



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

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**Energy Engineering and Management**

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# Abstrato

A utilização comercial de biomassa como recurso de energia renovável tem vindo a aumentar na última década. O desperdício de diferentes composições origina biomassa de baixa qualidade que, após a utilização térmica, pode ajudar a uma melhor disposição. As tecnologias térmicas incluem Combustão, Pirólise e Gasificação. O desafio mais crucial para essas tecnologias é garantir que as emissões estejam abaixo dos limites de regulação respectivos. As emissões de enxofre e gás ácido foram amplamente discutidas e a dessulfurização de gases de combustão (FGD) mostrou uma implementação bem sucedida em vários casos. Devido à composição diversa e, eventualmente, a natureza das emissões, a matéria-prima de biomassa requer o método de disposição de fonte específica.

Como parte deste trabalho de investigação, a Pirólise de Lodo de Esgoto com sorção in-situ de Cloro/Enxofre foi avaliada usando sorventes à base de Cálcio e Sódio. A investigação também examina a eficiência de utilizar sorção in-situ em comparação com o uso de um equipamento separado de limpeza de gás, após um estudo cuidadoso da literatura e obtenção de resultados experimentais. O Cloro está presente em quantidade significativa no feno de Trigo, portanto, requer uma pirólise para comparação com as emissões da pirólise das Lamas de Esgoto. Estudos sobre a utilização de sorção com Óxido de Cálcio (CaO) e Carbonato de Hidrogénio de Sódio (NaHCO<sub>3</sub>) foram conduzidos usando Planta Fixa e Pirólise de Parafuso Integrada (STYX).

Os resultados experimentais reflectem uma sorção notável de Cl e S na configuração STYX; No Reactor de Cama Fixa foram encontradas problemas de reprodutibilidade dos resultados desejados. O rendimento dos produtos de pirólise depende de diferentes condições como a natureza da matéria-prima, a temperatura de operação, o tipo de reactor, o tempo de residência, etc. A comparação do equilíbrio de massa entre utilização com e sem absorvente neste estudo demonstrou um aumento da fracção de gás Permanente, aumento ligeiro na quantidade de carvão, diminuição da fracção orgânica e fracção aquosa dos produtos líquidos obtidos.

Palavras-chave: Emissão de cloro, Reator de pirólise de parafuso integrado, Lodo de esgoto, Sorção in-situ.

# 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. Thermal utilization technologies are Combustion, Pyrolysis and Gasification. Most crucial challenge for these technologies is to ensure the emissions are below the respective regulation limits. Sulphur and acid gas emissions have been discussed widely and Flue Gas Desulphurization (FGD) has shown successful implementation in many cases. 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 Pyrolysis with in-situ sorption of Chlorine/Sulphur was evaluated using Calcium and Sodium based sorbents. The work also examines efficiency of using in-situ sorption as compared to using a separate gas cleaning equipment, after careful study of literature and obtained experimental results. Chlorine is present in significant amount in Wheat Straw, hence it is also pyrolyzed for comparison with the emissions from Sewage Sludge pyrolysis. Sorption studies with Calcium Oxide (CaO) and Sodium Hydrogen Carbonate (NaHCO<sub>3</sub>) were conducted using Fixed Bed and 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. Yield of pyrolysis products depends on conditions like nature of feedstock, temperature of operation, reactor type, residence time etc. The Mass Balance comparison between cases of with and without sorbent use, in this study, showed increase of fraction of Permanent gas, 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.

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# Abbreviations

1. BIGCC: Integrated Gasification Combined Cycle
2. CHP: Combined Heat and Power
3. EEA: European Economic Area
4. ESP: Electro Static Precipitator
5. EU: European Union
6. FBR: Fixed Bed Reactor
7. FGD: Flue Gas Desulphurisation
8. FID: Flame ionization detector
9. GC: Gas Chromatography
10. GC-MS: Gas Chromatography-Mass Spectroscopy
11. GHG: Green House Gases
12. IGCC: Integrated Gas Combined Cycle
13. MSW: Municipal Solid Waste
14. NS: No Sorbent
15. PAH: Polycyclic Aromatic Hydrocarbon
16. PCB: Poly-chlorinated Biphenyl
17. PCDD: Polychlorinated dibenzodioxins (dioxins)
18. P. Gas: Permanent Gas
19. SFG: Simulated Flue gas
20. SS: Sewage Sludge
21. STYX: (Integrated Pyrolysis Plant) Screw Pyrolysis Reactor with integrated hot gas filtration
22. TCD: Thermal Conductivity detector
23. WBA: World Biomass Association
24. WS: Wheat Straw

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# 1. Objective of the Work

## 1.1 Introduction

Growing energy demand and climate change have led to complex sustainability concerns. The green-house gas emissions and dwindling fossil fuel reserves and their costs have led to widespread research and commercial attention on *Biomass* as an energy resource. Currently, developing countries are the highest consumers of Bioenergy, traditionally in cooking and heating purposes, while modern usage of these resources can help in providing energy access and security to the world. The availability of feedstock in the form of MSW, agricultural waste, Organic waste etc. is not a concern but modern technologies are not accessible and affordable to most of the developing countries. Although there has been a shift in the regime of utilization of bio resources, but at the same time some arguments have been raised about three broad issues: Firstly, if Bioenergy translates to net GHG savings. Secondly, if large scale bioenergy exploitation adversely affects food security. Lastly, environmental ill-effects of using Bioenergy.

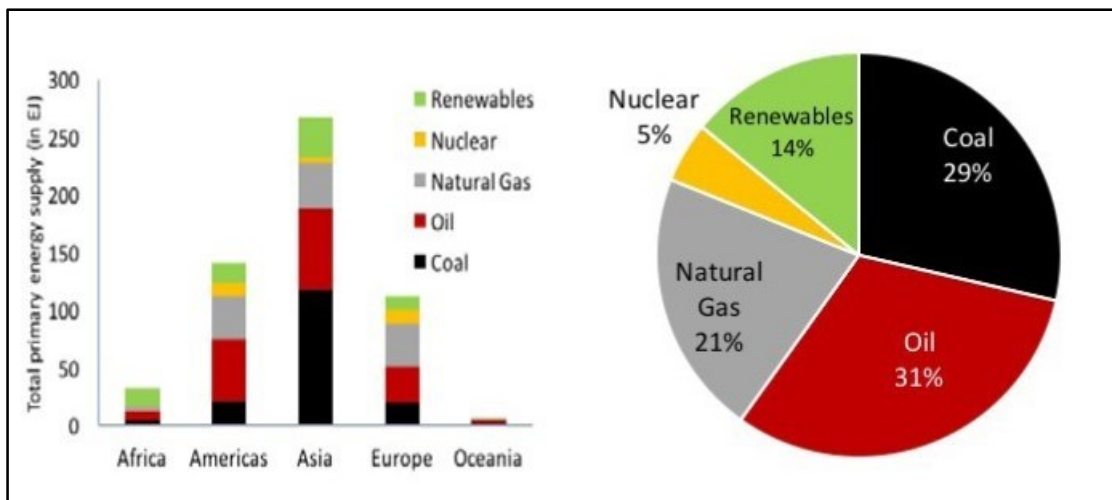


Figure 1: Total Energy Supply in the World, 2014 [1]

The Total Energy supplied as defined by WBA [1] in terms of energy content of the fuel, compares the total production of energy sources including imports, exports and storage facilities. The share of fossil fuel is the highest as shown in Figure 1., Asia has the highest total energy supply in the world along with the highest renewable energy supply. The African continent, due to its large use of biomass and hydropower, provides almost half of all the energy supply by renewable energy sources. In comparison, Europe has only 10.3% share of renewable resources in its energy supply statistics [1]. The Gross final energy consumption defined by WBA is, the sum of the following is [1]:

**Total Final Consumption + Electricity and Heat Consumption + Losses in distribution and transmission**

Where,

*Total Final Consumption* is the energy that is spent in the end uses sector, calculated using the energy content of the fuel and *Electricity and Heat consumption* is the heat and electricity generated in the power plants. Figure 2 below clearly shows that Africa has a major part of energy supplied by Biomass, whereas Oceania has the lowest share of biomass in the primary supply of energy. The main source of energy in Africa and poor parts of Asia, for cooking is wood and other agricultural residues. These low-grade fuels pose a threat to health and environment both.

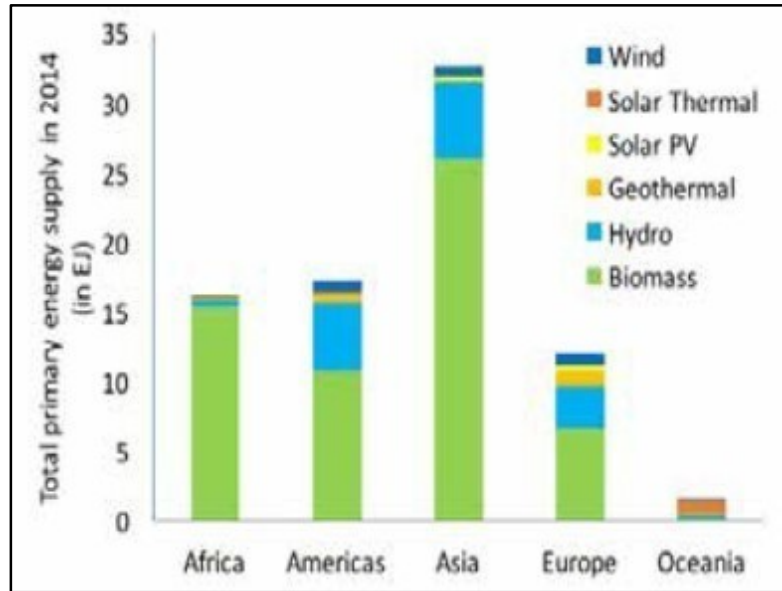


Figure 2: Gross Final Consumption of Energy Resources in 2014 [1]

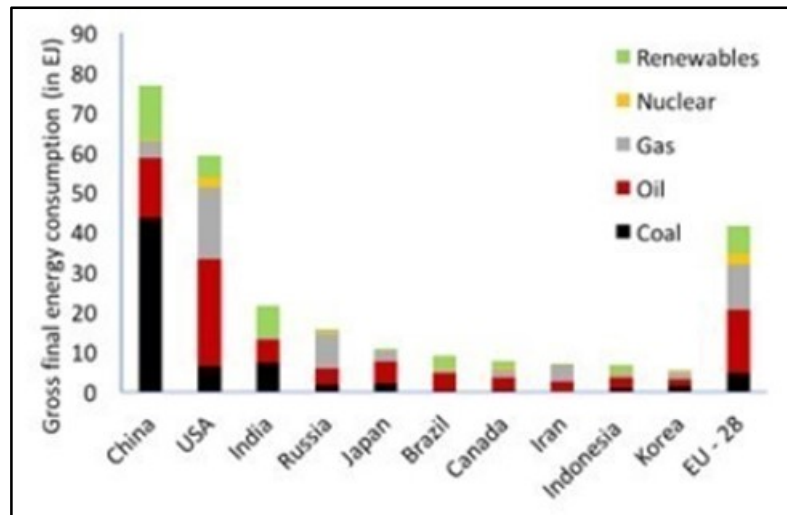


Figure 3: Gross Final Consumption comparing top 10 Countries, 2014 [1]

China consumes the highest amount of energy which accounts to 80 EJ, with global consumption of renewable resources accounting for a significant share. In Figure 3 it is important to note that the renewable resource use is not just in the electricity sector but in heating and transportation too.

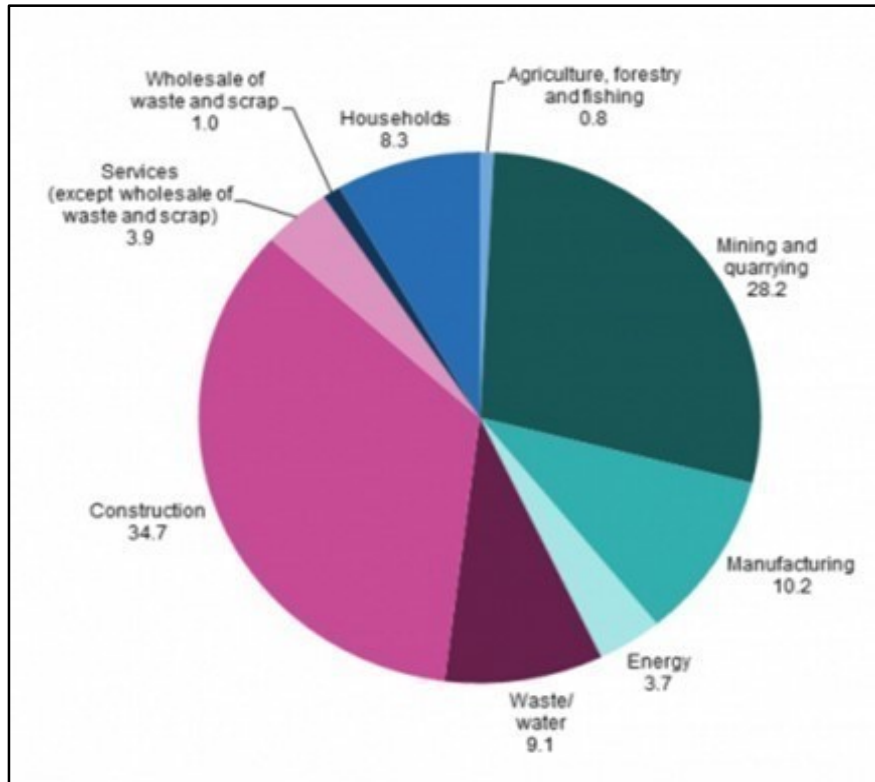


Figure 4: Waste generation by economic activities and households, EU-28, 2014 (%), Eurostat

Figure 4 and Figure 5 show the statistics of waste generation and utilization in the electricity sector in EU-28. Since there is a lot of attention given to minimizing waste and utilizing Biomass energy, the share of Biomass in electricity generation has increased over the years 2005-2015 (Figure 5). It is evident that a visible portion of the waste generated is waste water which is 9.1%, hence it is required that this water is treated ensuring that contaminants are well under the legal limit, by products are re-used and nutrients are recovered. 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.

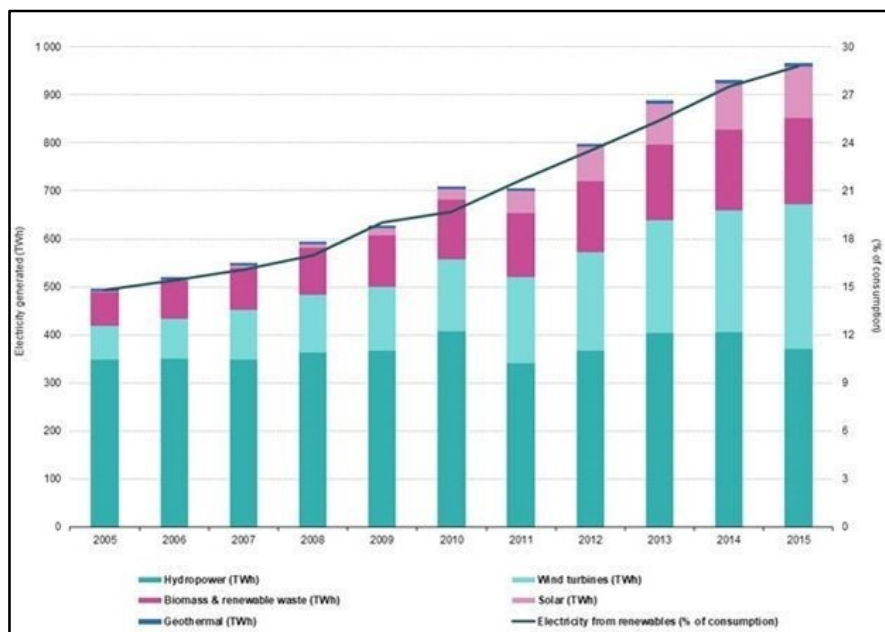


Figure 5: Electricity generated from renewable energy sources, EU-28, 2005-2015, Eurostat.

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 [2]. The products of sewage sludge pyrolysis can be utilized in soil quality enhancement (stabilized biochar) and the flue gas can be combusted to be used in energy generation applications [3]. However, there are concerns related to release of toxic polychlorinated compounds and acidic gases like HCl and H<sub>2</sub>S in the flue gas. Therefore, suitable methods should be employed post or pre-utilization so that the emissions are within the safe limits and the energy utilization efficiency is economically viable. The constraints of using sewage sludge for thermal treatments are not limited only to presence of pathogens and heavy metals but include also the corrosive effects of some compounds formed during pyrolysis and the acidic gases in flue gas. Alkali metals in the sewage sludge form metal chlorides responsible for corrosion and fouling of the reactor and hence even if chlorine is present in considerably small amounts in the sludge, it can form multiple compounds depending on process conditions that are hazardous for environment and health [4]. It has also been reported that torrefaction (low temperature pyrolysis) in the temperature range of 200-350°C causes the emission of nitrogen-containing compounds like N<sub>2</sub>O, NO, NO<sub>2</sub>, NH<sub>3</sub> and HCN, among which NO and HCN are the most common ones [5]. 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 [6]. Thermodynamic calculations on syn gas, carried out by Joseph Lee et al. [7] in the temperature range of 300-1500 K, Pressure 0.1-11 MPa and initial contaminant (HCl and H<sub>2</sub>S) concentration between 1-10000 ppm resulted in CaO, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> to be the four best candidates among 12 others for effective chlorine removal at moderate to high temperatures.

## 1.2 Research Objective

The objective of this study was to evaluate the so-called *In-situ* sorption of Chlorine/Sulphur by co-feeding Biomass and sorbent in a 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. This is relevant because it is evident that waste generation will increase and hence it is the need of the hour to invest in technologies for efficient utilization of it, without compromising environmental regulations. Sewage sludge combustion is practiced in some European countries but if the process and principle modifications can lead to energy generation without increasing toxic emissions then the process will be advantageous in an overall life cycle aspect. 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 [8].

## 1.3 Thesis Outline

This research work is presented in 2 sections, first is the *Literature Review* and second is the *Experimental Campaign with results and discussion*.

The thesis continues in **Chapter 2**, marking the beginning of Literature review. It consists of three sub chapters describing the basic concepts of biomass properties, composition and structure, Thermochemical Conversion processes respectively.

**Chapter 3** is dedicated for cradle to grave description of Sewage Sludge, divided in to 5 sub chapters. Since the feedstock examined in this thesis is sewage Sludge, knowing its characteristics, composition, treatment etc. is vital for the selection of suitable sorbent. The German and EU regulations are summarized in the last sub chapter 4.5, so that the quantification of results is relevant and as per the limits mentioned.

The evaluation of factors responsible for chlorine emission, Pyrolysis principles specific to sewage sludge and their comparison with combustion, are discussed elaborately in **Chapter 4**. This provides reasoning for the research work conducted as the root cause of emission is being addressed.

The last chapter in the literature review, **Chapter 5**, of this work mentions the significance and role of a range of sorbents studied in literature for sorption of Cl and S in combustion and pyrolysis. The chapter gives an insight for selection of sorbent to conduct this study. The extensive literature review focusing on use of sorbent, their characteristics and efficiency for combustion and pyrolysis, biomass feedstock composition and its effect on thermochemical conversion technologies are described in detail.

The second section of thesis starts from **Chapter 6**, which describes both the experimental set ups: fixed bed reactor and bench-scale Screw Pyrolysis (STYX<sup>1</sup>) reactor (developed by Institute of Technical Chemistry (ITC), Karlsruhe Institute of Technology (KIT), Germany). Experimental procedure to evaluate performance of sorbents for both Sewage Sludge (SS) and Wheat Straw (WS) is presented separately.

Lastly, the experimental results are presented in the **Chapter 7** for both reactor configurations. The sorbents tested are compared, overall mass balance is calculated and depicted in graphs. Comparison of the results produced in this study and the observations from literature is conducted, providing probable reasons for some deviations. The experiences and learning from the conduct of experiments and result analysis paved way for future work and outlook which are also listed in this last chapter.

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



## 2. Understanding Biomass and its Thermochemical Conversion

### 2.1 Biomass Characteristics

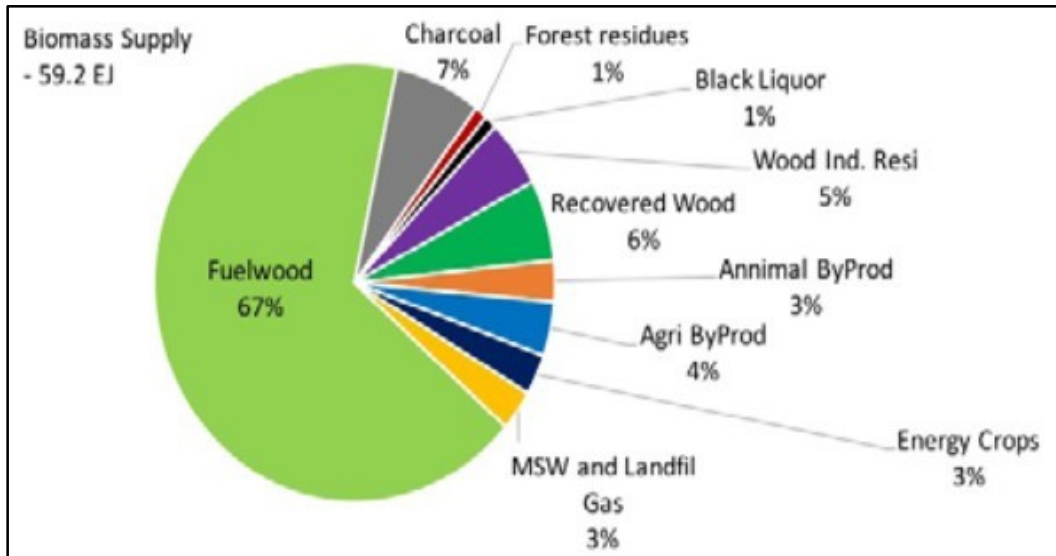


Figure 6: Sources of Biomass feedstock [1]

Biomass is a very general term and can be described as all organic matter (excluding the fossil fuels, which took millions of years to get transformed beneath the earth's surface[9] ) in which the energy derived from the Sun is stored in the form of chemical bonds, also including waste from agriculture, Industry and municipality [10]. It is an abundant raw resource, which requires processing depending on its use and composition. Biomass is a non-homogeneous type of resource because its composition is highly variable depending on the source, location, climate, season and other factors. The basic elements bonded together in the form of Biomass are C, H and O

According to WBA 2017 report [1], in the year 2014, 10.3% of all supply of energy in the world was from Biomass. As shown in Figure 6, the major source of Biomass is forestry that contributes to 87% of all the feedstock. The quality and utility of the Biomass depends on the compounds that make it up. McKendry [10] classified Biomass as: Woody Plants, Herbaceous Plants, Aquatic plants and Manure. In the recent decades, waste to energy applications have gained momentum and thus MSW, Sewage sludge, Dead animals, etc. can also be classified under Biomass. The use of Biomass is broadly obtaining Chemicals, Energy or Fuels, where different conversion processes are used to get the

desired product. As shown in Figure 7 below, Biomass feedstock can be of a variety of types and different researchers categorized it based on their analysis [10–12].

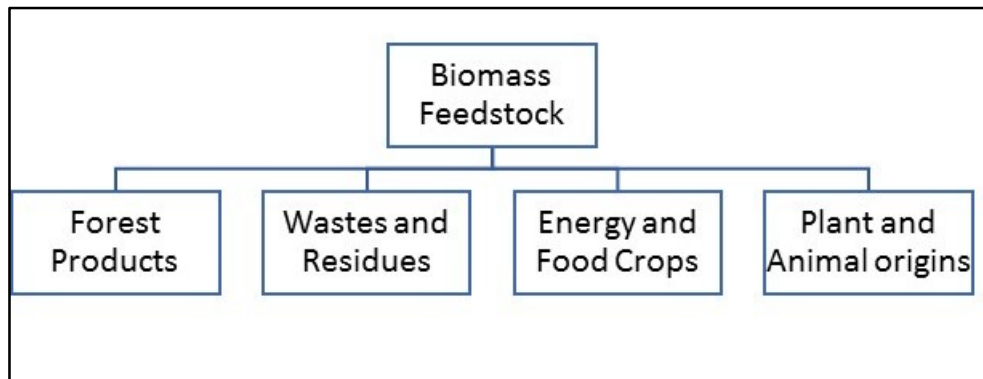


Figure 7: Basic Classification of Biomass Feedstock

**Forest Products:** Wood, dead trees and shrubs, Sawdust and Bark

**Wastes and Residues:** Organic waste from- Municipality, Industry, Hospitals, Agriculture. Manure and sewage sludge can also be included here.

**Energy and Food Crops:** Woody crops, Grasses, Starch and Sugar Crops, Oil seed crops, Grains.

**Plant and Animal Origin:** Aquatic animals and Plants, Algae, dead animals etc.

## 2.2 Biomass Composition

Biomass consists primarily of three types of macro molecules: Cellulose, Hemicellulose and Lignin. The first two are carbohydrates whereas Lignin is an important part of the cell wall of vascular plants, ferns, club mosses and has non-sugary polymeric units. For ease of understanding the diverse components of Biomass, one can classify its physicochemical properties, which are mentioned in the next sub section.

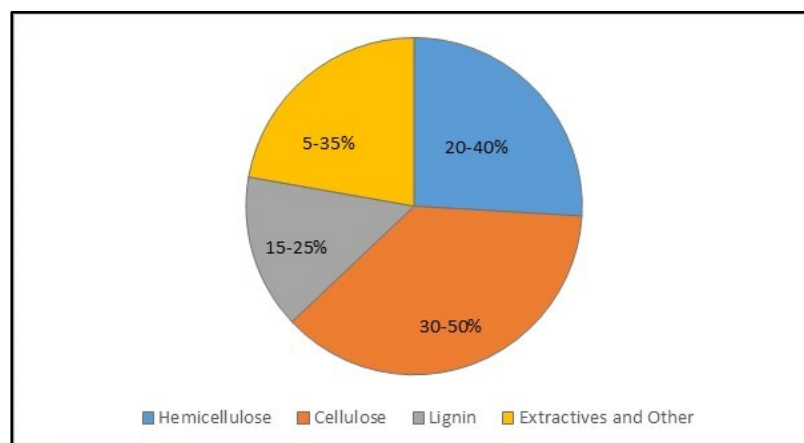


Figure 8: Distribution of the three most common components of lignocellulosic biomass dry matter [13]

### 2.2.1 Wood and Non-Wood Chemistry

Lignocellulosic Biomass consists of Cellulose as major constituent. Cellulose is a water-insoluble polymer composed of glucose units (>10 000), which are linked by  $\beta$ -(1-4)-glycosidic bonds [14].

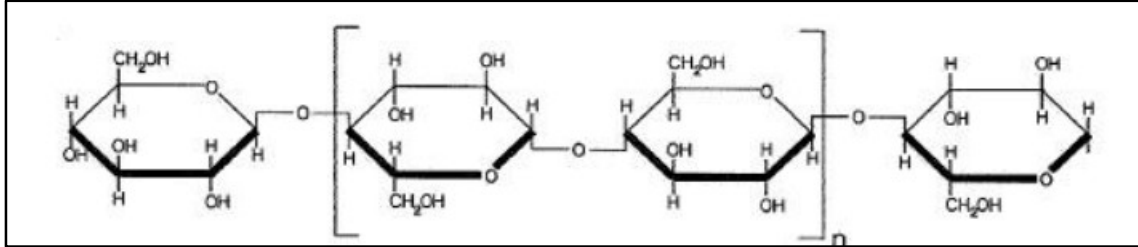


Figure 9: Polymeric Structure of Cellulose [15]

Hemicelluloses are heterogeneous polysaccharides made up of polymers of Pentoses (Xylose, Arabinose), Hexoses (Mannose, Glucose, Galactose) and sugar acids [16]. Hemicellulose is also composed by a number of different pentose and hexose monosaccharides and it tends to be much shorter in length than cellulose, with the molecular structure slightly branched [17]. As shown in Figure 9, all lignocellulosic Biomasses follow the general composition but it is a range of percentage because of variability in the carbohydrate content, which also leads to difference in yields of Biofuels and economics [13]. When Biomass is used for production of Biofuels or Bio-power, the overall energy content of the feed is a very important parameter for economics and yield. The carbohydrate content present in the feed is the main source of energy content but it is not explicitly used as a specification in thermochemical conversion processes.

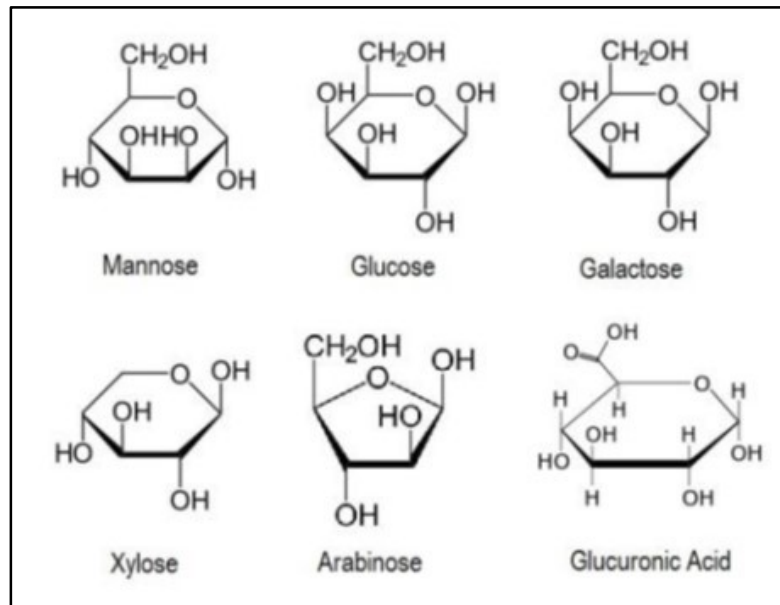


Figure 10: Polysaccharide units of Hemicellulose [9]

Lignin falls in the category of most abundant compounds on Earth after Cellulose and Chitin. It is a complex compound, hydrophobic and aromatic, with highly cross-linked units of hydroxyl-phenylpropane units, these being the phenol like structures acting as monomeric base. The important function of Lignin is to impart structural strength, sealing the water conducting system that links roots with leaves, and it also protects plants against degradation [18, 19]

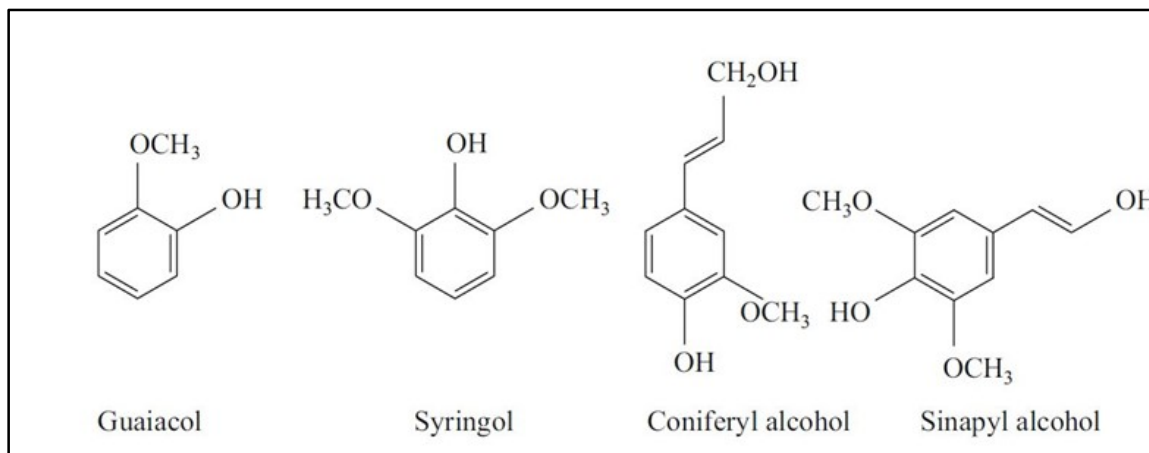


Figure 11: The four main mono-lignols composing Lignin structure [19]

The non-woody compounds present in biomass are broadly classified as Saccharides, Lipids and Proteins. These are the naturally occurring elements in plants and animals. Saccharides in the living organisms provide energy and also act as key code molecules in important functions of the body [19]. Lipids are a heterogeneous class of organic compounds that are insoluble in water but soluble in non-aqueous solvents like Chloroform, alcohol etc. They are naturally present in plants and animals used for direct production of Biodiesel [14]. Proteins are the most important compounds consisting of amino acids, which are needed by biological cells for functioning. Amino acids of 20 different types form the structure of proteins and based on them further thermochemical processes can have limitations. The presence of amine groups in proteins adversely affects the thermochemical technologies like pyrolysis, gasification etc. because the nitrogen leads to acidic gases causing pollution and corrosion [20].

### 2.2.2 Moisture content:

There are two types of moisture present in Biomass, namely: Intrinsic Moisture and Extrinsic Moisture [10]. As the name suggests, when moisture is present naturally then it is intrinsic whereas when it occurs because of climate and storage conditions then it is called extrinsic moisture. Moisture content has a different effect on the process depending on the desired end product and the technology used. For example, thermochemical processes require low moisture content biomass (less than 40%) while biochemical technologies like fermentation and digestion favor high moisture saturated biomass feedstock [19]. Hydrothermal processing technologies are developed for addressing the

high moisture biomass for thermal processing. One of the main disadvantages of moisture presence in biomass is the increase of transportation costs that adversely affects the economics [21].

### 2.2.1 Mineralogy

The agriculture based biomass can have several factors responsible for the mineral content like soil quality, use of fertilizers etc. In general, the mineral matter present in biomass is of inorganic nature but sometimes some organic compounds may also be present depending on the extent of contamination from industrial processes. The mineral matter represents the major constituent of post processing residues like Ash. Alkali metals, such as sodium (Na), potassium (K), calcium (Ca), phosphorous (P) and magnesium (Mg), are present in different forms and convert to different compounds depending on the type of thermal process. They also react with silica (SiO<sub>2</sub>) to produce a sticky and mobile liquid phase, which leads to blockage in Boilers [9]. The post processing residues can be utilised in other applications depending on the composition, if it is rich in N,P,K then it can be used as fertilizer, but if toxic metals are present then they can be a major limitation for further use [19]. The Table 1 shows typical ranges in percentage of different biomass feedstock for Mineral matter present and it is clear that the values vary drastically (2% woody trees to more than 45% for manure and sewage), this determines the suitability of the feed for the treatment and processes that can be considered.

Table 1: Typical Range of Mineral matter, wt% [12]

Feedstock	Minimum (%)	Maximum (%)	Average (%)
Wood Trees	0.1	6	2
Energy Crops(grasses)	1.1	17	6
Cereal Straw	1.3	20	7
Cereal Husks	1	20	9
Sewage	21	74	49
Manure	11	74	49

Ash has a negative effect on thermochemical conversion as it replaces carbohydrates that are valuable and hence the convertible biomass content decreases. When pyrolysis is used for thermochemical conversion of biomass, the ash specification is less than 1%, which clearly shows the disadvantage of having large percentages of ash as it can take the place of valuable carbohydrates [13].

### 2.2.2 Elemental composition of Organic matter

The organic matter elemental composition is determined by using two important methods (which were developed for the coal industry) Ultimate and Proximate analysis. Biomass is heated to 700°C in an inert atmosphere, which helps in classification of biomass in to volatiles, fixed carbon, ash and free moisture. The volatiles and moisture are released leaving behind the fixed carbon residue, and this is the proximate analysis of Biomass [22]. It is important

to know the content of volatiles and fixed carbon as they are important parameters for ignition and thermochemical conversion potential of the fuel. Ultimate analysis is done to find the elemental composition of volatile matter and fixed carbon. The major elements determined are C, H, N, S and O; N and S content is very important as they are the cause of environmental pollution. Generally, biomass has low S content (up to 1%) except Sewage sludge, Black liquor and some marine algae where S content is more than 1%, and in some cases sewage sludge can also lead to 6% or higher sulphur content. One of the disadvantages of biomass is that it has a higher N content compared to coal, 10-12% for some algae, sewage sludge and some seed and seed cakes [12]. Figure 12, shows the Van Krevelen atomic H/C to O/C diagram for different biomass types; Carbon and Hydrogen content help in estimating the calorific value of fuel and O determines the losses and CO<sub>2</sub> emission during processing. Carbon to carbon bond possess more energy than C-O and C-H bonds in the case of thermochemical conversion [10]

### 2.3 Thermochemical Conversion Processes

Pre-processing is required for economical use of Biomass in thermochemical processes. These include Density increase by compaction, thermal treatment through Torrefaction, Size reduction by crushing and grinding (although uniform size cannot be obtained, it can assure to be in a specific size range)[23].

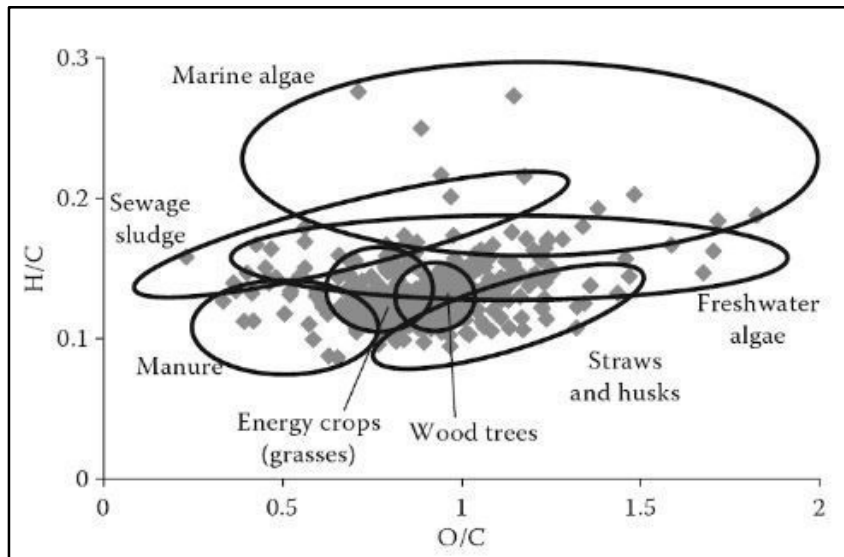


Figure 12: H/C vs O/C graph of Biomass Fuels [12]

Table 2: Thermochemical Conversion Processes

Thermochemical Processing Technology	Products
Combustion	Heat, Steam, Electricity
Gasification	Heat, Steam, Electricity, Methane, Hydrogen
Pyrolysis	Biogas, Bio-oil, Charcoal/Bio-char
Hydrothermal Processing	Biogas, Bio-oil, Charcoal

Thermochemical conversion of Biomass to produce fuel and CHP units have been widely researched giving rise to commercial scale plants in many developed parts of the world. Pyrolysis is one of the methods of thermal treatment in which the carbonaceous matter decomposes in the absence of oxygen. The products of this process consist of oil, gas and char of different compositions depending on the process (pyrolysis) conditions. Biomass appropriate for pyrolysis is lignocellulosic, chemically composed of cellulose and lignin, which forms the base hard structure of the plant matter and Hemicellulose binds the lignin and cellulose. Lignocellulosic biomass generally used for pyrolysis are- Crop residues, Forest residue, Organic MSW and sewage sludge [12].

### 2.3.1 Combustion

It is the most widely proven technology for production of heat and power in installations between a few kilowatts and more than 100 MW [24]. Combustion is burning biomass using an oxidant, leading to a series of complex exothermic reactions between the biomass fuel and oxidant. The commercial viability of this process is due to the high level technical maturity and considerable heat production, achieving economic feasibility [25]. The current research in combustion of biomass deals with optimization of furnace design, increase in control of combustion and overall efficiency. Early research on the commercial implementation of this process concluded that biomass combustion occurs via four basic stages: Drying, devolatilization, Combustion of volatile matter, Combustion of char [25].

Table 3: Bios-Bioenergy report, 2012 [24, 26]

Year/growth rate	Approximate Primary energy consumption, PJ(petajoule) per annum	Approximate Turnover of Biomass Combustion plants, Million Euros per annum		
		Turnover of Small scale plants	Turnover of Medium scale plants	Total Turnover
2008	3800	3500	2800	6300
2020	7700	9800	6700	16500
Expected growth rate from 2008 to 2020	100%	180%	140%	160%

### 2.3.2 Gasification

Biomass gasification is burning biomass fuel to combustible gases using a limited supply of oxygen on any other oxidant like CO<sub>2</sub> or steam. The gas thus obtained is composed by Hydrogen (12-20%), Carbon monoxide (17-22%), Methane (2-3%), Carbon dioxide (9-15%), water vapour, Nitrogen and other impurities depending on operating conditions and the type of gasifier [10]. Biomass gasification also involves complex chemical reactions taking place inside a gasifier, which has four separate zones: Drying zone, Pyrolysis zone, Partial Combustion zone and Reduction

zone [24]. The Figure 13 below shows that in total 24 biomass gasification plants have been constructed and supplied by ten major companies from four countries (Sweden, Finland, Germany and Austria).

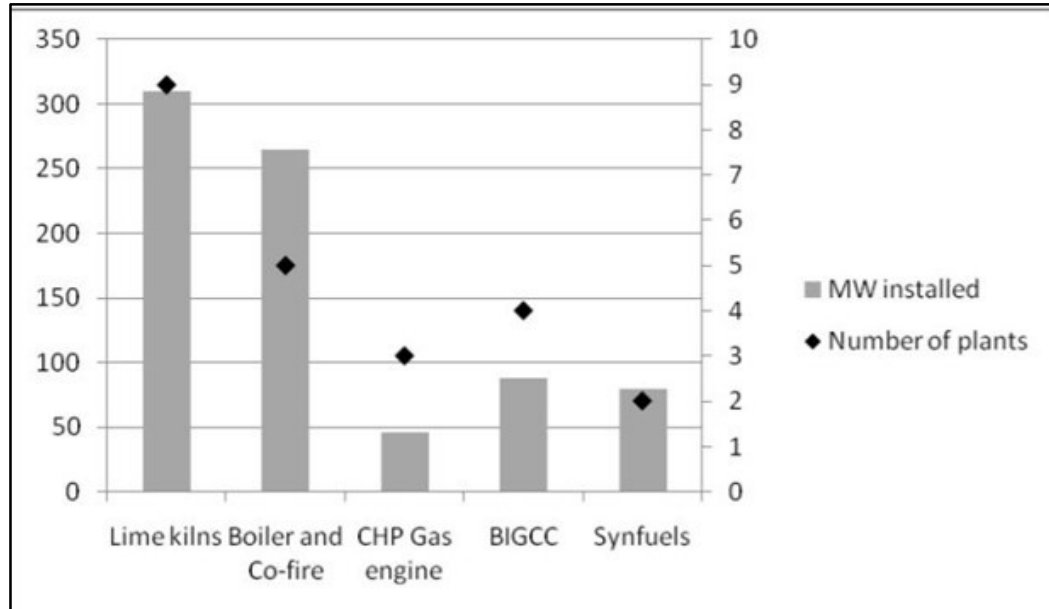


Figure 13: Accumulated experience in biomass gasification in terms of number of projects and MW [27]

### 2.3.3 Pyrolysis

Biomass pyrolysis has been explored throughout the world for hundreds of years and with time and technological progress better control over the process and products has been attained. Biomass Pyrolysis can operate in two different modes depending on the residence time and heating rate of the feed in the reactor: Fast Pyrolysis and Slow Pyrolysis. Slow pyrolysis is the conventional process, which yields a major portion of char and low level of liquids, whereas in fast pyrolysis high liquid yields can be obtained [20]. The heating rates in Slow pyrolysis can be several degrees per minute, temperature 500°C or less [28] and residence time is a few minutes [29]. Flash pyrolysis is another term for fast pyrolysis, which is characterized by reactor designs capable of providing short and intensive heat flux to small sized biomass particles. The solid and vapour residence times are very short and the temperature can range from 450-550°C [30]. The heating rate for fast pyrolysis is between 1000°C/s to 10,000°C/s [29] and for getting high liquid yields the temperature is between 500-520°C [30]. Fast pyrolysis yields a mixture of vapours and gases, vapours can be further condensed to separate the oils and aerosols. The share of liquids dominates with 50-80%, for fast pyrolysis of lignocellulosic biomass, the remainder being char and gases with approximately equal proportions [29–31]. Some pyrolytic processes are carried out in the intermediate regime of slow and fast pyrolysis and termed as *Intermediate Pyrolysis*. Some of the constraints that limit the use of both fast and slow pyrolysis are:



Feed preparation and pre-treatment according to size, drying and grinding, capital costs, product quality, scalability, low energy efficiency. At present, there are no reactor designs reported that can overcome these limitations [12].

Some of the factors playing a key role in thermal utilisation of Biomass are described below:

1. Particle size: In the case of slow pyrolysis there is no requirement for rapid heating and hence it can take particle size up to 50mm whereas in Fast pyrolysis, depending on the type of reactor used, the appropriate particle size changes. For ablative pyrolysis, its design can process biomass of sizes up to 20 mm as a result of constant shear on the particle, but for other reactors the feed particle size should be between 0.5-6mm in diameter [12].
2. Moisture Content in the Feed: It is one of the factors that causes an increase in the capital investment because drying is required to remove water, leading to decrease in the process efficiency as the latent heat of vaporisation of water cannot be recovered easily. It has been reported that typically the moisture content in harvested straw is 18% [32] and in wood chips 55% [33] hence requiring drying systems. The current pyrolysis reactor designs run with a feed moisture content of less than 10% [2].
3. Energy Efficiency: The energy requirement depends on feed quality, type and moisture content as the processes of drying and grinding are dependent on it. The cost and the process efficiency are affected most by drying, as it needs more than 10% of the energy value of raw Biomass when woody feedstocks are used [12]. Other types of restrictive factors are heat losses, which can be caused in case of external heating sources. If the mixing is also improper then heat transfer will be poor and will result in non-uniform temperature profile along the cross-section of reactor. The use of fossil fuels for the demand of feed preparation, heating rates etc decreases the overall output and therefore the current maximum efficiency obtained from Pyrolysis has several restrictions.
4. Scalability and Economics: The design of the reactor is an important limitation in scalability, especially for those that have a critical heating surface area to volume ratio. When these designs are used for an increased feed volume they are unable to provide the required area for optimum heat transfer. Some facilities have increased their capacity by using modular plants but this can be expensive if the design is cost intensive. Capital costs are high for a plant with complicated design and require a lot of auxiliary equipment for drying and grinding the feed. In most of the currently operational pyrolysis methods, the vapours have to be extracted, condensed and separated; this along with the gas handling systems increase the cost significantly [12].
5. Product Quality: In most of the lignocellulosic biomass pyrolysis, the quality of the oil is of concern because of the presence of oxygen, water and low pH. These factors make the oil difficult for upgrading to use as transport fuel and as feedstock for refineries. The oil can also contain some fine dust and charcoal particles that were not separated and hence it must be cleaned. The water content in the oil is an indicator of the moisture content of the feed [12].

# 3. Sewage Sludge: Characteristics and Disposal

## 3.1 Sewage sludge

Waste water treatment facilities generate Sewage Sludge, which differs in properties depending on the type of plant, physical and chemical properties of waste water used as feed. According to the European Council Directive 86/278/EEC, Sewage sludge can be defined as:

*a) Residual sludge from sewage plants that treat domestic or urban waste waters and from other sewage plants treating waste waters of a composition like domestic and urban waste waters;*

*b) Residual sludge from septic tanks and other similar installations for the treatment of sewage;*

*c) Residual sludge from sewage plants other than those mentioned in a) and b).*

Sewage contains a large amount of water but after it undergoes treatment the particulate matter and colloidal substances are concentrated to form sludge [34]. Thus, sludge contains a substantial fraction of water and studies have shown that it can be up to 90% of total wet weight [35]. Presence of water in high amount can hinder treatment processes like thermochemical conversion, hence the sludge obtained is dehydrated using suitable methods. The unit operations thus used to reduce water content of sludge are dependent on the type of moisture. Water in sludge can be of four types: Free moisture (which can be removed by mechanical processes like thickening and compression), Capillary Moisture (removed by thermal drying), Adhesive or surface moisture (also removed by thermal drying), Interstitial or chemically bonded water (which can only be separated by changing the chemical structure of sludge particles [35–37]). In general, 73-84% of moisture is present in dewatered sewage sludge. Before sending sludge for drying it is required that all the solids are aggregated and hence flocculants are used, like Lime, salts of trivalent Fe or Al [37]. Hence, one can find the reasons for inhomogeneity of Sewage sludge, tremendous differences in the concentrations of its components are observed leading to difficulties in determining or defining a standard composition for sewage sludge (mainly composed of organic compounds)[38].

Due to the physical and chemical treatment processes involved, sludge tends to concentrate heavy metals and poorly biodegradable trace organic compounds as well as potentially pathogenic organisms (viruses, bacteria, fungi etc.) present in waste water streams. It is also rich in nutrients, such as nitrogen and phosphorous, containing vital compounds and organic matter that is useful when soils are depleted or are subjected to erosion. This property of the sludge enables spreading of this kind of waste on agricultural land as a fertilizer [38]. Researchers have explored different methods of Sewage sludge disposal but there is no agreement as to which is the most appropriate method.

However, recent research has shown that energy recovery will dominate the treatment methods in the future [39]. The methods of disposal in EU are also not homogeneous depending on the level of implementation of directives and number of households connected to the sewers [40].

### 3.2 Treatment of Sewage

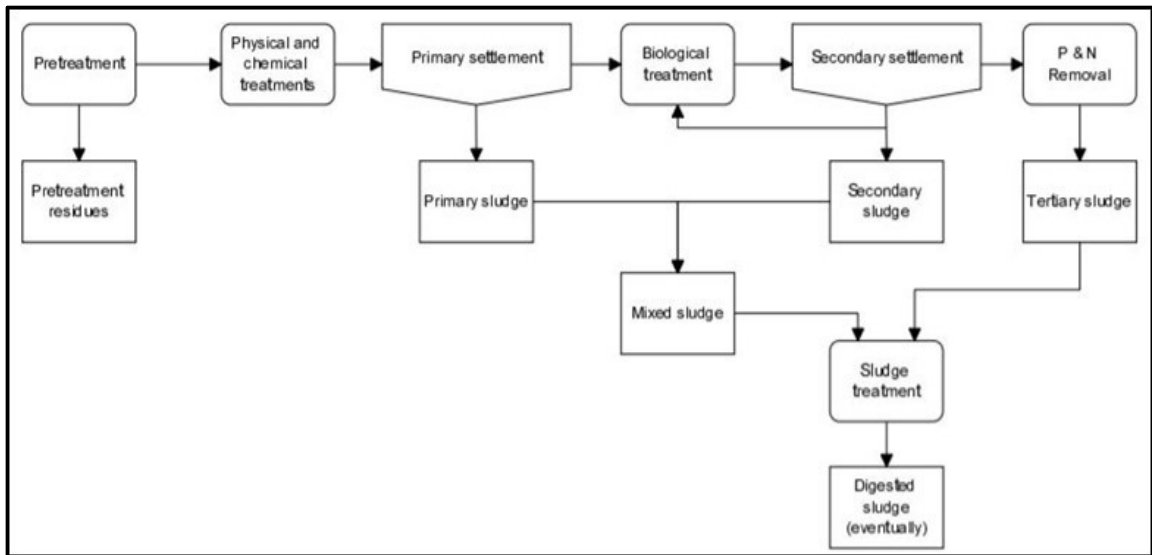


Figure 14: Detailed waste water treatment process [36]

As shown in Figure 14, waste water is treated using different methods targeted at different constituents (see list of sewage sludge composition in Table 5 and Table 6) to be removed or modified within the safe limits. Physical processes include Sedimentation, floatation; Chemical processes like Coagulation, Flocculation; Biological methods. The individual waste water treatment procedures are further distinguished as Primary, Secondary and Tertiary methods depending on the extent of removal of contaminants (following the EU regulations) [36](Figure 15).

Primary Sludge	Biological Sludge	Mixed Sludge	Tertiary Sludge
<ul style="list-style-type: none"> <li>•Heavy solids removed by sedimentation</li> <li>•lighter solids removed by floatation (settled material also removed here)</li> </ul>	<ul style="list-style-type: none"> <li>•Secondary treatment of water separated from solids, dissolved and suspended Biological matter removed</li> <li>•Micro-organisms used for treatment and are separated before tertiary treatment.</li> </ul>	<ul style="list-style-type: none"> <li>•The streams of sludge coming from Primary and Biological treatment are mixed to form mixed sludge</li> </ul>	<ul style="list-style-type: none"> <li>•Advanced waste water treatment; removal of unwanted nutrients N and P</li> <li>•High efficiency Chemical or bacterial processes used.</li> </ul>

Figure 15: Classification of Sewage Sludge treatment.

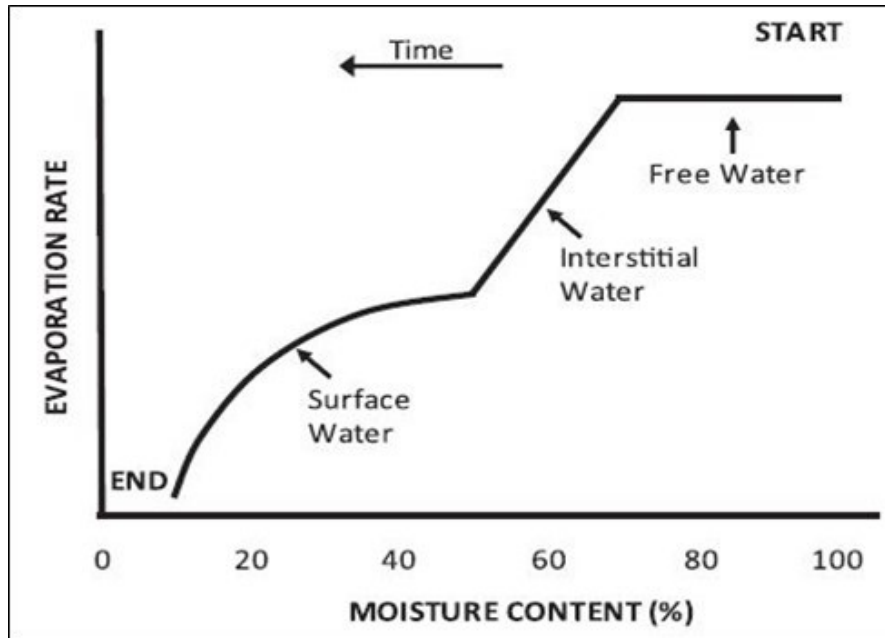


Figure 16: Typical Drying Curve for Sewage Sludge [35]

The drying curve, sketched in Figure 16, is an important characteristic of sewage sludge treatment. As mentioned in the previous section, water is associated with sewage sludge in four separate ways, so when it is subjected to drying, sewage sludge shows two falling rate intervals after the initial constant drying rate period. This is because of the difference in the way water is bound to sewage sludge, in the initial constant rate period the free moisture is evaporated. While interstitial water is removed in the first falling rate periods, the surface water is evaporated in the second period [41].

### 3.3 Composition of Sewage Sludge

Sewage sludge is a complex mixture of constituents; organic, inorganic and wide variety of micro-organisms. Hence, as discussed in the previous section, different treatment methods are used to ensure that regulations are met. Also, it should be noted that sewage sludge in dry form has a high calorific value, which is comparable to fossil coals [42]. Based on extensive research and review papers, Hassan and Wang et al. reported a comparison of calorific values, shown in Table 4 [41]. 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) [39–43]. The inorganic compounds present in the liquids are derived from soil and synthetic polymers having anthropogenic roots [44]. 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 [45]. Table 5 shows that dried sewage sludge can be a rich source of energy when compared to lignite coal and biomass (on average). However, 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 [41].

Table 4: Comparison of Calorific Values of Sewage Sludge and Biomass with coal [41]

Fuel	HHV, dry basis (MJ/Kg)	(wt%, dry basis)		(wt%, dry ash free basis)	
		Volatile Matter	Ash	N	S
Wood Pellet	18.30-19.60	82	17.4	1.5	0.9
Lignite	11.80-21.90	42.62	26.23	1.49	1.93
Bituminous coal	25.40-33.15	35.5	6.37	1.59	0.55
Wheat Straw	16	77.04	9.07	1.06	0.12
Sewage Sludge	11.10-22.10	48.41	43.99	7.15	1.41

There are diverse ways in which the sewage sludge is processed before thermochemical conversion and they are Digested and dry raw SS, Anaerobically digested and dry SS, chemical and activated sludge, etc. It has been reported that anaerobically digested and thermally dried SS is most widely used for pyrolysis experiments because this type of SS is produced in high capacity urban waste water treatment plants [39]. One of the basic purposes for drying the sewage sludge is that the resultant particles have good fluid-dynamic properties and hence can be used in applications like fluidization where particle size is a crucial parameter for operation [46].

Table 5: Basic characteristics and elemental composition of Sewage Sludge[43]

Constituent	A	B1	B2	C	D
Dry Matter (DM), g/l	12	9	7	10	30
Volatile Matter, % DM	65	67	77	72	50
Calorific Value, KWh/t DM	4200	4100	4800	4600	3000
pH, VM	6	7	7	6.5	7
C, % VM	51.5	52.5	53	51	49
H, % VM	7	6	6.7	7.4	7.7
O, % VM	35.5	33	33	33	35
S, % VM	1.5	1	1	1.5	2.1
N, % VM	4.5	7.5	6.3	7.1	6.2

Sewage sludge also contains a variety of heavy metals, which originate in industrial waste water, run off and corrosion of the sewer system. 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 [47]. As shown in Table 6, 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 [48].

Table 6: Organic and Inorganic components of Sewage Sludge [43]

Constituent	A	B1	B2	C	D
Protein, % DM	24	36	34	30	18
Fibers, % DM	16	17	10	13	10
Fat, % DM	18	8	10	14	10
P, % DM	2	2	2	2	2
Cl, % DM	0.8	0.8	0.8	0.8	0.8
Ca, % DM	10	10	10	10	10
K, % VM	0.3	0.3	0.3	0.3	0.3
Al, % VM	0.2	0.2	0.2	0.2	0.2
Fe, % DM	2	2	2	2	2
Mg, % DM	0.6	0.6	0.6	0.6	0.6

Heavy metals like Tin, Lead, Cobalt, Cadmium, Chromium, Nickel etc. are the major elements for rejection of Sewage sludge in agricultural purposes. If they are present in human bodies by making way from food chain, they can create detrimental effects to health. It is difficult to generalize any treatment method because the content of heavy metals varies significantly depending on the origin site. It was reported (Table 7) that Cd, Ni, Ti if present in low levels are safe as compared to Cr, Cu, Pb which are generally present in a toxic range [49]. (Table 7, on next page)

Table 7: Range of values for major heavy metals present in Sludge [40, 49]

Metal	Dry Sludge (mg/Kg)	
	Typical Range	Median Value
Tin	2.6-329	14
Lead	13-26,000	500
Cadmium	20-40	30
Cobalt	11.3-2490	30
Nickel	2-5300	80
Copper	84-17,000	800
Iron	1000-154,000	17,000
Molybdenum	0.1-214	4
Mercury	0.6-5.6	6

### 3.4 Disposal

Studies conducted in 2001, reported that there were 50,000 waste water treatment plants working in the European Union generating about 7.9 million tonnes of dry solids. By 2006, this number increased to 8.3 million tonnes dry solid per year, this clearly shows that implementation of the EU directive will lead to an increase in the amount of sludge[50]. Sewage sludge is a very challenging waste to be managed because of the inflated costs and environmental problems associated with it. There are several constraints in utilizing it for agriculture, although it is feasible from a policy perspective. The presence of heavy metals and pathogens restricts the use of sewage sludge as the quality is highly variable, which leads to high standard control and treatment measure. It is the need of the hour, for the policy makers to find a balance between preferred policy and sustainable development in environmental perspective. There are four methods to handle sewage sludge: Landfilling, Composting, and more than 60% of it is utilized in agriculture because of the presence of nutrients like P, N etc. [50, 51]. Countries like Austria, Netherlands, Germany, Slovenia use incineration as their major tool for disposal while, Malta, Italy, Romania use controlled landfill for the same, as shown in Figure 18. Biological methods of conversion of sewage sludge to useful product can be Anaerobic and aerobic digestion and composting; but constraints like odour, quality control, monitoring and heavy metal content make it difficult to be used. Although these methods help in phase separation of sewage sludge, they also need dewatering.

Table 8: Use and Disposal of Sludge based on method used [50].

Method	Examples	Constraints
Land Based	Agriculture, Forestry	Quality and variability, Impact, Vulnerability
Landfill	Mono and Co-Disposal	Leachate, Gas emissions, Potential resource loss
Thermal	Incineration, Gasification	High Costs, Ash disposal, Emissions, Public Perception

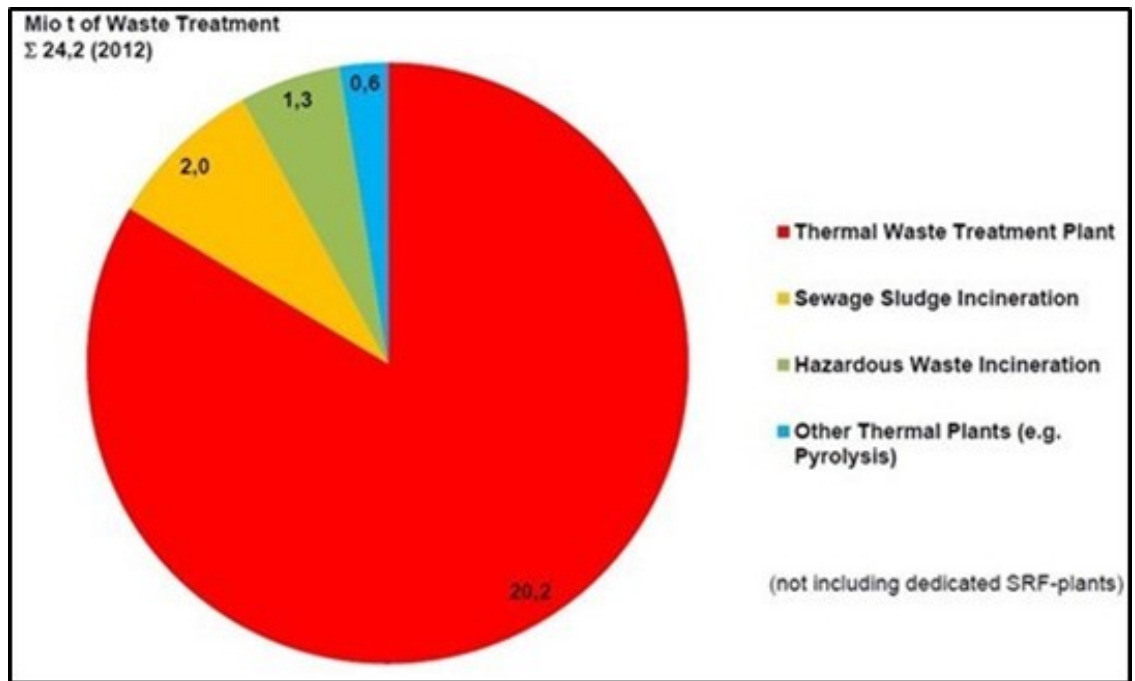


Figure 17: Thermal waste treatment in Germany, 2012 (Statistisches Bundesamt Wiesbaden 2015)

Incineration also has its share of criticism because of several reasons, it is said that incineration is just a way to minimize the sludge but it cannot completely dispose it. The ash produced by incineration is classified under hazardous waste and must be carefully handled and disposed in special landfills. The cost of the technology is also high and requires precise information of the calorific value, pre-treatment and should comply with emission standards. The presence of pollutants like PCB, PAH, PCDD, etc. require careful investigation, otherwise the sludge will fall under hazardous waste category [50].



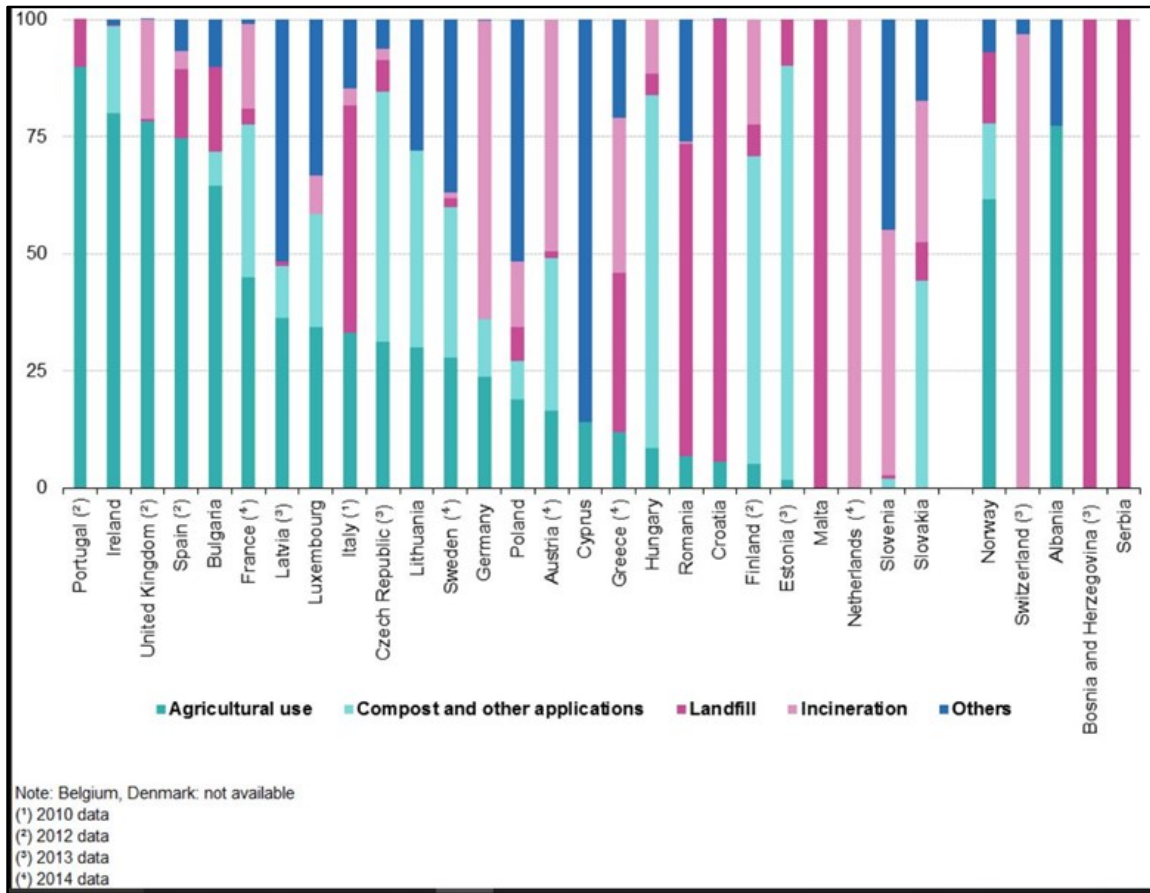


Figure 18: EEA Sewage sludge disposal by process used (% of total mass), EUROSTAT 2015

The cost increase of the incineration process is due to the high water content of the sewage sludge and the removal of water corresponds to an energy requirement. Table 9 below shows the methods of sewage sludge disposal used by some of the EU countries. Some countries prefer incineration over land use because of the harmful effects but at the same time they should take care of the ash disposal from incineration. As shown in the Figure 17, Germany used thermal treatment method to dispose most of its waste generated (total of 24.2 Million tonnes) in 2012. Also, sewage sludge has been increasing disposed in most sustainable method in German states, as reported by UmweltBundesamt in the year 2011 [38] (Figure 19).

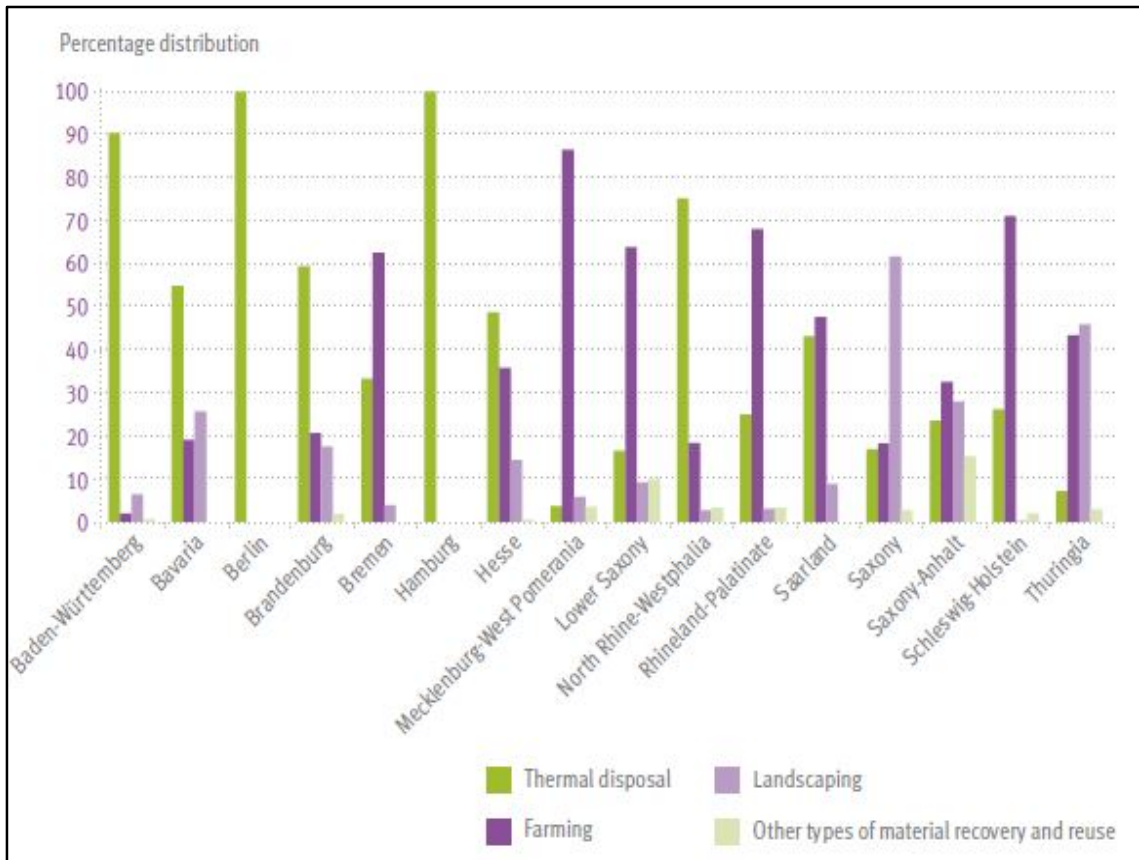


Figure 19: Percentage distribution of disposal methods in German regional states for 2011 (Umweltbundesamt)

Table 9: Disposal methods for sewage sludge in EU Member States as percentage [52]

Country	Year of data	Agriculture	Landfill	Incineration	Other
Germany	2003	30	3	38	29(i)
Austria	2005	18	1	47	34
Denmark	2002	55	2	43	
France	2002	62	16	20	3
Poland	2000	14	87		7
Netherlands	2006	0		60	40
Finland	2000	12		6	80(ii)
Belgium, Brussels Region	2002	32	2	66	

Where it should be noted that, (i) 3 out of 16 federal states intend to stop agricultural sludge use, (ii) While in 2004, there was still 9% of sludge recycled to agriculture, it decreased to 3% in 2005. In 2000, other outlets include 27% as landfill cover and 53% for landscaping.

### 3.5 EU Legislations for Sewage Sludge handling and disposal

1. Early in 1975, the member states were required to have environmentally friendly ways of disposal and waste prevention and management.
2. The Sewage sludge directive- 86/278/EEC laid rules for the use of sewage sludge in agricultural activities by defining the values of permissible limits of heavy metals like Cd, Cu, Hg, Ni, Pb, Zn in the sludge. It directed the member states to use sludge in agricultural activities by first treating it using biological, chemical or thermal treatments so that the extent of fermentation and health hazards are minimised [53].
3. In 1991 the EU also set up rules for handling hazardous waste and the Urban Waste water Directive- 91/271/EEC was amended to 98/15/EC, to be applicable from 2005. This amendment ensured stricter rules and quality standard for waste water with article 14 stating that member states should ensure that sewage sludge should no longer be disposed in water bodies and surface waters. It also directed that sludge should be re-used whenever appropriate [49, 54].
4. In 2005 the European Union also declared the implementation of the Directive, approved in 2000, for the reduction of dioxins by 90% emitted during incineration [40].
5. In 2001, the EU set up strict emission limits for the following components emitted during incineration of waste [55].

Table 10: Air emission limit values as per the 2001 Waste Incineration Directive.

Component	Incinerators, mg/m <sup>3</sup>	Cement Kilns mg/m <sup>3</sup>
Total Organic Carbon	10	10
Total Dust	10	30
HCl	10	10
CO	50	
HF	1	1
SO <sub>2</sub>	50	50
Dioxins and Furans	0.1ng/m <sup>3</sup>	0.1
Hg	0.05	0.05
Cd, Ti (total)	0.05	0.05
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V (total)	0.5	0.5
NO/NO <sub>2</sub>	Plants > 6t/h 200 Plants < 6t/h 400	Existing Plants 800 New plants 500

# 4. Chlorine emissions from Biomass Thermal Conversion

## 4.1 Release of Chlorine from different feedstock

Chlorine can be present in different forms depending on the origin and nature of fuel. In coal, the concentration of Cl varies from 50-2000 mg/Kg whereas the origin is from the ground water that percolates through layers below the surface during its formation [55]. The presence of Cl in coal was studied by different researchers but the problem is very complicated because of poor data agreement obtained by different methods. Chlorine is present in both inorganic and organic form in coal. The mineral chlorine present in coal is in the form of NaCl and oxychlorides [55]. It was also assumed by Crossley et al. [56] that water soluble chlorine exists in coal as NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> etc. While organic chlorine makes up the main part of the total Cl in coal. The organic Cl consists of two forms: 1. Water-insoluble Cl organic compounds, where Cl is covalently bonded with organic matter of coal, 2. Partly or fully water-soluble Cl which is sorbed on the pore surface of coal organic matter [55]. In the case of coal pyrolysis, Cl is released in the form of HCl mostly in the temperature range of 400-600°C. This released HCl can readily react with metal impurities (like Ca) to form inorganic and organic chlorine functionalities. Upon further increase of temperature these can release HCl again [57]. Coal combustion and the hot flue gas were studied extensively in the late 1980s to find suitable solutions for the undesirable and toxic components present in the flue gas. The presence of alkali vapours in the flue gas was a grave concern and hence its formation was studied for coal combustion at a temperature of 800°C. For this purpose Kaolinite was used as a sorbent to remove alkali chlorides from flue gas [58]. In this study the adsorption of NaCl and KCl vapours on kaolinite (under nitrogen and simulated flue gas atmospheres) was studied. The authors propose a model which suggests surface adsorption and diffusion through both the saturated product layer and pores of the active kaolinite. The conclusion was that Kaolinite is an effective sorbent for removing vapours of both NaCl and KCl from the syn gas produced by coal gasification and combustion.

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 [8, 59]. The extent of presence of chlorine determines its release behaviour as it was shown 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 [5]. Thermal utilization studies using different types of Biomass like straw, wood, agricultural residues etc. suggested that chlorine is released as several types of compounds because of the difference in the origin of feed. In the case of combustion or gasification of straw and sewage sludge separately, increasing the excess air coefficient led to an increase of chlorine emissions via KCl or NaCl formation. On the other hand, addition of Kaolin increases the release of HCl and significantly reduces the formation of KCl in straw combustion [60]. Pectin is a major component of the primary cell

wall of plants, which acts as a methyl donor for the formation of Chloromethane ( $\text{CH}_3\text{Cl}$ ) by abiotic conversion [61]. The emission of  $\text{CH}_3\text{Cl}$  during biomass combustion has been reported to be either a free radical process during combustion of cellulose or the coal-char catalysed reaction of methanol with HCl produced during pyrolysis [61]. Researchers also conducted study of chlorine release as a function of pectin content vs Cl/Pectin ratio and found that concentration of pectin in the biomass is not a rate limiting step and other organic compounds can also act as  $\text{CH}_3$  donors [60]. The inorganic chlorine released during biomass combustion is majorly in the form of HCl and particulate chlorine [5]. The predicted chlorinated compounds depend on the temperature of pyrolysis or combustion. Bjorkman et al. [8] reported that the distribution of chlorine between solid liquid and gaseous state is dependent on the process conditions, dominantly pressure and temperature. Also, they stated that composition of gaseous mixture after pyrolysis or gasification depends on the temperature, if it is below  $600^\circ\text{C}$  then HCl is the dominant product but above  $800^\circ\text{C}$  KCl and NaCl dominates (melting point of KCl is  $770^\circ\text{C}$  and that of NaCl is  $801^\circ\text{C}$  [5, 8]. Chlorine emission during pyrolysis of some selected Biomass feedstock: Sugarcane trash, switch grass, Lucerne, straw (rape) and synthetic waste were studied under pyrolysis conditions [8] and they released in to the gas phase, between 20-50% of all the chlorine content at  $400^\circ\text{C}$ , except straw (rape). The authors also made a very important point clear, that there was no significant difference in the emission of chlorine (mixture of inorganic and organic chlorides) from Biomass and synthetic waste. It has been found that for majority of biomass feedstock the torrefaction and pyrolysis (up to  $700^\circ\text{C}$ ) chlorine release is in the form of HCl [5]. Chlorine occurs in the form of alkali metal salts in the biomass and hence can readily convert in to vapour form during the pyrolysis and gasification processes. Most common is HCl which can further form compounds like  $\text{NH}_4\text{Cl}$  and NaCl causing fouling; hot corrosion of gas turbine blades which can occur with concentrations of chlorine and alkali even as low as 0.024 ppm [62]. The presence of potassium in biomass as shown in Figure 20 is high enough for the complete binding of chlorine as KCl [8].

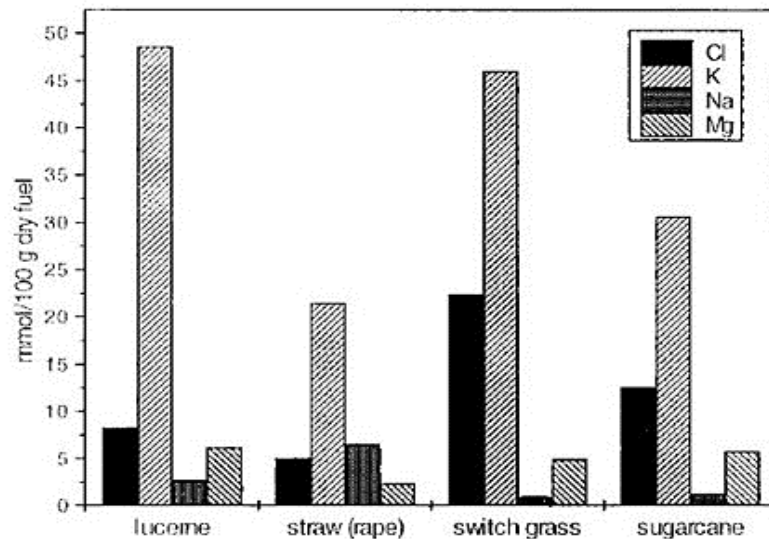
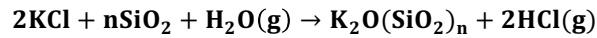
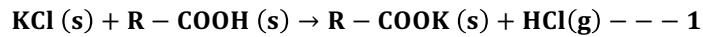


Figure 20: Alkali metal and Chloro atoms (mmol/100 g fuel) in Biomass [8]

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 [63]. 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 SiO<sub>2</sub>, at a temperature of 400°C this path of release of chlorine as HCl is significant [8].

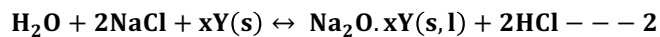


This also shows that even if the origin of chlorine in biomass is of inorganic nature it can release at a temperature less than the melting point of the salt [8, 63]. In the case of high chlorine biomass like corn Stover, more than 50 wt% of chlorine and Sulphur were released below 500°C. Since Sulphur 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 [64]) while in the case of chlorine it is mostly the ion exchange reaction leading to HCl formation [47]. 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 CH<sub>3</sub> donors [59]. Zintl et al. [65] 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 [47, 63]:

1. 60% Cl release between 200-400°C, (reaction 1) this step depends on the functional groups present in the organic matrix.
2. 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.



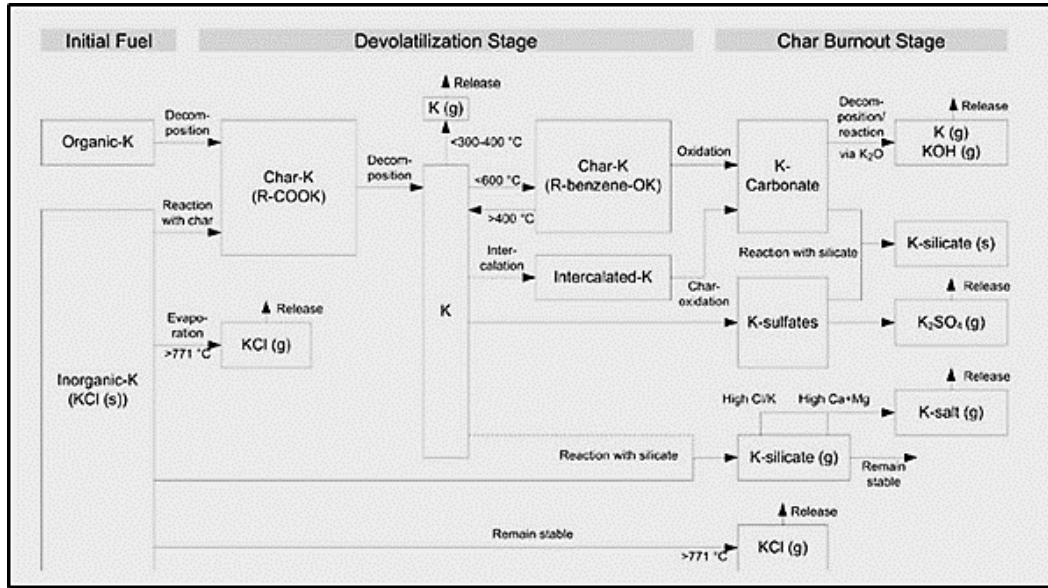


Figure 21: Possible reaction path for K release during devolatilization and combustion of annual crops [47]

As reported earlier, Potassium is one of the source of deposit formation in reactors. A closer look at the release mechanism as shown in the Figure 21, shows that it is a complex process which is related to the content of Si, S, Cl in the biomass. The organic fraction of K present in the biomass is released during the devolatilization stage and at elevated temperature KCl undergoes sublimation. The char burn out stage can lead to formation of K silicates or aluminosilicates. The alkali release in to the gas phase is slow and limited till 600°C because of the diffusional resistance offered by intact organic matrix [47]. It has also been showed that the increase of alkali metal content of biomass decreases the amounts of the combustion generated emissions of chlorine. Hence, the HCl emissions from the combustion of biomass are inversely proportional to their alkali to chlorine ratio [5].

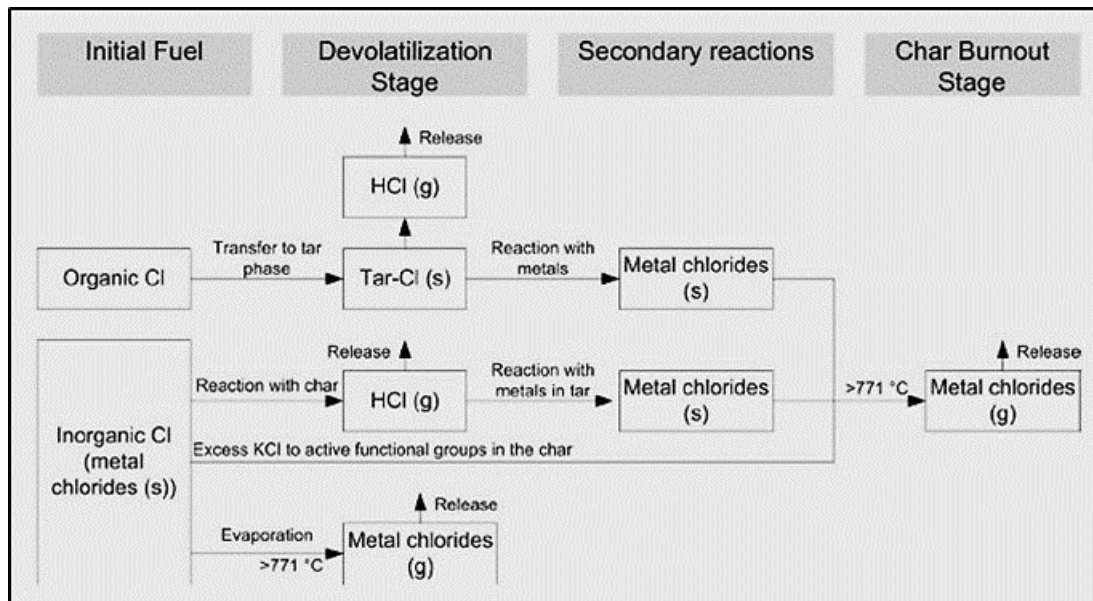
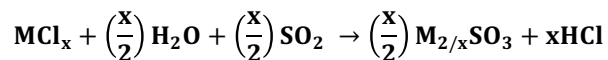


Figure 22: Possible reaction path for Cl release during devolatilization and combustion of annual crops [47]

## 4.2 Chlorine emissions from Sewage Sludge Pyrolysis

The motive of using thermo-chemical methods for disposal of sewage sludge is to extract the usable energy from it and reduce the harmful effects on the environment. In the case of for sewage sludge disposal, combustion has been researched and implemented extensively in Europe. Each thermal disposal technique has its own advantages and disadvantages but as mentioned in chapter 4, sewage sludge is highly variable in terms of composition, hence it is a crucial factor for choosing the technology to be used. 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 [66]. 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 [48]. It has also been found that co-incinerating MSW and sewage sludge reduces the cost of the process because sufficient energy can be produced for drying the sludge from MSW [66]. Approximately 30 wt% of the dry solids remain finally as ash in combustion of sewage sludge and this it does not contribute significantly to complete disposal [48]. 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 [67]. Pyrolysis has emerged as an efficient way for sewage sludge handling because it produces less emissions by the virtue of its process conditions, the heavy metal emission is nil in the gas phase as they are collected in the char which is also known as bio-char [68]. 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. [69] and confirmed by Kassmann et al. [70] when they carried out extensive thermodynamic studies considering all the possible reaction pathways. They reported that presence of SO<sub>3</sub> affects the formation of HCl from metal chlorides according to the following reaction [69]:



Chlorine and Sulphur emission reduction was studied since early 1990s as the acidic gases posed threat to environment and the reactors. Calcium based sorbents have been extensively studied for this purpose and wet scrubbing is reported to be a better choice when the biomass has high metal content [62].



## 5. Use of Sorbents for Chlorine Capture

Chlorine is a microelement present in the highest quantity when compared to other micro elements. It is absorbed as Cl<sup>-</sup> anion by the roots of the plants and then assimilated in the leaves and stem. Researchers have concluded that biomass having high percentage of Cl releases lower fraction of Cl than biomass with low percentage of Cl. Studies have also revealed that chlorine emissions from pyrolysis can be originating from both organic and inorganic contents of the biomass. Also, the release is strongly dependent on the inorganic constituents like alkali and alkaline earth metals in the biomass [71]. Another compound released in the form of CH<sub>3</sub>Cl is the cause of Cl emissions in the pyrolysis of woody and leafy biomass studied by Hamilton and co-workers [61]. They showed that the Pectin present in the leaves acts as a CH<sub>3</sub> donor and plays a key role in Cl emissions, this kind of release starts at a temperature of 150°C and increases up to 300°C. Also, pectin is not the only component for Cl release, they concluded that CH<sub>3</sub>Cl emissions during combustion of woody biomass can also be originated from the reaction of Cl<sup>-</sup> with lignin [61]. Chlorine emissions from pyrolysis of biomass in the form of hydrogen chloride or metal chlorides can be captured by using sorbents. These chemical substances undergo chemical reactions with chlorine or by physical adsorption removes chlorine from the flue gas. Based on the desired properties of sorbents like fast rate of adsorption, high loading capacity, irreversible adsorption, cost etc. studies have been conducted to check the capture efficiency and process calculations.

### 5.1 Removal of HCl and metal chlorides

In the early 1980s researchers observed the presence of alkali metal compounds in the vapour phase during gasification or combustion [72]. These compounds cause further process complications and damage for example, corrosion in the post process utilization. If content of chlorine in Biomass is high, then it can form depositions of alkali chlorides on the walls of the boiler which slows down the heat transfer. Chlorine in the form of HCl, in flue gas which is utilized for combined cycle process, can cause corrosion of the turbine parts [58]. Since a sizeable portion of chlorine in the flue gas is associated with alkali metals, reports were published illustrating bench scale and lab scale experiments under different reactor and process set up.

Aluminosilicates became popular as catalysts because of their high surface area and porosity, hence Kaolinite was investigated as a sorbent for removal of alkali chlorides from hot flue gases. The experiment used nitrogen and simulated flue gas environment to capture NaCl at 800°C. Mathematical models suggested that the initial rate of adsorption is directly proportional to the alkali concentration in the bulk gas, also it is nearly the same for both environments considered. The adsorption is irreversible and depends on the gas composition. As in a SFG environment only sodium was retained, unlike with N<sub>2</sub> atmosphere, it was proposed that the adsorbed NaCl would have reacted with Kaolinite in the presence of water to form nephelite and HCl vapours [58]. Sorbents that contain a high percentage of Silica could adsorb irreversibly just the alkali and not chlorine, releasing it as HCl. Activated bauxite and emathlite in the diameter range of 2.4-3.4-mm were used for alkali removal, they also demonstrated

that the product gas chlorine concentration was unaffected or was reduced to half in the best case scenario, while K and Na removal efficiency were 98% and 92% respectively [73].

## 5.2 Alkali and Alkaline earth metals as sorbents

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 [74]. Similarly, alkaline earth metals (BaO, CaO, MgO) also showed to be thermodynamically feasible for removal of halides [75].

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 [76]. The sorbent selection also depends on cost, hence sodium based compounds like sodium bicarbonate, sodium carbonate,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$  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 [77]. Ketov et al. (1968) [78] showed that there is an optimum temperature range, which leads to maximum  $\text{CaCO}_3$  to  $\text{CaCl}_2$  conversion (depending on the kind of lime taken), that was found to be between 540-550°C. On pilot scale the use of slaked lime particles as a sorbent for flue gas demonstrated. The results were monitored at a temperature of 260-400°C, HCl retention was in the range of 40-100% which increased based on the temperature increase, water content in the gas and with decreasing particle diameter from 11-39 $\mu\text{m}$ . The lime conversion rate was rapid in the beginning as most of the HCl in the gas was absorbed, after some time it decreased and then gradually became constant (depending on other reaction parameters) as shown by Figure 23 [79]. Duo et al. (1994) [80] studied the reaction between  $\text{CaCO}_3$  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  $\text{CaCO}_3$  at 400°C, while they also tested  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  [81]. The concentration of  $\text{CO}_2$  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.  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  was found to be better than  $\text{Na}_2\text{CO}_3$  because of high porosity of its dehydrated compound [81].

A study of binding of HCl with the sorbent particles was done by Claus and co-workers; the sorbents used were slaked Lime and Limestone. The binding capacity was dependent on chemical equilibrium of solid and gas above 500°C, it was independent of the particle size and slightly dependent on specific surface area. In the temperature range of 500-600°C and below 150°C the binding capacity was highest, almost full conversion of lime to  $\text{CaCl}_2$  was observed. The kinetics was dependent on the diffusion inside the solid particles and followed unreacted grain-core model [82].

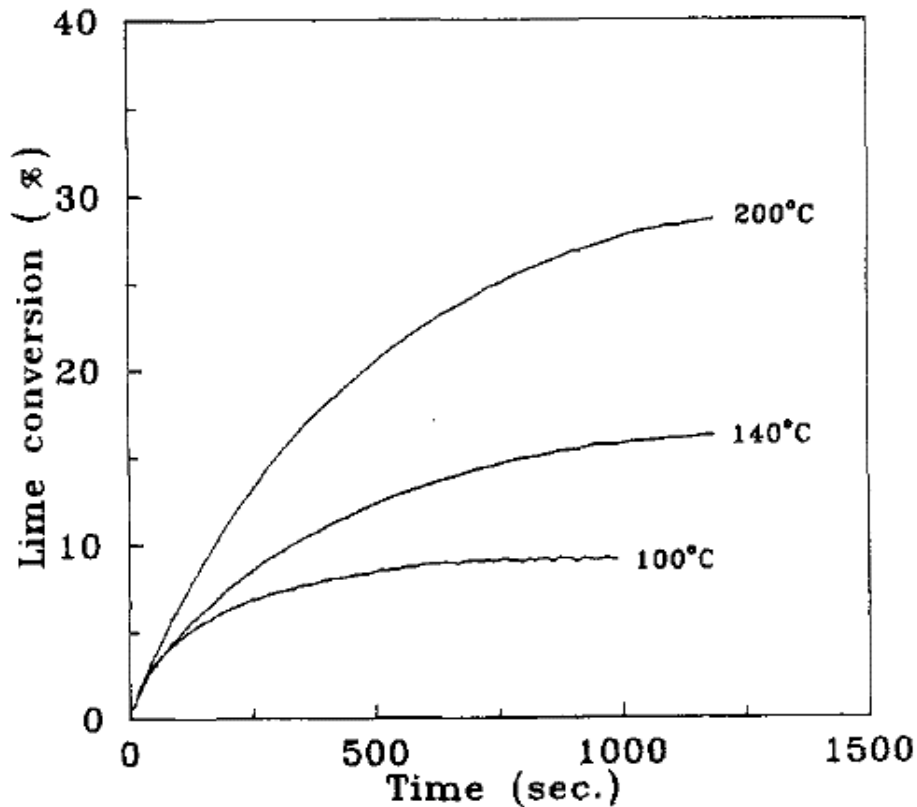


Figure 23: Lime conversion for different temperature with respect to time [79]

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  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgO}$  etc. could reduce the HCl vapour concentration from  $10^{-3}$  to  $10^{-6}$  at a temperature of  $500^\circ\text{C}$  and space velocity of  $3000\text{h}^{-1}$ . The reaction kinetics followed first order with respect to initial HCl concentration [76]. Another study of HCl removal in fixed bed using  $\text{NaHCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}_2\text{O}_3$  was conducted at a temperature of  $550^\circ\text{C}$ , showing significant reduction of less than 2 wt% in downstream as compared to fully saturated upstream end [83]. Sorbent  $\text{ECl}_1$  as depicted in Table 11, showed higher adsorption capacity, probably because of the composition and structure, as the reactive component was 87 wt% while in  $\text{ECl}_2$  it is 11 wt%. The combination of Dolomite and Silica as a catalyst for decomposition of pyrolysis tar showed good efficiency even at high temperature [84]. Karlsson et al. (1981) [85] studied  $\text{Ca}(\text{OH})_2$  as a sorbent in fixed bed reactor from  $150$  -  $400^\circ\text{C}$ , confirming that the reaction follows first order kinetics, as previously mentioned by others, also the available maximum  $\text{Ca}(\text{OH})_2$  for the sorption was around 55%. A magazine report [86] published in 2014, showed the advantages of retrofitting acid gas removal systems of two waste to energy plants in Germany. The old systems used  $\text{Ca}(\text{OH})_2$  as sorbent which was replaced with  $\text{NaHCO}_3$ . The results showed better efficiency of removal of HCl with comparable economic feasibility.

Table 11: Composition of Sorbents used [83]

	Sorbent	
	EC <sub>1</sub>	EC <sub>2</sub>
Main Components	NaHCO <sub>3</sub> , CaCO <sub>3</sub> , Ca(OH) <sub>2</sub> , Mg(OH) <sub>2</sub> : 87%	Ca(OH) <sub>2</sub> , 11%, Al <sub>2</sub> O <sub>3</sub> , 89%
Preparation	Dry mixing	Wet impregnation
Bulk Density (g/cm <sup>3</sup> )	0.66	0.73
Surface Area (m <sup>2</sup> /g)	3.24	127.89
Average Pore diameter (Å)	247.80	47.34

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. The sorbents were powdered calcium formate (CF), calcium magnesium acetate (CMA), calcium propionate (CP), calcium oxide (CX), and calcium carbonate (CC). The sorbents fluidized in a stream of air were introduced in the furnace concurrently, showing relative utilization of 80%. Calcium carbonate and calcium oxide were the inexpensive and low porosity sorbents, they performed well with CaCO<sub>3</sub> 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 CO<sub>2</sub>. The remaining CaCO<sub>3</sub> reacts with HCl as follows [77]:



The thermodynamic studies were done in the 2000s to compare sorbents and their efficiency by varying process parameters. Nicola et al. [87] conducted incineration experiment, to remove pollutants in flue gas in an in-duct dry removal set up to compare Ca and Na based sorbents by establishing theoretical limits achieved by them, thermodynamically. They checked the limiting values of equilibrium vapour pressures of the pollutants (with both NaHCO<sub>3</sub> and Ca(OH)<sub>2</sub>) by varying the temperature from 100-600°C and kept the molar ratio between amount of sorbent injected and the amount of pollutants in the gas, constant. The second case kept the temperature constant and varied the molar ratio from 0-1.2. As shown in Figure 24, NaHCO<sub>3</sub> is superior to Ca(OH)<sub>2</sub> 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. NaHCO<sub>3</sub> was found to be effective even at 600°C reducing HCl to NaCl. When the molar ratio of sodium bicarbonate was increased the decreasing value of HCl in the gas showed that it is better than Lime [87].

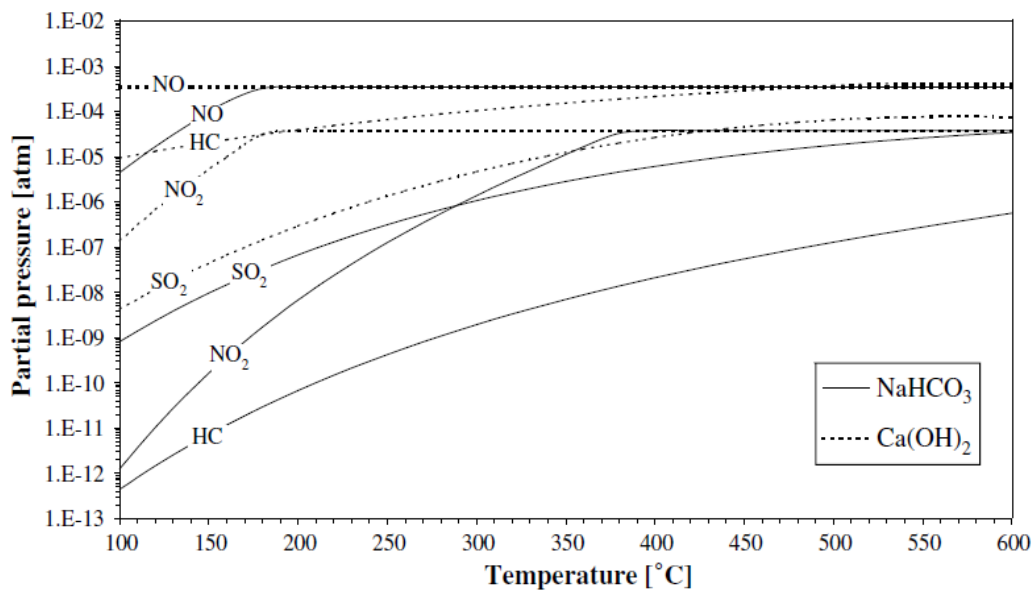


Figure 24: Performance of sorbents with the pollutant partial pressures [87]

Another study was conducted by the same authors in a fixed bed reactor system with the reaction conditions: 550°C, space velocity 3000h<sup>-1</sup> and inlet HCl concentration of 1000 mg/m<sup>3</sup>. As shown in Table 13, the breakthrough point for sorbent E1 was the best for the temperature of 550°C and it was able to reduce the outlet concentration to 1mg/m<sup>3</sup>, which is near to the desirable limit of less than 1 mg/m<sup>3</sup> [88].

Table 12: Sorbent properties [88]

	Sorbent	Composition wt%	Surface Area (m <sup>2</sup> /g)	Pore volume (mL/g)	Pore diameter(Å)
HCl removal	E1	MgO, 30%; MMT, 70%	136.20	0.20	89.80
	E2	Commercial catalyst	127.90	0.15	47.30
	E3	MgO, 50%; MMT, 50%	12.10	0.05	300.8
	E4	MgO, 70%; MMT, 30%	16.40	0.07	289.2

Table 13: Breakthrough point for Chlorine [88]

Sorbent	E1	E2	E3	E4
Breakthrough time (h)	7.20	4.00	2.10	2.00
Breakthrough chlorine content (%)	8.60	3.60	3.20	3.00
Saturation chlorine content (%)	48.3	32.15	19.70	19.20

# 6. Experimental Set Up

This chapter provides the detailed description of the reactor configuration used for the experiments, the process conditions, feed characteristics and Integral Mass Balance equation.

The pyrolysis experiments were conducted using two different reactor configurations: Fixed bed batch Reactor and Screw Pyrolysis Reactor (STYX). The feed used was Sewage Sludge, obtained from a waste water treatment facility in Germany, having particle size in the range of 4-8 mm. Wheat straw was also used to carry out same experiments as alternative feed for comparison purposes. 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.

## 6.1 Fixed Bed Reactor

The fixed bed reactor set up used for pyrolysis experiments consisted of a cylindrical reactor made up of stainless steel coiled with tubes all round its outer surface. These coils carried nitrogen gas which was injected from the top. The mantle, as shown in the Figure 25 below, was the source of heating, temperature ramp was programmed up to 500°C and held constant until the experiment was completed.



Figure 25: Laboratory scale fixed bed reactor

Three positions were chosen for measuring the temperature inside the reactor (one in the mid of the reactor and two on the sides) using thermocouples. The pyrolysis liquid containing some volatile matter was condensed and collected beneath the reactor, with the help of a condenser (maintained at 7-10°C) having parallel tubes inside and a mixture of ethylene glycol and water as the cooling fluid. The next stage involved capture of aerosols, using Electrostatic Precipitator (ESP), from the volatile gaseous mixture coming from the condensation stage. An absorber column was used with NaOH solution to remove HCl vapours from the flue gas before it was sent to a gas analyser and subsequently out to the atmosphere. The change in pH of this solution indicated the presence of HCl in the gas stream entering the column.

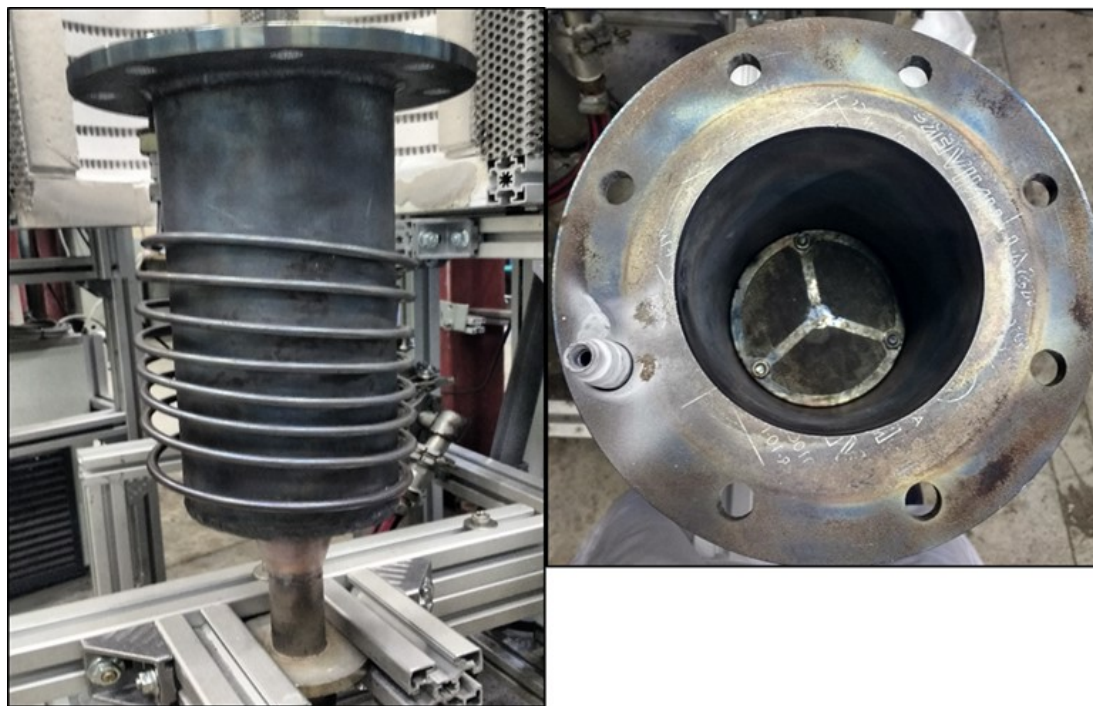


Figure 26: Reactor outside and inside view

### 6.1.1 Experimental Procedure

Pyrolysis of the Sewage sludge (Klärschlamm) or of Wheat Straw (Weizen stroh) was carried out with and without the use of a sorbent. The sorbents used in this study were Sodium Hydrogen Carbonate ( $\text{NaHCO}_3$ ) and Calcium oxide (CaO), varied with respect to the molar ratio of feed/sorbent. The temperature of the reactor was maintained at 500°C and the temperature of the oven was 670°C. The feedstock in each experiment was weighed to 100 g precision, mixed with suitable amount of sorbent (based on molar calculations) and then introduced to the reactor. A washing solution of NaOH 0.1 M was used in the absorber column, measuring its initial pH value. The empty condensate glass bottle was connected to the end of the condenser. The cooling system was switched on for the condenser with the

temperature set as 9°C. The nitrogen connection tube was screwed tightly and the flow rate controlled as desired, generally 5 liters per minute (L/min). The voltage value for the electrostatic precipitator was not more than 7 kV initially, but once the gas started filling it could be increased to a maximum of 14 kV. After the reactor reached 500°C, it was allowed to run for 15-20 min and then the oven shut off. The pH change of the absorber column solution was monitored. After the experimental setup cooled overnight, the filled condensate bottle and the char were weighed for the necessary mass balance.

## 6.2 Screw Pyrolysis Reactor (STYX)

The bench scale Screw Pyrolysis Reactor with integrated hot gas filtration (STYX<sup>2</sup>) was developed by the Institute of Technical Chemistry (ITC), Karlsruhe Institute of Technology (Karlsruher Institut für Technologie), in Germany. It was used in the study of intermediate pyrolysis of low grade biogenic residues in an isothermal reaction environment. It consisted of a feeding system, through screw reactor, char collection drum, condensation units and gas analysis systems. The significance of using a screw reactor is that it enables the feed to have a well-defined residence time by virtue of its design. The feeding zone was purged with nitrogen so that oxygen was removed from the bulk of biomass feed. The reactor contained two main units, first the screw conveyor and second the sequential extraction and filtration unit. Thermocouples were located throughout the length of the reactor at fixed positions to measure the temperature and control it when required. Since the reactor assembly has a filtration unit, the raw vapours generated were extracted from the reactor and the solid particles collected separately as char. After filtration, the clean gas mixture was extracted through a pipe, which was 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 pyrolysis vapours. The condensation assembly consisted of two parallel condensers maintained at 15°C and an ESP (Electrostatic Precipitator), which provided capture of aerosols and thus removed the last residues of tar. The flow rate, temperature and absolute pressure of the permanent gas was determined by using a flow meter, a thermocouple and a manometer, respectively. A gas analysis device by Swedish company, ABB, was used to determine the composition of the permanent gas in volume% (methane, carbon-dioxide, carbon-monoxide, oxygen). For this purpose, a small part of the gas was withdrawn as sample and pumped into the assembly. The stream of permanent gas was sent to a torch via a suction train.

The reactor was constructed of steel alloy EN 1.4571 and could handle up to 15 kg/h of sewage sludge (thermal input 45kW<sub>TH</sub>). Isothermal conditions inside the reactor were maintained and controlled by thermocouples located on the bed of the screw and in the filter units. The reactor temperature was held constant with the temperature control system that controlled the heating elements for a total heating capacity of 40 kW. The reactor was divided in 7 segments. The maximum number of filtration elements could be 14, in this study there were 6 filter cartridges

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<sup>2</sup> 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.



present in the 2,4 and 6 segments of the reactor. The description of individual vital components of the experimental apparatus is described in the next sections.

The specifications of the reactor assembly are tabulated below in Table 14 :

Table 14: Reactor Specifications

Heated Length	2 m
Diameter	0.15 m
Residence Time (in this study)	7.5 min
Number of filter elements	14
Number of segments in the reactor	7
Temperature	500°C (maximum 600°C)
Flow rate (in this study)	2 kg/h (maximum is 10 kg/h)
Length of filter elements	200 mm
Diameter of filter elements	60 mm
Maximum Electric Power	40 kW
Relative Pressure drop	Ca. -2 .... -20 mbar rel.

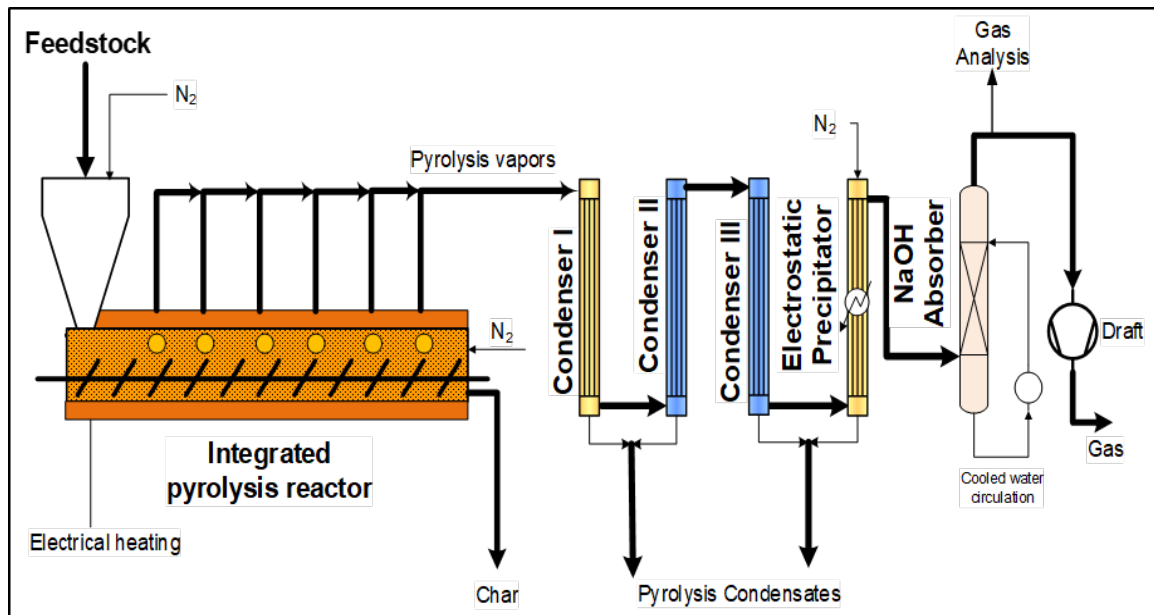


Figure 27:Flow diagram of the Bench scale Pyrolysis Reactor (STYX)

### **6.2.1 Feeding System**

The plant was designed for processing different type and grade of biomass. In this study, SS and WS were used, which have different composition, particle size and moisture content. Hence, the feeding unit consisted of a lock-hopper and a dosing screw conveyor. The feeding system was provided with four independent inlets, which enables injecting multiple feedstocks and additives (in this case, sorbent).

The lock- hopper is the crucial element, consisting of two mixers. The first one had a vertical axis and was attached to the plug such that it was directly introduced in the lock-hopper. The second one was placed at the same level of the dosing screw was located in the chamber behind the lock-hopper. These mixers were driven by electric motors for a total power of 100W. The screw conveyor functioned as dosing device and did not contain a shaft. The dosing protocol (correlation between rotation speed and flow rate) was previously calculated and was provided by setting the rotational speed of the motor driving the screw conveyor

### **6.2.2 Sequential Extraction and Filtration unit**

The presence of filters inside the reactor was one of the striking features of the STYX used. The inclusion of such a filtration has advantages like particle free condensates, which makes them stable and less prone to ageing. Also, it avoids the clogging and fouling of the pipelines, which is a major constraint in thermal processing of biomass.

The filtration unit was located above the screw conveyor and directly inside the reactor. It was divided in seven segments and each segment accommodated two filter candles. The hot gas filtration unit was equipped with an automatic online re-cleaning system to maintain suitable pressure drop among the filters. The filter candles were constructed with a coarse-grained support made of silicon carbide associated with fine alumino-silicate filter membrane; candles had two openings: one for the hot vapours that are extracted from the reactor and the other side worked as the inlet for re-cleaning gas (heated nitrogen was used for re-cleaning). Referring to Figure 28, there were two gas collection sections: one for the clean gas and the other for the nitrogen used to clean the filters. The filter candles were placed perpendicular to the screw axis. The raw pyrolysis gas was sucked from the reaction chamber to the filters while the cleaned vapours were sent to the condensation unit.

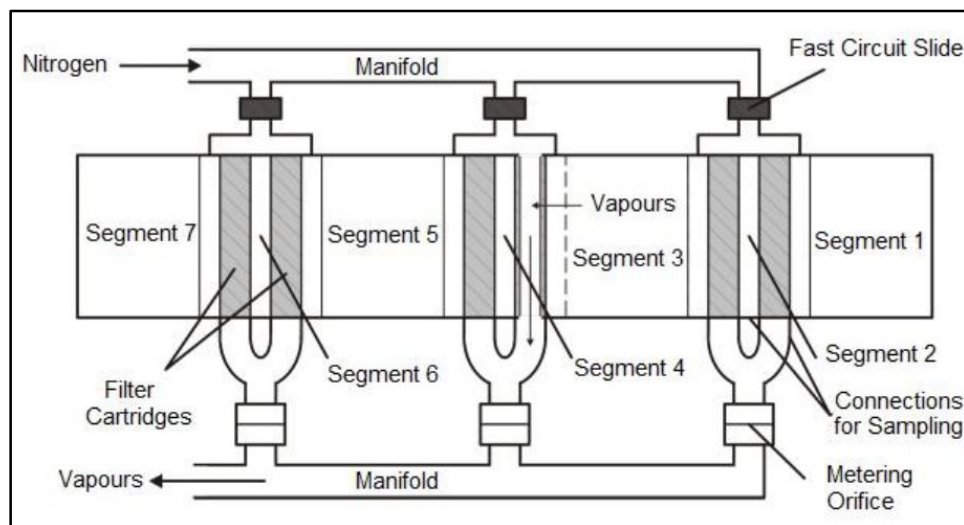


Figure 28: Schematic diagram of Hot gas Filtration Assembly [9]

### 6.2.3 Condensation Assembly

The condensation unit consisted of two condensers placed in series, leading to an Electrostatic precipitator (ESP) at the end. As the mixture coming to the condenser has recoverable components, the condensation occurred in two stages. In the first stage, heavy oil and the aqueous condensate were recovered, they were collected in a glass bottle located outside the reactor as shown in Figure 29, while in the second stage the vapours were cooled down to 15°C and moved to the Electrostatic precipitator (ESP). The function of the electrostatic precipitator was to remove the aerosols from the non-condensable gases (also known as permanent gases). The condensates get naturally separated in organic and aqueous phases. In some cases, when it is difficult to separate naturally the oil and aqueous phases, a decanter could be used.

### 6.2.4 Online Gas Analysis

After the ESP unit the gas entered the analysis unit where the combustion calorimeter CDW200 was used to measure density, Wobbe index and the LHV; BINOS 100-M measured the volumetric concentrations of CO, CO<sub>2</sub>; OXYNOS 100 was used to measure the concentration of molecular oxygen (O<sub>2</sub>). The concentration of hydrocarbons, particularly methane, was measured by the gas analysis facility using a flame ionization detector (FID), Agilent/HP 6890 GC, for the precision.

### 6.2.5 Experimental Procedure

The sewage sludge was fed through the feeding unit and it transported with the screws inside the reactor. The mass flow rate of the feed was set to 2kg/h in all the experiments. The mass flow rate of the feedstock was determined before conducting the 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<sub>3</sub>) was used as a sorbent to conduct experiments using sewage sludge and wheat straw and was fed with the

biomass after manual mixing. The nitrogen flow rate was set to 6 litres per minute and the screw rotation speed set according to the dosing curve. The feed moved along the axis with the screw (which provides well defined residence time of the solids) by adjusting its rotation, leading to a residence time of 7.5 minutes. The amount of char collected was weighed while the condensates were 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.



Figure 29: Bench scale experimental set up (actual pictures from KIT)

### 6.3 Feedstock Properties

a) Sewage sludge was the feed of primary focus while wheat straw was used for comparison purposes as it contains a significant amount of chlorine. The ultimate and proximate analysis of both feeds were done and are shown in Table 15 and Table 16 below. It can be clearly seen that the sewage sludge has a high content of Nitrogen, Sulphur and Phosphorous, while the ash was rich in Silicon, Calcium and Phosphorous present as  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{P}_2\text{O}_5$  respectively. Chlorine content was also comparatively high, and it, arises from the treatment and disinfection process of the waste water. The low heating value was attributed to a high ash content and low fixed carbon of the sewage sludge [89].

Table 15: Ultimate and Proximate analysis, Heating Value of dried sewage sludge

Ultimate Analysis wt % on dry basis				Halogens mg/kg on dry basis	
C	H	N	S	Cl	F
30.10	4.27	4.95	1.32	1260	299
Proximate Analysis wt % as received basis				Heating Value KJ/Kg as received basis	
Moisture	Ash (550°C)	Volatile Matter	Fixed Carbon	HHV	LHV
10.30	39.40	47.60	2.80	11708	10630

Table 16: Ash Analysis of sewage sludge

Ash Composition, wt% of ash on dry basis							
SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
29.7	13.30	0.40	1.30	10.40	2.10	5.40	15.50

The German law (AbfKlärV 2010) specifies the permissible limit of various metals in sewage sludge. It is clear from the Table 18 below that the amount of Chromium, Copper, Manganese and Nickel was higher than the allowed standards. The rest of the metals were below the desired requirements. Extensive and elaborate research has been done on phosphorous recovery from sewage sludge and according to German Sewage Sludge statistics a large amount of inorganic phosphorous can be recovered [37].

Table 17: Estimated Phosphorous Recycling Potential in Germany

Nature of sewage Sludge	Estimated Phosphorous Recovery, tonnes/year
Industrial Sewage	15,000
Municipal Sewage Sludge	50,000
Manure	444,000
Estimated Phosphorous Demand in Germany	170

Table 18: Metal concentration in this study and comparison with German permissible amount [37]

Metal name	Sewage Sludge used for this study (mg/Kg)	Allowed in Soil (mg/Kg)	Allowed in Sewage sludge (mg/Kg)
Lead	61	40-100	150
Antimony	7	-	-
Copper	390	20-60	800
Mercury	0.60	0.1-1	2
Nickel	110	15-70	100
Chromium	230	30-100	120
Thallium	0.2	-	1.5
Manganese	740	-	-
Cobalt	8	-	-
Arsenic	6.3	-	18
Cadmium	1.2	0.4-1.5	3
Tin	20	-	-

b) Wheat Straw

Wheat straw was used for pyrolysis experiments with Screw reactor and comparison with the results from Sewage sludge pyrolysis. It is evident from Table 20 that the ash from wheat straw had a significant amount of Potassium, which has been reported to promote the formation of KCl and cause deposit formation inside reactors [63, 64]. The ultimate and proximate analysis of the wheat straw used as feed for this study (Table 19) shows that chlorine is present in substantial amounts compared to Sulphur, on weight basis.

Table 19: Ultimate and Proximate analysis, Heating Value of Wheat Straw

Ultimate Analysis wt % on dry basis				Halogens mg/Kg on dry basis	
C	H	N	S	Cl	F
43.60	5.80	0.55	0.04	1420	<10
Proximate Analysis wt % as received basis				Heating Value KJ/Kg as received basis	
Moisture	Ash (550°C)	Volatile Matter	Fixed Carbon	HHV	LHV
8.60	11.60	65.50	14.40	15260	13880

Table 20: Ash Analysis of Wheat Straw

Ash Composition, wt% of ash on dry basis							
SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
72.70	3.70	<0.10	11.30	0.50	1.00	1.30	1.10

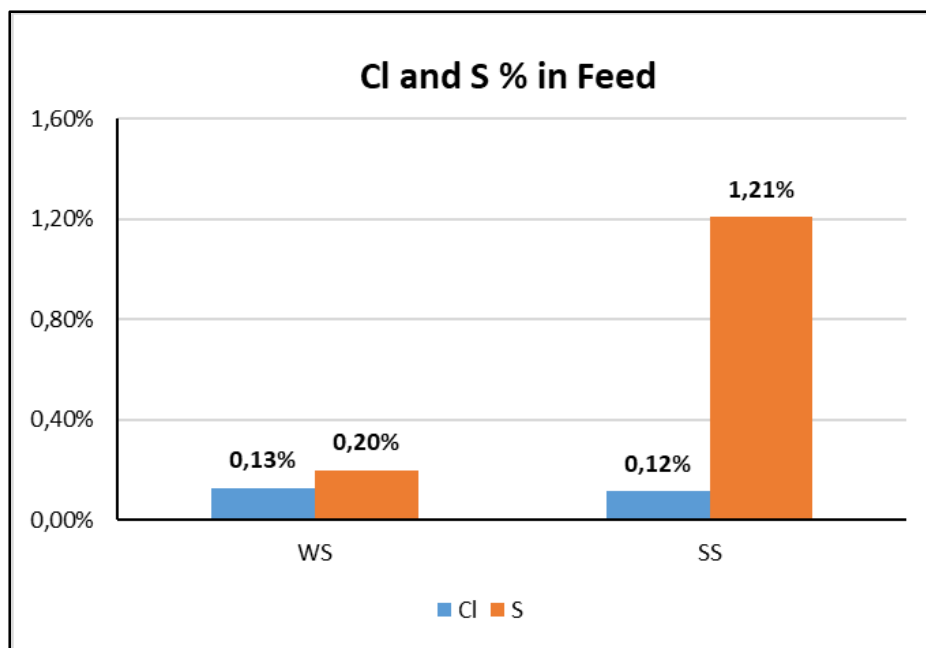


Figure 30: Cl and S in Feed

#### 6.4 Chemical Analysis of the Products

Samples of the products were collected depending on their physical state and analysis method to be used. For liquids, the collection was done simultaneously during the experiment, but the separation and analysis was done after the experiment has finished. The solid product, char, was collected in a drum, weighed and sent for analysis after the experiment. Gaseous samples were collected during the experiment for GC analysis later. Sewage sludge has non-homogenous composition and hence reproducibility of results is a challenge. Wheat straw composition does not pose a problem, but the char obtained undergoes chemical changes and in turn gets heated up. Also, the nature of bio-oils obtained from wheat straw and sewage sludge differ in physical and chemical properties. Both solid and liquid products are characterized by elemental and proximate analysis. The liquid products consist of organic and aqueous phase, analysed by Gas Chromatography-Mass Spectroscopy (GC-MS), (Agilent 5975C VL MSD with 6890 GC) and pH determination. The solid product, char, was characterised by ash and metal content analysis. The permanent gases were analysed online by using a gas volume % detector and by GC analysis by Agilent/HP 6890 GC (TCD and FID detectors).

# 7. Results and Discussion

In this study, in situ sorption of Cl and S is examined using two types of experimental apparatus for low grade biogenic feedstock (in this case, SS and WS). The basic screening of suitable sorbents was done taking into account observations in literature, the feed characteristics and desired limit of emission as per German Standards. The effect and performance of the sorbents on reducing emissions was evaluated based on the amount of Cl and S in the pyrolysis vapours and char.

The experiments carried out using two reactor configurations (Fixed bed reactor and STYX) are summarized below. The results are discussed in terms the following points:

- Efficiency of using *in situ* sorption for reduction of acid gas from pyrolysis vapours.
- Reactor configuration and its influence on the sorption performance of the sorbent.
- Mass balance showing distribution of the products obtained in both the reactor configurations.
- Comparison of char obtained from using and not using sorbent.
- Composition of pyrolysis vapours and potential of using it for gas turbine operation.

## 7.1 Fixed Bed Reactor

Experiments were divided in two categories: 1. No Sorbent used 2. Using sorbent. Table 21 shows a summary of the experiments conducted at a fixed temperature of 500°C in the fixed bed reactor system.

Table 21: Summary of Experiments in FBR system

Feed (Biomass + Sorbent)	Amount (Biomass + Sorbent), g	Temperature
Sewage Sludge	100 + 0	500°C
Sewage Sludge + NaHCO <sub>3</sub>	100 + (0.3, 6, 15, 30)	
Sewage Sludge + CaO	100 + (26.1, 52.3)	
Wheat Straw	100 + 0	
Wheat Straw + NaHCO <sub>3</sub>	100 + 30	

CaO is tested in fixed bed reactor only while NaHCO<sub>3</sub> was used as sorbent both in FBR and STYX configurations. There are two reasons for this selection, first is the extensive literature reported on efficiency of both sorbents and NaHCO<sub>3</sub> 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<sub>3</sub> for Wheat Straw, in capturing Cl from 50% to 70% approximately.



### 7.1.1 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. Nevertheless, since the motive of these experiments was to test the efficiency of Cl sorption, char and gas analysis were the most crucial measurements.

Overall mass balance of sorbent and no sorbent case from Figure 31, shows that the fraction of gas products increase 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. Throughout the experiments, the best case was selected for sorbent to feed molar ratio which is (Na or Ca): Cl molar = 349.60

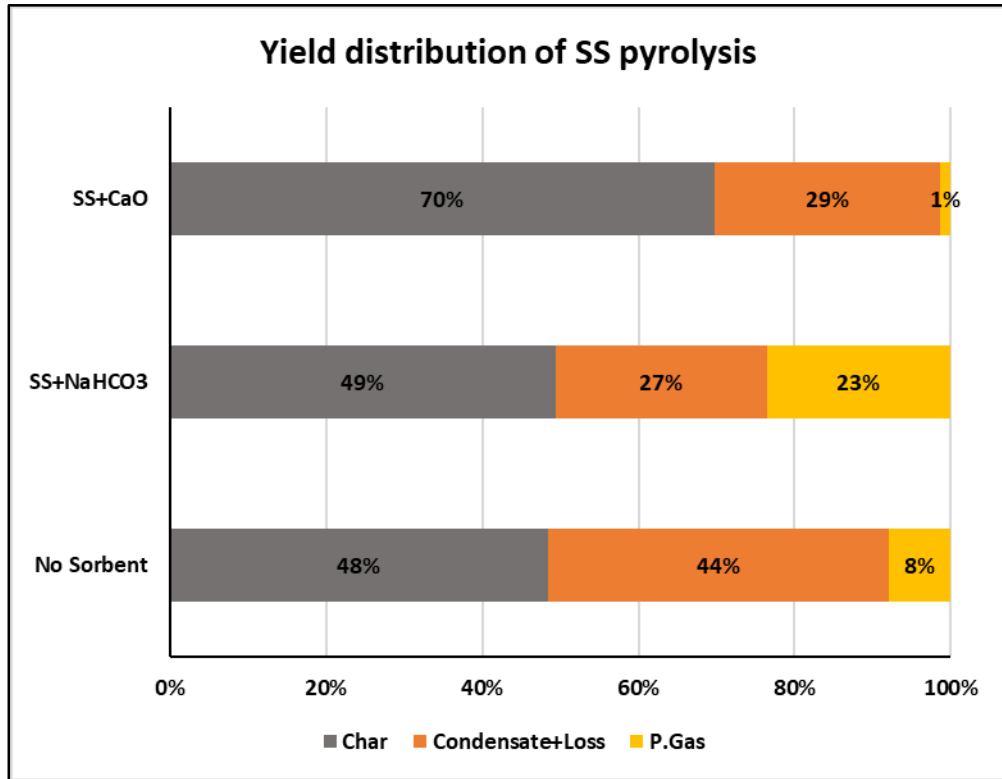


Figure 31: Overall Mass Balance for SS

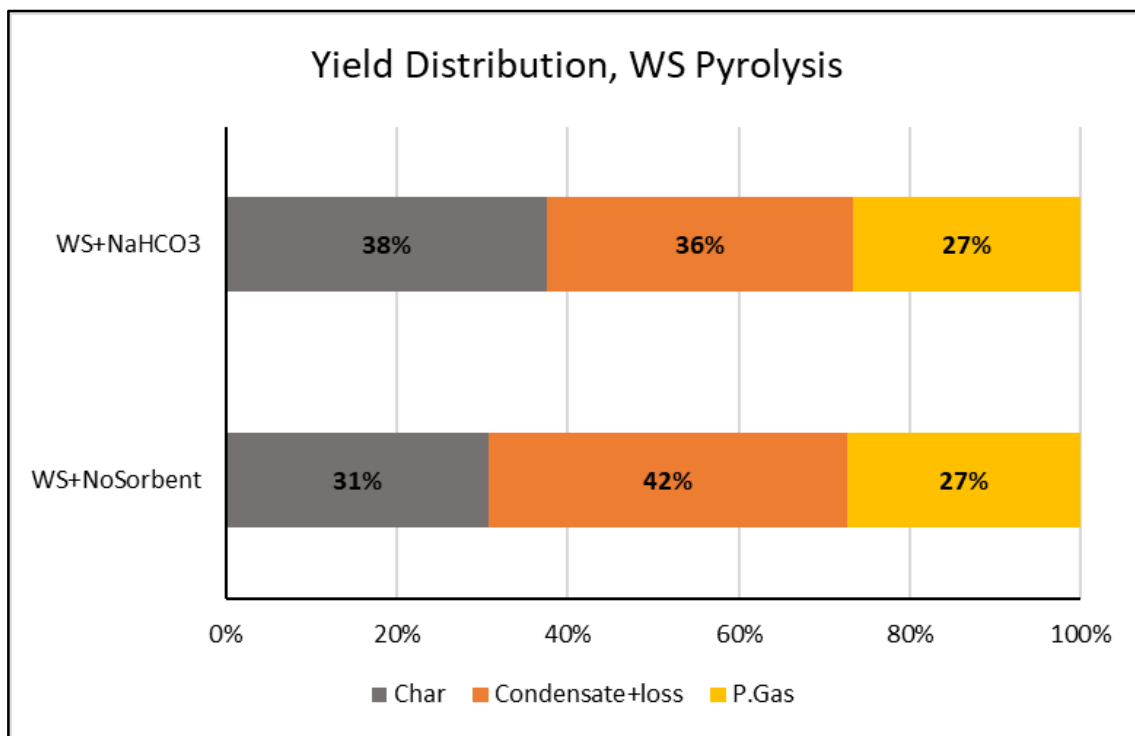
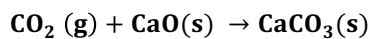


Figure 32: Overall Mass Balance for WS Pyrolysis

The results of gas measurement system which gives online volume % of CO<sub>2</sub> produced are shown in Figure 33. The comparison between CO<sub>2</sub> release shows that significant amount is contributed by sorbent decomposition. A comparison is made between the amounts of CO<sub>2</sub> released when CO<sub>2</sub> was used as sorbent and when no sorbent was used, shown in Figure 34. The amount of CO<sub>2</sub> released in vol% of P. Gas is far less than no sorbent case. This is because of the occurrence of following reaction:



Hence, major fraction of CO<sub>2</sub> is captured by the sorbent. Because of which, while in the case of NaHCO<sub>3</sub>+SS the share of P. Gas increases from 71.03 to 95.35 g/Kg feed, in the case of CaO+SS it decreases from 71.03 to 2.53g/Kg feed, refer figure Figure 37.

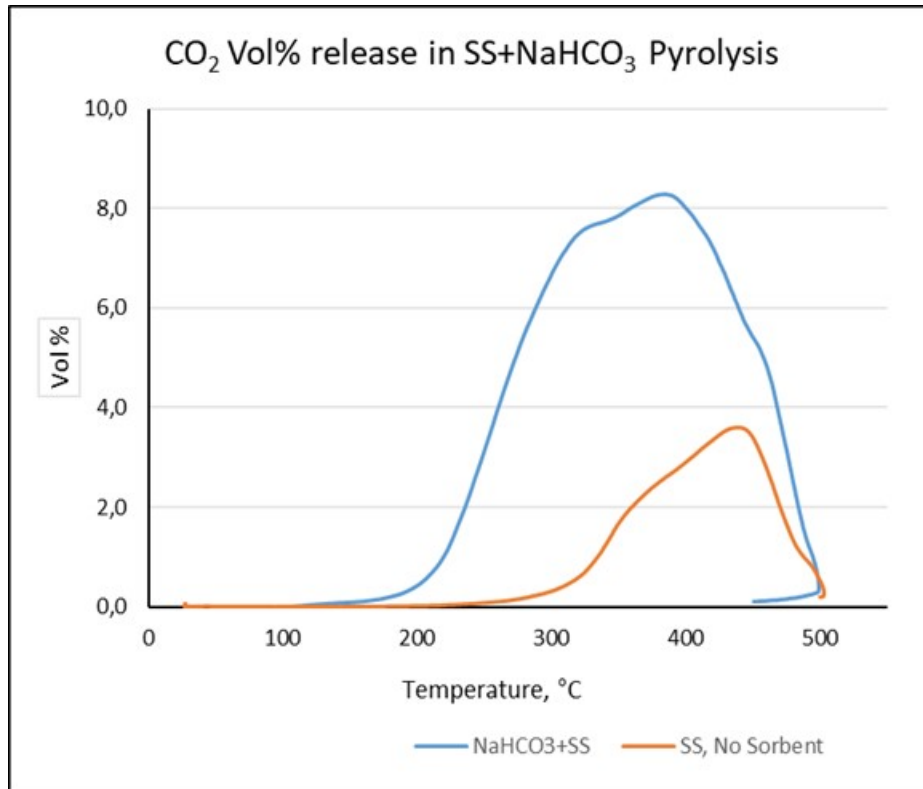


Figure 33: Volume % Distribution of P. Gas, SS+NaHCO<sub>3</sub>

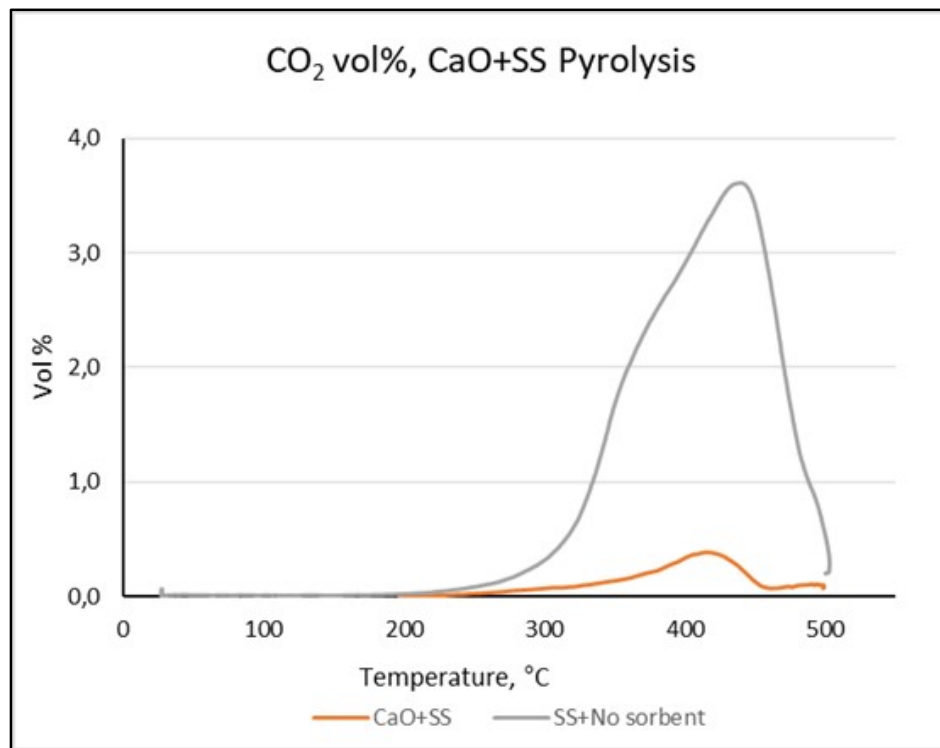


Figure 34: Vol% CO<sub>2</sub> Released

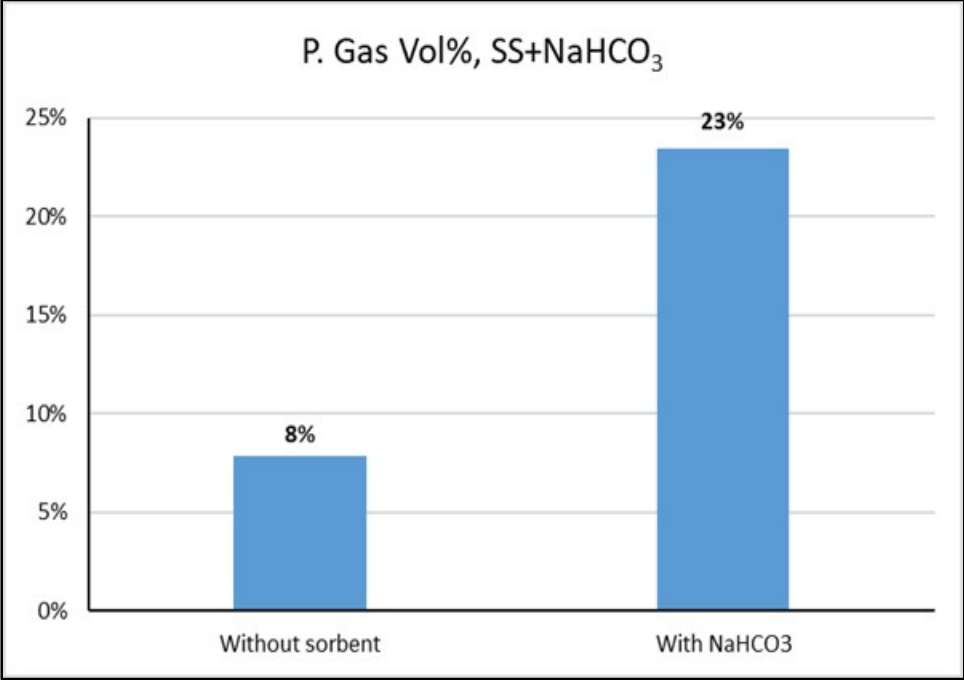


Figure 35: Increase in P. Gas for SS and NaHCO<sub>3</sub>

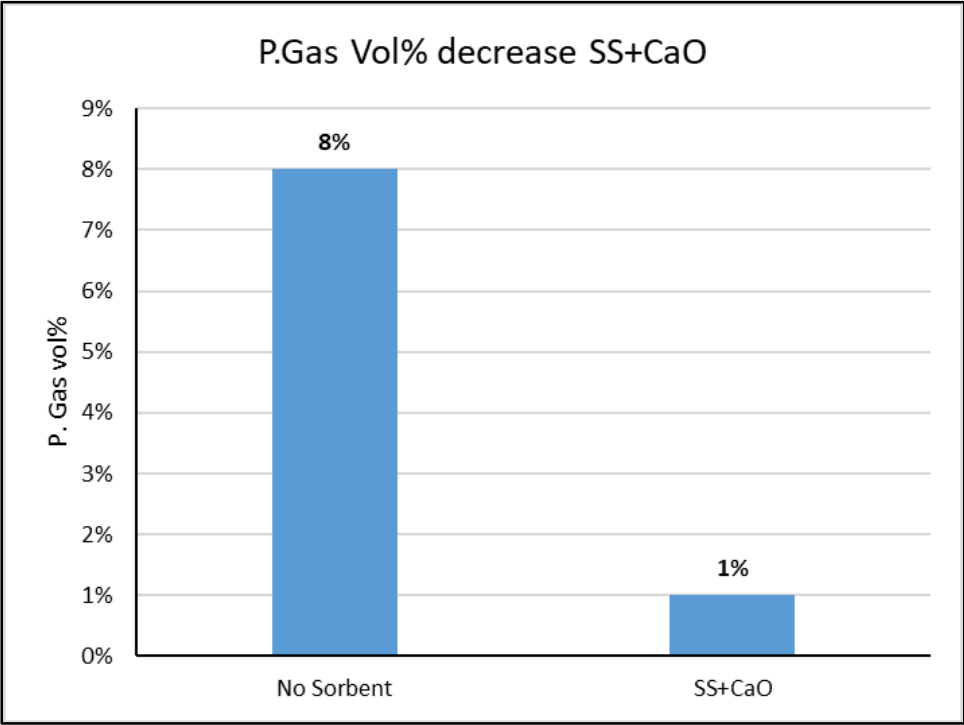


Figure 36: P. Gas decrease in the case of SS+CaO

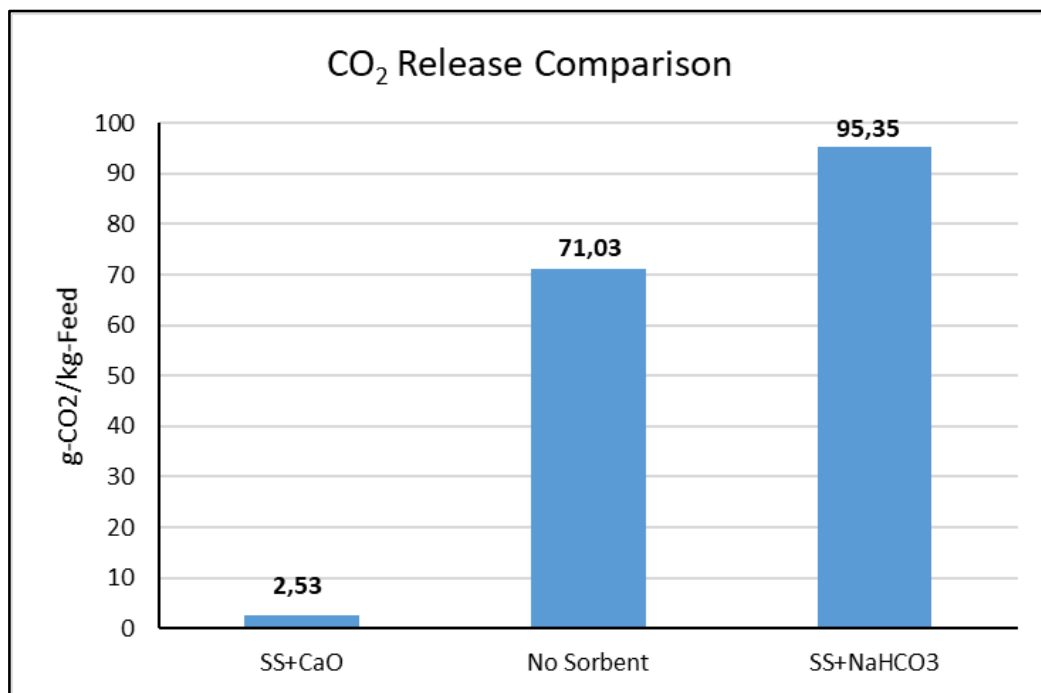


Figure 37: Tabulation of g-CO<sub>2</sub> released per Kg feed

### 7.1.2 Sorbent Efficiency Comparison for SS and WS

Two sorbents (NaHCO<sub>3</sub> 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 38 below, the quantities of sorbent used (NaHCO<sub>3</sub>) 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:

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

Changing the amount of NaHCO<sub>3</sub> used, affected S and Cl capture in diverse ways. For Cl the trend was not clear and was abrupt in the extent of increase or decrease. While for 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 an increase in yield of Sulphur. This increase in S yield agrees with literature [89, 90] previously reported for the dry sorbent injection to target SO<sub>2</sub> removal. According to such expectations, an increase in the ratio of Na/S or Ca/S should increase the Sulphur capture because of availability of more surface area for adsorption, due to increase in sorbent amount. According to other studies [91], 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 NaHCO<sub>3</sub>-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  $\text{NaHCO}_3$  was used as sorbent the S capture in char increased from 42% to 52%.

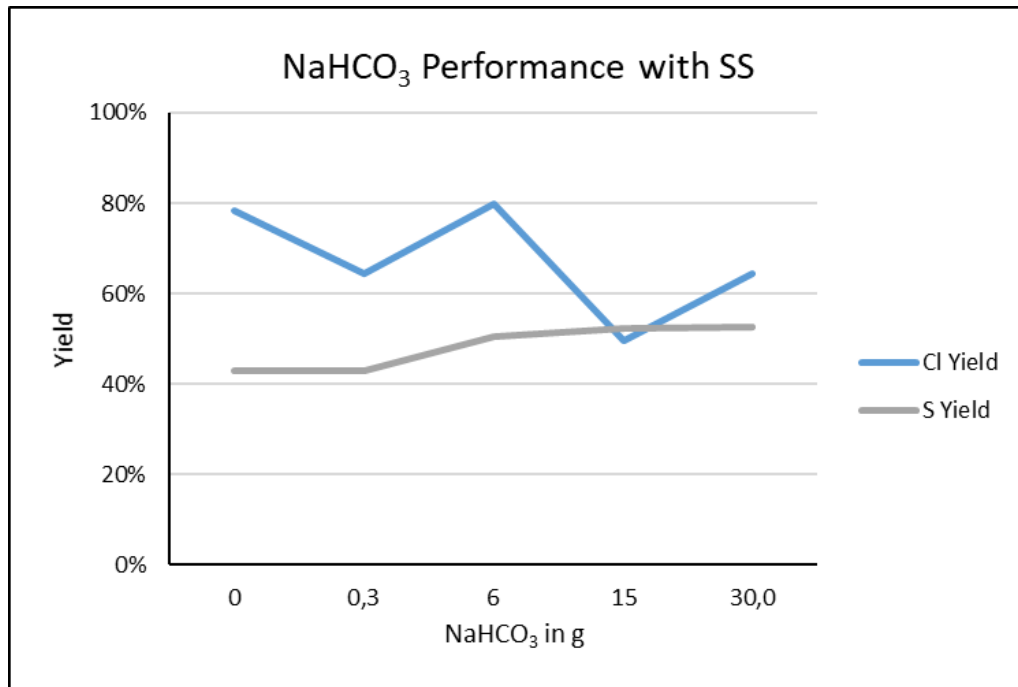


Figure 38:  $\text{NaHCO}_3$  Performance in the case of SS

For the clear understanding of Cl capture with increase of sorbent amount, two modes of sorbent use were considered. One, in which the sorbent and SS were mixed manually, and the other, in which separate layers of SS and sorbent were placed in the reactor one upon another. In both methods, the trend was not as expected and reported in literature. The reason for such a behaviour is not clear. Some possibilities can be the occurrence of secondary reactions between  $\text{NaHCO}_3$  and char matrix [47] thereby decreasing the amount available for Cl adsorption (it has been reported [90, 91] that a high stoichiometric amount of  $\text{NaHCO}_3$  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 [66]). Hence, further analytical and structural analysis of the char and liquid products needs to be done to understand the cause. Sorbent/ SS ratio was varied from 0.003 to 0.3 in the case of the FBR- $\text{NaHCO}_3$  system, which showed abrupt and non-conclusive results for Cl sorption probably because of uneven distribution of sorbent even after manual mixing or the analysed char sample to be not a representative one. However, S capture in the char was initially constant for Sorbent/SS ratio in the range of 0.003-0.06 but, it increased steadily when the sorbent amount was increased. Literature reports mentioned that in the case of  $\text{NaHCO}_3$  as sorbent higher stoichiometric ratios are desirable as they show better efficiency.

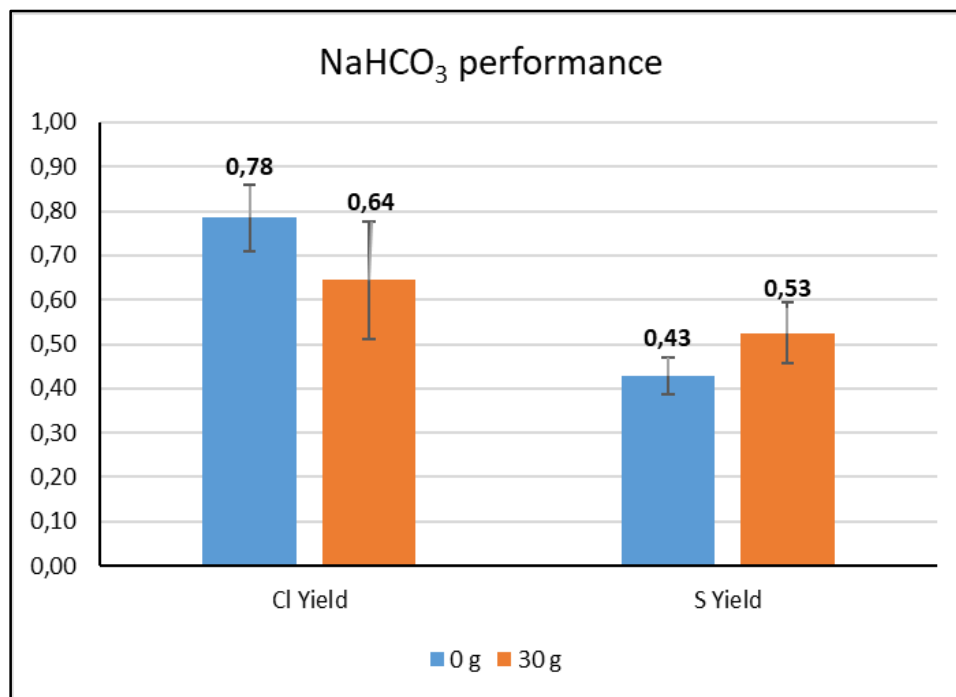


Figure 39: Standard deviation for the case of SS and NaHCO<sub>3</sub>

Results obtained agreed with literature that the sorption reaction rate of CaO is lower for acid gases as compared to NaHCO<sub>3</sub>. 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 CO<sub>2</sub> capture when compared to no sorbent case of SS pyrolysis, Figure 34 and Figure 37

The Sulphur capture increased significantly with the amount of CaO increase, from approximately 42% to 72. This could be attributed to high affinity of alkali and alkaline earth metals towards Sulphur compounds, the alkali metals present in the char also contribute to fixing of Sulphur by favourable reactions [92]. Release of Sulphur in pyrolysis is thermodynamically favoured towards formation of reduced Sulphur compounds as the stable ones and not the gaseous form of S [87]. In the range of 175-500°C most of the organically bound S is released following the devolatilization stage and if the system temperature reaches as high as 1000°C then char burn out contributes to further release of S [47]. 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<sub>3</sub> 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 [47, 63, 93]. The chlorine release in wheat straw was higher than SS and hence the sorbent can capture most of it in char. This causes the increase of precision with which it can be detected in the char analysis done later. When both the feedstocks are compared in

terms of Cl and S capture yield, for the case of  $\text{NaHCO}_3$  as sorbent, WS shows better yield for yield of both Cl and S than SS.

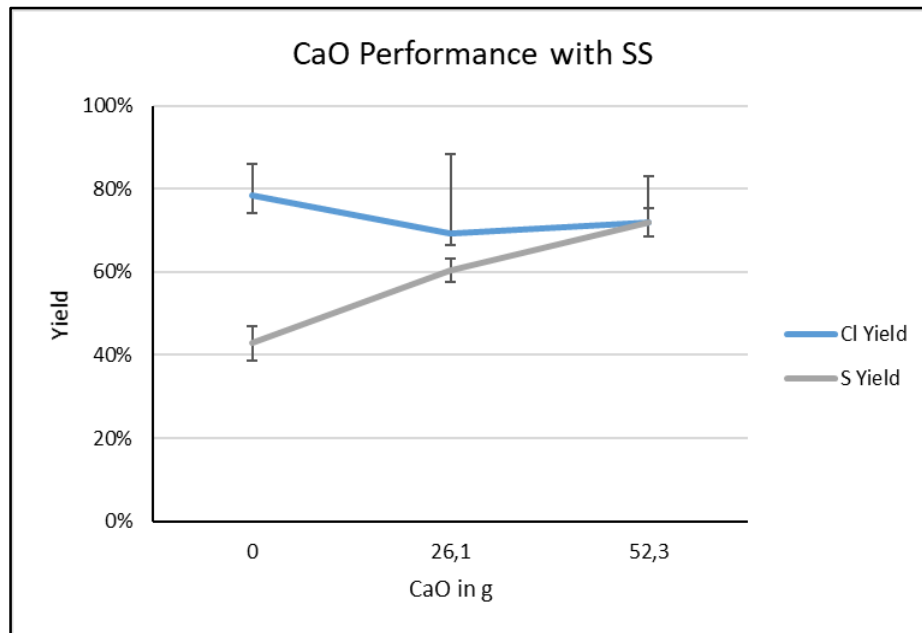


Figure 40: Performance and Standard Deviation, SS+CaO

In the FBR-WS system, only  $\text{NaHCO}_3$  was tested as the previous experiments showed  $\text{NaHCO}_3$  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.

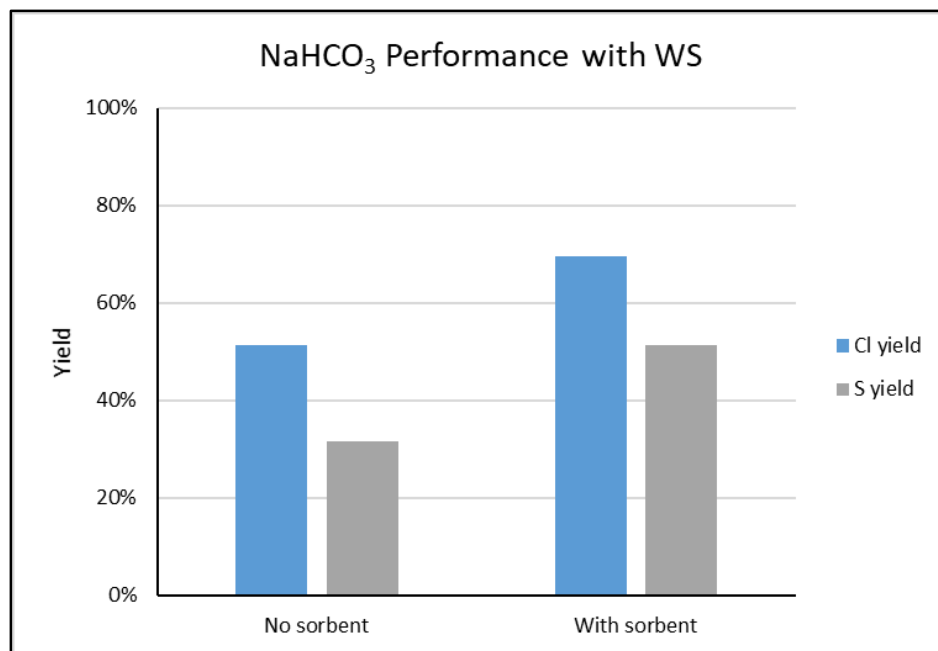


Figure 41: Performance of  $\text{NaHCO}_3$  in case of WS



Standard deviation is a measure of the extent of deviation or dispersion of results obtained from performing the same experiment multiple times. In this case, it gives an insight on the abrupt values obtained in the case of Cl capture for SS using both  $\text{NaHCO}_3$  and  $\text{CaO}$ . 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

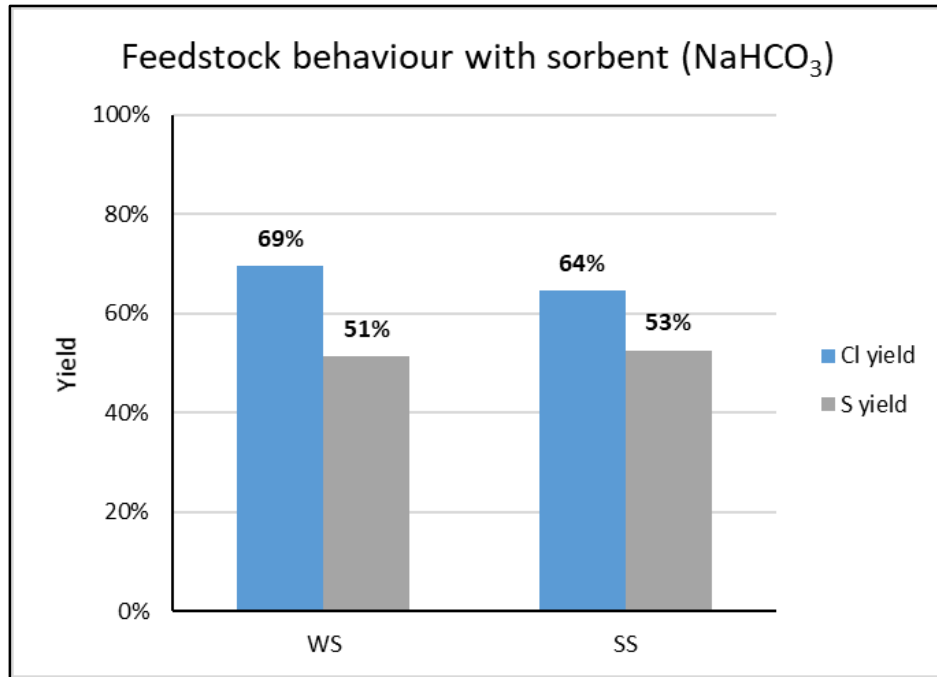


Figure 42: Comparison of Feedstock with respect to Cl and S emissions and their sorption

The analytical error can be justified by the low content of Cl 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 the better precision observed in the latter case).

## 7.2 STYX Experimental Reactor

The in-situ sorption of Cl and S were investigated at the bench-scale screw pyrolysis reactor STYX, adopting  $\text{NaHCO}_3$  as sorbent. This selection was a combination of observations from the small scale FBR experiments and the extensive literature published already. Four experiments were carried out (2 repetition of each one). The process conditions are enlisted in Table 22

Table 22: List of Experiments performed on STYX

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 <sub>3</sub>	4000 + (1199.7)			
Wheat Straw	4000 + 0			
Wheat Straw + NaHCO <sub>3</sub>	4000 + (1199.7)			

The mass ratio of feed to Sorbent was held constant as it was in the experiments with FBR configuration. In the following paragraphs, the mass balances will be first discussed, then the sorbent performance evaluation.

### 7.2.1 Mass Balance

The results of the mass balance are shown in the Figure 43. The balance is with respect to the feed which includes both the biomass feedstock and the sorbent. Two sets of experiment were conducted with both the biomass feedstock separately. 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<sub>3</sub> and pyrolyzed at the same process conditions. The depiction of the mass balance of the experiments performed in the Integrated pyrolysis STYX plant are demarcated as shown in Figure 43 and Figure 44. The yields of solid, liquid and gaseous products for both cases are compared; due to release of CO<sub>2</sub> from the decomposition of NaHCO<sub>3</sub> the gas fraction of SS+NaHCO<sub>3</sub>, is higher than the no sorbent experiment and lead to an overall balance of 108 wt%). 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 [40]. Also, the increase in P. Gas for SS+NaHCO<sub>3</sub> and WS+NaHCO<sub>3</sub> 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 [38, 40, 44]. 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 44 represents P. Gas+ loss.

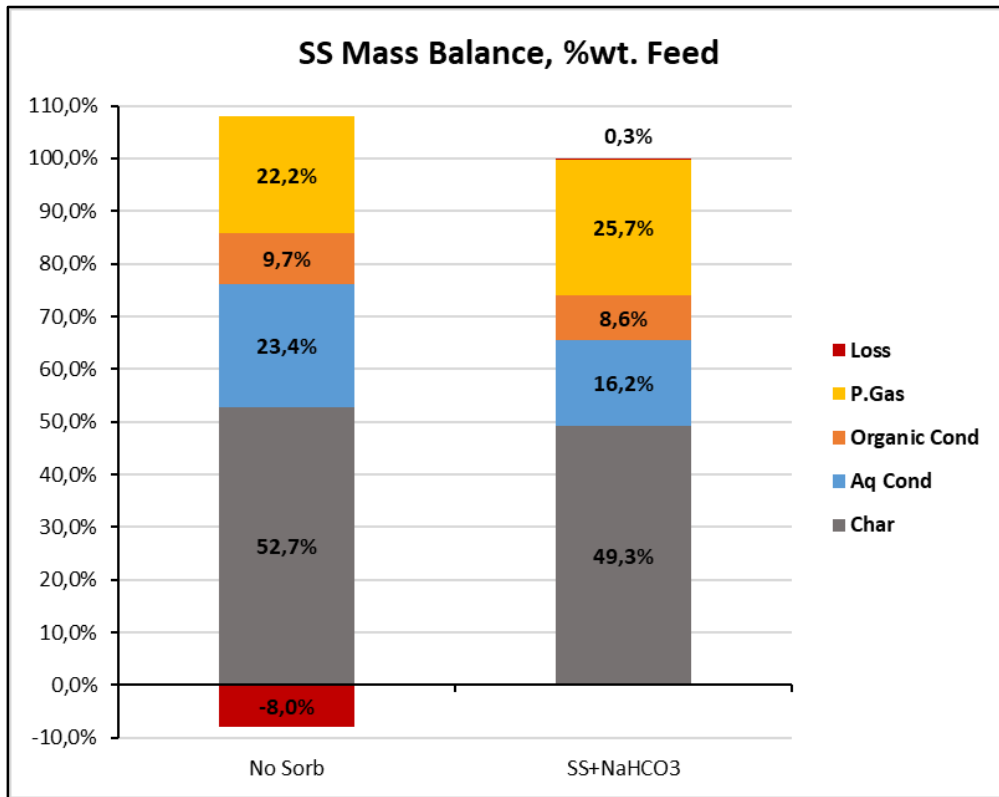


Figure 43: Mass Balance and Yield distribution of experiments using STYX

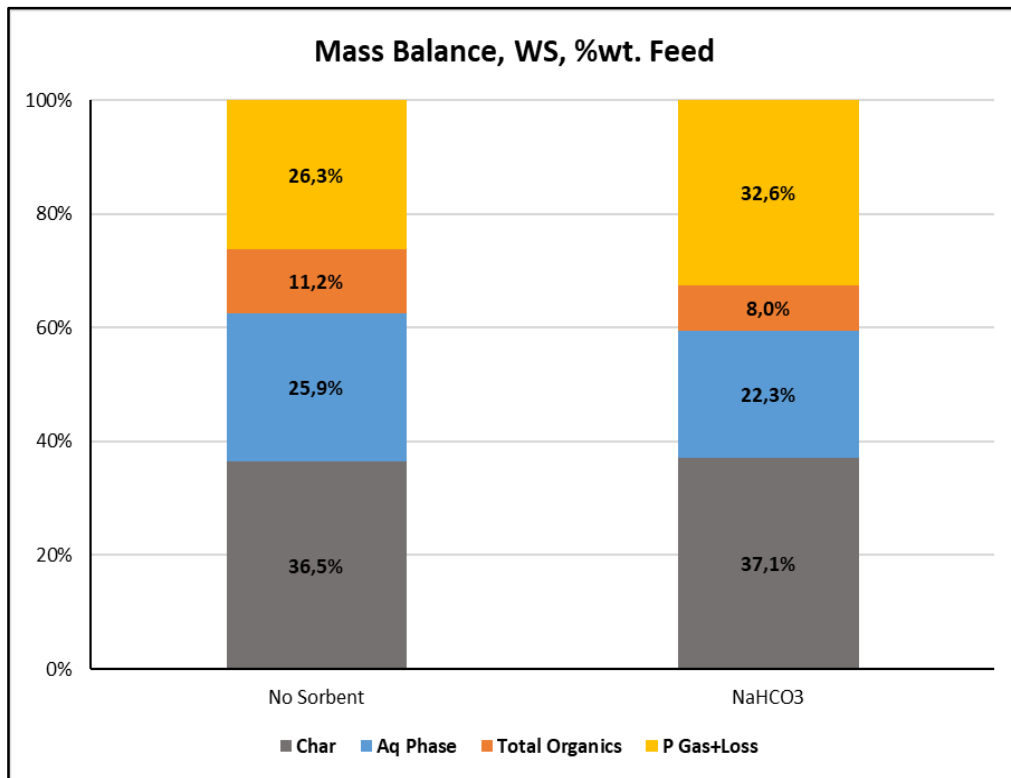


Figure 44: Mass Balance WS for STYX experiments

### 7.2.2 Sorbent Performance

Since release of chlorine compounds, in this study, mainly takes place between 350-550°C [94], Intermediate pyrolysis with hot gas filtration led to an increase of P. Gas because of low heat rates and high residence time as compared to fast pyrolysis [95]. Using NaHCO<sub>3</sub> as sorbent with Sewage Sludge, increased the capture of Cl in char from 83% to 93% approximately as shown in Figure 45.

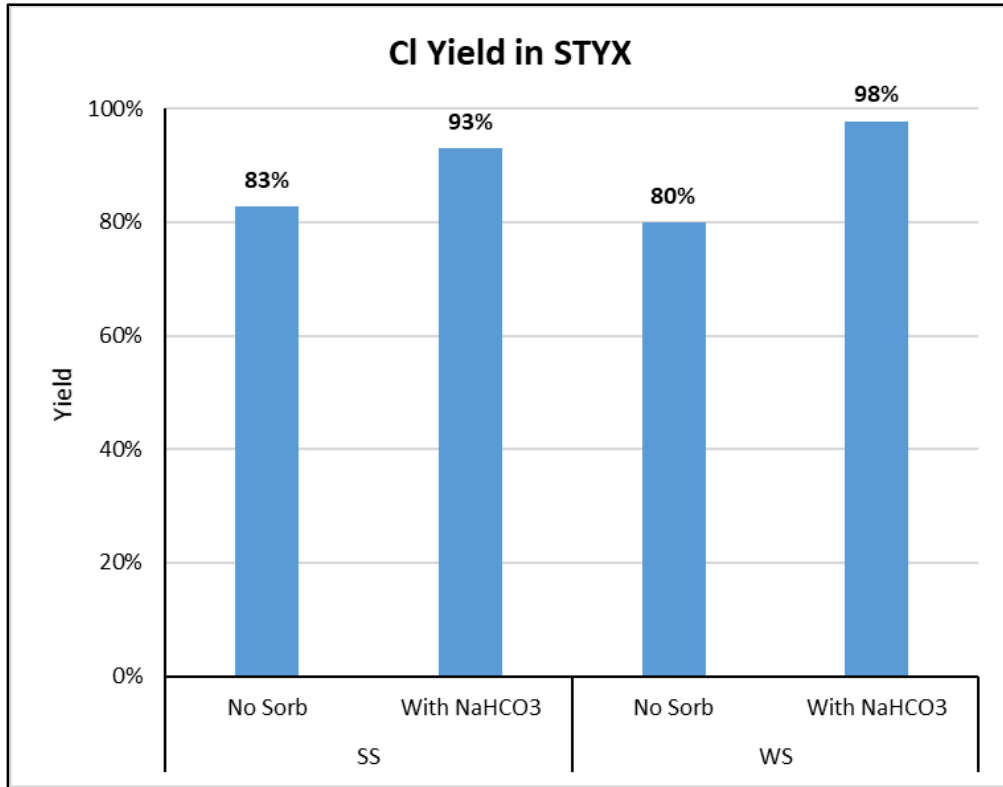


Figure 45: Comparison of Chlorine Yield for SS and WS for STYX

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 46. The presence of alkali metals in the reactor in the form of NaOH or NaHCO<sub>3</sub> reduces the emission of H<sub>2</sub>S 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 sulphate in char, further reducing the release of sulfur into gas phase [92]. Hence, these reports explain the reduction of S in the gas phase when sorbent is used, in this study.

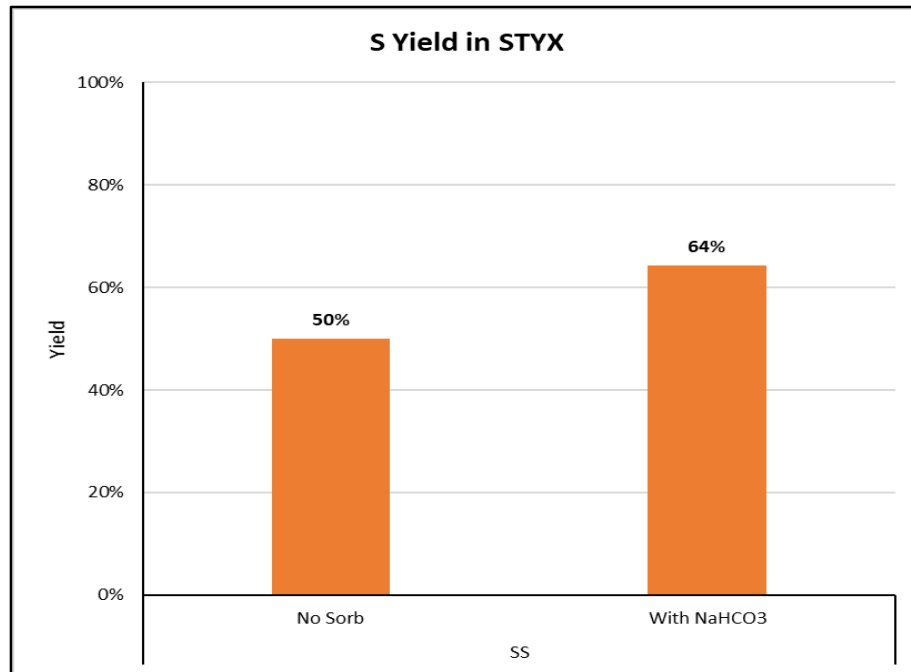


Figure 46: Comparison of Sulphur Yield for SS

### 7.2.3 Permanent Gas Combustion

In order to evaluate the reduction of the emissions due to the implementation of the in-situ sorption, calculations of permanent gas combustion were carried out. The permanent generated by sewage sludge pyrolysis in STYX reactor, were analysed using GC by Agilent/HP 6890 GC (FID and TCD detectors). The composition of the P. Gas is evaluated into details. Quantitative analysis of N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub> and the hydrocarbons up to C<sub>4</sub> was possible (see Figure 47).

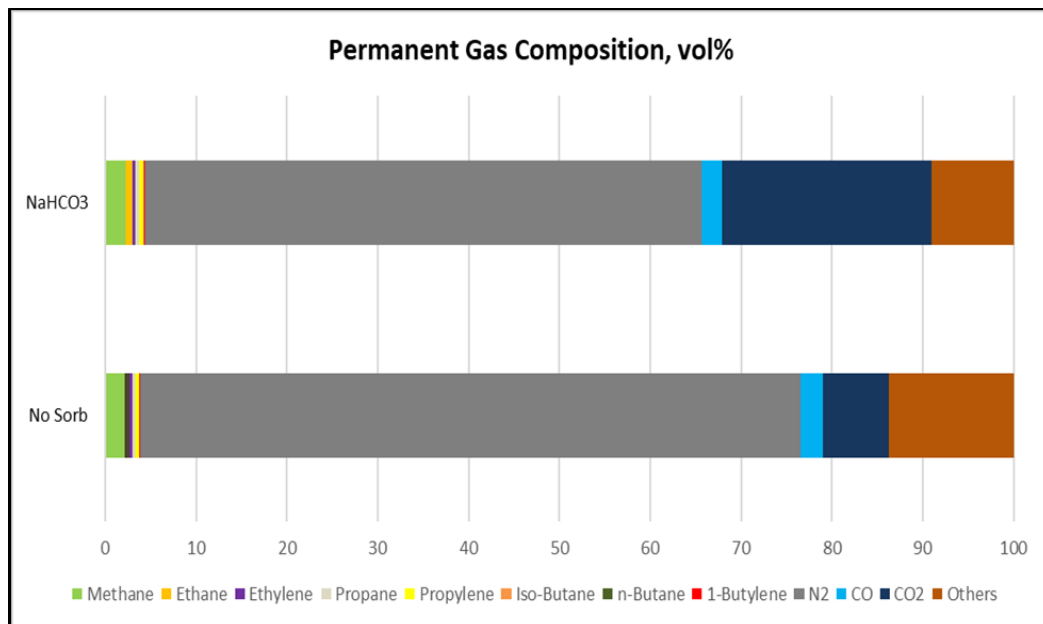


Figure 47: Permanent gas, vol%

It was also observed that share of hydrocarbons contributing to the calorific value, increased in the case of use of NaHCO<sub>3</sub> even considering that additional CO<sub>2</sub> is released in such situation. (Note: The permanent gas is the non-condensable part of the pyrolysis vapours. Upon combustion of this permanent gas we get the flue gas which is being analysed as per the German regulations)

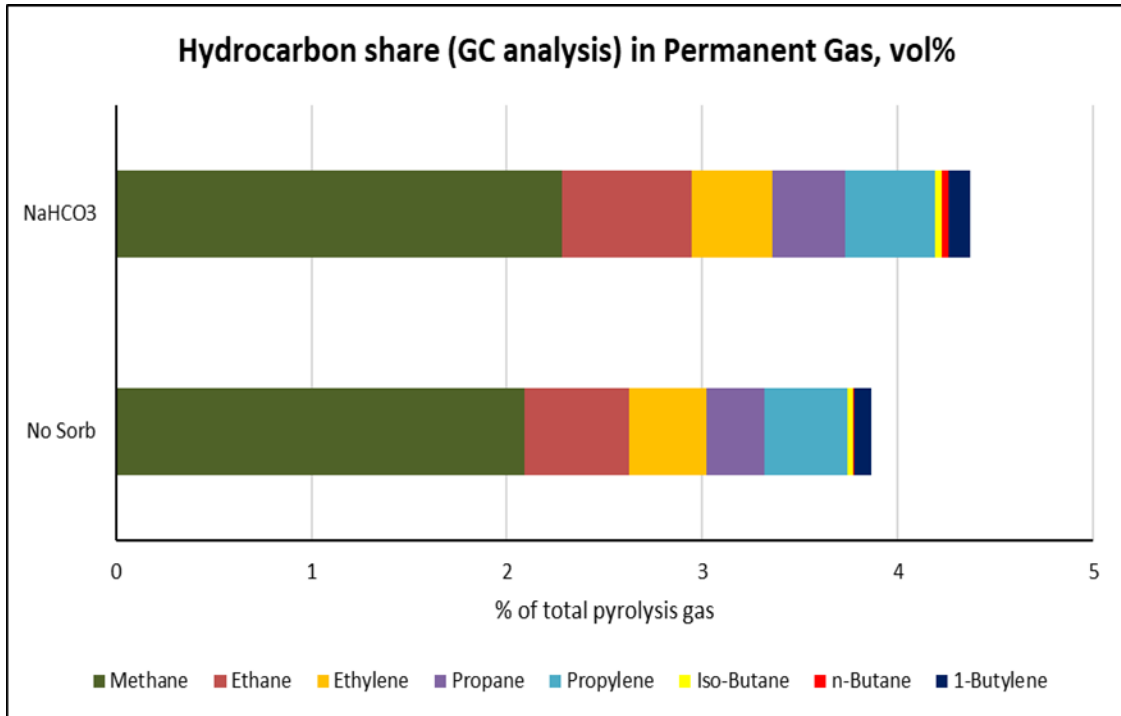


Figure 48: Hydrocarbon share of the Permanent gas in Figure 47

Combustion of permanent gas using excess air as per the guidelines mentioned in 17. BImSchV [96] limits the HCl and SO<sub>2</sub> emissions to be not more than 10 and 50 mg/m<sup>3</sup> respectively. 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. General combustion equations for the range of hydrocarbons and H<sub>2</sub>S present in the permanent gas are shown below Table 23.

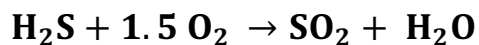
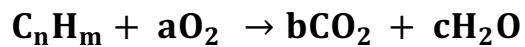


Table 23: Tabulated values of SO<sub>2</sub> and HCl emissions from Combustion

Experiment Type	SO <sub>2</sub> emission (mg/m <sup>3</sup> )		HCl emission (mg/m <sup>3</sup> )	
	Calculated in this Study	17. BImSchV regulation (11% O <sub>2</sub> )	Calculated in this Study	17. BImSchV regulation (11% O <sub>2</sub> )
No Sorbent, SS	36044.49	17164.04	231.69	110.33
NaHCO <sub>3</sub> +SS	24867.20	11841.52	81.90	39.00

In Table 23, the emissions are reported both under stoichiometric conditions as well as after the German 17. BImSchV regulation (11% O<sub>2</sub>) [96]. Emissions of HCl are reduced by a factor 3. 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. On the other hand, the emissions of SO<sub>2</sub> 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 appears a suitable approach; however, optimization is required. In the case of combined removal of Cl and S from the P. Gas, the in-situ sorption approach showed limited results.

## 8. Conclusions

In this thesis, Pyrolysis of Sewage Sludge (SS) and Wheat Straw (WS) was carried out with focus on in-situ sorption of Cl and S using Sodium Hydrogen carbonate ( $\text{NaHCO}_3$ ) and Calcium Oxide ( $\text{CaO}$ ) as sorbents. The following informative remarks and conclusions can be drawn from the studies conducted:

- a) Use of  $\text{NaHCO}_3$  and  $\text{CaO}$  as sorbents for Cl and S capture in the FBR showed varying results and issues of reproducibility. The standard deviation of Cl capture in char showed that an analytical error is the predicted cause of the dwindling values. The relative amount of Cl is small as compared to S in the SS feedstock which gives rise to decrease of precision while measurement in a small-scale experiment (100 g SS as feed).
- b) Higher stoichiometric ratio of Sorbent and Feed could lead to better capture of Cl and S, literature reports mentioned that, in the case of  $\text{NaHCO}_3$  higher stoichiometric ratios are desirable as they show better efficiency. However, economic considerations may also be considered.
- c) Calcium Oxide as sorbent for both SS and WS showed competitive sorption of  $\text{CO}_2$  and acid gases. The capture of S in the char using  $\text{CaO}$ , 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.  $\text{CaO}$  undergoes other competitive reactions for example, with  $\text{CO}_2$  to form  $\text{CaCO}_3$  at the reaction conditions, which was mentioned in literature before. When  $\text{CaO}/\text{SS}$  ratio was increased from 0.26 to 0.52, the S capture showed significant increase as more sorbent was available for reaction.
- d) In the FBR-WS system, only  $\text{NaHCO}_3$  was tested as the previous experiments showed  $\text{NaHCO}_3$  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. Hence, it was concluded that  $\text{NaHCO}_3$  due to its superior performance, will also be tested in STYX experiments for capture of S and Cl.
- e) When Sewage Sludge and wheat straw is used as feed and Sodium Hydrogen Carbonate ( $\text{NaHCO}_3$ ) as sorbent in STYX, chlorine removal trend is increasing from no sorbent to using a sorbent. In the case of Sulphur 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  $\text{NaHCO}_3$ +SS system for STYX pyrolysis plant to get higher efficiency of Cl sorption.
- f) Combustion Calculations of permanent gas from SS obtained from two streams: With  $\text{NaHCO}_3$  as sorbent and without a sorbent, showed that the values of  $\text{SO}_2$  and HCl emissions are above the regulation limit. The limitations in HCl emissions appear achievable by optimization of the process. The removal of Sulphur requires a different strategy. Further component balance from the analysis of bio-oil and aqueous phase can lead to better understanding of the efficiency of sorbent and the pathways of formation of Cl and S compounds.



## 9. Future Work

Future works related to the reduction Cl emissions should follow two main strategies. On the one hand, an optimization of the in-situ sorption is required:

- Improvement and optimization of the sorbent/feed ratio
- Evaluation of more economic sorbents, such as  $\text{CaCO}_3$  or dolomite.

Moreover, the analysis of the bio-oil will assess the chance of direct combustion of the pyrolysis vapours as an alternative to the combustion of the P. Gas. In the case of limited Cl content in the liquids, the increase of the mass flow would help to achieve the emissions targets.

The second strategy that should be investigated consists of investigating different approaches for the removal of Cl from the pyrolysis vapours or from the P. Gas.

The dry injection of the sorbent in the gas-phase (entrained flow sorption) appears to be an interesting alternative for the STYX reactor. The presence of the high temperature filters will remove the reacted sorbent from the gas. The sorbent will be retained on the surface of the filter generating an additional opportunity for sorption. This approach appears interesting in both the case of direct combustion of the pyrolysis vapours or of the P. Gas after condensation of the bio-oil.

In the case of combustion of the P. Gas, the utilization of an absorbent after the condensation of the bio-oil might also be a suitable option. In this case, both Cl and S can be reduced to very low levels. However, an additional aqueous waste stream is generated; therefore, a techno-economic comparison of the described options is mandatory for the overall optimization of the process.

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