

Gasification of Sewage Sludge in a Rotary Kiln Reactor – A Case Study with Incorporation of Sewage Sludge Ash in Brick Production



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The gasification of sewage sludge (SS) was studied in a semi-industrial pilot plant consisting of a rotary kiln reactor. The gasification process was preceded by drying the SS in an integrated tubular rotating structure with built-in worm conveyors, to increase the dry matter (DM) content in the SS (> 90 wt.%). The released hydrogen-rich syngas from the gasification process of SS had low heating value (LHV) of approximately 8.83 MJ N⁻¹ m⁻³ (equal to 2.45 kWh N⁻¹ m⁻³) due to the high content of combustible gases H₂ (41.5 vol.%) and CH₄ (3.2 vol.%). Also investigated was the incorporation of sewage sludge ash (SSA) generated in the process of gasification as a partial substitute for clay in the production of clay bricks. Amounts of 5 wt.%, 10 wt.%, 20 wt.% of clay were replaced by SSA. By incorporating SSA at 5 wt.%, the new brick product achieved 4.5 % higher compressive strength compared to the control brick.

Keywords:

sewage sludge, gasification, syngas, sewage sludge ash, brick production, circular economy

Introduction

The trend towards the construction of wastewater treatment plants (WWTPs) has led to problems with the formation of significant quantities of sewage sludge (SS). According to EUROSTAT statistics, the total production of SS in the EU28 can be estimated at about 10 million tons of dry matter (DM).¹ The disposal of SS poses challenges to WWTPs, which must be addressed with traditional disposal methods or the application of innovative methods of use and/or recycling SS. There are two main solutions: disposing SS as solid waste in landfills, and using SS as fertilizer in agriculture. The direct use of SS in agriculture as a fertilizer or soil amendment is suitable due to its high organic matter content (>50 %) and the presence of nutrients (e.g., nitrogen (N) and phosphorus (P)) that can improve soil fertility.^{2,3} However, despite these advantages, this practice has been abandoned in many countries due to the environmental and health risks caused by the presence of potentially toxic substances in SS. The presence of heavy metals, trace elements,

pathogenic microorganisms, and organic pollutants limits the use of SS on agricultural and non-agricultural land.^{2,4} The limit for heavy metals in SS has been gradually tightened in many European countries, and this trend is expected to continue. The quality of SS has improved significantly over the last 30 years, with concentrations of some heavy metals trending downward. Although heavy metal pollution of SS has remained constant or even decreased in recent years, other pollutants are increasing. These include organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), microplastics, detergents and drug residues, personal care products, endocrine disruptors, anabolic steroids, and pathogens.^{3,5} The disposal of SS from WWTPs is also restricted under the new laws due to limited land resources and potential negative environmental impacts.^{4,6} Heating value (also called calorific value) is one of the most important factors in the suitability of SS as a solid fuel. Due to the volatile organic matter content, which ranges from 21–48 %, the heating value of stabilized and dehydrated SS reported in the literature varies in the range of 11–22 MJ kg⁻¹, indicating equal or higher

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values compared to various biomass samples.⁷ One of the waste residues with the highest phosphorus content in the world is SS, so many EU countries are enacting new laws requiring thermal treatment of SS and recovery (extraction) of phosphorus from sewage sludge ash (SSA), for example Sweden and Germany.^{5,8} Thermochemical treatment of SS at high temperatures reduces the mass and volume of SS and removes or destroys potentially hazardous materials from SS, promotes reuse and recycling of by-products to conserve landfills, optimizes land use, reduces CO₂ emissions, and protects groundwater. The main objectives of thermal treatment of SS can be considered as the following:

- Reduction of organic matter content in SS;
- Destruction of persistent organic pollutants;
- Extraction of inorganic substances (phosphorus, metals, etc.);
- Reduction of mass and volume;
- Utilization of energy stored in SS;
- Possibility of easier use and/or recycling of recovered SSA

Nowadays, three basic processes are mainly used for thermochemical treatment of SS – incineration (co- incineration), pyrolysis, and gasification. In the last two decades, more attention has been paid to the gasification process, which produces syngas as a clean fuel and solid residue SSA and/or biochar as a potentially hazardous waste that can be disposed of properly.

Some studies point out the advantages of gasification technology over other thermochemical treatment methods.⁸ Like other thermochemical treatment processes, SS gasification requires a lower moisture content, e.g., pre-drying SS, which involves significant energy consumption. To maximize the energy efficiency of the entire process, the heat released during SS gasification is usually used for pre-drying SS. In gasification, organic compounds are thermochemically transformed by partial oxidation at high temperatures (650–1000 °C) to maximize the gaseous products.^{6,9,10} There are three basic reactor types for gasification – fixed-bed downdraft, fixed-bed updraft, and fluidized-bed gasifier.^{11–13} The fluidized bed reactor achieves instantaneous entry of all phases required for the complete gasification process, making it superior to other reactors. Fluidized bed reactors can be a bubbling fluidized bed (BFB) or a circulating fluidized bed (CFB). The type of reactor also affects the efficiency of the process and consequently the concentration of tar and impurities in the product.^{9,14} The SS characteristics and various process parameters, such as equivalence ratio (ER), gas residence time, catalyst efficiency, and operating temperature influence the gasification efficiency, i.e., maximize gas

yield, improve gas quality, minimize tar yield, and improve overall process efficiency.¹⁴ High temperatures contribute to the yield of gaseous products and the reduction of tar and char, as well as the overall efficiency of the process.¹⁴ The major challenges in SS gasification are SS composition (moisture content, heavy metals, nitrogen, and sulfur), SSA disposal due to high content of inorganic substances (heavy metals), and minimization of tar content.^{9,14}

The heating value of the gases varied from 4 to 28 MJ N⁻¹ m⁻³ depending on the gasification system and the operating temperature.¹⁴ According to studies, the gasification agent was found to have a significant effect on the heating value of the synthesis gas produced.^{13,14} The gasification agent can be air, carbon dioxide, oxygen, steam, or a mixture thereof. After purification, the resulting gas can be used for various purposes, such as combined heat and power (CHP) or further processing and conversion of syngas into liquid fuel, or to produce ammonia, hydrogen, as well as for power generation with integrated gasification fuel cells (IGFC). The result is an electrical efficiency of about 21 % to 65 % with a minimum lifetime of 20 years.^{15–18} Solid residue, SSA, consists of particles the size of fine sand and silt, and is used in the ceramics industry as a filler or substitute for clay.¹⁹ The oxides present in SSA also make it a good substitute material for clay. Regarding the heavy metals present in SSA during the sintering process of ceramic products, the risk of possible leaching of hazardous compounds from SSA can be significantly reduced, resulting in a construction product of satisfactory quality, and avoiding disposal in landfills.^{19–21}

There are few publications on gasification of SS in a rotary kiln reactor, and in general there are no studies on gasification of SS in the Republic of Croatia.^{22,23}

The aim of this research was to investigate SS gasification in a semi-industrial pilot plant consisting of a rotary reactor as a way to dispose of SS in a safe and environmentally friendly manner. The quality of the synthesis gas produced and the solid residue, SSA, was determined. Subsequently, the reuse of SSA as a clay substitute in brick production was investigated for the assessment of potential recycling and management according to the new EU circular economy action plan.

Materials and methods

The SS samples used in this study were obtained from the Zagreb WWTP (1.2 million PE with secondary treatment stage), after anaerobic digestion and dewatering (with about 31 % DM), collected in May 2020. The physicochemical properties of

SS are listed in Table 1. The pH was determined by method HRN EN 15933:2013, TOC was determined by method HRN EN 15936:2013, TP by method HRN EN 15309:2008, DM by method HRN EN 12880:2005, and TN by method HRN EN 16169:2013. The higher and lower heating values of SS were determined by method HRN EN 15170:2010.

The organic and inorganic pollutants in the SS were determined, and are listed in Table 2. The heavy metals, copper, zinc, nickel, lead, cadmium, cobalt, arsenic, mercury, molybdenum, and selenium in the SS raw material were determined by method HRN EN 13657:2008, potassium by meth-

od HRN EN ISO 14911:2001, and chromate (Cr^{6+}) by method HRN ISO 11083:1998. Total petroleum hydrocarbons TPH (mineral oil) were determined by method HRN EN 14345:2005, polycyclic aromatic hydrocarbons (PAH) were determined by method SOP -145-053 (I), polychlorinated biphenyls (PCBs) by method EPA 8082, and hexachlorocyclohexane (HCH) and hexachlorobenzene (HCB) were determined by method EPA 8081 A.

Gasification of SS was carried out in a pilot plant, Fig. 1. The plant was designed and manufactured by the company Dok-Ing Energo Ltd. The plant consisted of the following units: Control cabinet, drying system (double rotating screw conveyors), main gasification reactor with rotary kiln, syngas cleaning system with cyclone and wet scrubbers (scrubbing liquid – water), and solids residue storage system.

The SS was fed into a drying system with double rotating screw conveyors (rotation of the inner screw and rotation of the outer conveyors) in a hot air stream $< 200\text{ }^\circ\text{C}$. The dried SS was fed into the main gasification reactor, which consisted of three chambers heated by silicon carbide (SiC) heating elements. Studies dealing with the gasification of SS show that the temperature at which the SS is gasified plays an important role in the composition and yield of the syngas. In other words, higher gasification temperatures result in higher gas yield due to higher conversion efficiency.²² Therefore in this study, SS gasification was carried out at $T = 900\text{ }^\circ\text{C}$. Gasification of SS with air is easy to handle and inexpensive.²⁴ An ER is the actual mass ratio of air to SS used in gasification relative to the mass ratio of air to SS required for stoichiometric combustion.²⁵ According to studies, lower ER causes incomplete gasification, resulting in high levels of liquid tar product and solid char residue. Performing gasification at higher ERs results in a better oxidation atmosphere that promotes combustion of higher fractions of tar and char, which influences higher yields of gaseous CO_2 and H_2O products and release of thermal energy, but also has an effect on syngas production and its heating value. A high ER causes the reduction of syngas yield. Therefore, it is important to achieve an optimal ER. According to some studies, the optimal ER is 0.2–0.4, and influences the maximization of CO , H_2 , CH_4 products, and some light hydrocarbons.^{25,26} The experimental tests were carried out with 10 kg of SS (with a moisture content of 8 %), the reactor was operated at atmospheric pressure, and under a limited oxidation atmosphere of maximum 6 % of the air supply in the reactor, without using steam. The SS gasification process was also performed without the use of a catalyst. During the experiment, SS was rapidly gasified to produce a gas mixture of hydrogen, car-

Table 1 – Physicochemical properties of SS

Parameters	SS sample	Unit
pH	12.5	
Total organic carbon (TOC)	25.9	wt. %
Total phosphorus (TP)	1.71	wt. %
Dry matter (DM)	33.2	wt. %
Total nitrogen (TN)	3.5	wt. %
Calorific value	HHV	11.74 MJ kg^{-1}
	LHV	10.80 MJ kg^{-1}

Table 2 – Organic and inorganic pollutants in SS sample

Parameters	SS sample	Unit
Total petroleum hydrocarbons TPH (Mineral oil)	31.4	mg kg^{-1}
Polycyclic aromatic hydrocarbon (PAH)	0.12	mg kg^{-1}
Polychlorinated biphenyl (PCB)	<1	mg kg^{-1} DM
Hexachlorocyclohexane (HCH)	<0.05	mg kg^{-1} DM
Hexachlorobenzene (HCB)	<0.05	mg kg^{-1} DM
Potassium	<0.05	wt. % DM
Chromate Cr^{6+}	<0.5	mg kg^{-1} DM
Chromium	21.8	mg kg^{-1} DM
Copper	452	mg kg^{-1} DM
Zinc	511	mg kg^{-1} DM
Nickel	24.6	mg kg^{-1} DM
Lead	61.7	mg kg^{-1} DM
Cadmium	<2	mg kg^{-1} DM
Cobalt	<10	mg kg^{-1} DM
Arsenic	1.32	mg kg^{-1} DM
Mercury	1.54	mg kg^{-1} DM
Molybdenum	2	mg kg^{-1} DM
Selenium	1.1	mg kg^{-1} DM

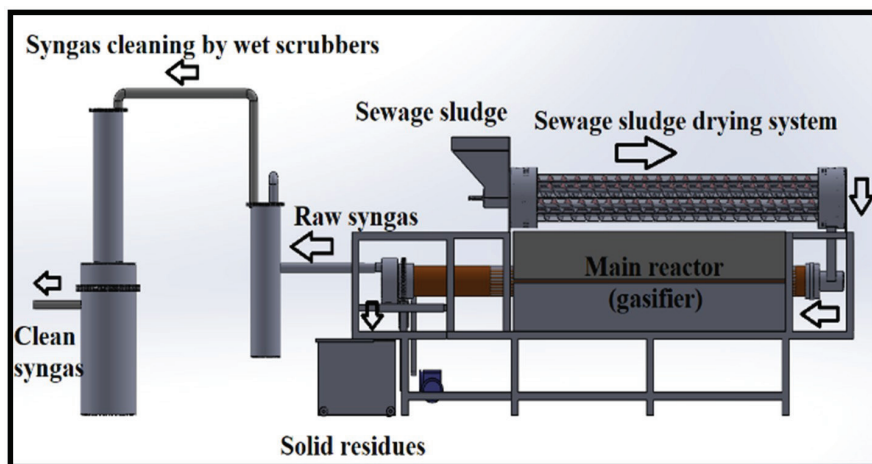


Fig. 1 – Gasification pilot plant

bon monoxide, carbon dioxide, and methane, as well as hydrogen sulfide, and other trace impurities. The syngas produced passed through a gas purification system with a cyclone and wet scrubbers. After wet scrubbing, the synthesis gas sample was taken in a gas sampling bag with valve, and its qualitative and quantitative composition was determined in the accredited laboratory Dr. Graner & Partner GmbH, Munich, according to DIN EN ISO 17025 – D- PL-18601-01-0. The composition of syngas is given in the Results section. The volume fraction of argon, hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, propane, i-butane, n-butane was determined according to DIN 51872-4 (GC-WLD). LHV was determined by calculation (DIN EN ISO 6976). Hydrogen sulfide and ammonia were determined by colorimetric method. Tetramethylsilane, trimethylsilane, hexamethyldisiloxane (L2), hexamethylcyclotrisiloxane (D3), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (L4) were determined by the method of i.A. VDI 3865 Bl.4 (GC-MS). Total chlorine, total fluorine, and total sulfur are determined according to DIN EN 38409 – H8 / DIN EN 10304. Total silicon and the sum of the organic silicon compounds were determined by calculation. The by-product of SS gasification is the solid residue, SSA. The resulting SSA was subjected to further physicochemical analysis with the determination of oxides and heavy metals to test the substitute material for clay in the production of bricks. Subsequently, it was tested whether the produced SSA could substitute clay in a proportion of 5 wt.%, 10 wt.%, and 20 wt.% in the manufacture of bricks. The proportions of each oxide are listed in the Results section in Table 5, and compared with the oxide proportions in the clay. The oxides were determined by atomic absorption spectroscopic analysis (AAAnalyst 200, PerkinElmer) performed by the Laboratory for Synthesis of New Materials, Division of Materials

Chemistry, Ruder Bošković Institute. The individual samples were first dissolved by boiling in an acid mixture in a steel autoclave with a Teflon cartridge, then diluted to the desired amount and measured. The proportions of heavy metals in the resulting SSA are listed in the Results section and compared with the proportions of heavy metals in the clay. The heavy metals in SSA and clay were determined by X-ray fluorescence (XRF) in the Laboratory of Nuclear Analytical Methods, Division of Experimental Physics of the Ruder Bošković Institute. Samples were crushed with a mortar and pestle, dry sieved ($\phi=45\ \mu\text{m}$), and pressed into thick pellets ($\phi=2.5\ \text{cm}$) weighing approximately 2 g. Subsequently, all samples were analyzed by EDXRF technique, where the excitation source was a Siemens X-ray tube with Mo anode and Mo secondary target in orthogonal geometry. The X-ray tube operated at 45 kV and 35 mA. Samples were irradiated in vacuum for 1000 s, and spectra were recorded using a Canberra Si (Li) detector with 3 mm thickness, 30 mm² active area, 0.025 mm Be window thickness, and 170 eV resolution (FWHM) at 5.9 keV. Spectra were analyzed using the software IAEA QXAS, and concentrations of K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb, and Th were determined by direct comparison of count rates with the standard reference material IAEA-SL -1 (Trace and minor elements in lake sediment).

The organic content in the SSA was determined using the loss on ignition (LOI) method, which is based on the mass loss at 550 °C to a constant mass.

Manufacture of bricks

In the Hydrotechnical Laboratory of the Faculty of Civil Engineering of the University of Zagreb, the laboratory production of bricks (full bricks) was carried out. The SSA was added to the clay mixture in a proportion of 5 %, 10 %, 20 % by weight as a

Table 3 – Proportions of raw materials and water in the brick mixture (wt.%)

Raw materials	Control brick	5 % SSA brick	10 % SSA brick	20 % SSA brick
clay	100	95	90	80
SSA	0	5	10	20
H ₂ O	31	34	30	35

replacement raw material. Clay used for the experiment was provided by Termoterra from Topusko. The dried raw materials were ground and then sieved through a 707 μm sieve. Four types of bricks were produced: Control brick (100 % clay), and 5 % SSA brick, 10 % SSA brick, 20 % SSA brick. Water requirements for handmade brick production are slightly higher than for machine production, as shown in Table 3. Due to the low plasticity and high CaO content in the composition, SSA has a high water absorption capacity. Therefore, mixtures containing SSA require a higher water content to be workable and moldable. However, it can be seen from Table 3 that these were insignificant deviations from the control brick.

After preparing the raw materials and adding water, the mixture was stirred. When the mixture was compact enough to be molded, it was manually pressed into molds. The bricks were then dried ($T = 105\text{ }^{\circ}\text{C}$, $t = 24\text{ h}$) and fired ($T = 950\text{ }^{\circ}\text{C}$ at a temperature rise of $5\text{ }^{\circ}\text{C min}^{-1}$) under the same conditions as the control bricks (100 % clay).²⁷ Disc-shaped bricks were produced, dimensions: diameter $d = 50\text{ mm}$, thickness $s = 14\text{ mm}$, weight $m = 46\text{--}48\text{ g}$. The compressive strength of bricks was tested in the Laboratory of Materials of the Faculty of Civil Engineering of the University of Zagreb, and is listed in the Results section. Compressive strength is defined as the resistance of an element to failure under a given load. The preparation of the samples and the tests were performed according to HRN EN 772-1. The test was performed on 3 samples.

Results and discussion

Results of the SS gasification process

Analysis of the produced syngas

During gasification, the organic part was converted into gaseous products, while the inorganic part remained mainly in the SSA. Table 4 shows the main components of the product gas, the main value of the syngas components, and some miscellaneous minor components.

Syngas is a mixture of carbon monoxide and hydrogen in various ratios, while in this case, it was

Table 4 – Composition of syngas

Gas composition	Result	L.O.Q.	Unit
Argon	0.2	0.1	vol. %
Hydrogen	41.5	0.1	vol. %
Oxygen	1	0.1	vol. %
Nitrogen	18.2	0.1	vol. %
Carbon monoxide	25.3	0.1	vol. %
Carbon dioxide	10.6	0.1	vol. %
Methane	3.2	0.1	vol. %
Ethane	< L.O.Q.*	0.01	vol. %
Propane	< L.O.Q.*	0.01	vol. %
i-Butane	< L.O.Q.*	0.01	vol. %
n-Butane	< L.O.Q.*	0.01	vol. %
Low calorific value Hi	8830		$\text{kJ N}^{-1}\text{ m}^{-3}$
Low calorific value Hi	2.45		$\text{kWh N}^{-1}\text{ m}^{-3}$
Hydrogen sulfide	720	1	mg m^{-3}
Ammonia	< L.O.Q.*	1	mg m^{-3}
Tetramethylsilane	< L.O.Q.*	0.1	mg m^{-3}
Trimethylsilanol	< L.O.Q.*	0.1	mg m^{-3}
Hexamethyldisiloxane (L2)	< L.O.Q.*	0.1	mg m^{-3}
Hexamethylcyclotrisiloxane (D3)	< L.O.Q.*	0.1	mg m^{-3}
Octamethyltrisiloxane (L3)	< L.O.Q.*	0.1	mg m^{-3}
Octamethylcyclotetrasiloxane (D4)	< L.O.Q.*	0.1	mg m^{-3}
Decamethyltetrasiloxane (L4)	< L.O.Q.*	0.1	mg m^{-3}
Decamethylcyclopentasiloxane (D5)	< L.O.Q.*	0.1	mg m^{-3}
Sum of org. silicium compounds	0		mg m^{-3}
Sum of silicium	0		mg m^{-3}
Chlorine total	< L.O.Q.*	1	mg m^{-3}
Fluorine total	< L.O.Q.*	1	mg m^{-3}
Sulfur total	680	1	mg m^{-3}

*L.O.Q – limit of quantitation

in the ratio $\text{CO}/\text{H}_2 = 1/1.6$. The composition of the gases had a high hydrogen content of 41.5 vol.% and of carbon monoxide 25.3 vol.%. The calorific value of the analyzed syngas was $8.8\text{ MJ N}^{-1}\text{ m}^{-3}$, which is within the range of literature values (4 to $28\text{ MJ N}^{-1}\text{ m}^{-3}$).¹⁴

Fig. 2 shows a comparison of syngas composition for this research and experimental data from the literature.^{22,28–30}

The volume fraction of hydrogen produced in this study was significantly higher compared to other SS gasification experiments under similar conditions. The high hydrogen content in syngas can be explained as follows. Similar studies on biomass

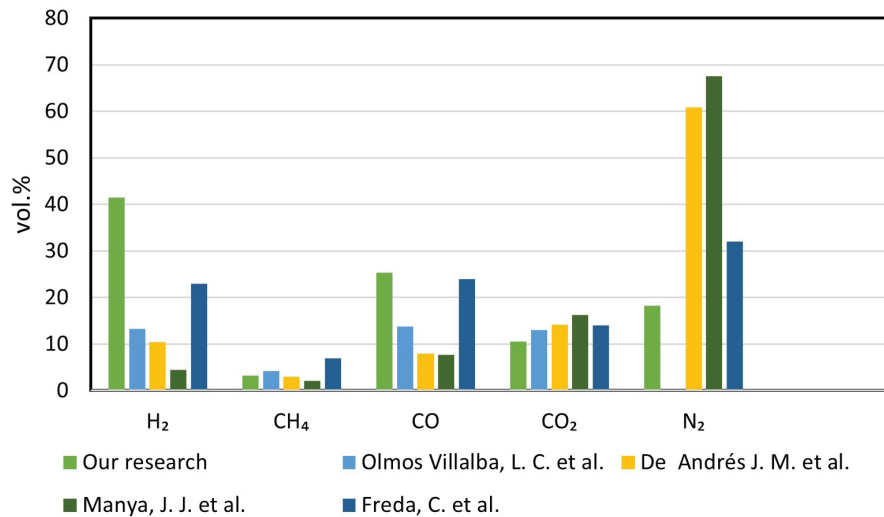


Fig. 2 – Comparison of syngas composition from Zagreb SS gasification and experimental data from the literature

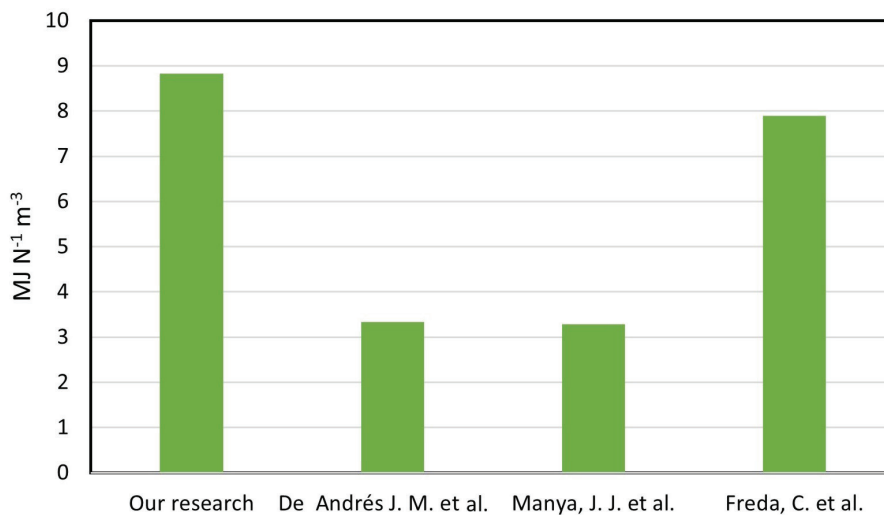


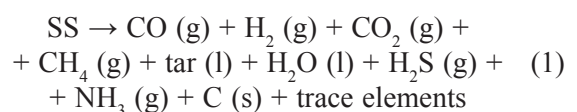
Fig. 3 – Comparison of LHV value of syngas from gasification of SS Zagreb with experimental data from literature

gasification show that a temperature of 900 °C increases H₂ content and decreases CH₄ and CO₂ content.¹⁴ This was confirmed in this study. Temperatures above 800 °C favor the prevalence of Boudouard reactions.³¹ Other studies have also shown that a temperature increase of 750–850 °C leads to an increase in energy and better conversion of carbon utilization, and thus to an increase in hydrogen content in the syngas mixture.²⁹ The gasification temperature has a significant impact on the quality of the synthesis gas. It should be recalled that high temperatures contribute to better conversion of char, but too high temperatures can lead to ash agglomeration and excessive oxidation of combustible gases.^{26,31} CO in the syngas produced in our experiment was also higher than in similar experiments in the literature. This could also be due to the choice of the optimal ER, as many researchers have found that the hydrogen and carbon monoxide content is higher at lower ER. The amount of N₂ in syn-

gas was significantly lower compared to other experiments, as was the amount of CO₂. Fig. 3 shows the LHV value of the syngas obtained in our experiment, which was also higher than other experiments in the literature.^{22,29,30}

The chemistry of SS gasification is complex and proceeds in the following stages: drying, pyrolysis or devolatilization, followed by partial oxidation and reduction.

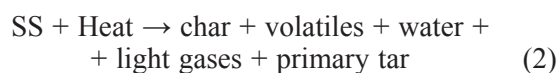
The main gasification reaction is represented in Equation 1.^{32–34}



The drying phase occurs mainly at temperatures up to 200 °C, with free moisture evaporating to water vapor SS. The pyrolysis or devolatilization phase is an endothermic process in which SS is

decomposed by heat transfer and occurs at temperatures of 350–600 °C.³¹ In the pyrolysis phase, 75–95 % of the organic matter and other volatile compounds are converted into gaseous and liquid products (hydrocarbons) and solid char (carbon).³¹

The drying/devolatilization reaction is represented by Equation 2.³¹



The volatile organics (C, O, H) contained in SS are believed to produce dry gases (CO, CO₂, CH₄, H₂), water vapor, solids (ash-bound oxygen, charcoal), and liquids (tar).²⁶

Heavy polycyclic aromatic hydrocarbons are the main reason for the effects of dirt and clogging in the gas lines of the gasification plant products and equipment. The term tar refers to the compounds benzene, phenol, naphthalene. Thermal cracking of tar and oxidation of tar have a significant impact on the final composition of the synthesis gas. According to Schmid *et al.*, high SS gasification temperatures of 850–900 °C lead to a high yield of released synthesis gas, and to minimization of tar formation.²⁵ The non-volatile part of the SS in the form of char and the released hydrocarbons are oxidized, releasing heat, and this phase represents the oxidation phase. This is followed by a reduction phase in which the char is converted to CO and H₂ by partial oxidation.

The results show that neither ammonia nor total fluorine or chlorine were detected in the gas produced. According to some studies, it is assumed that nitrogen is released from the SS (fuel) in the form of N₂, while others assume that 50–60 % of the nitrogen from the SS is converted to NH₃.²⁶ In our case, the results show that nitrogen from the SS was converted to N₂, which is consistent with the first assumption. According to some authors, the oxides Fe₂O₃ and CaO present in SS influence the reduction of NH₃ and HCN gases to N₂ during the gasification process of SS.³¹

The content of acid gases such as hydrogen sulfide is characteristic for the processes of thermal treatment of SS.⁹ Syngas analysis shows 720 mg m⁻³ of hydrogen sulfide and 620 mg m⁻³ of total sulfur. This indicates that additional purification of acid gases is required. Therefore, wet processes with a solution of hydroxide (NaOH) or slaked lime (CaOH₂) are usually used.⁹ HCl can be formed as a product of chlorine contained in the SS when reactor temperatures are below 920 °C.³¹ The results show that total chlorine in syngas is below the detection limits. This confirms the claim that the gas from thermal treatment SS is characterized by low HCl concentrations.⁹

Tetramethylsilane, trimethylsilane, hexamethyldisiloxane (L2), hexamethylcyclotrisiloxane (D3), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (L4) form siloxanes. These compounds are used in products such as deodorants and shampoos, and therefore may be present in the syngas from the gasification of SS. These compounds can cause serious combustion problems in gas engines or incinerators. However, the results of the syngas analysis show that all siloxane compounds are below the detection limits.

The impurities in the syngas could be due to the high content of nitrogen and sulfur, which is characteristic of SS. The results of the syngas analysis show the good quality of the produced syngas with very few impurities (e.g., H₂S, total sulfur). This could be due to the suitable operating conditions under which the gasification process was carried out. In addition, a cyclone was used to remove dust particles, and scrubbers were used to remove other impurities in the syngas (e.g., CO₂, H₂S, NH₃). In addition, some authors state that the significant content of oxides CaO and Fe₂O₃ in the SS leads to a reduction of pollutants in syngas.³¹

Analysis of the solid residue-SSA

SSA has been shown to have similar chemical properties to conventional ceramic materials, e.g., clay, and to achieve the desired densification, strength increase, and absorption reduction upon heat treatment. Table 5 shows that SSA contained a high proportion of SiO₂ of 47.55 % and Al₂O₃ of 11.80 %, oxides commonly found in clay, and other ceramic materials, although the SSA material had a higher CaO content with a value of 14.24 % compared to clay 0.72 %. Fe₂O₃ is another important oxide in SSA with a content of 7.37 %, which is also commonly found in ceramic materials. Oxides such as Fe₂O₃, CaO and P₂O₅ can lead to additional benefits as they can lower the melting temperature of the mixture during sintering, thus reducing energy costs.²⁰ P₂O₅ and SO₃ are also typical oxides that contain SSA but are not normally found in clay.²⁰ However, they were not determined in this analysis. The total oxide content was only slightly lower in SSA compared to clay. The content of organic matter in SSA was determined as 11.2 wt.%.

The inorganic pollutants (heavy metals) detected in SS were also found in the solid residues of gasification – SSA. In addition, it was documented that the concentrations of some heavy metals increased significantly due to thermal treatment (Tables 2 and 5).

Comparison of heavy metal concentrations in samples of SSA and clay showed that heavy metals are also present in clay. The concentrations were

Table 5 – Chemical composition of SSA and clay (oxides) (wt.%)

Oxide content	SSA	Clay
K ₂ O	1.51	2.23
MgO	4.31	0.63
Fe ₂ O ₃	7.37	5.49
CaO	14.24	0.72
Na ₂ O	1.11	1.49
SiO ₂	47.55	66.52
Al ₂ O ₃	11.80	14.59
TiO ₂	1	1.36
Total	88.89	93.02

slightly lower compared to SSA, but it can be seen that heavy metals such as As, Cr and V were present in clay samples in higher concentrations than in SSA. Industry has a major impact on the concentration of heavy metals in SS, as does the treatment of industrial wastewater before it is discharged into the sewer system. The average content of some heavy metals in the SSA from the literature data was compared with the content of heavy metals from the Zagreb SSA, as shown in Fig. 4.³⁵

According to the ATSDR, the most potentially toxic heavy metals include arsenic, lead, mercury, and cadmium. Heavy metals, unlike organic pollutants, are not biodegradable, which contributes to their accumulation potential. They can dissolve and contaminate the environment even at low concentrations, indicating the need for safe disposal of the materials.^{19–21,35} Many authors point out the good effect of the fixation of heavy metals inside the brick body, which occurs due to the structural change during the sintering process.^{19–21}

Table 6 – Chemical composition of SSA and clay (heavy metals)

Heavy metals	SSA	Clay	Unit
Toxic			
Fe	4.11	4.15	wt.%
Zn	923.39	111.9	mg kg ⁻¹ DM
Cu	379.81	55	mg kg ⁻¹ DM
Cr	64.42	90.5	mg kg ⁻¹ DM
Sr	201.22	97	mg kg ⁻¹ DM
Pb	209.29	31.6	mg kg ⁻¹ DM
Ni	76.71	48.9	mg kg ⁻¹ DM
V	83.19	177.4	mg kg ⁻¹ DM
As	6.84	16.8	mg kg ⁻¹ DM
Nontoxic			
K	1.53	1.96	wt.%
Ca	7.98	0.25	wt.%
Ti	3966.89	6721	mg kg ⁻¹ DM
Mn	985.11	313	mg kg ⁻¹ DM
Ga	13.36	22.8	mg kg ⁻¹ DM
Br	74.19	<0.5	mg kg ⁻¹ DM
Rb	61.78	144.2	mg kg ⁻¹ DM
Y	50.08	106.9	mg kg ⁻¹ DM
Zr	333.71	632	mg kg ⁻¹ DM
Th	9.54	17.35	mg kg ⁻¹ DM

Testing of manufactured bricks

Compressive strength is an important parameter in testing brick quality. Although the compressive strength is primarily influenced by the firing temperature of the brick, the results in Fig. 5 show

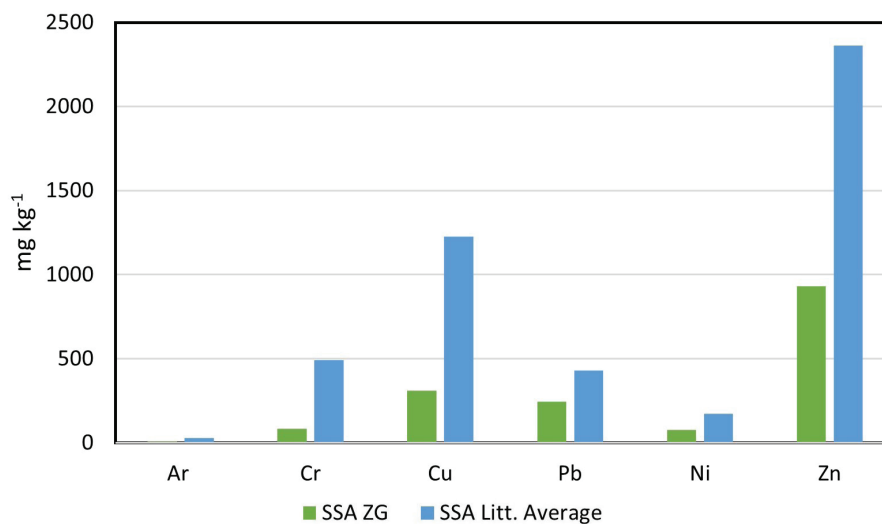


Fig. 4 – Comparison of heavy metals from SSA Zagreb with experimental data from the literature

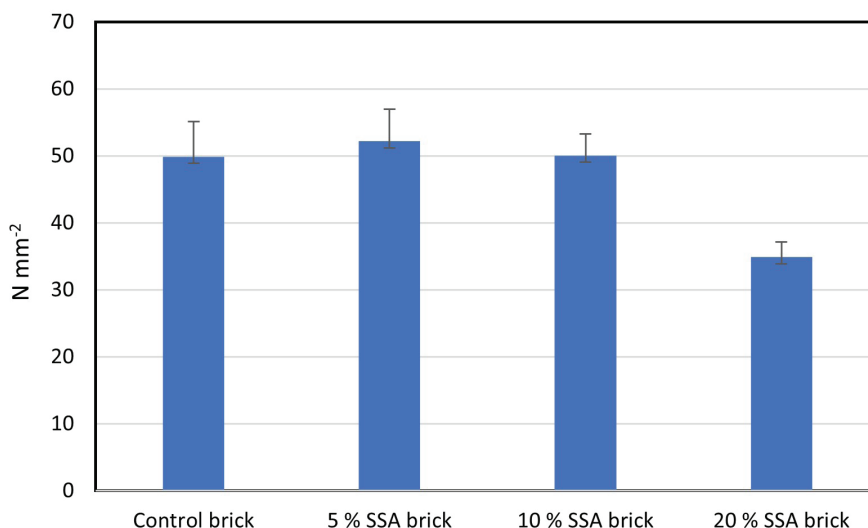


Fig. 5 – Compressive strength of the manufactured bricks

that the composition of the raw material also plays an important role.^{19,27} The bricks were prepared and manufactured under the same conditions. The brick with an SSA content of 5 wt.% had a better compressive strength than the control brick and the bricks with a higher SSA content. With the addition of a mass fraction of 20 % SSA, the compressive strength of the brick decreased. Although the achieved compressive strength was lower compared to other bricks, the bricks with 20 % SSA still had good compressive strength. The minimum value recommended for a brick specimen according to the US and Canadian standards for bricks is 17.20 N mm⁻².

Conclusion

SS gasification is a promising technology for thermochemical conversion of organic matter contained in SS into valuable syngas. The tests were conducted in a pilot-scale rotating reactor. The fuel used was SS from the Zagreb WWTP and gasification was carried out at a temperature of 900 °C. The produced syngas consisted of 41.5 vol.% H₂, 25.3 vol.% CO, 3.2 vol.% CH₄, and 10.6 vol.% CO₂, the LHV was 8.8 MJ N⁻¹ m⁻³, which corresponds to 2.45 kWh N⁻¹ m⁻³. The high content of hydrogen and the very low content of impurities indicate high quality of the syngas. The solid residue, SSA, from the gasification process is a valuable waste material. Moreover, the recovered SSA can be used as a raw material in the construction industry. By replacing clay with SSA, higher compressive strength was obtained in the production of bricks with 5 wt.% and 10 wt.% than the control bricks. However, besides compressive strength, other tests on SSA bricks are required to confirm the quality of SSA bricks. It is also very important to

determine the safety of such products by testing for leaching metals. The research results indicate the sustainability of the gasification process as one of the thermal treatment processes of SS, achieving a high degree of energy and material recovery from SS in the circular economy: Waste → Processing → Hydrogen + Raw Materials → Recycling → New Product. SS is a promising solid fuel because WWTPs currently have to pay for disposal, and the price of disposal is steadily increasing.

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Abbreviations

WWTP	– Wastewater treatment plant
SS	– Sewage sludge
SSA	– Sewage sludge ash
DM	– Dry matter
LHV	– Low heating value
HHV	– Higher heating value
CHP	– Combined heat and power
Eurostat	– European statistical office
EU28	– European Union (EU) which consists of 28 countries

PAH	– Polycyclic aromatic hydrocarbons
PCDD/Fs	– Dioxins and furans
PCB	– Polychlorinated biphenyls
BFB	– Bubbling fluidized bed
CFB	– Circulating fluidized bed
ER	– Equivalence ratio
IGFC	– Integrated gasification fuel cells
PE	– Population equivalent
TOC	– Total organic carbon
TN	– Total nitrogen
TP	– Total phosphorus
TPH	– Total petroleum hydrocarbons
HCH	– Hexachlorocyclohexane
HCB	– Hexachlorobenzene
SIC	– Silicon carbide
SYNGAS	– Synthesis gas
XRF	– X-ray fluorescence
LOI	– Loss on ignition
ATSDR	– Agency for toxic substances and disease registry

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