

Pyrolysis of low grade biogenic feedstock and *in-situ* sorption of Chlorine for emission reduction

Yasha Dave

yasha.dave@tecnico.ulisboa.pt

Instituto Superior Técnico, Universidade de Lisboa, Portugal

November 2017

Abstract

Commercial attention on Biomass, as an energy resource has increased in the past decade. Waste of different nature and origin represents low grade biomass which upon thermal utilisation can aid in better disposal. Most crucial challenge for this is to ensure the emissions are below the respective regulation limits. Due to the diverse composition and eventually nature of emissions, biomass feedstock requires *source specific* disposal method.

As part of this research work, Sewage Sludge (SS) Pyrolysis with *in-situ* sorption of Chlorine/Sulphur was evaluated using Calcium and Sodium based sorbents. Chlorine is present in significant amount in Wheat Straw (WS), hence it is also pyrolyzed for comparison with the emissions from Sewage Sludge pyrolysis. Sorption studies with Calcium Oxide (CaO) and Sodium Hydrogen Carbonate (NaHCO₃) were conducted using Fixed Bed. After analysis of results, Sodium Hydrogen Carbonate was selected as the sorbent for sewage sludge Cl capture, to be tested on Integrated Screw Pyrolysis (STYX) plant.

The results of experimental campaign reflected notable sorption of Cl and S in STYX configuration; in the Fixed Bed Reactor issues of reproducibility of desired results were encountered. The Mass Balance comparison between cases of with and without sorbent use for NaHCO₃, showed increase of fraction of Permanent gas (from 8 to 23%), slight increase in the char amount, decrease in the organic and aqueous fraction of liquid products obtained.

Keywords: Chlorine emission, Integrated Screw Pyrolysis Reactor, Sewage Sludge, In-Situ Sorption.

1. Introduction

Sewage sludge disposal technologies are currently discussed and implemented in the EU because of the harmful effects caused by landfilling sewage sludge. The landfill gas and the leachates are toxic for the environment, plants and ground water table. One of the most technologically mature processes of sludge utilization is anaerobic digestion, which produces biogas. One of the key concerns with this technology is that the digestate matter after digestion still has energy and nutrient content that can be recovered using thermal utilization techniques. Pyrolysis is one of the thermal processes used for utilization of energy from the organic content present in the sludge; as pyrolysis is endothermic in nature it should be noted that a high energy yield does not correspond to higher efficiency because the products get their energy from the external heat of pyrolysis that is

being supplied. Pyrolysis is preferred over gasification and incineration because of its versatility and also the efficient use of the products obtained, for example, the pyrolysis oils upon further processing can be used as transport fuels [1]. Gas cleaning and feed pre-treatment methods are prevalent in Biomass to energy applications but if the feed is mixed with a sorbent that can capture the chlorine in biomass to concentrate it in the ash, it can prove to be an interesting alternative. Use of suitable compounds as sorbents like Kaolin, Bauxite, Limestone etc. have been reported to release Chlorine from alkali metal chlorides and hence avoid deposit formation [2]. Thermodynamic calculations on syn gas, carried out by Joseph Lee et al. [3] in the temperature range of 300-1500 K, Pressure 0.1-11 MPa and initial contaminant (HCl and H₂S) concentration between 1-10000 ppm resulted in CaO, K₂CO₃, Na₂CO₃ and NaHCO₃ to be the four best candidates

among 12 others for effective chlorine removal at moderate to high temperatures.

1.1 Sewage Sludge (SS)

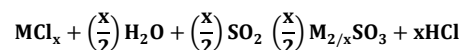
Sewage sludge is a complex mixture of constituents; organic, inorganic and wide variety of micro-organisms. Also, it should be noted that sewage sludge in dry form has a high calorific value, which is comparable to fossil coals [4]. Based on extensive research and review papers Hassan and Wang et al. reported that calorific value of SS can range from 11.1 – 22.1 MJ/kg HHV on dry basis which is comparable to Lignite (11.80-21.90 MJ/kg) [5]. The presence of undigested organics, such as paper, plant residues, oils, faecal material, is one of the causes of pollution and toxicity associated with sewage sludge, because it contains highly complex molecules of phenolic, aromatic, aliphatic structures and poly cyclic aromatic hydrocarbons (micro organic pollutants) [6, 7]. The inorganic compounds present in the liquids are derived from soil and synthetic polymers having anthropogenic roots [8]. Therefore, the composition of the sewage sludge samples obtained from different treatment plants can vary even if the same waste water treatment procedures are employed [9]. Sewage sludge has a high N content, which it gets from proteins, peptides, acid etc. whereas the S content of sewage sludge is significantly higher than the Biomass average, but comparable to Lignite [5].

It has been reported that approximately 50-80% of the heavy metal content in the waste water is concentrated in the sewage sludge by different treatment methods [10]. K, Al, Ca, Mg content in sewage sludge is comparable to that of Cl; on one hand metals like Al and Ca tend to retain Cl whereas on the other hand it has been reported that the release of Chlorine is dependent on K content [11].

1.2 Sewage Sludge Pyrolysis

Combustion is one of the most researched method concerning sewage sludge as it reduces the disposal volume and complete destruction of pathogens. But the main drawback of using combustion is the generation of hazardous air pollutants in the flue gas, combustor designs are hence made taking care of the chlorine content of

sludge [12]. Co-incineration is one of the suggested ways to deal with sewage sludge as it can be used in combination with other fuels like coal and MSW etc. to generate energy [13]. The kinetics of pyrolysis suggests that reaction configuration and residence time are crucial in determining the final residue and pollutants in the flue gas. This is because primary (raw material decomposition) and secondary reactions are two basic steps occurring during pyrolysis where secondary reactions (primary volatiles react with the char) are a result of high residence time and high temperatures [14]. Sewage sludge composition is very important parameter for determining the thermodynamic feasibility of the reactions leading to emission of HCl. One such observation was reported by Matsuda et al. and confirmed by Kassmann et al. [15] when they carried out extensive thermodynamic studies considering all the possible reaction pathways. They reported that presence of SO₃ affects the formation of HCl from metal chlorides according to the following reaction [16]:



Calcium based sorbents have been extensively studied for the purpose of Cl and S emission reduction and wet scrubbing is reported to be a better choice when the biomass has high metal content [17]. Presence of chlorine in the sewage sludge catalyses some crucial processes: promotes the mobility of inorganic compounds like Potassium, Sodium etc., Cl can form gas phase metal chlorides, which are stable in nature, HCl and other carbon compounds are the precursors for dioxin formation and this occurs mainly in the post combustion zone [18].

1.3 Research Objective

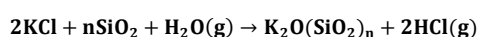
The objective of this study is to evaluate the so-called In-situ sorption of Chlorine/Sulphur by co-feeding Biomass and sorbent in Pyrolysis process. To attain this objective, laboratory scale and bench scale (STYX) experiments were conducted using Sewage Sludge (SS) and Wheat Straw (WS) as feed and finding a suitable sorbent to reduce Chlorine and Sulphur emissions.

2. Chlorine release and capture

2.1 Release of chlorine

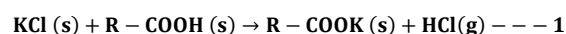
In the case of Biomass, Chlorine content varies from less than 200 mg/Kg to a maximum of 7000 mg/Kg; pyrolysis of woody biomass leads to complete release of Chlorine at 350°C, which confirmed the results of studies stating that the fraction of chlorine released is higher for low Cl content biomass [18, 19]. The extent of presence of chlorine determines its release behaviour as it was showed in a research that with biomass of moderate alkali content, the increase of Calcium content seems to be more effective in decreasing the HCl emissions than increasing the K content [20].

The release of chlorine from the biomass matrix depends largely on the particle size and heating rate; it has also been shown that the pyrolysis of a mixture of KCl with chlorine free biomass lead to release of chlorine (30-50%) even at temperatures below 400°C, this is because of reaction between KCl and the carboxylic groups in biomass [21]. Another observation about release of chlorine from biomass with considerable silicon content is the reaction between KCl and steam (formed by drying of biomass), since the equilibrium of this reaction is largely affected by the presence of acidic SiO₂, at a temperature of 400°C this path of release of chlorine as HCl is significant [18].

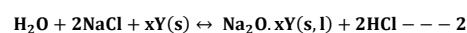


This also shows that even if the origin of chlorine in biomass is of inorganic nature it can release at a temperature less than the melting point of the salt [18, 21]. In the case of high chlorine biomass like corn Stover, more than 50 wt% of chlorine and Sulphur were released below 500°C. Since Sulphur is also associated with the organic matrix of the biomass which decomposes at 500°C hence the release of Sulphur at considerably low temperature was observed (S exists in a range of oxidation states from -2 to +4 both organic and inorganic in nature [22]) while in the case of chlorine it is mostly the ion exchange reaction leading to HCl formation [11]. Recent pyrolysis studies of Cl and S release using two different reactor configurations (Rotary and Fixed bed reactor) showed that 20% of

Cl was released from straw at a temperature of 250°C and 64% at 350°C, the low temperature release of Cl was attributed to presence of CH₃ donors [19]. Zintl et al. [23] performed reactions of KCl and wood in the temperature range of 200-700°C and proposed that the initial low temperature Chlorine release was a result of a reaction between KCl and carboxylic groups (shown below).



To understand the release of Chlorine from straw and corn Stover pyrolysis in a nitrogen atmosphere, between 200-1050°C, in a systematic manner, Jensen et al. reported two-step process of chlorine release [11, 21]. First occurs when, 60% Cl release between 200-400°C, (reaction 1) this step depends on the functional groups present in the organic matrix. The rest between 700-900°C, (reaction 2) aluminosilicates reacts with alkali metals (at moderate temperature this step is kinetically limited and at temperature above 700°C it competes with the alkali chloride evaporation). In the reaction below Y(s) can be silica, alumina or a combination of both.



2.2 Use of Sorbent for reducing Cl emissions

Alkali metal sorbents are increasingly used for halide removal, commonly HCl removal resulting from thermochemical conversion of Biomass. These metal sorbents form salts like NaCl, KCl etc. on reaction with halides and hence prove to be useful [24]. Similarly, alkaline earth metals (BaO, CaO, MgO) also showed to be thermodynamically feasible for removal of halides [25].

Some fixed bed reactor studies were done in the context of Chlorine removal and the reaction kinetics; one suggested that the tested alkali and alkaline earth metal sorbents like Na₂CO₃, CaCO₃, MgO etc. could reduce the HCl vapor concentration from 10⁻³ to 10⁻⁶ at a temperature of 500°C and space velocity of 3000h⁻¹. The reaction kinetics followed first order with respect to initial HCl concentration [26]. Another study of HCl removal in fixed bed using NaHCO₃, CaCO₃, Ca(OH)₂, Mg(OH)₂ and Al₂O₃ was conducted at a temperature of 550°C, showing significant

reduction of less than 2 wt% in downstream as compared to fully saturated upstream end [27]

HCl formed during pyrolysis is found to be removed most efficiently in the temperature range of 500-550°C because of the chemical equilibrium conditions between the constituent gases and solids involved [26]. The sorbent selection also depends on cost, hence sodium based compounds like sodium bicarbonate, sodium carbonate, Ca(OH)₂, Mg(OH)₂ and their calcined versions of CaO, MgO are reported to be useful and inexpensive. Experiments using calcium based sorbents have shown 80% removal of HCl. Duo et al. (1994) [28] studied the reaction between CaCO₃ and HCl and due to the low value of chemical potential concluded that the reaction was slow, as well as the sorbent conversion. Another study by same authors, for IGCC Fuel gas cleaning sorbent also confirmed the above results of low conversion of CaCO₃ at 400°C, while they also tested Na₂CO₃, NaHCO₃ and Na₂CO₃.10H₂O [29]. The concentration of CO₂ affects the Ca based sorbents showing better results in oxygen blown than air blown fuel gases, while it does not affect the Na based sorbents in the temperature range of 300-600°C. Na₂CO₃.10H₂O was found to be better than Na₂CO₃ because of high porosity of its dehydrated compound [29].

Karlsson et al. (1981) [30] studied Ca(OH)₂ as a sorbent in fixed bed reactor from 150-400°C, confirming that the reaction follows first order kinetics, as previously mentioned by others, also the available maximum Ca(OH)₂ for the sorption was around 55%. A magazine report [31] published in 2014, showed the advantages of retrofitting acid gas removal systems of two waste to energy plants in Germany. The old systems used Ca(OH)₂ as sorbent which was replaced with NaHCO₃. The results showed better efficiency of removal of HCl with comparable economic feasibility.

Dry injection of Calcium based sorbents in laboratory scale furnace experiments at gas temperatures of 600-1000°C were conducted to check the HCl capture. Calcium carbonate and calcium oxide were the inexpensive and low porosity sorbents, they performed well with CaCO₃ utilization of 54% at mid temperature range and CaO of 80% in the lowest temperature of

investigation. Calcium salts volatilize in the temperature range of 300-460°C to form calcium carbonate, which is stable up to 700°C and above it forms CaO and liberates CO₂. The remaining CaCO₃ reacts with HCl as follows [32]:



The thermodynamic and equilibrium studies were done in 2000s to compare sorbents and their efficiency by varying process parameters. As shown in the Figure 1, NaHCO₃ is superior to Ca(OH)₂ in the entire temperature range considered because bicarbonate allows to obtain theoretical limits for HCl at comparatively lower value (six orders of magnitude) than with Lime. . When the molar ratio of sodium bicarbonate was increased the decreasing value of HCl in the gas showed that it is better than Lime [33].

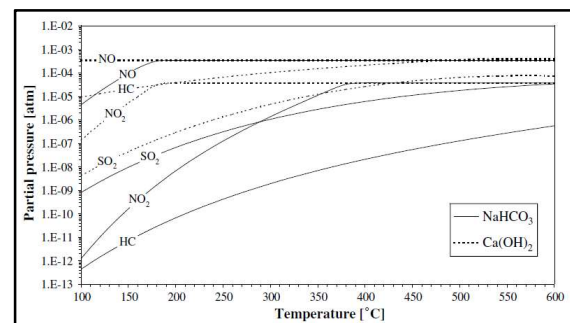


Figure 1: Performance of the sorbents with the pollutant partial pressures [33]

3. Experimental Set Up

The pyrolysis experiments were conducted using two different reactor configurations: Fixed bed batch Reactor and Screw Pyrolysis Reactor (STYX). The feed used is Sewage Sludge, obtained from a waste water treatment facility in Germany having particle size in the range of 4-8 mm. Wheat straw is also used to carry out same experiments as Sewage sludge for comparison purpose. The feedstock samples were analysed by ultimate and proximate analysis according to German standards. The metal, halogens and other compounds in ash were also analysed as per DIN 22022-1 and DIN 51729-1 standards. The next sub heading will discuss both the reactor configuration in detail along with the experimental procedure.

3.1 Fixed Bed Reactor

Pyrolysis of the Sewage sludge and Wheat Straw was carried out with and without using a sorbent. The sorbents used in this study are Sodium Hydrogen Carbonate (NaHCO_3) and Calcium oxide (CaO), varied with respect to the molar ratio of feed/sorbent. The temperature of the reactor is maintained at 500°C and the temperature of oven is 670°C . The feedstock in each experiment is weighed accurately to 100 g, mixed with suitable amount of sorbent (based on molar calculations) and then introduced in to the reactor. The washing solution of NaOH 0.1 M is used in the absorber column by measuring its initial pH value. The empty condensate glass bottle is connected to the end of the condenser. The cooling system is switched on for condenser and the temperature is set as 9°C . The nitrogen connection tube is screwed tightly and the flow rate to be as desired, generally 5 litres per minute (lpm). The voltage value for the electro static precipitator initially will not be more than 7 kV, but once the gas starts filling it can be increased to maximum 14 kV. After the reactor reaches 500°C , it is run for 15-20 min and then oven is shut off. The pH change of the absorber column solution is checked and noted down. After the experimental setup is cooled overnight, the filled condensate bottle and the char is weighed for the necessary mass balance.

Feed (Biomass + Sorbent)	Amount (Biomass + Sorbent), g
Sewage Sludge	100 + 0
Sewage Sludge + NaHCO_3	100 + (0.3, 6, 15, 30)
Sewage Sludge + CaO	100 + (26.1, 52.3)
Wheat Straw	100 + 0
Wheat Straw + NaHCO_3	100 30

Figure 2: Summary of Experiments in FBR system

3.2 Screw Pyrolysis Reactor (STYX)

3.2.1 Reactor Configuration

The bench scale Screw Pyrolysis Reactor with integrated hot gas filtration (STYX¹) was developed by Institute of Technical Chemistry (ITC), Karlsruhe

Institute of Technology in Germany. It is used in the study for intermediate pyrolysis of low grade biogenic residues in an isothermal reaction environment. It consists of a feeding system, through screw reactor, char collection drum, condensation units and gas analysis systems. The significance of using screw reactor is that it enables the feed to have a well-defined residence time because of its design. The feeding zone is purged with nitrogen so that oxygen is removed from the bulk of biomass feed. The reactor contains two main units, first is the screw conveyor and second is the sequential extraction and filtration unit. Thermocouples are located throughout the length of the reactor at fixed positions to measure the temperature and control it when required. Since the reactor assembly has filtration unit, the raw vapours generated are extracted from the reactor and the solid particles are collected separately as char. After filtration, the clean gas mixture is extracted through a pipe, which is positioned inside the oven to maintain the same temperature as the reactor. This is necessary to avoid any possibility of condensation or cracking of the ours. The condensation assembly consists of two parallel condensers maintained at 15°C and an ESP (Electrostatic Precipitator) which provides capture of aerosols and thus removes the last residues of tar. The flow rate, temperature and absolute pressure of the permanent gas is determined by using a flow meter, a thermocouple and a manometer respectively. Gas analysis assembly is used to find the composition of permanent gas in vol% (methane, carbon-dioxide, carbon-monoxide, oxygen). For this purpose, a small part of the gas is withdrawn as sample and pumped in to the assembly. The stream of permanent gas further is sent to the torch via a suction train.

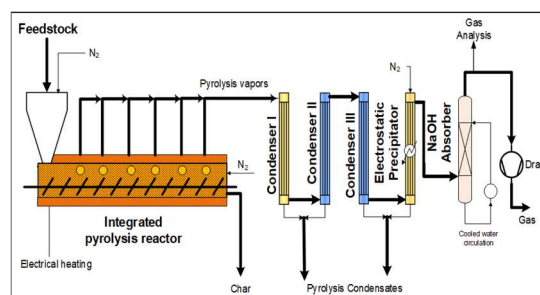


Figure 3: Flow diagram of Bench scale Pyrolysis Reactor (STYX)

¹ STYX stands for the river of the Greek mythology. It is the river over which Charon, the ferryman, transports the death souls from the Earth to a new life in the Underworld.

3.2.2 Experimental Procedure of STYX

The sewage sludge is fed through the feeding unit and it is transported with the screws present inside the reactor. The mass flow rate of feed was set to be 2kg/h in all the experiments performed. The mass flow rate of the feedstock is determined before conducting experiments based on the dosing protocol. About 4 kg of feed (sewage sludge or wheat straw) was taken with suitable amount of sorbent to be pyrolyzed at a temperature of 500°C. Sodium Hydrogen carbonate (NaHCO_3) is used as a sorbent to conduct experiments using sewage sludge and wheat straw and is fed with the biomass after manual mixing. The nitrogen flow rate is set to be 6 litres per minute and the screw rotation speed is set according to the dosing curve. The feed moves along the axis with the screw (which provides well defined residence time of the solids) by adjusting its rotation leading to residence time of 7.5 minutes. The amount of char collected is weighed while the condensates are separated and weighed. The composition and density of the permanent gases were measured online, samples were also taken to be analysed by Gas Chromatography (GC), for getting the detailed gas composition.

Feed (Biomass + Sorbent)	Amount (Biomass + Sorbent), g	Temperature	Residence Time (min)	Flow Rate of Feed
Sewage Sludge	4000 + 0	500°C	7.5	2kg/h
Sewage Sludge + NaHCO_3	4000 + (1199.7)			
Wheat Straw	4000 + 0			
Wheat Straw + NaHCO_3	4000 + (1199.7)			

Figure 4: List of Experiments performed on STYX

4. Results

The effect and performance of sorbent on reduction of emissions is evaluated based on the amount of Cl and S in the pyrolysis gas and char.

4.1 Fixed Bed Reactor

Experiments were divided in to two categories: 1. No Sorbent used 2. Using sorbent. Figure 2, below shows summary of the experiments conducted at a fixed temperature of 500°C in the fixed bed reactor system.

4.1.1 Mass Balance

The mass balance of each experiment was carried out. Due to the size of the design of the condenser,

the recovery of the liquid was challenging. Therefore, the condensate is calculated by difference. Overall mass balance of sorbent and no sorbent case from Figure 5, shows that the fraction of gas products increases when sorbent is used. This is a desirable result as this gas after cleaning can be combusted and used for energy generation. Moreover, the amount of S and Cl retained in char allows for considering sorption as an effective process.

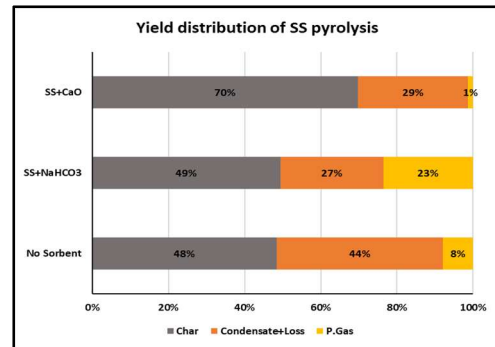


Figure 5: Overall Mass Balance for SS Pyrolysis

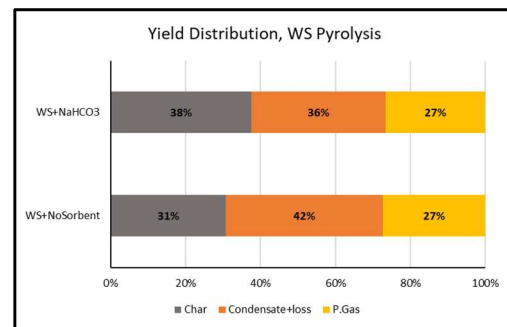


Figure 6: Overall Mass Balance for WS Pyrolysis

The results of gas measurement system which gives online volume % of CO_2 produced are shown in Figure 7. The comparison between CO_2 release shows that significant amount is contributed by sorbent decomposition.

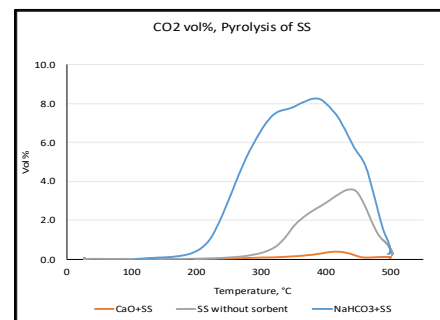


Figure 7: Volume % Distribution of P.Gas, SS+NaHCO₃

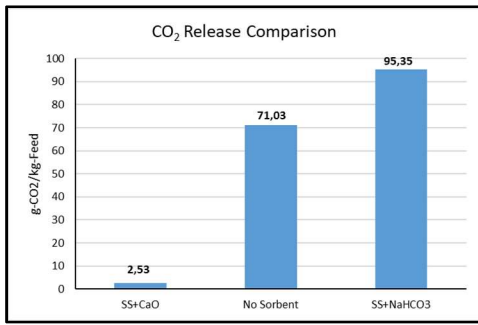


Figure 8: Tabulation of g-CO₂ released per Kg-feed

4.1.2 Sorbent Efficiency Comparison

Two sorbents (NaHCO₃ and CaO) were selected for in situ sorption pyrolysis experiments with Sewage Sludge after careful screening of information from literature. The Sorbent/Feed mass ratio was set based on theoretical calculations and the effect of changing this ratio was examined. As shown in the Figure 9 below, the quantities of sorbent used (NaHCO₃) is varied from 0.3-30 g with 100 g (fixed) of Sewage sludge. Y axis shows the yield of the desired element with respect to the change of sorbent amount and is defined as follows:

$$\text{Yield of Cl or S} = \frac{\text{Amount retained in the char, g}}{\text{Amount present in the feed, g}}$$

In case of S, initial increase from 0.3 to 6 g did not show any effect but further increase to 15 and 30 g of sorbent showed increase in yield of Sulphur. This increase in S yield agrees with literature [34, 35] previously reported for the dry sorbent injection to target SO₂ removal. According to which increase in the ratio of Na/S or Ca/S should increase the Sulphur capture because of availability of more surface area of adsorption, due to increase in sorbent amount. According to other studies [36], Sulphur capture is very sensitive to temperature and is maximum in the range of 120-175°C, it decreases with further increase of temperature in a NaHCO₃-S system. In-Situ sorption of Cl, in Fixed Bed Reactor (FBR) Pyrolysis of Sewage Sludge showed varying efficiency (from 80% capture of Cl in char to as low as 49%) even though 3-5 repetitions of the same experiment were carried out. While the S capture in char showed a mild increase from No Sorbent (NS) case to using a sorbent case. When NaHCO₃ was used as sorbent the S capture in char increased from 42% to 52%.

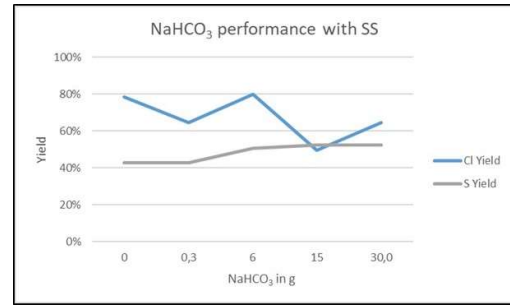


Figure 9: NaHCO₃ Performance in the case of SS

Some possibilities to explain the Cl trend can be the occurrence of secondary reactions between NaHCO₃ and char matrix [11] thereby decreasing the amount available for Cl adsorption (it has been reported [34, 36] that high stoichiometric amount of NaHCO₃ is required for effective sorption efficiency of Cl, typically more than 90%), the contacting pattern and flow regime between solid-gas components (low HCl concentration in incinerators have reported modification in design of reactor such that the contact between ash and flue gas is enhanced[12]).

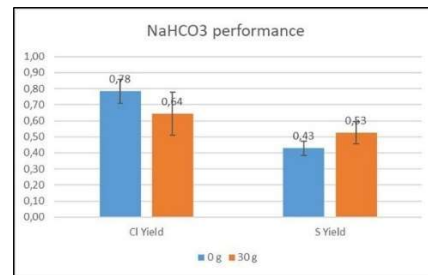


Figure 10: NaHCO₃ Performance in the case of SS

Results obtained in the case of CaO as sorbent, agreed with literature that the sorption reaction rate of CaO is lower for acid gases as compared to NaHCO₃. Chlorine capture was marginal (69% to 72%) when compared to Sulphur which increased from 41% to 76%. When CaO/SS ratio was increased from 0.26 to 0.52, the S capture showed significant increase as more sorbent was available for reaction. Another important result in this case is affinity of CaO towards CO₂ capture when compared to no sorbent case of SS pyrolysis, Figure 7 and Figure 8.

The Sulphur capture increases significantly with the amount of CaO increase, from approximately 42% to 72%. Sulphur capture in both feedstock follow this release pattern mentioned in literature

and maximum amount of the released S is captured at the pyrolysis temperature. When wheat straw was used as feed for pyrolysis and NaHCO_3 used as sorbent in the FBR system the chlorine yield was visibly higher and the same was the case with S, which is an expected result and has been reported elsewhere [11, 21, 37].

In the FBR-WS system, only NaHCO_3 was tested as the previous experiments showed NaHCO_3 to be relatively better sorbent. The Cl capture in char increased from 51% to 69%, S capture from 25% to 51%; which is a decent efficiency as compared to FBR-SS system.

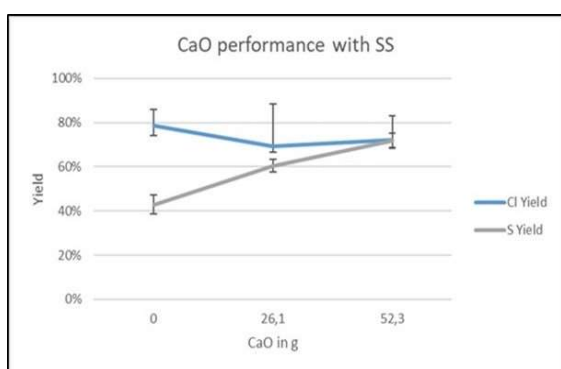


Figure 11: Performance and Standard Deviation, SS+CaO

Standard deviation is a measure of extent of deviation or dispersion of results obtained from performing the same experiment multiple times. In this case, it gives an insight to the abrupt values obtained in the case of Cl capture for SS using both NaHCO_3 and CaO. This deviation can be because of analytical error and inhomogeneity in char composition in the sample taken for analysis. Analytical error can be justified by the low content of Cl as compared to S in the feedstock which is challenging to be determined with precision using the available instruments for analysis.

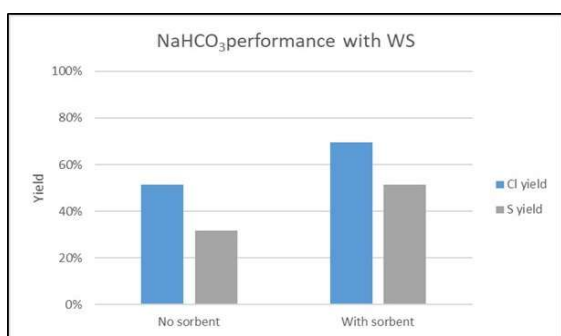


Figure 12: Performance of NaHCO_3 in case of WS

Analytical error can be justified by the low content of Cl as compared to S in the feedstock which is challenging to be determined with precision using the available instruments for analysis (also the feed used is 100 g in FBR and approximately 2 kg in STYX, hence better precision observed in latter case).

4.2 STYX Experimental Reactor

The in-situ sorption of Cl and S is investigated adopting NaHCO_3 as sorbent but not CaO. There are two reasons for this selection, first is the extensive literature reported on efficiency of both sorbents and NaHCO_3 being superior in performance. Second is, the results obtained during experiments on FBR showed low reproducibility in using both sorbents, but visible efficiency of NaHCO_3 for Wheat Straw, in capturing Cl from 50% to 70% approximately.

Four experiments were carried out (2 repetition of each one) mentioned in Figure 4. The mass ratio of feed to Sorbent was held constant as it was in the experiments with FBR configuration.

4.2.1 Mass Balance

The results of overall mass balance are shown in the Figure 13. The balance is with respect to the feed which includes both the biomass feedstock and the sorbent. Biomass feedstock studied were Sewage Sludge (SS) and Wheat Straw (WS). First experiment was done to know how much Cl is released during pyrolysis of the respective feedstock without sorbent. Then both the feedstocks were mixed with NaHCO_3 and pyrolyzed at the same process conditions. The depiction of the mass balance of the experiments (residence time was 7.5 minutes) performed in the Integrated pyrolysis STYX plant are demarcated as shown in Figure 13. The yields of solid, liquid and gaseous products for both cases are compared; due to release of CO_2 from the decomposition of NaHCO_3 the gas fraction of SS+ NaHCO_3 , is higher than the no sorbent experiment. (%). Sorbent addition increases the cracking reactions between volatiles and char leading to breakdown of higher hydrocarbons to lighter ones, eventually increasing the share of gas [5]. Also, the increase in P. Gas for SS+ NaHCO_3 and WS+ NaHCO_3 is compensated by a decrease in the content of liquid products (Organic

and Aqueous fractions). The reason for the decrease in the liquid yield for the case when sorbent is used with both the feedstocks, is attributed to the presence of alkali metals and alkaline earth metals in the reaction mixture. These species promote secondary reactions (cracking) of volatiles with the char [5, 6, 9]. In the case of sewage sludge without the utilization of sorbent, the yield of the char was 52%. While, in the case of Utilization of the sorbent, yield of char decreased to 49.3%. Wheat straw showed slightly different response towards using a sorbent. The increase in P. Gas yield was significant (from 26.3% to 32.6%) while increase in the yield of char was marginal (36.5% to 37). It should be noted that since the pyrolysis gas from WS experiments were not analysed by GC, the yellow component in Figure 13 represents P. Gas+ loss.

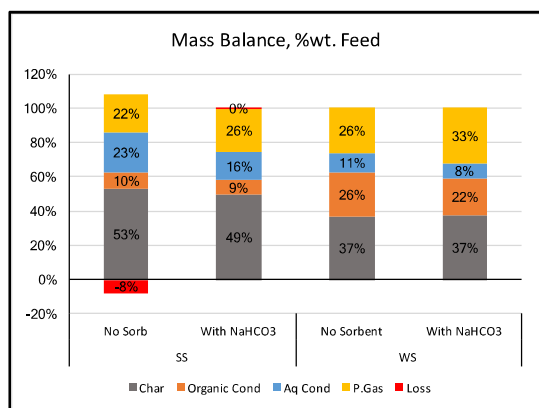


Figure 13: Mass Balance and Yield distribution of experiments using STYX

4.2.2 Sorbent Performance

Since release of Chlorine compounds, in this study, mainly takes place between 350-550°C [38], Intermediate pyrolysis with hot gas filtration led to an increase of Permanent Gas (P. Gas) because of low heat rates and high residence time as compared to fast pyrolysis [39]. Using NaHCO₃ as sorbent with Sewage Sludge, increased the capture of Cl in char from 82% to 92% approximately as shown in Figure 14.

As discussed previously, in case of FBR Cl capture in char could not be measured with high precision because of issues related to mixing and sampling (less Cl content), different heating program and temperature distribution in the bulk solid also contributed to this problem. Nevertheless, in case

of SS which has high S content, sorbent has shown reliable performance of in-situ sorption (from 50% to 68%) depicted in Figure 15. The presence of alkali metals in the reactor in the form of NaOH or NaHCO₃ reduces the emission of H₂S in two ways. First is the oxidation of unstable aliphatic and aromatic sulphurs to more stable sulphoxides and sulphonic acid at a temperature of 250°C. Second is the fixation of sulphur in the form of in-organic sulfide and sulfate in char, further reducing the release of sulfur into gas phase [40]. Hence, these reports explain the reduction of S in the gas phase when sorbent is used, in this study.

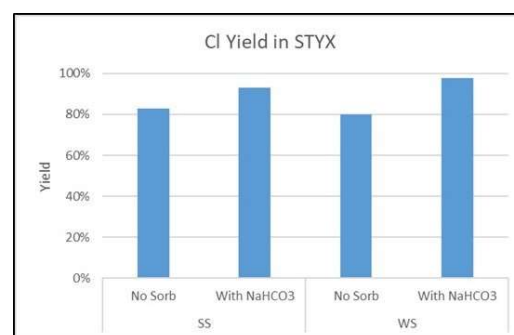


Figure 14: Comparison of Cl Yield for SS and WS for STYX

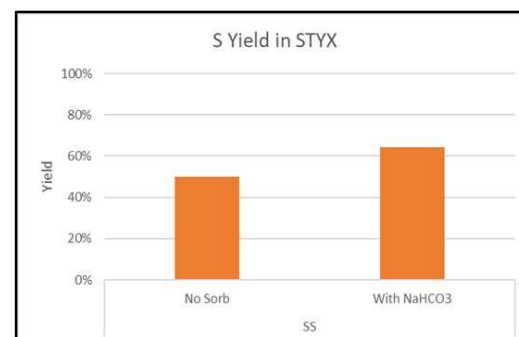


Figure 15: Comparison of Sulphur Yield for SS

4.2.3 Permanent gas Combustion

The permanent gas generated by sewage sludge pyrolysis in STYX reactor, were analysed using GC (FID and TCD) detectors to find the composition. In the Figure 16, leaving aside Nitrogen, share of CO₂ increases when sorbent is used. It was also observed that share of hydrocarbons contributing to the calorific value, increased in the case of use of NaHCO₃. Combustion of permanent gas using excess air as per the guidelines mentioned in 17. BlmSchV, limits the HCl and SO₂ emissions to be not more than 10 and 50 mg/m₃ respectively. [41]

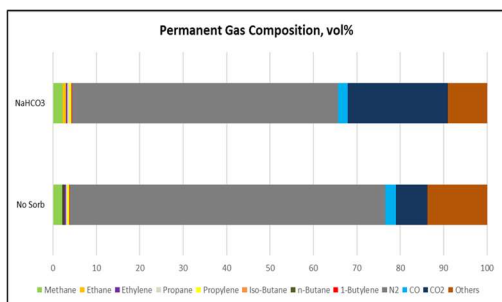


Figure 16: Breakdown of Hydrocarbons in Pyrolysis gas

It also precisely mentions the amount of oxygen present in the flue gas. The oxygen content present in the flue gas should be 11% and hence the required amount of air is re-calculated based on this value. Using these guidelines and the equation below, combustions calculations were done. In Figure 18 and Figure 19, the emissions are reported both under stoichiometric conditions as well as after the German 17. BImSchV regulation [41] (11% O₂). Emissions of HCl are reduced by a factor 3.

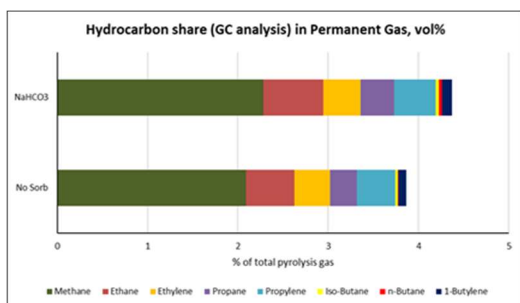


Figure 17: Hydrocarbon share in the P.gas

However, it was not possible to meet the required emission limits. Nevertheless, the target appears achievable by improving the mixing quality as well as by slightly increasing the sorbent to feed ratio.

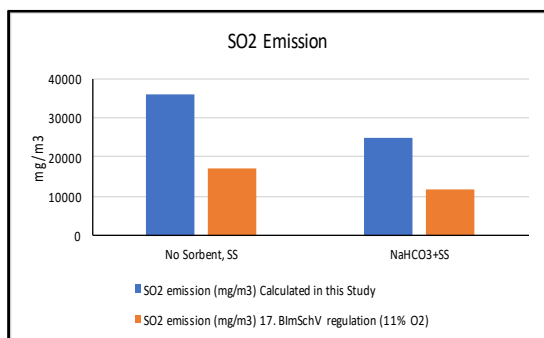


Figure 18: SO₂ Emission

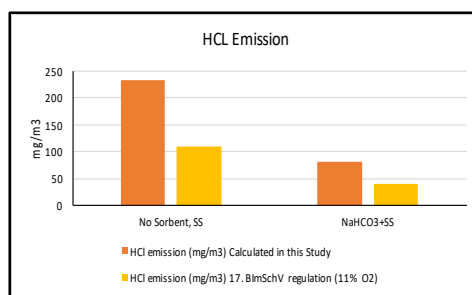


Figure 19: HCl emissions

On the other hand, the emissions of SO₂ are far away from the required target. Alternative strategies for the removal of sulphur from the P. Gas need to be investigated. In conclusion, the co-feeding of sorbent for the reduction of Cl emission, is a promising option requiring optimization. In the case of combined removal of Cl and S from the P. Gas, the in-situ sorption approach showed limited results.

5. Conclusions

- Use of NaHCO₃ and CaO as sorbents for Cl and S capture in the FBR showed varying results and issues of reproducibility. The relative amount of Cl is small as compared to S in the SS feedstock which gives rise to decrease of precision.
- Higher stoichiometric ratio of Sorbent and Feed could lead to better capture of Cl and S. However, economic considerations may also be considered.
- Calcium Oxide as sorbent for both SS and WS showed competitive sorption of CO₂ and acid gases. The capture of S in the char using CaO, was more efficient than Cl, for sewage sludge. This is because of the high amount of S present in SS, which enables better analysis of the contents in char.
- In the FBR-WS system, the Cl capture in char increased from 51% to 69%, S capture from 25% to 51%; which is a decent efficiency as compared to FBR-SS system. Hence, it was concluded that NaHCO₃ due to its superior performance, will also be tested in STYX experiments for capture of S and Cl.

- e) When SS and WS are used as feed, NaHCO₃ as sorbent in STYX, chlorine removal trend is increasing from no sorbent to using a sorbent. In the case of S which is present in very high amount in SS visibly high S sorption efficiency was observed. Hence, it was concluded that further studies must be conducted on NaHCO₃+SS system for STYX pyrolysis plant to get higher efficiency of Cl sorption.
- f) Combustion Calculations of Permanent gas showed that the values of SO₂ and HCl emissions are above the regulation limit. The removal of Sulphur requires a different strategy.

References

- Bridgwater, A.V.: Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal* (2003). doi: 10.1016/S1385-8947(02)00142-0
- Coda, B., Aho, M., Berger, R., Hein, K.R.G.: Behavior of Chlorine and Enrichment of Risky Elements in Bubbling Fluidized Bed Combustion of Biomass and Waste Assisted by Additives. *Energy Fuels* (2001). doi: 10.1021/ef000213
- Lee, J., Feng, B.: A thermodynamic study of the removal of HCl and H₂S from syngas. *Frontiers of Chemical Science and Engineering* (2012). doi: 10.1007/s11705-011-1162-4
- Horan, N.J.: Biological wastewater treatment systems. Theory and operation. John Wiley & Sons Ltd (1989)
- Hassan, S.S.A., Wang, Y., Hu, S., Su, S., Xiang, J.: Thermochemical processing of sewage sludge to energy and fuel Fundamentals, challenges and considerations. *Renewable and Sustainable Energy Reviews* (2017). doi: 10.1016/j.rser.2017.05.262
- Fonts, I., Gea, G., Azuara, M., Ábrego, J., Arauzo, J.: Sewage sludge pyrolysis for liquid production: A review. *Renewable and Sustainable Energy Reviews* (2012). doi: 10.1016/j.rser.2012.02.070
- European Commission: Disposal and recycling routes for sewage sludge. Part 3 - Scientific and technical sub-component report. Scientific and technical sub-component report. European Commission Environment, Luxembourg. http://ec.europa.eu/environment/archives/waste/sludge/pdf/sludge_disposal3.pdf (2001)
- Grøn, C.: Organic contaminants from sewage sludge applied to agricultural soils. False alarm regarding possible problems for food safety?(8 pp). *Environmental Science and Pollution Research* **14**, 53–60 (2007)
- Fonts, I., Azuara, M., Gea, G., Murillo, M.B.: Study of the pyrolysis liquids obtained from different sewage sludge. *Journal of Analytical and Applied Pyrolysis* **85**(1), 184–191 (2009)
- Lester, J.N., Sterritt, R.M., Kirk, P.W.W.: Significance and behaviour of heavy metals in waste water treatment processes II. Sludge treatment and disposal. *Science of the total environment* **30**, 45–83 (1983)
- Johansen, J.M., Jakobsen, J.G., Frandsen, F.J., Glarborg, P.: Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass. *Energy Fuels* (2011). doi: 10.1021/ef201098n
- Fullana, A., Conesa, J.A., Font, R., Sidhu, S.: Formation and Destruction of Chlorinated Pollutants during Sewage Sludge Incineration. *Environ. Sci. Technol.* (2004). doi: 10.1021/es034896u
- Fytili, D., Zabaniotou, A.: Utilization of sewage sludge in EU application of old and new methods—A review. *Renewable and Sustainable Energy Reviews* (2008). doi: 10.1016/j.rser.2006.05.014
- Conesa, J.: Kinetics Study of the Pyrolysis of Sewage Sludge. *Waste Management & Research* (1997). doi: 10.1006/wmre.1996.0085
- Kassman, H.: Strategies to reduce gaseous KCl and chlorine in deposits during combustion of biomass in fluidised bed boilers. Zugl.: Göteborg, Univ., Diss., 2012, Chalmers University of Technology (2012)
- Matsuda, H., Ozawa, S., Naruse, K., Ito, K., Kojima, Y., Yanase, T.: Kinetics of HCl emission from inorganic chlorides in simulated municipal wastes incineration conditions. *Chemical Engineering Science* (2005). doi: 10.1016/j.ces.2004.07.131
- Woolcock, P.J., Brown, R.C.: A review of cleaning technologies for biomass-derived syngas. *Biomass and Bioenergy* (2013). doi: 10.1016/j.biombioe.2013.02.036
- Björkman, E., Strömberg, B.: Release of Chlorine from Biomass at Pyrolysis and Gasification Conditions. *Energy Fuels* (1997). doi: 10.1021/ef970031o
- Saleh, S.B., Flensburg, J.P., Shoulaifar, T.K., Sárossy, Z., Hansen, B.B., Egsgaard, H., DeMartini, N., Jensen, P.A., Glarborg, P., Dam-Johansen, K.: Release of Chlorine and Sulfur during Biomass Torrefaction and

- Pyrolysis. *Energy Fuels* (2014). doi: 10.1021/ef4021262
20. Ren, X., Sun, R., Chi, H.-H., Meng, X., Li, Y., Levendis, Y.A.: Hydrogen chloride emissions from combustion of raw and torrefied biomass. *Fuel* (2017). doi: 10.1016/j.fuel.2017.03.040
 21. Jensen, P.A., Frandsen, F.J., Dam-Johansen, K., Sander, B.: Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis. *Energy Fuels* (2000). doi: 10.1021/ef000104v
 22. Knudsen, J.N., Jensen, P.A., Lin, W., Frandsen, F.J., Dam-Johansen, K.: Sulfur Transformations during Thermal Conversion of Herbaceous Biomass. *Energy Fuels* (2004). doi: 10.1021/ef034085b
 23. Kopetz, K., Weber, T., Palz, W., Chartier, P., Ferrero, G.L. (eds.): *Biomass for Energy and Industry*. 10th European Conference and Technology Exhibition, Würzburg, Germany, June 8-11 1998. C.A.R.M.E.N (1998)
 24. Liu, Q., Chmely, S.C., Abdoulmoumine, N.: Biomass Treatment Strategies for Thermochemical Conversion. *Energy Fuels* (2017). doi: 10.1021/acs.energyfuels.7b00258
 25. Abdoulmoumine, N., Adhikari, S., Kulkarni, A., Chattanathan, S.: A review on biomass gasification syngas cleanup. *Applied Energy* (2015). doi: 10.1016/j.apenergy.2015.05.095
 26. Dou, B.-l., Gao, J.-s., Sha, X.-z.: A study on the reaction kinetics of HCl removal from high-temperature coal gas. *Fuel Processing Technology* (2001). doi: 10.1016/S0378-3820(01)00176-X
 27. Dou, B., Gao, J., Baek, S.W., Sha, X.: High-Temperature HCl Removal with Sorbents in a Fixed-Bed Reactor. *Energy Fuels* (2003). doi: 10.1021/ef010294p
 28. Duo, W., Seville, J.P.K., Kirkby, N.F., Clift, R.: Formation of product layers in solid-gas reactions for removal of acid gases. *Chemical Engineering Science* **49**(24), 4429–4442 (1994)
 29. Duo, W., Kirkby, N., Seville, J.P.K., Kiel, J.H.A., Bos, A., Den Uil, H.: Kinetics of HCl reactions with Calcium and Sodium based sorbents for IGCC fuel gas cleaning. *Chemical Engineering Science* **51**, 2541-2546, (1996)
 30. Karlsson, H.T., Klingspor, J., Bjerle, I.: Adsorption of Hydrochloric Acid on Solid Slaked Lime for Flue Gas Clean Up. *Journal of the Air Pollution Control Association* (1981). doi: 10.1080/00022470.1981.10465343
 31. Quicker, P., Rotheut, M., Noel, Y., Schulten, M., Athmann, U.: *Treating WTE Plant Flue Gases with Sodium Bicarbonate*. Power, Business & Technology for the Global Generation Industry Since 1882, Aachen, Germany (2014)
 32. Shemwell, B., Levendis, Y.A., Simons, G.A.: Laboratory study on the high-temperature capture of HCl gas by dry-injection of calcium-based sorbents. *Chemosphere* (2001). doi: 10.1016/S0045-6535(00)00252-6
 33. Verdone, N., Filippis, P. de: Thermodynamic behaviour of sodium and calcium based sorbents in the emission control of waste incinerators. *Chemosphere* (2004). doi: 10.1016/j.chemosphere.2003.09.041
 34. Kong, Y., Wood, M.: *Dry Injection of soDium sorbents for Dry Injection of Sodium Sorbents for Air pollution control*, New York
 35. Yassin, L., Lettieri, P., Simons, S.J.R., Germanà, A.: Study of the Process Design and Flue Gas Treatment of an Industrial-Scale Energy-from-Waste Combustion Plant. *Ind. Eng. Chem. Res.* (2007). doi: 10.1021/ie060929d
 36. Fellows, K.T., Pilat, M.J.: HCl Sorption by Dry NaHCO₃ for Incinerator Emissions Control. *Journal of the Air & Waste Management Association* (2012). doi: 10.1080/10473289.1990.10466734
 37. Wang, X., Si, J., Tan, H., Ma, L., Pourkashanian, M., Xu, T.: Nitrogen, Sulfur, and Chlorine Transformations during the Pyrolysis of Straw. *Energy Fuels* (2010). doi: 10.1021/ef1007215
 38. Morgano, M.T., Leibold, H., Richter, F., Stapf, D., Seifert, H.: Screw pyrolysis technology for sewage sludge treatment. *Waste Management* (2017). doi: 10.1016/j.wasman.2017.05.049
 39. Bridgwater, A.V.: Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* (2012). doi: 10.1016/j.biombioe.2011.01.048
 40. Cheng, S., Qiao, Y., Huang, J., Cao, L., Yang, H., Liu, H., Yu, Y., Xu, M.: Effect of alkali addition on sulfur transformation during low temperature pyrolysis of sewage sludge. *Proceedings of the Combustion Institute* (2017). doi: 10.1016/j.proci.2016.06.124
 41. Bundesministeriums der Justiz, juris GmbH: Siebzehnte Verordnung zur Durchführung des BundesImmissionsschutzgesetzes (Verordnung über die Verbrennung und die Mitverbrennung von Abfällen - 17. BImSchV), Germany (2013)