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Low temperature circulating fluidized bed gasification and co-gasification of municipal sewage sludge. Part 1: Process performance and gas product characterization

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1 **Low Temperature Circulating Fluidized Bed gasification and co-gasification of**

2 **Municipal Sewage Sludge. Part 1: Process performance and gas product**

3 **characterization**

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9 **Abstract**

10 The study is part 1 of 2 that investigates gasification of municipal sewage sludge (MSS) as well as co-gasification

11 of MSS and cereal straw in low temperature gasifiers. Results from five experimental campaigns with Low

12 Temperature Circulating Fluidized Bed (LT-CFB) gasification of straw and/or MSS from three different Danish

13 municipal waste water treatment plants in pilot and demonstration scale are analyzed and compared. The

14 gasification process is characterized with respect to process stability, process performance and gas product

15 characteristics.

16 A total of 8600 kg of MSS dry matter was gasified during 133 hours of LT-CFB operation test with MSS fuels.

17 The short term stability of all campaigns was excellent. LT-CFB gasification of dry MSS lead to substantial

18 accumulation of coarse and rigid, but un-sintered, ash particles in the system, and these particles may

19 negatively affect long term operation due to problems with decreased fluidization and circulation. Co-

20 gasification of MSS with sufficient amounts of cereal straw was found to be an effective way to mitigate these

21 issues by substantially reducing the potential accumultion of oversize MSS ash particles and thereby also

22 reducing the need for other means to control the bed composition. Characterization of gas products and

23 process performance showed that even though gas composition varied substantially, hot gas efficiencies of

24 around 90% could be achieved for all MSS fuel types.

25 **Keywords:** Municipal sewage sludge; cereal straw; thermal gasification; process performance; gas product

26 characterization

27 **1   Introduction**

28 Modern techniques for cleaning municipal wastewater lead inevitably to production of municipal sewage

29 sludge (MSS). The annual production of MSS in Europe, North America and Japan amounts to around 30 million

30 ton dry matter, while the annual global production has been estimated to be around 50 million ton dry matter

31 (Krüger and Adam, 2015; Zsirai, 2011). The global MSS production is increasing rapidly, driven by improved

32 wastewater cleaning techniques, a growing global population, increasing wealth in developing parts of the

33 world, and more strict regulations on emissions from wastewater treatment to the environment (Kelessidis and

34 Stasinakis, 2012; Samolada and Zabaniotou, 2014). To avoid problems with pathogens, xenobiotics and toxins,

35 greenhouse gases and foul odor, the produced sewage sludge requires appropriate handling. The benefits of

thermal MSS management systems can include; i) energy recovery, ii) mass- and volume reduction, iii) odor reduction, iv) sterilization and purification by destruction of pathogens and organic xenobiotics (microplastics, pharmaceuticals, phthalates, flame retardants etc.), and, v) a general reduction of product variations and associated risks, providing increased robustness of the disposal system (Donatello and Cheeseman, 2013; Fytili and Zabaniotou, 2008; Samolada and Zabaniotou, 2014). Thermal gasification is one of the emerging thermal MSS management alternatives. The process has the same general advantages as other thermal processes plus some additional desirable qualities including: i) A flexible energy product range with a potential for gaseous, liquid and solid energy products, ii) High electric efficiency, even in very small scale with gas engines or fuel cells (Ahrenfeldt et al., 2013; Thomsen et al., 2015), iii) Reduced emissions and/or exhaust gas cleaning costs in combustion systems when pretreating the gas prior to combustion (Jenkins, 2015; Kang et al., 2011; Samolada and Zabaniotou, 2014), iv) Potential conservation and recycling of the critical nutrient phosphorous (P) and other valuable macro and micro nutrients in fertilizer ashes with high carbon content to increase security of supply, enhance soil quality and sequester carbon (Cordell and White, 2014; Hansen et al., 2016, 2015).

Several different thermal MSS gasification designs are currently under development including down-draft gasification (Arjharn et al., 2013), two-stage gasification (Mun et al., 2013; Mun and Kim, 2013), three-stage gasification (Choi et al., 2016), fluidized bed gasification (Calvo et al., 2013; Kang et al., 2011), Dual Fluidized Bed gasification (Xiaoxu et al., 2012) as well as fixed bed gasification (Werle, 2015) and fixed bed co-gasification of MSS and woody biomass (Ong et al., 2015; M. Seggiani et al., 2012). On a commercial or near-commercial level, the designs under development and testing include among others the SÜLZLE Kopf SynGas bubbling fluidized bed gasifier (Judex et al., 2012) and Outotec's dual-circulating fluidized bed gasifier (Buchholz, 2015).

There are several challenges related to efficient MSS management, and in systems with thermal gasification, these issues commonly relates to a very high content of moisture, ashes, and heavy metals combined with high heterogeneity and constant fluctuations in the MSS fuel characteristics as function of season and geography. The implications of these issues may be ash melting, bed agglomeration, low efficiency and/or substantial variations in the process performance and/or product composition and quality (Calvo et al., 2013; Krüger et al., 2014; Krüger and Adam, 2015; M. Seggiani et al., 2012; Maurizia Seggiani et al., 2012).

In this study it is hypothesized that co-gasification of MSS with straw in low temperature gasifiers with downstream gas combustion in CHP boilers may be an efficient way to mitigate some of the common issues related to MSS gasification. Mixing MSS and straw may reduce the practical impact of high ash content and heavy metal content in the MSS. In addition, mixing dewatered MSS and dry straw may reduce or eliminate MSS drying requirements. Finally, a proper mixture of MSS and straw may reduce fluctuations in fuel characteristics and process performance and product quality, and increase the fertilizer value of the ashes from the process by improving the phosphorus-potassium nutrient relationship and positively modify P plant availability. A low temperature process will make it possible to convert high alkali straw in fluidized bed systems, and direct downstream combustion of the gas product in existing medium to large CHP boilers may provide a more optimal combination of energy efficiency, emissions and economy. Such a system could prove to be a very interesting MSS management alternative in Denmark and other countries with similar resources of herbaceous biomass.

74 Five experimental campaigns with cereal straw gasification, MSS gasification and MSS/cereal straw co-
75 gasification in two Low-Temperature Circulating Fluidized Bed (LT-CFB) gasifiers of very different scale are
76 analyzed and compared in this work. The study is divided into two parts:

77 - Part 1: Process performance, product distribution and gas product characteristics (this study)
78 - Part 2: Ash product characteristics (composition, pH and P fertilizer quality) and estimation of
79   elemental balances for selected elements and heavy metals (Thomsen et al., 2017)

2   Materials and Method

2.1   About the LT-CFB gasifier

82 The LT-CFB process was selected for the investigation as it is a very fuel flexible platform that has been proven
83 to operate on many different fuels including cereal straw, biogas- and manure fibers and organic residues from
84 industry. Schematics of the process are provided in Figure 1, and a more details on the LT-CFB process design
85 and previous operational results can be found in literature (Ahrenfeldt et al., 2013; Kuligowski et al., 2008;
86 Narayan et al., 2016; Nielsen, 2007; Stoholm et al., 2008).

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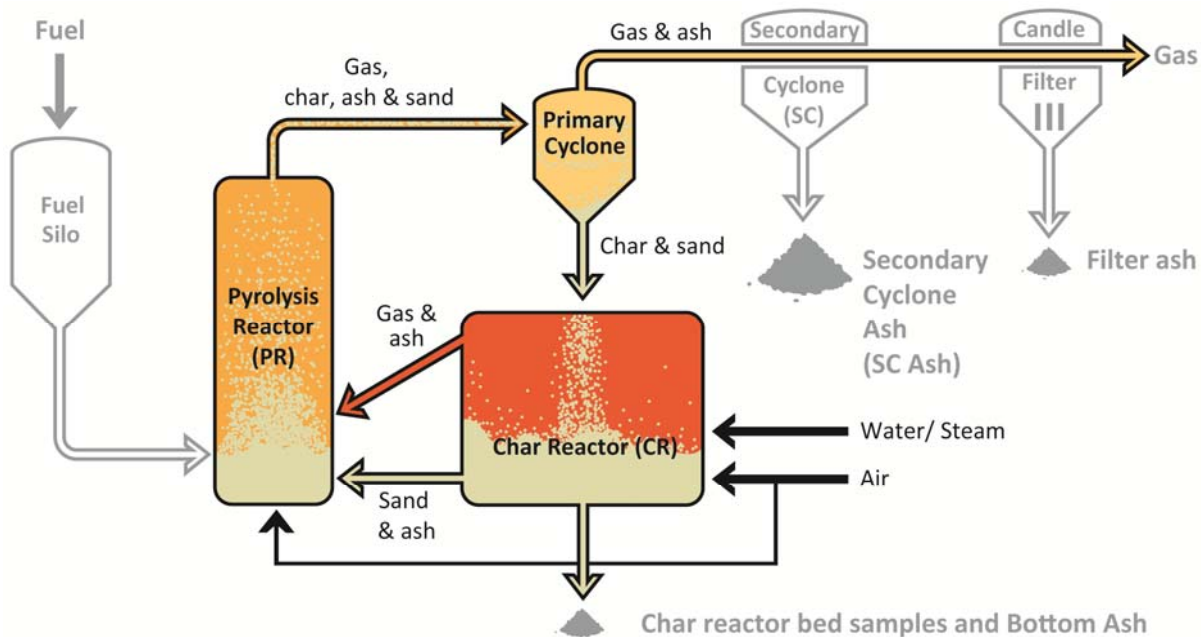
Figure 1: Low Temperature Circulating Fluidized Bed (LT-CFB) gasification system. Modified from (Thomsen et al., 2015).

89 The LT-CFB technology has been under development for almost 20 years and has been bought and
90 commercialized by DONG Energy under the alias Pyroneer in recent years. The largest LT-CFB built has a
91 thermal capacity (TH) of 6 MW and is located at Asnaes Power Plant in Kalundborg, Denmark. When operating,
92 the 6 MW unit supplies product gas to a suspension-fired coal boiler, thereby substituting coal in a high
93 efficiency CHP system (DONG Energy Power A/S, 2012). In addition to the 6 MW$_{TH}$ unit, a 100 kW$_{TH}$ pilot scale

94 LT-CFB unit exist at the Technical University of Denmark (DTU) at Campus Risø near Roskilde. The 100 kW unit
95 has an option for hot gas filtration in a candle filter. The present study includes data from campaigns
96 conducted at both of these LT-CFBs using quartz sand without additives as bed material (DanSand.dk, 2013).

97 **2.2 About the campaigns and fuels**

98 Results from five campaigns are included in the present study. Two of the campaigns were conducted on dry
99 MSS granules, two were conducted on mixes of dry or dewatered MSS and dry Danish wheat straw, and one
100 was conducted on dry Danish wheat straw alone. The MSS fuel campaigns ranged between 17 and 40 hours of
101 operation, and the MSS consumption varied between 45 and 7500 kg MSS dry matter. A brief description of the
102 campaigns is provided in Table 1. A hot gas candle filter made from inorganically bonded granular minerals
103 (TENMAT FIREFLY, Manchester, UK) was applied in two of the campaigns to further clean the product gas of
104 particulate material. Four MSS samples have been gasified during the five campaigns. The MSS samples
105 originate from three different Danish wastewater treatment plants (WWTPs) in Randers (Randers WWTP),
106 Aabenraa (Stegholt WWTP), and, Roskilde (Bjergmarken WWTP). The WWTPs are described in detail in part
107 two of the study (Thomsen et al., 2017). Proximate analysis data on the five test fuels are provided in Table 2.

108 **Table 1: Overview of Low Temperature Circulating Fluid Bed (LT-CFB) campaigns. ST: Stegholt WWTP. BJ: Bjergmarken WWTP. RA:**
109 **Randers WWTP. WWTP: Wastewater treatment plant. Th: Thermal capacity. MSS: Municipal sewage sludge**

Name	Fuel type	LT-CFB plant	Filter
REF	Crushed wheat straw pellets	Risø DTU, 100 kW$_{Th}$	Yes
MIX-ST	Mix: Dewatered MSS (ST) + crushed straw pellets	Risø DTU, 100 kW$_{Th}$	No
MIX-BJ	Mix: Dry MSS pellets (BJ) + straw pellets	Asnaes Power plant, 6 MW$_{Th}$	No
SLU-BJ	Dry MSS granules (BJ)	Risø DTU, 100 kW$_{Th}$	Yes
SLU-RA	Dry MSS granules (RA)	Risø DTU, 100 kW$_{Th}$	No

110

111 **Table 2: Fuel characterization. DM: Dry Matter. D.a.f: Dry, ash free.**

		Reference	MIX-ST[1]	MIX-BJ[1]	SLU-BJ	SLU-RA
MSS:Dry straw mixing ratio	% wet	0:100	30:70	21:79	100:0	100:0
	% DM	0:100	11:89	14:86	100:0	100:0
Moisture	% wet	10.6	29.9	12.5	12.5	4.6
Volatiles	% DM	68.4	67.7	66.5	42.7	43.1
Fixed carbon	% DM	23.8	22.5	20.1	14.2	15.2
Ash	% DM	7.9	9.8	13.3	43.1	43.8
HHV, wet	MJ/kg	16.1	13.2	14.8	11.4	12.2
HHV, d.a.f	MJ/kg	19.6	20.9	19.5	22.9	22.0

2.3 Description of analytical procedures

Proximate compositions of fuels were determined as follows: Moisture content (ASTM D3173-73, DS/EN 14774-3 (2009) and EN 12880), Volatile matter: ASTM D3175-73 and Ash content: (ASTM D3174-73, DS/EN 14775 (2009) and EN 15169 (2007)).

Fuel and ash higher heating values were determined by bomb calorimetry on a Parr 6300 Bomb Calorimeter (Parr Instrument Company, Moline, Illinois, USA). In samples with very low heating values, a mixture of solid benzoic acid (26.454 MJ/kg HHV) and ash (50/50% by weight) was prepared and combusted in the bomb calorimeter.

All data from operation of the 100 kW plant (fuel feeding rate, system temperatures, system pressures, SC ash production rate, air flows, nitrogen flows and water/steam flows) was logged using National Instruments Labview 2015 software. Data from the 6 MW plant was provided by DONG Energy A/S, Denmark using a process control and data acquisition system from 2012 developed and implemented by SIEMENS, Germany.

Analysis of product gas from the 100 kW unit, was performed with an Advance Optima 2020 Modular continuous process gas analyzer system, applying a Caldos 15 cell for H_2 analysis and an Uras 14 cell for CO, CO_2, and CH_4 (ABB, Switzerland). Content of O_2 was determined using a PMA 10 O_2-Analyser. Prior to analysis gas was cleaned in a system composed of a bobble flask with tap water and two serial twist-filters before conditioning in a CSS-V Sampling-system (M&C TechGroup, Germany). Heating Values of the cold gas products were calculated using calorific values for the included gas components representative at 25 °C and 1 atm (Turns, 2012).

Gas sampling for simple hydrocarbon was performed using conservatively flushed gas pipettes. Three samples were extracted from the product gas before the gas analyzer. The samples were analyzed for simple hydrocarbons using a GC system with flame ionization detection (FID) and GC-MS. A series of 10 simple hydrocarbons from ethane up until benzene were measured using this system.

Quantification of the tar and water content in the product gas was done using a simple method developed at DTU Chemical Engineering. The method combines cooling and condensation with gas volume determination and calorimetry. The experimental setup is illustrated in Figure 2. All the applied equipment (Figure 2) was cleaned and weighted before and after the experiment. The time of the experiment was recorded and the total non-condensing gas volume measured by the gas meter. Total condensate was quantified and divided into two main fractions i.e. light and heavy, and the tar-water ratio of the two fractions determined by calorimetry using a Parr 6300 Bomb Calorimeter with paraffin coated ignition threads. A dry tar HHV of 27 MJ/kg was assumed based on previous experience with LT-CFB tar and published literature on the heating value of the oil phase collected from MSS pyrolysis (Fonts et al., 2012). GC was used to verify that tar composition in the two fractions were identical. Condensate in the filter and filter casing was assumed to resemble that in the flask.

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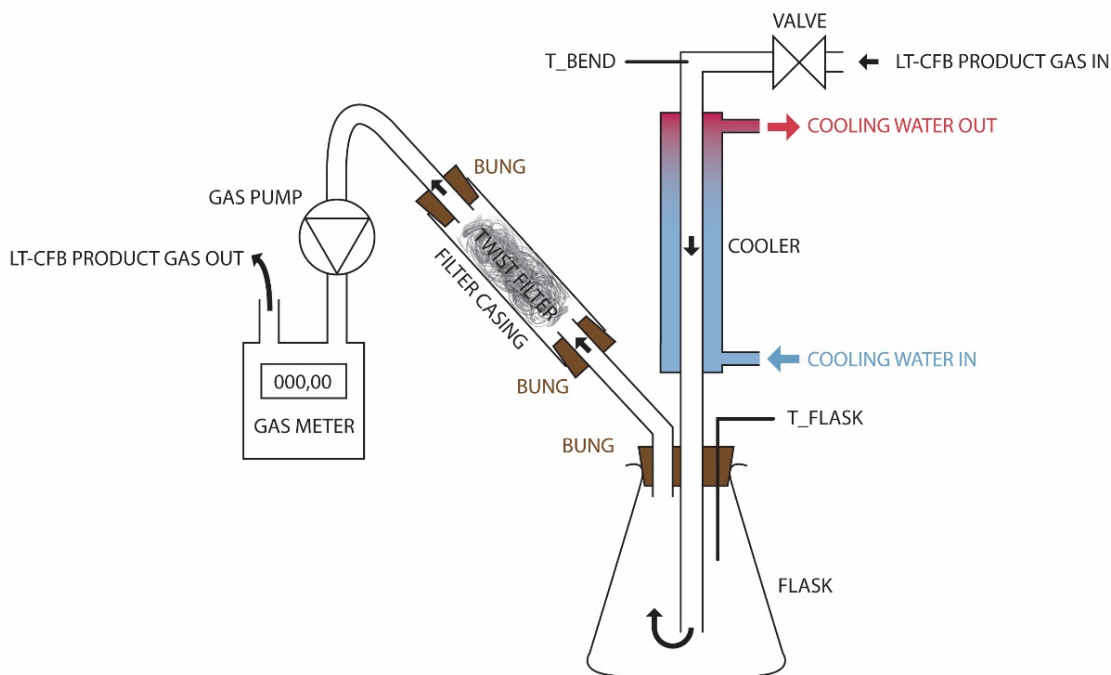
Figure 2: Experimental setup for quantification of total tar and water in gasification product gas. LT-CFB: Low temperature circulating fluidized bed gasifier. T: Temperature measurement point.

Tar collection for characterization and gravimetric tar measurements was done by bubbling product gas through acetone in a Petersen column (Grosch et al., 2015). The acetone was transferred to a measurement flask, and the weight difference between the clean flask and the same flask with dry tar residues after evaporation and thermal drying of the content was calculated and considered as total gravimetric tar. The analysis was done in duplicate.

Determination of phenolics was performed on a mixture of the acetone sample and deuterated phenol (phenol d5) solution. Samples were extracted with cyclohexane after pH increase and the cyclohexane phase discharged with diethyl-ether. The sample was extracted again with diethyl-ether after lowering pH and the ether phase was collected and traces of water removed. The samples were analyzed with a Hewlett Packard HP 6890 gas chromatograph interfaced to a HP5973 Mass Selective Detector with a HP 7683 autosampler (Agilent, Denmark). Product separation was done using a 0.32-mm i.d.×30 m WCOT-fused silica column coated with VF-23ms at a thickness of 0.25 μm (Analytical, Denmark). Quantification was performed using the instrument responses and the known amount of deuterium labeled added standards.

Determination of polycyclic aromatic hydrocarbons (PAH) was performed on a mixture of the collected acetone sample and a standard solution with deuterated naphthalene, acenaphtene, fluorene, phenantrene, anthracene, fluoranthene and pyrene. Cyclohexane was added to the mixture and after mixing, 2 M NaOH solution was added. The cyclohexane phase was separated and traces of water were removed by adding Na_2SO_4. The samples were then analyzed using GC-MS as described above. The products were separated using

6

167   a 0.32-mm i.d.×25 m WCOT-fused silica column coated with CP-SIL at a thickness of 0.25 μm (Analytical,

168   Denmark). PAH compounds were identified using the NIST search engine version 2.0 f. (Agilent, Denmark).

169   Content of total N and ammonia was measured in the condensable fraction of the product gas by bubbling part

170   of the hot product gas through three impinger bottles in series containing demineralized water. The bottles

171   were cooled in ice bath and all condensable compounds were extracted from the gas. The concentrations of

172   ammonium (NH_4^+) and nitrate (NO_3^-) as well as total dissolved N (TDN) were analyzed by standard colorimetric

173   procedures on an AutoAnalyzer 3 (Bran+Luebbe, Norderstedt, Germany). The completeness of the

174   condensation was determined by comparing the concentrations in the three flasks.

175   Simple mass and energy balances were performed using data on relevant process inputs (Fuel (mass and HHV),

176   fresh bed material (mass), total air supply (mass) and total water supply (mass)) and process outputs (SC ash

177   (mass and HHV), Filter ash (mass and HHV), Char reactor bed draining (mass and HHV), final bed composition

178   (mass and HHV)). Total gas product mass was estimated by balance. Subsequently, the total mass of the gas

179   product was divided into tar, steam and dry, tar-free gas using the results from the tar and water

180   quantification. The Higher Heating Value of dry tar was assumed to be 27 MJ kg^{-1} (Fonts et al., 2012), and the

181   specific heat capacity of tar 1.47 kJ kg^{-1} K^{-1} at 500-600 °C (Engineeringtoolbox.com, 2016a). The specific heat

182   capacity of the dry, tar-free gas was assumed described by the content and heat capacity of N_2 and CO_2 alone

183   (1.11-1.12 and 1.15-1.20 kJ kg^{-1} K^{-1} respectively at 500-600 °C (Engineeringtoolbox.com, 2016b, 2016c)). Finally,

184   the specific heat capacity of steam at 500-600 °C was assumed to be 2.11-2.18 kJ kg^{-1} K^{-1}

185   (Engineeringtoolbox.com, 2016d) and the enthalpy of evaporation of the water to be 2.30 MJ kg^{-1} (Chang and

186   College, 2002). Air, water and fuel were assumed to have a temperature of 25 °C before entering the system.

187   The potential evaporation of inorganics is estimated based on laboratory study approximations (Thomsen et

188   al., 2015). This approach was chosen because a fully satisfactory energy balance based on enthalpy was not

189   possible to establish due to the complexity of the hot product gas.

190

191   **3   Results and discussion**

192   **3.1   Fuel feeding and thermal loads**

193   A total of 8600 kg MSS dry matter was gasified during a total of 133 hours of operation distributed with 45 kg in

194   28 hours in the MIX-ST campaign, 7500 kg in 48 hours in the MIX-BJ campaign, 240 kg in 17 hours in the SLU-BJ

195   campaign and 800 kg in 40 hours in the SLU-RA campaign. The feeding systems worked well for all fuel types.

196   Based on the fuel heating value and the fuel feeding rate, the fuel input thermal load of the LT-CFB gasifiers

197   during the different campaigns has been estimated. These results are provided on basis of HHV in Table 3.

198   In general, a higher thermal load was achieved in the straw campaign (REF) and the co-gasification campaigns

199   (MIX-ST & MIX-BJ) than in the MSS-only campaigns (Table 3). Extensive experiences with operation on straw as

200   well as a system designed for this purpose is part of the reason behind this difference. Also, the higher heating

201   value of the straw-based fuels led to higher thermal loads at comparable mass based feeding rates. Finally, the

202 lower ash content in the straw and straw-MSS mix required less effort to maintain a stable system mass and
203 gave fewer restrictions on the feeding rate in regard to potential mass accumulation in the system.

204 **Table 3: Nominal thermal capacity and recorded thermal load of the gasifiers during the assessed campaigns. Based on Higher**
205 **Heating Value of fuels.**

	Nominal thermal capacity	Average thermal load	Peak thermal load
	kW_{TH}	kW_{TH}	kW_{TH}
REF	100	88	99
MIX-ST	100	77	95
MIX-BJ	6000	6158	N.A
SLU-BJ	100	62	73
SLU-RA	100	71	81

206

207 All tested MSS fuels gave good preliminary operational results. However, efficient LT-CFB gasification requires a
208 relatively dry fuel or fuel mix with a maximum of 25-30 wt% moisture (Ahrenfeldt et al., 2013). The feasible
209 range of MSS-straw mixing ratios that can be converted in LT-CFB gasifiers is thereby limited by the moisture
210 content of both the MSS and the straw.

211 **3.2   Product distribution**

212 Mass based product distribution results are provided in Figure 3.

■ SC ash ■ Filter ash* □ Accumulated + drained CR bed   □ Total gas product
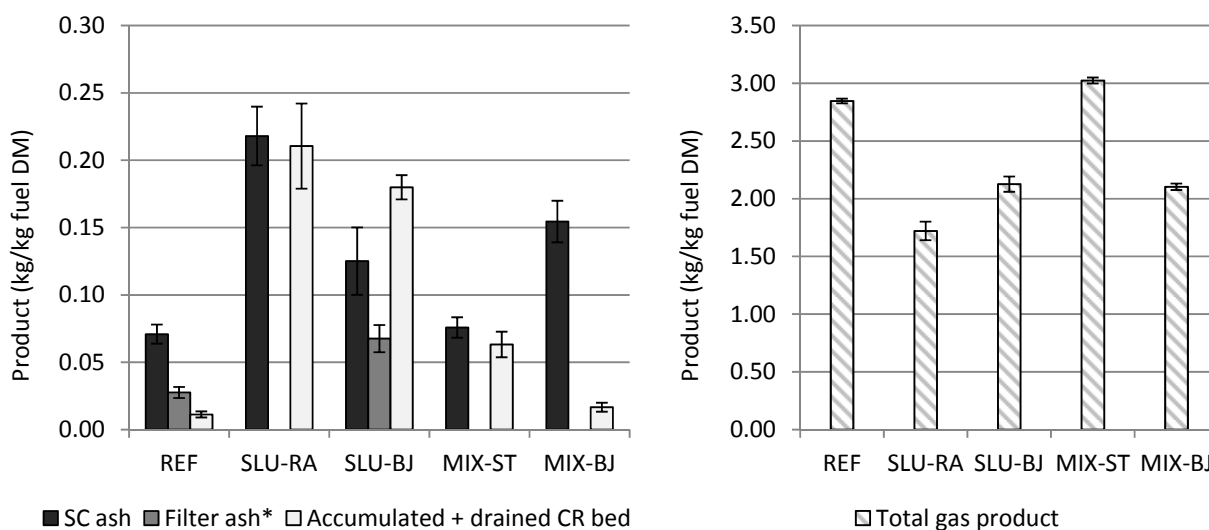
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214 **Figure 3: Mass distribution of products in the assessed low temperature gasification campaigns. Results on basis of dry fuel feed.**
215 **Accumulated + drained CR bed: Sum of fuel mass accumulated in the bed or drained as bottom ashes from the Char Reactor (CR). SC:**
216 **Secondary Cyclone. * Filter ash only collected in REF and SLU-BJ campaigns.**

217 Variations in total mass of gas product are due to differences in supply of air and water among the campaigns,
218 combined with differences in fuel ash and moisture content. There are also characteristic differences among
219 the production of SC ash, and the sum of bed material, accumulating and drained as bottom ashes. Both of
220 these product fractions increase severely, when operating on sludge only as a consequence of the very high ash
221 content in the dry sludge fuels (Table 2).

222 **3.3   Process stability**

223 3.3.1   Temperatures and pressures

224 The temperatures recorded in the char reactor (see Figure 1) were very stable with maximum temperatures of
225 735-750 °C across all campaigns. The temperature fluctuations in the char reactor were generally smaller in
226 straw and straw/MSS campaigns (10-15 °C) than in the MSS-only campaigns (35-40 °C) whereas the
227 temperature fluctuations in the pyrolysis reactor was comparable in the REF and SLU campaigns (20-30 °C) and
228 substantially higher in the MIX-ST campaign (50 °C). The vertical temperature gradients in the char reactor bed
229 was just 5-10 °C in all campaigns while the temperature difference between the bed and the freeboard ranged
230 from 20-50 °C in the SLU campaigns to 60 °C in the REF campaign and almost 80 °C in the MIX-ST campaign. The
231 vertical temperature gradients in the pyrolysis reactor was generally the same in all campaigns (10-20 °C
232 difference from top to bottom) except for the MIX-ST campaign where it was at least 5 times as high (around
233 100 °C) due primarily to the cooling effect of the water in the fuel. Similarly, there was a noticeably larger
234 difference between the average temperatures in the char reactor and pyrolysis reactor in the MIX-ST campaign
235 (160 °C) than in the other campaigns (25-50 °C) owing mainly to higher water content in the MIX-ST fuel.
236 Towards the end of the two SLU campaigns the temperature difference between the char and pyrolysis
237 reactors started to increase continuously indicating reduced circulation of bed mass. The development in the
238 SLU-BJ temperatures and the difference towards the MIX-ST temperatures are illustrated in Figure 4 with data
239 from 10 aggregated periods of 30-60 minutes covering the full campaign periods.
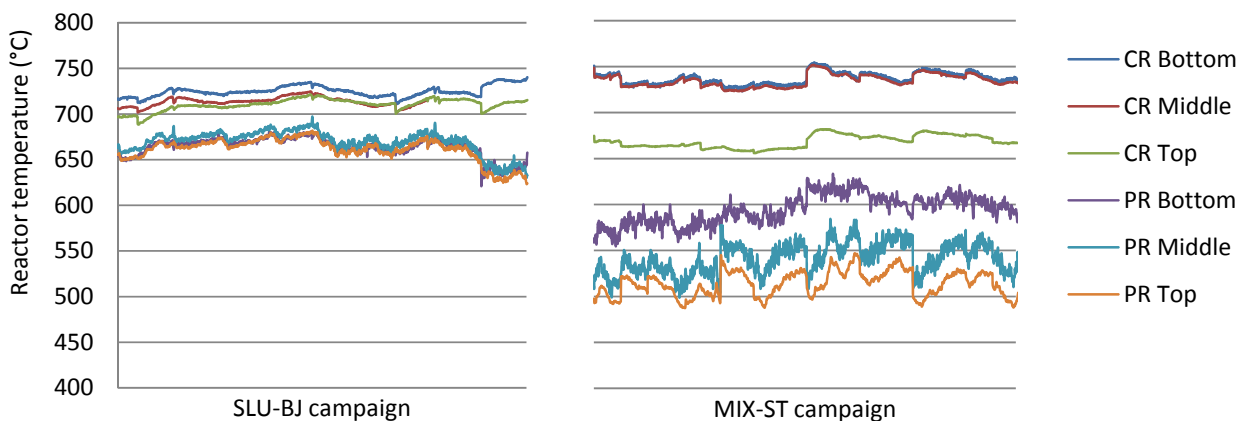
241 **Figure 4: Pyrolysis reactor (PR) and char reactor (CR) data curves from SLU-BJ campaign (left) and MIX-ST campaign (right). Data**
242 **aggregated from 10 periods of 30-60 minutes totaling 8 hours out of a total operation data set of 17 hours (SLU-BJ campaign) and 28**
243 **hours (MIX-ST campaign).**

244   The reduced circulation at the end of the SLU campaigns was accompanied by development in the system
245   pressures. In general these were quite stable in all campaigns with high pressure drops across the bed in the
246   char reactor as well as pyrolysis reactor, indicating full fluidization. However, there was a continuously
247   decreasing pressure difference across the char reactor in the last part of the two SLU campaigns, which was not
248   observed in the REF and MIX campaigns. Declining pressure drop indicates declining bed mass and density
249   and/or incomplete fluidization, which can be due to increasing bed particle sizes (Kunii and Levenspiel, 1991).
250   The development (example in Figure 5) follows the increased temperature differences between the reactors
251   and in combination this also indicates reduced circulation. This development is only evident in the MSS-only
252   campaigns, and therefore co-gasification MSS with straw in proper mixing ratios seem to be a simple and
253   efficient way to mitigate this issue and avoid the need for other bed particle management efforts.
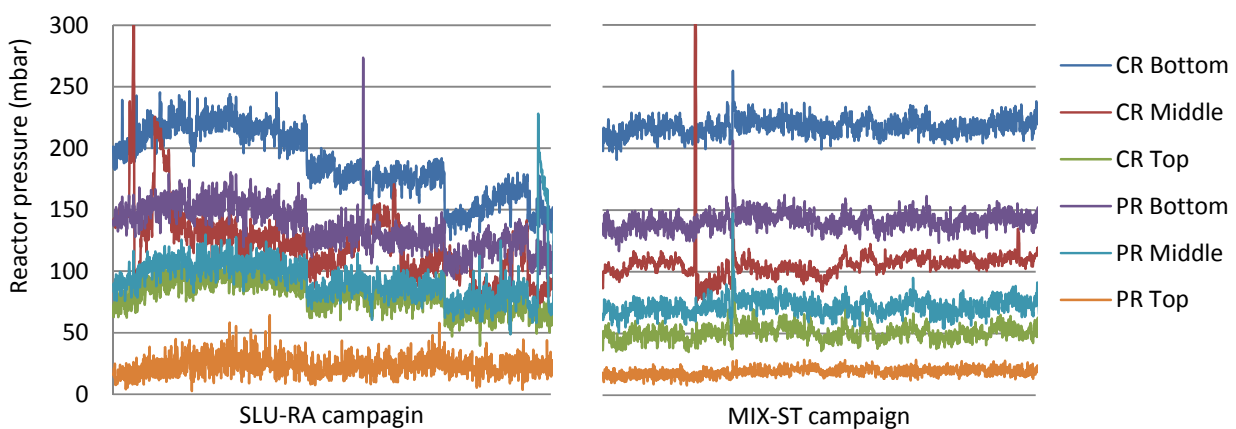

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255   **Figure 5: Pyrolysis reactor (PR) and char reactor (CR) pressure curves from SLU-RA campaign (left) and MIX-ST campaign (right). Data**
256   **aggregated from 10 periods of 30-60 minutes totaling 8 hours out of a total operation data set of 40 hours (SLU-RA campaign) and 28**
257   **hours (MIX-ST campaign).**

258

259   3.3.2   Stability of internal system mass and volume

260   Stability of the system operation impels a somewhat stable internal mass and volume of particles.
261   Accumulation of mass is a common phenomenon in fluid bed systems, especially when using extremely ash-
262   rich fuels like MSS, which has also been observed in the study by Calvo et al. from 2013 (Calvo et al., 2013). The
263   simplest way to counteract such accumulation is to drain out surplus bed material.

264   The potential influence of the MSS fuel composition on the rate of bed draining required to maintain a
265   constant inorganic mass within the system has been estimated by simple inorganic mass balances of the five
266   campaigns. The goal was to determine if there was significant correlation and if such a correlation was linear or
267   non-linear. Results are provided in Figure 6.
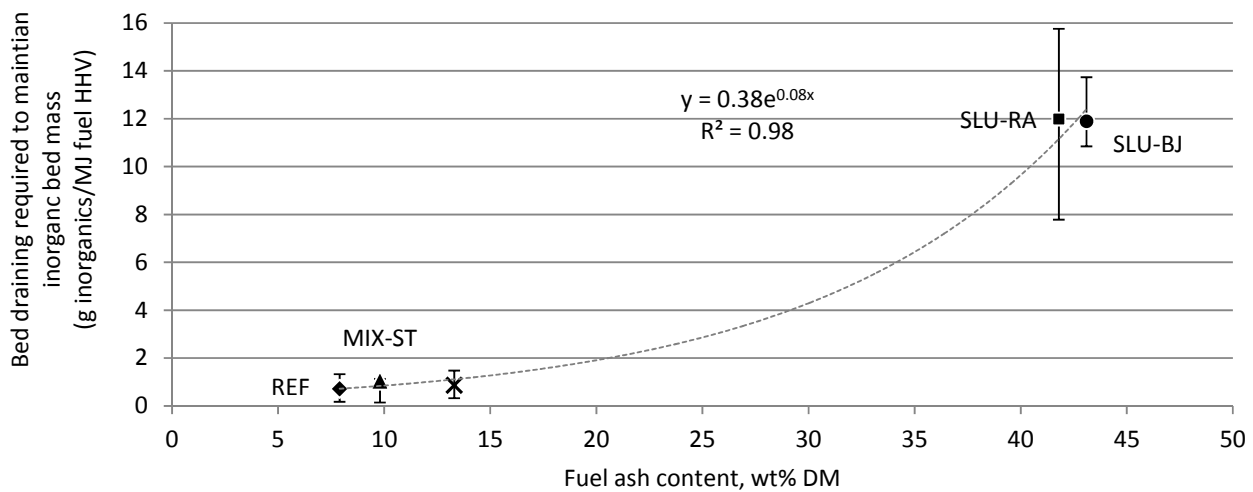
Figure 6: Rate of bed draining required to maintain a stable mass of inorganics in the bed as function of fuel ash content during five LT-CFB campaigns with different fuels. DM: Dry matter. HHV: Higher Heating Value.

Despite the uncertainties there is a strong trend in the results and a very significant difference between MSS-only campaigns on one side and straw and MSS/straw campaigns on the other (Figure 6). There is no significant difference between the potential accumulation of inorganics during the REF, MIX-ST and MIX-BJ campaigns, and also no significant difference between the two MSS-only campaigns. Part of the explanation behind this effect is obviously differences in absolute fuel ash input and perhaps especially absolute MSS ash input. Another important part of the explanation is that the reduced amount of ash in the co-firing system allows for longer retention time of the large ash particles in the system. A long retention time increase the degree of mechanical particle attrition thus also increasing the chance that relatively more small ash particles leave via the cyclones.

It should be notised, that during the reported test campaigns, the goal was not to keep a constant bed mass or volume but rather to keep the bed particle inventory within the limits allowing for sufficient particle circulation and consequently a proper temperature level in the pyrolysis reactor. Hence, bed draining requirements cannot be sufficiently analyzed by monitoring the total bed mass alone. Despite these reservations, the combined set of results from the five LT-CFB campaigns indicate substantial benefits of co-gasification of MSS and cereal straw with regard to stability of bed mass (Figure 6) and fluidization (Figure 4 and Figure 5).

3.4   Gas quality and composition

3.4.1   Composition of dry, tar-free gas

In each campaign, the dry, tar-free product gas composition has been recorded for periods of at least 1.5-3 hours. A summary is provided in Figure 7.

There are some significant differences in the gas composition and heating value, between the different fuel types (SLU >< MIX >< REF), and while the gas products from the two SLU campaigns are very comparable, there

11

292 are profound differences among the MIX campaigns which is probably mainly due to the high moisture content
293 in the MIX-ST fuel mix (Figure 7). Generally, the most significant differences are in the H_2 ($\approx$1-7 vol%) and CO
294 content ($\approx$4-11 vol%), and higher heating value (2 to 5 MJ/ Nm^3) whereas the contents of CH_4 ($\approx$2-3 vol%) and
295 CO_2 ($\approx$ 16-18 vol%) are more uniform among the campaigns. O_2 content in all products is practically zero (data
296 not shown). N_2 is not quantified, but can be expected to constitute the vast majority of the composition
297 balance. The content of simple hydrocarbons ($C_{2-6}H_{2-10}$) in the REF campaign constituted 2.3 vol% of the gas but
298 almost 40% of the total energy potential in the dry, tar-free gas. As the content of simple hydrocarbons was
299 not measured in the other gas products, the LHV and HHV results from these campaigns should be used with
300 caution. The main $C_{2-6}H_{2-10}$ contributors in the REF gas products were ethylene (13% of total HHV), propene
301 (9%), 2-butene (7%), ethane (4%) and cyclopentane (4%). The content of simple hydrocarbons in product gas
302 from MSS gasification has been investigated in three previously published studies, and was found to constitute
303 from 0.1 to as much as 7 vol% of the cold, dry gas (Choi et al., 2016; Mun et al., 2013; Roche et al., 2014). The
304 influence of tar and simple hydrocarbons is expected to substantially influence the H_2 concentration as varying
305 amounts of hydrogen may be fixed in simple hydrocarbons and tars and thereby not identified as H_2 in the cold,
306 dry gas product.
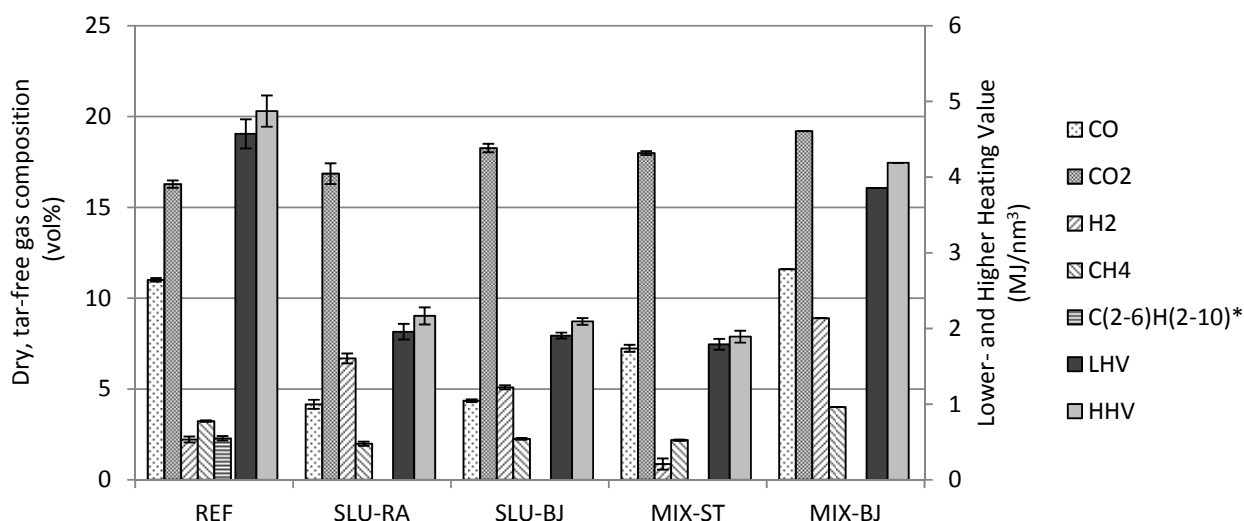
307

308 **Figure 7: Composition of dry, tar-free product gas. N_2 major balancing gas component. LHV: Lower Heating Value. HHV: Higher**
309 **Heating Value. *: Content of simple hydrocarbons with compositions $C_{2-6}H_{4-10}$ has only been measured in the REF campaign.**

310 3.4.2   Tar quantification and characterization

311 During the REF and SLU-BJ campaigns comparable amounts of gravimetric tars were collected, whereas the
312 MIX-ST yielded 20-30 times as much gravimetric tar (Table 4 A). The amount of tar collected is substantially
313 higher than those reported in the published literature. Roche et al (2014) and Mun et al (2013) produced 3400-
314 10000 mg/Nm^3 and around 6000 mg/Nm^3 respectively in lab scale fluidized bed gasifiers, converting sludge at
315 temperatures around 800 °C (Mun et al., 2013; Roche et al., 2014). The low pyrolysis temperature during the
316 MIX-ST campaign is the main driver behind the large tar content in the product gas of this campaign as

317 discussed below. Furthermore, there were several tar-reducing initiatives in the experimental setup in the
318 previously published studies, while the LT-FCB product gas is untreated.

319 **Table 4. A) Quantification of gravimetric tar, phenol and PAH contents in tar collected during the REF, MIX-ST and SLU-BJ campaigns**
320 **using a Petersen column. B) Quantification of total tar, water and permanent gases in gas products from the REF and MIX-ST**
321 **campaigns using condensation, calorimetry and gas volume measurements (Figure 2). PG: Product gas. N.A.: Not Analyzed.**

		REF	MIX-ST	SLU-BJ
A) Gravimetric tar	mg/Nm^3 PG	33·10^3	N.A.	26·10^3
Phenol content	mg/Nm^3 PG	883	N.A.	390
PAH content	mg/Nm^3 PG	136	N.A.	226
B) Total tar	wt%, PG	1±1	12±2	N.A.
Water	wt%, PG	14±3	24±2	N.A.
Permanent gases	wt%, PG	84±5	64±2	N.A.

322

323 The results from quantification of total tar, water and permanent gases using an in-house method (Table 4 B)
324 largely support the previously determined difference in the tar content of the two gas products from the REF
325 and MIX-ST campaigns. From the results in Table 4, it is clear that the high moisture content of the
326 sludge/straw mix fuel, and the related low pyrolysis temperatures, have a pronounced effect on the total tar
327 and water content in the product gas. The temperatures in the middle and upper part of the pyrolysis reactor,
328 where the sludge pyrolysis takes place were around 650-700 °C in the REF and SLU campaigns, while it was
329 500-550 °C in the MIX-ST campaign. Pyrolysis temperatures around 500-550 °C, have previously been reported
330 as optimum temperatures for pyrolysis oil production from fast pyrolysis of sewage sludge and straw (Alvarez
331 et al., 2015; Xie et al., 2014; Xin-bin et al., 2012). The pyrolysis process taking place in the LT-CFB occurs rapidly,
332 as the heat transfer from the hot sand to the biomass or sludge, is extremely high. In general, such high heating
333 rates combined with pyrolysis temperatures around 500-550 °C and short vapor residence times are regarded
334 as beneficial conversion characteristics for pyrolysis oil production (Bridgwater et al., 1999). This supports the
335 finding of very high tar content in the product gas from the MIX-ST campaign. If the tar characteristics can be
336 optimized, then this system might be highly suitable for production of bio-oil from co-gasification of dewatered
337 MSS and dry straw. The effective heating rate could be further increased and an even higher tar production
338 probably be seen if the fuel was applied as finer and more dry particles.

339 GC-MS chromatograms (example in Figure 8) indicate that oxygenated compounds and phenols are the main
340 constituents of the characterized tars from the REF campaign while a significantly different pattern was
341 observed in the MIX-ST campaign: besides the phenols, a high amount of anhydro-carbohydrates such as
342 levoglucosan appeared. This shows a good correlation with the higher water content of the straw-sludge
343 mixture as well as the low pyrolysis temperature. The tar compounds in the MIX-ST gas were found to largely
344 resemble a bio-oil composition considering the appearance of anhydrosugars, acetic acid, furfural and several
345 phenols with a lower amount of PAHs (Trinh et al., 2013). Tars from the SLU-BJ campaign on the other hand
346 clearly indicate that the fuel had a higher N-content than that of straw or straw-sewage sludge mixtures. High
347 amounts of N-containing heterocyclic compounds were clearly present including pyrrole and indole and their
348 methyl derivatives. Very similar compounds were found during gasification of Danish sewage sludge by
349 Adegoroye et al. (Adegoroye et al., 2004). In another study by Zuo et al. sewage sludge was pyrolyzed in a

350 fluidized bed reactor and the formation of nitrogenated compounds was studied with special focus on
351 heterocyclic compounds. In this study a significant presence of pyrrole and also pyridine derivatives were also
352 identified (Zuo et al., 2013).

353 Based on these results, it seems to be characteristic for tars from sludge gasification that they contain more
354 PAHs and a lot of N-heterocyclic compounds compared to the reference straw tar. During co-gasification of
355 dewatered sludge and straw at the assessed mixing ratio, the resulting tars seem to be very similar to the
356 regular straw gasification tars and have bio-oil like characteristics.
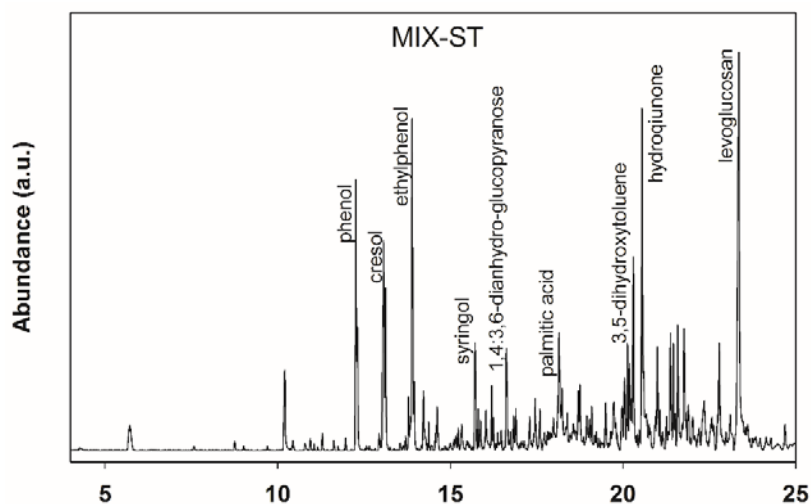
357

358 **Figure 8: Example of GC-MS chromatogram of the tar fractions from the MIX-ST campaign.**

359 3.4.3   NH$_3$ and total N in gas product

360 2.1 g total N and 2.0 g NH$_3$-N was recovered per Nm^3 of dry gas in the REF campaign while the recovery was
361 only 0.07 g total-N and 0.06 g NH$_3$-N per m^3 of dry gas in the MIX-ST campaign. The concentration of total N
362 and NH$_3$-N was thereby around a factor of 30 higher in the REF product gas than in the MIX-ST product gas. The
363 large difference becomes even more profound when considering that the content of fuel N has been found to
364 be a factor of 6 higher in MSS than in wheat straw on average across more than 40 samples measured per dry
365 mass (ECN, 2016a, 2016b). The very large differences between the two sets of results are probably related to
366 differences in allocation of N in the gas between tar-N, NH$_3$, HCN and N$_2$ in the two campaigns. While all tar
367 and tar-N species as well as NH$_3$ is expected to condense in the impinger bottles, none of the produced N$_2$ will
368 be captured, and the contribution of HCN-N to total-N results is most likely severely underestimated as the
369 bobble-flask approach may be inadequate of recovering HCN due to a very low boiling point (around 26 °C).

370 It is generally agreed, that the vast majority of fuel-N in gas from sludge pyrolysis is in the form of NH$_3$, HCN
371 and tar-bound N (Cao et al., 2010; Zhang et al., 2014). The production of NO$_X$ in MSS pyrolysis has been found
372 to be very low (< 0.5% of fuel N, (Tian et al., 2002)) but the NH$_3$, HCN and tar-bound N are all potential
373 precursors for post-pyrolysis NO$_X$ formation in downstream gas combustion (Glarborg et al., 2003; Whitty et al.,
374 2008). There are substantial differences in the distribution of fuel-N, between NH$_3$ and HCN while tar-bound N

375 consequently represent around 1/3 of total N in four studies of MSS pyrolysis (Cao et al., 2010; Chen et al.,
376 2011; Tian et al., 2002; Zhang et al., 2014). In two cases it is found that NH_3 constituted significantly more N
377 than HCN (Cao et al., 2010; Zhang et al., 2014) where the exact opposite was the case in the other two studies
378 (Chen et al., 2011; Tian et al., 2002). Two of the studies also found a significant content of N_2 in the product
379 gas, constituting 2-18% of fuel N depending on the pyrolysis process (Cao et al., 2010; Chen et al., 2011). The
380 formation of N_2 in MSS pyrolysis has been found to rely on high temperature decomposition of NH_3 as well as
381 catalytic effects of iron-containing minerals, quartz and recalcitrant carbon (Chen et al., 2011; Tsubouchi and
382 Ohtsuka, 2008). In a study by Mura et al (2013) it was found that the formation of NO_X from combustion of NH_3
383 rich gas from MSS pyrolysis was very limited at combustion temperatures up to 950 °C. Only 7% of the total N
384 in the MSS pyrolysis gas was emitted in the exhaust as NO_X at air excess ratios of 1.1. This increased with more
385 than a factor of 3 when the air excess ratio was increased from 1.1 to 2.3. The remaining N was present in the
386 exhaust gas predominately as N_2. Mura et al proposed a spontaneous selective non-catalytic reduction reaction
387 (SNCR) as the main driver for the low NO_X content in the exhaust (Mura et al., 2013).

388 From this assessment it seems as there is a substantial potential for production of NO_X-precursors during
389 thermal gasification of MSS based fuels, but also that the practical implications of this concern may become
390 small if the pyrolysis/gasification and gas combustion processes are optimized in this regard.

391 **3.5   Process performance**

392 3.5.1   Overall energy balance and energy efficiency

393 As the LT-CFB product gas is mainly intended for being combusted without prior cooling it makes sense to
394 regard the hot-gas efficiency of the process. This is estimated from an energy based distribution of products
395 and results are provided in Table 5.

396 **Table 5: Carbon conversion rates and allocation of fuel energy potential in products and unaccounted fractions during selected Low**
397 **Temperature Fluidized Bed gasification campaigns. SC: Secondary cyclone.**

	SC ash carbon	Filter ash carbon	Bed carbon (incl. drained)	Hot gas (efficiency[c])	Unaccounted (balance)	Carbon conversion
	MJ/MJ fuel	MJ/MJ fuel	MJ/MJ fuel	MJ/MJ fuel	MJ/MJ fuel	%
REF	0.06	0.03	0.02	0.82	0.07	86[b]
MIX-ST	0.04	N.A.	0.00	0.90	0.06	95[b]
MIX-BJ	0.08	N.A.	0.01	0.88	0.04	91[b]
SLU-BJ[a]	0.02	0.01	0.04	0.88	0.06	93[b]

398

399 The unaccounted fraction of the fuel energy input (Table 5) includes i.e. surface heat loss not fully
400 compensated by electric surface heat tracing , loss of thermal enthalpy in ash products, enthalpy losses in
401 phase changes (in addition to that of water) and the sum is finally influenced by substantial uncertainties in all
402 parameters. SC ash carbon content is found to constitute 2-8% of the original fuel energy and seems to
403 increase with straw content. Combined with the filter ash carbon and the carbon in the bed material, these

404   losses account for a total of approximately 5-10% of the fuel energy. Carbon conversion rates on basis of total
405   carbon mass in the fuels were in the range 85-95% and increase in processes with high ash or moisture levels in
406   the fuels which is mainly due to the need for higher air to fuel ratio and therefor more oxidising conditions in
407   the char reactor. Carbon conversion rates from 48-85% were obtained in a study by Seggiani et al. on co-
408   gasification of MSS and wood while carbon conversion rates of 65-93% were obtained in four recent studies on
409   mono-gasification of MSS in various types of gasifiers (Choi et al., 2016; Kang et al., 2011; Mun et al., 2013;
410   Roche et al., 2014; M. Seggiani et al., 2012). The estimated hot-gas efficiencies in the MSS campaigns were
411   around 88-90% and highest in the MIX-ST campaign. The efficiency of the LT-CFB MSS process is in the high end
412   regardless of the MSS fuel composition when compared to the previously published literature on MSS
413   gasification. Hot gas efficiencies of 40-70% and cold gas efficiencies from 30-89% have been stated in a series
414   of previous studies on MSS gasification involving several different types of gasifiers (Calvo et al., 2013; Choi et
415   al., 2016; Kang et al., 2011; Mun et al., 2013; Werle, 2015).

416

Conclusions

418   Process performance and gas product quality and quantity have been compared across five successful
419   experimental Low Temperature Circulating Fluidized Bed (LT-CFB) campaigns operated on different fuels and
420   LT-CFB plants. Four of the fuels were municipal sewage sludge (MSS) or a mix of MSS and cereal straw. The fifth
421   fuel was a reference cereal straw fuel. No bed agglomeration or ash sintering was observed in the assessed
422   temperature regime. Regardless of substantial differences in the hot gas composition and tar content of the
423   gas products from the different LT-CFB campaigns, hot gas energy efficiencies close to 90% and carbon
424   conversion rates in the range of 90-95% were documented in all assessed cases with MSS fuels or fuel mixes.

425   Many other gasification concepts have also been tested successfully on MSS fuels, but in general fluidized bed
426   based gasifiers obtains the highest thermal efficiencies. Among these highly efficient systems, the LT-CFB has a
427   distinct characteristic in the very low operation temperature which allows for mixing the MSS with straw and
428   other high alkali biomass residues. This approach can be used to mitigate two common problems with MSS
429   gasification in fluidized bed systems; i) MSS gasification can lead to accumulation of large amounts of inorganic
430   material from the fuel in the bed, requiring extensive extraction of bed material and in some cases addition of
431   fresh bed material to allow for continuous operation. However, co-gasification of MSS with straw was found to
432   be an effective way to mitigate this issue; ii) Co-gasification of dewatered MSS and straw seems to be sufficient
433   to avoid the expense of thermal drying of MSS prior to thermal gasification.

434   When mixing wet or dewatered MSS with straw, the relatively high moisture content of the mixed fuel did have
435   an expectable influence on the process conditions, especially in the pyrolysis reactor. A very high tar
436   production was documented in this campaign, owing mainly to low temperatures in the pyrolysis reactor.
437   Characterization of the tar has indicated a potential use as a liquid fuel (bio-oil) if condensed and separated
438   from the product gas. With further investigation this could increase the process flexibility by expanding the
439   potential product range.

The overall conclusion of this study is that LT-CFB gasification of MSS and especially co-gasification of MSS and cereal straw is a highly efficient way to manage MSS and utilize the energy potential in this resource. The low temperature gasifier can convert MSS or MSS/straw mixtures into a combustible and/or condensable product gas, and the product gas characteristics can be altered substantially by changing the fuel composition.

The prospect of utilizing the ashes produced in the described LT-CFB campaigns as phosphorus fertilizer and soil improvement agents is the subject of part 2 of the current study.

References

Adegoroye, A., Paterson, N., Li, X., Morgan, T., Herod, A.A., Dugwell, D.R., Kandiyoti, R., 2004. The characterisation of tars produced during the gasification of sewage sludge in a spouted bed reactor. Fuel 83, 1949–1960. doi:10.1016/j.fuel.2004.04.006

Ahrenfeldt, J., Thomsen, T.P., Henriksen, U., Clausen, L.R., 2013. Biomass gasification cogeneration – A review of state of the art technology and near future perspectives. Appl. Therm. Eng. 50, 1407–1417. doi:10.1016/j.applthermaleng.2011.12.040

Alvarez, J., Amutio, M., Lopez, G., Barbarias, I., Bilbao, J., Olazar, M., 2015. Sewage sludge valorization by flash pyrolysis in a conical spouted bed reactor. Chem. Eng. J. 273, 173–183. doi:10.1016/j.cej.2015.03.047

Arjharn, W., Hinsui, T., Liplap, P., Raghavan, G.S.V., 2013. Evaluation of an Energy Production System from Sewage Sludge Using a Pilot-Scale Downdraft Gasifier. Energy & Fuels 27, 229–236.

Bridgwater, A. V., Meier, D., Radlein, D., 1999. An overview of fast pyrolysis of biomass. Org. Geochem. 30, 1479–1493.

Buchholz, D., 2015. Gasifying sludge and slurry: Europe's circular economy in action. Renew. Energy Focus 16, 147–149. doi:10.1016/j.ref.2015.10.019

Calvo, L.F., García, A.I., Otero, M., 2013. An Experimental Investigation of Sewage Sludge Gasification in a Fluidized Bed Reactor. Sci. World J. 2013, 1–8.

Cao, J.-P., Li, L.-Y., Morishita, K., Xiao, X.-B., Zhao, X.-Y., Wei, X.-Y., Takarada, T., 2010. Nitrogen transformations during fast pyrolysis of sewage sludge. Fuel 104, 1–6. doi:10.1016/j.fuel.2010.08.015

Chang, R., College, W., 2002. Chemistry, 7th ed. McGraw Hill, New York, NY.

Chen, H., Namioka, T., Yoshikawa, K., 2011. Characteristics of tar, NOx precursors and their absorption performance with different scrubbing solvents during the pyrolysis of sewage sludge. Appl. Energy 88, 5032–5041. doi:10.1016/j.apenergy.2011.07.007

Choi, Y.-K., Mun, T.-Y., Cho, M.-H., Kim, J.-S., 2016. Gasification of dried sewage sludge in a newly developed three-stage gasifier: Effect of each reactor temperature on the producer gas composition and impurity removal. Energy 114, 121–128. doi:10.1016/j.energy.2016.07.166

473 Cordell, D., White, S., 2014. Life's Bottleneck: Sustaining the World's Phosphorus for a Food Secure Future.
474   Annu. Rev. Environ. Resour. Vol 39 39, 161–188. doi:DOI 10.1146/annurev-environ-010213-113300

475 DanSand.dk, 2013. SIEVE ANALYSIS Sand 13 [WWW Document]. DanSand. URL
476   http://www.dansand.dk/fileadmin/content/DATABLADE_PDF/S_V_13.eng.pdf (accessed 7.25.16).

477 Donatello, S., Cheeseman, C.R., 2013. Recycling and recovery routes for incinerated sewage sludge ash (ISSA): A
478   review. Waste Manag. 33, 2328–2340. doi:10.1016/j.wasman.2013.05.024

479 DONG Energy Power A/S, 2012. Pyroneer, A new Gasolution - Biomass gasification [WWW Document]. URL
480   http://www.pyroneer.com/en (accessed 9.23.16).

481 ECN, 2016a. Phyllis2 - Database for biomass and waste [WWW Document]. URL
482   https://www.ecn.nl/phyllis2/Browse/Standard/ECN-Phyllis#sewage sludge (accessed 8.16.16).

483 ECN, 2016b. Phyllis2 - Database for biomass and waste [WWW Document]. URL
484   https://www.ecn.nl/phyllis2/Browse/Standard/ECN-Phyllis#wheat straw (accessed 8.16.16).

485 Engineeringtoolbox.com, 2016a. The Engineering ToolBox - Solids - Specific Heats [WWW Document]. URL
486   http://www.engineeringtoolbox.com/specific-heat-solids-d_154.html (accessed 10.14.16).

487 Engineeringtoolbox.com, 2016b. The Engineering ToolBox - Nitrogen - Specific Heat [WWW Document]. URL
488   http://www.engineeringtoolbox.com/nitrogen-d_977.html (accessed 10.4.16).

489 Engineeringtoolbox.com, 2016c. The Engineering ToolBox - Carbon Dioxide Gas - Specific Heat [WWW
490   Document]. URL http://www.engineeringtoolbox.com/carbon-dioxide-d_974.html (accessed 10.4.16).

491 Engineeringtoolbox.com, 2016d. The Engineering ToolBox - Water Vapor - Specific Heat [WWW Document].
492   URL http://www.engineeringtoolbox.com/water-vapor-d_979.html (accessed 10.4.16).

493 Fonts, I., Gea, G., Azuara, M., Ábrego, J., Arauzo, J., 2012. Sewage sludge pyrolysis for liquid production: A
494   review. Renew. Sustain. Energy Rev. 16, 2781–2805. doi:10.1016/j.rser.2012.02.070

495 Fytili, D., Zabaniotou, A., 2008. Utilization of sewage sludge in EU application of old and new methods-A review.
496   Renew. Sustain. Energy Rev. 12, 116–140. doi:10.1016/j.rser.2006.05.014

497 Glarborg, P., Jensen, A.D., Johnsson, J.E., 2003. Fuel nitrogen conversion in solid fuel fired systems. Prog.
498   Energy Combust. Sci. 29, 89–113. doi:10.1016/S0360-1285(02)00031-X

499 Grosch, H., Sárossy, Z., Egsgaard, H., Fateev, A., 2015. UV absorption cross-sections of phenol and naphthalene
500   at temperatures up to 500 °C. J. Quant. Spectrosc. Radiat. Transf. 156, 17–23.

501 Hansen, V., Hauggaard-Nielsen, H., Petersen, C.T., Mikkelsen, T.N., Müller-Stöver, D., 2016. Effects of
502   gasification biochar on plant-available water capacity and plant growth in two contrasting soil types. Soil
503   Tillage Res. 161, 1–9. doi:10.1016/j.still.2016.03.002

504 Hansen, V., Müller-Stöver, D., Ahrenfeldt, J., Holm, J.K., Henriksen, U.B., Hauggaard-Nielsen, H., 2015.
505   Gasification biochar as a valuable by-product for carbon sequestration and soil amendment. Biomass
506   Bioeng. 72, 300–308. doi:10.1016/j.biombioe.2014.10.013

507   Jenkins, R.G., 2015. Thermal Gasification of Biomass – A Primer. Bioenergy Biomass to biofuels 261–286.
508   doi:10.1016/B978-0-12-407909-0.00016-X

509   Judex, J.W., Gaiffi, M., Burgbacher, H.C., 2012. Gasification of dried sewage sludge: Status of the demonstration
510   and the pilot plant. Waste Manag. 32, 719–723. doi:10.1016/j.wasman.2011.12.023

511   Kang, S.W., Dong, J.I., Kim, J.M., Lee, W.C., Hwang, W.G., 2011. Gasification and its emission characteristics for
512   dried sewage sludge utilizing a fluidized bed gasifier. J. Mater. Cycles Waste Manag. 13, 180–185.
513   doi:10.1007/s10163-011-0016-y

514   Kelessidis, A., Stasinakis, A.S., 2012. Comparative study of the methods used for treatment and final disposal of
515   sewage sludge in European countries. Waste Manag. 32, 1186–1195. doi:10.1016/j.wasman.2012.01.012

516   Krüger, O., Adam, C., 2015. Recovery potential of German sewage sludge ash. Waste Manag. Urban Mini, 400–
517   406. doi:10.1016/j.wasman.2015.01.025

518   Krüger, O., Grabner, A., Adam, C., 2014. Complete Survey of German Sewage Sludge Ash. Environ. Sci. Technol.
519   48, 11811–11818.

520   Kuligowski, K., Poulsen, T.G., Stoholm, P., Pind, N., Laursen, J., 2008. Nutrients and heavy metals distribution in
521   thermally treated pig manure. Waste Manag. Res. 26, 347–354. doi:10.1177/0734242X08090075

522   Kunii, D., Levenspiel, O., 1991. Fluidization Engineering, Second. ed. Butterworth-Heinemann, Newton.

523   Mun, T.Y., Kim, J.S., 2013. Air gasification of dried sewage sludge in a two-stage gasifier. Part 2: Calcined
524   dolomite as a bed material and effect of moisture content of dried sewage sludge for the hydrogen
525   production and tar removal. Int. J. Hydrogen Energy 38, 5235–5242. doi:10.1016/j.ijhydene.2013.02.073

526   Mun, T.Y., Kim, J.W., Kim, J.S., 2013. Air gasification of dried sewage sludge in a two-stage gasifier: Part 1. the
527   effects and reusability of additives on the removal of tar and hydrogen production. Int. J. Hydrogen
528   Energy 38, 5226–5234. doi:10.1016/j.ijhydene.2012.10.120

529   Mura, E., Debono, O., Villot, A., Paviet, F., 2013. Pyrolysis of biomass in a semi-industrial scale reactor: Study of
530   the fuel-nitrogen oxidation during combustion of volatiles. Biomass Bioeng. 59, 187–194.
531   doi:10.1016/j.biombioe.2013.09.001

532   Narayan, V., Jensen, P.A., Henriksen, U.B., Egsgaard, H., Nielsen, R.G., Glarborg, P., 2016. Behavior of Alkali
533   Metals and Ash in a Low-Temperature Circulating Fluidized Bed (LTCFB) Gasifier. Energy and Fuels 30,
534   1050–1061. doi:10.1021/acs.energyfuels.5b02464

535   Nielsen, R.G., 2007. Optimering af Lav Temperatur Cirkulerende Fluid Bed forgasningsprocessen til biomasse
536   med højt askeindhold (Eng.: Optimizing Low Temperature Circulating Fluidized Bed gasification for high
537   alkali biomass). Technical University of Denmark, Lyngby, Denmark.

538   Ong, Z., Cheng, Y., Maneerung, T., Yao, Z., Tong, Y.W., Wang, C.-H., Dai, Y., 2015. Co-gasification of woody
539   biomass and sewage sludge in a fixed-bed downdraft gasifier. AIChE J. 61, 2508–2521.
540   doi:10.1002/aic.14836

541   Roche, E., De Andrés, J.M., Narros, A., Rodríguez, M.E., 2014. Air and air-steam gasification of sewage sludge.

542   The influence of dolomite and throughput in tar production and composition. Fuel 115, 54–61.
543   doi:10.1016/j.fuel.2013.07.003

544   Samolada, M.C., Zabaniotou, A.A., 2014. Comparative assessment of municipal sewage sludge incineration,
545   gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. Waste Manag. 34,
546   411–420. doi:10.1016/j.wasman.2013.11.003

547   Seggiani, M., Puccini, M., Raggio, G., Vitolo, S., 2012. Effect of sewage sludge content on gas quality and solid
548   residues produced by cogasification in an updraft gasifier. Waste Manag. 32, 1826–1834.
549   doi:10.1016/j.wasman.2012.04.018

550   Seggiani, M., Vitolo, S., Puccini, M., Bellini, A., 2012. Cogasification of sewage sludge in an updraft gasifier. Fuel
551   93, 486–491. doi:10.1016/j.fuel.2011.08.054

552   Stoholm, P., Ahrenfeldt, J., Henriksen, U., Gómez, A., Krogh, J., Nielsen, R.G., Sander, B., 2008. The Low
553   Temperature CFB Gasifier - 500 kW test on Biogas Fiber Residue, in: 16th European Biomass Conference &
554   Exhibition, 2-6 June 2008, Valencia, Spain. pp. 720–723.

555   Thomsen, T.P., Hauggaard-Nielsen, H., Gøbel, B., Stoholm, P., Ahrenfeldt, J., Henriksen, U.B., Müller-Stöver,
556   D.S., 2017. Low Temperature Circulating Fluidized Bed gasification and co-gasification of Municipal
557   Sewage Sludge. Part 2: Evaluation of ash materials as phosphorus fertilizer. Waste Manag. In Press.

558   Thomsen, T.P., Ravenni, G., Holm, J.K., Ahrenfeldt, J., Hauggaard-Nielsen, H., Henriksen, U.B., 2015. Screening
559   of various low-grade biomass materials for low temperature gasification: Method development and
560   application. Biomass Bioeng. 79, 128–144. doi:10.1016/j.biombioe.2014.12.019

561   Tian, F.J., Li, B.Q., Chen, Y., Li, C.Z., 2002. Formation of NOx precursors during the pyrolysis of coal and biomass.
562   Part V - Pyrolysis of a sewage sludge. Fuel 81, 2203–2208. doi:10.1016/S0016-2361(02)00139-4

563   Trinh, T.N., Jensen, P.A., Sárossy, Z., Dam-Johansen, K., Knudsen, N.O., Sørensen, H.R., Egsgaard, H., 2013. Fast
564   pyrolysis of lignin using a pyrolysis centrifuge reactor. Energy and Fuels 27, 3802–3810.
565   doi:10.1021/ef400527k

566   Tsubouchi, N., Ohtsuka, Y., 2008. Nitrogen chemistry in coal pyrolysis: Catalytic roles of metal cations in
567   secondary reactions of volatile nitrogen and char nitrogen. Fuel Process. Technol. 89, 379–390.
568   doi:10.1016/j.fuproc.2007.11.011

569   Turns, S.R., 2012. An Introduction to Combustion - Concepts and Applications, Third. ed. McGraw-Hill, New
570   York, NY.

571   Werle, S., 2015. Gasification of a Dried Sewage Sludge in a Laboratory Scale Fixed Bed Reactor. Energies 8,
572   8562–8572. doi:10.3390/en8088562

573   Whitty, K.J., Zhang, H.R., Eddings, E.G., 2008. Emissions from Syngas Combustion. Combust. Sci. Technol. 180,
574   1117–1136. doi:10.1080/00102200801963326

575   Xiaoxu, F., Leizhe, C., Liguo, Y., 2012. Dried Municiple Sewage Sludge Gasification Experiment in Dual Fluidized
576   Bed. Adv. Mater. Res. 390, 3799–3804. doi:10.4028/www.scientific.net/AMR.383-390.3799

577 Xie, Q., Peng, P., Liu, S., Min, M., Cheng, Y., Wan, Y., Li, Y., Lin, X., Liu, Y., Chen, P., Ruan, R., 2014. Fast
578   microwave-assisted catalytic pyrolysis of sewage sludge for bio-oil production. Bioresour. Technol. 172,
579   162–168. doi:10.1016/j.biortech.2014.09.006

580 Xin-bin, Z., Jian-guo, H., Yong-xiang, Z., Wei-ming, S., 2012. Genotypic variation of rape in phosphorus uptake
581   from sparingly soluble phosphate and its active mechanism. African J. Biotechnol. 11, 3061–3069.
582   doi:10.5897/AJB11.3043

583 Zhang, J., Tian, Y., Zhu, J., Zuo, W., Yin, L., 2014. Characterization of nitrogen transformation during microwave-
584   induced pyrolysis of sewage sludge. J. Anal. Appl. Pyrolysis 105, 335–341. doi:10.1016/j.jaap.2013.11.021

585 Zsirai, I., 2011. Sewage Sludge as Renewable Energy. J. Residuals Sci. Technol. 8, 165–179.

586 Zuo, W., Jin, B., Huang, Y., Sun, Y., Li, R., Jia, J., 2013. Pyrolysis of high-ash sewage sludge in a circulating
587   fluidized bed reactor for production of liquids rich in heterocyclic nitrogenated compounds. Bioresour.
588   Technol. 127, 44–48. doi:10.1016/j.biortech.2012.09.017

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