/75/EU). The systematic mapping identified several knowledge gaps that need to be addressed to inform relevant environmental policymaking, technology development, and the adoption of best practices for the mitigation of emissions from pyrolysis plants.

Keywords: emission limit value; mitigation strategies; particulate matter; PCDD/Fs; pyrolysis; regulation; VOCs; waste management

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1. Introduction

Pyrolysis is a thermochemical process commonly used to convert waste materials into useful resources such as pyrolysis gas, oil, and char. The pyrolysis process is considered a sustainable environmental practice, as it can reduce the carbon footprint associated with waste disposal while contributing to the circular economy by creating closed-loop waste management systems [1]. There are three main types of pyrolysis; namely slow, fast, and flash. Slow pyrolysis employs a relatively long residence time (>1 h) and low heating rate (<10 °C/min) for producing char as the major product [2]. Slow pyrolysis produces a small amount of pyrolysis gas rich in carbon dioxide (CO_2), carbon monoxide (CO), and light hydrocarbons, with yields usually less than 25%; however, this can vary depending upon the biomass utilized [3]. This process is crucial in mitigating climate change by limiting greenhouse gas (GHG) emissions, particularly in the synthesis of biochar from biomass whose carbon (C) content is very stable [4]. Biochar has been reported to improve soil health through improvements in soil physiochemical and hydraulic properties and, therefore, soil function [5]. On the contrary, fast pyrolysis uses high heating rates (>60 °C/min) over a short residence time (<10 s) and rapid cooling to produce high-yielding oil [2,6], while flash pyrolysis results mainly in gases and oil, which are produced at higher heating rates (>1000 °C/min) and a very short residence time (<3 s) [6,7].

The development of pyrolysis plants has seen rapid expansion in recent years, driven by the need to implement environmentally friendly waste disposal approaches for greater resource recovery and renewable energy generation; but, it has also raised concerns about the risks associated with air pollution [8,9]. Figure 1 illustrates the air-polluting emissions generated by pyrolysis plants and the factors that affect these emissions, including, importantly, the characteristics of the feedstock, the operating temperature, residence time, and the technology used to control emissions [10]. Other factors influencing the emissions of the pyrolysis plants include the condensation stage and the design of the pyrolysis reactor [11,12]. Pyrolysis gases are a combination of CO_2, CO, H_2, CH_4, and heavier hydrocarbons [13], which are combusted directly to provide energy or heating. When pyrolysis occurs at high temperatures (>650 °C), hydrocarbon cracking leads to substantial production of pyrolysis gas and the breakdown of oxygen (O_2) molecules produces CO_2 and CO [6], while tars and heavy hydrocarbons undergo vapor phase cracking and reforming processes, which produce C_2H_4, CH_4, and C_2H_6 [6].

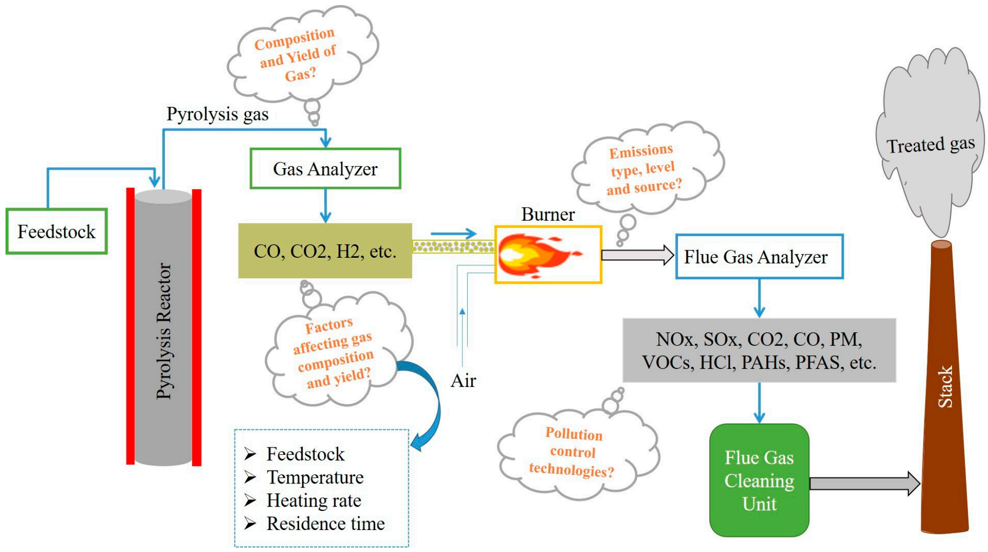


Figure 1. Air-polluting emissions from pyrolysis plants and the main factors affecting the concentration of air pollutants.

Figure 1 shows that combustion of pyrolysis gas can result in significant NO_x, SO_x, CO_2, CH_4, particulate matter, volatile organic compounds (VOCs), HF, N_2O, HCN, NH_3, HCl, and CO emissions [2,14,15].

The literature [16–18] indicates that VOCs such as benzene, toluene, and formaldehyde present in pyrolysis gas from municipal solid waste (MSW) increase concurrently with operating temperature. These VOCs are pollutants of concern to human health and the environment. Additionally, NO_x and SO_2 can cause acid rain. However, the emissions of these gases can be reduced by optimizing the pyrolysis operating conditions, as the production of NO_x and CO is affected by the burners' configuration. Elevated temperatures can lead to NO_x production, while incomplete combustion favors the production of CO. The combustion air must be controlled and residual oxygen levels monitored to ensure that CO and NO_x levels are kept within the allowable limits [2,10]. The concentration of chlorine (Cl) in the feedstock is crucial during the pyrolysis of MSW, notably, food waste and polyvinyl chloride. When polyvinyl chloride is thermally decomposed (between 200 °C and 360 °C), it produces HCl [19]. In flue gases, Cl manifests as heavy metal chlorides, alkali chlorides, and HCl [20]. The presence of Cl in flue gases is considered a serious environmental and health risk as it encourages the subsequent formation of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) [19]. Particulate matter (PM) emissions following combustion of pyrolysis gas (after condensation) were found to be modest when compared with combustion of pyrolysis gases without condensation, suggesting that direct combustion of pyrolysis gas without the condensed liquid phase may increase PM emissions [10]. However, temperatures exceeding 500 °C during pyrolysis can efficiently decrease or eliminate long-lasting organic contaminants from the feedstock, including polychlorinated biphenyls (PCBs), perfluoroalkyl and polyfluoroalkyl substances (PFAS), and microplastics [21,22]. Furthermore, a robust oxidation rate and prolonged residence time can lower the content of VOCs [23]. Novel technologies such as scrubbers and electrostatic precipitators have been reported to be effective in controlling the amount of emissions from pyrolysis plants, particularly PM, SO_x, HCl, and VOCs, which can be significantly reduced from flue gases with the use of electrostatic precipitation [23,24].

Comparison of air-polluting emissions from pyrolysis plants with current regulatory frameworks is important for determining the extent of compliance and assessing whether permissible levels of air pollutants are being exceeded. Furthermore, such analysis can help determine whether emissions could be reduced by narrowing the existing technology gap or improving operations and management practices at the plant. Figure 2 shows the average daily emission limit values (ELV) of major air pollutants emitted from waste incineration plants in the United States [25], China [26], India [27], Canada [25], and the European Union (EU) [28]. The most stringent regulations appear to be in the EU and Canada. While ELVs in China and India are high, the ELVs listed here for India are the half-hourly average values for all air pollutants (except CO). The ELV for dioxins is the same (0.1 ng/Nm^3) in all countries except for the United States (0.009 ng/Nm^3) and Canada (0.07 ng/Nm^3), while the HF values for the EU and India are 1 mg/Nm^3 and 4 mg/Nm^3, respectively.

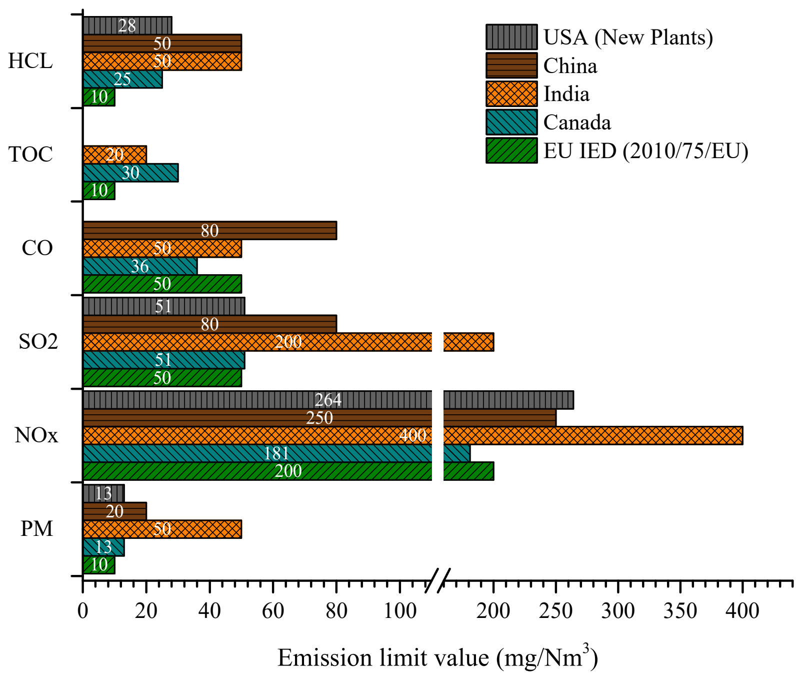


Figure 2. Emission limit values for major air pollutants emitted from waste incineration plants in different regions.

The EU Industrial Emission Directive (IED) (2010/75/EU) [28] is used in the literature [29,30] to compare pyrolysis emissions with waste incineration plants because there is no specific regulatory framework related to pyrolysis plants. Despite this, the EU IED (2010/75/EU) does not specify ELV for small-scale biomass plants (<20 MW) and some countries (e.g., Austria, Germany, Italy, Switzerland, and Sweden) have adopted country-specific limit values. For example, Table 1 presents the ELV for small-scale biomass plants established by the Italian government [31].

Table 1. Air daily average ELV (mg/Nm^3) for small-scale biomass plants in Italy [31].

Polluting Substances	for Plants Using Biomass (O_2 in the Effluent Gaseous by 11%)			
	>0.15 to <3 MW	>3 to <6 MW	>6 to <20 MW	>20 MW
NO_2	500	500	300	200
SO_2	200	200	200	200
CO	350	300	150	100
Dust (PM)	100 [1]	30	30	30

[1] PM for 0.035 to 0.15 MW is 200 mg/Nm^3.

Prior to conducting this work, a literature search in major databases returned no systematic maps on the theme of air-polluting emissions from pyrolysis plants. The work reported in this article presents a systematic mapping of studies related to air-polluting emissions from pyrolysis plants and it was conducted through a systematic search of articles published between 2003 and 2024. The identification of knowledge gaps, patterns, and trends was made possible by this systematic analysis, which offers insightful information for follow-up R&D studies and to inform technology development aimed at mitigating emissions from pyrolysis plants. The primary questions formulated as part of this analysis were as follows:

(1) What evidence is available on the type and concentration of air pollutants emitted by pyrolysis plants and how does the pyrolysis process configuration affect such emissions?
(2) What air pollution control technologies are available to reduce emissions and therefore minimize environmental and health risks?

2. Materials and Methods

This study followed the standard methodology developed for systematic mapping in a subject area related to environmental and agricultural sciences [32–34]. The current systematic mapping adopted the Collaboration for Environmental Evidence (CEE) framework and the Reporting Criteria for Systematic Evidence Syntheses (ROSES) [35,36]. The ROSES flow data are provided in the Supplementary File SF-1.

2.1. Environmental Evidence Search

The Scopus bibliographic database was used to search for available evidence. Additionally, the search was performed using Google Scholar (search engine) and complemented through direct contact with several organizations and industries that agreed to participate in this study and provided non-confidential information often not available in the public domain. The University of Padova (Italy) subscription was used to access the bibliographic database. The search was limited to publications published in English only and covered 21 years (between 2003 and 2024) to gather relevant environmental evidence. Book chapters and review articles were excluded during the search process. The Publish or Perish (PoP) software (V 8.2.3944) [37] was used to extract citations from Google Scholar. Table 2 represents the search string developed in Scopus to find the evidence. Additional details regarding the search in the bibliographic database and other sources are provided in Supplementary File SF-2. Furthermore, to ascertain the comprehensiveness of the search, 15 pertinent publications (benchmarks) were evaluated against the findings of a scoping search. The search phrases were looked up and adjusted in the search string to see if any articles were missing. The list of these 15 articles is available in the Supplementary File SF-2. Before the screening process, data collected from Scopus and Google Scholar were combined on the EPPI reviewer web [38] to remove duplicate articles.

Table 2. Search string used in the bibliographic database Scopus and search engine Google Scholar.

Source	Search Type	Search String
Scopus	TITLE-ABS-KEY	(“pyrolysis”) AND (“biomass” OR “sludge” OR “wood” OR “tyre” OR “MSW” OR “tire” OR “waste” OR “plastic”) AND (“air emissions” OR “air pollutants” OR “air pollution”)
Google Scholar	General	1—Emissions; Pyrolysis, 2—Air Pollutants; Pyrolysis, 3—Air Emissions; Pyrolysis

2.2. Article Screening and Eligibility Criteria

The articles were screened based on title and abstract and those that seemed relevant but whose full text was not available or inaccessible were retrieved. The articles that were not retrieved are mentioned in Supplementary File SF-3 with reasons as to why full text may not be available. Furthermore, full-text screening was performed on the free-accessible and retrieved articles.

Eligible articles were identified and subsequently included in the analysis based on the criteria presented in Table 3. The list of articles excluded at the full-text screening stage (with reasons for their exclusion) is available in the Supplementary File SF-3.

Table 3. Inclusion criteria adopted in the systematic mapping database.

Criteria	Inclusion Criteria
Population (P)	Studies relevant to pyrolysis plants.
Intervention (I)	Studies focused on air pollutants emitted from pyrolysis plants, the aspects that influence the emissions of air pollutants, and control strategies implemented to reduce emission levels.
Study type	Primary research, excluding systematic reviews

2.3. Critical Appraisal and Data Coding Strategy

The accuracy of the data reported in the articles and the scientific rigor were not evaluated in this systematic map, as it was considered to be out of the scope (this merits a separate analysis using appropriate methods), and the data coding strategy is provided in the database as Supplementary File SF-4.

2.4. Data Mapping Method

The knowledge gaps and clusters were identified and the scope of the research was defined based on the systematic map database. Descriptive statistics and an extensive database were used to identify evidence. An evidence atlas was also developed, which served to visualize research on an interactive map using the study location (i.e., latitude and longitude extracted from Google Earth). The location of the corresponding author was utilized to find the longitude and latitude of the study. Through cross-tabulations, knowledge gaps and clusters were identified and the number of studies in each table cell was examined to determine the strength of the evidence. The correlations between studies based on term co-occurrence were visualized using VOSviewer software (V 1.6.20) [39].

3. Results and Discussion

3.1. Methods of Determining Air Pollutant Emissions

There are several methods commonly used to determine air pollutant emissions from pyrolysis plants. However, our analysis focused on the most prevalent methods documented in the scientific literature. In laboratory-scale investigations, it is reported that gas samples are collected from pyrolysis plants in gas bags (usually Tedlar bags) or stainless-steel cylinders. The gas sample is then manually transferred or syringed into the injection port of a gas chromatograph (GC). The starting temperature of the injection port and the GC oven should initially be kept low and then progressively increased according to the program [40]. A mass spectrometer (MS) coupled with GC is used to detect the composition of gas. Several approaches are used to detect PM in the gas stream, such as filter-based and laser light scattering methods. In the filter-based approach, the filters are pre-weighed before the exhaust gases are drawn through filters that catch PM, such as glass fibers or Teflon filters. Filters are then weighed to ascertain the mass of previously collected PM [41]. In laser light scattering, a particle counter detects PM in the flue gases. First, it warms up the particle counter for a few minutes to stabilize the sensors and laser. The particle counter is then placed near the steady flow rate of the pyrolysis reactor exhaust gases. When gas-containing particles flow through the sample chamber of a particle counter, they scatter laser light. The photodetector processes the data based on scattered laser light to identify the quantity and size of particles [40].

For small-scale pyrolysis power plants, a gas probe is introduced into the gas stream to collect a sample and a sample line is used to transport the gas sample from the probe to the analyzer. The sample line features a particle filter and cyclones that capture PM while protecting the analyzer from adverse effects. To keep the sample gas flow to the analyzer constant, a choked critical orifice is used in conjunction with a diaphragm vacuum pump. Various instruments are used to detect air pollutants, such as nondispersive infrared (NDIR) analyzers to measure CO_2 and CO, flame ionization detectors (FIDs) to measure THC, chemiluminescence analyzers to measure NO_x emissions, and colorimetric gas detection tubes to measure SO_x emissions [10]. However, on an industrial scale, sampling and analysis processes are highly automated, with continuous real-time monitoring to maintain air pollutant emissions under the permitted levels.

3.2. Literature-Based Evidence

3.2.1. Types and Levels of Air Pollutants

The database (SF-4) highlights the air pollutants emitted during pyrolysis of various feedstocks in different process configurations. All studies presented in the database examined the types of air pollutants and the air pollutants identified during the pyrolysis process were CO_2, SO_2, CH_4, PM, HCl, VOCs (benzene, toluene, H_2S, HCN, and NH_3), and persistent organic pollutants (PCDD/Fs, polycyclic aromatic hydrocarbons (PAHs), PCBs, and brominated phenols (BrPhs), and brominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), PFAS). Table 4 shows 10 of the most relevant studies from the database, illustrating the types of air pollutants emitted from the pyrolysis of various feedstock (see also Supplementary File SF-4). More than 25 different types of air pollutants were identified and the types of pollutants emitted were found to be dependent on the feedstock utilized.

Table 4. Pyrolysis air-polluting emissions from various feedstock.

Article ID (Database)	Feedstock	Air Pollutants Studied
1	Coconut shell	CO, CO_2, CH_4
4	Shredded tire rubber	PM, NO_x, SO_2, CO, TOC, HCl, HF, PCDD/Fs
25	Viscoelastic memory foam	PAHs, dl-PCBs, PCDD/Fs, SVOCs
26	Medical waste	PCDD/Fs
31	Plastic waste	PCBs, PCDD/Fs
49	E-waste (PCB)	PCDD/Fs, dl-PCBs, SVOCs, PAHs, ClBzs, CIPhs, BrPhs
59	Waste timber	PAHs, CO, NO_2, VOCs, CO_2, PM
60	MSW	PM, HCl, NO_x, SO_x, PCDD/Fs
61	Waste tires	PM, NO_x, CO, SO_2, HCl, HF, TOC, PCDD/Fs
63	Bark	CO_2, PM, NO_x, CO, SO_2, CH_4, PCDD/Fs, PAHs

The level of air pollutants emitted depends on the pyrolysis process parameters and the configuration of the reactor or burner. The level of air pollutants emitted was recorded by 51 studies in the database, while 12 studies only indicated the type of air pollutant released during pyrolysis without specifying the level of air pollutants. The units of pollutants emitted and the measurement techniques were different according to the scale of the study (lab-scale, small-scale, and industrial scale). Figure 3 shows the concentration of air pollutants released from the pyrolysis of various feedstocks following the combustion of the pyrolysis gas in the burner. From this information, it could be seen that NO_x emissions were dominant in three feedstocks (bark [42], waste tires [43], and shredded rubber from tires [44]), while the other two studies (MSW [45] and waste timber [2]) did not report the NO_x concentration. The NO_x concentration was 244 mg/Nm^3 for waste tires, 240 mg/Nm^3 for bark, and 118 mg/Nm^3 for shredded tire rubber. The SO_2 concentration was high in bark (72 mg/Nm^3), followed by waste tires (33 mg/Nm^3) and waste timber (28.1 mg/Nm^3). Additionally, the CO emissions were highest in waste tires (52 mg/Nm^3) while other feedstock observed low concentrations (<5 mg/Nm^3). Some studies available in the scientific literature [2,10,11] considered CO as a pollutant when it was present in flue gases, likely reflecting inefficient pyrolysis conditions, incomplete pyrolysis, or incomplete combustion of pyrolysis gas [12]. Figure 3 shows that the concentration of PM in all feedstocks was less than 6.94 mg/Nm^3, while the concentration of HCl for shredded tire rubber, MSW, and waste timber was 12 mg/Nm^3, 11.6 mg/Nm^3, and 10.2 mg/Nm^3, respectively. Usually, high Cl content in MSW explains high HCl emissions during pyrolysis; for example, food waste is reported to emit more HCl (0.14 ± 0.09 g HCl/kg) due to its Cl content (e.g., 2.6 ± 0.2 g Cl/kg) [2]. Therefore, control strategies need to be implemented to minimize HCl emissions when using MSW or mixed waste for pyrolysis. The concentrations of PCDD/Fs, PAHs, CH_4, non-methane volatile organic compounds (NMVOC), and HF air pollutants were low. Figure 3 illustrates the ELV of air pollutants (dotted red line) according to the EU IED (2010/75/EU). Figure 3 depicts the type and level of air pollutant emissions, rather than directly comparing emissions from different feedstocks. Since available research on the scientific literature was conducted on different experimental or operational scales, care must be taken when reviewing this information to avoid misinterpretation of such results.

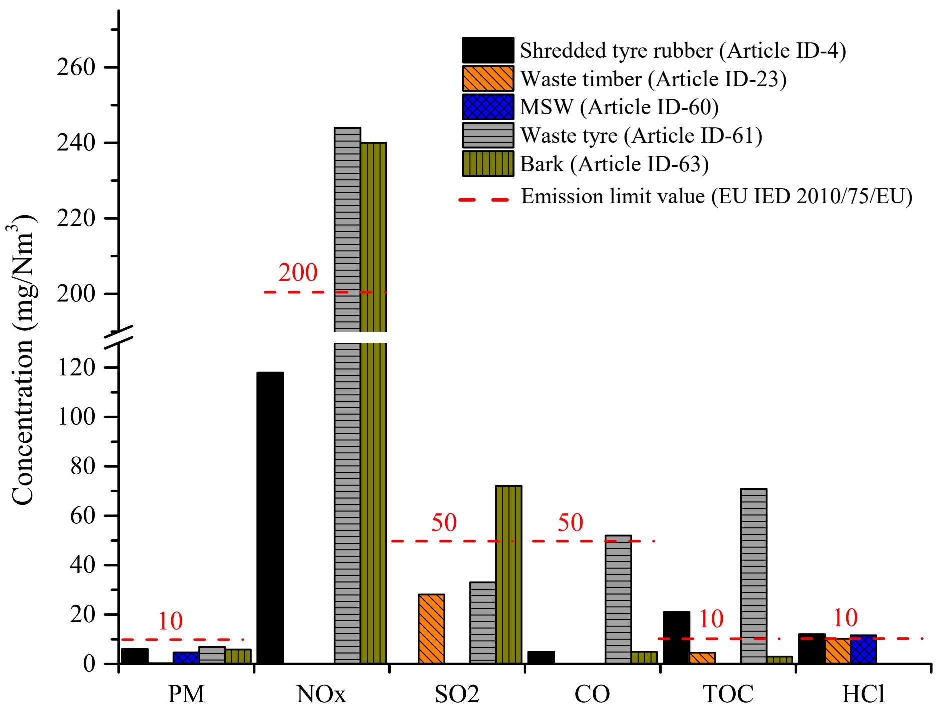


Figure 3. Concentration of air pollutants encountered during the pyrolysis of various feedstock after pyrolysis gas burner. The emission limit value (ELV) of air pollutants quoted in the graph is based on the EU IED (2010/75/EU) [28] and is represented by the red dotted lines.

In certain situations, published research on specific feedstocks was limited or non-existent; therefore, caution should be exercised when interpreting the data reported herein (Figure 3) as it may not be representative of wider industry practice, particularly in relation to the type of feedstocks. Further information about the type and concentration of air pollutants based on the feedstock type and pyrolysis process conditions for other studies is available in the Supplementary File SF-4.

3.2.2. Factors Affecting Air Pollution Emissions

The main factors that affect air-polluting emissions are (1) feedstock and pyrolysis gas compositions, (2) operating temperature, (3) heating rate, and (4) residence time. Most of the studies presented in the database evaluated air-polluting emissions of biomass feedstock. However, knowledge about the composition of feedstock is vital when analyzing and interpreting air-polluting emissions data. Only 11 studies in the database used different feedstocks under the same pyrolysis conditions, which were helpful in observing the effect of the feedstock's composition on the resultant air pollution emissions. The pyrolysis of rice husk and grape pruning revealed that variability in the biomass composition, such as nitrogen, sulfur, volatile matter, and ash concentration, can have a significant effect on the levels of PM and gaseous pollutants, including SO_2, NO_2, and H_2S [46]. Therefore, knowledge of the composition of the feedstock is thus important to determine what measures can be implemented to reduce the concentration of pollutants. For example, in the co-pyrolysis of wood and PVC film, the hemicellulose found in the wood can absorb a significant amount of Cl, consequently reducing HCl emissions [47]. The composition of pyrolysis gas used in the burner for combustion can have an impact on air pollution emissions. There are 26 studies in the database (SF-4) that analyzed the composition of the pyrolysis gas before combustion, while another 25 studies investigated the pyrolysis gas after the combustion and recirculation process. The main components of pyrolysis gas are H_2, CH_4, CO, and CO_2, along with other trace gases. Table 5 presents the pyrolysis gas composition and yield from some of the pyrolysis studies available in the database. For this study, the pyrolysis plants were divided into three scales: laboratory, small, and industrial. Pyrolysis plants with a feeding rate up to 70 kg/h were considered as small scale, while those with a feeding rate greater than 70 kg/h were referred to as industrial scale. The yield of pyrolysis gas depends on the type of feedstock and the specific characteristics of the process. There were no studies available in the database that explored the effect of pyrolysis gas composition on post-combustion air-polluting emissions. It is therefore critical that research into such effects be conducted, as larger concentrations of hydrocarbons in pyrolysis gas can result in increased CO and VOC emissions, while the presence of nitrogen-containing compounds in pyrolysis gas may lead to increased NO_x emissions.

The operating temperature influences the concentration of air pollutants emitted during pyrolysis. The database contains 33 studies that evaluated the concentration of air pollutants at various operating temperatures. For instance, a pyrolysis study of waste tires performed at 600 °C and 850 °C found that higher temperatures reduced the PCDD/Fs and PBDD/Fs air pollutants while increasing the PAHs and CIBz pollutants [48]. Additionally, a pyrolysis study of limed sewage sludge (LSS) and digested sewage sludge (DSS-1) measured the PFAS emissions factor at various temperatures. The results indicated that the PFAS emission factor was 0.0096 ± 0.0005 g Mg^{-1} and 0.9 ± 0.2 g Mg^{-1} for LSS at 600 °C and 750 °C, respectively. For DSS-1, the PFAS emission factor was 0.2 ± 0.1 g Mg^{-1}, 3.1 ± 1.6 g Mg^{-1}, and 1.2 ± 0.8 g Mg^{-1} at 500 °C, 600 °C, and 700 °C, respectively [49]. The pyrolysis operating temperature has a positive or negative impact on PFAS air pollutant emissions. For example, PFAS emissions in DSS-1 increased from 500 °C to 600 °C but dropped when the temperature was increased to 700 °C. No studies in the database evaluated the concentration of air pollutants at various heating rates and residence times. This is a potential research gap that should be addressed in future studies.

Table 5. Pyrolysis gas compositions and yield from a range of studies on pyrolysis as recorded in the database.

Article ID	Feedstock	Scale	Temperature	Composition	Yield (%)
4	Shredded tire rubber	Laboratory	600 °C	H_2 CO CO_2 CH_4	30.40 2.38 2.90 23.27
20	Grape pruning	Laboratory	600 °C	H_2 CO CO_2 CH_4	10.30 10.00 21.50 8.30
21	Rice husk	Laboratory	600 °C	H_2 CO CO_2 CH_4	5.40 24.30 12.30 3.80
23	Waste timber	Small [1]	500–800 °C	H_2 CO CO_2 CH_4	3–18 32–35 20–35 15–20
23	Food waste	Small [1]	500 °C and 800 °C	H_2 CO CO_2 CH_4	15–19 15–20 12–18 21–23
56	MSW	Small [1]	500 °C	H_2 CO CO_2 CH_4	19 30 25 10

[1] Feeding rate $\leq$ 70 kg/h.

The condensation phase in pyrolysis plants can affect the air pollutants emissions. Pyrolysis gas usually contains air pollutants such as higher hydrocarbons, VOCs, and PM [50]. The gas may cause corrosion, fouling, and plugging problems on the surface of the heat exchanger, which may reduce the efficiency of pyrolysis plants. As a result of condensation, a proportion of the pyrolysis gas is converted to liquid, which usually contains a higher hydrocarbon concentration than the gas. Therefore, the total volume of gas is reduced, concurrently reducing air pollutants that may otherwise be present in the gas [11]. The published data available in the literature indicated that the efficacy of condensation in capturing pollutants can reach 50% for PM and 98% for hydrocarbons [50]. The direct combustion of pyrolysis gas without first undergoing the condensation stage can increase PM emissions compared with the combustion of pyrolysis gas after the condensation stage [2]. Therefore, the condensation stage can act as a pretreatment device to reduce the air pollutant emissions from pyrolysis plants.

Pyrolysis reactors can also affect the level of air pollutants emitted during pyrolysis. At present, there are several types of commercially available pyrolysis reactors; however, their development has mainly focused on improving product yield and quality and, to a lesser extent, reducing air pollutants emitted during the pyrolysis process. Pyrolysis reactors are available in a variety of designs and configurations, which influence the resultant air pollutant emissions. For instance, fluidized bed reactors are often utilized in pyrolysis due to their excellent heat transfer mechanism but they can generate more NO_x emissions from the feedstock than other designs due to the rapid reaction and higher temperature built inside the reactor [51]. When fixed-bed reactors are used, PAH and VOC emissions can increase as a result of limited heat and mass transfer inside the reactor, which may cause incomplete pyrolysis [12]. The arrangement of rotary-kiln reactors allows for the uniform distribution of temperature on the feedstock surface. However, the length of the kiln and fluctuation in heating zones may lead to increased emissions of pollutants such as hydrocarbons, CO_2, and CO [12,52]. Compared to the traditional kiln, for example, the downdraft reactor produced less hydrocarbons, CO_2, and CO during the pyrolysis of coconut shells [53]. Improving reactor design is an important engineering consideration for reducing air pollution emissions.

3.2.3. Mitigation Strategies and Technologies

When the amount of air pollutants released into the environment has the potential to exceed the acceptable limits set out by regulations in place, the operation can be compromised and, therefore, strategies to reduce such levels need to be implemented. There were 26 studies in the database that either proposed or implemented a range of mitigation practices to maintain air pollutants within permissible levels. Different techniques have been developed to minimize air-polluting emissions from pyrolysis plants and some of these include (1) the optimization of operational conditions, (2) the use of catalysts, and (3) the implementation of emission control technology such as electrostatic precipitators, wet scrubbers (WSB), and baghouse filters. Table 6 presents the mitigation strategies that some of the studies compiled in the database adopted to reduce the concentration of air pollutants. It can be seen that most of the studies used selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) to reduce NO_x emissions through the conversion of NO_x to water, CO_2, and nitrogen [54]. NO_x can also be controlled by the temperature of the flame inside the burner when pyrolysis gas is used for combustion to produce heat for the process, as NO_x emissions tend to decrease with a decrease in the flame temperature [2]. Acid gas cleaning devices such as flue gas desulphurization (FGD) and a baghouse filter with an injection of lime can be used to reduce the concentration of SO_2 and HCl emissions [54]. To reduce the concentration of PM and VOC emissions in the atmosphere, studies suggested the WSB and baghouse filter technologies. Also, the PAH emissions from the pyrolysis unit can be reduced by utilizing a particle scrubber or filter [29]. Some studies emphasize the use of catalysts such as Zn $(Ac)_2$ to reduce the concentration of H_2S emissions [55]. The removal efficiency of mitigation technology indicates by how much air pollution is reduced and to what extent limit values, as stated in regulatory frameworks and guidelines, can be met. However, the database included in this work contained only a few studies that reported the removal efficiency of mitigating technology (due to published information being rather limited). In a study on scrap tire pyrolysis, the removal efficiencies of total PAHs by WSB and flare were approximately 75% and 68%, respectively [10]. The removal efficiency of a high-temperature ceramic process gas filter for fine dust was greater than 99% and the removal efficiency of a baghouse with carbon dosing before the release of flue gases into the atmosphere was 95%, as indicated in Table 6. A study has suggested that, in order to reduce PBDD/Fs emissions, elevated temperature and CaO addition may be employed along with air pollution control devices (APCDs) and three-stage glass PUF cartridge adsorption [56]. The study found that the total removal efficiencies of PBDD/Fs were 58% at 700 °C and 40% at 1200 °C [56]. Furthermore, a lab-scale study reported that NO_x emissions can be reduced in the pyrolysis of sewage sludge by adding $ZnCl_2$, while the addition of KOH can be effective in reducing SO_x emissions [57]. However, in laboratory-scale studies, air-polluting emissions from pyrolysis often tend to ignore or overlook potential mitigation techniques. Monitoring air-polluting emissions is critical to ensure that the pyrolysis plant is operated in an environmentally friendly manner while complying with regulatory frameworks; this can be facilitated by the use of appropriate technology (Table 6).

Table 6. Mitigation strategies and technology adopted to reduce air-polluting emissions from pyrolysis plants.

Article ID	Feedstock	Study Scale	Mitigation Strategy	Removal Efficiency
4	Shredded tire rubber	Laboratory	FGD to reduce the HCl and SO_2 concentration	-
8	Scrap tires	Small [1]	WSB and a flare	PAHs by WSB = 76.2%, Flare = 66.8%
23	Various feedstocks	Small [1]	Flue gas recirculation, SNCR, or SCR to reduce the NO_x emissions	-
28	RDF	Small [1]	Caustic Scrubber and electrostatic precipitator (ESP) to reduce PM emissions	-
60	MSW	Industrial [2]	SNCR unit for NO_x control, a baghouse for PM control, and a scrubber unit for control of acid gases and volatile metals	-
61	Waste tires	Industrial [2]	Baghouse filter to reduce PM emissions (below 5 mg/Nm^3)	-
62	MSW	Industrial [2]	Ion exchange scrubber followed by a baghouse with carbon dosing before discharge of the flue gases to the atmosphere	Filtration system = 90%, carbon based gas cleaning system = 95%
63	Bark	Industrial [2]	SNCR/SCR for NO_x reduction, high-temperature ceramic process gas filter adsorbs >99% of the fine dust, for SO_x, additional gas cleaning module (which is standard for sewage sludge applications) to reduce acidic components of the exhaust gas with caustic soda	For fine dust is >99%

[1] Feeding rate ≤ 70 kg/h; [2] Feeding rate > 70 kg/h.

3.2.4. Comparison of Air-Polluting Emissions

The comparison of air-polluting emissions from pyrolysis plants with alternatives such as waste combustion or incineration plants is an important consideration to help assess their environmental performance and is subsequently used to determine their feasibility from a sustainability perspective. In the database, 25 studies compared pyrolysis air-polluting emissions with regulatory frameworks and waste combustion. For instance, a small-scale pyrolysis plant study that utilized several types of feedstocks compared air-polluting emissions with the EU IED (2010/75/EU) for waste incineration plants [2]. The NO_x emission value from pyrolysis of waste wood, garden waste, sludge (DSS-2), and food waste was 365 mg/Nm^3, 410 mg/Nm^3, 350 mg/Nm^3, and 454 mg/Nm^3 at 800 °C, respectively. The SO_x emission values from pyrolysis of waste timber, garden waste, sludge (DSS-2), and food waste were 28.1 mg/Nm^3, 18.9 mg/Nm^3, 198.3 mg/Nm^3, and 73.2 mg/Nm^3 at 800 °C, respectively. The findings from that study [2] indicated that the pyrolysis of all the waste feedstock tested surpassed the EU IED (2010/75/EU) ELV for NO_x (which is 200 mg/Nm^3 for waste incineration plants) while sludge (DSS-2) and food waste also exceeded the SO_2 ELV (which is 50 mg/Nm^3) for waste incineration plants. Another pyrolysis and combustion study of viscoelastic memory foam reported that NO_x emission levels in pyrolysis were within the range specified in the EU IED (2010/75/EU) while NO_x emission limits were exceeded with combustion [30].

3.3. Review Process

The search string was employed in the Scopus advance search and the limits were applied according to the study type inclusion criteria. Figure 4 illustrates the flow diagram of the search and screening strategy adopted to synthesize evidence and develop the database on air-polluting emissions from pyrolysis. The Scopus search returned 539 primary research articles (which excluded review articles) and the Google Scholar search on the PoP software (V 8.2.3944) [37] returned 450 articles (but including review articles). The search results were combined in the EPPI-reviewer web [38] where 95 articles were traced as duplicates. The screening based on the article titles and abstracts found 756 articles unrelated to the inclusion criteria. Most of the irrelevant articles were returned after the Google Scholar search as it was not possible to insert or develop a search string. The full-text screening was performed on 137 articles. However, of these, 77 articles were excluded with reasoning (see Supplementary File SF-3) and most of them did not discuss or examine air-polluting emissions. The articles that were excluded based on intervention had the potential to conduct further research in the domain of air pollution emissions because these articles were relevant to pyrolysis, but did not discuss the air-polluting emissions during the production of biofuels. Additional data were provided by four industries operating pyrolysis plants. Figure 4 shows that the database consists of 63 studies of which 57 were journal articles (see Appendix A), 2 conference proceedings, and 4 industry reports.

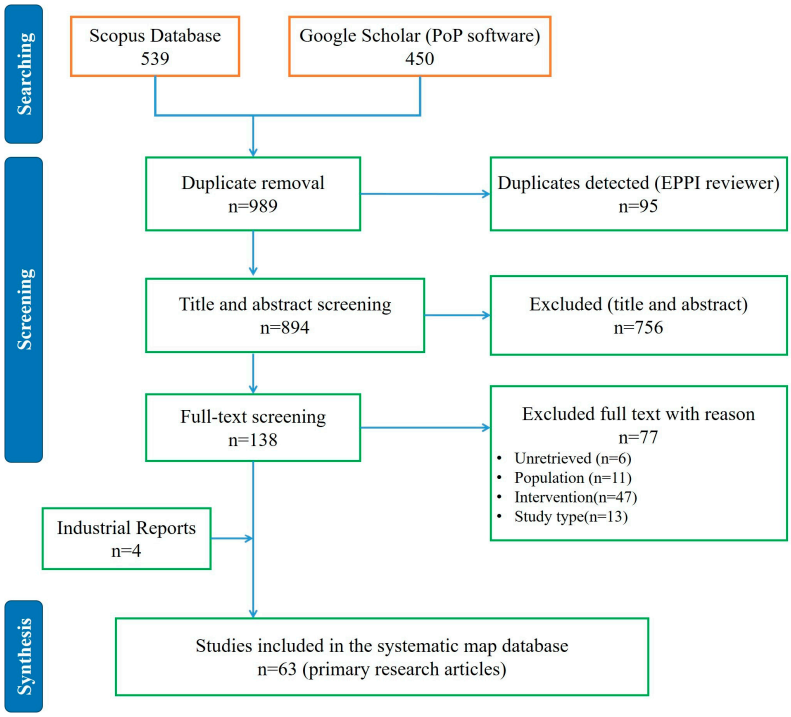


Figure 4. Flow diagram for evidence search, screening, and synthesis.

3.4. Statistic Analysis

Figure 5 shows the evidence atlas (EviAtlas) map, which was created to illustrate the locations of studies and provide the overview of the main findings of studies that were included in the systematic mapping database. The full map is available at https://pyropollutants.github.io/ (accessed on 4 December 2023). The EviAtlas shows that most of the studies on air-polluting emissions from pyrolysis were conducted in Asia (China and Taiwan) and Europe (Spain and Norway). China (14) and Spain (14) published the majority of articles, followed by Taiwan (6), Norway (5), Australia (4), the Republic of Korea (4), and the USA (2), while other countries (10) also contributed to this field. The EviAtlas map provided a summary for each study such as year of publication, journal name, pyrolysis reactor type, pyrolysis type, feedstock type, air-polluting emissions, and mitigation strategies (Figure 5). Overall, the EviAtlas map was regarded as a convenient tool as it provided quick access to the relevant literature.

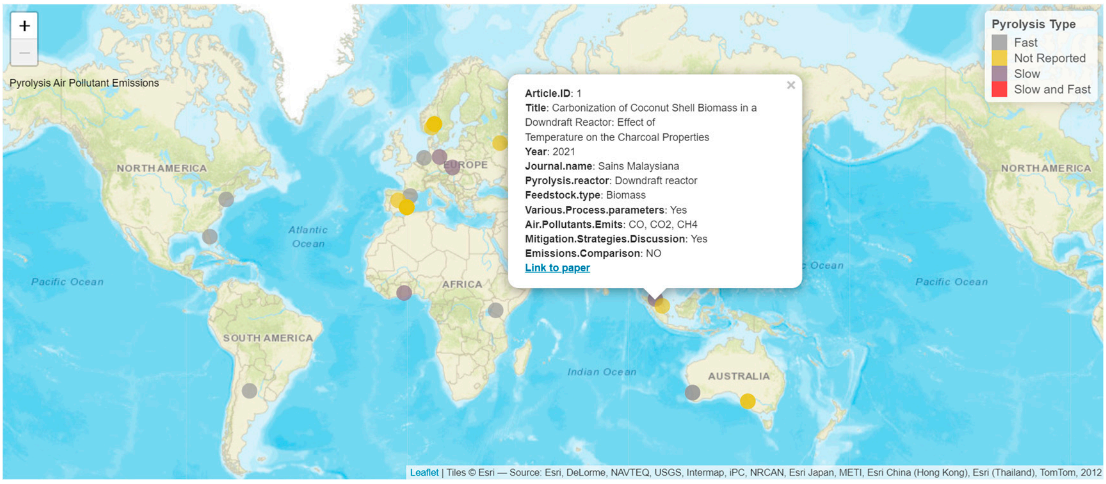
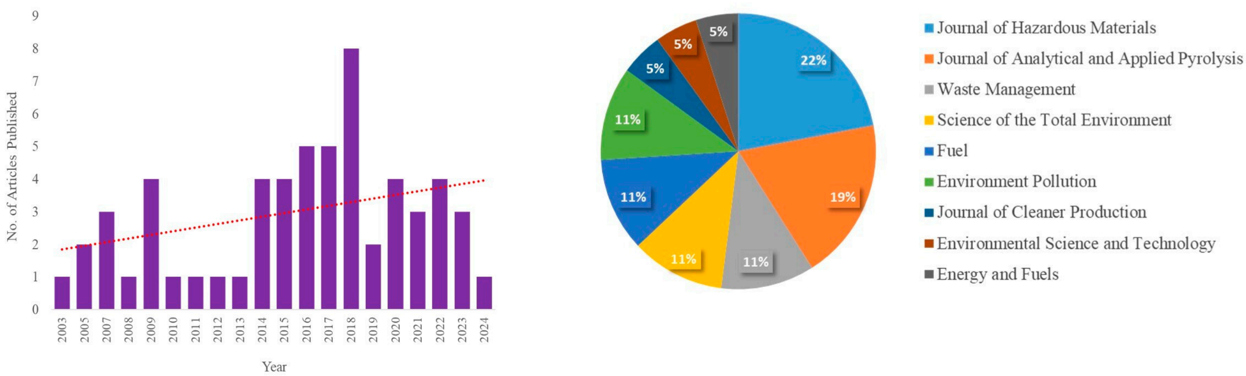


Figure 5. A map showing the geographic spread of reported studies on air-polluting emissions from pyrolysis plants. The full map details are available at https://pyropollutants.github.io/ (accessed on 4 December 2023).

Figure 6 illustrates the exploratory data analysis of database articles. Figure 6a shows the number of articles published from 2003 to 2024, excluding 2004 and 2006, as there were no articles that met the search criteria during those two years. The trend line of the prediction (red dotted line) shows that the number of articles increased over the years. During the study period, most articles were published in 2018, after which the number of publications per year decreased to an average of three articles per year between 2019 and 2024. However, the number of articles published each year has not changed significantly, suggesting that research into air-polluting emissions from the pyrolysis plants has not been prioritized and therefore that the problem is not being addressed during the production of biofuels. Figure 6b shows the percentage of articles published in subject-relevant scientific journals. Most of the articles were published in the Journal of Hazardous Materials (22%), followed by the Journal of Analytical and Applied Pyrolysis (19%), Waste Management (11%), Science of the Total Environment (11%), Fuel (11%), Environment Pollution (11%), Journal of Cleaner Production (5%), Environmental Science and Technology (5%), Applied Energy (5%), and Energy and Fuels (5%). Scientific journals that returned less than two publications were excluded from Figure 6b. The results indicated that the Journal of Hazardous Materials and the Journal of Analytical and Applied Pyrolysis were the dominant journals in which articles on air-polluting emissions from pyrolysis plants were published.



(**a**) (**b**)

Figure 6. Exploratory data analysis derived from a database of scientific articles dealing with air pollution emissions from pyrolysis plants. (**a**) Number of publications by year of publication and (**b**) percentage of subject-relevant publications per journal.

Figure 7 shows the type of feedstock used in the database articles to evaluate air-polluting emissions. Biomass feedstock had the highest number of articles (18), followed by e-waste (9), plastics (8), MSW (7), rubber tires (6), oily sludge (5), meat and bone meal (2), sludge (2), sewage sludge (1), and medical waste (1). It can be seen that most of the articles used biomass feedstock to analyze air pollution during pyrolysis, which might be due to their availability and cost. Biomass is divided into several types that include woody, aquatic, animal-based, herbaceous, and lignocellulose. The majority of the published research in the database used lignocellulosic and woody biomass. Lignocellulose biomass, such as agricultural residue, mainly consists of cellulose, hemicellulose, and lignin. This type of biomass is readily available and contains high energy compared to other types of biomass. Consequently, efficient utilization of lignocellulose wastes for bioenergy production can assist in reducing greenhouse gas emissions and promoting sustainability. There is a growing interest in evaluating air pollution during the pyrolysis of several hazardous materials such as plastics, tires, and e-waste. Most of the studies found in the literature focused on biochar production from sewage sludge and analyzed the heavy metals and other potentially toxic elements present in biochar; however, none of these studies evaluated the impact on air pollution during biochar production. Certain products such as medical waste are used for pyrolysis but such materials are known to include hazardous substances and therefore the assessment of their potential to cause air pollution is required.

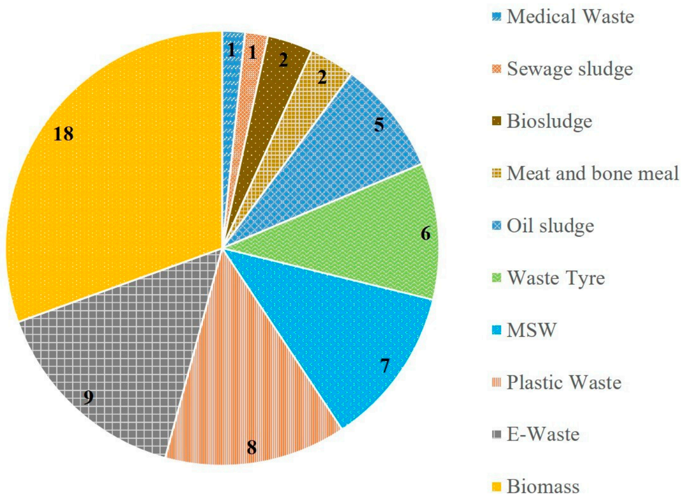


Figure 7. The range of feedstocks reported in the studies included in the database used to evaluate air-polluting emissions from pyrolysis plants.

Figure 8 illustrates the number of articles in the database that discussed or did not discuss the essential aspects when examining the impact of pyrolysis on air pollution. The 33 studies examined how air-polluting emissions from pyrolysis changed in response to variations in process configurations such as temperature, heating rate, and residence duration. However, no research has determined the air-polluting emissions by altering the heating rate and residence time; these studies assess air-polluting emissions by altering the operating temperature. The composition of pyrolysis gas was analyzed in 26 articles, while 25 articles utilized pyrolysis gas for the combustion and recirculation process. Additionally, 26 articles in the database suggested or implemented various mitigation strategies. Most of the studies conducted at the laboratory scale only suggested mitigation strategies. In contrast, studies on small and industrial scales adopted available mitigation technology to reduce air pollutants emitted from pyrolysis plants. As shown in Figure 8, only 25 studies compared air-polluting emissions with other thermochemical processes (e.g., combustion or incineration) and regulatory frameworks. Most of the studies available from the database compared emission levels from the regulatory framework for waste combustion and incineration plants, which may be explained by a lack of regulatory frameworks for pyrolysis plants.

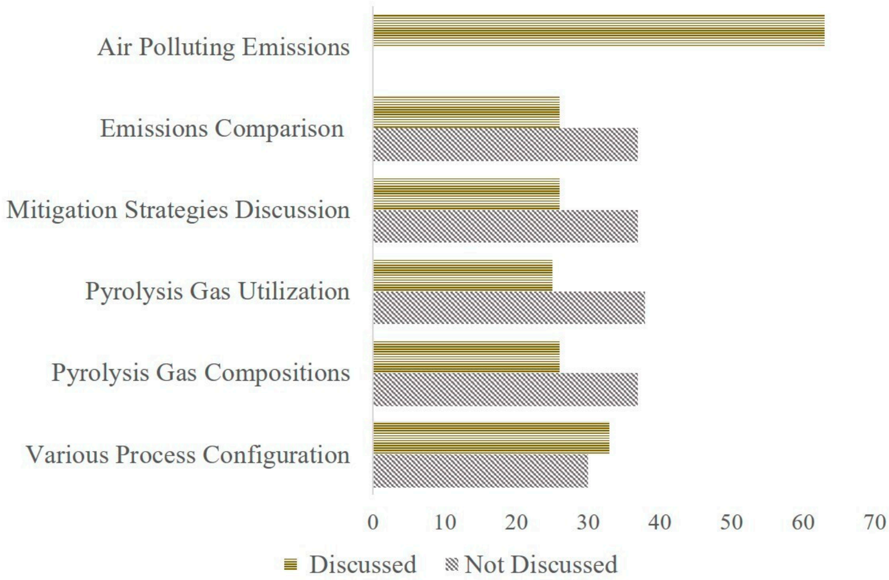


Figure 8. The number of articles in the database that discussed and did not discuss important aspects that needs to be considered for the evaluation of pyrolysis plants. The studies included the evaluation of pyrolysis for air-polluting emissions at various operating temperatures.

3.5. Potential Research Gap

Figure 9 represents the cluster of keywords in the title and abstract of articles that were recorded from the Scopus database and evaluated using VOSviewer software (V 1.6.20). The software identified 250 terms in the title and abstract of the selected papers after applying occurrence 6 times. The terms that occurred the most were detected and 53 terms met the conditions. Subsequently, the network line was drawn based on the co-occurrence of keywords (at least 28 times). VOSviewer provides a network map in which nodes represent keywords and links that reflect the strength of co-occurrence. Clusters of words that are closely related are grouped and have the same color. There are four cluster groups identified for this study, as shown by the colors in Figure 9. The keyword pyrolysis is the research's main keyword followed by biomass and air pollutants, which shows the higher frequency of these keywords in the dataset. There are strong connection lines between pyrolysis and biomass, pyrolysis, and process parameters, which reveals the strong co-occurrence or relationship between these keywords. The keywords, having smaller sizes and showing a thin connection line with the core keyword, indicate areas with fewer studies or less focus. Furthermore, the distance between keywords reveals the similarity and vice versa. As shown in Figure 9, the keywords polycyclic aromatic hydrocarbons, volatile organic compounds, particulate matter, flue gases, climate change, and air pollution control are less frequent and illustrate weaker connectivity with pyrolysis. The keywords 'heating rate' and 'residence time' show less connection with air pollutants and other pollutants. Considering pyrolysis air-polluting emissions, the results from VOSviewer indicated potential research gaps that should be examined in future studies for the dual purpose of human and environmental health.

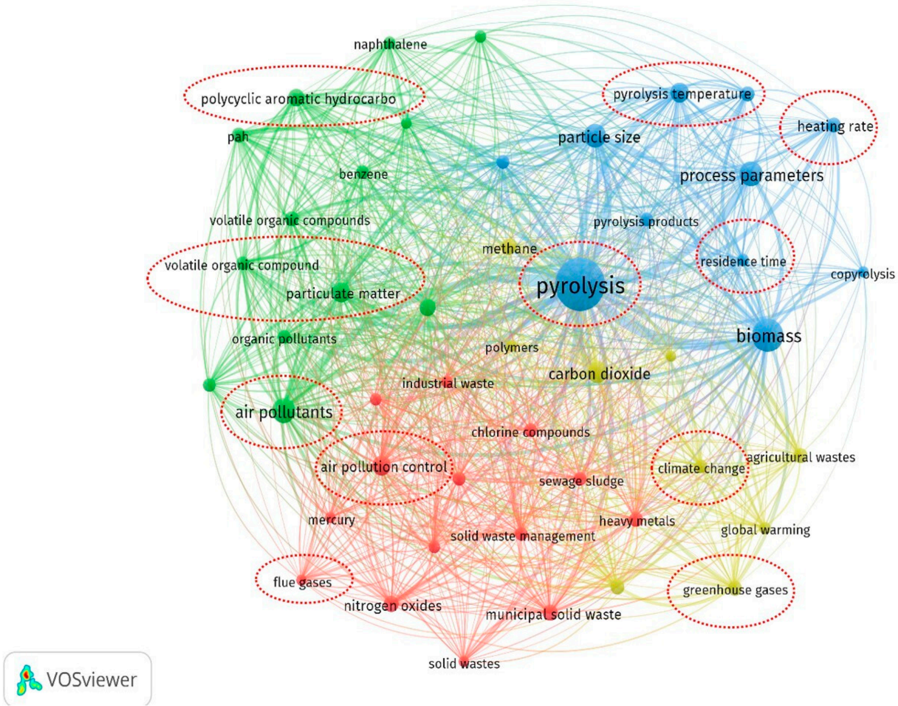


Figure 9. The keywords cluster in the title and abstract of the articles.

Some of such needs are summarized below, as follows:

- An improved understanding of the impact of the heating rate and residence time on air-polluting emissions from pyrolysis plants is required. This will show how pyrolysis operational parameters (collectively) affect air-polluting emissions;
- The effects of feedstock characteristics and pyrolysis gas composition on post-combustion emissions must be quantified. As different feedstock compositions alter the properties of pyrolysis gas, which affects air pollution as it burns, it is critical to optimize combustion operations in order to effectively reduce the environmental impact;
- Measurement of air pollutants from pyrolysis plants should be standardized across different scales (that is, from the laboratory scale to the small and industrial scale) because this would facilitate interpretation and cross-comparison of air-polluting emissions from a diverse range of pyrolysis scales;
- The efficacy of mitigation strategies is often neglected in lab-scale research but it needs to be considered as an essential component of emission control strategies;
- There is an urgent need to develop a regulatory framework for pyrolysis plants as, currently, no regulations are available. Pyrolysis studies frequently compare emission levels to existing waste incineration and combustion regulatory frameworks; therefore, comparisons may not be relevant.

4. Conclusions

Air pollution from pyrolysis plants is a growing environmental concern and knowledge of air pollution risks is required prior to obtaining pyrolysis plant authorization by ensuring that the plant will comply with environmental regulations. The number of studies on air-polluting emissions from pyrolysis plants decreased to an average of three articles per year after 2018, suggesting that research on the topic has not been prioritized and that the problem does not appear to have been addressed. Key air pollutants emitted during pyrolysis, as identified in our study, were CO, CO_2, SO_2, CH_4, PM, HCl, VOCs (benzene, toluene, H_2S, HCN, and NH_3), and persistent organic pollutants (namely PCDD/Fs, PAHs, PCBs, BrPhs, PBDD/Fs, and PFAS). The concentration of individual air pollutants emitted during pyrolysis is significantly affected by the composition of feedstock and the process parameters. Studies that compared air-polluting emissions from pyrolysis plants with those from combustion and incineration plants showed that the resulting PCDD/Fs concentrations during combustion and pyrolysis at high temperatures were similar and both relatively low (~106 ± 23 pg/g of sample). A comparison of incineration and pyrolysis showed that the PCDD/Fs yield was much lower with pyrolysis and that pyrolysis plants emit more VOCs than combustion plants. This is because the process of pyrolysis takes place in an oxygen-limited atmosphere and it can release VOCs as part of the thermal decomposition of organic materials. On the contrary, the combustion process occurs in an oxygen-rich atmosphere, which, therefore, contributes to the oxidation of VOCs and increased production of CO_2. The studies available in the database involved a range of approaches (e.g., catalysts, electrostatic precipitators, wet scrubbers, and baghouse filters) to reduce emissions. Monitoring air-polluting emissions within the prevailing regulatory framework is an important practical consideration to ensure that pyrolysis plants can operate in an environmentally friendly and compliant manner, which can be facilitated by implementing best management practices, including the adoption of suitable mitigation technology. This article highlighted several technical and knowledge gaps and opportunities that were evident in the literature consulted. The most important is the urgent need to develop a regulatory framework for pyrolysis plants, as no regulations are currently available.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/environments11070149/s1. Supplementary Files: ROSES data (SF-1), bibliographic database and benchmark (SF-2), list of excluded articles with reasoning (SF-3), and database (SF-4), which are attached along with the article.

Author Contributions: Conceptualization, A.P. and H.G.; methodology, A.P. and A.S.; software, H.G.; validation, D.L.A., S.C. and G.B.; formal analysis, H.G.; investigation, H.G.; resources, P.R. and W.P.; data curation, H.G.; writing—original draft preparation, H.G.; writing—review and editing, D.L.A., S.C., F.D.M. and M.C.L.; visualization, H.G.; supervision, A.P., M.C.L. and G.B.; project administration, M.C.L.; funding acquisition, A.P. and M.C.L. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: No new data were created or analyzed in this study.

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Conflicts of Interest: Philipp Reichardt is employed by the company PYREG GmbH. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in the article:

APCDs	Air pollution control devices
BrPhs	Brominated phenols
ClPhs	Chlorophenols
ClBzs	Chlorobenzenes
ELV	Emission limit values
FGD	Flue gas desulphurization
IED	Industrial Emission Directive
NMVOCs	Non-methane volatile organic compounds
PAHs	Polycyclic aromatic hydrocarbons

PBDD/Fs	Polybrominated dibenzo-p-dioxins and dibenzofurans
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and furans
PFAS	Perfluoroalkyl and Polyfluoroalkyl Substances
PM	Particulate matter
SVOCs	Semi-volatile organic compounds
VOCs	Volatile organic compounds

Appendix A. The Selected Primary Studies

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