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Entrained Flow Plasma Gasification of Sewage Sludge–Proof-of-Concept and Fate of Inorganics

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Abstract: Sewage sludge is a residue of wastewater processing that is biologically active and consists of water, organic matter, including dead and living pathogens, polycyclic aromatic hydrocarbons, and heavy metals, as well as organic and inorganic pollutants. Landfilling is on the decline, giving way to more environmentally friendly utilisation routes. This paper presents the results of a two-stage gasification–vitrification system, using a prototype-entrained flow plasma-assisted gasification reactor along with ex situ plasma vitrification. The results show that the use of plasma has a considerable influence on the quality of gas, with a higher heating value of dry gas exceeding 7.5 MJ/m_N^3, excluding nitrogen dilution. However, dilution from plasma gases becomes the main problem, giving a lower heating value of dry gas with the highest value being 5.36 MJ/m_N^3 when dilution by nitrogen from plasma torches is taken into account. An analysis of the residues showed a very low leaching inclination of ex-situ vitrified residues. This suggests that such a system could be used to avoid the problem of landfilling significant amounts of ash from sewage sludge incineration by turning inorganic residues into a by-product that has potential use as a construction aggregate.

Keywords: gasification; plasma; sewage sludge; inorganics; leaching

1. Introduction

Sewage sludge is a residue created during wastewater treatment and is becoming increasingly troublesome. Water, organic matter, as well as organic and inorganic contaminants, including polycyclic aromatic hydrocarbons (PAHs) and heavy metals, can be found in sewage sludge in various concentrations [1,2]. The possibility of biological activity in sewage sludge must be considered when it is used. As a result, a great deal of study has been done on sewage sludge deactivation and stabilisation [3–8] through many different thermal utilisation routes: thermal hydrolysis [9], hydrothermal carbonisation (HTC) [10–12], HTC integrated with anaerobic digestion [13,14], torrefaction [15,16], pelletising [17], pyrolysis and co-pyrolysis [18,19], gasification [20–23], and combustion [24].

Sewage sludge is regulated at both the European Union (EU) and national levels due to a variety of environmental, health, and safety issues. In the case of national rules, some are more stringent than the criteria laid down by EU legislation [25–27]. Figure 1, which is based on Eurostat's official statistics [28], shows the production of sewage sludge in all EU countries and the amounts currently applied in agriculture and incineration. There are approx. 60,000 wastewater treatment plants across Europe [29], and the location of plants might not always be logistically favourable when application in agriculture (land spreading) is considered, which is related to the high moisture content of the material. Agricultural application is also limited by the permissible limits on heavy metal content, i.e., 20 mg/kg$_{dry}$ of Cd, 1000 mg/kg$_{dry}$ of Cu, 16 mg/kg$_{dry}$ of Hg, 300 mg/kg$_{dry}$ of Ni, 750 mg/kg$_{dry}$ of Pb, and 2500 mg/kg$_{dry}$ of Zn, as specified in European Council Directive 86/278/EEC [30]. For agricultural use, the threat of microplastics should also be taken into serious consideration [31].

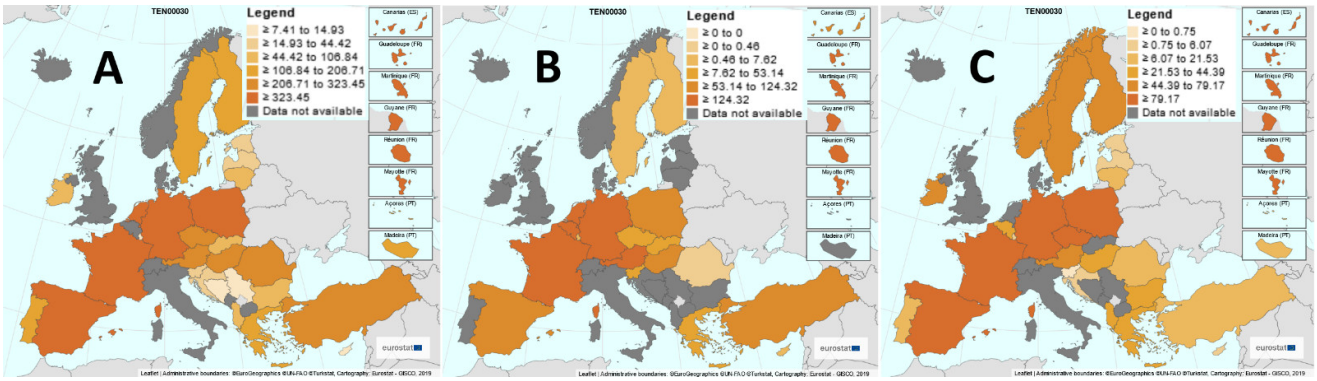

Figure 1. Sewage sludge production and disposal from urban wastewater (unit–thousand tonnes of dry mass) in 2016 based on the Eurostat Database [28]: (**A**) sewage sludge production (total); (**B**) sewage sludge utilisation by incineration; (**C**) sewage sludge disposal by agricultural use (data for later years not reported by many countries).

The following regulations are important on the EU level [26,27]:

- The Water Framework Directive (2000/60/EC)
- Directive 91/271/EEC (amended by Council Directive 2013/64/EU of 17 December 2013)
- Integrated pollution prevention and control directive (Directive 96/61/EC),
- Waste Landfilling Directive (99/31/EC)
- Sludge Use in Agriculture Directive (86/278/EEC)

Conversion of solid fuel to gas is the main point of gasification [32,33]. When air is used as a gasification agent, the main product called "producer gas" consists mainly of H_2, CO, CO_2, and N_2 [34–36]. Hydrocarbons are also present, among which methane is the most significant of all non-condensable gases [37,38]. Phenols, toluene, naphthalene, benzene, and other aromatic chemicals, as well as more complex condensable compounds, are also present [39–42]. Compounds with an atomic mass higher than benzene are often referred to as tars [43–46]. Gasification has been investigated extensively for many different materials [47–54].

Intensive investigation into the gasification of sewage sludge and the subsequent use of producer gas has been performed for many years. Werle discovered that the laminar flame speed rose along with the hydrogen level in the producer gas from sewage sludge [55]. Such gas could be usedin spark-ignition engines [56]. Nonetheless, to get adequate performance out of a spark-ignition engine, producer gas from sewage sludge requires a 40% addition of methane, according to Szwaja et al. [57].

According to Werle and Dudziak, phenols and their derivatives make up the great bulk of tars produced by gasification of sewage sludge [58]. Pawlak-Kruczek et al. [59] recommended using a tar-deposition diagram to predict the potential severity of tar de-

position problems in gas coolers. Using this tool, the study demonstrated that significant torrefaction of sewage sludge prior to steam gasification reduced the content of tars with melting points above 40 °C [59]. In terms of sewage sludge thermal utilisation, gasification has been considered as an interesting alternative to incineration, with some works even proposing such a thermal route, leading to gas-powered plants with negative CO_2 emissions [60].

The amount of information available in the literature on commercial sewage sludge gasification plants is quite minimal. A case study on the commercial-scale gasification of sewage sludge for the Greek island of Psittaleia was conducted using the Gasif Eq equilibrium model, which was performed by Montouris et al. [61]. It was discovered that plasma gasification of sewage sludge could result in net power production [61]. The calculation, which was carried out for a hypothetical plant with a processing rate of 250 tonnes per day (moisture content 68%), revealed the possibility of supplying 2.85 MW of electricity [61]. Experiments using two-step plasma processing units were effective for several research groups [62,63], proving the concept's general practicality in a lab setting and the prospect of lowering the tar level to 90 mg/m_N^3 [63]. Brachi et al. [64] determined that gasification of sewage sludge, with the combustion of the gas in a CHP unit, could be economically feasible for a real wastewater treatment plant that serves a 1.2 million population equivalent in Southern Italy.

2. Aim of the Study and Justification

State-of-the-art incineration of sewage sludge is capable of significantly reducing its mass. However, the content of incombustible inorganics (ash) in sewage sludge may reach a value as high as a quarter or even a third of its dry mass (e.g., see Table 1). Moreover, combustion is never complete, which adds to the total mass of the waste still left after combustion. Therefore, it is plausible to state that incineration is only a partial solution to the sewage sludge problem because a significant part of the mass of the original waste stream still needs to be landfilled.

Table 1. Range of values for proximate and ultimate analysis of sewage sludge, based on our own analyses using samples from wastewater treatment plants in Wrocław (Janówek) and Brzeg (all data given on dry basis).

Proximate Analysis	
Volatile Matter content	56.0–58.1%$_{dry}$
Fixed Carbon	9.4–17.8%$_{dry}$
Ash content	26.2–32.5%$_{dry}$
Higher Heating Value	13.66–15.70 MJ/kg
Ultimate Analysis	
C content	27.89–32.16%$_{dry}$
H content	2.86–6.67%$_{dry}$
N content	4.36–4.83%$_{dry}$
S content	0.29–0.81%$_{dry}$
O content	28.80–33.14%$_{dry}$

After incineration, both bottom and fly ash have their own respective waste codes, according to the European Parliament and Council Regulation (EC) No 2150/2002 on waste statistics, enacted on 25 November 2002. Hazardous and non-hazardous bottom ash and slag receive the waste codes 19 01 11 and 19 01 12, respectively. Similarly, fly ash receives the code 19 01 13 or 19 01 14, depending on the hazard involved. Such waste is then deemed ready to be directed to the appropriate landfill which is selected based on Council Decision 2003/33/EC of 19 December 2002, which establishing procedures and criteria for accepting waste at landfills. The document states specific limits regarding leaching limits for different

types of landfills. This implies a certain cost, i.e., gate fees associated with landfilling along with the transportation cost of the waste to an appropriate landfill site.

Such cost can be avoided if the waste is turned into a product, which is possible based on Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008. In Article 6, the directive outlines the requirements for obtaining end-of-waste status: waste which has undergone a recycling or other recovery operation is considered to have ceased to be waste if it complies with the following conditions:

- the substance or object is to be used for specific purposes,
- a market or demand exists for such a substance or object,
- the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products, and
- the use of the substance or object will not lead to overall adverse environmental or human health impacts.

Moreover, promoting such an approach is beneficial for member states because turning sewage sludge into fuel is not counted towards the attainment of the recycling targets, as stated by the directive: (Article 11a–Rules on the calculation of the attainment of the targets).

The outcome would not be much different for technologies competitive with incineration, such as gasification, in which unconverted carbon would also significantly contribute to the amount of waste left after the process. Therefore, in the case of gasification, the possibility to turn post-process solid waste into a product should not be overlooked. However, such a product would still need to comply with the requirements regarding avoiding adverse environmental or human health impacts and the existing market for such product. Environmental and human health impacts could be effectively minimised if the waste is inert, which could be determined based on requirements set by the Council Decision 2003/33/EC of 19 December 2002 (see Table 2).

Table 2. Leaching limit values for inert waste (for different allowed test procedures) set by the Council Decision 2003/33/EC of 19 December 2002 [65] (dry substance—data given on dry basis).

Component	Test		
	L/S = 2 dm^3/kg	L/S = 10 dm^3/kg	C0 (Percolation Test)
	mg/kg $_{dry\ substance}$	mg/kg $_{dry\ substance}$	mg/dm^3
As	0.1	0.5	0.06
Ba	7	20	4
Cd	0.03	0.04	0.02
Cr $_{total}$	0.2	0.5	0.1
Cu	0.9	2	0.6
Hg	0.003	0.01	0.002
Mo	0.3	0.5	0.2
Ni	0.2	0.4	0.12
Pb	0.2	0.5	0.15
Sb	0.02	0.06	0.1
Se	0.06	0.1	0.04
Zn	2	4	1.2
Chloride	550	800	460
Fluoride	4	10	2.5
Sulphate	560	1 000	1 500
Phenol index	0.5	1	0.3

One of the promising ways to obtain such values is by vitrification, which changes the structure of waste, such as ash, in a way that makes its structure resemble amorphous crystals, such as glass. Such a structure could effectively immobilise hazardous waste components, such as heavy metals, and significantly decrease the rate of leaching, thus enabling the possibility of such waste to be considered inert.

The aim of this study is to provide a proof-of-concept for the two-step plasma gasification of sewage sludge with vitrification of inorganic residues, thereby allowing the residue to be turned into a valuable product that complies with all norms regarding its influence on the environment.

3. Materials and Methods

The gasification of sewage sludge was performed using a bespoke rig as shown in Figure 2. The rig was equipped with a plasma torch, using N_2 to generate the plasma. The reactor wall was built of stainless steel with a ceramic refractory. The temperature at the edge of the refractory was measured using a K-type thermocouple inserted into the top revisory hole. Gasification in the reactor was performed in an entrained flow, with residence time on the order of magnitude of 1 s. Pre-dried sewage sludge was brought from the Municipal Wastewater Treatment plant in Janówek (near Wrocław, Poland). The plant in Janówek is equipped with anaerobic digestion reactors. After anaerobic digestion, the sludge is dried in a rotary drum dryer. Samples of pre-dried sewage sludge were taken at the outlet of the drier.

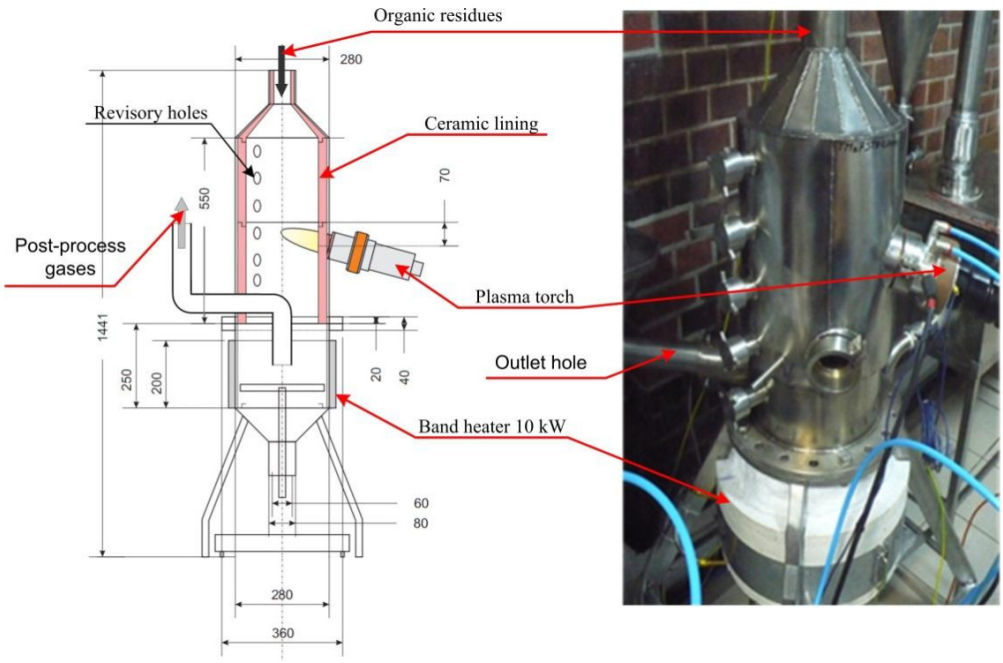

Figure 2. Experimental rig for plasma gasification of sewage sludge.

An experimental matrix for performed entrained flow plasma-assisted gasification experiments is provided in Table 3. Gasification was performed with different plasma-gas-to-fuel ratios (PGFR) as well as different air-to-fuel ratios (AFR). Mass flow rates of plasma gas were calculated using flow rates measured with rotameters and density of nitrogen in normal conditions. Additionally, during gasification, air was supplied to the reactor along with fine particles of sewage sludge (d < 1 mm), entrained from the auger located on the top of the gasifier. The two-phase mixture was fed from the top of the reactor into the freeboard, located over the streams of hot plasma, generated by plasma torches. The producer gas was removed from the bottom of the reactor (see Figure 2). Tangential placements of plasma torches enforced cyclonic flow inside of the reactor.

Table 3. Experimental matrix for plasma-assisted gasification of pre-dried sewage sludge (R-wall indicates refractory wall).

Exp. ID	AFR	PGFR	I	$T_{R\text{-}wall}$
	–	–	A	°C
I	0.43	6.73	100	650
II	0.33	7.36	80	620
III	0.29	6.73	100	680
IV	0.33	7.85	100	680
V	0.29	6.31	80	620

Ex situ vitrification experiments were performed using a plasma torch located over a pile of post-gasification residues in a simple rectangular reactor, built using heat resistant bricks. Post-gasification residues, gathered during gasification experiments, sintered and melted, whereas any additional gases created during the process were directed into the fume hood and subsequently to the ventilation system. The vitrified residue was subsequently removed from the reactor using a chisel. Furthermore, a chisel was used to chip off any small fragments of brick lining from the vitrified sample. Subsequently, leaching tests were performed in an external laboratory, in compliance with methods outlined by the EU in the Council Decision 2003/33/EC of 19 December 2002.

Proximate analysis was performed using a Perkin–Elmer Diamond TGA (thermogravimetric analyser). The following program was applied during tests:

- Heat to 105 °C; ramp at 10 °C/min + hold for 10 min
- (2 a) Air was used to determine ash content: Heat to 815 °C; ramp at 50 °C/min + hold for 15 min
- (2 b) N_2 was used to determine the volatile matter content: Heat to 850 °C; ramp at 50 °C/min + hold for 15 min

The IKA C2000 basic bomb calorimeter was used to calculate the higher heating value, in compliance with ISO 1928. The isoperibolic method was used. Ultimate analysis was performed using Perkin–Elmer 2400 analyser, according to polish standard PKN-ISO/TS 12902:2007.

Oxide analysis was performed using the Atomic Absorption Spectrometry method, with AAnalyst 400 analyser. Samples were burned in the oven under the ashing temperature equal to 815 °C (residence time–3 h). Afterwards, between 100 and 150 mg of ash were diluted in 5 mL of HNO_3 and 3 mL of HF and subsequently mineralized in a Multiwave 3000 microwave oven, under 250 °C and 60 bar (pressure ramp 0.5 bar/s) for 80 min. Mineralized samples were diluted in 18 mL of saturated boric acid to bind free fluorides. Then the solution was diluted using distilled water (18.2 MΩ·cm) to obtain the final sample volume of 100 mL.

4. Results and Discussion

4.1. Two-Stage Sewage Sludge Utilisation Process–Stage I: Plasma-Assisted Gasification

The pre-dried sewage sludge from the wastewater treatment plant in Janówek, near Wrocław, was characterised, and the results of the proximate and ultimate analysis of the gasification feedstock are reported in Table 4.

The results for each of the plasma-assisted gasification experiments are shown in Table 4 and Figures 3–7. It can be clearly seen that the dilution strongly influenced the lower heating values of the producer gas (Table 5). However, results of calculations performed for the dry producer gas, without taking inert nitrogen into account, showed that the use of plasma positively influenced the heating value of the producer gas since values of HHV, close to 8 MJ/m_N^3 could be achieved. The real LHV values (Table 5) are similar to those obtained by Striūgas et al. [63], who performed plasma-assisted gasification of sewage sludge and achieved an LHV of 4.82 MJ/m_N^3.

Table 4. Proximate and ultimate analysis of the pre-dried sewage sludge from Municipal Wastewater Treatment plant in Janówek (near Wrocław, Poland): HHV–Higher Heating Value; C–carbon content; H–hydrogen content; N–nitrogen content; S–sulphur content; O–oxygen content] (dry—data given on dry basis; as received—data given on as received basis).

	Value	Unit
Volatile matter	56.0	$\%_{dry}$
Fixed carbon	17.8	$\%_{dry}$
Ash	26.2	$\%_{dry}$
Moisture	7.5	$\%_{as\ received}$
HHV	13.658	MJ/kg
C	32.16	$\%_{dry}$
H	2.86	$\%_{dry}$
N	4.83	$\%_{dry}$
S	0.81	$\%_{dry}$
O	33.14	$\%_{dry}$

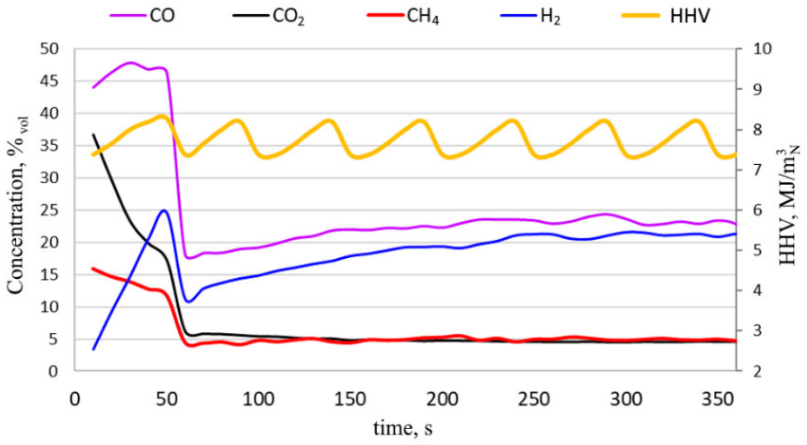

Figure 3. Plasma assisted gasification of sewage sludge–ID I (concentrations after excluding nitrogen supplied by plasma torch).

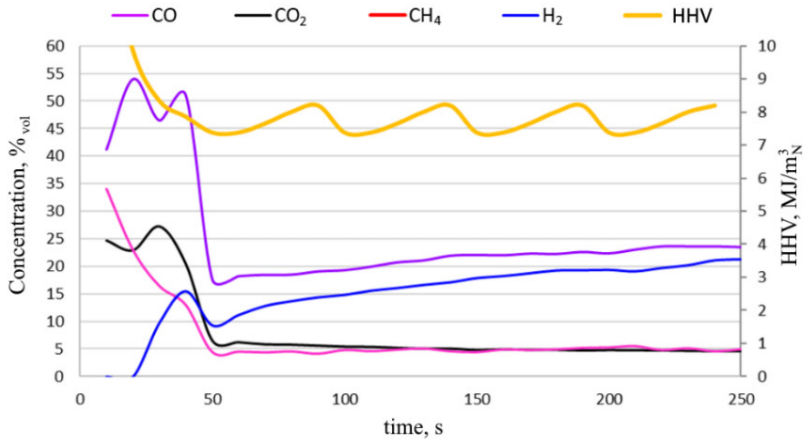

Figure 4. Plasma assisted gasification of sewage sludge–ID II (concentrations after excluding nitrogen supplied by plasma torch).

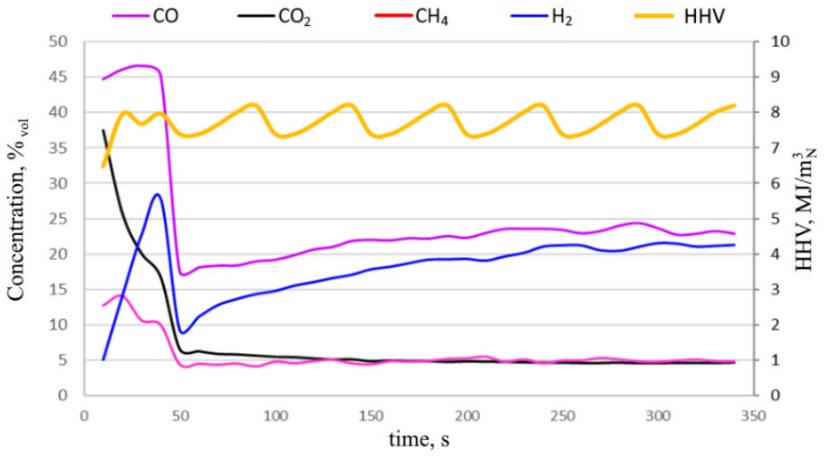

Figure 5. Plasma assisted gasification of sewage sludge–ID III (concentrations after excluding nitrogen supplied by plasma torch).

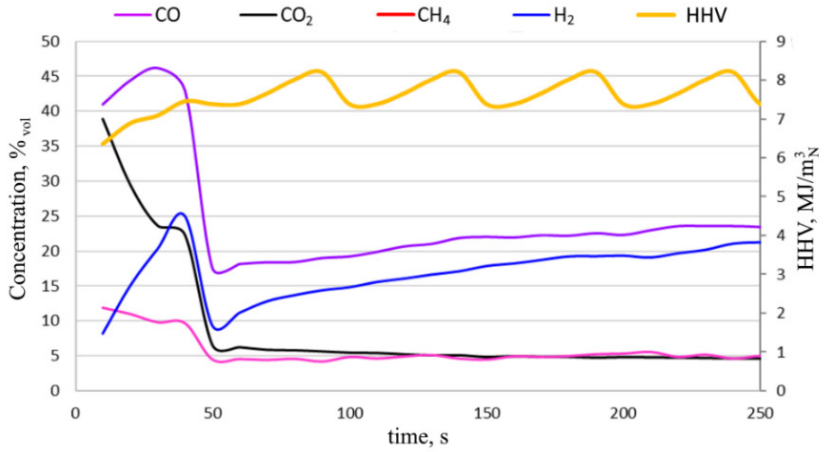

Figure 6. Plasma assisted gasification of sewage sludge–ID IV (concentrations after excluding nitrogen supplied by plasma torch).

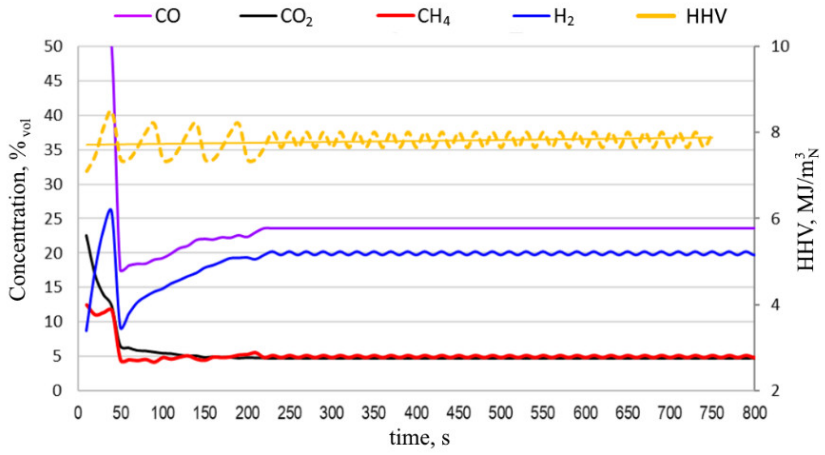

Figure 7. Plasma assisted gasification of sewage sludge–ID V (concentrations after excluding nitrogen supplied by plasma torch).

Table 5. Lower heating value (LHV) of dry producer gas for each test.

Experiment ID	Average LHV of the Gas, MJ/m_N^3
I	4.80
II	4.00
III	4.70
IV	3.96
V	5.36

Temperature is important in the gasification process, which is also the case for sewage sludge gasification [66]. Werle noticed a decrease in temperature and an increase in the concentration of combustible components in the producer gas with an increased oxygen content of the sludge [67]. Moreover, increased air temperature at the entrance of a fixed bed gasifier, according to observation, enhanced the production of combustible chemicals during the gasification of sewage sludge [68]. However, the temperature of the walls of the reactor was between 620 and 680 °C, which suggested that the average temperature in the reactor was much smaller than for Striūgas et al. [63], where the temperature at the exit was 1100 °C [63]. The hydrogen content in the gas was higher in comparison to the work of Striūgas et al. [63], reaching 20%$_{vol}$ compared to approx. 14.5%$_{vol}$ [63]. This was much less than in the case of fluidised bed gasification and fixed bed gasification, where observed concentrations of hydrogen were higher than 40% [69] and 30% [70], respectively. This suggested that the plasma treatment slightly decreased hydrogen content in the treated producer gas. This was in qualitative agreement with the results of Wnukowski et al. [71], who reported treatment of a model (artificially prepared) producer gas with microwave plasma and observed a slight decrease in H_2 content [71]. In the work of Striūgas et al. [63], plasma was applied to gas from a downdraft gasifier in a separate reactor. In the work of Chun and Song, microwave-induced fixed gasification of sewage sludge was performed, also giving an H_2 content close to 20%$_{vol}$ [72]. This suggested that the presence of gasified sewage sludge particles in the plasma also has some influence on the composition of the gas and on reaction pathways. This could suggest some autocatalytic effect and requires further investigation.

In each of the cases, the startup took only about 50 s. After the startup, an initial stabilisation period was observed when the gasifier was not fully in equilibrium and conditions were gradually changing, with the heating value of the gas changing in a cycle. Such cycles can be explained by changes in C_xH_y in the composition of the gas, caused by pyrolysis of relatively heavy sewage sludge that was falling at the bottom of the reactor. After devolatilisation, the particles of char from sewage sludge subsequently became lighter and were entrained. Such a stabilisation period took an additional 200 s, depending on the temperature (Figures 3–7). It was followed by a steady-state period, which was distinguished by the decreased amplitude of cycling the HHV of syngas. The longest test was performed for 13 min (Figure 7), so it could reasonably be expected that long-term stable operation of the unit is possible, provided the variability in the fuel quality is not high and the wear on the plasma torches is not significant.

4.2. Two-Stage Sewage Sludge Utilisation Process—Stage II: Plasma Vitrification

In general, vitrification aimed at obtaining an aggregate that could be used as a construction material can be performed in two different ways: in situ and ex situ. Ex situ vitrification can be performed for the residue after gasification, as well as for the ash after incineration. Ex situ vitrification has some disadvantages, as unburned carbon can still be converted during this process by oxidation, which could result in gaseous by-products, which would contribute to emissions of the installation. Conversion could be avoided with the introduction of an inert atmosphere for vitrification. However, in such a case, a high cost would be involved with the production or purchase of nitrogen. Furthermore, this would mean an additional unit operation in the process chain. On the other hand, in situ vitrification can be applied for gasification inside the reactor if temperatures are

sufficiently high. This is possible if sufficiently high amounts of heat are provided to the gasification reactor, which could be achieved using plasma torches. Benefits include high carbon conversion and stabilisation of the process, which offers better controllability, making it less sensitive to poor-quality fuels. Such an effect could also be achieved by using oxygen or air pre-heated to high temperatures as a gasifying agent.

The results (Table 6) showed that vitrified residues could be considered inert material. Only the content of phenols exceeded the limits. This was probably a result of soot depositions created from residual carbon, but overall, this can be amended by improvements in the offtake of gases from vitrification.

Table 6. Leaching for vitrified residues after plasma gasification of sewage sludge from the wastewater treatment plant in Wrocław–Janówek (leaching performed with L/S = 10 L/kg; dry substance—data given on dry basis).

Component	Obtained Value	Limit for Inert Materials
	mg/kg $_{\text{dry substance}}$	mg/kg $_{\text{dry substance}}$
As	<0.10	0.5
Ba	0.09 ± 0.03	20
Cd	<0.01	0.04
Cr total	<0.01	0.5
Cu	0.050 ± 0.016	2
Hg	<0.0001	0.01
Mo	<0.20	0.5
Ni	<0.01	0.4
Pb	<0.01	0.5
Sb	<0.20	0.06
Se	<0.20	0.1
Zn	<0.01	4
Chloride	<10.0	800
Fluoride	<1.00	10
Sulphate	394 ± 118	1 000
Phenol index	54 ± 12	1

It could be noticed that the composition of ash in post-gasification residues did not deviate significantly with respect to raw sewage sludge (see Table 7). The temperature of the reactor did not seem to have a significant influence on the ash composition as only two tests deviated significantly from the rest, namely ID II and ID IV. The temperature of the reactor during ID II was relatively low, looking at the temperature of the edge of the wall (see Table 4), whereas the temperature during ID IV was among the highest. During ID II, the concentration of Al_2O_3 was slightly higher, whereas for ID IV the concentration of SiO_2 was slightly higher compared to other tests. Moreover, for ID IV, the concentration of CaO was slightly lower than in other tests, as well as for the raw sewage sludge sample. The inhomogeneous character of sewage sludge seems to be the most plausible explanation for such behaviour.

Table 7. Ash composition for residues from different gasification trials.

Sample	K_2O	Na_2O	CaO	Mn_3O_4	Fe_2O_3	MgO	Al_2O_3	TiO_2	SiO_2
ID I	1.71	0.20	26.7	0.19	16.1	3.43	7.84	1.30	42.57
ID II	1.88	0.85	24.6	0.19	15.7	2.70	12.00	1.32	40.72
ID III	1.74	0.76	25.3	0.18	15.7	2.77	6.80	1.27	45.43
ID IV	1.57	0.93	19.0	0.17	14.5	3.16	7.97	1.10	51.55
ID V	1.54	0.67	25.5	0.19	15.3	2.71	7.86	1.28	44.98
Raw sewage sludge	1.63	0.44	28.2	0.18	16.4	3.46	6.99	1.22	41.45

5. Conclusions

Overall, the results of the leaching experiments using ex situ vitrified post-gasification residues, showed that the two-stage plasma gasification system can be efficiently used to make the inorganic part of sewage sludge inert. This showed that such a 2-stage system could be used for the thermal treatment of sewage sludge, allowing its use for energy purposes, with a possibility of the inorganic part reaching end-of-waste status, thus becoming a marketable product. Thus, the work could be considered a proof-of-concept. Nonetheless, the results of phenol leaching indicated that the off-gases from the second stage of the process (vitrification) could be problematic. Therefore, it seems plausible to suspect that a single-stage system with in situ vitrification could bring some additional benefits. Alternatively, a combination of non-plasma gasification and plasma vitrification would consume less electricity and still offer the benefits of fulfilling an end-of-waste protocol for inorganic residues and turning them into a marketable product. Plasma gasification makes sense only when the plasma-generating agent is not inert, which has a positive influence on the heating value of the gas without diluting it. Furthermore, additional valorisation, e.g., hydrothermal carbonization, and its influence on plasma gasification is a promising area for future studies. Moreover, additional work is recommended to prove the feasibility of the concept from an economic standpoint.

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