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## Review

# Review of the Current State of Pyrolysis and Biochar Utilization in Europe: A Scientific Perspective

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**Abstract:** This scientific paper provides an overview of the current state of pyrolysis in Europe, with a focus on mapping the key research areas and technologies employed. This research relied on search equations that centered on the utilization of biomass and plastics as primary feedstocks in pyrolysis, with a particular emphasis on biochar generation and different technologies applied. The results showed that both plastic and biomass pyrolysis can contribute to reducing waste and mitigating greenhouse gas emissions. However, plastic pyrolysis can release harmful pollutants due to the presence of chlorine and other additives in plastics, which requires sophisticated emission control systems to be implemented. The production of biochar from sewage sludge is identified as a promising approach for phosphorus recovery, which can subsequently be utilized as a valuable fertilizer in agricultural applications. The data from this study contribute to exploring future applications at pilot and industrial scales for pyrolysis, with a critical assessment of the use of feedstocks. Moreover, this work provides information about current companies that are already operating on a large scale with pyrolysis and a map of the principal countries in Europe engaged in pyrolysis research, correlating the characteristics of the pyrolysis processes investigated.

**Keywords:** Europe pyrolysis; biochar; sewage sludge; TCR; plastic pyrolysis; biofuels



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## 1. Introduction

In an era characterized by a pronounced dependence on fossil fuels in the total primary energy supply, coupled with an ongoing escalation of waste generation and the urgent need to mitigate climate change, sustainable solutions for resource recovery and energy production are of paramount importance. To achieve a more environmentally conscious and resilient future, innovative approaches that not only reduce waste and carbon emissions but also promote circular economy principles have become imperative, highlighting the significance of finding efficient and effective technologies. Within this context, pyrolysis, a thermochemical conversion process, offers a promising avenue for addressing these challenges.

Pyrolysis involves the thermal decomposition of organic matter at moderate temperatures (typically 200–600 °C) by adding heat in the absence or limited supply of an oxidizing agent. During pyrolysis, the complex molecular structure of biomass breaks down into smaller and simpler molecular structures than its original form, resulting in the formation of a vapor phase and a solid phase.

The solid phase, known as either char (derived from non-biogenic feedstocks) or biochar (derived from biogenic feedstocks), usually has a high carbon content (>65%), highly porous structure, significant amounts of extractable humic, fulvic acids, and other nutrients (calcium, potassium, phosphorus, etc.), and a high cation exchange capacity.

Certain biochars can provide nutrients to the soil and perform a slow release for plants, benefiting their growth [1]. Some parameters define the quality and stability of biochar depending on the type of application.

The condensed vapor phase from pyrolysis is usually referred to as bio-oil or bio-crude, and presents a distribution of different compounds, including carboxylic acids, alcohols, esters, aliphatic, furans, phenolics, aldehydes, ketones, etc.; the non-condensable vapor phase, also known as synthesis gas, consists of various permanent gases and light hydrocarbon gases ( $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{C}_x\text{H}_y$ ). Bio-oil can be used in various sectors of the chemical industry, such as in the production of fertilizers and biofuels (synthetic gasoline, diesel, and kerosene), asphalt, and polymers [2]. Maximizing the desired products from pyrolysis and the efficiency of the thermochemical conversion process depends on several factors, including the characteristics of the raw material (seasonality, available quantity, moisture content, ash content, etc.) and the operational conditions (temperature, pressure, composition of the carrier gas, reactor, etc.) [3]. The products possess immense potential for various applications, including energy generation, soil improvement, and the production of valuable chemicals [4].

The importance of pyrolysis lies in its ability to enable the transition toward a circular economy by transforming waste materials into valuable resources. It provides an opportunity to utilize organic waste, agricultural residues, and biomass feedstocks to generate energy and high-value products while reducing the reliance on fossil fuels. Furthermore, pyrolysis can contribute to mitigating greenhouse gas emissions by enhancing the existing technologies utilized in solid waste management and reducing the need for fossil fuel extraction [4].

In recent years, pyrolysis has emerged as a prominent research area in Europe, driven by the urgent need to address environmental concerns, achieve resource efficiency, and transition towards a sustainable circular economy. Although some research was curtailed during the COVID global pandemic, the year 2023 witnessed a substantial rebound in progress in understanding and optimizing pyrolysis technologies. This resurgence has led to a deeper exploration of their potential applications and benefits, further driving the advancement of sustainable practices.

Europe, renowned for its commitment to environmental sustainability and renewable energy, has been at the forefront of pyrolysis research. Numerous studies have been conducted across various European countries, encompassing a wide range of feedstocks, pyrolysis techniques, technologies, and end-product utilization. These studies have focused on enhancing the pyrolysis process efficiency and assessing its potential applications in energy generation through bio-refining concepts in agriculture and environmental remediation [5–7].

In the face of this context, this paper aims to present a comprehensive review of the research conducted on pyrolysis in Europe from 2020 to 2023. Through an analysis of published studies, our aim is to synthesize the key findings, highlight notable advancements, and identify emerging research trends. Furthermore, this review will shed light on some of the key challenges encountered and propose potential areas for future research and innovation. Thus, the primary objectives of this scientific work were as follows: (1) to identify the overarching themes regarding key pyrolysis studies conducted in Europe through a literature review; (2) to provide detailed insights into the major works, aiming to construct a comprehensive map of Europe for the easy identification of countries and their prevalent research trends; (3) to conduct a critical analysis, delving more deeply into topics that emerged with greater frequency during the review. In this manner, the results can serve as a valuable resource for future research in pyrolysis, as well as for the scaling-up and rapid deployment of processes for specific industrial applications.

## 2. Overview: Main Pyrolysis Studies in Europe

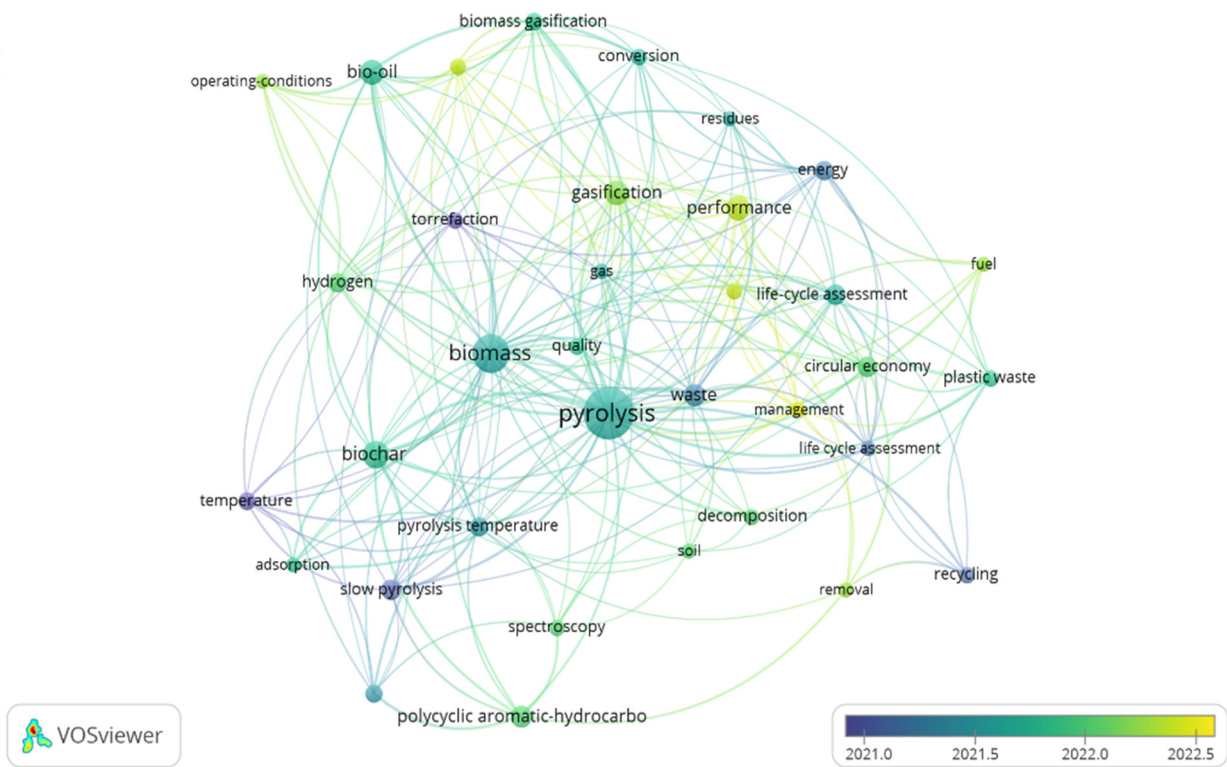
This study employed a methodology based on a bibliographic review of key articles pertaining to pyrolysis in Europe from the years 2021 to 2023. Scientific articles were

sought on research platforms such as ScienceDirect and Web of Science, utilizing keywords such as “Pyrolysis”, “Europe”, “Biomass”, “Biochar”, and “Plastic Waste”. The search filters on these platforms were applied to include articles from European countries. Based on the initial investigation conducted using the search term “Pyrolysis and Europe”, the VosViewer tool was utilized to create maps that would help to integrate all the keywords from the scientific articles. Figure 1a shows the map generated, which resulted in the identification of four clusters. The first cluster included related words such as bio-oil, pyrolysis, conversion, gasification, and biomass gasification. The second cluster contained words such as circular economy, plastic waste, performance, recycling, and technologies. The third cluster included words such as biomass, energy, fuel, waste, and soil. Finally, the fourth and last cluster included words such as biochar, adsorption, and slow pyrolysis. Within each cluster, the words with the highest density of connections were pyrolysis, biomass gasification, biomass, biochar, and plastic waste. Furthermore, we observed connection points between certain words such as pyrolysis–biomass, pyrolysis–plastic waste, and biomass–biochar. Given this context, and following a quick search for each keyword in the literature, it was decided to use the following search equations: “Pyrolysis and Biomass” and “Pyrolysis and Plastic waste” due to the demand of the works found. Figure 1b was generated from the works found for the search equation “Pyrolysis and Biomass”, resulting in six major clusters with numerous keywords ranging from 64 to 19. Among the words with a higher density, in cluster 3, words such as biochar and pyrolysis stood out, while in cluster 4, broader terms such as biomass, biochar, temperature, and sewage sludge were prominent. The strongest connection between words was observed for biochar, sewage sludge, and biomass. In the search equation “Pyrolysis and Plastic Waste”, as shown in Figure 1c, six clusters were also obtained, featuring a variety of keywords (ranging from 35 to 15). The words with the highest density included pyrolysis, catalytic pyrolysis, polyethylene, and noteworthy relationships with plastic waste, biochar, and biomass pyrolysis. Given the abundance of keywords, a quick literature search was conducted to assess which works were most prevalent. Biomass and plastic topics within pyrolysis emerged prominently in titles and abstracts. In light of this investigation, it was decided to emphasize two approaches in this research: the utilization of biomass and plastic to perform pyrolysis followed by a focus on biochar, sewage sludge, and catalytic reforming as a technology. Despite the extensive range of topics associated with pyrolysis, the focus was narrowed down to technologies employed in Europe and the substrates used for pyrolysis product generation, with a specific emphasis on biochar.

The selected works predominantly focused on the pyrolysis of plastics and various biomass sources. To steer the investigation towards biochar, emphasis was given to studies with a primary objective of biochar production from sewage sludge, particularly those associated with phosphorus recovery—a recurrent technique in biochar utilization. Another focus applied in this study was the exploration of activities conducted using thermo-catalytic reforming (TCR), which has demonstrated promise for catalytic reforming in pyrolysis, enhancing the quality of the resulting products. This advancement further aids in the scaling-up process.

In light of these findings, this study is structured into the following sections: Plastic Pyrolysis, Biomass Pyrolysis, Biochar, Sewage Sludge and Biochar, Thermo-Catalytic Reforming (TCR) Approach, Importance of Phosphorus, and phosphorus Recovery through Biochar. Figure 2 displays a diagram illustrating the pyrolysis process, featuring the obtained bio-products, utilized substrates, and a brief summary of the researched works, along with the types of technology employed.

a



b

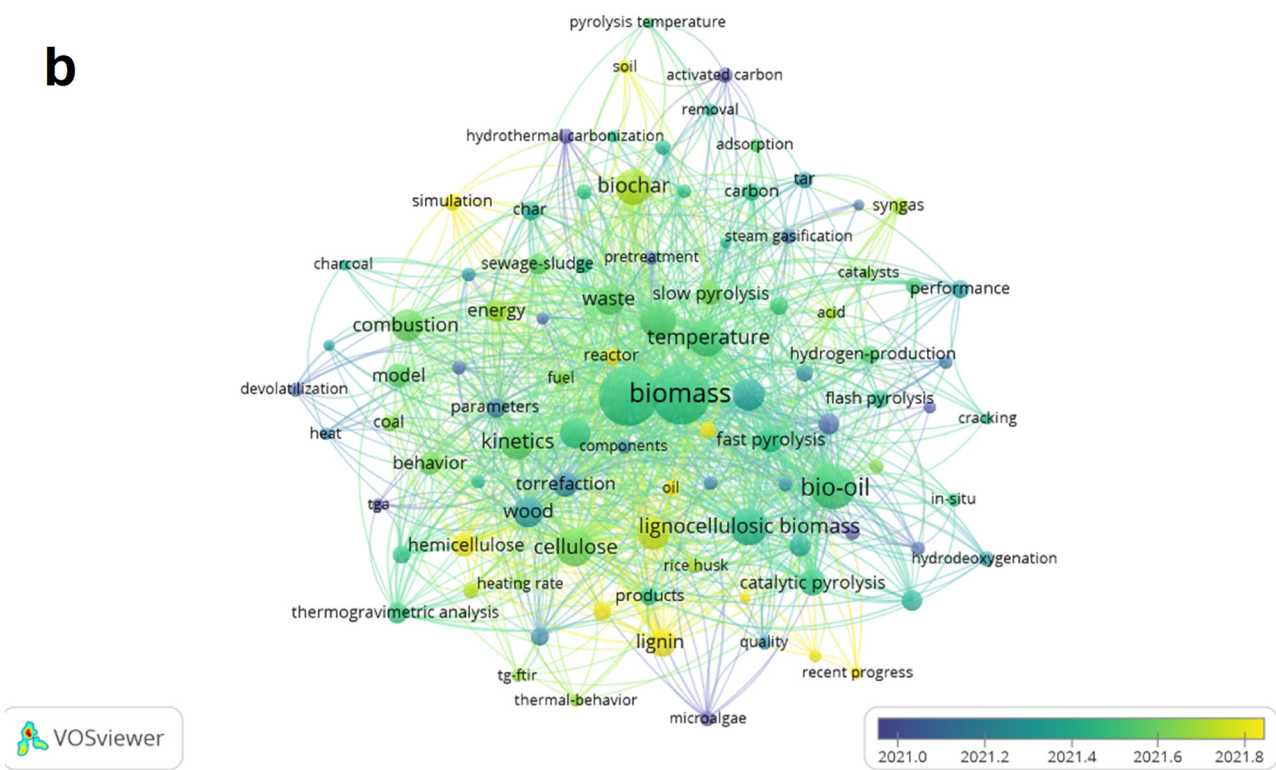
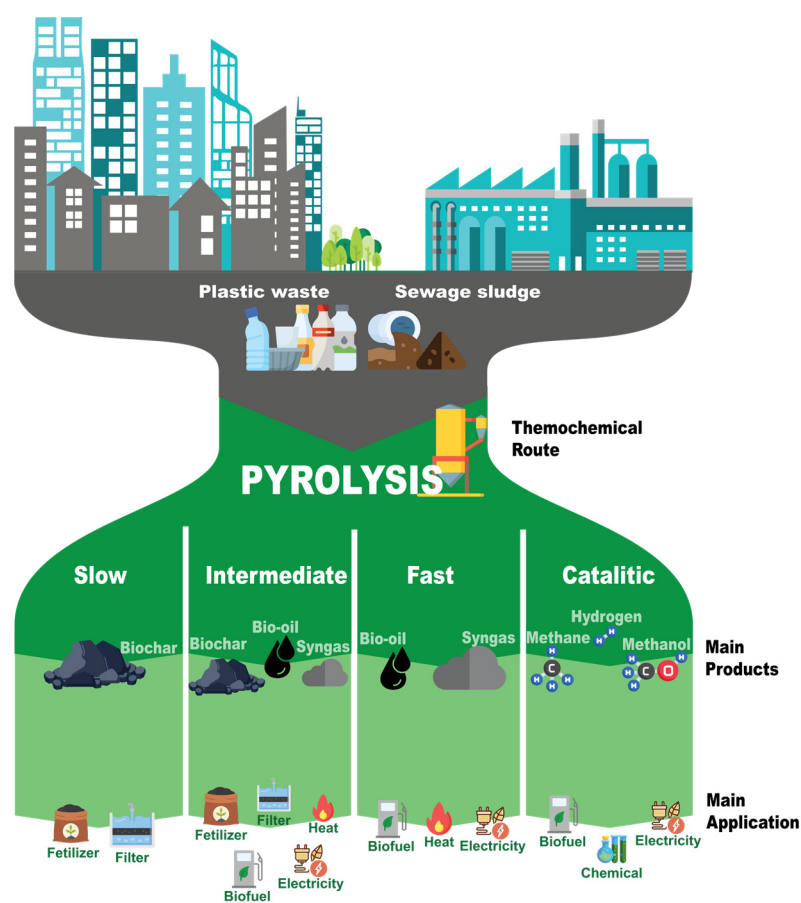
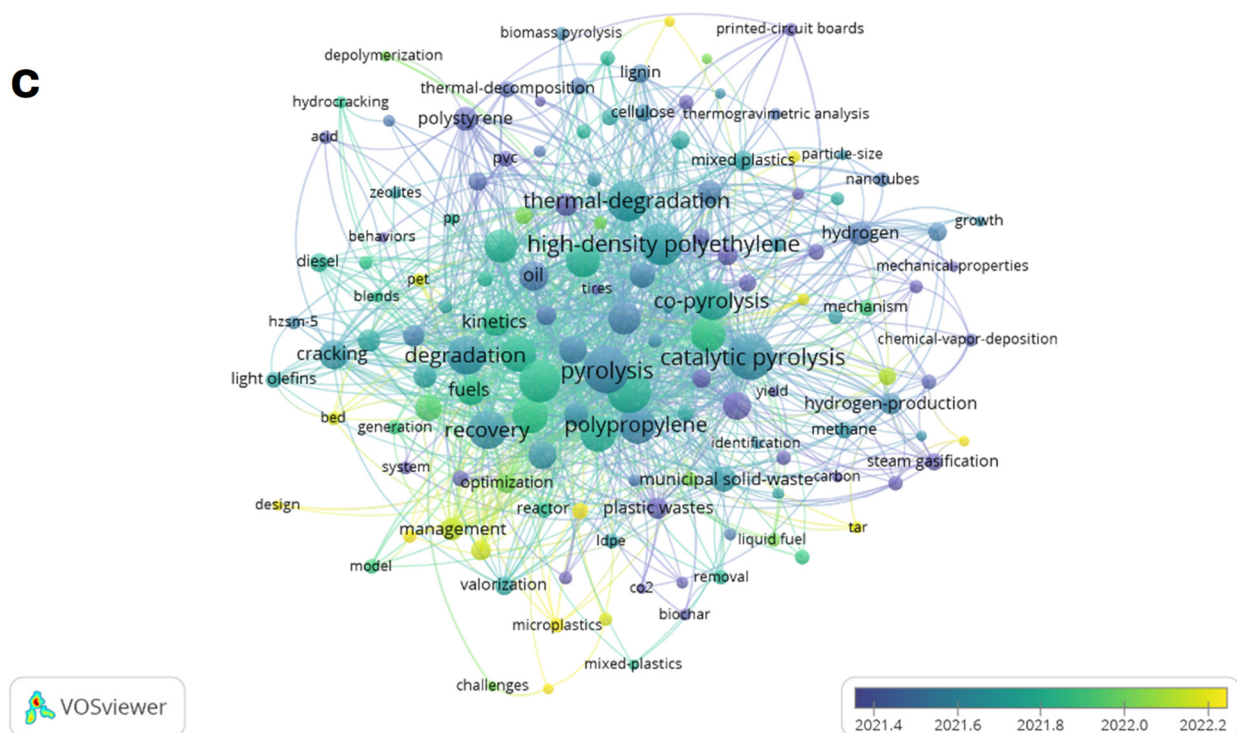


Figure 1. Cont.





### 2.1. Plastic Pyrolysis

Pyrolysis is an efficient and flexible method for extracting both energy and chemical value from waste materials, generating potentially valuable products suitable for future reuse. This flexibility is due to the possibility of maximizing a specific product by altering the reaction conditions of the process, such as the temperature, residence times, and pressure. To increase the contribution of pyrolysis within a circular economy, it is crucial to develop new methodologies [5]. The escalating use of plastics has become a significant environmental concern, with Europe accounting for approximately 17% of global plastic production, amounting to 62 million tons in 2018 [8].

Among the plastics produced in Europe, polypropylene (PP), high-density polyethylene (HDPE), and low-density polyethylene (LDPE) comprise approximately half of the total production. In the same year, Europe collected 29.1 million tons of plastic waste, with 32.5% being recycled, 42.6% used in energy recovery facilities, and 25% ending up in landfill. The non-biodegradable nature of plastic presents significant environmental challenges, especially when disposed of in landfills [9]. Although plastic recycling is perceived as a viable solution, its effectiveness is often compromised due to the incorporation of additives, and the quality of recycled plastic is frequently comparable to that of disposed plastic [9]. One potential solution to reduce plastic pollution is the conversion of plastic into synthetic fuel, achievable through the pyrolysis process. In general, the plastic wastes are converted into syngas, oil, and char, when they are treated at 500–650 °C. Mostly, plastic waste produces pyrolysis oil with identical physical properties (viscosity, calorific, and longer chain of hydrocarbons) to that of heavy oil [10].

In this context, the chemical recycling of plastic waste through pyrolysis is considered an attractive technology for reducing plastic waste and greenhouse gas emissions, and promoting the circular economy. However, greater care must be taken when using mixed plastic wastes as feedstocks, as the use of such can lead to melting and agglomeration at lower heating rates, thus blocking key reactor components, as well as leading to the inconsistent or significant variation of final fuel properties.

Ortega et al. [11] conducted a study on the pyrolysis of surgical masks and filtering face piece masks (FFP2) commonly used during the 2020 pandemic. The masks were collected immediately after use and subjected to pyrolysis at temperatures of 450, 500, and 550 °C in a horizontal tubular furnace. The results demonstrated the influence of temperature on subproduct formation, particularly biochar. With increasing temperature, the concentration of biochar decreased for both surgical masks and FFP2 masks due to the increase in temperature promoting cracking reactions. The maximum bio-oil yield was observed at 500 °C, while the maximum syngas yield was obtained at 550 °C with yields of 50% bio-oil, 40% syngas, and 0.4% biochar *w/w*%. In addition, the major compound recovered in bio-oil was 2,4-Dimethyl-1-heptene during the thermal pyrolysis of masks (>10%). Furthermore, cembrane, 3-Eicosene, (E)-, 5-Eicosene, (E)-, and 1,2-Epoxyhexadecane appeared in a concentration greater than 3% in thermal pyrolysis bio-oils from face masks. For the biochar composition, a high carbon content was observed (from 50.0 to 70.9%), lower nitrogen (from 1.1 to 5.4%) and hydrogen content (from 3.1 to 9.4%), and no sulfur. The study also investigated the effect of using a low-cost catalyst, sepiolite, during pyrolysis. Generally, the use of sepiolite increased the syngas yield at the expense of bio-oil. Moreover, the catalytic pyrolysis led to an increase in the isoparaaffinic content of the bio-oil, with a decrease in naphthenes and paraaffins. The gases derived from the thermal and catalytic pyrolysis of surgical masks and FFP2 masks exhibited a molar composition of hydrocarbon (methane, ethane, ethylene, propane, and propyne) of over 75% that resulted in a high calorific value (over than 40 MJ Nm<sup>-3</sup>), making them suitable as fuels for various applications with methane (48.5%) as the main compound.

Ligeiro et al. [12] produced an activated carbon from biochar derived from the pyrolysis of a post-consumer contaminated mixture of plastic waste. The study examined different temperatures for the activation process at the lab scale. The main composition was liquid (oil, 57.3%), solid (char, 6.2%), and gas (36.5%). The results indicated that the

temperature significantly influenced the CO<sub>2</sub> adsorption uptake. Physical activation using N<sub>2</sub> or CO<sub>2</sub> showed the highest CO<sub>2</sub> uptakes at 720 °C, while chemical activation required higher temperatures of 760 °C for KOH and 800 °C for NaOH. The chemical treatment with alkali hydroxide demonstrated superior results in developing a porous material, with KOH showing better performance than NaOH. Additionally, optimizing the char: KOH ratio revealed that a ratio of 2:1 yielded the highest CO<sub>2</sub> uptake performance of 50 mg g<sup>-1</sup>. Still on the same issue of using discarded plastics and evaluating the potential of the products that can be obtained from pyrolysis, Palomar-Torres et al. [13] conducted a pyrolysis study on municipal plastic waste, focusing on the production of bio-oil and the use of catalysts, such as ZAP zeolite, at the lab scale. They discovered that the use of a catalyst reduced the production of pyrolysis oil and solid residues while slightly affecting the characteristics of the obtained oils, such as the calorific value, density, surface tension, and kinematic viscosity. The main composition of bio-oil was less than 0.1% for N and less than 0.5% for S, and consisted mainly of alkanes very similar to gasoline and diesel fuel with an elemental composition of 66% C and 10% H. Despite the reduction in the pyrolysis oil yield, the oil remained suitable for use in combustion engines or as fuel additives.

Considering that simulation using mathematical data can provide facilities for obtaining results and predicting behaviors, works in the field of pyrolysis like these have shown great promise. Yapici et al. [5] investigated gas production predictions in pyrolysis based on various conditions such as waste types, temperature, heating rate, catalyst type, and quantity. Mathematical models were utilized to predict the yield of pyrolysis gas products. The results indicated a strong negative correlation between liquid and gas product yields, a negative correlation between solid product yields and temperature, and a positive correlation between the heating rate and gas product yield. The efficiency of the pyrolysis process was found to depend on the process parameters, highlighting the need for intensive experimental work. Mathematical predictions, specifically Gaussian processes with an exponential kernel, exhibited superior performance in forecasting gas product yields, facilitating experiment optimization and increased productivity.

The utilization of waste plastics for hydrogen production through chemical recycling mechanisms, such as pyrolysis, offers innovative opportunities for creating a valuable product. Hydrogen serves as a versatile commodity chemical with applications in various industries, including oil refining, fertilizer manufacturing, plastics production, and pharmaceuticals. The demand for hydrogen is projected to increase in the clean energy sectors, such as road transportation and fuel cell utilization, as part of efforts to decarbonize the economy and mitigate climate change [14]. Aminu et al. [14] investigated hydrogen generation through non-thermal plasma/catalytic steam reforming of different types of real-world industrial and commercial waste plastics. Polyolefin plastics, including high-density polyethylene, low-density polyethylene, and polypropylene, exhibited the highest hydrogen yields among the plastics tested. At the lab scale with a two-stage experimental reactor system, a 1st stage pyrolysis reactor and a 2nd stage non-thermal plasma reactor were implemented using pyrolysis. The results showed that the main H<sub>2</sub> production was from HDPE plastic pyrolysis, with 18 mmol g<sup>-1</sup> plastic and 43% of H<sub>2</sub> composition. On the other hand, the PET and PS which contain aromatic groups in their structures produced the lowest amount of hydrogen, and for PET, a higher amount of CO and CO<sub>2</sub>.

The real-world application of plastic waste to produce value-added products was assessed in [15]. The authors produced bio-oil from non-chlorinated and non-brominated plastic waste derived from MSW (predominantly composed of PE, PP, and PS) and stored it for 5 years to evaluate its performance in CHP combustion engines. Pyrolysis of 5–7 tons of plastic waste was conducted in a 35 m<sup>3</sup> rotary kiln operated at 400 °C, with the process initiated using diesel burners and sustained with non-condensable gases. In the reactor, bio-oil yields ranged from 45% to 55% (with a high content of alkenes) and a biochar yield smaller than 30% was observed. However, during storage, the authors noted that these compounds tended to polymerize, resulting in long-chain saturated hydrocarbons, consequently increasing the viscosity and boiling point of the bio-oil upon distillation.



Polymerization led to an increase in the distillation temperature at atmospheric pressure, reaching 500 °C after a 5-year storage period, which was 125 °C higher than observed when the bio-oil was stored for 6 months. Overall, the bio-oil produced and stored for 5 years maintained characteristics similar to diesel, but with higher viscosity, sulfur content, nitrogen content, and water content, along with a lower flash point. Based on these findings, the authors highlighted that challenges still exist regarding the practical applications of bio-oil in current diesel combustion engines. Similarly, Januszewicz et al. [16] carried out the pyrolysis of PP and PS in a fixed-bed reactor operated between 400 and 500 °C, and obtained a bio-oil yield of over 90%. This fuel could not be directly used in diesel engines due to its low viscosity and flash point; however, the utilization of a mixture between PP bio-oil and diesel in proportions of 1:5 and 2:5 presents commercial feasibility as the emission characteristics and combustion profiles do not undergo significant changes.

Overall, these studies highlight the potential of pyrolysis as a promising technology for the chemical recycling of plastic waste. This technology enables the production of valuable products, a reduction in environmental impact, and a contribution to the circular economy. Table 1 provides a summary of the main pyrolysis technologies for plastics currently being carried out in Europe, while Figure 3 displays the countries carrying out these works. Further research and optimization of process parameters are necessary to enhance the efficiency and to provide environmental benefits, specifically with respect to scaling up and upgrading plastic derived bio-oils for compatibility as fuels in conventional unmodified engines. It is worth noting that, in addition to scientific research, some patents have been filed in European countries related to the pyrolysis of plastic waste. For example, Kyung's [17] patent was deposited in European countries and addresses the selection of plastic waste containing polyethylene, polypropylene, or a mixture thereof. The plastic waste is passed through a pyrolysis reactor to thermally break down at least a portion of the polyolefin waste and produce a pyrolyzed effluent. The pyrolyzed effluent is separated into residual gas, a pyrolysis oil composed of naphtha, diesel, and heavy fractions, and charcoal. The focus is more on studying the process itself rather than the technologies used. The patent from Sudipto et al. [18] essentially discusses the plastic conversion process through pyrolysis, emphasizing the initial plastic melting and its subsequent use in the pyrolysis reactor, with a focus on maintaining the initial plastic homogeneity under specific conditions. In general, major petrochemical industries have been implementing plastic pyrolysis techniques, aiming for products similar to petrochemicals and the utilization of renewable energy.

**Table 1.** Overview of key pyrolysis parameters for plastic pyrolysis in Europe in 2023.

Number in Map	Type of Pyrolysis	Feedstock	Product	Reactor Type	TRL Level *	Temperature	Reference
1	Fast and Catalytic	Surgical and FFP2 masks	Syngas Bio-oil Biochar	Horizontal tubular furnace	2–3	450, 500, and 550 °C	[11]
2	Fast	Dirty and wet mixture of post-consumer plastic waste	Activated carbon form biochar	Tubular furnace	2–3	500 °C	[12]
3	Catalytic with ZAP USY zeolite	Plastic from Municipal waste	Bio-oil	Single-batch fixed-bed pyrolysis reactor	2–3	400 °C ± 30 °C	[13]
4	Catalytic with Ni/MCM-41	HDPE, PP, OS, PET plastics which were recycled waste plastics donated by Regain Polymers Castleford, UK	Gas, liquid, and char, but the main one is gas (H <sub>2</sub> )	Two-stage experimental reactor system 1st stage pyrolysis reactor and a 2nd stage non-thermal plasma reactor	2–3	750 °C	[14]
5	Intermediate	Polypropylene—PP	Biochar Bio-oil	Glass semi-batch reactor	2–3	480 °C	[19]

Table 1. Cont.

Number in Map	Type of Pyrolysis	Feedstock	Product	Reactor Type	TRL Level *	Temperature	Reference
6	Slow	Rubber	Char Oil (mainly composed of C10, benzene, D-limonene, cyclohexadiene, and cyclo-heptane) Gas, mainly H <sub>2</sub> and CH <sub>4</sub>	Horizontal batch mechanically fluidized reactor (MFR)	2–3	300–500 °C	[20]
7	Intermediate	Plastic from Municipal waste	Bio-oil Biochar	Rotary kiln	6–7	400 °C	[15]
8	Slow	Polypropylene—PP Polystyrene—PS	Bio-oil	Single-batch fixed-bed pyrolysis reactor	2–3	400–500 °C	[16]

Note: \*: TRL Level: 2–3 = Lab-scale fundamental research; 6–7 = Demonstration scale;

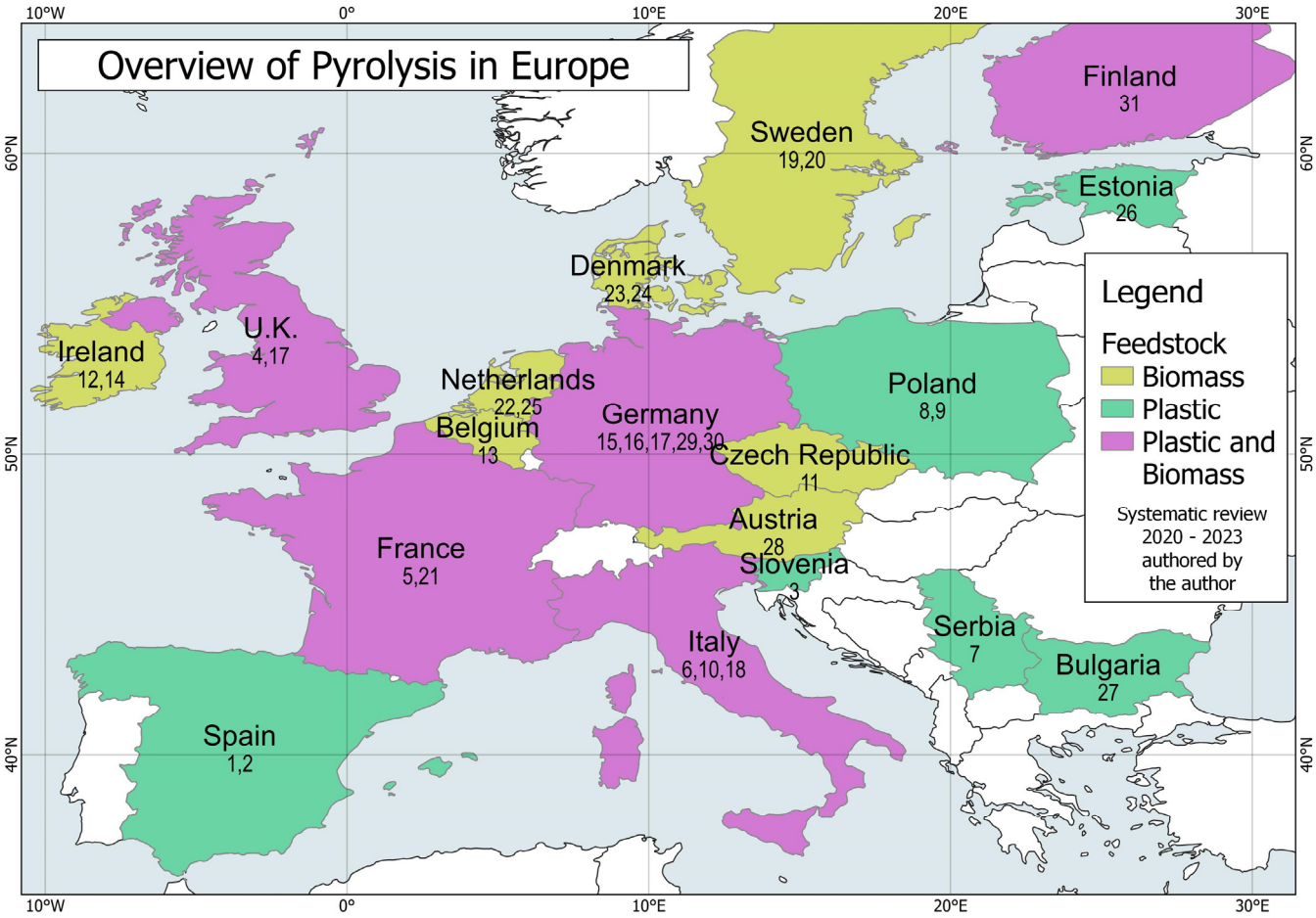


Figure 3. Geographical distribution of pyrolysis research in Europe: focus on key investigating countries. The numbers on the map refer to the countries listed in Tables 1–3.

2.2. Biomass Pyrolysis

The pyrolysis of biomass is a promising and environmentally sustainable approach for the conversion of renewable organic materials into valuable products. Biomass, such as agricultural residues, forestry waste, energy crops, and dedicated energy crops, offers significant potential as a feedstock for pyrolysis due to its abundance, low cost, and reduced greenhouse gas emissions compared to fossil fuels. However, unlike plastic waste, biomass exhibits a high complexity in its chemical composition, which can vary among different types of biomass, directly impacting the distribution, composition, and applicability of the products [21]. Biochar from biomass pyrolysis can be utilized as a soil conditioner for the amendment of soil properties. Biochar improves soil fertility and

carbon sequestration due to its physicochemical characteristics (alkalinity, specific surface area, high carbon concentration, adsorbent characteristics, etc.), while bio-oil can serve as a renewable source of liquid fuel or as a feedstock for further refinement into chemicals and materials. Syngas, consisting mainly of methane, hydrogen, carbon monoxide, and carbon dioxide, has applications in heat and power (CHP) generation, platform chemical production for alcohols and methane, and liquid transportation fuels production through Fischer Tropsch, or can be used to produce heat both to sustain the parasitic heat load in the pyrolysis process as well as providing excess heat [21]. The versatility and wide range of potential applications make biomass pyrolysis an attractive pathway for achieving sustainable energy production within a biorefinery setting whilst mitigating climate change.

The cultivation of *Miscanthus × giganteus* (M × g) in soils contaminated with diesel was investigated by Burdová et al. [22] in the context of organic matter utilization and pyrolysis. M × g plants are known for their ability to grow in contaminated soils, and the plant material underwent pyrolysis. The study revealed that the specific surface area of biochar did not significantly change for leaves and roots. The CO<sub>2</sub> (2–7% g/d.w. yield) and CO (1–4% g/d.w. yield) were the main evolved gases during pyrolysis, and significant differences in the gas composition were observed between below ground and above ground plant parts due to increasing contamination with polycyclic aromatic hydrocarbons (PAHs). Although the product yields of pyrolysis (bio-oil, biochar, pyrolysis gas) were similar in contaminated and clean variants, significant differences were found in the surface area of biochar, gas quality, and bio-oil composition. The main representative compounds groups for bio-oil were acids, furans, ketones, phenols, and esters, with a 50% yield, and a 30–40% yield for biochar. Nevertheless, the biomass of M × g from diesel-contaminated soil can be considered a renewable source suitable for the production of green chemicals compared to biomass from non-polluted soils, since the carbon derived from diesel will be converted into biomass and subsequently into bio-products through pyrolysis.

The energy expenditure associated with pyrolysis and its compensatory potential in relation to the energetic products generated were investigated by Costa et al. [23]. The pyrolysis of spruce, pine, and larch residues at different particle ranges and temperatures was analyzed, focusing on bio-oil, synthesis gas, and biochar production, as well as the life cycle analysis of the overall process. The results showed a bio-oil yield of between 18 and 30%, while the synthesis gas was between 38 and 62% and biochar was 20–35%. The potential for acidification and eutrophication also exhibited a low environmental impact, thus extending the product's life cycle. The total social cost per 1 MJ of bio-oil amounts to 0.16 euros, representing 17% of the total environmental cost of biofuel production. The study revealed that pyrolysis is indeed energy-intensive in terms of external heat consumption. However, the production of synthesis gas can provide the required conversion process heat through concurrent reuse, and the excess energy in the form of biochar can compensate for the electricity demand of the process. Another aspect often overlooked by researchers is the energy required for pre-treatment (drying of the biomass). Typically, biomass should be dried down as low as possible before pyrolysis to conserve energy and maximize pyrolysis efficiencies, with an average moisture content of the biomass ranging between 10 and 15 wt.% recommended before pyrolysis; therefore, questions concerning whether there is sufficient energy available within the bio-products to satisfy the pre-treatment heat demand of drying in addition to pyrolysis requires further investigation. Using externally sourced heat can dramatically impact the overall carbon intensity and sustainability of the process and therefore this must not be overlooked. One option to ensure sustainability is to utilize the energy from synthesis gas for pyrolysis and use biochar as a co-gasification fuel for the surplus heat production for drying biomass.

In the pursuit of organic materials for pyrolysis, Qiu et al. [6] investigated the co-pyrolysis of pig manure with Japanese knotweed (JK), an invasive plant. The study aimed to find a final disposal method for the plant while addressing the low carbon properties and risks associated with heavy metals (HMs) in manure-derived biochars. Different temperatures and substrate ratios were examined, and the co-pyrolysis biochar exhibited

higher carbon fixation compared to biochar derived solely from pig manure. The biochar derived from pig manure achieved the highest yield at 400 °C, reaching around 50%. On the other hand, JK alone obtained the lowest yields (30–40%), while the combinations of both residues yielded results ranging from 35 to 45%. The biochar also demonstrated the ability to retain essential macronutrients, such as K, Ca, Mg, and P, highlighting its potential value. Pyrolysis preserved P, Ca, K, and Mg in biochars, as mineral alkali salts were released from the pyrolytic structure during the pyrolysis process. The combination of pig manure and JK in a 3:1 ratio produced biochar with approximately 60 g<sub>P</sub> kg<sup>-1</sup>. The presence of such metals in biochar opens an important route to new catalytic pyrolysis research, as these metals are all active catalysts known to effect pyrolysis behavior and the formation of specific end products, especially in bio-oil. Therefore, the manipulation of metals within the char can be an effective means of acquiring higher yields of the desired biofuel products.

Several pyrolysis technologies and reactor designs have been studied in the field of biomass conversion in Europe, aiming to obtain bio-products. Shi et al. [24] investigated the upgrading of vapors resulting from pyrolysis in a fluidized bed reactor operated at 0.5 kg h<sup>-1</sup> and 500 °C, and integrated with a catalytic bed (HZSM + Al<sub>2</sub>O<sub>3</sub> and Y-zeolite + Al<sub>2</sub>O<sub>3</sub>). The experiments observed that the biochar yield was 19%. The bio-oil yield was 50%, and the synthesis gas yield was 31% for the non-catalytic process, while the use of a catalytic bed resulted in a reduction in the bio-oil yield. The condensable vapors resulting from pyrolysis in the catalytic bed were deoxygenated and produced water-insoluble compounds (heavy bio-oil at 4–10% and light bio-oil at 21–25%) and valuable compounds, such as naphthalene and olefins, that were not obtained in the experiments without a catalyst; however, the catalysts resulted in a notable concentration of PAHs (polycyclic aromatic hydrocarbons). The synthesis gas was mainly composed of CH<sub>4</sub>, CO, and CO<sub>2</sub>, with an increase in CO production when the catalytic bed was used. That could be attributed to the hydrocarbon deoxygenation. Johansson et al. [25] demonstrated that the co-refining of bio-oil produced from fast pyrolysis (ablative pyrolysis pilot plant) of willow (*Salix* spp.) can be feasible. In this study, pyrolysis produced 42.5% bio-oil, 13.6% biochar, and 21.9% syngas. The bio-oil refinement was carried out through fluid catalytic cracking (FCC) with a 1:5 mixture of bio-oil to conventional fossil feed. The products were composed mainly of gasoline/naphtha, and the C<sup>14</sup> analysis showed that the bio-oil produced 18% coke, 44% liquid, and 38% gas. However, the success in gasoline conversion revealed a reduction in the yield of gasoline/naphtha compared to the use of conventional fossil FCC feed. Chataigner et al. [26] developed and evaluated a new reactor design for biochar production through the partial oxidation (equivalence ratio of 0.09–0.12) of pyrolysis gases. The developed reactor consists of concentric cylinders that separate the pyrolysis zones and utilize the gas produced by the pyrolysis itself to generate heat for the decomposition reactions, rendering the reactor autothermic. This reactor could produce 19–21% biochar, 48–56% synthesis gas, and 20–27% bio-oil from pine bark with diameters ranging from 4 to 15 mm.

These studies enhance the comprehension of organic matter conversion via pyrolysis, demonstrating the potential of various waste biomass sources and pyrolysis technologies, and highlighting their application in sustainable and value-added processes. Furthermore, it is important to highlight that there are still improvements to be made for the effective application of products from the pyrolysis biomass, particularly in utilizing bio-oil to produce biofuels within the current refining processes of the petrochemical industry, as well as advancing the current TRLs of the most promising technologies, as most studies were carried out at relatively early stage TRLs. Table 2 shows a summary of the main scientific works with pyrolysis technologies for biomass that are currently being carried out in Europe. The map in Figure 3 makes it possible to visualize which countries are carrying out these works.



**Table 2.** Overview of key pyrolysis parameters for biomass pyrolysis.

Number in Map	Type of Pyrolysis	Feedstock	Product	Reactor Type	TRL Level *	Temperature	Reference
9	Slow	Refuse-derived fuel, paper, sewage sludge, and rubber, and waste wood biomass (hornbeam leaves, pine, and spruce bark)	Biochar	Tube-furnace heated; lab Scale	2–3	300 °C	[27]
10	Slow	Sewage sludge	Biochar P recuperation	Pilot plant designed and operated by RE-CORD, called SPYRO (Slow Pyrolysis Reactor)—auger type reactor	4–5	450 °C	[28]
11	Fast	Energy crop <i>Miscanthus</i> × <i>giganteus</i> (M × g)	Biochar Bio-oil Syngas	Muffle oven (LAC, Ht205) (a), a glass tube used as a reactor (b), cooler with flowing cold water (c), round bottom flask (d) three wash bottles filled with acetone (e)	2–3	600 °C	[22]
12	Slow and Intermediate	Spruce, pine, and larch	Biochar Bio-oil Syngas	Lab-scale cylindrical fixed-bed pyrolysis chamber	2–3	300, 400 and 500 °C	[23]
13	Slow	Pig manure and invasive plant Japanese knotweed	Biochar	Fixed-bed slow pyrolysis experiments were conducted with a modular stainless steel container	2–3	400–700 °C	[6]
14	Slow	Disposal of waste-activated sludge from wastewater treatment of an effluent from five milk processing plant	Biochar	Quartz tube reactor (wrapped with a heating tape and high-temperature insulation) coupled with a condenser cooler (cooled through circulation of a refrigerated liquid at 0 °C) and a twin-neck round-bottom receiving flask where the pyrolysis liquid was collected	2–3 and 4–5	600–700 °C	[7]
15	Intermediate	Hardwood pellets, softwood pellets, and chips	Biochar Bio-oil Syngas	TCR reactors	2–3	400 °C and 500 °C.	[29]
16	Intermediate	Spent coffee grounds	Syngas (H <sub>2</sub> ) Bio-oil	TCR reactors	2–3	500 and 700 °C	[30]
17	Intermediate	Sewage Sludge	Bio-oil	TCR reactors	4–5	450 °C pyrolysis and 700 °C post-reforming temperature	[31]
18	Intermediate	Sewage sludge	Bio-oil Biochar Syngas	TCR reactors	4–5	500–600 °C and 700 °C	[32]
19	Fast	Sawdust	Biochar Bio-oil Syngas	Fluidized bed	2–3	500 °C	[24]
20	Fast	Willow ( <i>Salix</i> spp.)	Biochar Bio-oil Syngas	Abrative reactor	4–5	750 °C	[25]
21	Intermediate	Pine bark	Biochar Bio-oil Syngas	Pyrolysis prototype named “Ariane” composed by an interlocking of three cylinders forming three distinct temperature zones	2–3	350 °C pyrolysis zone inlet 780 °C maximum temperature	[26]

Note: \*: TRL Level 2–3 = Lab-scale Fundamental research; 4–5 = Pilot scale.

It is also worth noting that numerous patents are being filed with biomass throughout Europe, such as a patent from Carsten [33], which outlines a friction-based biomass pyrolysis process where friction itself heats the biomass and initiates the pyrolysis. There are also patents discussing the reforming process of pyrolysis byproducts, exemplified in a patent from Paradowski [34], which involves treating the gas derived from pyrolysis of both biomass and plastic through different washes and drying methods. Pyrolysis and its byproducts have already found applications in major industries, showcasing their

significant potential for energy generation and producing value-added products. Table 3 presents several European industries actively engaged in the market employing pyrolysis, utilizing feedstocks such as biomass and plastics. The table includes information on the TRL and the European country of operation, providing an overview of large-scale pyrolysis operations in Europe. These details illustrate the dissemination of both pyrolysis research and its industrial applications, emphasizing their significance in the global energy transition. Furthermore, this information underscores the role played by European countries in this transition. In Figure 3, it is possible to visualize the countries detailed in Table 3.

**Table 3.** Pyrolysis-engaged industries in the market.

Number in Map	Company	Feedstock	Products	TRL *	Country
22	Biorizon-TNO	Lignocelulosic biomass	Bio-aromatics	4–5	The Netherlands
23	Project AquaGreen PCE	Sewage sludge	Syngas; biochar	6–7	Denmark
24	Springkildeprojektet	Agricultural waste	Syngas; Biochar	6–7	Denmark
25	BTGBioliquids	Biomass: sawdust, sunflower husk, roadside grass, and straw	Bio-oil	8–9	The Netherlands
26	GreenEco	Tire plastic	Bio-oil, biochar, syngas, steel	8–9	Estonia
27	Modulbg	Tire plastic	Bio-oil, biochar, syngas, steel	8–9	Bulgaria
28	NGE material morphing technology	Sewage sludge	Coke, Syngas	8–9	Austria
29	Fraunhofer	Biomass and plastic	Bio-oil; Syngas	4–5	Germany
30	Karlsruhe Institute of Technology	Plastic	Bio-oil; Syngas	4–5	Germany
31	VTT Technical research center of Finland	Biomass and plastic	Bio-oil-	4–5	Finland

Note: \*: TRL Level: 4–5 = Pilot scale; 6–7 = Demonstration scale; 8–9 = Flagship plant;.

### 3. Biochar: Sewage Sludge, Thermal Conversion Processes (TCR), and Phosphorus Recovery

Biochar has emerged as a prominent product of pyrolysis in the current literature due to its adsorptive capability for soil and water, enabling the removal of heavy metals and promoting increased carbon sequestration. It also serves as an additive for compounds, such as phosphorus. In the conducted research, biochar gained prominence in its use, particularly in biomass, such as in its production from sewage sludge pyrolysis, and its application for phosphorus recovery in agriculture. However, other applications for biochar should also be emphasized, such as its use in the production of ferroalloys in the metallurgical industry.

Currently, fossil fuels are utilized as reducers for the construction of ferroalloys, essential for steel production. To replace carbon reducers from fossil fuels in the ferroalloy industry, biochar with specific chemical, mechanical, and electrical properties is required. Biochar from woody or herbaceous biomass has shown promise for this role. When biomass is operated at 550–600 °C, it produces biochar with a fixed carbon content exceeding 85%, and pyrolysis byproducts are used to provide thermal heat for the process. Biochar produced under these conditions can be directly used in open hearth furnaces for the production of ferrosilicon and silicon [35]. However, handling and transportation issues must be considered as these materials are more fragile. Mousa et al. [36] also highlighted the possibility of using biochar in blast furnaces in the metallurgical industry to replace

pulverized coal, demonstrating the potential to replace the entire system by optimizing the biochar moisture content.

Despite the various applications of biochar, the majority of research has focused on using sewage sludge for biochar generation and phosphorus recovery for agricultural use. As a result, the following sections will be centered on this topic. Additionally, the recurring technology in Europe, TCR, will be explored as it has a significant application in biochar production while also allowing for the generation of bio-oil and syngas. Therefore, attention will also be given to this promising technology that can complement the pyrolysis process and its scaling.

### 3.1. Sewage Sludge and Pyrolysis

Sewage sludge is a complex mixture of water, organic and inorganic substances, and microorganisms that are dissolved in the liquid phase [37]. After a biological and chemical treatment process in wastewater treatment, the sewage is dewatered through a mechanical process, such as a screw press, and the so-called “biosolid” appears. Biosolids are essentially the solid fraction obtained after treatment at sewage treatment plants, and this solid exhibits a structure and a bulk density that usually falls within the range of 650 to 800 kg m<sup>-3</sup> [1].

The inorganic material found in the sludge derives mainly from the soil and anthropogenic polymers, while the organic molecules are derived mainly from polysaccharides, lipids, proteins, plant macromolecules, and some micropollutants [37]. The composition of each material can vary depending on the type of sewage treatment and the geographical region from which the sewage originates.

The organic matter content of the sludge when it contains human faeces and food remains can reach values of 73% in the sewage with a humidity of 90–98%. Mineral elements, such as phosphorus and nitrogen, are generally between 30 and 50% by weight in dry sludge, with phosphorus (P) occupying 0.5–2.5% and nitrogen varying between 3.4 and 9% [1,25]. In untreated sludge, the presence of P does not vary much, being in a fraction close to 3% [1]. Phosphorous species in sewage sludge can generally be classified as inorganic phosphorus (IP), polyphosphate (poly-P), and organic phosphorus (OP). Poly-P and OP are usually generated during biological phosphorus removal, whereas IP is usually derived from chemical phosphorus removal and raw wastewater [38].

The amount of phosphorus that is present in sewage sludge can satisfy 12–15% of the total phosphorus demand after recovery [38]. Several techniques have been studied to remove phosphorus directly from sewage sludge [39]; however, the application of these methods is generally limited by their cost and recovery efficiency, which are highly dependent on the phosphorus species and fractions [38]. Phosphorous, as other inorganic elements, is concentrated in char after sludge pyrolysis, indicating that it is associated with the inorganic fraction of char [28]. Linked to this context, as sewage sludge has several types of microorganisms, including some that are pathogens for plants and humans, there is a need to treat this sewage sludge so that it can have an adequate final deposition and at the same time ensuring that these bacteria, viruses, and fungi are killed, causing no environmental damage. Incineration, pyrolysis, and landfill deposition are common treatment alternatives for sewage sludge. Although incineration brings advantages, such as reducing the volume of sewage sludge by 70% and the degradation of pathogens and toxic compounds, it still has some points that make it expensive, such as the emissions of some gases that can generate air pollution, depending on the location [1]. Landfill is another alternative that is often viewed unfavorably due to its potential to emit greenhouse gases, such as methane, generate leachate that can lead to soil contamination, and contribute to rising land prices [1]. In this context, sewage sludge pyrolysis has gained more prominence, as it has a lower carbon footprint, has less combustion gas compared to incineration, and eliminates the pathogens contained in sewage sludge, reducing the volume of carbonaceous waste, in addition to producing energy and chemicals [37].

In general, pyrolysis can be summarized by three kinds of operation: slow pyrolysis, characterized by extended residence times and lower temperatures (250–350 °C), which

optimizes the production of biochar or activated carbon when an activating agent is introduced; intermediate pyrolysis, which implements moderate heating rates and residence times to give an even distribution of all products; and fast pyrolysis, which involves rapid heating rates at higher temperatures to maximize the yield of bio-oil and gaseous fractions [1]. Among the factors that affect pyrolysis, such as the heating rate, moisture content, residence time, and temperature, the latter is the most impactful and studied. During sewage sludge pyrolysis, the temperature increase can lead to the formation of compounds, such as  $\text{SO}_x$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and  $\text{HCN}$ , which are not desirable [37]. Consequently, careful consideration must always be given to ensure the production of high-quality biochar, which has several beneficial applications in the environment.

In a study conducted by Fristak et al. [40], sewage sludge was utilized for pyrolysis with a focus on nutrient recovery and the utilization of biochar as a fertilizer source for agriculture. The pyrolyzed sludge was evaluated in terms of phosphorus concentration and heavy metal content. Despite slightly elevated concentrations of zinc (Zn) and iron (Fe), the researchers concluded that the pyrolyzed sludge facilitated the growth of lettuce plants. Therefore, the process effectively reduces the bioavailability of heavy metals to soil ecosystems when employed as an alternative fertilizer or soil additive. The sewage sludge biochar had significant amounts of nutrients, among which phosphorus stood out.

Kwapinska et al. [7] focused on utilizing dairy processing sludge (DPS) for pyrolysis and assessing the resulting biochar's elemental properties and contaminants for its potential use as a fertilizer in agriculture. Slow pyrolysis at temperatures of 600 and 700 °C, and residence times of 10 and 20 min were employed to produce the biochars in a laboratory-scale setup and in a pilot-scale facility. The study found that DPS biochars have relatively high contents of Ca (5–10%) and Na (0.9–2%), and contain Fe (814–315, 487 ppm) and Mn (57–665). The heavy metal content in DPS biochars is very low. Moreover, some of the biochars exhibited a high phosphorus (P) content (9–24% as phosphorus pentoxide), indicating their ability to retain P and suggesting their potential as a P source for future extractions.

In the study conducted by Salimbeni et al. [28], slow pyrolysis of sewage sludge was carried out in a pilot-scale reactor to obtain biochar and extract phosphorus from this biochar, thereby enabling the utilization of the mineral-rich liquid and the improved biochar. The results revealed a biochar yield of 57.9%, with a carbon content of approximately 14.4% and a nitrogen content of 2.4%. Furthermore, the biochar exhibited a phosphorus concentration of 47%, along with elevated concentrations of calcium and iron (36 vs. 16 mg  $\text{kg}_{\text{d.b.}}^{-1}$ ).

### 3.2. Thermo-Catalytic Reforming (TCR) Approach

One of the newest technologies that Europe has been leading in research is thermo-catalytic reforming (TCR). Fraunhofer UMSICHT, based in Germany, has developed a novel technology called thermo-catalytic reforming (TCR) under patent number (WO 2015/158732) that enables the processing of various types of problematic waste biomass. TCR combines intermediate pyrolysis with post-catalytic reforming to convert waste biomass into valuable bio-oil, syngas, and biochar. Unlike traditional approaches that rely on forest wood or energy crops from agricultural land, TCR allows the utilization of alternative feedstocks, such as sewage sludge, digestate from AD plants, or livestock slurries/manure, to produce valuable biofuels. In the context of anaerobic digestion, TCR can optimize the economic feasibility by processing the solid residue fraction from AD as a feedstock, thus producing valuable biofuels [41].

This process has been widely used for biochar production, primarily due to its operational characteristics and the temperature range at which it operates. The TCR system consists of two critical steps: intermediate pyrolysis carried out at temperatures ranging from 400 to 500 °C, with solid residence times between 5 and 10 min, where the feedstock undergoes thermal heating in the absence of oxygen; and a reforming (treatment) step, conducted at elevated temperatures above 600 °C, promoting vapor catalytic cracking to enhance the formation of syngas and organic vapors with enhanced physicochemical



properties [41]. In the first stage of the process, gas, vapors, and char are obtained during the pyrolysis phase. However, in the second stage, the gases and vapors pass through a bed of catalyst which can either be the biochar itself or a combination of biochar and conventional catalysts, significantly enhancing the final quality of the bio-oil and gas produced. Additionally, TCR facilitates the easier separation of water from bio-oil, which readily phase separates [42].

In the study conducted by Elmously et al. [30], TCR (thermo-catalytic reforming) was performed on spent coffee grounds to evaluate the potential for improved product quality (biochar, bio-oil, and syngas) compared to traditional technology. A slight increase in the heating value of bio-oil was observed, from 36 to 36.8 MJ kg<sup>-1</sup> at temperatures ranging from 500 °C to 700 °C, respectively. The quality of TCR-bio-oil demonstrated significant superiority in comparison to fast pyrolysis. Bio-oils produced through fast pyrolysis showed higher oxygen content within the range of 35–59% and water content ranging from 10% to 23% by weight. Conversely, TCR-bio-oil had lower nitrogen and sulfur yields. The reforming temperature contributed to an increase in the hydrogen content in the gas composition (0.5% vs. 38%) and reduced the concentration of carbon dioxide. Compared to both slow and fast pyrolysis, the char produced from TCR technology was found to be of higher quality due to catalytic reforming reactions between the char and condensable/non-condensable gases. TCR biochar exhibited a lower oxygen content and H/C ratio. The low H/C ratio contributes to the stability of TCR char, making it suitable for carbon storage in soil.

In the study conducted by Gill et al. [29], they utilized three biomass feedstocks sourced from Alberta (hardwood pellets, softwood pellets, and chips) within a laboratory-scale TCR plant operating at a rate of 2 kg h<sup>-1</sup>. The results suggested that the chemical composition of the biomass exerts a minimal influence on both the yield and quality of the resulting products. The TCR gases exhibited an elevated calorific value ranging from 12.5 to 12.8 MJ kg<sup>-1</sup>, alongside a hydrogen content within the range of 13 to 15 vol%. The resultant TCR bio-oil demonstrated a reduced water content of approximately 5 wt.% and possessed a heating value ranging from 32 to 34 MJ kg<sup>-1</sup>. The superior quality of the bio-oil was evident from its low O/C ratio of 0.15 and total acid number (TAN) falling between 6 and 15 mg<sub>KOH</sub> g<sup>-1</sup>. Moreover, the TCR biochar derived from all three feedstocks exhibited a notable calorific value and a substantial carbon content, consequently exhibiting low O/C and H/C ratios [43].

Sewage sludge, as mentioned in this study, has been one of the biomass sources with the most focus on pyrolysis currently in Europe, mainly due to being a waste generated in high volumes that can pose problems in its disposal. Its use as a substrate for TCR and the conversion of bio-oils that can be used as aviation fuel was investigated by Bashir et al. [31]. The sewage sludge was pre-conditioned and processed through a TCR system (2 kg h<sup>-1</sup>) at a 450 °C pyrolysis temperature and 700 °C post-reforming temperature to produce a biocrude oil. The raw biocrude oil was subsequently conditioned and upgraded through consecutive hydro-processing in two stages, comprising hydrodeoxygenation and hydrocracking as separate unit operations. A total of 6% by weight of the dried sewage sludge was converted into TCR crude oil, separated by phases; 25.4% by weight was converted into synthesis gas composed of CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and C<sub>x</sub>H<sub>y</sub>l; 48.5% by weight converted into char; and the remaining 20.1% by weight converted into wastewater effluent. The crude oil had a higher heating value (HHV) of 39.4 MJ kg<sup>-1</sup> and after hydro-processing it reached 43 MJ kg<sup>-1</sup>. Kick et al. [43] conducted a study demonstrating that TCR technology effectively mitigates the aqueous phase generated during sewage sludge pyrolysis, which typically exhibits high concentrations and is influenced by the biomass moisture content. Typically, the aqueous phase comprises both organic and inorganic compounds, and when TCR is employed, secondary reactions between the pyrolysis gas and the catalyst begin to occur at approximately 600 °C. These reactions consume a portion of the produced water, resulting in a reduction in the volume of the aqueous phase. The TCR aqueous phase, characterized by a higher heating value < 2.4 MJ kg<sup>-1</sup>, consists of over

70% by weight of water, while the remaining fraction is composed of organic and inorganic compounds. The TCR technology has a global warming impact of  $3 \text{ g}_{\text{CO}_2} \text{ MJ}^{-1}$ , while the fossil fuels have approximately  $94 \text{ g}_{\text{CO}_2} \text{ MJ}^{-1}$  according to the renewable energy directive (RED2), being significantly higher than biofuels.

Sewage sludge has the potential to become a renewable energy source through the use of new thermochemical technologies, such as pyrolysis followed by a reforming process. A net energy yield of approximately 2 MJ per kilogram of ash-free dried sludge can be achieved by directly processing the sludge without an intermediate anaerobic digestion step and using the TCR products to provide heat and energy to the system. This processing configuration has been shown to avoid greenhouse gas emissions of approximately  $0.5 \text{ kg}_{\text{CO}_2\text{eq}}$  per kilogram of ash-free dried sludge. The reduction in waste volume and weight obtained through the process is substantial, which helps operators save on disposal fees [32].

TCR has emerged as a leading technique in Europe for the utilization of sewage sludge, as exemplified by the H2020 To-Syn-Fuel project [44]. The central goal is to introduce an environmentally sustainable process that effectively converts biomass waste, specifically sewage sludge, into renewable liquid transport fuels, biochar for soil amendment and carbon sequestration, and hydrogen for fuels and chemical synthesis. The liquid bio-oil can be further refined to produce green fuels that meet the EN fuel standards, enabling their direct use in internal combustion engines without requiring any modifications.

### 3.3. Importance of Phosphorus and Biochar as P Recycling and P Fertilizer

Phosphorus is the second most important nutrient for plant growth, second only to nitrogen, with approximately 30–40% of soils worldwide exhibiting low concentrations of phosphorus. The use of mineral fertilizers such as phosphate fertilizers has become necessary to provide the necessary nutrients for plant growth, as a consequence of population expansion and the need for enhanced agricultural productivity. However, only some fertilizers can effectively supply phosphorus to plants due to its interactions with soil microorganisms, adsorption processes, and erosion [45]. This complexity is due to the fact that the ionic forms of these nutrients available to plants are susceptible to loss via leaching (i.e., ortho-P  $\text{H}_2\text{PO}_4$  ions and  $\text{HPO}_4^{2-}$ ), and fixation or precipitation reactions (i.e., precipitation of ortho-P ions with calcium carbonate in alkaline soils and with aluminum and iron oxides in acidic soils) [46].

The soil biogeochemical cycle facilitates the production of bioavailable phosphorus, also known as ortho-P. This process involves the hydrolysis of organic phosphorus and the solubilization of inorganic phosphate, which are mediated by various agents such as free-living microorganisms, root symbionts, and plant roots. These agents produce hydrolytic enzymes and organic acids. Ortho-P present in the soil solution can either diffuse towards neighboring plant roots or be captured by arbuscular mycorrhizal fungi's high-affinity transporters, which subsequently transfer it to the host plant. The introduction of biochar amendments can influence this hydrolysis and solubilization reactions, as well as the transport of ortho-P by mycorrhiza [46].

Pyrophosphate availability in biochar refers to the presence or potential release of pyrophosphate within the biochar matrix. Pyrophosphate ( $\text{P}_2\text{O}_7^{2-}$ ) is a chemical compound that contains two phosphate ions connected by a high-energy pyrophosphate bond. In the context of biochar, pyrophosphate availability can have implications for plant nutrition and soil fertility. The availability of pyrophosphate in biochar can influence plant nutrient uptake and phosphorus cycling in the soil. Once pyrophosphate is released from biochar, it holds the potential to be accessed by both plants and microorganisms, contributing to nutrient availability. However, the specific mechanisms and extent of pyrophosphate release, along with its subsequent effects on plant growth and soil dynamics, may vary depending on several factors such as biochar characteristics, soil conditions, and management practices.

Research has demonstrated that a viable approach to acquiring and enhancing the availability of phosphorus for soils and plants involves the utilization of biochar. Depending on the concentration of existing anions, biochar can aid in the facilitation of the mineral's release process within the soil, thus addressing phosphorus-related issues. Moreover, several conditions of pyrolysis temperature can exert an influence on the release of this mineral [47]. Another highly significant application for phosphorus is its utilization as a catalyst for biofuels. Most biofuels derived from biomass have a high oxygen content, as they contain compounds such as ketones, aldehydes, and carboxylic acids, which, when compared to petroleum-based fuels, make them have a relatively low calorific value, low stability, low flash point, and high viscosity [48]. In this context, one of the most effective and low-cost methods for deoxygenating biofuels is catalytic cracking.

Among various types of biochars, sewage sludge biochar is notably rich in phosphorus content in comparison to other biochars derived from sources such as animal waste or crop residues [49]. In addition, biochar can increase the phosphorus content by adsorption in its porous structure, reaching values between 4 and 13 mg of P [45]. The main characteristics of biochar derived from sewage sludge are 21% C, 1% H, 3% N, and 7% O [50].

The literature also provides various methodologies for P extraction from biochar, with the majority of methods utilizing chemical reagents for these washes. Among the commonly employed methods is the use of sodium bicarbonate ( $\text{NaHCO}_3$ ) or the presence of acids such as sulfuric acid, formic acid, or citric acid [51,52]. In the study by Zhang et al. [53], the results revealed that the amount of extractable P with  $\text{NaHCO}_3$  was similar to that obtained with water in most biochar samples. However, the amount of P extracted with the  $\text{H}_2\text{SO}_4$  solution was significantly higher than the P extractable with water or  $\text{NaHCO}_3$ , suggesting that the available P in the biochar samples primarily consisted of soluble phosphates and water-soluble P. Other methods for P extraction from biochar involve sequential washes with  $\text{H}_2\text{O}$ ,  $\text{NaHCO}_3$  (0.5 M),  $\text{NaOH}$  (0.1 M),  $\text{HCl}$  (1.0 M), and aqua regia, as described by Adhikari et al. [52]. However, since the P present in biochar from sewage sludge is typically in an inorganic form, the application of techniques used to quantify P in mineral fertilizers can be useful for utilizing sewage sludge as a P source for plants. Therefore, Figueredo et al. [51] decided to conduct a study using citric acid (CA) and neutral ammonium citrate (NAC), typically used to evaluate P solubility in mineral fertilizers, to assess the effect of different extractors on the solubility of P in sewage sludge biochar prepared over a wide temperature range. The results showed that the P fraction soluble in neutral ammonium citrate (P-NAC) exhibited a higher proportion of P compared to the P fraction soluble in citric acid (P-CA). In general, the techniques employed for P extraction from biochar involve washes. However, it is crucial to consider the forms in which this P will be available in biochar (organic, inorganic) and the temperature conditions under which these biochars were produced to ensure a more effective extraction.

In addition, the literature has shown that biochar can serve as a phosphorus reservoir for soils, and that a fraction of this P is in plant-available forms [53]. However, the extent of biochar's effects on soil and phosphorus availability varies significantly with the type of biochar, mainly the raw material, pyrolysis temperature, and P extractor used, as there are several methodologies for this [51]. In one part of the TO-SYN-FUEL project [41], ryegrass biomass was cultivated in pot trials using different fertilizers: TCR sewage sludge biochar, pyrolysis ashes, and full fertilization. The plant growth with the different fertilizers demonstrated that biomass production in the first growth cycle was highest with full fertilization, closely followed by TCR fertilization. Initially, biochar-TCR showed slightly poorer activity, but it significantly caught up in cycles 2–4 and achieved similarly good results as full fertilization. One of the key explanations for this behavior is that biochar can store the available phosphorus when loaded with synthetic fertilizers and release it over a longer period. The initial lower performance can be attributed to the low concentration of water-soluble and plant-available phosphorus in TCR biochar, suggesting a mild phosphorus deficiency in the early stages. These findings confirm the ability of biochar to store and release phosphorus and highlight its potential role as a fertilizer.

### 3.4. Shutdown: Possible Scenarios for Biochar Applications

Considering the research from scientific articles and insights from many industries, the main scenarios that can be considered for biochar realistic potential are as follows:

1. **Agricultural enhancement:** Biochar plays a crucial role in agriculture by enhancing soil fertility, nutrient retention, and water retention. It facilitates nutrient release to the soil, aiding in the fertilization process.
2. **Carbon sequestration for climate mitigation:** Biochar emerges as a significant tool for carbon sequestration, contributing to climate change mitigation efforts. Its ability to capture and store carbon positions it as a promising solution in the fight against climate change.
3. **Industrial applications—metallurgy and construction:** Biochar demonstrates promise in industrial applications, particularly in metallurgy and construction. Its use in the production of materials, such as ferroalloys, showcases its versatility and potential as a substitute for coal in various industrial processes.
4. **Energy production and co-firing:** Biochar's role in energy production, either through direct combustion or co-firing with other biomass sources, presents an opportunity for renewable energy generation. It can serve as both a renewable energy source and a co-substrate to control process conditions when used in conjunction with biomass.

While these are the primary scenarios, it is essential to note that the versatility of biochar allows for exploration in various fields, and new applications may emerge with ongoing research and technological advancements. The actual impact and widespread adoption will depend on factors such as technological developments, regulatory support, and market acceptance.

## 4. Comparison between Pyrolysis from Plastic and Biomass: Impacts and Overview

Currently in Europe, approximately over 5 million tons of plastic waste is mechanically recycled and only around 50,000 tons of plastic waste is chemically recycled. Typical plastic waste recycling systems are logistically more complex, with separate collections and several different flows than other traditional waste processing systems, such as metals or paper, which results in higher plastic waste management costs. They have the capability to treat various kinds of plastic waste ranging from packaging waste to more complex materials, such as rubber and plastics from WEEE (waste electrical and electronic equipment), hospital waste, and ELV (end of life vehicle), which are contaminated with toxic and hazardous substances such as halides. The pyrolysis of plastics, besides liquid products, also generates hydrocarbon-rich gas, which has, depending on the feed and conditions, a heating value of  $25\text{--}45\text{ MJ kg}^{-1}$ , making it ideal for energy recovery. Therefore, in many cases the pyrolysis gas is circulated back into the process to extract the energy for the heating purpose [54].

Pre-treatments are essential in the pyrolysis of plastics to ensure the removal of contaminants, such as heavy metals, and to achieve particle size uniformity for optimal performance in the pyrolysis reactor. The pre-sorting of plastic waste is crucial to maintain the economic viability of a Plastic to Fuel (PTF) plant. Moreover, the origin of the plastic waste plays a significant role, as plastics sourced from different origins exhibit variations in shape and size [54].

Various types of reactors are commonly employed in plastic pyrolysis, including fluidized bed reactors, auger reactors (a variant of rotary kilns), melting vessels or stirred-tank reactors (STR), and microwave reactors. The operating temperature typically ranges between 400 and 600 °C [54].

According to Qureshi et al. [54], an existing pyrolysis plant in Spain utilizes plastic energy technology, focusing on the production of raw diesel, light oil, and synthetic gas components using an STR reactor. In contrast, a 500 kg/h TCR plant in Germany adopts a screw reactor, targeting the production of products such as green crude, diesel, gasoline, and jet fuel.

In the context of current advancements in plastic pyrolysis in Europe, it is important to highlight the significant role of biomass, specifically sewage sludge, as a valuable resource.



The utilization of TCR technology presents a novel approach that enables the production of high-quality products, including biochar and bio-oil. These products exhibit favorable characteristics that facilitate their direct application in combustion engines without requiring additional post-treatments. This technological innovation not only offers a sustainable solution for the effective utilization of biomass, but also contributes to the development of a more efficient and environmentally friendly energy system. Furthermore, the production of biochar and bio-oil through TCR demonstrates the potential for valorizing sewage sludge and highlights the feasibility of implementing this technology as a viable alternative in the transition towards a circular economy. Another important aspect that must be made regarding the use of biomass within the pyrolysis process, is that it is part of the carbon cycle, effectively restoring the organic fraction of carbon released into the environment through pyrolysis, thereby reducing greenhouse gas emissions.

Table 4 presents a comprehensive comparison of products, substrates, and technologies employed for both biomass and plastic pyrolysis. Notably, biomass pyrolysis stands out for its exceptional potential as a source of fertilizers, owing to its high nutrient content. On the other hand, plastics have the capacity to generate gases with elevated nitrogen yields and potentially produce oils characterized by higher hydrocarbon concentrations and lower oxygen levels, thereby enhancing their overall quality. It is crucial to emphasize that the selection of waste material to be processed depends on the specific interests of the industry, taking into account the potential for bioenergy generation and the availability of these materials.

**Table 4.** Comparison between plastic and biomass pyrolysis.

Characteristic	Plastic	Biomass
Feedstock	Pyrolysis involves the thermal decomposition of plastic waste	Pyrolysis involves the conversion of organic materials such as wood, agricultural residues, and energy crops.
Composition	Primarily made of carbon and hydrogen	Contains a mixture of carbon, hydrogen, oxygen, and other elements, including nitrogen and sulphur
Energy Content	Higher energy content compared to biomass (more energy-rich products)	Lower energy content compared to plastic
Process and Products	Plastics are typically heated in the absence of oxygen, leading to the production of liquid fuels, gases, and a solid residue (char).	Follows a similar plastic process, but due to the varied composition of biomass, the product yield and composition can differ. Biomass pyrolysis can produce bio-oils, gases (including syngas), and biochar.
Environmental Impact	Both plastic and biomass pyrolysis can contribute to reducing waste and mitigating greenhouse gas emissions. However, plastic pyrolysis can release harmful pollutants due to the presence of chlorine and other additives in plastics, which requires proper emission control systems	On the other hand, it is generally considered more environmentally friendly due to the renewable nature of biomass and its potential to be carbon neutral
Applications	The products derived from plastic pyrolysis, such as pyrolysis oil, can be used as a feedstock in refineries or as an alternative fuel	Biomass pyrolysis products, such as biochar, can be use as fertilizer in agriculture and syngas can be applied as biofuel

In general, pyrolysis, regardless of the substrate used (plastic, biomass, or otherwise), is crucial for the advancement of renewable and sustainable energy, not only in Europe but worldwide. The Paris Agreement holds significant implications for Europe, where nations actively pursue the reduction of greenhouse gas emissions by a minimum of 40% below 1990 levels by 2030. Concurrently, there is a concerted effort to advance the deployment of renewable energy sources. Notably, Europe has emerged as a trailblazer in instituting carbon market initiatives, exemplified by the EU Emissions Trading System (EU ETS),

strategically designed to instigate economic incentives conducive to emission reductions, thereby contributing to the circular economy. Within this context, pyrolysis has garnered attention among European nations as a viable technology to attain emission reduction targets and facilitate decarbonization. Additionally, this involves the use of substrates that were previously considered waste and generates value-added products, such as biochar, bio-oil, and syngas. This circulates the products, leading to economic gains in the process and contributing to the circular economy. The work of Surup et al. [55], for example, clearly illustrates how pyrolysis contributes to the circular economy, as they demonstrate that bio-oil can be used as a binder for pellets composed of coal, which are employed in ferroalloy industries. Its attractiveness stems from its low capital requirements and minimal spatial footprint, presenting a pragmatic avenue for diminishing the reliance on fossil fuels. The utilization of both biomass and plastics holds promise in advancing these objectives, thereby aiding Europe in fulfilling the stringent requirements set forth by the Paris Agreement.

## 5. Conclusions

In conclusion, this study highlights Europe's leadership in pyrolysis research concerning biomass and plastics, with a focus on bio-oil, biochar, and syngas as the main products. The literature demonstrates a significant research interest in utilizing plastic as a feedstock for pyrolysis due to its adverse environmental impacts and the challenges associated with its proper disposal. Despite recycling efforts, a substantial portion of plastic waste remains unrecycled and is consequently discarded. Pyrolysis presents a promising avenue for the environmentally sound management of plastic waste, offering the potential to convert materials such as COVID pandemic masks into valuable energy products including bio-oils, biochar, and syngas.

In addition to plastics, biomass resources, including crop residues and sewage sludge, have garnered considerable attention and investigation in Europe. These biomass sources offer the potential for producing high-value biochar, characterized by elevated levels of micronutrients. Of particular interest, biochar derived from sewage sludge exhibits a pronounced phosphorus content, making it a potentially valuable fertilizer. Furthermore, the presence of key alkali metals such as Ca, K, and Mg within the biochar matrix opens up new avenues for catalytic pyrolysis research, with potential applications in utilizing biochar as a catalyst for bio-oil production.

Among the various pyrolysis technologies, TCR stands out for its ability to generate high-quality bio-oil, syngas, and biochar without the need for extensive purification, generating time and money savings, showing even more viable alternatives for the application of pyrolysis in a biorefinery setting. The Technology Readiness Levels (TRLs) employed in plastic pyrolysis predominantly remain at the laboratory/pilot scale, indicating a primary focus on experimental investigations, with very few commercial plants operational. In contrast, the utilization of biomass resources has witnessed notable progress, with significant advancements achieved at the pilot scale, specifically emphasizing the implementation of TCR technology. The versatility of pyrolysis in terms of substrates and technological applications makes it increasingly appealing for the production of bioenergy and biofuels.

This literature review holds the potential to significantly contribute to the advancement of pyrolysis in Europe, particularly concerning the utilization of technologies and the scaling-up of the process. Through the developed mapping, it becomes feasible to discern the specific focus of each country in their pyrolysis development, thereby aiding in prospective research endeavors and potentially influencing future patent applications, industrial advancements, and technology implementations. Moreover, this comprehensive visualization of pyrolysis in Europe may foster collaboration among nations, facilitating progress in the use of renewable fuels and aligning with the requirements outlined in the Paris Agreement and the Sustainable Development Goals (SDGs).

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