energies

Article

Evaluation of the Feasibility of Using TCR-Derived Chars from Selected Biomass Wastes and MSW Fractions in CO_2 Sequestration on Degraded and Post-Industrial Areas

Marcin Sajdak [1,*], Artur Majewski [2], Francesca Di Gruttola [3], Grzegorz Gałko [4], Edyta Misztal [4], Michał Rejdak [4], Andreas Hornung [5] and Miloud Ouadi [2,*]

1 Department of Air Protection, Faculty of Energy and Environmental Engineering, Silesian University of Technology, 44-100 Gliwice, Poland
2 School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
3 Astronautical, Electrical and Energy Engineering Department (DIAEE), Sapienza University of Rome, 00185 Rome, Italy
4 Institute of Energy and Fuel Processing Technology, Zamkowa 1, 41-803 Zabrze, Poland; ggalko@itpe.pl (G.G.)
5 Fraunhofer UMSICHT, An Der Maxhutte 1, 92237 Sulzbach Rosenberg, Germany
* Correspondence: marcin.sajdak@polsl.pl (M.S.); m.ouadi@bham.ac.uk (M.O.)

Abstract: Protection of the natural environment is one of the most significant global challenges for the international community. World problems arising as a result of the incineration of fossil fuels, excessive CO_2 emissions, erosion and soil degradation, as well as air pollution with the accelerating greenhouse effect and changes to the climate condition, make it necessary to take action at many levels. Environmental protection and the protection of natural resources need to follow the principles of sustainable development. Looking for alternative energy sources is appropriate but not sufficient and should be conducted in various areas since natural environmental changes are accelerating with many consequences. Therefore, there is demand for implementation of applications aimed at protecting air, and soil, preventing waste formation and combating the greenhouse effect. Therefore, the multi-directional use of various biocarbon substances for activities related to renewable energy, land reclamation, and carbon dioxide capture from the atmosphere is a promising and significant direction. This paper presents multidirectional analysis related to the use of biocarbon obtained from biomass and MSW waste.

Keywords: TCR; char; thermal conversion of biomass and waste; CO_2 sequestration

Citation: Sajdak, M.; Majewski, A.; Di Gruttola, F.; Gałko, G.; Misztal, E.; Rejdak, M.; Hornung, A.; Ouadi, M. Evaluation of the Feasibility of Using TCR-Derived Chars from Selected Biomass Wastes and MSW Fractions in CO_2 Sequestration on Degraded and Post-Industrial Areas. *Energies* **2023**, *16*, 2964. https://doi.org/10.3390/en16072964

Academic Editor: Alberto Coz

Received: 3 March 2023
Revised: 21 March 2023
Accepted: 22 March 2023
Published: 24 March 2023

1. Introduction

Biomass wastes, including some fractions of municipal solid waste (MSW) and sewage sludge, are currently a significant challenge to environmental protection. In terms of morphology, they are characterized by large diversity. MSW consists of different morphological fractions such as plastics, biomass, textiles and inorganic substances in the form of metal, glass, and other substances [1–3]. There are several possibilities for the disposal of this type of waste, and there is currently a growing move towards their use in thermal conversion processes. It is important to obtain fuel with the highest calorific value and the lowest ash and moisture content. Fuel properties, mainly its proximate and ultimate characteristics, determine its further usability. In the thermal conversion processes, pyrolytic oils, syngas (or pyrolytic gas) and a solid fraction (carbonite) are obtained [4–10]. These fractions mostly depend on the type of applied thermal process for material conversion, the process conditions and the feed material itself. In thermal conversion, apart from gasification and incineration, one of the most significant processes is pyrolysis. This process's characteristic feature is thermal degradation without the presence of oxygen or other additive reagents. However, to increase the process efficiency, and the yield of valuable products, some modifications are required to develop a novel and innovative technological solution. One of the most promising directions is catalytic pyrolysis. An example of this is the Thermo-Catalytic Reforming (TCR) technology developed by A. Hornung and Fraunhofer UMSICHT, Germany [11,12] that combines intermediate pyrolysis with catalytic reforming to convert waste biomass to valuable products. The process includes heating biomass with a catalyst present in a controlled environment to create a highly porous and stable char, as well as valuable liquid and gaseous products. In the TCR system, intermediate pyrolysis at mild temperatures (300–500 °C) is followed by the reforming step at elevated temperatures (500–800 °C), where catalytic cracking of gases and vapours generated in the first step occurs. Part of the produced char can be recycled back into the process as a catalyst. Biochar's end-use properties can be fine-tuned through manipulation of the process parameters such as temperature, pressure, and reaction time.

Agriculture, soil improvement, carbon sequestration, and contaminated soil remediation are just a few of the many uses for biochar, which is created through the thermochemical conversion of biomass and wastes. Biochars obtained from MSW have many additional possible directions of application, with significant potential to reduce environmental problems. An interesting opportunity is the application as a green adsorbent for preventing contaminants migration and limitation of withstanding nutrients in the soil for plant uptake and retention. Therefore, MSW biochar introduction to the soil has been proven to enhance plant growth to attain a higher yield [13]. It can enhance agricultural soil's fertility, water-holding capacity, and structural integrity. Greenhouse gas emissions can be lowered because carbon is sequestered in the soil for a long time. Since it has a high adsorption capacity, it can also be used to clean up polluted soil. Due to its significant share of mineral fraction (ash), it can also be used as a useful fertiliser. By reclaiming previously unusable land for agricultural purposes, char usage improves crop yields and the overall agricultural productivity of an area. The presence of micronutrients in manufactured biochar greatly enhances soil fertility properties. Nitrogen (N), phosphorus (P), potassium (K), and calcium (Ca) are the four main nutrients for plants present in MSW-derived biochar [14]. In conclusion, the Thermo-Catalytic Reforming (TCR) of biomass provides a highly controlled and efficient approach to the production of biochar with enhanced physical and chemical properties.

The purpose of this manuscript is both the valuation of chars from different origins based on literature data, and discussion of their potential applications to suggest where they might be most valuable. Possibilities of using various types of biochar obtained from a diverse range of raw materials, along with their potential further use and possible effects of such action, are presented. This manuscript presents the novel approach of TCR-biochar being used as a valuable resource for atmospheric (CO_2 sequestration) and pedosphere protection (source of organic carbon, soil improver). Application of novel aspects of biochar products from municipal solid waste correlates with the actual trend of waste formation prevention in accordance with the circular economy, sustainable development and some aspects of cradle-to-cradle novel methodology, which is significantly different to the traditional approaches (energy and metallurgy usage). The importance of the problem and the need to take immediate action to protect the environment and climate has been taken into account.

2. Materials and Methods

2.1. Thermo-Catalytic Reforming

In the context of technology, thermo-catalytic reforming is distinguished by combining pyrolysis and reforming processes. At typical operating conditions, the pyrolysis stage operates at temperatures between 400 and 500 °C, while the reforming stage operates at temperatures between 600 and 700 °C, as presented in Figure 1.

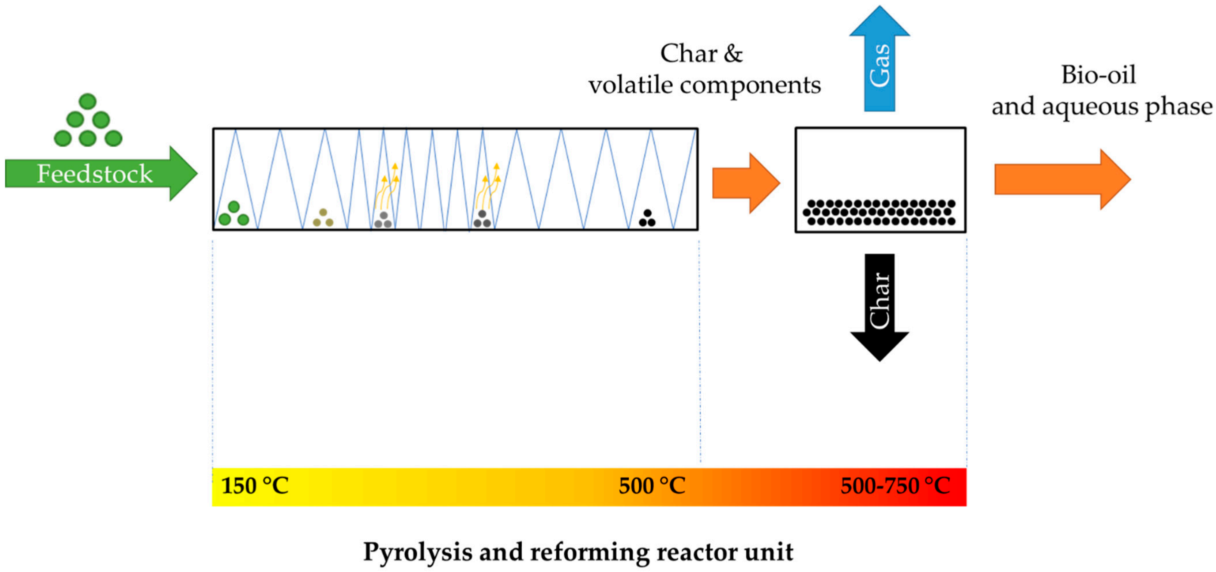

Figure 1. Thermo-catalytic reforming reactor with a partial char loop as a catalyst.

Gas, vapours and char are created during the pyrolysis stage. In the second step, the off-gases and vapours are upgraded by passing through a bed of char that is continuously removed from the reformer, which results in the production of syngas and oil of a higher quality. The efficiency, quality, and properties of the process's end products can be controlled by adjusting the temperatures used throughout the process. These factors define how the by-products of the TCR process are utilised going forward. Upgrading allows for easier separation of water from the bio-oil fraction. High-energy syngas with a high concentration of H_2 and high-quality char can be produced via TCR technology, which is an advantage over the combustion process. These materials have utility for energy storage or as building blocks for development into transportation fuels in liquid form. Many scientific reports [2,3] have investigated the TCR procedure using a wide range of substrates. As previously stated, waste feedstock for catalytic pyrolysis is a heterogeneous blend of various fractions made up of plastics, biomass, metals, glass, paper, textiles, soil, and food processing residues. It is necessary to standardise the charge in terms of physical properties and granulation for the TCR of biomass-based materials and the waste blend process for optimal functionality due to the charge materials' heterogeneous nature. In the first step of biomass wastes and MSW processing, separation of fractions such metals and glass, which is handled by solutions such as material recycling, is the most desirable action. Next, the carbonization process can employ the homogenised charge, which consists of different waste fractions. The efficiency of the TCR process, as well as the nature of the waste that is used, determine the yields of the obtained fractions. The obtained chars thus have varied amounts of the mineral fraction and the carbon fraction. The process is meant to improve the quality of the bio-oil obtained compared to that achieved by fast pyrolysis, while simultaneously increasing the yield of liquid and gaseous products. However, regardless of the feedstock, a solid fraction in the form of carbonate is always produced, and is frequently a valuable product that can be recycled. The average mass flow share of valuable fractions is depicted in a Sankey diagram in Figure 2.

According to the average values acquired from the literature data for 12 experiments [3,11,15–17], the average biochar yield is 27.01% m/m, the average liquid fraction is 28.88%, of which about 53% is bio-oil (organic fraction), and the remaining, 44.04% m/m, is post-process gas.

Regardless of the final use of both gas and liquid products, nearly one-third of the biomass material forms biochar that can be used as a soil additive to promote carbon sequestration.

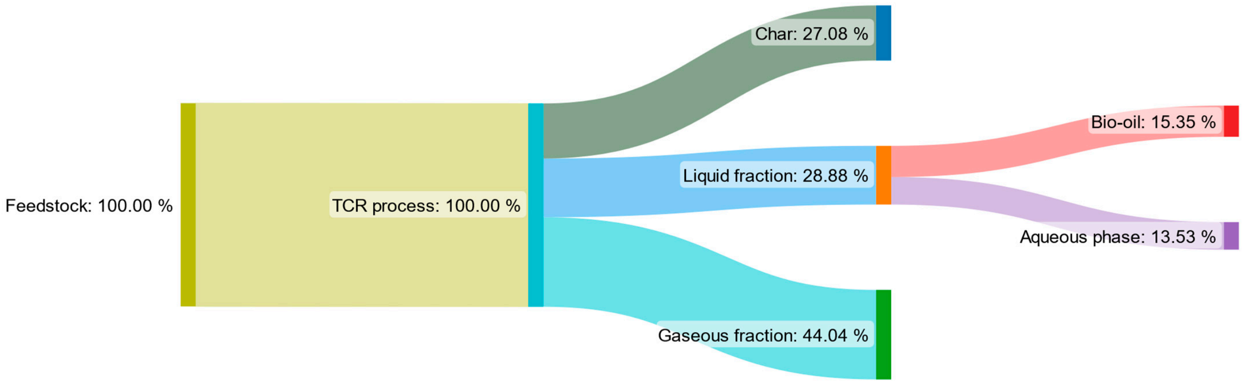

Figure 2. Sankey diagram for average biomass-based feedstock applied to the TCR process (based on literature data—see reference in Table 1).

2.2. Properties of Various Chars Obtained from TCR Technologies

To obtain a char that meets functional properties, biomass should be subjected to a thermal transformation with the implementation of solutions that allow for increased carbon content in the ultimate product. One of the most promising existing solutions is Thermo-Catalytic Reforming (TCR) technology which uses two-step pyrolysis mechanisms to obtain valuable products. TCR technology effectiveness was assessed based on the basic indicators used in the assessment of solid fuels. The main direction is to determine the proportion between the content of combustible and non-combustible substances, which is an important aspect that determines the further use of the obtained char. It also determines its further application. As previously indicated, char's high mineral content (ash) is favourable for agricultural purposes. On the other hand, demand for solid fuels for thermal processing requires mostly material that contains the highest possible proportion of combustible substances (high carbon content). The qualitative parameters of chars manufactured with the TCR technology are shown in Table 1. Research on TCR application and obtained products for various feedstock materials have been presented in different scientific reports [3,11,18–21]. In some reports it was indicated that Thermo-Catalytic Reforming (TCR) was developed and applied as a link between renewable fuels and waste management [22]. Such technology additionally allows upgrading the technological parameters of biofuel residue obtained from biomass [23].

The physicochemical properties of the raw material are fundamental to establish its suitability for further applications of the char produced. Their values have a direct impact on the efficiency and quality of each type of thermal process carried out and further interaction with surroundings. The most important parameters are the elemental composition of the combustible substance, which includes the content of elements such as carbon, hydrogen, nitrogen, sulphur, and oxygen. Carbon and hydrogen are the dominant elements. Their content in fuel mostly determines the caloric suitability measured by assessment of heat of combustion and calorific value determined on this basis [24].

The basic function of the TCR process is to increase functional properties determined in terms of further energy use as a result of the cycle of transformations. The presented data show that the chars produced by TCR technology from waste clean wipes, wood, and wheat husk have very valuable properties. In all these cases, the produced chars had a high content of elemental carbon (C > 70%) and a very high LHV value (>25 MJ/kg). In this aspect, these values are similar to some coals, which is the desired feature. However, unlike coal, chars from biomass fractions and waste have different origins of raw materials. The existence of by-products determines their further use and their destination. All this affects the utilisation of wastes as feedstock for thermal conversion, which is desirable in the context of the principles of sustainable development and ecology. In practice, the properties of the chars obtained depend on the initial parameters of the raw materials used in the process. The raw materials suitable for processing may vary as well as their composition. However, in practice, the better the quality of the initial raw material, the easier it is to obtain high-quality char.

Table 1. Properties of various chars from TCR technology.

Material	Proximate Analysis				Ultimate Analysis							Ref
	A	VM	FC	M	C	H	N	S	O	LHV	HHV	
					[%]					MJ/kg		
MSW Blend char	44.9	-	-	1.6	47.3	0.8	1.0	0.3	5.7	16.7	17.0	[3]
Waste clean wipes	4.1	-	-	-	83.9	1.66	0.49	0.06	1.9	30.42	30.79	[11]
Paper waste (pulper rejects)	26.1	-	-	2.6	66.7	1.69	0.45	0.12	4.94	24.79	25.16	[15]
Wheat husk	11.8	-	-	-	76.5	2.2	3.3	0.1	6.1	-	28.4	[18]
FMW	24.6	-	-	-	63.75	2.05	4.36	0.45	4.79	23.47	23.64	[25]
DIS Dre-ink sludge (char)	82.1	-	-	-	16.85	0.62	0.1	0.1	0.24	6.54	6.67	[16]
Wood	4.2	-	-	-	90.18	1.57	0.32	0.1	3.62	32.86	33.2	[16]
Digestate pellets	29.1	-	-	0.7	65.0	1.2	1.5	0.3	2.2	23.5	23.9	[17]
RSB biochar	32.46	-	-	-	63.63	1.31	0.55	0.21	-	-	22.1	[26]
RSB at 500 °C	30.5	-	-	-	67.90	1.60	0.52	0.51	-	-	24.0	[26]
RSB at 600 °C	32.57	-	-	-	65.84	0.87	0.48	0.04	-	-	23.1	[26]
RSB at 700 °C	32.15	-	-	-	64.47	0.70	0.54	0.03	-	-	21.2	[26]
Sewage sludge	74.4	-	-		22.2	0.9	2.0	1.0	0.0	18.2	-	[12]
Digestate	32.0	-	-		64.0	1.0	1.4	0.5	0.7	23.0	-	[12]
Brewer spent grain	17.5	-	-	-	72.6	0.1	4.6	0.4	4.9	26.0	-	[12]
Wood	3.1	-	-	-	89.8	2.2	0.3	0.1	4.5	34.4	-	[12]
Straw biochar at 500 °C	14.83	23.69	57.85	3.63	65.50	3.51	11.03	1.29	0.21	-	25.07	[27]
Straw biochar at 700 °C	16.93	6.99	74.87	1.21	69.02	1.92	9.51	1.18	0.23	-	25.61	[27]
Straw biomass	4.78	70.50	18.19	6.53	43.80	5.48	38.69	0.62	0.10	-	17.52	[27]

A—ash, VM—volatile matter, FC—fixed carbon, M—moisture, C—carbon content, H—hydrogen content, N—nitrogen content, S—sulphur content, O—oxygen content, LHV—lower heating value, HHV—high heating value.

Char's heavy metal content is the deciding factor if carbon dioxide sequestration in agricultural and forestry soils is one of the char management options being considered.

Several countries' statutory legislation and international legal frameworks precisely define the maximum concentrations of heavy metals in the agrosystem. Limitations apply to all agricultural product distribution channels to reduce the potential harm by phytotoxicity and to human health. Although the implementation of regulatory controls has contributed to a modest reduction in industrial emissions, the overall rate of intake of most metals in soil and aquatic systems has not been reduced but has grown. Some heavy metal concentrations in soils are extremely high in urban and developed industrial locations [28].

The EU Regulation on environmental protection and land (86/278/EEC) requires Member States [29] to adhere to specific values for heavy metals in soil, as shown in Table 2.

Table 2. Limit values of heavy metals [28].

Parameters	Limit Values (mg/kg)
Cadmium	1–3
Copper	50–140
Nickel	30–75
Lead	50–300
Zink	150–300
Mercury	1–1.5

A summary of heavy metals in produced chars from various feedstocks is compiled in Table 3.

Table 3. Heavy metals in chars obtained from different materials.

Material	Cd (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Hg (mg/kg)	Ref
MSW Blend char	2.59	354.84	45.17	161.3	-	0.13	[3]
Digestate	<0.2	68	3	<2	300	<0.07	[12]
Demolition wood char 350	2.2	51.5	8.7	409.7	785.1	-	[24]
Demolition wood char 550	0.9	31.7	17.9	561.6	1047.9	-	[24]
Straw pellets char 550	0.2	16.0	91.3	11.3	43.4		[24]
Biochar Beech wood	0.2	10.0	6.0	10.0	5.0	0.1	[24]
Pepper residues biochar 670	0.2	29.0	7.0	63.0	25.0	0.1	[24]
Pepper residues biochar 600	0.2	26.5	12.8	12.3	68.0	-	[24]
Pepper residues biochar 700	0.2	28.0	8.0	8.0	26.0	-	[24]
Charcoal briquette	0.2	21.4	3.1	12.1	0.6	-	[24]
Oak wood biochar 400	0.3	23.9	14.6	19.0	83.0	-	[24]
Straw pellets char 350	0.3	11.4	6.8	12.0	33.1	-	[24]
Willow char 550	0.3	13.7	4.0	1.3	261.7	-	[24]
Willow char 350	4.8	9.2	27.4	4.9	151.0	-	[24]

3. Biochar's Application in Mitigating the Impacts of Environmental Degradation

3.1. Utilisation of Biochar in the Remediation of Degraded Post-Industrial Areas

It is becoming increasingly common practice to employ carbonates for functions other than from thermal applications. The main limitation of using biochar for thermal processes is typically the presence of ballast content, which consists of ash and moisture. While it is possible to reduce the moisture content by drying the biochar, ash is a solid element that is difficult to minimise. Because of this, additional options are needed that can make use of biochar, as in agricultural settings, provided that it satisfies the environmental standards discussed in the prior section. The fact that biochar is a nutrient for microorganisms is unquestionably an advantage for incorporating biochar into the soil. This advantage cannot be overstated. The development of microorganisms is aided by increased biochar content, which is an example of where the addition of biochar can be beneficial [16]. Such benefits can be seen in fermentation processes.

In addition, the presence of biochar causes beneficial changes by improving soil properties, such as limiting the loss of soil nutrients, thereby extending their fertilising properties, and improving the conditions for stimulating plant growth [30]. Additionally, elemental carbon might be a source of food for microorganisms under favourable conditions. Biochar's presence also causes beneficial changes by improving the conditions in which plants are stimulated.

When specific biomass types are used to obtain certain kinds of biochar, either alkaline or acidic material is produced as a by-product. In this way, the proportion of biochar in the soil could be also responsible for a change in soil pH, and the magnitude of this shift is mostly determined by the proportion of biochar used as well as the type of biochar [31]. In this scenario, the utilisation of char is advantageous because, in addition to enhancing the adaptability of the soil, it prevents soil erosion and eutrophication (the excessive production of biogenic chemicals) [32], It is also capable of improving the soil's potential for agricultural usage. The migration of organic compounds in the soil solution is primarily dependent on its structure and, more than anything else, on the presence of three phases: solid being the soil solution, liquid water in the soil, and air present in the soil pores, occupying spaces whose volume depends on the degree of compaction [33]. The soil solution has solid, liquid, and air components. Because of these properties, on the one hand, a soil buffer is created, but on the other hand, the risk of pollutant migration in the soil solution is reduced. Despite reported results on limitation to the migration of pollutants, it is difficult for biochar to properly homogenise with the soil solution.

This lays the groundwork for the utilisation of products that should not harm the quality of the soil. In addition to qualitative criteria, the enrichment of the soil with a particular biochar should be considered. Due to the high concentration of elemental nitrogen, biochar also has the potential to be a source of total nitrogen, especially char from strow (Table 1). This component, along with carbon, is considered to be a macroelement of the soil [34,35].

The waste origin of biomass material (sewage sludge or the biomass fraction of municipal waste) results in the chemical composition of the obtained biochar (being a by-product of waste processing by the TCR method or another thermal conversion method) that may exceed permissible limits in terms of the concentration of heavy metals, affecting the possibililty of its use as an additive to agricultural soils.

This relates to its viability as a helpful addition to badly degraded and post-industrial soils, of which there are many in Europe and around the world. These kinds of soils are characterised by high levels of harmful contaminants such as heavy metals, pesticides, hydrocarbons, and so on. Basic cations are found in the biomass that is used in the production of biochar. When biochar is worked into the soil, the cations that it contains are transmitted into the soil. By increasing the surface area of the soil, this improves the cation exchange capacity of the soil allowing it to absorb more cations. Additionally, the high concentrations of calcium, potassium, nitrogen, and phosphorus that are found in biochar allow it to be used as a source of nutrients for the microbial population in the soil.

In addition, the presence of organic fractions in biochar enables the formation of stable organic complexes. These complexes promote the immobilisation of heavy metals that are present in soils in post-industrial and degraded areas, which in turn lowers the concentration of these metals in the soil solution. It is also important to note that an increase in pH, which is proportional to the increase in biochar, leads to an increase in the adsorption of heavy metals and their immobilisation [36]. The lower solubility of the pollutants that are present in the highly degraded soil is mostly attributable to the increased adsorption that takes place on the surface of biochar, as well as the creation of insoluble forms. One of the reasons for this could be the binding of lead to the Fe-Mn oxides that are present in the carbonates, with the carbonates in question constituting the ash components. This is most likely due to the chemical affinity that lead has with iron and manganese oxides [37,38].

In the literature are several observations that indicate biochar's ability to immobilise heavy metals. Despite this, the precise mechanism responsible for this effect has not yet been fully elucidated. The primary reason for this is that biochar generated under different temperature settings, process conditions, and from a variety of biomass components, including waste materials, has a very different characteristics. It is now thought that the action of biochar in soil is connected to [37]:

- chemical interaction between ions on the surface of the biochar;
- creation of complexes with active functional groups;
- physical adsorption on the surface of the biochar;
- the precipitation of phosphate ions on the surface of the biochar;
- the precipitation of insoluble compounds generated by an increase in pH in the contaminated soil, particularly when the soil is acidic.

Each mechanism has a distinct response to one or more of the various pollutants in the soil. The characteristics of the contaminant in the soil determine whether or not it is activated. For example, Cd in most cases is predominantly absorbed on the surface of the biochar, whereas Cu is chemically linked to the biochar surface. But Pb was reported to precipitate as a result of complexing with biochar functional groups [37]. When biochar is used as a soil supplement, the percentage of the soil composed of pores grows. The growth of bacteria takes place in the pore fraction, which increases the time that moisture, air, and nutrients remain there. This, in turn, promotes the growth, survival, and activity of microbes, which in turn leads to the growth of plants [39].

Biochar created at high temperatures is more resistant to degradation and remains in the soil for a longer period compared to biochar that is formed at low temperatures.

It is possible to use mixtures of waste of biomass origin, including some fractions of MSW containing more than 35% moisture. To obtain the right raw material before further processing, it is necessary to study physical properties (moisture content, granulation) through pre-treatment step processes, i.e., drying, sorting, shredding, and pelletizing. Before mechanical treatment, it is recommended that the used waste be separated into fractions that are potentially difficult for further processing and contain a high content of inorganic substances. Preliminary compaction of various types of waste fractions and homogenization in the form of pellets with a specific geometry helps to significantly reduce the moisture content of the initial material (max 10% m/m) [40]. The main challenge in terms of the use of waste thermally treated by this type of process (TCR) as a component of the soil solution is the presence of heavy metals. To reduce their negative impact, it is necessary to use additives that enable their absorption. According to reports [41], such adsorbents can be compounds such as humic acids naturally present in soils, the effectiveness of which is described by the mechanism of the adsorption process using Langmuir and Freundlich models. The effectiveness of the adsorption mechanism depends on the difference between the molecules of the adsorbent surface and the energy of the particles inside it. A model of the surface layer at the phase boundary is presented in Figure 3.

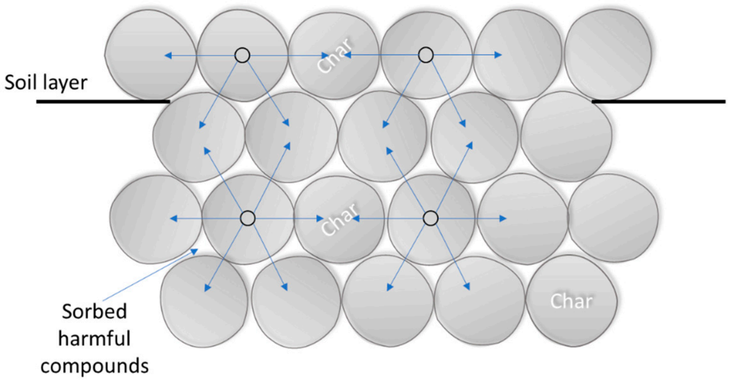

Figure 3. Surface absorption layer model.

The adsorption mechanism is important because susceptibility to accumulated harmful compounds in soils is mainly dependent on the density and permeability of the deposit. On one hand, the advantage of adsorption allows the uptake of beneficial plant compounds such as macro and microelements that can stimulate plant growth. On the other hand, compounds in the form of heavy metals migrate and adsorb in a similar way. Therefore, to assess the suitability of char as a soil additive, it is important to analyse metal compounds or the possibility of using components that allow their accumulation in compounds.

3.2. Biochar Application in CO_2 Soil Sequestration

Concern over climate change is driving efforts to reduce CO_2 emissions. The carbon cycle, which directly affects climate change, is directly influenced by the role that soil performs. Carbon sequestration is a strategy that shows a lot of promise for lowering CO_2 emissions and depositing carbon in the soil [42]. One of the significant aspects of TCR-derived manufacturing is that such manufacturing should be economically justified with beneficial aspects. Waste management is a significant aspect of social activity, and TCR technology can be treated as a material recycling technology where novel materials can be obtained from discarded waste. Due to aromatic structures in biochar, it is only slightly resistant to breakdown by microbes; hence, biochar demonstrates positive results in terms of carbon sequestration in soil. Both liable and recalcitrant forms of carbon can be found in biochar, which are the two categories that can be used to describe its carbon content. During the application of biochar, microorganisms have an easier time using soluble carbon, which results in greater carbon mineralization at the beginning of the process. As a result, the use of biochar enhances the carbon mineralization process. On the other hand, recalcitrant carbon stays in the soil for a significantly longer period [43]. Because of this, the amount of carbon that is fixed due to the application of biochar is greater than the amount of carbon that is released due to liable carbon mineralization. It is not yet clear how much impact biochar properties have on the amount of carbon that can be sequestered.

Such physical and chemical qualities make biochar a carbon source that is far more resistant to biological degradation processes than the pure biomass from which it is generated. However, partially due to the price and scarcity of pyrolysis equipment, biomass carbonate is not yet commonly employed as a way to absorb and sequestrate CO_2.

Nonetheless, it is expected that over the following decade, a greater number of biomass pyrolysis facilities will be constructed. Biochar can store between 2.1 and 4.8 tonnes of carbon dioxide per one tonne of biochar, depending on the environment and the sort of thermal conversion methods used for biomass and biomass-derived waste [44]. This is because different thermal conversion technologies, such as TCR technology, produce biochar with different degrees of carbonization, and because organic matter reduces the total mass of biochar to a lesser extent than elemental carbon. Considering the temperature range prevailing in the TCR process (500 °C pyrolysis with 750 °C reforming), the biochar obtained in this process is characterised by a high degree of carbonisation, a fairly low oxygen content, and other components, which significantly translate into an increase in resistance to degradation. Due to the greater stability of biochar created by thermal conversion processes compared to organic matter deposited in soil, the rate at which CO_2 is re-emitted into the atmosphere is greatly reduced over time [45].

Availability and competitiveness with other markets for its use, such as fuel for commercial power generation and residential heating, may be the factor limiting the current low acceptance of biochar. Some estimates put the annual potential for carbon sequestration in the world's soils at between two and five billion metric tonnes of CO_2 ($GtCO_2$) by 2050, with a total potential of 104 to 130 $GtCO_2$ by the end of the century. The literature has more optimistic estimates of sequestration rates, with total estimates ranging from 78 $GtCO_2$ to 477 $GtCO_2$ [46,47]. To accomplish this it is necessary to make use of all sources of biomass materials, including agricultural waste, the biodegradable component of household trash, sewage sludge, and many more. Biochar made from waste biomass may occasionally have levels of Cd, Cu, Ni, Zn, Pb, and Hg that are undesirable for use in agriculture. However, this would not prevent them from being used in post-industrial and degraded environments, where they might not only aid in carbon sequestration but also enhance land quality by immobilising heavy metals and toxins in contaminated soil.

This would make possible the revitalisation of degraded land by allowing for planting trees, hastening the process, and increasing the amount of CO_2 removed from the air. Therefore, the potential for such applications is substantial.

It is challenging to estimate the overall area of degraded and brownfield land in Europe despite reliable information from European authorities. This is because the definition of these categories varies among countries and regions. Degraded land covers almost 4.5 million hectares across the European Union, according to 2019 research by the European Environment Agency [48]. Degradation is defined in this report as the decline in soil, water, or ecosystem quality brought about by either human actions or natural occurrences. Brownfield areas, on the other hand, are estimated to cover about 2.5 million hectares across Europe, according to the European Commission's 2020 report on sustainable transformation and economic recovery, and are areas formerly utilised for industrial purposes but now left unoccupied, usually because of pollution and safety concerns. These numbers may be low since they don't account for post-industrial and decaying areas in nations outside the EU and in some parts of Europe where reliable statistics are scarce.

In addition, while these projections are accurate as of 2021, the actual outcome may differ depending on the success of efforts to revitalise and restore the ecosystems in these regions.

According to the Food and Agriculture Organization of the United Nations (FAO) and one of the most thorough sources of information on the topic (Global Land Outlook 2017), roughly 20% of the world's land area (roughly 2 billion hectares) is degraded, and more than half of the land area is at risk of degradation [49]. Unfortunately, there is also a deficiency of reliable international statistics on brownfield sites. The UN Environment's 2019 report is one of the few available resources on the topic, and it estimates that there are about 14 million hectares of brownfields in need of rehabilitation around the world. It should be highlighted, however, that this estimate is likely to be low because it does not account for deteriorated and brownfield sites in regions where reliable data are lacking.

With all of this in mind, and considering that biochar can be used as an additive in proportions ranging from 30 to 60 t per hectare, its potential for use in CO_2 sequestration and clean-up is considerable.

4. Potential of the Use of Different Carbonates Produced by TCR Technology—Future Perspective and Challenges

As illustrated in Figure 4, biochar accounts for approximately one-third of the total mass of feedstock directed to the TCR process. This represents the average value of 12 studies, and different proportions of different solid fractions can be predicted depending on the kind of feedstock, biomass, biomass-derived trash, or selected MSW components. Furthermore, when considering biochar as a material for soil carbon sequestration, the elemental carbon content of the produced biochar is the most essential metric. Three versions (based on the available literature) were chosen to show the opportunities of CO_2 sequestration by biochar formed during the TCR process of diverse materials of both biomass and waste origin, an average and two extremes. They correspond to the three materials utilised in the TCR process, resulting in different numbers of chars with different carbon concentrations. Figure 4 shows the findings of this investigation in the form of a Sankey diagram for the various feed materials. At a maximum temperature of 700 °C, the process conditions were comparable.

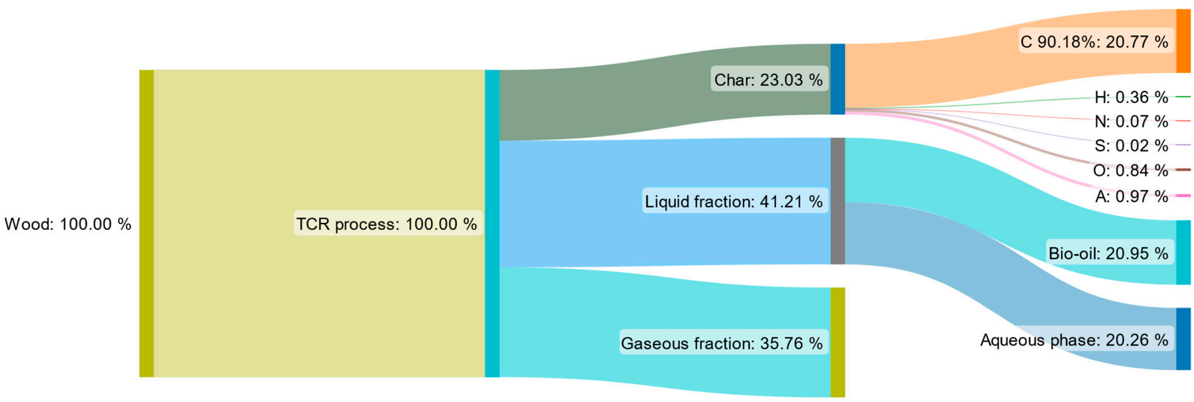

Figure 4. Sankey diagram for pine wood as a feedstock in the TCR process (based on data from [16]).

As can be observed, when pine wood is used in the TCR process, biochar has high content of elemental carbon [16]. In this example, 23% of the biochar yield is comprised of more than 90% of elemental carbon. The application of such biochar for carbon dioxide sequestration would allow for the removal and storage of more than 3.3 tonnes of CO_2/ton of biochar in the soil.

The situation is considerably different in the case of cleaning wipes (Figure 5). This waste contains roughly 30% polypropylene and 70% wood pulp fibres, which contribute to the large yield of gaseous products and the poor yield of liquid products, and particularly low biochar yield of only 8% [11]. However, the biochar obtained has a comparatively significant elemental carbon content of over 84%. The application of such biochar for carbon dioxide sequestration would allow for the removal and storage of more than 3.1 tons of CO_2/ton of biochar in the soil.

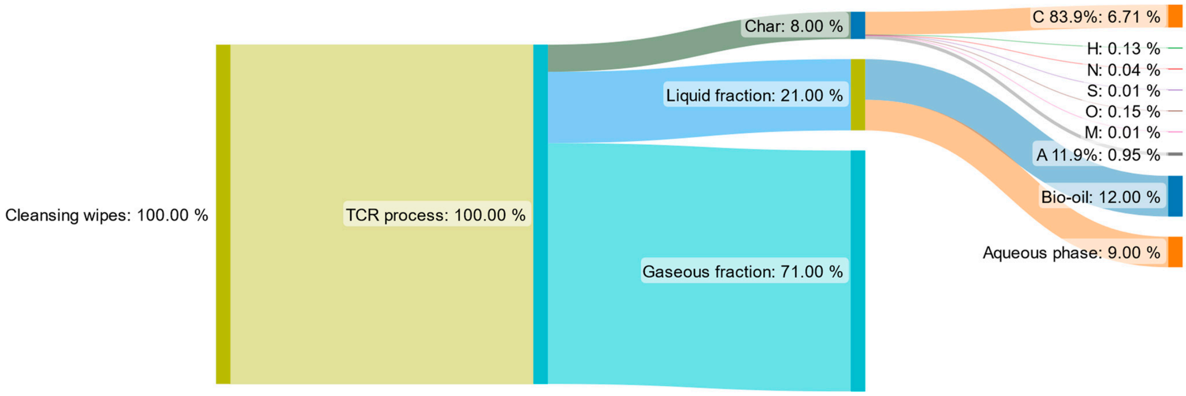

Figure 5. Sankey diagram for cleaning wipes as a feedstock in the TCR process (based on data from [11]).

Biodegradable Municipal Solid Waste fractions obtained during the MSW [3] separation process could constitute another waste. Fractions could comprise up to 50% of biomass-derived material with polymeric waste and mineral ballast in them. There is slight danger in the case of polymeric waste in that at the TCR temperature conditions, all polymeric materials decompose into volatile components, leaving only a small amount of elemental carbon, which may be the result of secondary reactions, or the presence of carbon black added to the polymeric material during the processing stage. The TCR process of the MSW material provides 31% char, which contains only 47.3% elemental carbon and high 44.9% inorganic ballast ash in the scenario under discussion (Figure 6). The use of such char for carbon dioxide sequestration would allow more than 1.7 tonnes of CO_2/ton of carbon black created in the soil to be removed and stored.

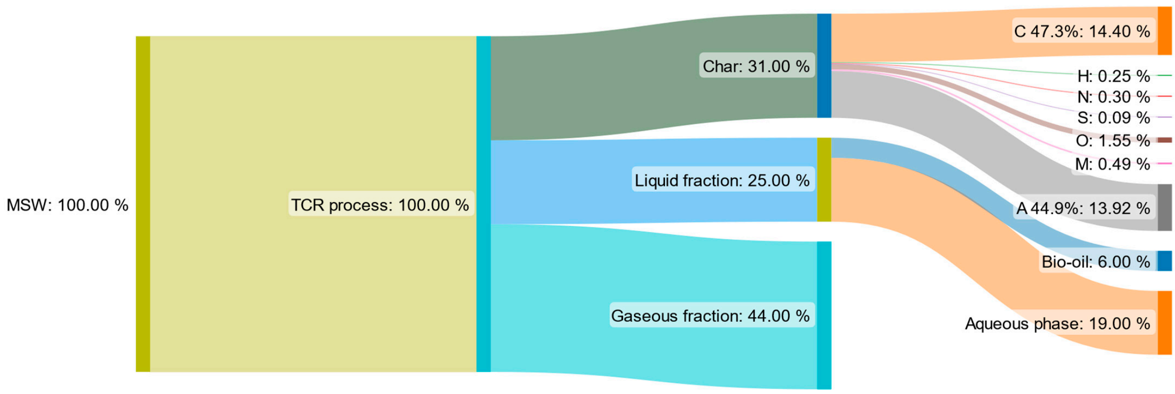

Figure 6. Sankey diagram for MSW as a feedstock in the TCR process (based on data from [3]).

As can be shown, biochar/char generated through thermal conversion processes, notably the TCR process, has the potential to be a major component for carbon sequestration in soil, particularly for degraded and post-industrial sites. Using the previously mentioned numbers for Europe's degraded and post-industrial land of 4.5 million hectares, and assuming that up to 20 tonnes of biochar/char can be used per hectare of such soils, more than 24 million tonnes of CO_2 could be sequestered with only 10% coverage of the area in question.

5. Conclusions

Our analysis shows that apart from the technological usability of biochar in energy systems there are applications for char. One is biochar application to soil. Applications of biochar obtained from waste and other alternative by-products improve waste management and the production of high-quality biochar. Biochar use depends on the quality of raw materials and technological opportunities. Different fractions have different uses. Biochar soil application may address ecological issues such as air and soil treatment, as well as improving soil's agricultural properties. Proper processing of raw material to obtain biochar may increase the efficiency of sequestration of CO_2. However, in such cases, the presence of heavy metals originating from the raw materials is important. Biochar constitutes 30% as a solid fraction obtained from the TCR process, which also determines its application. One important use is for char application in the reclamation of polluted and degraded soils, and famine relief through improved agriculture. The potential for biochar applications is determined by the initial quality of the soil, further processing and agricultural plans. Apart from improving the agricultural properties of soil, biochar could applied for accelerating mechanisms of self-renewal of soils, which usually takes a long time. Reduction of CO_2 emissions by soil sequestration via biochar application has huge potential in mitigating climate changes. In future decades, processing biochar will have a significant role in the prevention of climate and environmental deterioration. The many applications of manufactured biochar represent a promising direction for environmental protection, natural resource rationalization and sustainable development.

Author Contributions: Conceptualization, M.S., G.G. and M.O.; methodology, M.S.; formal analysis, M.S.; resources, M.S., G.G., M.O., A.M., A.H., F.D.G. and E.M.; writing—original draft preparation, M.S., G.G. and M.R.; writing—review and editing, M.S., G.G., M.R., M.O., A.M., A.H., F.D.G. and E.M.; visualization, M.S. and G.G.; supervision, M.S. and G.G.; funding acquisition, M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was performed under the project sponsored by the Polish National Agency for Academic Exchange under the Bekker Program, Project no. NAWA BPN/BEK/2021/1/00103.

Data Availability Statement: Not applicable.

Acknowledgments: This research was supported by the Faculty of Energy and Environmental Engineering, Silesian University of Technology (statutory research).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Keppert, M.; Tydlitát, V.; Volfová, P.; Šyc, M.; Černý, R. Characterization of Solid Waste Materials from Municipal Solid Waste Incineration Facility. In Proceedings of the 2nd International Conference on Sustainable Construction Materials and Technologies, Ancona, Italy, 28–30 June 2010; pp. 737–743.
2. Anthraper, D.; McLaren, J.; Baroutian, S.; Munir, M.T.; Young, B.R. Hydrothermal Deconstruction of Municipal Solid Waste for Solid Reduction and Value Production. *J. Clean. Prod.* **2018**, *201*, 812–819. [CrossRef]
3. Ouadi, M.; Jaeger, N.; Greenhalf, C.; Santos, J.; Conti, R.; Hornung, A. Thermo-Catalytic Reforming of Municipal Solid Waste. *Waste Manag.* **2017**, *68*, 198–206. [CrossRef] [PubMed]
4. Sajdak, M. Characteristics of Chars from Biomass and Waste Co-Pyrolysis. In Proceedings of the ASME 2018 Power Conference collocated with the ASME 2018 12th International Conference on Energy Sustainability and the ASME 2018 Nuclear Forum, Lake Buena Vista, FL, USA, 24–28 June 2018; Volume 2. [CrossRef]
5. Sajdak, M. Porosity and Pore Size Distribution of Biochar from Straw Biomass—Data for DOE. *Mendeley Data* **2022**, *1*. [CrossRef]
6. Sajdak, M. Application of Chemometrics to Identifying Solid Fuels and Their Origin. *Cent. Eur. J. Chem.* **2013**, *11*, 151–159. [CrossRef]
7. Sajdak, M. Impact of Plastic Blends on the Product Yield from Co-Pyrolysis of Lignin-Rich Materials. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 415–425. [CrossRef]
8. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic Biomass Pyrolysis: A Review of Product Properties and Effects of Pyrolysis Parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
9. Fahmy, T.Y.A.; Fahmy, Y.; Mobarak, F.; El-Sakhawy, M.; Abou-Zeid, R.E. Biomass Pyrolysis: Past, Present, and Future. *Environ. Dev. Sustain.* **2020**, *22*, 17–32. [CrossRef]
10. Muhammad, C.; Onwudili, J.A.; Williams, P.T. Thermal Degradation of Real-World Waste Plastics and Simulated Mixed Plastics in a Two-Stage Pyrolysis-Catalysis Reactor for Fuel Production. *Energy Fuels* **2015**, *29*, 2601–2609. [CrossRef]
11. Ouadi, M.; Greenhalf, C.; Jaeger, N.; Speranza, L.G.; Hornung, A. Thermo-Catalytic Reforming of Co-Form®Rejects (Waste Cleansing Wipes). *J. Anal. Appl. Pyrolysis* **2018**, *132*, 33–39. [CrossRef]

12. Schmitt, N.; Apfelbacher, A.; Jäger, N.; Daschner, R.; Stenzel, F.; Hornung, A. Thermo-Chemical Conversion of Biomass and Upgrading to Biofuel: The Thermo-Catalytic Reforming Process—A Review. *Biofuels Bioprod. Biorefin.* **2019**, *13*, 822–837. [CrossRef]
13. Gunarathne, V.; Ashiq, A.; Ramanayaka, S.; Wijekoon, P.; Vithanage, M. Biochar from Municipal Solid Waste for Resource Recovery and Pollution Remediation. *Environ. Chem. Lett.* **2019**, *17*, 1225–1235. [CrossRef]
14. Huang, Y.; Anderson, M.; McIlveen-Wright, D.; Lyons, G.A.; McRoberts, W.C.; Wang, Y.D.; Roskilly, A.P.; Hewitt, N.J. Biochar and Renewable Energy Generation from Poultry Litter Waste: A Technical and Economic Analysis Based on Computational Simulations. *Appl. Energy* **2015**, *160*, 656–663. [CrossRef]
15. Ouadi, M.; Greenhalf, C.; Jaeger, N.; Speranza, L.G.; Hornung, A. Thermo-Catalytic Reforming of Pulper Rejects from a Secondary Fibre Mill. *Renew. Energy Focus* **2018**, *26*, 39–45. [CrossRef]
16. Fivga, A.; Jahangiri, H.; Bashir, M.A.; Majewski, A.J.; Hornung, A.; Ouadi, M. Demonstration of Catalytic Properties of De-Inking Sludge Char as a Carbon Based Sacrificial Catalyst. *J. Anal. Appl. Pyrolysis* **2020**, *146*, 104773. [CrossRef]
17. Neumann, J.; Binder, S.; Apfelbacher, A.; Gasson, J.R.; Ramírez García, P.; Hornung, A. Production and Characterization of a New Quality Pyrolysis Oil, Char and Syngas from Digestate—Introducing the Thermo-Catalytic Reforming Process. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 137–142. [CrossRef]
18. Santos, J.; Ouadi, M.; Jahangiri, H.; Hornung, A. Integrated Intermediate Catalytic Pyrolysis of Wheat Husk. *Food Bioprod. Process.* **2019**, *114*, 23–30. [CrossRef]
19. Król, D.; Gałko, G. Stoichometric Equilibrium Model of Sewage Sludge Gasification with Athmospheric Air. *Przem. Chem.* **2018**, *97*, 1698–1702. [CrossRef]
20. Wang, S.; Faravelli, T.; Yang, H. Special Issue of Thermo-Chemical Conversion of Biomass. *Appl. Energy Combust. Sci.* **2022**, *11*, 100075. [CrossRef]
21. Gill, M.; Kurian, V.; Kumar, A.; Stenzel, F.; Hornung, A.; Gupta, R. Thermo-Catalytic Reforming of Alberta-Based Biomass Feedstock to Produce Biofuels. *Biomass Bioenergy* **2021**, *152*, 106203. [CrossRef]
22. Hornung, A.; Jahangiri, H.; Ouadi, M.; Kick, C.; Deinert, L.; Meyer, B.; Grunwald, J.; Daschner, R.; Apfelbacher, A.; Meiller, M.; et al. Thermo-Catalytic Reforming (TCR)–An Important Link between Waste Management and Renewable Fuels as Part of the Energy Transition. *Appl. Energy Combust. Sci.* **2022**, *12*, 100088. [CrossRef]
23. Neumann, J.; Jäger, N.; Apfelbacher, A.; Daschner, R.; Binder, S.; Hornung, A. Upgraded Biofuel from Residue Biomass by Thermo-Catalytic Reforming and Hydrodeoxygenation. *Biomass Bioenergy* **2016**, *89*, 91–97. [CrossRef]
24. Phyllis2. Available online: https://phyllis.nl/ (accessed on 5 December 2019).
25. Ouadi, M.; Bashir, M.A.; Speranza, L.G.; Jahangiri, H.; Hornung, A. Food and Market Waste-A Pathway to Sustainable Fuels and Waste Valorization. *Energy Fuels* **2019**, *33*, 9843–9850. [CrossRef] [PubMed]
26. Ahmad, E.; Jäger, N.; Apfelbacher, A.; Daschner, R.; Hornung, A.; Pant, K.K. Integrated Thermo-Catalytic Reforming of Residual Sugarcane Bagasse in a Laboratory Scale Reactor. *Fuel Process. Technol.* **2018**, *171*, 277–286. [CrossRef]
27. Muzyka, R.; Misztal, E.; Hrabak, J.; Banks, S.W.; Sajdak, M. Various Biomass Pyrolysis Conditions Influence the Porosity and Pore Size Distribution of Biochar. *Energy* **2023**, *263*, 126128. [CrossRef]
28. Guinée, J.B.; van den Bergh, J.C.J.M.; Boelens, J.; Fraanje, P.J.; Huppes, G.; Kandelaars, P.P.A.A.H.; Lexmond, T.M.; Moolenaar, S.W.; Olsthoorn, A.A.; Udo De Haes, H.A.; et al. Evaluation of Risks of Metal Flows and Accumulation in Economy and Environment. *Ecol. Econ.* **1999**, *30*, 47–65. [CrossRef]
29. *EUR-Lex-31986L0278-EN*. Council Directive 86/278/EEC of 12 June 1986 on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge Is Used in Agriculture. Official Journal L 181, 04/07/1986 P. 0006-0012; Finnish Ppecial Edition: Chapter 15 Volume 7 P. 0127; Swedish special edition: Chapter 15 Volume 7 P. 0127. Available online: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31986L0278:EN:HTML (accessed on 19 February 2023).
30. Wang, C.; Luo, D.; Zhang, X.; Huang, R.; Cao, Y.; Liu, G.; Zhang, Y.; Wang, H. Biochar-Based Slow-Release of Fertilizers for Sustainable Agriculture: A Mini Review. *Environ. Sci. Ecotechnol.* **2022**, *10*, 100167. [CrossRef]
31. Wijitkosum, S. Biochar Derived from Agricultural Wastes and Wood Residues for Sustainable Agricultural and Environmental Applications. *Int. Soil Water Conserv. Res.* **2022**, *10*, 335–341. [CrossRef]
32. Sánchez-Reinoso, A.D.; Ávila-Pedraza, E.Á.; Restrepo-Díaz, H. Use of Biochar in Agriculture. *Acta Biol. Colomb.* **2020**, *25*, 327–338. [CrossRef]
33. Gałko, G. The influence of infiltration of leachate from landfills on the changes of chemical parameters of the soil. *J. Ecol. Eng.* **2015**, *16*, 198–205. [CrossRef]
34. Tabak, M.; Lisowska, A.; Filipek-Mazur, B.; Antonkiewicz, J. The Effect of Amending Soil with Waste Elemental Sulfur on the Availability of Selected Macroelements and Heavy Metals. *Processes* **2020**, *8*, 1245. [CrossRef]
35. Yu, Y.; Yang, B.; Petropoulos, E.; Duan, J.; Yang, L.; Xue, L. The Potential of Biochar as N Carrier to Recover N from Wastewater for Reuse in Planting Soil: Adsorption Capacity and Bioavailability Analysis. *Separations* **2022**, *9*, 337. [CrossRef]
36. Khan, S.; Naushad, M.; Lima, E.C.; Zhang, S.; Shaheen, S.M.; Rinklebe, J. Global Soil Pollution by Toxic Elements: Current Status and Future Perspectives on the Risk Assessment and Remediation Strategies—A Review. *J. Hazard. Mater.* **2021**, *417*, 126039. [CrossRef]
37. Liang, M.; Lu, L.; He, H.; Li, J.; Zhu, Z.; Zhu, Y. Applications of Biochar and Modified Biochar in Heavy Metal Contaminated Soil: A Descriptive Review. *Sustainability* **2021**, *13*, 14041. [CrossRef]

38. Amoah-Antwi, C.; Kwiatkowska-Malina, J.; Thornton, S.F.; Fenton, O.; Malina, G.; Szara, E. Restoration of Soil Quality Using Biochar and Brown Coal Waste: A Review. *Sci. Total Environ.* **2020**, *722*, 137852. [CrossRef]
39. Yaashikaa, P.R.; Kumar, P.S.; Varjani, S.; Saravanan, A. A Critical Review on the Biochar Production Techniques, Characterization, Stability and Applications for Circular Bioeconomy. *Biotechnol. Rep.* **2020**, *28*, e00570. [CrossRef]
40. Stringfellow, A.; Powrie, W.; Tejada, W.C.; Whatmore, S.; Gilbert, A.; Manser, R.; Maslen, R. Mechanical Heat Treatment of Municipal Solid Waste. *Proc. Inst. Civ. Eng. Waste Resour. Manag.* **2015**, *164*, 179–190. [CrossRef]
41. Mulyani, O.; Joy, B.; Kurnia, D. The Various Forms of Cow Manure Waste as Adsorbents of Heavy Metals. *Appl. Sci.* **2022**, *12*, 5763. [CrossRef]
42. Méndez, A.; Gómez, A.; Paz-Ferreiro, J.; Gascó, G. Effects of Sewage Sludge Biochar on Plant Metal Availability after Application to a Mediterranean Soil. *Chemosphere* **2012**, *89*, 1354–1359. [CrossRef]
43. Puga, A.P.; Abreu, C.A.; Melo, L.C.A.; Beesley, L. Biochar Application to a Contaminated Soil Reduces the Availability and Plant Uptake of Zinc, Lead and Cadmium. *J. Environ. Manag.* **2015**, *159*, 86–93. [CrossRef]
44. van Zwieten, L.; Kimber, S.; Downie, A.; Morris, S.; Petty, S.; Rust, J.; Chan, K.Y. A Glasshouse Study on the Interaction of Low Mineral Ash Biochar with Nitrogen in a Sandy Soil. *Soil Res.* **2010**, *48*, 569–576. [CrossRef]
45. Chan, K.Y.; van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S. Agronomic Values of Greenwaste Biochar as a Soil Amendment. *Soil Res.* **2007**, *45*, 629–634. [CrossRef]
46. Fuss, S.; Lamb, W.F.; Callaghan, M.W.; Hilaire, J.; Creutzig, F.; Amann, T.; Beringer, T.; de Oliveira Garcia, W.; Hartmann, J.; Khanna, T.; et al. Negative Emissions—Part 2: Costs, Potentials and Side Effects. *Environ. Res. Lett.* **2018**, *13*, 63002. [CrossRef]
47. Smith, P. Soil Carbon Sequestration and Biochar as Negative Emission Technologies. *Glob. Chang. Biol.* **2016**, *22*, 1315–1324. [CrossRef] [PubMed]
48. EEA SIGNALS 2019—Land and Soil in Europe—European Environment Agency. Available online: https://www.eea.europa.eu/publications/eea-signals-2019-land (accessed on 19 February 2023).
49. Global Land Outlook | UNCCD. Available online: https://www.unccd.int/resources/global-land-outlook/overview (accessed on 19 February 2023).