separations

Article

The Effect of the Elemental Composition of Municipal Sewage Sludge on the Phosphorus Recycling during Pyrolysis, with a Focus on the Char Chemistry—Modeling and Experiments

Naeimeh Vali [1,*], Aurélie Combres [1], Aida Hosseinian [2] and Anita Pettersson [1]

[1] Swedish Centre for Resource Recovery, University of Borås, 501 90 Borås, Sweden
[2] Water, Energy and Environmental Engineering Research Unit, Faculty of Technology, University of Oulu, 90014 Oulu, Finland
* Correspondence: naeimeh.vali@hb.se; Tel.: +46739391375

Abstract: The present study investigates how the original sewage sludge characteristics influence the composition of sewage sludge-based chars for land applications. Sewage sludge from two different wastewater treatment plants in Sweden was pyrolyzed at 500, 700, and 900 °C, and the resulting chars were analyzed. Thermodynamic equilibrium calculations (TEC), together with chemical fractionation, were implemented to simulate the char after the pyrolysis process at different temperatures. The results showed that, in general, for both the municipal sewage sludge (MSS), phosphorus (P) was significantly retained in the char at various temperatures. However, no specific correlation could be found between the pyrolysis temperature and the amount of P remaining. With regard to the heavy metals removed from the char after the pyrolysis reaction, the concentrations of copper, chromium, lead, nickel, zinc, and cadmium were below the limits of the Swedish regulations for farmland application.

Keywords: pyrolysis; phosphorous recovery; char; municipal sewage sludge; thermodynamics equilibrium calculations; heavy metals; waste recycling; chemical fractionations

Citation: Vali, N.; Combres, A.; Hosseinian, A.; Pettersson, A. The Effect of the Elemental Composition of Municipal Sewage Sludge on the Phosphorus Recycling during Pyrolysis, with a Focus on the Char Chemistry—Modeling and Experiments. *Separations* **2023**, *10*, 31. https://doi.org/10.3390/separations10010031

Academic Editor: Zaira Chowdhury

Received: 19 November 2022
Revised: 19 December 2022
Accepted: 30 December 2022
Published: 4 January 2023

1. Introduction

In recent years, a growing concern about our planet's limited resources and the impact of greenhouse gas emissions on climate changes has been witnessed [1]. Phosphate rock and phosphorous (P) have been mentioned in the list of critical raw materials (CRMs), which specifies the minerals and metals of importance for the European economy that indicate a high risk of a supply shortage in the future [2,3]. P is among the primary macronutrients for plant growth and plant health, required from the seedling stage to maturity. In addition, P plays a crucial role in complex energy transformations, necessary for all living organisms and is a central component of DNA; moreover, it is essential for building proteins and other compounds [4,5]. The current linear pattern of P consumption, where most of the P used in fertilizers is a mineral and extracted from limited reserves, in addition to a low efficiency in the usage, leads to a high environmental impact and endangers the economy and independence of each country. Therefore, to maintain the security of P-based fertilizers and sustain the food production chain, developing new methods and technologies for P recovery from secondary resources has become an essential objective in the EU [2,6]. Closing the P loop requires safeguarding the value of P products and minimizing waste generation; therefore, every waste flow that contains an adequate quantity and quality of P could be a potential resource for P recycling. In this context, there are four main waste-based flows that could be categorized as secondary P resources: food waste, mining waste, manure, and sewage sludge. Among these resources, the most promising is municipal sewage sludge (MSS), as a huge amount of byproducts in every municipal wastewater treatment plant (WWTP) contains high concentrations of P. With regard to the adequate P quality, the recovery is feasible, and its concentration is comparable with P minerals [6]. Therefore, a farmland application of MSS may be an excellent option for P recycling. However, it also contains pollutants, such as pesticides (DTT, PCB), micro-plastics, resistant bacteria, heavy metals from industries, etc., polluting the soil and water. P recovery from sewage sludge is possible via different methods, such as composting, anaerobic digestion, and thermal treatments (incineration, gasification, and pyrolysis). By thermal treatment of the sewage sludge, all the organic pollutants could be destroyed [7,8], with only the metals remaining [9–11]. The pyrolysis process may be designed to act as a purification process with the release of the heavy metals from MSS in the produced municipal sewage sludge biochar (MSSC), and the emission of trace elements during the pyrolysis process could be affected by reaction conditions, such as residence time and heating rate or sample compositions [12,13]. In that case, the P-containing biochar is converted into a soil improver and fertilizer. Yet, the biochar is not included on the list of eligible fertilizers in the EU regulations due to the fact that the evidence of organic contamination removal is insufficient. However, the commission delegated regulation (EU)2021/2088 has recently revealed the eligible criteria for adding pyrolysis and gasification materials as a component material category in EU fertilizing products. Pyrolysis of MSS is an interesting alternative since it has the advantage of reducing the cost of the plant operation. Pyrolysis can save the sludge disposal costs; it can be used to recover energy or valuable chemical products. Furthermore, the harmful organic compounds can be destroyed, and heavy metals can be separated from the P-rich char without any complex and costly treatments [14]. Therefore, there is a need for more investigation on the effectiveness of contamination removal from sewage sludge by pyrolysis. Generally, the composition of sewage sludge and, consequently, the properties of the char after the pyrolysis reaction, strongly depends on the sewage source and wastewater treatment techniques. The nutrient recovery (NR) from the char residue may be influenced by P speciation in the char for several reasons. First of all, the most commonly used mineral fertilizers contain nitrogen, potassium, and phosphorous (N-K-P) elements; therefore, the physical and chemical properties of the resulted chars to be used as a soil improver are highly affected by the concentration of P and K and other inorganic elements such as Ca, Mg, Al, Fe in the raw sewage sludge. Furthermore, one of the operational challenges during pyrolysis is char handling, related to char viscosity. Generally, K and Calcium (Ca) are considered detrimental elements in thermal conversion. In the combustion of sewage sludge with a higher amount of K, low-melting temperature compounds will be formed and increase viscosity; conversely, the Ca contributes to forming ashes with lower viscosity [15,16]. Therefore, the melt formation is of importance in industrial MSS pyrolysis and should be investigated. This could be performed using both theoretical and experimental analysis to support process assurance in removing heavy metals and predict the chemical association of P for sewage sludges from different sources [4]. According to the literature review, the process temperature, the feedstock's residence duration, and the properties of the raw materials have the biggest effects on the relative weights and yields of the three pyrolysis products [17]. However, despite so many studies on the pyrolysis of sewage sludge, no studies have investigated simultaneous application of chemical fractionation analysis and thermodynamics equilibrium which are dominating the investigated temperature range.

In this research project, simultaneous application of chemical fractionation analysis and thermodynamics equilibrium calculations was compared with the pyrolysis of two different digested and undigested municipal sewage sludges. The objective of this work was to perform the pyrolysis of MSS from two WWTPs in order to obtain a P-rich char residue for soil improvement. This implies a high content of P and Carbon (C) and a low concentration of heavy metals. The reason for choosing these two MSS is one of the strong points of this study, which is that the samples are from different WWTPs, at different locations with different compositions, one in the north and one in the southwest of Sweden. They undergo different treatments, with one being digested biologically and the other is undigested. After pyrolysis, the concentrations of C, P, and the heavy metals in the char are experimentally investigated in order to evaluate the effectiveness of the pyrolysis treatment on the sewage sludge. Furthermore, thermodynamic equilibrium calculations (TECs) are conducted, focusing on the influence of the sewage sludge composition, gas atmosphere, and the process temperature on the melting formation and the P speciation in the char.

2. Materials and Methods

2.1. Sewage Sludge and Sample Preparation

A scheme of the steps of the research procedure applied in the study is shown in Figure 1.

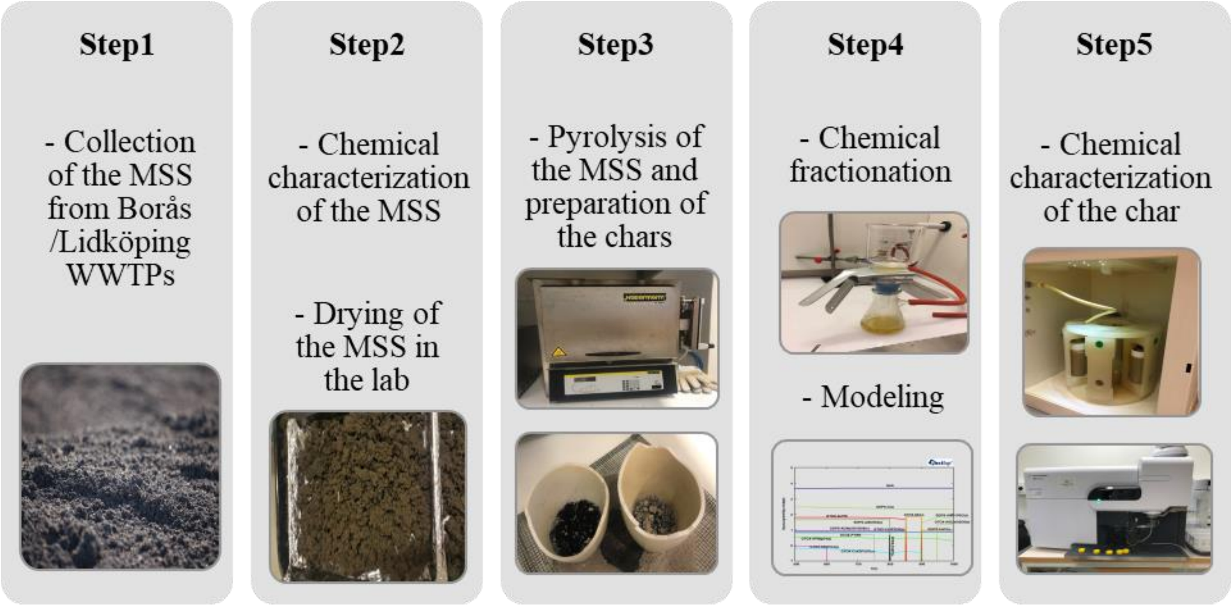


Figure 1. Schematics of the steps in the current study.

Two MSS samples were used in this study. The MSS was collected from WWTPs located in different regions in Sweden: Lidköping (58°30′ N 13°11′ E) and Borås (57°43′16″ N 12°56′25″ E). The chemical characteristics of the sewage sludge samples are shown in Table 1. Because the Borås sewage sludge was anaerobically digested, some of C had already been used for methane production. The sewage sludge samples were de-watered to a moisture content of around 70–80% in a moving drier at the site. Then, before the pyrolysis process, it was dried at 105 °C in the lab using a drier oven until a moisture content of 1% was reached. Thereafter, the dried MSS samples were ground by a laboratory crushing mill and stored in sealed Polyethylene containers before pyrolysis. In this research, the size of the MSS particles was less than 0.2 mm.

Table 1. MSS characteristics.

Wastewater Treatment Plant Location	Lidköping, Sweden	Borås, Sweden
P Removal Method in WWTP	Undigested, Chemical P removal	Anaerobic Digested, biological P removal
Ash content in dry matter [1]	21.5	38.0
Moisture content (wt%) [1,2]	79	71
Ash analysis (g/kg DSS [2])		
Al	38 ± 6.7	50.5 ± 14
Ca	9.9 ± 1.8	12.7 ± 3
Fe	7.1 ± 1.4	9.8 ± 2
K	2.1 ± 0.5	2.5 ± 0.5
Mg	1.7 ± 0.6	2.4 ± 0.5
Na	1.6 ± 0.2	1.6 ± 0.2
P	17.6 ± 2.7	29.1 ± 5
Si	17.8 ± 3.2	17.5 ± 5.2
Ti	0.6 ± 0.1	1.6 ± 0.3
Cl	0.3	0.19
Trace elements (mg/kg DSS [3])		
As		3 ± 0.7
Cd	3.2 ± 1.25	0.6 ± 0.195
Co	0.3 ± 0.069	3.7 ± 1.6
Cr	2.2 ± 0.70	32.9 ± 11.4
Cu	24.5 ± 5.4	280 ± 70
V	139 ± 30	10.5 ± 2.7
Mo	8.3 ± 1.21	6.3 ± 1
Ni	2.9 ± 0.62	14.8 ± 3.5
Pb	9.2 2.06	16.8 ± 4
Zn	7.4 1.85	596 ± 25

[1] Wt.%; [2] as received; [3] dry basis.

2.2. Pyrolysis Procedure and Preparation of Chars and Thermogravimetric Analysis (TGA)

The two types of sludge, Lidköping sewage sludge (LSS) and Borås sewage sludge (BSS), were subjected to the pyrolysis process with a N_2-atmosphere inside a laboratory high-temperature oven (Nabertherm P330) for about one hour. Sewage sludge chars (SSC) were prepared at 500, 700, and 900 °C. For each LSS and BSS, three samples were pyrolyzed at each temperature; also, for each experiment, a total of 10 g of MSS was put in a quartz crucible. Three heating programs were used with different ending temperatures: 500 °C, 700 °C, and 900 °C, for each sample. During the pyrolysis process, there were no analyses of the gases and liquid production. An oxygen-free gas atmosphere was achieved inside the furnace during the pyrolysis process by a constant 20 mL/min N_2 gas flow. After the pyrolysis process, the prepared Borås SSC (BSSC) and Lidköping SSC (LSSC) were weighed. The pattern setting of the heating program is shown in Figure 2.

In Figure 2, the process parameters for the samples were set as follows:

Time 1: holding time 20 min; Time 2: holding time 30 min (T1: 105 °C); Time 3: holding time varies based on the final pyrolysis temperature, 40 min (T2: 500 °C) and 60 min (T2: 700 °C), or 1 h 20 min (T2: 900 °C) (the heating rate was 10 °C/min and unchanged); Time 4: 30 min.

To investigate the kinetics behavior of pyrolysis process, both dried BSS and LSS were analyzed by a thermogravimetric analyzer (Q500 from TA instrument supplied by Waters LLC/TGA). A crucible containing around 17 mg of each of the two dried sewage sludges was loaded and heated in TG equipment using N_2 atmosphere at a heating rate of 10 °C per minute from 30 °C to 900 °C. N_2 flow was maintained at 20 mL/min. The TG curves were numerically deduced to produce the differential thermogravimetric (DTG) curves.

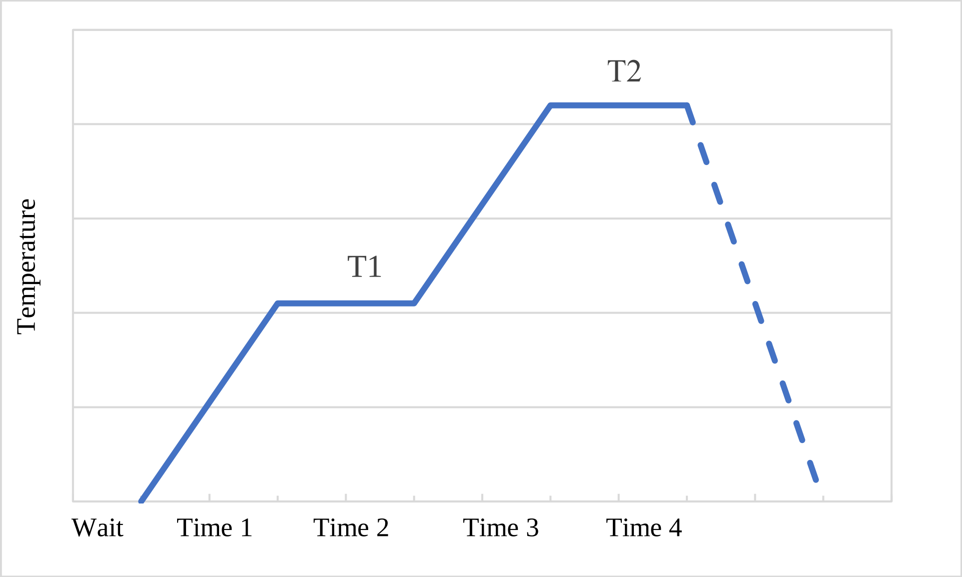


Figure 2. The pattern setting of the heating program.

2.3. Heating Value Measurements with a Bomb Calorimeter

The Bomb Calorimeter IKA 2000 (IKA-Werke GmbH & Co. KG, Staufen im Breisgau, Germany) was used to estimate the heating value of the char residue obtained from the pyrolysis. The heating corresponds to the amount of heat released during the entire process of char combustion. The energy released after the pyrolysis corresponds to the amount of solid C and some other elements remaining in the char fraction that is oxidized during combustion in the calorimeter. Three experiments were performed on the char residue for each temperature (500, 700, and 900 °C) and for both sludges.

2.4. Chemical Treatments and MP-AES Analysis

Microwave Plasma–Atomic Emission Spectroscopy (MP-AES, Agilent technologies, Santa Clara, CA, USA) was used to analyze the content of the char residue of selected metals, such as the main elements (P, Mg, Ca, K, Na, Fe, Al, and Si) and trace elements (Cd, Cu, Cr, Zn, Pb, Ni, As, Co, and Mn). The char residues were subjected to digestion by an acid solution containing 6 mL of 65% nitric acid (HNO_3), 2 mL of 37% hydrochloric acid (HCl), 1 mL of 30% hydrogen peroxide (H_2O_2), and 1 mL of hydro-fluoric acid 48% (HF) by using microwave digestion (Milestone ETHOS UP microwave oven, Acquisition Corp, Hatfield, PA, USA). Finally, the resultant solutions were filtered (0.20 µm) and diluted to 50 mL with Milli-Q water and analyzed by MP-AES. The concentration of elements in the char was analyzed in mg/kg of char residue after the pyrolysis and then correlated with the available amount of sludge before the pyrolysis. Consequently, the mg/kg TS refers to the mass of the dried sewage sludge before the pyrolysis.

2.5. Chemical Fractionations of the Dried Municipal Sewage Sludge (DMSS)

Chemical fractionations, as an advanced analytical approach, were performed on the dried municipal sewage sludges (DMSS) to provide information about the chemical forms and association of ash-forming elements during thermal conversions based on their solubility in H_2O (aq), NH_4Ac (1M), and HCl (1M), respectfully. Chemical fractionation analysis was originally used for fossil fuels and was later modified to analyze the behavior of inorganic elements in biofuels to predict their contribution in the ash and emissions during thermal conversion of biofuels [18,19]. A schematic representation of the method is shown in Figure 3 [18]. Generally, water-soluble salts, including alkali sulphates, carbonates, and chlorides, are leached out in the first step. In the second step, ion exchangeable elements, which are believed to be typically associated with Ca, Na, K, and Mg, are leached out by NH_4Ac. In the third step, acid-soluble compounds, such as alkaline carbonates and alkali sulphates, are extracted. The remaining part is a solid residue consisting of silicates, oxides, sulphides, and other minerals [20]. However, in this study, only H_2O and NH_4Ac were used; furthermore, the last step, leaching with HCl, was omitted. This is because the solid residue after leaching with NH_4Ac contains the ash forming elements in the char after the pyrolysis process. The leached liquids and solid residue were analyzed for inorganic ash formic elements in the MSS, such as Ca, Cl, Fe, K, Mg, Na, S, Si, Al, Ag, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Zn, and Ti. Thereafter, based on the level of their reactivity, they were used in the calculation. Generally, the water- and ammonium-acetate-soluble fractions are considered to be the reactive part, and the solid residue is considered to be the non-reactive part [21] for the purposes of finding the non-reactive fractions of elements for the input for thermodynamics calculations.

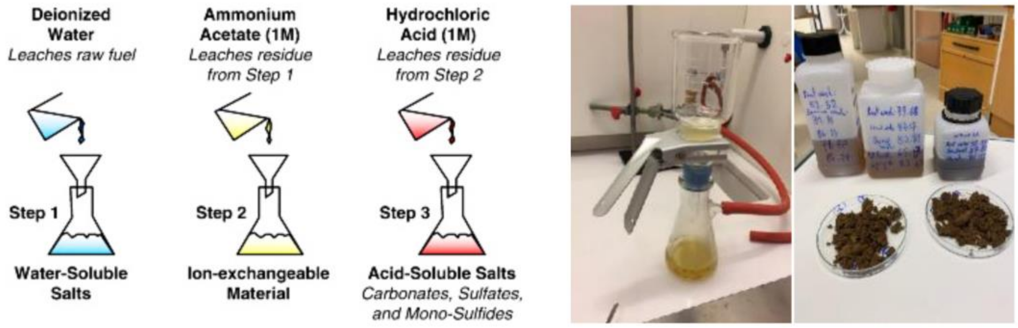


Figure 3. Chemical fractionation procedure of solid fuel.

2.6. Thermodynamic Modeling

TECs were performed applying the software FactSage 7.3 [22] to determine the P component in the char. Novel TEC databases with enhanced applicability in P-rich inorganic systems, GTOX (P-containing compound, developed by GTT and FZ-Julich) and SGPS (SGTE pure substance database), were employed. GTOX was selected as a primary database for the prediction of stoichiometric compounds and the solution phase in the char. The oxide melt model from the GTOX database was used for the prediction of molten phases, and the gas phase produced was modeled using GTOX. Subsequently, SGPS was selected as a complementary database for H bearing compounds and gaseous species (Table 2). The modeling strategy is focused on the prediction of the P and the inorganic compounds in the char residue. Therefore, chemical fractionation analysis was used to separate the reactive elements from the non-reactive elements in the sewage sludge and, thereafter, apply the non-reactive elements in the modeling. The atmospheric conditions for the calculations were set to guarantee an inert atmosphere with an inlet gas composition identical to the one in the pyrolysis process with 100 vol.% N_2. The calculation was performed over a temperature range between 500 °C and 900 °C to investigate the distribution of P-bearing compounds during char formation at various temperatures. The initial melt formation was calculated to investigate the char melting behavior, and the fate of P in the char was predicted.

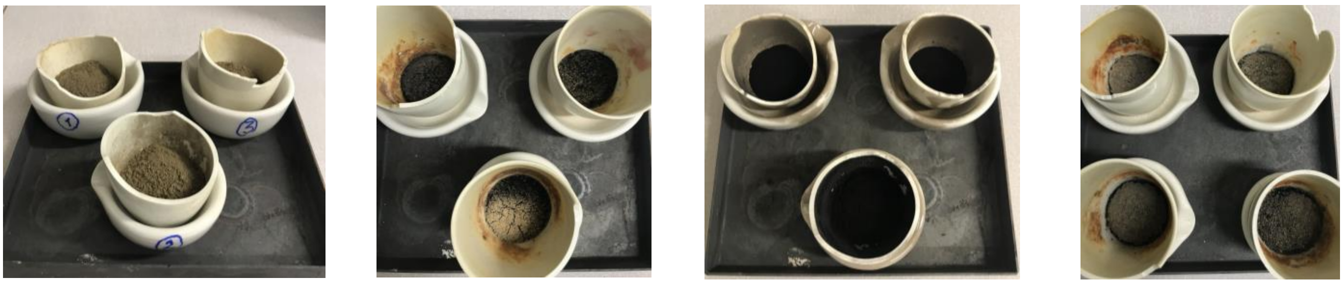
Table 2. Elements, compounds, and solution models used for the thermodynamics equilibrium calculations in FactSage.

Elements	
H, C, N, O, Na, Mg, Al, Si, P, K, Ca, Fe, Zn, S	
Database—GTOX (solution models)	
Slag (liquid phase containing oxides, metals, sulphides, sulphates of existing elements)	
ALPM (Al, Si)(P, Si)O_4	C3PL (Ca, Mg, Zn)$_3$(PO_4)$_2$
CORU (Al, Fe)$_2O_3$	PYRR (MgS, FeS)
MEO CaO, MgO, K_2O, Al_2O_3, FeO, ZnO	MULL Al_2(Al, Fe, Si)O_5
OLIV (Ca, Fe, Mg, Zn)SiO_4	CMP (Ca, Mg) CaP_2O_7
Gases: CO_2, H_2O, H_2	Stoichiometric solid compounds
Database—SGPS	
Gas compounds	
Stoichiometric solid compounds	

3. Results and Discussion

3.1. Characteristics of the Sewage Sludge and the Char Residues

The visual properties of the original Borås and Lidköping MSS and the char obtained from the pyrolysis at different temperatures are presented in Figures 4 and 5, respectively. Both the Borås and Lidköping MSS were milled to a powder form before pyrolysis to promote more homogenous samples. After pyrolysis, the physical characteristics of the chars were directly related to the ending temperature of the pyrolysis. As shown in Figure 4b, for LSS, an entirely dark powder is obtained, which means that the pyrolysis reaction was fully performed and efficient at an ending temperature of 500 °C. In contrast, in Figure 4c,d, at 700 °C and 900 °C, respectively, some ash was found on top of the sludge's char residue. Ash formation could be because more C is volatilized at higher temperatures, and the inorganic part captured in the C is revealed, according to a previous study [23]. This is also in line with the ash content in both the BSSC and the LSSC increasing with the rising treatment temperature. These results are congruent with those from other studies [24]. Regarding BSSC in Figure 4, more gray ash is found at each of the three temperatures compared to LSSC. The darker part is related to C and the organic part. Since BSSC is a digested sludge, it contains a higher amount of the inorganic compound in comparison with the LSSC, which was an undigested sludge.



(**a**) (**b**) (**c**) (**d**)

Figure 4. (**a**) Lidköping sludge sample before pyrolysis; and char after pyrolysis at (**b**) 500 °C, (**c**) 700 °C, and (**d**) 900 °C.

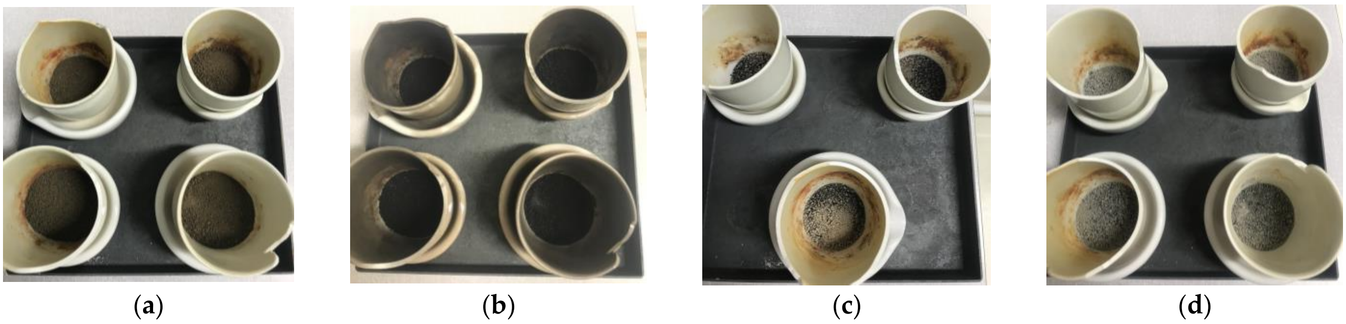

(**a**) (**b**) (**c**) (**d**)

Figure 5. (**a**) Borås sludge sample before pyrolysis, (**b**) Char after pyrolysis at 500 °C, (**c**) 700 °C, and (**d**) 900 °C.

The ash fractions of MSS collected from combustion in the calorimeter and the heating value of the MSS are presented in Table 3, together with the percentage of char residue obtained after the pyrolysis at different temperatures. This value corresponds to the amount of obtained char residue relative to the original amount of sludge, given in percentage. The average percentage of heating value refers to the percentage of heating value of generated chars at various temperatures relative to the heating value of the raw MSS. Table 3 shows that the average percentage of the heating value decreases from 71 to 59% for LSSC and 76 to 56% for BSSC when the pyrolysis temperature is increased from 500 to 900 °C. This shows that the ash content of the chars increases along with decreasing the organic char contents by the increasing pyrolysis temperature. It is clear that the higher the pyrolysis temperature, the lower the char residue content. This could be affiliated mainly with the higher evaporation rate of the organic matter and other elements at a higher temperature. The average percentage of char residue at 500, 700, and 900 °C for LSS was 42, 34, and 30 percent, respectively, and that of BSS was 60, 52, and 47 percent, respectively, for the three temperatures. Considering Table 3, for both the BSSC and LSSC, the percentage of average heating value with respect to the raw sewage sludge decreased with increasing temperature. BSS had a lower heating value than LSS, since it was biologically digested at the WWTP, as mentioned before; therefore, some of the carbon in the sewage sludge was converted into methane gas during the digestion process. Comparing the change in the heating value of BSS and LSS, they both decreased at higher pyrolysis temperatures. This correlates with results showing that a greater amount of carbon is released at a higher pyrolysis temperatures. It can be observed that BSSC lost slightly less carbon than LSSC, which is explained by the lower primary heating value of the sludge.

Figure 6 shows the appearance of the ash fraction of the BSS and LSS obtained from combustion in the calorimeter. The grain size of the ashes was bigger in the BSS than in the LSS, and they were more agglomerated than those of the LSS. This could be a result of the amount of dry ash matter, which was higher in the BSSC; moreover, the BSSC contained a high proportion of metals at the higher temperature, compared to the LSSC.

The difference between the heating values of these two sludges showed that the Borås sewage sludge was already lower in C from the start because of anaerobic digestion.

3.2. Elemental Analysis

The chemical composition results of the SSC samples are presented in Tables 4 and 5. A high concentration of nutrients characterizes the SSC from the two MSSs investigated. The Borås sludge showed a high P recovery rate in all of the samples (97 to 99.7% remaining in the char samples) after pyrolysis at 900 °C. The lowest P concentration in the analyzed sample was detected in the char residues of LSS after pyrolysis at 900 °C.

Table 3. Characterizations of char residues obtained from the pyrolysis of Lidköping and Borås sewage sludge.

	Percentage of Char Residue	Heating Value (kJ/g)	Average of Heating Value (kJ/g)	Average% of Heating Value
LSS	Non-applicable	19.4	19.4	Non-applicable
LSSC 500 °C, 1	41	13.8	13.7	71
LSSC 500 °C, 2	44	13.6		
LSSC 500 °C, 3	44	13.8		
LSSC 700 °C, 1	34	12.3	12.4	64
LSSC 700 °C, 2	34	12.5		
LSSC 700 °C, 3	34	12.5		
LSSC 900 °C, 1	29	10.2	11.4	59
LSSC 900 °C, 2	31	11.8		
LSSC 900 °C, 3	31	12.1		
BSS	Non-applicable	12.7	12.6	Non-applicable
Borås 500 °C, 1	59.4	10.1	9.6	76
Borås 500 °C, 2	59.1	10.1		
Borås 500 °C, 3	61.1	9.1		
Borås 700 °C, 1	51.7	8.3	8.6	68
Borås 700 °C, 2	52.1	8.8		
Borås 700 °C, 3	52.0	8.9		
Borås 900 °C, 1	47.9	7.4	7.1	56
Borås 900 °C, 2	47.9	7.4		
Borås 900 °C, 3	46.0	6.6		

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

Figure 6. Appearance of the ash fractions collected from combustion in the bomb calorimeter: (**a**) Lidköping sludge ashes and (**b**) Borås sludge ash.

Table 4. The content of the main elements in the municipal sewage sludge (MSS) and sewage sludge chars (SSC) produced at various temperatures (500, 700, and 900 °C) with standard deviations.

Element	P [g × (kg TS)$^{-1}$]	Fe [g × (kg TS)$^{-1}$]	Mg [g × (kg TS)$^{-1}$]	Na [g × (kg TS)$^{-1}$]	Mn [g × (kg TS)$^{-1}$]	K [g × (kg TS)$^{-1}$]	Ca [g × (kg TS)$^{-1}$]
LSS	17.5	6.9	1.5	1570	0.15 ± 0.01	2.2 ± 0.1	9.3 ± 1.0
LSSC 500 °C	36 ± 0.5	15 ± 0.5	0.40 ± 0.01	24 ± 0.7	0.23 ± 0.01	9.8 ±1.0	7.5 ± 0.5
LSSC 700 °C	44 ± 0.3	17 ± 0.5	0.40 ± 0.01	24 ± 0.6	0.28 ± 0.05	10 ± 1.0	6.5 ± 1.0
LSSC 900 °C	46 ± 0.2	18 ± 1	0.80 ± 0.40	24 ± 0.5	0.3± 0.05	11 ± 0.5	8.5 ± 0.5
BSS	29	9.8	2.4	1.6	2.8	2.6	12.7
BSSC 500 °C	44 ± 0.6	18 ± 0.1	0.51 ± 0.01	32 ± 0.2	0.4 ± 0.01	14 ± 1.0	10 ± 1.1
BSSC 700 °C	53 ± 1.0	21 ± 1.4	0.52 ± 0.01	31 ± 0.4	0.4 ± 0.02	14 ±1.0	9.4 ± 1.2
BSSC 900 °C	61 ± 0.5	25 ± 2.0	0.91 ± 0.16	31 ± 0.5	0.5 ± 0.02	15 ± 0.5	12 ± 1.2

Table 5. The content of heavy metals in municipal sewage sludge (MSS) and sewage sludge chars (SSC) produced at various temperatures (500, 700, and 900 °C) with standard deviations.

Element	Cu [mg × (kg TS)$^{-1}$]	Cr [mg × (kg TS)$^{-1}$]	Pb [mg × (kg TS)$^{-1}$]	Ni [mg × (kg TS)$^{-1}$]	Zn [mg × (kg TS)$^{-1}$]	Cd [mg × (kg TS)$^{-1}$]
LSS	140 ± 3.0	22 ± 2	8	10 ± 1	206 ± 6	
LSSC 500 °C	300 ± 3.0	50 ± 5	30 ± 3	20 ± 3	190 ± 27	0
LSSC 700 °C	370 ± 5.0	55 ± 3	40 ± 1	24 ± 1	280 ± 17	0
LSSC 900 °C	450 ± 4.0	170 ± 20	75 ± 13	99 ± 11	300 ± 20	0
BSS	280	33	17	15	596	
BSSC 500 °C	440 ± 5.0	60 ± 5	60 ± 9	11 ± 5	500 ± 72	~0
BSSC 700 °C	500 ± 6.0	65 ± 2	65 ± 4	13 ± 5	580 ± 74	~0
BSSC 900 °C	540 ± 4.0	100 ± 6	70 ± 3	40 ± 4	550 ± 72	~0
[1] EU 2019/1009	600	2	120	100	1500	3
[2] Sweden farmland regulation SFS 1998:994	600	100	100	50	800	2

[1] Regulation (EU) 2019/1009 regulates the concentration of heavy metals in inorganic macronutrient fertilizers; [2] limits set by the Swedish government for the amount of heavy metals in sewage sludge implemented in farmland.

As can be seen from Table 4, P was enriched and exhibited a much higher concentration in the SSC compared to in the MSS. However, according to calculations of the total amount, around 11.5% of the total P in the original MSS was lost at 500 °C, whereas the P contents in the SSC samples at 700 and 900 °C had a P loss of up to 20%. When comparing the P recovered in both the SSCs, the concentration of P decreased slightly with the pyrolysis temperature in the LSS; however, it increased in the BSS. The difference in behavior between the two MSS samples may be explained by the differences in treatment in the different WWTPs from which they are derived. There are differences in P precipitation with wastewater treatment. Moreover, the BSS was digested before pyrolysis, but not the LSS. These differences in treatment could have resulted in BSSC containing more stable P compounds than the LSSC. This result is congruent with other research findings suggesting that the fate of P in pyrolysis is closely related to the P originating in the raw SS, whether it is organically bounded or inorganically bounded P. Additionally, this affects the P's sensitivity to the treatment temperature at high temperatures, which leads to conversion to the gas phase or decomposition and transformation into the other more condensed functional groups. Considering the P concentration in the BSSC and LSSC in Table 4, it seems that the LSS, which is undigested, contains more organic P sources, and therefore can easily be converted to the gas phase. However, it did not dissolve in the water and ammonium acetate during chemical fractionation analysis, and it has been predicted by thermodynamic equilibrium calculations that P will start to release in the gas, as shown here in the modeling section. In contrast, the BSS, with more inorganic P-bearing compounds, undergoes reactions which lead to decomposition and the formation of a more condensed functional group. In the current study, particular attention was paid to the chemical composition of the char; not only the values of the P contents, but also those of other elements, were of interest. The distribution of components varies in the LSS and BSS. The lowest amount of K and Na in both the BSSC and LSSC was found after pyrolysis at 700 °C, which is in line with the results from a previous study [23]. The analyzed samples of the LSSC and BSSC were characterized by a relatively high Iron (Fe) content. Regarding Magnesium (Mg), it was found that about 80 to 90% of Mg was evaporated during the pyrolysis process at a temperature above 500 °C. Regarding Ca, more than half of the content was released in all char residues. However, Manganese (Mn) was found in somewhat lower concentrations in the LSSC samples compared to the LSS, but the concentrations in the BSSC were the same as in the BSS. The legislated maximum concentrations of heavy metals in the sewage sludge for direct use on agricultural farmland are found in EU 86/278/EEC, and the Swedish regulations are found in the document Regulation 1998:994. These limits and the content of heavy metals in both MSSs and SSCs are shown in Table 5.

As a result of the decomposition of heavy metal compounds during the pyrolysis process and the removal of the volatile compounds, the concentration of heavy metals in the LSSC were lower than those stipulated in the Swedish regulations except for Cr, which was too high in one case. For both the BSS and the BSSC, the concentrations of heavy metals were a little higher, but remained below those stipulated in the Swedish legislation, by a good margin. The concentration of Cadmium (Cd) was below the detection limit, which is low. Thus, it was treated as being below the legislated limits.

3.3. Thermogravimetric Analysis

The TG (wt%) and derivative weight (wt%/°C) curves of the sludges during heating from 20 to 900 °C at a heating rate 10 °C/min are shown in Figure 7. According to the TG analysis in the current work and the kinetics analysis in a previous study [23], above 500 °C, the rate of total lost weight is almost constant for both sludges, it shows that under the pyrolysis conditions employed in this work at temperature of 500 to 900 °C, the pyrolysis process is not governed by the kinetics, but is rather dominated by thermodynamics.

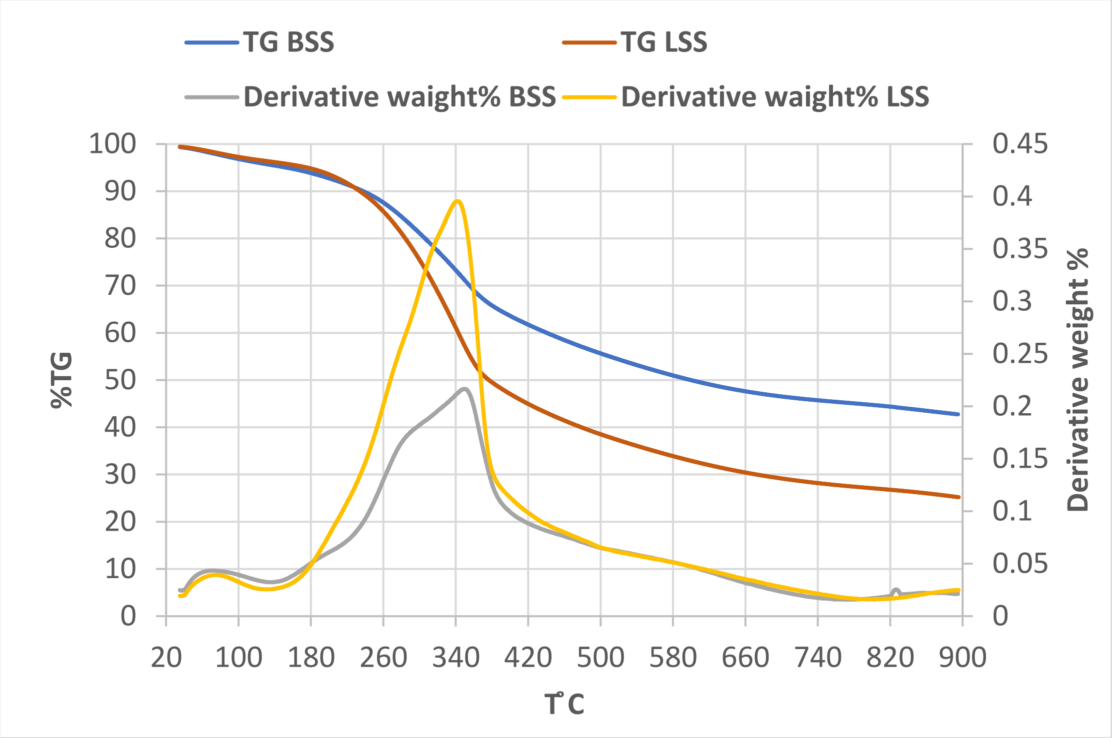


Figure 7. Thermogravimetric analysis of BSS and LSS.

3.4. Chemical Fractionation Analysis and Modeling Results

3.4.1. The Prediction of Reactivity of Ash-Forming Elements during Pyrolysis

Chemical fractionation was successfully performed to distinguish the less reactive (non-volatile species) fractions of ash-forming elements from the reactive (volatile species) during the thermal process in each MSS.

The results are shown in Figure 8. It can be seen that most of the P has remained in the solid residue/char after the pyrolysis reaction. According to literature reviews describing the results of Olsson et al. and Häggström et al. [25,26], who found that, during thermal conversion of P-enriched biomasses such as sewage sludge, the main part of P remains in the char during de-volatilization (pyrolysis), this might be explained by the fact that the P in both sewage sludge is in the form of P organic compounds (e.g., phytic acids) [27]. According to the results shown in Figure 8 for both MSS samples, only slight amounts of aluminum (Al), silicon (Si), and Fe were soluble in the sequences leached with water and acetate. This is compatible with the less reactive nature of these elements in the biomass. Ca and Mg showed similar chemical behaviors to those of Na and K [16]. The predicted less reactive ash-forming elements remaining in the char after the pyrolysis reactions consist of Al, Ca, Fe, K, Mg, Na, P, Si, S, and Ti.

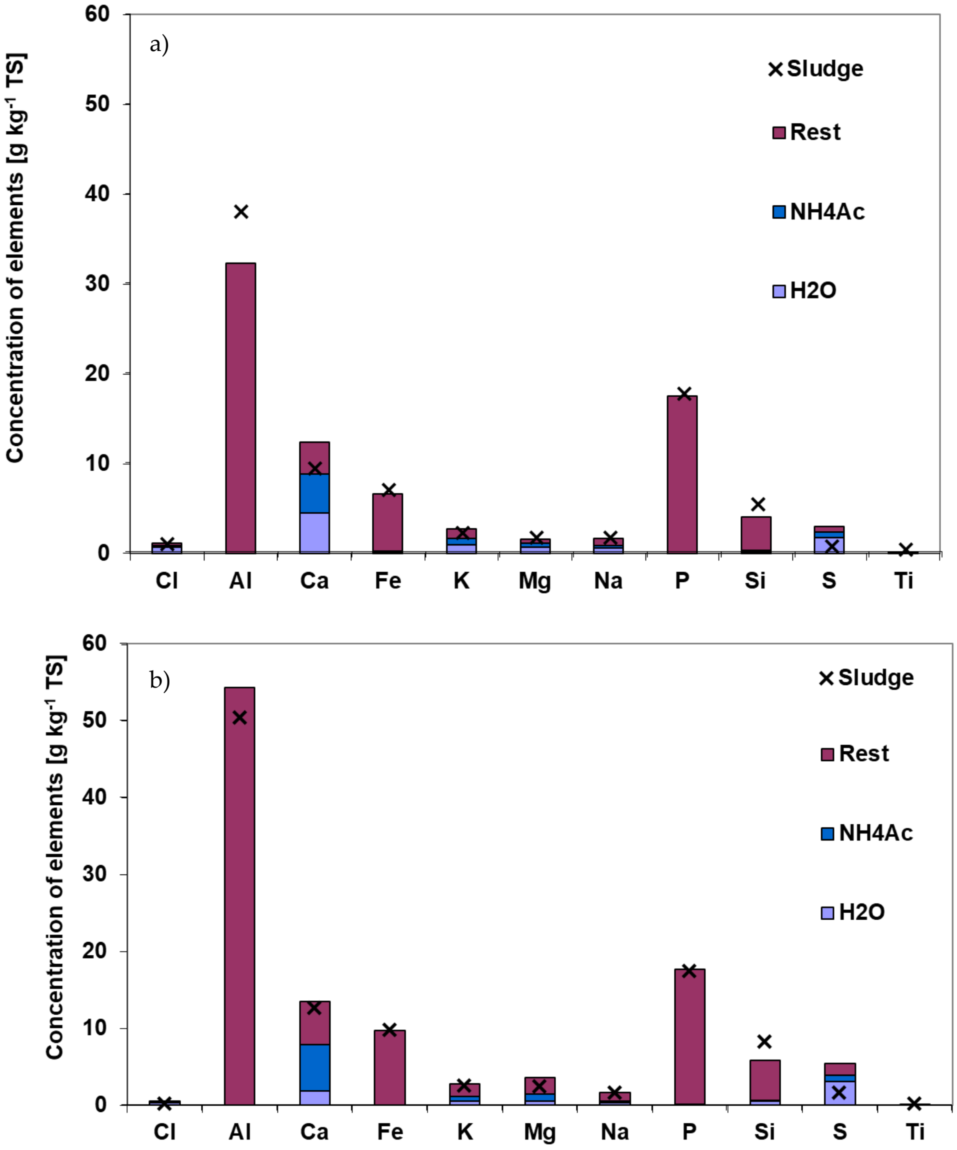
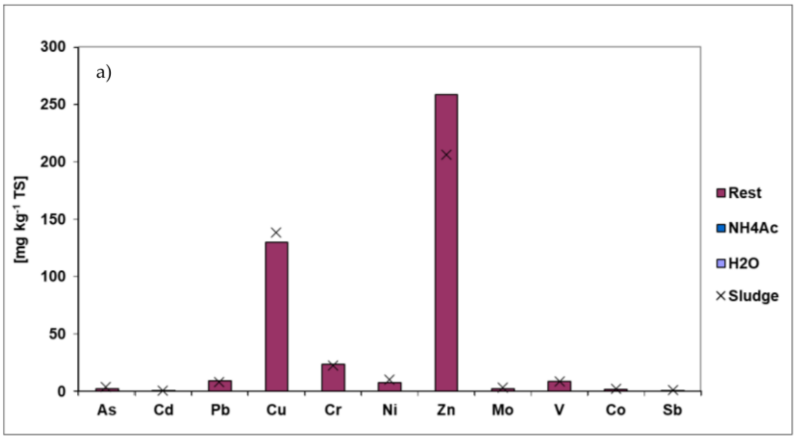


Figure 8. Results of the chemical fractionation of sewage sludge (main elements) in g kg^{-1} TS. Crosses (X) represent the total concentration of the element in the sewage sludge (**a**) LSS and (**b**) BSS.

According to Figure 9, the amount of heavy metals remaining in the char is much lower compared to the main elements presented in Figure 8. Regarding the fate of the heavy metals, most of the heavy metals associated in the reactions are volatilized to the gaseous during the pyrolysis process; therefore, the assumption is that these elements are reactive elements in the process. According to these results, and compared with other studies, Cl can be considered to be 100% reactive. Cu and Zn had the highest concentration in the MSS compared to other heavy metals, and they remained in the solid residue. Studies have also shown that 60% of Zn could be reactive during thermal conversion, which was taken into account [20,28]. The fractions of elements that were considered to be non-reactive, and thus used as input for the modeling part, is shown in Figure 10 for LSS and BSS, respectively.



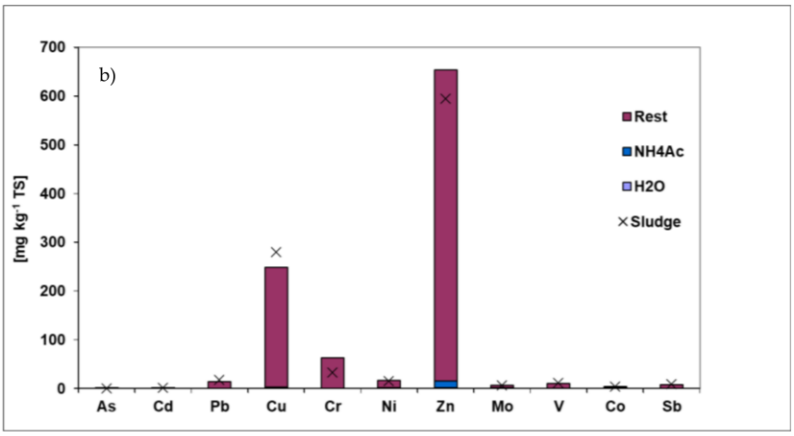
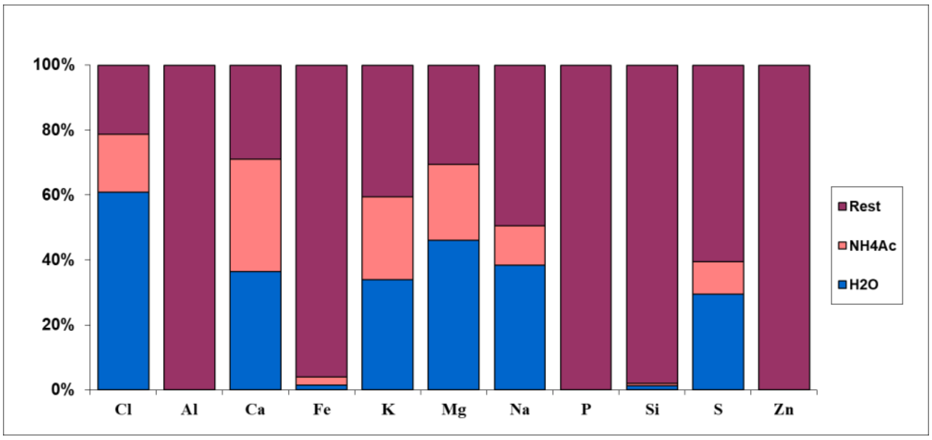
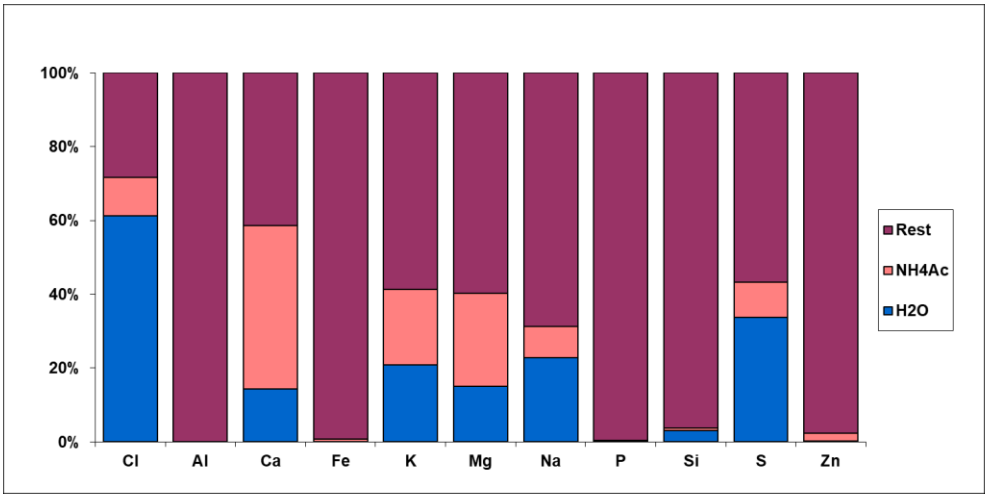


Figure 9. Results of the chemical fractionation of sewage sludge (heavy metals) in mg kg^{-1} TS. Crosses (X) represent the total concentration of the element in the sewage sludge (**a**) LSS and (**b**) BSS.



(**a**)

Figure 10. *Cont*.



(**b**)

Figure 10. Prediction of the percentage of non-reactive and reactive fractions of the ash-forming elements in the char: (**a**) LSS and (**b**) BSS.

According to Figure 10, the values for both sludges are close to one another, and the less reactive fraction is based on the percentage of different ash-forming elements in the leachates that are non-soluble and which remain in the rest solids after chemical fractionations. The water- and acetate-soluble fractions presented in Figure 9 are considered to be reactive.

3.4.2. Initial Melt Formation (IMF) Obtained by Thermodynamics Modeling

Figure 11 shows the influence of the MSS composition on the melt formation during the pyrolysis of BSS and LSS. The temperature at which the first sticky molten phases (slag) appear depends on the sewage sludge characteristics.

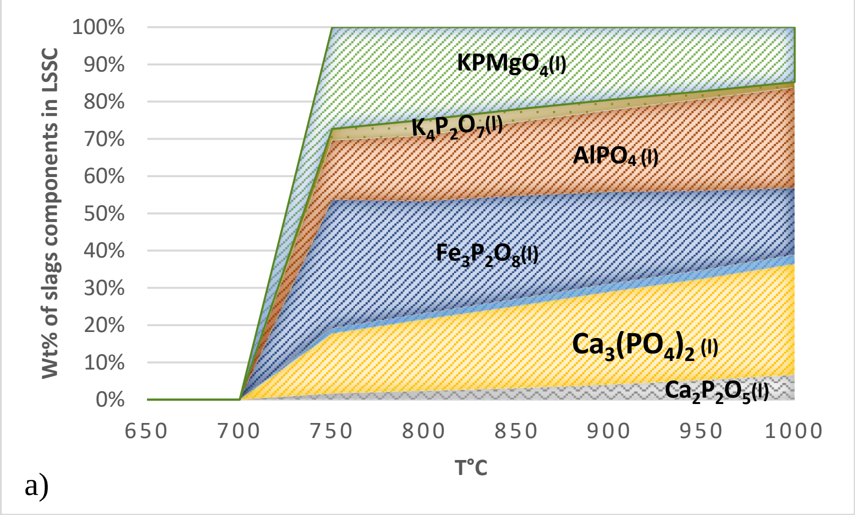


Figure 11. *Cont*.

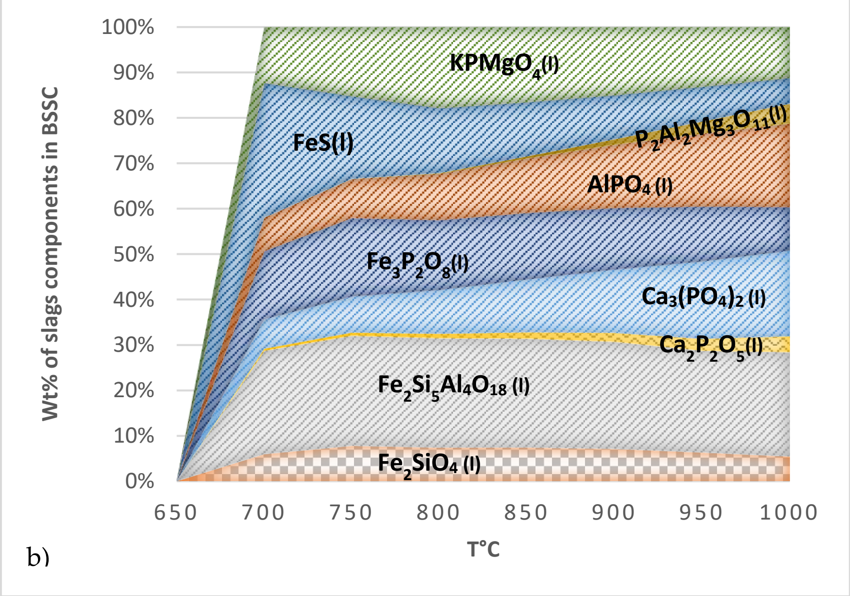


Figure 11. The calculated equilibrium composition of slag compounds (liquid species) during the pyrolysis of sewage sludge at different temperatures: (**a**) LSSC and (**b**) BSSC.

The initially formed melts mainly contain P, K, Mg, Al, and Fe in both of the MSS samples investigated. Figure 11 presents the percentage of the different compounds in the slags at different temperatures. Regarding the initial melt formation (IMF), each MSS behaved differently depending on its chemical composition. Neither LSS nor BSS exhibited slag formation at 500 °C; BSS started to form a liquid (l) at 650 °C, and the amount of melt increased significantly at 700 °C, whereas LSS started to liquefy at 700 °C.

Figure 12 shows the equilibrium composition of the chars as a function of temperature. The stoichiometric (pure solids) compounds in the char at the temperature ranges of 500 to 900 °C showed that Al_2O_5Si(s), $Al_6O_{13}Si_2$(s), $Al_2Na_2O_{16}Si_6$(s), $Al_6P_2O_{14}$(s), $KPMgO_4$(s), $K_4P_6Mg_4O_{21}$(s), $Ca_3P_2O_8$(s), CaP_2MgO_7(s), and $Ca_3P_4Mg_3O_{16}$(s) were predicted. An earlier study by Xia et al. [11] confirmed the formation of some of the predicted solid compounds, such as Al_2SiO_5.

Considering Figures 11 and 12, the association of P with Al/Fe and Mg/Ca compounds reveals that P has a special reaction potential for combining with Ca and Mg at higher temperature in a reduced atmosphere (under stoichiometric conditions), and prefers Fe and Al as well. Therefore, the concentration of Ca and Mg in the raw sewage sludge is crucial in the fate of P captured in the resulting chars. These results are in line with experiments by Han et al. [29], which show that adding CaO is effective for increasing the P recovery from sewage sludge. Regarding the BSSC, the percentage of alkali–P compounds is lower than that of the LSSC due to the additional Fe and Al in the LSS. Moreover, the fate of P in the liquid phase during pyrolysis reactions shows a significant dependence on the ratio of Mg + Ca/Al + Fe. In the equilibrium conditions and a reduced atmosphere, Fe and Al compete for the P, and the same behavior can be observed for Mg and Ca. Thermodynamically, P-K-Ca or P-K-Mg are the most stable phases in slag, provided that additional Ca, Mg, and K are available. It has been estimated by other researchers that the mobility and the plants' fraction of available P are highly dependent on its speciation; furthermore, chars containing P that are compounded with alkali, especially K and Na, are more readily available to the plants [30].

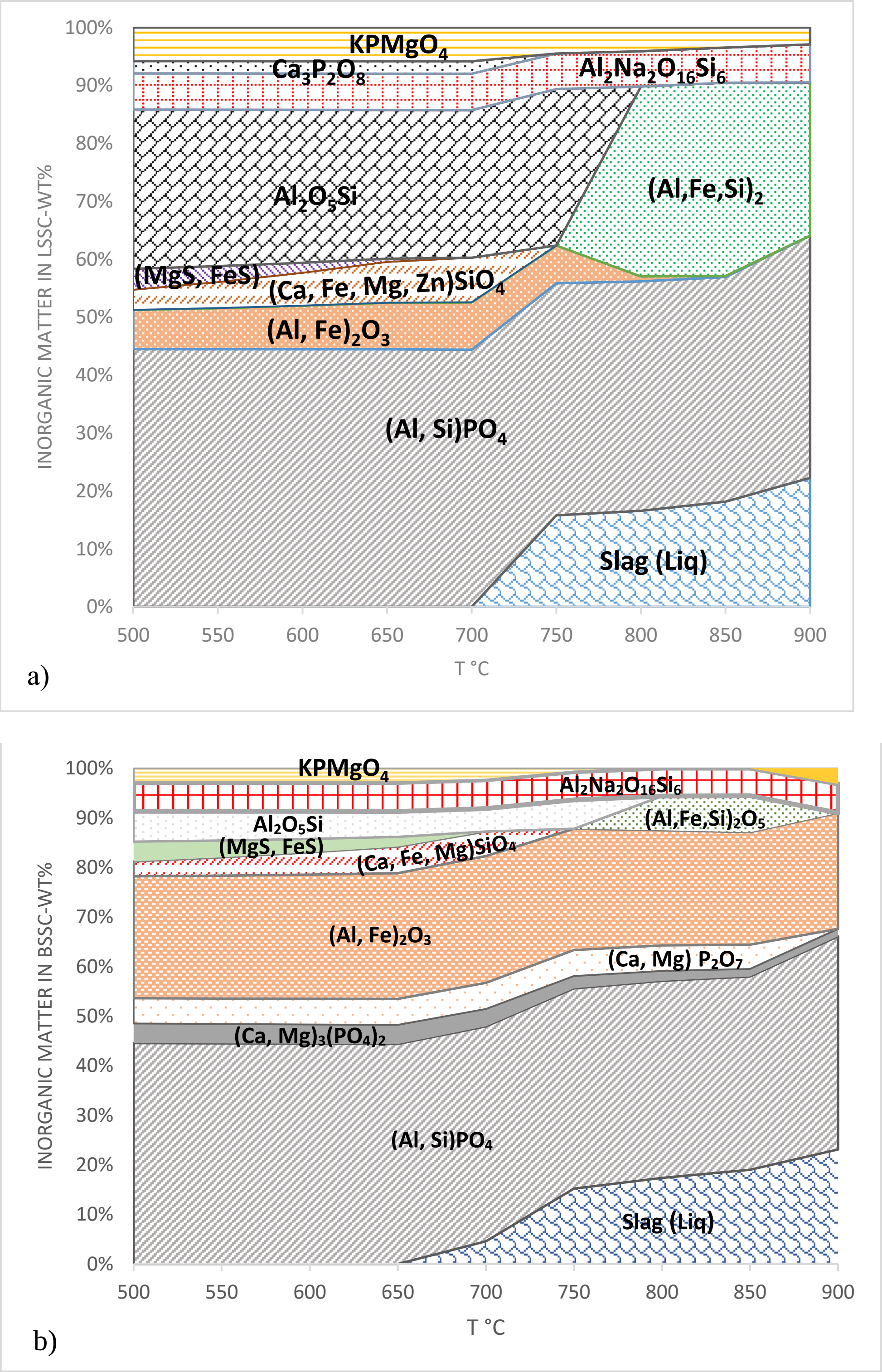


Figure 12. The calculated equilibrium composition of char after pyrolysis at different temperatures: (**a**) LSSC and (**b**) BSSC.

As mentioned before, some of the P associated with the gaseous phase, to the best of our knowledge and according to the literature [19,31], belongs to organic P-bounded compounds such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, and Al^{3+} phosphate. However, the chemical fractionation results did not show any presence of organically associated P (Figures 9 and 10). The modeling results show that P may be directly released into the gas product or can be found in the form of slag. In practice, it may be evaporated from slag and released into the gases, which might be one of the reasons why the concentration of P was lower in the chars, especially in LSSC, compared to the original MSS (Table 4). In Figure 13, the distribution of P in the different phases during pyrolysis has been shown for each sewage sludge. According to the graph, most of the P remained constant in the char at temperatures lower than 650 °C; thereafter, the P increased considerably in the slag and gaseous products.

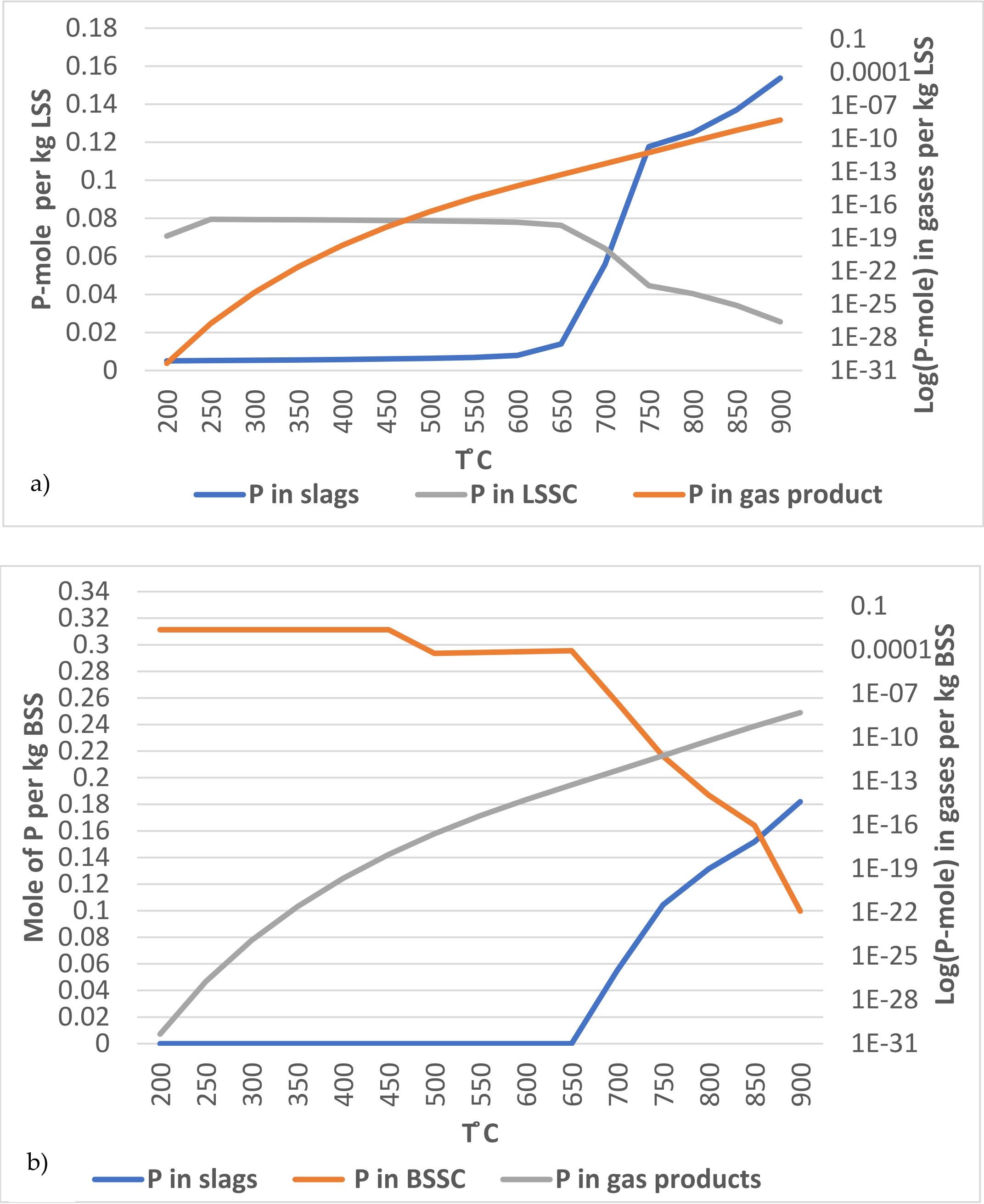


Figure 13. Distribution of P in the char, slags, and gaseous product during pyrolysis: (**a**) LSS and (**b**) BSS.

4. Conclusions

This study shows that char residue from pyrolyzed sewage sludge is interesting as a source of P for soil improvement. The amount of char residues in the Borås sludge is higher than in the Lidköping sludge, which corresponds to its higher ash content. In addition, it can clearly be seen that the Borås sludge has a lower heating value because it has been digested, in contrast to the Lidköping sludge. A loss of 30% of the C content was noticed in the char after the pyrolysis at 500 °C, while 35% was lost at 700 °C, and more than 40% was lost at 900 °C. The concentration of Zn was significantly reduced after the pyrolysis process in all samples; however, regarding Cu concentration, no substantial reduction was observed. However, the concentrations of all measured heavy metals were lower than those stated in the Swedish legislation. According to the thermodynamic calculation modeling, the initial melting formation and the fate of P are strongly dependent on the temperature and elemental composition, especially the concentration of alkali elements in the sewage sludge.

Author Contributions: Conceptualization, methodology, and formal analysis, N.V., A.C., A.H. and A.P.; investigation, N.V., A.C., A.H. and A.P.; validation, N.V., A.C., A.H. and A.P.; writing—original draft preparation, N.V.; writing—review and editing, A.H. and A.P.; visualization, N.V.; supervision, A.P.; project administration A.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not necessary.

Acknowledgments: The authors would also like to acknowledge the research facilities and technical assistance of the Energy lab at the University of Borås for the support and equipment employed for the lab-scale experiments. The authors would also like to give a special acknowledgement to waste water treatment plants in Borås and Lidköåing to the supply of municipal sewage sludge.

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

References

1. Shaddel, S.; Bakhtiary-Davijany, H.; Kabbe, C.; Dadgar, F.; Østerhus, S.W. Sustainable Sewage Sludge Management: From Current Practices to Emerging Nutrient Recovery Technologies. *Sustainability* **2019**, *11*, 3435. [CrossRef]
2. Kelessidis, A.; Stasinakis, A.S. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Manag.* **2012**, *32*, 1186–1195. [CrossRef] [PubMed]
3. Smol, M.; Adam, C.; Kugler, S.A. Thermochemical Treatment of Sewage Sludge Ash (SSA)-Potential and Perspective in Poland. *Energies* **2020**, *13*, 5461. [CrossRef]
4. Hannl, T.K.; Sefidari, H.; Kuba, M.; Skoglund, N.; Öhman, M. Thermochemical equilibrium study of ash transformation during combustion and gasification of sewage sludge mixtures with agricultural residues with focus on the phosphorus speciation. *Biomass Convers. Biorefinery* **2021**, *11*, 57–68. [CrossRef]
5. Hedayati, A.; Lindgren, R.; Skoglund, N.; Boman, C.; Kienzl, N.; Öhman, M. Ash Transformation during Single-Pellet Combustion of Agricultural Biomass with a Focus on Potassium and Phosphorus. *Energy Fuels* **2021**, *35*, 1449–1464. [CrossRef]
6. Hosseinian, A.; Ylä-Mella, J.; Pongrácz, E. Current Status of Circular Economy Research in Finland. *Resources* **2021**, *10*, 40. [CrossRef]
7. Hoffman, T.C.; Zitomer, D.H.; McNamara, P.J. Pyrolysis of wastewater biosolids significantly reduces estrogenicity. *J. Hazard. Mater.* **2016**, *317*, 579–584. [CrossRef]
8. Moško, J.; Pohořelý, M.; Cajthaml, T.; Jeremiáš, M.; Robles-Aguilar, A.A.; Skoblia, S.; Beňo, Z.; Innemanová, P.; Linhartová, L.; Michalíková, K.; et al. Effect of pyrolysis temperature on removal of organic pollutants present in anaerobically stabilized sewage sludge. *Chemosphere* **2021**, *265*, 129082. [CrossRef]
9. Jeon, S.; Kim, D.-J. Enhanced phosphorus bioavailability and heavy metal removal from sewage sludge ash through thermochemical treatment with chlorine donors. *J. Ind. Eng. Chem.* **2018**, *58*, 216–221. [CrossRef]
10. Gorazda, K.; Tarko, B.; Werle, S.; Wzorek, Z. Sewage sludge as a fuel and raw material for phosphorus recovery: Combined process of gasification and P extraction. *Waste Manag.* **2018**, *73*, 404–415. [CrossRef]
11. Xia, Y.; Tang, Y.; Shih, K.; Li, B. Enhanced phosphorus availability and heavy metal removal by chlorination during sewage sludge pyrolysis. *J. Hazard. Mater.* **2020**, *382*, 121110. [CrossRef] [PubMed]
12. Han, H.; Hu, S.; Syed-Hassan, S.S.A.; Xiao, Y.; Wang, Y.; Xu, J.; Jiang, L.; Su, S.; Xiang, J. Effects of reaction conditions on the emission behaviors of arsenic, cadmium and lead during sewage sludge pyrolysis. *Bioresour. Technol.* **2017**, *236*, 138–145. [CrossRef] [PubMed]
13. Chen, T.; Zhang, Y.; Wang, H.; Lu, W.; Zhou, Z.; Zhang, Y.; Ren, L. Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresour. Technol.* **2014**, *164*, 47–54. [CrossRef] [PubMed]

14. Meng, X.; Huang, Q.; Xu, J.; Gao, H.; Yan, J. A review of phosphorus recovery from different thermal treatment products of sewage sludge. *Waste Dispos. Sustain. Energy* **2019**, *1*, 99–115. [CrossRef]
15. Skoglund, N. Ash Chemistry and Fuel Design Focusing on Combustion of Phosphorus-Rich Biomass. Ph.D. Thesis, Comprehensive Summary. Umeå Universitet, Umea, Sweden, 2014.
16. Skoglund, N.; Grimm, A.; Ohman, M.; Boström, D. Effects on Ash Chemistry when Co-firing Municipal Sewage Sludge and Wheat Straw in a Fluidized Bed: Influence on the Ash Chemistry by Fuel Mixing. *Energy Fuels* **2013**, *27*, 5725–5732. [CrossRef]
17. Khiari, B.; Marias, F.; Zagrouba, F.; Vaxelaire, J. Analytical study of the pyrolysis process in a wastewater treatment pilot station. *Desalination* **2004**, *167*, 39–47. [CrossRef]
18. Miller, S.F.; Miller, B.G. The occurrence of inorganic elements in various biofuels and its effect on ash chemistry and behavior and use in combustion products. *Fuel Process. Technol.* **2007**, *88*, 1155–1164. [CrossRef]
19. Zevenhoven, M.; Yrjas, P.; Skrifvars, B.-J.; Hupa, M. Characterization of Ash-Forming Matter in Various Solid Fuels by Selective Leaching and Its Implications for Fluidized-Bed Combustion. *Energy Fuels* **2012**, *26*, 6366–6386. [CrossRef]
20. Pettersson, A. Characterisation of Fuels and Fly Ashes from Co-Combustion of Biofuels and Waste Fuels in a Fluidised Bed Boiler. A Phosphorus and Alkali Perspective. Ph.D. Thesis, Chalmers Tekniska Högskola, Göteborg, Sweden, 2008.
21. Moradian, F.; Tchoffor, P.A.; Davidsson, K.O.; Pettersson, A.; Backman, R. Thermodynamic equilibrium prediction of bed agglomeration tendency in dual fluidized-bed gasification of forest residues. *Fuel Process. Technol.* **2016**, *154*, 82–90. [CrossRef]
22. Bale, C.W.; Bélisle, E.; Chartrand, P.; Decterov, S.A.; Eriksson, G.; Gheribi, A.E.; Hack, K.; Jung, I.H.; Kang, Y.B.; Melançon, J.; et al. FactSage thermochemical software and databases, 2010–2016. *Calphad* **2016**, *54*, 35–53. [CrossRef]
23. Vali, N.; Lars-Erik, A.; Combres, A.; Richards, T.; Pettersson, A. Pyrolysis of Municipal Sewage Sludge to Investigate Char and Phosphorous Yield together with Heavy-Metal Removal-Experimental and by Thermodynamic Calculations. *Energies* **2021**, *14*, 1477. [CrossRef]
24. Gascó, G.; Paz-Ferreiro, J.; Méndez, A. Thermal analysis of soil amended with sewage sludge and biochar from sewage sludge pyrolysis. *J. Anal. Calor.* **2012**, *108*, 769–775. [CrossRef]
25. Lidman Olsson, E.O.; Glarborg, P.; Leion, H.; Dam-Johansen, K.; Wu, H. Release of P from Pyrolysis, Combustion, and Gasification of Biomass A Model Compound Study. *Energy Fuels* **2021**, *35*, 15817–15830. [CrossRef]
26. Häggström, G.; Hannl, T.K.; Hedayati, A.; Kuba, M.; Skoglund, N.; Öhman, M. Single Pellet Combustion of Sewage Sludge and Agricultural Residues with a Focus on Phosphorus. *Energy Fuels* **2021**, *35*, 10009–10022. [CrossRef]
27. Raboy, V. Approaches and challenges to engineering seed phytate and total phosphorus. *Plant Sci.* **2009**, *177*, 281–296. [CrossRef]
28. Pedersen, A.J.; van Lith, S.C.; Frandsen, F.J.; Steinsen, S.D.; Holgersen, L.B. Release to the gas phase of metals, S and Cl during combustion of dedicated waste fractions. *Fuel Process. Technol.* **2010**, *91*, 1062–1072. [CrossRef]
29. Han, J.; Xu, M.; Yao, H.; Furuuchi, M.; Sakano, T.; Kanchanapiya, P.; Kanaoka, C. Partition of Heavy and Alkali Metals during Sewage Sludge Incineration. *Energy Fuels* **2006**, *20*, 583–590. [CrossRef]
30. Kumpiene, J.; Brännvall, E.; Wolters, M.; Skoglund, N.; Čirba, S.; Aksamitauskas, V.Č. Phosphorus and cadmium availability in soil fertilized with biosolids and ashes. *Chemosphere* **2016**, *151*, 124–132. [CrossRef]
31. Hupa, M. Ash-Related Issues in Fluidized-Bed Combustion of Biomasses: Recent Research Highlights. *Energy Fuels* **2012**, *26*, 4–14. [CrossRef]