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Industrially relevant pyrolysis of diverse contaminated organic wastes: Gas compositions and emissions to air

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ABSTRACT

Pyrolysis is a promising waste handling technique compared to incineration, especially due to its potential for greenhouse gas reduction through biochar carbon removal. This study investigated greenhouse gas and air pollutant emissions and emission factors from waste feedstocks and a reference clean wood pyrolyzed at 500-800 °C in an industrially relevant small version Biogreen® unit with condensation prior to pyrolysis gas combustion. Emissions were generally lower than literature values, except for nitrogen oxides (NO_X) and sulfur dioxide (SO2). Methane (CH4) and nitrous oxide (N2O) emissions ranged 30-570 mg CH4 and 0-32 mg N2O per kg biochar produced. Waste lignocellulosics (waste timber and garden waste) had comparable emissions to clean wood, except for higher NO_X emissions. All waste feedstocks exceeded the EU NO_X emission limit value for waste incineration (>200 mg NO_X/Nm³ at 11% oxygen, O₂), while no carbon monoxide (CO) was measured (<0.6 mg/ Nm³) suggesting possible compliance with EU emission limit values for waste incineration with simple pollution control measures such as air-to-fuel ratio regulation, or other NO_X reducing measures such as flue gas recirculation or selective (non-)catalytic reduction. Sludges and food waste reject also exceeded the SO2 EU emission limit value (50 mg SO₂/Nm³ at 11% O₂) for waste incineration, emissions ranging 61–298 mg SO₂/Nm³ at 11% O₂, indicating the potential need for SO₂ pollution control. In conclusion, this study shows continuous pyrolysis with condensation as a promising alternative for waste management with potential for simplified air pollution control compared to incineration. Future work should focus on optimized combustion systems for waste pyrolysis and emissions from waste pyrolysis without condensation.

1. Introduction

Waste management is a global challenge that has grown increasingly urgent due to the rise of population and urbanization. Landfilling and incineration are among the commonly used techniques for managing waste, but both have limitations, including environmental pollution and health risks (Istrate et al., 2020; Makarichi et al., 2018; Stoiber et al., 2020; Vaverková, 2019). Pyrolysis for waste management has emerged as a promising alternative to these methods. Pyrolysis involves heating organic waste in the absence of oxygen, which results in the formation of biochar, a stable carbon-rich solid, and other gaseous and liquid by-products (pyrolysis gas and condensate) (Elkhalifa et al., 2019; Liu et al., 2017; Roberts et al., 2017; Singh et al., 2022). Pyrolysis gas is typically a mixture of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), methane (CH₄) and some heavier hydrocarbons. This mixed gas could be used for further synthesis such as conversion to CH₄ through catalytic methanation (Salman et al., 2017) or anaerobic digestion (Torri et al., 2020), but it is commonly combusted directly to produce energy, e.g. to run the pyrolysis process or heat water. In addition, pyrolysis provides an opportunity for biochar carbon removal (BCR), which involves capturing CO₂ emissions by converting biomass into biochar. BCR involves biological carbon capture, using natural

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processes to capture and store carbon from the atmosphere, such as through photosynthesis in plants (Lehmann et al., 2021). At pyrolysis temperatures above 500 °C, persistent organic pollutants such as microplastics, PFAS and PCBs present in the feedstock can be removed or reduced to much lower and safer concentrations in the biochar (Buss, 2021; Moško et al., 2021; Sørmo et al., 2023b, 2023c). Biochar also has numerous uses, especially in agriculture or as sorbents of pollutants in water or soil (Ahmad et al., 2014; Beesley et al., 2011; Krahn et al., 2023; Shaaban et al., 2018). Quality standards such as the European Biochar Certificate makes it possible to categorize biochar qualities based on properties and to a large degree independent of feedstock source, making materials recycling of previously incinerated waste possible (EBC, 2012).

To make BCR-estimates more accurate, GHG emissions associated with the pyrolysis process, such as the emissions from the combustion of pyrolysis gas needs to be investigated. Important GHGs that may be emitted from the combustion of pyrolysis gases included in this study are CO₂, CH₄ and nitrous oxide (N₂O). Other pollutants investigated in the present work can affect the environment and human health and are therefore relevant for waste management and environmental policy perspectives. Nitrogen oxides (NO_x) and sulfur dioxide (SO₂) are contributors to local air pollution such as acid rain and can cause respiratory problems. Total suspended particulates (TSP) and non-methane volatile organic compounds (NMVOC) are also harmful to human health and the environment. TSP can cause respiratory problems and NMVOCs can lead to the formation of ground-level ozone, which is also harmful to human health and the environment (Manisalidis et al., 2020). In addition to these, carbon monoxide (CO), hydrogen cyanide (HCN), hydrogen chloride (HCl), ammonia (NH₃) and hydrogen fluoride (HF) are all considered air pollutants with varying negative effects on health and the environment. All the gases included in this study are important when considering the life cycle impacts of the pyrolysis process (USNRC, 2002; WHO, 2021).

Previous studies have reported on emissions from pyrolysis of various waste materials. For example, a study by Sørmo et al. (2020) compared the emissions from pyrolysis of waste timber to a reference wood in Pyreg continuous pyrolysis unit with a FLOX burner. The air-fuel-ratio (AFR) was relatively low (1.01), causing CO to be the dominating pollutant (Sehn and Gerber, 2007). These emissions were still much lower than those from a "Kon-Tiki" Flame Curtain biochar kiln (Cornelissen et al., 2016), with emission factors of products of incomplete combustion (PIC) at 6–10 g/kg biochar for the continuous unit and 51 g/kg biochar for the best kiln tested. Dunnigan et al. (2018) investigated the particulate emissions from the combustion of raw pyrolysis volatiles produced during the production of biochar from rice husk. The study showed that particulate emissions from pyrolysis were lower than those from combustion of raw biomass. Several studies have investigated the formation of HCN and NH3 in pyrolysis as NOX and N2O precursors (Ren et al., 2010; Tan and Li, 2000; Tian et al., 2013), but residual emissions of these after combustion of pyrolysis gas and their emission factors is currently lacking in the literature.

In this study, we present pyrolysis emission concentrations and emission factors for a wide range of GHGs and air pollutants, waste feedstocks and pyrolysis temperatures from a continuous pyrolysis unit with condensation. The pyrolysis unit used in this work is a smaller version of the commercially available Biogreen® Technology, making the results more industrially relevant than laboratory-scale studies done with e.g. tube or muffle furnaces, or thermogravimetric analysis (TGA). The study includes various waste streams from biogas plants (food waste reject and digested sewage sludge) that are relevant for the circular economy and for moving upwards in the waste hierarchy by increasing the reuse of waste. These data can help improve the reliability of life cycle assessments figuring pyrolysis and support environmental management and policy making.

To our knowledge, there is currently no similarly comprehensive study detailing emissions and emission factors for air pollutants from industrially relevant pyrolysis of such a wide range of waste materials, pyrolysis temperatures and air pollutants.

Combustion of waste is more strictly regulated than combustion of clean wood biomass because of higher risk of air pollutants such as $\rm NO_X$ and SO₂. We hypothesize that pyrolysis of waste materials leads to higher air emissions compared to pyrolysis of clean wood. To test this, we compared emissions from pyrolysis of waste materials to clean wood biomass at temperatures from 500 to 800 $^\circ C.$

2. Materials and methods

Seven different feedstocks: Waste timber (WT), garden waste (GW), biosolids from three different anaerobic digestion facilities, and the "reject" waste fraction before anaerobic digestion of food waste (FWR) were dried, pelletized and later pyrolyzed at 2–4 different temperatures. Table 1 explains the experimental setup. The three different biosolids were all from anaerobically digested sewage sludge (DSS). DSS-1 went through thermal hydrolysis prior to digestion and includes sewage sludge, residual fats and food waste and DSS-2 was from anaerobically digested primary sludge. Limed sewage sludge (LSS) was additionally stabilized by about 39 % wt lime after anaerobic digestion. The feedstocks were dried (<15% moisture) and made into pellets (diameter 8 mm, length 40 mm) prior to pyrolysis.

The temperature range 500–800 $^{\circ}$ C was selected to ensure reduction or removal of persistent organic pollutants in the feedstocks while studying the effect of temperature on emissions in a range that was practically feasible and possible for the equipment used.

A detailed description of the pyrolysis experimental system (A.1), sample preparation and analytical methods (A.2) and data analysis (A.3) is available in the supplementary materials section A.

3. Results and discussion

3.1. Mass yields and carbon balance

Characterizing data including % TS, % Ash, mass yields, C, H, N, S, O and higher heating values for feedstocks, biochars, condensates and gas are presented in the SM (section B, Tables S1, S2 and S3). The following section will show data from moisture corrected feedstock unless otherwise specified. The SM additionally present actual values (including moisture) and values on dry, ash free basis (Section B.1, Tables S1–3).

Pyrolysis gas mass yield increased, and biochar mass yield decreased with temperature for most of the feedstocks, but this was not a clear trend for the sludges (Fig. 1). Only the waste timber had a significant linear biochar mass yield decrease ($R^2 = 0.98$, p = 0.01) and gas yield increase ($R^2 = 0.95$, p = 0.03) by temperature.

The sludges had a much higher ash content (32–51% TS) than the lignocellulosics (0.6–10% TS), and most of this ash ends up in the char. Consequently, sludge char yield varied between 40% (DSS-2-800) to 70% (DSS-1-760), while the lignocellulosics (CWC, WT and GW) varied between 16% (CWC-750) and 32% (GW-600). DSS-1 seemed to even have a slight increase in yield by temperature (however, not a significant linear relationship $R^2 = 0.43$, p = 0.35), which could be due to heterogeneity of the feedstock with its higher variation in ash content. The food waste reject was somewhere in between with regards to ash content (24% TS) and gave a biochar mass yield of 35%. The varying ash content also affected the gas production, with a much lower gas yield for the sludges, varying between 10% (DSS-1-760) to 32% (LSS-770) compared to 22% (WT-500) to 71% (CWC-750) and FWR with gas yields between 41 and 43%. Condensate yields ranged between 13% (CWC-750) and 48% (WT-500) across all feedstocks and temperatures.

The char yields from the lignocellulosic materials correspond to reported yields from similar temperatures for intermediate/fast, fixed bed pyrolysis with similar maximum temperatures (Kan et al., 2016; Kim et al., 2011; Li et al., 2019). For example, Sørmo et al. (2020) reported 25% char yield for a similar waste timber at 600 °C using a continuous

Table 1

Adapted from (Sørmo et al.,	, 2023b). Feedstocks and	temperatures tested on	1 the Biogreen ® aug	er pyrolysis system.
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Feedstock	Abbrev.	Description	Pyrolysis temperatures (°C)	Pyrolysis residence time (min)	Solid phases sampled	Pyrolysis condensate sampled	Pyrolysis gas analysed	Flue gas sampled
Wood chips	CWC	Pellets produced from pine/spruce wood chips from forestry/logging.	530, 600, 700 and 750	20	Yes	Yes, for 600 °C treatment	Yes, in parallel tests	Yes, for all treatments
Waste timber	WT	Discarded wood products and objects from private households, businesses, and construction/demolition (no chemically impregnated wood)	500, 600, 700 and 800	20	Yes	Yes, for 600 °C treatment	Yes, for all treatments	Yes, for all treatments
Garden waste	GW	Gardening waste from private households and businesses. Fraction includes twigs, leaves, roots and some sand/gravel.	500, 600 and 800	20	Yes	Yes, for all treatments	Yes, for all treatments	Yes, for 500 and 800 °C treatments
Digested sewage sludge	DSS-1	Sewage sludge and food waste gone through thermal hydrolysis (155 °C, 20 min) before anaerobic digestion	500, 600, 700 and 770	20	Yes	Yes, for 500, 600 and 700 °C treatments	Yes, for all treatments	Yes, for all treatments (excl. particles for 760 °C)
Digested sewage sludge	DSS-2	Sewage sludge gone through anaerobic digestion	500, 600, 700 and 800	20	Yes	Yes, for all treatments	Yes, for 500, 600, 800, and parallel test for 700	Yes, for all treatments
Limed sewage sludge	LSS	Sewage sludge gone through anaerobic digestion, then added lime (39%) for stabilization and hygienization	600 and 760	20	Yes	Yes, for all treatments	Yes, for all treatments	Yes, for all treatments
Reject from food waste biogas production	FWR	Fraction of food waste rejected for biogas production. Consists of material that does not pass an initial sieving process to reject plastics and other too large or non-digestible items.	600 and 800	20	Yes	Yes, for 800 °C treatment	Yes, for all treatments	Yes, for all treatments

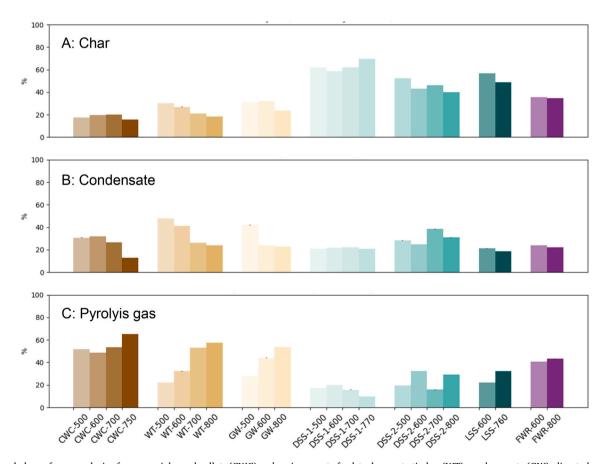


Fig. 1. Mass balance from pyrolysis of commercial wood pellets (CWC) and various waste feedstocks: waste timber (WT), garden waste (GW), digested sewage sludge 1 (DSS-1), digested sewage sludge 2 (DSS-2), limed sewage sludge (LSS) and food waste reject (FWR). A: Char yield (% mass of dry feedstock). B: Condensate yield (% mass of dry feedstock), calculated by difference. Each feedstock is sorted by increasing temperature.

G.Ø. Flatabø et al.

Pyreg unit with a residence time of 20 min, comparable to the 27% yield of the current study.

The liquid yields for lignocellulosics were lower than what is typical for fast pyrolysis but somewhat higher than typical for slow pyrolysis. Fast pyrolysis, characterized by high heating rates (typically >60 °C/min) and short residence times (typically <10 s), tends to maximize the production of liquid products. This is because it rapidly heats the biomass and then quickly cools it, helping to condense the volatile compounds produced into liquid form. Slow pyrolysis, however, with lower heating rates and longer residence times (typically >1 h), allows for secondary reactions to occur, where volatile compounds react further to form non-condensable gases and solid residue, thus yielding less liquid product (Williams and Besler, 1996). For this study, lignocellulosics yielded 31–48% liquid at 500 °C, compared to the typical 20–30% liquid yield for slow pyrolysis and 60–70% for fast pyrolysis at this temperature (Kan et al., 2016; Panopoulos et al., 2022; Yogalakshmi et al., 2022).

The char yields of DSS-2 corresponds well to literature values from pyrolysis of sewage sludge with similar ash content (Zhang et al., 2015). Li et al. (2019) synthesized data from a range of pyrolysis studies and found that biosolids char yields ranged between 25 and 70%. The yield range 40–70% for the current study is in line with this. The food waste reject biochar follows the trend found in Li et al. (2019) of ash increase by temperature for feedstock with similar ash content.

Pyrolysis concentrates ash in the char, causing the ash content of the feedstock to influence mass yields. Higher ash content gives higher char yields when the total char yield is calculated as a fraction of the total mass, which in turn decreases the calculated gas yields. To eliminate the influence of ash content, mass yields can be compared on a dry, ash free basis.

Table S3 shows the mass yields on dry, ash free basis. Irrespective of the type of feedstock, biochar yields ranged within 10–33%, and gas yields within 23–72%, similar to published dry, ash free yields (Dall'ora et al., 2008; Fonts et al., 2009). On dry ash free basis, the pyrolysis temperature is what mainly influences the biochar yield (Dall'ora et al.,

2008; Fonts et al., 2009; Russell et al., 2017; Ryu et al., 2007). The separation between gas and liquid, however, were additionally affected by feedstock type, since average gas yield was slightly lower for the digestates than the lignocellulosics (50% for lignocellulosics and 38% for digestates), while the digestates produced more condensate (30% average for lignocellulosics and 43% average for digestates).

The carbon balance followed the same trends as the mass balance (Fig. S2, right hand side). The aforementioned Li et al. (2019) data synthesis from a multitude of pyrolysis studies showed trends of increased C concentration in biochar by temperature, while the C concentration of sludge chars decreased by pyrolysis temperature. For our sample set, only the GW showed a significant linear trend of increasing C in char by temperature ($R^2 = 0.99$, p < 0.05). The C concentration of DSS-2 char decreased by temperature, but with no significant linear trend ($R^2 = 0.66$, p = 0.19).

3.2. Pyrolysis gas composition

The composition of the pyrolysis gas, before post-combustion, indicates a decrease in CO_2 and increase in H_2 by temperature (Fig. 2). The composition was also affected by feedstock, with the sludges generally causing higher CO_2 (sludges: 15–45%, lignocellulosics: 16–35%) and H_2 (sludges: 12–24%, lignocellulosics: 2–18%) concentrations, while the lignocellulosics had higher CO (sludges: 8–35%, lignocellulosics: 30–35%) concentrations. This implies that it is possible to influence and modify pyrolysis gas composition by temperature and feedstock, as confirmed by several authors (Honus et al., 2014; Jaramillo-Arango et al., 2016; Netzer and Løvås, 2022; Santamaria et al., 2021).

Jaramillo-Arango et al. (2016) pyrolyzed digested sewage sludge in a fluidized bed pyrolysis reactor between 500 and 800 °C and found an increase with temperature between 30 and 50% vol of H₂, and an increase from 1.5 to 3% vol of C₂H₄. The sludges in this study showed the same trends when comparing changes in gas composition by temperature, but the analysed concentration of C₂H₄ (15–20% vol) was more than 10 percentage points higher, while H₂ (measured at 15–25% vol)

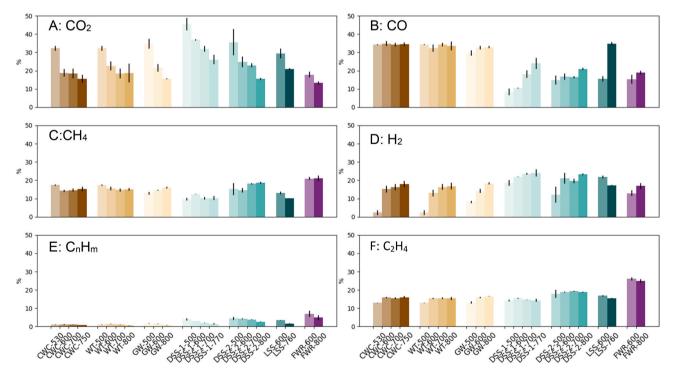


Fig. 2. Mean gas compositions of pyrolysis gas measured by gas analyser. A: $CO_2\%$ vol, B: CO% vol, C: $CH_4\%$ vol, D: H_2 , E: CnHm, the sum of C_2H_6 , C_3H_8 and C_4H_{10} (% vol), F: $C_2H_4\%$ vol. The x-axis starts with commercial wood pellets (CWC), then the following waste feedstocks: waste timber (WT), garden waste (GW), digested sewage sludge 1 (DSS-1), digested sewage sludge 2 (DSS-2), limed sewage sludge (LSS) and food waste reject (FWR). Each feedstock is sorted by increasing temperature. Error bars represent the standard deviation of the measurement (n \approx 240 per treatment).

was more than 10 percentage points lower than reported in literature from similar conditions (Jaramillo-Arango et al., 2016). Honus et al. (2014) pyrolyzed biomass pellets in an auger pyrolysis reactor between 500 and 650 °C and measured an increasing CH₄ and H₂ concentration (12-15% vol CH₄ and 6-20% vol for H₂), decreasing CO₂ (20-16% vol) while CO and C2H4 varied (8-30% vol for CO and 3.7-4.9% vol for C₂H₄). In a study with a fluidized bed reactor, higher temperature (600-800 °C) wood pellets pyrolysis gave higher CO₂, H₂ and CO concentrations (15-20% vol CO2 and H2, 50-40% vol for CO) and similar CH₄ concentration (15-10% vol) for pyrolyzed wood pellets. The composition of C2-C4-compounds was analysed to decrease from 7% to 5% by temperature (Santamaria et al., 2021). These values are similar to the measured gas compositions from lignocellulosics in this study, with the exception of C₂H₄ which, similar to the sludges, was measured to 9-18% vol, more than 10 percentage points higher than reported in literature for similar pyrolysis conditions (Honus et al., 2014; Santamaria et al., 2021). During TCD detection of H₂ without separation such as chromatography, C₂H₄ may interfere with the measurement, so the sensors may need more frequent calibration (Sluder et al., 2004). The inaccuracy in the gas composition measurements may impact the calculated C from gas composition; however, the differences are minor

when comparing to the C-yield based on difference from measured condensate composition (Table S4).

3.3. Emissions from pyrolysis gas combustion

3.3.1. Emissions concentrations

Carbon monoxide, particulates (TSP), methane and other volatile compounds, are typically products of incomplete combustion. Fig. 3 gives an overview of the measured concentrations of these compounds related to estimated flue gas volume. Most of the pyrolysis gases were completely combusted, with only small amounts of particulates (0–0.3 mg/Nm³, as TSP), CO (0–2.8 mg/Nm³) and volatiles (CH₄ 0.2–1.8 mgC/Nm³, NMVOC 0.3–3.3 mgC/Nm³) (Fig. 3). Two samples had less complete combustion (CWC-500 and LSS-760) shown by more volatiles (7.2 mgC/Nm³ NMVOC for CWC-500 and 15 mg C/Nm³ CH₄ for LSS-760). The CWC-samples had also comparatively less complete combustion, which we see from the slightly higher number for products of incomplete combustion (PIC). This is mostly from the CO detected (1.1–2.6 mg/Nm³), while CO was below detection limit (<0.6 mg/Nm³) for the other samples. Compared to the pyrolysis of the clean reference material (CWC), waste material pyrolysis, both lignocellulosic and sludge based,

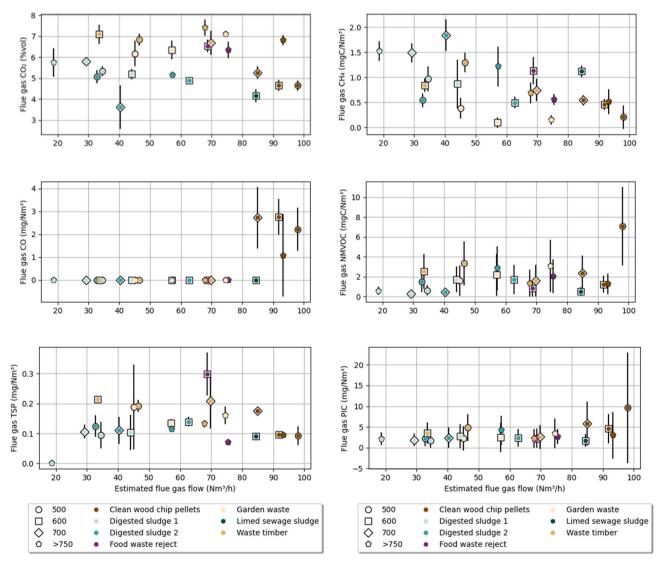


Fig. 3. C-containing gas emission concentrations related to estimated flue gas flow, mean values with standard deviation represented by the error bars. From the top of the left column: CO_2 (% vol), CO (mg/Nm3), TSP (mg/Nm³). From the top of the right column: CH_4 (mg/Nm³), NMVOC (mg/Nm3), PIC (mg/Nm³). LSS-760 is omitted from the plot for better resolution, due to its high flue gas flow ($357 \pm 15 \text{ Nm}^3$ /h) see emission values in Table S6). The flue gas flow is estimated assuming the relative contribution from co-fired propane is negligible. See SM section A.4 and B.4 on estimates regarding propane.

did not lead to higher emission concentrations of any of the carbonbased flue gases.

Waste incineration typically causes much higher particulate emissions than measured in the current study. Yoo et al. (2002) listed values of 17–349 mg/Sm³ of PM₁₀ emitted from small incinerators of municipal solid waste, even when using cyclone as air pollution control device. Modern waste incinerators, however, employ more efficient air pollution control devices to stay within regulatory limits.

The measured N-containing gases were related to the mass flow of N in the pyrolysis gas calculated by difference (Fig. 4). See section 3.4 for a discussion of NO, NO₂ and their sum (NO_X). Compared to the CWC, most of the waste materials gave higher concentrations of NH₃ (CWC 0–1.0 mg/Nm³, all other feedstocks 0.02–1.5 mg/Nm³) and HCN (CWC 0.01–4.6, all other feedstocks 2–14 mg/Nm³). However, between the waste materials, there was no statistically significant linear correlation (R² < 0.2, p > 0.08 for all N-containing gases normalized to 11% O₂, NO_X represented NO and NO₂) between available fuel nitrogen and the concentrations of the N-containing flue gases.

Sørmo et al. (2020) measured emissions from pyrolysis of waste timber and a reference wood in a Pyreg unit with a FLOX burner and

recorded higher CO concentrations (50-100 mg/Nm³) and very low NO_x-concentrations (around 10 mg/Nm³) compared to this study. The authors indicated that a low air-to-fuel ratio (approx. 1.01, O2-concentration not given) might be an explanation for the high CO and low NO_X. In the current study, the burner was not flameless, and parts of the flame might be a higher temperature, promoting NO_X-formation (Sehn and Gerber, 2007). The combustion also had a much higher air intake, with estimated oxygen levels of >10% (Table S14). Additionally, Sørmo et al. (2020) found significant differences between the CO, NMVOC and PM₁₀ emission concentrations from the waste timber and the clean wood reference. CO and NMVOC were significantly higher for the waste timber (80-100 ppm CO for WT and 50 ppm for reference wood, and 10-20 ppm NMVOC for WT and 3 ppm for the reference) and PM₁₀ emission concentrations were significantly lower for WT (2–8 mg/m^3 for WT and 12 mg/m^3 for reference wood). No such trends were observed in the current study.

Fig. 5 shows the emission concentrations of HCl and SO₂, related to Cl- and S-load from feedstock (g/h), respectively. These compounds are dependent on fuel Cl and S to form. SO₂ concentrations were higher from the sludge and FWR (61–298 mg/Nm³ at 11% O₂) than the reference

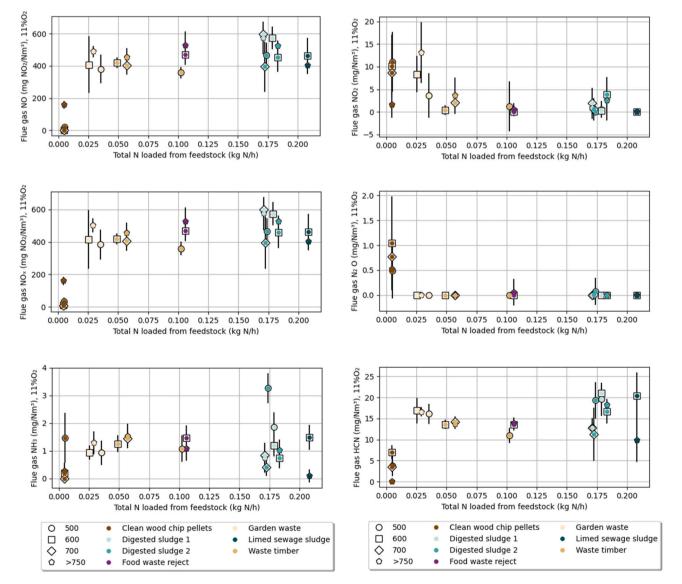


Fig. 4. N-containing gas emissions as a function of feed N load (kg N/h), mean values with standard deviation represented by the error bars. Normalized to $11\% O_2$ by Eq. 12 (SM A.3). From the top of the left column: NO (mg NO₂/Nm³), NO_X (mg NO₂/Nm³), NH₃ (mg/Nm³). From the top of the right column: NO₂ (mg/Nm³), NO₂ (mg/Nm³), HCN (mg/Nm³).

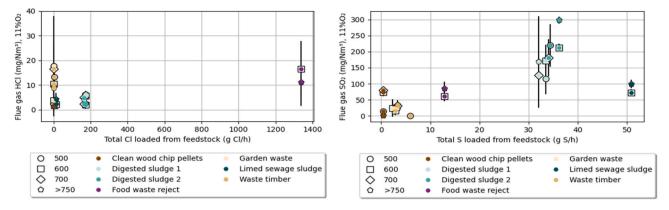


Fig. 5. HCl emissions (mg/Nm³, left) as a function of Cl load from feedstock (g Cl/h). SO₂ emissions (mg/Nm³, right) as a function of S load from feedstock (g S/h).

CWC (0.4–79 mg/Nm³ at 11% O₂). For HCl, except for DSS-2, all the waste materials gave higher HCl concentrations (2.2–18 mg/Nm³ at 11% O₂) than the CWC reference (1.3–2.5 mg/Nm³ at 11% O₂). SO₂ concentration (at 11% O₂) was correlated to fuel S (R² = 0.51, p = 0.0001). However, there was no statistically significant correlation between fuel Cl and HCl concentration (R² = 0.13, p = 0.1), most likely due to the heterogeneity of the feedstocks and partitioning of the feedstock Cl content into the char and condensate instead of the gas.

We did not measure HF above the detection limit (1 mg/Nm³) in any of the samples. HF in the flue gas could have risen from e.g. PFAS contamination in the feedstock (Sørmo et al., 2023b). Although the PFAS concentrations were relatively high in some of the feedstocks (e.g. 4 mg kg⁻¹ in the CWC), this would only amount to about 0.14 mg/Nm³ HF in the flue gas assuming everything was converted.

Emission concentrations were measured in co-combustion with propane, due to the requirements of the burner. This might have diluted some of the measured concentrations (see SM section B.4). For example, TSP concentrations recalculated without propane at 11% O₂ increased

1–12 times but increased on average 3.6 times, and the highest recalculated value at 4.5 ± 1.7 (LSS-760). However, some emissions are more dependent on combustion temperature, air-fuel ratio, and combustion chamber size, so it is unlikely that there is a linear relationship between emission concentrations and propane contribution. For example, Shi et al. (2022) tested combustion of CH₄/NH₃ mixes and got 30 times less NO_X emissions when using a different distribution method between the fuel gas and combustion air. Using chemical kinetic simulations, the authors could suggest the differences in chemical reactions leading to these results. In our sample set, burner parameters were not optimized for the various feedstocks and corresponding gas flows. For most of the samples, propane/fuel ratio was well below 1 (average 0.5), and possible dilution would be minor. However, future work using chemical kinetic simulations could shed light on the impact of the propane co-fuel and how to optimize the combustion process to minimize emissions.

3.3.2. Emissions factors

Fig. 6 summarizes the emission factors from the C-containing flue

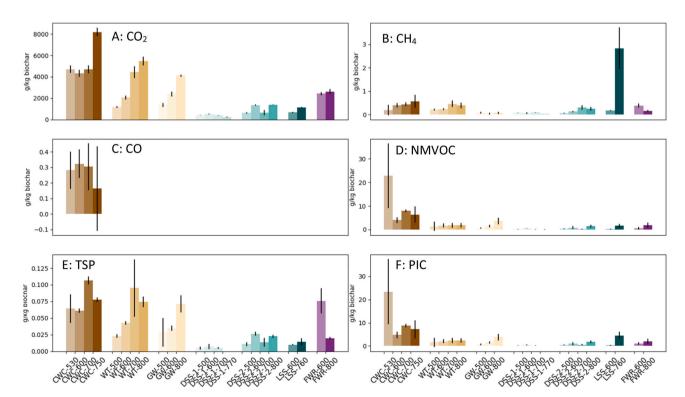


Fig. 6. Mean emission factors in g compound based on kg biochar produced. The error bars represent the standard deviation. A: CO_2 , B: CH4, C: CO, D: NMVOC, E: TSP, F: PIC. The missing data point for CO were below detection limit (<0.01 mg/Nm³), expressed as 0 in the figure. Values are tabulated in SM section B.3, Table S10.

gases. The emissions factors generally follow the pyrolysis gas mass yield, which increases by temperature. The sludge samples mainly have lower emission factors than the lignocellulosics, due to the lower amount of pyrolysis gas produced per kg biochar. The emission factors were also affected by differences in combustion, where the CWC had less complete combustion as seen from the higher PIC value. The PIC and NMVOC emission factors were similar to the values found in Sørmo et al. (2020), with slightly less complete combustion in CWC, however CH₄ was not detected in that study, most likely due to the high limit of detection (500 ppm).

The methane detected in this study was all 30-200 times lower than the detection limit of Sørmo et al. (2020), offering better resolution for greenhouse gas budgeting. CH4 from common charcoal-making earth mound kilns in Kenya were as high as 45 g CH₄/kg char produced (Pennise et al., 2001), compared to <1 g CH₄/kg char from the lignocellulosic feedstocks in the present work, clearly demonstrating the advantage of a continuous process with controlled combustion with regards to greenhouse gas emissions. CH₄ emissions from LSS-760 were much higher than from the other tests, while other products of incomplete combustion were unaffected. This test was an outlier in several ways: Due to the high concentration CaCO₃ in this sample, calcination, a temperature dependant (>650 °C), endothermic process occurred during pyrolysis. Additionally, the exhaust gas was diluted to 18.6% residual O₂ (Table S14), indicating a large flow of combustion air in the burner. This could potentially have cooled the burner causing CH₄-spikes, but the burner temperature sensor did not register unusually cool temperatures. Further tests are needed in the future to conclude whether these CH₄ emissions are representative for pyrolysis of CaCO₃ -treated sludge at such temperatures.

TSP emission factors were about 10 times as low as from the Pyreg unit in Sørmo et al. (2020), about 100 times as low as a Kon-Tiki Flame Curtain Kiln (Cornelissen et al., 2016) and about 300 times as low as from common charcoal-making earth mound kilns in Kenya (Pennise et al., 2001). Compared to the above-mentioned studies, the TSP in this study might have been slightly diluted by the co-firing with propane, but this cannot explain more than a doubling of the current values (Fig. S3). Another difference is the condensation of the pyrolysis gas and removal of pyrolysis condensate in the current set up, which was not part of the Pyreg or Kon-Tiki, or charcoal kiln setups. The presence of tars and water in the pyrolysis gas during combustion could promote more particle emissions. Schwartz et al. (2020) tested combustion of pyrolysis products separately, concluding that the particulate emissions from the gas phase was negligible and similar to burning clean gases such as propane, while PM-emissions from pyrolysis oil were 39 mg/m3 (at 7% O_2). This indicates that uncondensed liquid phase in pyrolysis gas may increase particulate emissions if combusted directly, compared to only combusting the incondensable gas.

Conesa et al. (2009) studied emissions from combustion of various wastes and found NMVOC emission factors per fuel at 72, 48 and 63 g/kg feedstock and methane emission factors at 1.2, 17 and 35 g/kg feedstock for two different sludges and cotton waste. In comparison, emission factors for NMVOC and CH₄ for the sludges in the current study were 0.02–0.8 and 0.02–1.3 g/kg feedstock, respectively. For the lignocellulosics the corresponding emission factors were 0.2–3.9 and 0.01–0.09 g/kg feedstock, respectively (Table S12). Combustion of pyrolysis gas is more similar to gas combustion, where fuel-air mixing is more efficient and complete combustion is simpler to attain, compared to e.g. waste incineration where a solid matrix is combusted.

The emission factors for N-containing gases were mainly affected by pyrolysis gas yield (Fig. 8), so even the sludges that had the highest relative N-content (Fig. 5) had lower emission factors than waste timber and garden waste (Fig. 7), while the CWC was lower due to its limited N-content (more in section 3.4). Nitrous oxide (N₂O) was only detected from the CWC at 15–30 μ g/kg biochar produced. In comparison, N₂O emission factors from Kenyan earth mound kilns were 150 μ g/kg char produced (Pennise et al., 2001).

HCl emission factors (Fig. 8, left) follows the same trend as the emission concentrations (Fig. 5, left), where more is produced from waste timber and food waste reject. DSS-2 had the highest SO_2 concentration (Fig. 6, B) and the highest gas yields of the sludge feedstocks, also reflected in the SO_2 emission factors (Fig. 9, B). Surprisingly, CWC (600 and 700), which had the lowest S-concentration of all the feedstocks, gave similar emission factors as DSS-2, which had a much higher S-concentration. The reason for this observation is unclear. It can be

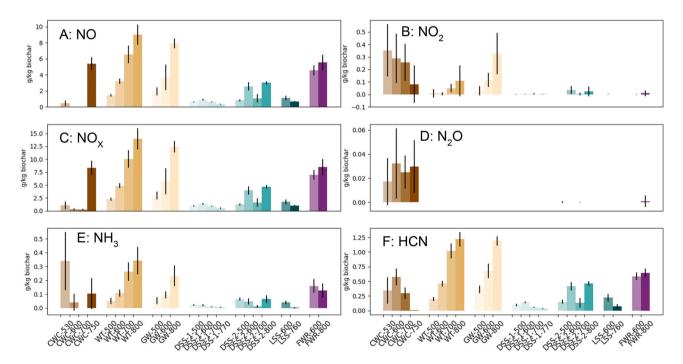


Fig. 7. Mean emission factors in g compound based on kg biochar produced. The error bars represent the standard deviation. A: NO, B: NO₂, C: NO_x, D: N₂O, E: NH₃, F: HCN. The missing data points for NO₂ and N₂O were below detection limit ($<0.01 \text{ mg/Nm}^3$), expressed as 0 in the figure. Values are tabulated in SM section B.3, Table S11.

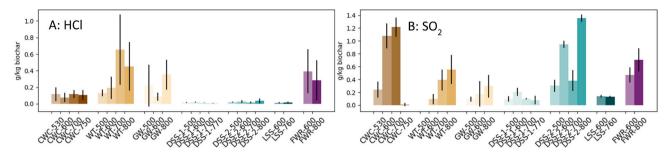


Fig. 8. Mean emission factors in g compound based on kg biochar produced. The error bars represent the standard deviation. A: HCl, B: SO₂. Values are tabulated in SM section B.3, Table S10.

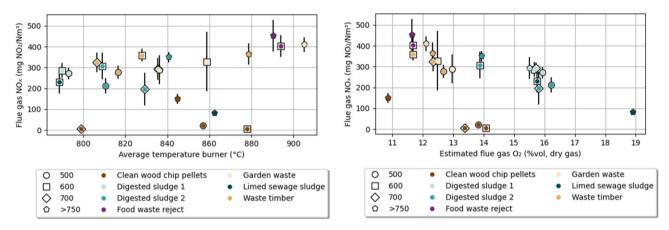


Fig. 9. Measured mean NO_X (mg NO_2/Nm^3) related to average measured burner temperature (left) and measured NO_X related to estimated flue gas O_2 concentration (right). The error bars represent the standard deviation.

speculated that it is connected to the ash content, which was much higher in the other feedstocks than in CWC: Metals such as iron, commonly present in sewage sludge, can form sulphides, preventing the feedstock S to form SO₂ (Dong et al., 2015). Also the presence of alkali such as Ca and K can reduce SO₂ emissions from combustion of biomass (Wolf et al., 2005). Both metals and alkali were present in the other feedstocks in higher concentrations, e.g. Fe concentration in CWC was 0.02 g/kg while ranging 1–130 g/kg in the other feedstocks and Ca concentration in CWC was 1.5 g/kg, while ranging 3–153 g/kg in the other feedstocks (Sørmo et al., 2023a, submitted). The CWC has a very low ash content, so most of the feedstock S could be formed into SO₂. When comparing the SO₂ emission factors per feedstock to the theoretical SO₂-emission based on all feedstock S, only 0.6–4% of the theoretical SO₂ was formed from the sludges, while the CWC-700 formed 100% of theoretical SO₂.

3.4. NO_X , CO and burner conditions

NO_X and CO are two pollutants whose formation are highly affected by burner conditions. CO is formed as a production of incomplete combustion, usually when air-to-fuel ratio is < 1.06, with CO increasing as the air-to-fuel ratio and temperature goes down (Sehn and Gerber, 2007). High air-to-fuel ratios and temperature typically promote more NO_X-formation, so monitoring of residual oxygen and regulation of combustion air is essential to keep the balance between CO and NO_X within the legal framework (section 3.5). There was no significant correlation between available fuel N and NO_X emissions between the various waste feedstocks (R² = 0.17, p = 0.08, Fig. 4). Without normalizing for the O₂-concentation, however, NO_X concentrations from the waste materials increased with average burner temperature (R² = 0.24, p = 0.03, Fig. 9, left) and decreased with estimated O₂ concentration (R² = 0.76, p = 1 × 10⁻⁶, Fig. 9, right). O₂ concentration reflects

excess air flow to the burner and in effect dilutes the NO_X concentration and cools down the burner temperature. However, the normalization (Eq. 12, SM A.3) evens out the dilution effect (Fig. 10), making low O₂ concentrations (<11%) and lower temperatures optimal for low NO_X-concentrations normalized by Eq. 12 (SM A.3).

The CWC NO_X concentrations are also correlated with the O₂-concentration ($R^2 = 0.94$, p = 0.03), but at a lower emissions range (6.2-149 mg/Nm3 for CWC, 81-454 mg/Nm3 for waste feedstocks) compared to the waste feedstocks. This is most likely due to the very limited fuel N available in the CWC feedstock. When converting CWC feedstock N load to corresponding NO₂ and dividing it by estimated flue gas volume, the maximum theoretical NO_X concentration possible to produce from the CWC feedstock was 176 mg/Nm³ (CWC-700), and only 4-92% of fuel N was converted to NO_X. Since flame temperatures need to be very high, above 1000 °C, for NO_X to be produced from N₂ in air, the current burner conditions only produced NO_X from fuel N, keeping the CWC NO_X values lower than the waste feedstocks. The waste feedstocks loaded much more fuel N, but only converted 1-4% (for sludges) or 4-32% (for FWR and lignocellulosics) of it into NO_X emissions with the current burner conditions. This shows that above a certain nitrogen level in the fuel, such as the level for waste materials, combustion conditions such as temperature, combustion air flow and residence time of the pyrolysis gas needs fine tuning to attain NO_X-concentrations within the legal framework (see section 3.5 for discussion on the legal framework).

3.5. Regulatory and industrial implications

3.5.1. EU emission limit values

To compare the emission concentrations with current EU legal requirements for waste incineration plants, they need to be normalized to 11% vol O₂ (dry flue gas). The EU Directive 2010/75/EU

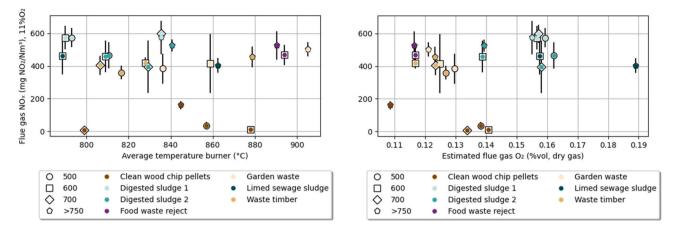


Fig. 10. NO_X -concentrations normalized to 11% residual oxygen per dry flue gas (mg NO_2/Nm^3) related to average measured burner temperature (left), and measured NO_X related to estimated flue gas O_2 concentration (right). The error bars represent the standard deviation.

on industrial emissions (integrated pollution prevention and control) Annex VI (European Council, 2010) presents emission limit values (ELV) for concentrations of total suspended particle emissions (TSP), total organic carbon (NMVOC + CH₄ expressed as C), HCl, CO, SO₂ and NO_X. HF also has an ELV (1 mg/Nm³) but was below detection limit (<1 mg/Nm³) in our tests and was therefore not included. The EU ELVs are shown as red line and compared to the emissions from the current study in Fig. 11.

With the current burner setup, all the feedstocks tested were within the ELVs for total suspended particles (TSP, or "total dust" in the EU Directive) and CO. However, HCl might be an issue when pyrolyzing waste with high or varying Cl content, especially given the variability observed in HCl emissions from pyrolysis of waste timber, garden waste and food waste reject (relative standard deviations 29–115%), most likely due to the heterogeneity of these feedstocks. Food waste reject had the highest measured Cl-level (2.6 \pm 0.2 g Cl/kg feedstock, Table S1), probably due to salt from food waste, and emitted the most HCl per feedstock (0.14 \pm 0.09 g HCl/kg dry feedstock for FWR-600, Table S12). Waste timber, often waste from demolition of buildings, might be contaminated with Cl-containing adhesives, binders or paints, and this contamination level might be more variable than the low Cl levels measured in this study (0.005 \pm 0.009 g Cl/kg feedstock, Table S1). For feedstocks with high Cl-levels, such as mixed wastes including food waste, HCl pollution control might be needed.

The highest-temperature limed sludge biochar (LSS-760) showed very high CH₄ emission concentrations (76 \pm 24 mg/Nm³, 11% O₂). Additionally, we estimated unusual high amounts of co-firing propane (4.7 kg/h compared to 0.4 kg/h average for sludge feedstocks, Table S14) and combustion air use for this sample, resulting in an estimated flue gas volume of 357 Nm³/h compared to the average of 60

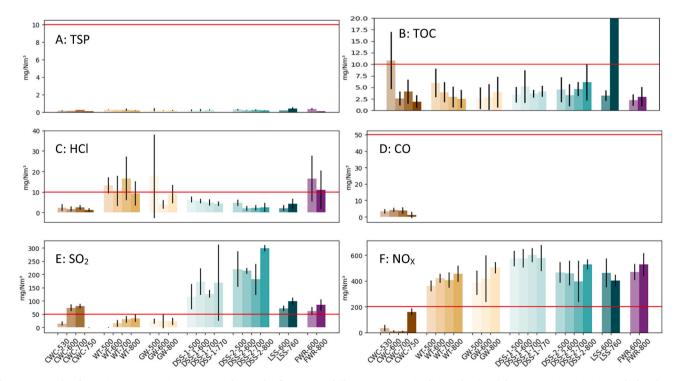


Fig. 11. Normalized emission concentrations to 11% vol O_2 in dry flue gas. EU daily average emission limit value (ELV) for waste incineration is marked with a red, horizontal line on each figure. The black, vertical lines represent the standard deviation. A: TSP (mg/Nm³), ELV: 10 mg/Nm3, B: TOC (NMVOC + CH₄ as mgC/Nm³), ELV: 10 mg/Nm³, C: HCl, (mg/Nm³), ELV: 10 mg/Nm³, D: CO, (mg/Nm³), ELV: 50 mg/Nm3, ELV: 50 mg/Nm³, ELV: 50 mg/Nm³, F: NO_x (mg NO₂/Nm³), ELV: 200 mg/Nm³. The TOC value of LSS-760 is out of scale at 76 ± 24 mg/Nm³.

Nm³/h (Table S14). Further tests are needed to conclude whether the CH₄-emissions were a consequence of the pyrolysis of this feedstock itself or whether it was a consequence of changed combustion conditions. During the pyrolysis, CaCO₃ in this sample was converted into CaO and CO₂, a temperature dependant (>650 °C), endothermic process. This increased the energy demand for the pyrolysis process and produced a highly reactive biochar product. To avoid this, limed sludge should not be pyrolyzed above 650 °C.

3.5.2. NO_X emissions and control

The NO_X values were above the ELV for all the waste feedstocks (Fig. 11F), but optimising the burner conditions, such as reducing the air-to-fuel ratio to reduce the normalized NO_X values while increasing the now negligible CO values somewhat, could make it possible for these waste feedstocks to reduce NO_X to within the ELV. The current EU regulation for incineration gas temperature and retention time is 850 $^\circ C$ for 2 s (European Council, 2010). These should be low enough to allow a reduction of NO_x-concentrations by lowering the air-to-fuel-ratio. If the combustion process goes above 1000 °C, there is potential for significant amounts of fuel NO_x from feedstock N in addition to thermal NO_x from ambient N₂. For plants that need high combustion temperatures, such as for hazardous waste where the combustion temperature needs to be raised to 1100 °C (European Council, 2010), the EU Commission Best Available Techniques (European Commission, 2019) recommends selective (non-)catalytic reduction (SCR/SNCR) as the most efficient technique for reducing NO_X.

3.5.3. SO₂ emissions and control

The measured SO₂-concentrations indicate that pyrolysis of high Sfeedstocks such as sewage sludge might need SO₂ pollution control to adhere to the ELV for waste incineration. Biomass combustion (installed power >50 MW), which is more relevant for CWC, is subjected to an SO₂ ELV of 133 mg/Nm³ (200 mg/Nm³ at 6% O₂), which is within reach for the lignocellulosics (highest SO₂ concentration at 79 \pm 8 mg/Nm³ at 11% O₂ for CWC-700). Large pyrolysis plants planning to include sludge or other high S-feedstocks should consider a SO₂ reduction method such as a wet scrubber or dry sorbent injection (Kaminski, 2003). Such methods are easy to implement, highly efficient and could also reduce HCl-levels (European Commission, 2019).

3.5.4. Comparing pyrolysis and incineration

Compared to incineration, the air emissions measured from pyrolysis of waste, with condensation, were very low, especially for particulates and TOC (Conesa et al., 2009; Yoo et al., 2002). The legal framework limiting air pollution for waste incineration makes it necessary to install advanced air pollution control devices on waste incinerators. Usually, the investment cost of modern waste incinerators makes it necessary to build large, centralized units where air pollution can be controlled and monitored, and the combustion energy can be used for example for district heating (Makarichi et al., 2018).

Based on the results from this study, waste pyrolysis with condensation, especially pyrolysis of lignocellulosic waste, does not need as advanced air pollution control as waste incineration. Compared to clean wood pellet pyrolysis, where fuel-NO_X can mostly be avoided by keeping combustion temperature low, waste feedstocks need careful monitoring of O₂-levels and air intake, such as using a lambda sensor, in addition to combustion temperature, to stay within NO_X ELV. This should be documented in future studies on pyrolysis air emissions.

Sørmo, Adli et al. (2023, submitted) investigated heavy metal emissions from pyrolysis of the same feedstocks as in the present work and found that the measured sum of HMs emitted upon pyrolysis were 30–300 times lower than the EU threshold of 500 μ g/m³ for waste incineration (European Council, 2010), although they did not quantify the ultrafine particle fraction. Another parallel study by our group (Sørmo, Krahn et al., 2023; submitted), reported emissions of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzodioxins and

furans (PCDD/Fs) well below the EU thresholds for waste incineration. However, emissions of per and polyfluorinated alkylsubstances (PFAS) were found to be in the range of 0.01–3.1 mg/tonne of biochar, and there were furthermore uncertainties related to the release of PFAS degradation products (Sørmo et al., 2023b).

3.5.5. Recommendations and implications for industry

Given the findings, industries considering pyrolysis of high S-feedstocks like sewage sludge should implement SO_2 pollution control. It is likely that application of wet scrubber technology for SO_2 and HCl pollution control could reduce the concentrations of heavy metals, PAHs, PCDD/Fs and PFAS by scavenging particles from the flue gas, but this needs to be confirmed by further studies. More research is needed on optimized combustion of pyrolysis gases to reduce NO_X emissions from waste pyrolysis, however techniques like selective (non-)catalytic reduction (SCR/SNCR) would ensure effective NO_X reduction for waste pyrolysis. By aligning practices with regulatory standards and implementing recommended pollution control measures, industries can ensure both environmental compliance and operational efficiency.

4. Conclusions

Our study demonstrated that pyrolysis with condensation is a promising waste management alternative for various waste types. Compared to incineration, this method simplifies air pollution control, with emissions generally lower than those reported in previous literature (Cornelissen et al., 2016; Dunnigan et al., 2018; Pennise et al., 2001; Sørmo et al., 2020). The exception is NO_X emissions, which require careful air-to-fuel ratio regulation to balance CO and NO_X production, or implementation of other NO_X reducing measures such as flue gas recirculation, SNCR or SCR.

While emissions from lignocellulosic waste materials were similar to those from the clean wood reference, sludge feedstocks and food waste reject emitted more SO₂ than the clean wood reference, exceeding the EU emission limit for waste incineration. This suggests that SO₂ air pollution control measures should be considered for industrial-scale pyrolysis of these waste types. SO₂ control measures are not only easy to implement and highly efficient, but they and can also reduce HCl concentrations, which we found can fluctuate significantly from heterogeneous wastes such as waste timber and food waste reject.

Previous studies on these feedstocks have shown low PFAS emissions (Sørmo et al., 2023b) and heavy metal, PAHs, and PCDD/F emissions well below existing ELVs for waste incineration (Sørmo, Adli et al., 2023; submitted; Sørmo, Krahn et al., 2023; submitted). However, to fully understand the environmental impacts, a life cycle perspective comparison of pyrolysis of these different feedstocks is necessary.

In light of these findings, we recommend further research into life cycle impacts of pyrolysis for waste feedstocks, as well as research into emissions from condensed and non-condensed pyrolysis gas from waste feedstocks using optimized industrially relevant combustion systems and chemical kinetic simulations. Ultimately, our research paves the way for a more sustainable future, highlighting pyrolysis as a viable and environmentally friendly alternative for waste management that could potentially reduce the environmental footprint of organic waste treatment.

CRediT authorship contribution statement

Gudny Øyre Flatabø: Writing – original draft, Conceptualization, Formal analysis, Investigation, Resources, Visualization. Gerard Cornelissen: Conceptualization, Methodology, Investigation, Supervision, Writing – review & editing, Project administration, Funding acquisition. Per Carlsson: Resources, Writing – review & editing. Pål Jahre Nilsen: Resources, Writing – review & editing. Dhruv Tapasvi: Resources, Writing – review & editing. Wenche Hennie Bergland: Writing – review & editing. Erlend Sørmo: Conceptualization, Methodology,

Journal of Cleaner Production 423 (2023) 138777

Formal analysis, Investigation, Writing – review & editing, Visualization, Supervision, Funding acquisition.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the first author used OpenAI ChatGPT-4 in order to generally improve language of introduction, conclusion and abstract. Dall-E 2 was used to create a few of the illustrations integrated into the graphical abstract. After using these tools, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gudny Oeyre Flataboe reports financial support was provided by VOW ASA. Per Carlsson reports financial support was provided by VOW ASA. Paal Jahre Nilsen reports financial support was provided by VOW ASA. Dhruv Tapasvi reports financial support was provided by Lindum As. The authors Per Carlsson and Pål Jahre Nilsen are employed by VOW ASA, distributor of the "Biogreen (R)" technology used for performing this study. Their salaries were paid by VOW ASA, but all research activities and measurements were funded through a regulated publicprivate-collaboration research project and managed by Norwegian Geotechnical Institute. Gudny Øyre Flatabø is also employed by VOW ASA, but her salary is paid through an "Industrial PhD"-program with joint private-public funding. Dhruv Tapasvi is employed by Lindum AS who distributed some of the test materials and have interests in the results. His salary was paid by them.

Data availability

Most raw data is supplied through Supplementary Material. More can be supplied upon request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2023.138777.

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