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Upscale of a TCR® plant to industrial scale – characterisation and pre-testing of gas-scrubbing unit

Experimental degree thesis

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Abstract

The Fraunhofer Institute for Environmental, Safety, and Energy Technology (Fraunhofer UMSICHT) at Sulzbach-Rosenberg, is developing a new method of intermediate pyrolysis, followed by reforming. The patented process, called Thermo-Catalytic-Reforming (TCR®), is the core technology in the To-Syn-Fuel project. The aim of the project is the production of advanced synthetic fuels from residual and waste materials (in particular sewage sludge), which are converted into the products bio-oil, as well as hydrogen, by means of the TCR®- plans. On the laboratory and pilot scale, the potential of this process for the generation of high-quality fuels according to the European standards EN 228 (for gasoline fuel) and EN 590 (for diesel fuel) has been already demonstrated, now the scale up of the plant is in the phase of commissioning. The aim of this work is to demonstrate the feasibility of TCR® gas cleaning from H_2S and NH_3 through the use of a scrubber. Several experiments have been carried out using $FeCl_2$ as a scrubbing agent, from laboratory small scale to the real size scale plant, simulating the ideal gas concentration and operating condition of TCR500 plant. The best conditions for scrubbing H_2S and NH_3 have been investigated testing the stoichiometric reaction capacity of $FeCl_2$ and the best environment inside the reactor. Moreover, new upgrades, such as sedimentation tank, filter, working bulk-absorption system, and a bypass, are tested to improve the scrubbing system in order to establish more efficient results and as well as have fewer issues related to lower byproduct formation, and decreasing of the maintenance time requested by the scrubber.

These experiments reached 95% scrubbing efficiency and let a deep know-how for the control of the cleaning system and a good starting point for its integration in the plant start-up.

Scope

The task personally researched and developed during the internship period spent at the Fraunhofer Umsicht institute was dedicated to cleaning the gas in the scrubber unit, obtained from the TCR® process. The hydrogen sulphide and ammonia gas produced are not only toxic but also harmful and degrading for the structural mechanical parts and their products derived. The final goal of the TO-SYN-FUEL project is to obtain advanced biofuel from sewage sludge with a hydrodeoxygenation process by upgrading the TCR®-oil previously produced. For this reason, the hydrogen deriving from the gaseous phase of the reaction, which is therefore intended to be used, must be as clean as possible from those contaminants. Cause-effect experimental work to start-up the purification system and obtain the best possible cleaning efficiency was conducted in the dedicated plant: the scrubber. The results obtained are shown in the following Thesis and provide a broad overview of the reactor in question and deep know-how available for the future automation phases of the entire system.

Preface

Table of content

Symbols

Formula symbol	**Unit**	**Explanation**
C	mol/L	Mole concentration
Hi	J / kg	Calorific value
ΔH_r^0	J / mol	Enthalpy standard of reaction
Kd	1	Dissociation constant
K_F *air / nitrogen*	1	Conversion factor air / nitrogen
m_B	kg	Mass of the substance B
$\dot{m}$	kg / s	Mass flow
M	kg / mol	Molar mass
$\dot{n}$	mol / s	Material flow
p	Pa	Pressure
p_{is}	Pa	Operating pressure
p_k	Pa	Pressure (calibration)
p_{Ks}	1	Acid constant
p_n	Pa	Pressure (standard condition)
$\dot{Q}$	J / s	Heat flow
T	K	Thermodynamic temperature
Tn	K	Thermodynamic temperature (standard condition)
V	m^3	Volume
$\dot{V}$	m^3/ s	Volume flow
$\dot{V}_{Max}$	m^3/ s	Maximum volume flow
$\dot{V}n$	m^3/ s	Volume flow (standard condition)
$\dot{V}n_{is}$	m^3/ s	Actual volume flow (standard condition)
$\dot{V}n_{target}$	m^3/ s	Target volume flow (standard condition)
ϑ	° C	Temperature
ϑis	° C	Operating temperature
ϑk	° C	Temperature (calibration)
ϑ_{target}	° C	Target temperature
κ	S / m	Electrical conductivity
λ	1	Air ratio
Λ	Sm^2/ mol	Molar conductivity
$\xi_{A/B}$	1	Mass fraction of ash in the component B
$\xi_{C/B}$	1	Mass fraction of carbon in the component B
$\xi_{H/B}$	1	Mass fraction of hydrogen in the component B
$\xi_{i/B}$	1	Mass fraction of the element i in the component B
$\xi_{N/B}$	1	Mass fraction of nitrogen in the component B
$\xi_{O/B}$	1	Mass fraction of oxygen in the component B
$\xi_{S/B}$	1	Mass fraction of sulfur in the component B
ρ	kg/m^3	Density
φ	1	Volume fraction
φ_{BM}	1	Volume fraction of Bellamethan
ω	1	Mass fraction

Abbreviations

Abbreviation	**Description**
Biokraft-NachV	Biofuel Sustainability Ordinance Germany
EP	Equivalence point
BM	bellamethane
$CaCl_2$	Calcium chloride
CH_4	Methane
C_mH_n	Hydrocarbons
CO	Carbon monoxide
CO_2	Carbon dioxide
$FeCl_2$	Ferrous chloride
$Fe(OH)_2$	Ferrous hydroxide
$Fe(OH)_3$	Ferric hydroxide
FeS	Ferrous sulfide
GC / MS	Gas chromatograph with mass spectrometer
HCl	Hydrogen chloride
H_2O	Water
$H3O^+$	Hydronium
HS^-	Hydrogen sulfide ion
H_2S	Hydrogen sulfide
HDN	Hydrodenitrogenation
HDM	Hydrodemetallization
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
NaCl	Sodium chloride
NH_3	Ammonia
$NH_4{}^+$	Ammonium
NO_x	Nitrogen oxides
OCl^-	Hypochlorite ion
OH^-	hydroxide
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PCDD / PCDF	Polychlorinated dibenzodioxins / furans
$PO_3{}^-$	Phosphate
Pr	Post reformer
R	Hydrocarbon residue
SO_2	Sulfur dioxide
TCR®	Thermo-catalytic reforming
TE	Toxicity equivalent
DM	Dry matter
DS	Dry substance
waf	Water and ash free

1 Introduction

The world population has increased in the past 200 years from just over a billion to a current level of approximately 7.5 billion people. Due to this rapid increase in combination with higher prosperity levels, bottlenecks in the global supply of sufficient food, energy and raw materials are inevitable, moreover, the amount of waste will also rise steadily. Considering an average result in global human demands, we already need around 1.6 earths to ensure our current standard of living in the long term. The scarcity of fossil raw materials and the advancing climate change are only two aspects that result from anthropogenic activity, that require fast and effective replies [1] [2] [3] [4].

World states are facing this situation sometimes with ambiguous and different approaches, but what is for sure real is that in the next years our daily demand will be supplied by new potential raw material uptake. Despite the different political governments, 194 countries have committed themselves to the “Accord de Paris” (Paris Agreement) in order to limit global warming and reduce greenhouse gas emissions to less than 2 °C above the pre-industrial level by 2050 [5]. For the sake of completeness, the last IPCC’s Sixth Assessment Report launched in summer 2021 finds that global warming of 1.5°C and 2°C will be exceeded during the 21st century unless deep reductions in carbon dioxide (CO_2) and other greenhouse gas (GHG) emissions occur in the coming decades. It's clear that the urgency of action to reverse climate change and regenerate our planet, pushing for net-zero by 2030 to avoid further catastrophes. For this, we urgently need to accelerate and implement innovation for climate action at all scales and in integrated, holistic ways [6].

Today and in the near future, fossil fuels are likely to remain of great importance to the international community, in particular, crude oil and the products made from it have become indispensable in the chemical industry and mobility. For this reason, efforts have been made for a long time to develop new technologies and alternative raw material sources in order to avoid the environmental pollution caused by the use of crude oil, so far. However, no approach on a large scale has prevailed. On one hand, there is a conflict of interest between the production of food and feed as well as energy crops on the available area that influences the choice of raw materials. On the other hand, the quality of the products obtained is of great importance and can severely limit their widespread use. Complete substitution of fossil diesel and gasoline fuels by conventional pyrolysis oils would not make sense or would involve greater effort due to the unfavourable product properties and composition. With the introduction of the "Renewable Energy Directive ", the European Union stated that the proportion of conventional biofuels is to be reduced and replaced by advanced biofuels [7] [8] [9].

The system concept developed by Fraunhofer UMSICHT for the thermal conversion of sewage sludge, consisting of thermal catalytic reforming (TCR®) in combination with a fixed bed gasifier and a combined heat and power unit (CHP), addresses the given challenge of sewage sludge utilization and combines this with the politically required reduction of greenhouse gases. However, the previous systems have only been used successfully developed on a laboratory, and pilot scale [10] [11]. The next step is to optimize and start up a pre-commercial TCR®-Plant with a sewage sludge throughput of 500 kg/h. The main objective is to ensure long-term, stable operation of the entire demonstration plant while at the same time meeting the product yield and quality achieved on a smaller scale. For this purpose, all system components must also be checked for their functionality, so that the plant can work towards an autonomous mode of operation, and if successful results will be obtained, the next step would be the full commercial application of this technology in the market.

As part of this master thesis, pre-testing of components in order to prepare the plant for hot commissioning were done during the internship period spent at the Fraunhofer Umsicht institute. Specifically, the task that was personally researched and developed was dedicated to cleaning the gas obtained from the TCR® process. It is well known that pyrolysis oils contain significant percentages of organic compounds, sulphur and nitrogen, which in turn, due to high temperatures, can flow into the gaseous phase of the products. The consequent formation of hydrogen sulphide and ammonia are not only toxic but also harmful and degrading for the structure of the plant itself and its products derived. Since the final goal is to obtain advanced biofuel with a hydrodeoxygenation process by upgrading the TCR-oil previously produced, for this reason, the hydrogen deriving from the gaseous phase of the reaction which is therefore intended to be used, must be as clean as possible. Experimentation work to obtain the best possible efficiency and start-up the purification system was conducted in the dedicated plant: the scrubber. The results obtained are shown in the following

Thesis and provide a broad overview of the reactor in question and deep know-how available for the future automation phases of the entire system.

2 Theoretical foundations

2.1. Thermochemical conversion

Thermochemical conversion is a process in which the input material is converted into valuable products in the form of heat or energy sources [12] [13]. All types of organic substances can be used as feedstock, those with low moisture content are the most appropriate [14] [15]. In general, biomass conversion can be divided into primary and secondary conversion technologies. The primary conversion has the aim to generate energy sources or release directly the heat; it takes place at high temperatures, and occasionally high pressure, in the course of *combustion, liquefaction, gasification or pyrolysis* [12] [13]. Depending on the process, there is a different yield and quality. In secondary conversion, the products of the first conversion step are converted into other energy carriers (e.g. fuel) or another form of energy (electrical energy, etc.) [13]. For the sake of completeness, it should be pointed out that there are other methods to convert biomass that are based on other principles: bio-chemical (anaerobic fermentation, fermentation, bio-photolysis) or also physico-chemical processes (mechanical press, extraction) [16].

Concerning the four primary conversion processes we have:

1) The direct *combustion* of the feedstock for energetic use, which is a proven, cost-effective process with high reliability [17]. Biomass combustion consists of the following steps: heating, drying, degassing to produce charcoal and volatile substances, and burning of these last ones [18]. However, it can cause serious environmental problems due to the release of incomplete converted carbon-containing particles and nitrogen oxides (NO_x), coming under unfavourable reaction conditions [18]. In addition, biomass can contain sulfur, which causes the risk of formation of sulfur dioxide (SO_2) and acid rain [14].

2) In order to obtain a liquid product, the *liquefaction* process can be achieved at low temperatures (250-470 °C), high pressure (50- 150 bar), long dwell time (5 – 30 min) and using a catalyst [10], [16]. As a result of these reaction conditions, the starting material is split into smaller reactive molecules, which are then converted into an oil-like mixture through polymerization [19]. Several reactions take place simultaneously, such as depolymerization, thermal decomposition, dehydration, decarboxylation,

hydrogenolysis and hydrogenation [20]. Interest in this method is rather low, as it is a cost-intensive and complex process due to this combination of parameters [21] [17].

3) In a *gasification* process, a solid carbonaceous feedstock is converted in a reducing atmosphere at temperatures above 1000K into synthesis gas, which can be used as a fuel gas or chemical feedstock [17] [22] [23]. The synthesis gas, with a calorific value of 4 to 11 MJ/m^3, is composed mainly of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2) and tar [24] [25]. If oxygen or air is present, combustion and gasification are similar; however, gasification is an incomplete combustion with the aim of forming a high-quality gas mixture [10].

4) The *Pyrolysis* is a reaction in which molecules with a high molar mass of organic material are broken down into smaller molecules after drying by rapid heating to a higher temperature (up to 750 K) and, differently from gasification, it operates under a lack of oxygen ($\lambda \approx 0$) [14] [15] [26]. The main products of the pyrolysis of biomass are: Biochar, Pyrolysis oil, Gases (CH_4, H_2, CO and CO_2) and water [10].

The relationships and intermediate steps of the thermochemical conversion are shown in Figure 2.1.

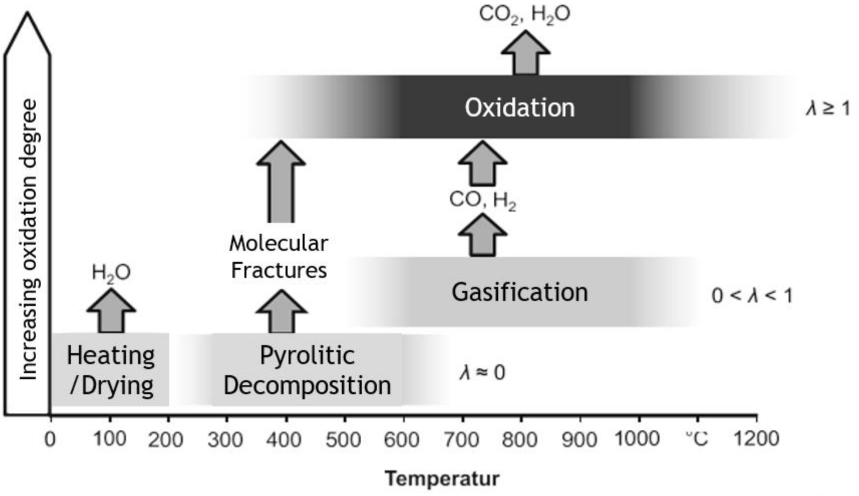


Figure 2.1: Process of thermo-chemical conversion. Representation of the oxidation degree depending on the temperature and the air ratio including essential intermediate products / groups; lighter boxes: endothermic conversion process; darker box: exothermic conversion process. Picture translated from [27]

Pyrolysis ($\lambda \approx 0$), gasification ($0 < \lambda < 1$) and combustion (Oxidation with $\lambda \geq 1$) differ in the temperature range and in the state of the gaseous atmosphere wherein the individual subprocesses occur. Lambda is used as a description of the relationship between the ratio of the supplied air to the stoichiometrically necessary ($\lambda = 1$) air supply. Exclusively combustion takes place completely in the ideal condition and reaches the maximum degree of oxidation. It is also the only stage of the exothermic process in the thermochemical conversion process.

In the first phase of "***heating***", the feedstock is reacted endothermically, and the free and bounded water escapes completely. The subsequent second phase of the "***pyrolytic decomposition***" leads to the cleavage of the covalent bonds of the macromolecules: when the heat is supplied from outside, the resulting molecular fragments leave the fuel in the form of volatile components. The volatile components are mainly organic substances, which have a low boiling point. Further reactions (cleavage, polymerization) in the gas phase produce not only simple compounds (carbon monoxide and water) but also higher molecular compounds. After complete pyrolytic decomposition *coke* is formed as a result of this thermochemical conversion process. Following the pyrolytic decomposition "***Gasification***" can occur. Here it is necessary to supply a limited amount of air or oxygen ($\lambda < 1$) with a temperature high enough to partially oxidize the remaining coke, carbon monoxide is then produced from the carbon bound to solid form in the coke. In order to achieve "***Oxidation***" the intermediate products that have arisen up to now, sufficient air must be supplied with a stoichiometric mixture. The strongly exothermic reaction of the oxidation provides the necessary energy for the three preceding phases during combustion. [28] [29]

2.2. Pyrolysis

The pyrolysis of biomass can be split into *primary* and *secondary mechanisms* [30]. The *primary mechanism* is made up of carbon formation, depolymerization and fragmentation [31]. As a result of the pyrolytic decomposition, the macromolecules of the components contained in the biomass experience a dissociation of the bonds due to strong thermal stimulation. The result is an occasional irreversible splitting of the chemical bonds within the macromolecules and the formation of smaller molecule fragments which leave the solid starting material as gas or vapour. As a result, this depolymerization leads to a reduction in the degree of polymerization, with the process continuing if volatile compounds are released [32]. During coal formation, benzene rings are first formed, secondly from them solid residue biochar with an aromatic-polycyclic structure is created [33] [34] [35]. During the decomposition, oxygen bounded can be released and be available for further reactions. However, the escaping product gas usually prevents the process from being impaired by oxygen. The endothermic reaction begins at temperatures of 150 to 220 °C, after completion of the process at around 500 °C, a solid residue remains, which consists mainly of carbon and ash. The other (intermediate) products are under normal conditions in the liquid and gaseous aggregate condition. The gas mixture is mainly composed of CO, CO_2, CH_4, H_2, short-chain hydrocarbons and other gases. The liquid phase represents a complex mixture of long-chain and/or polyaromatic hydrocarbon compounds, which may be contaminated with water, carbon and ash particles. The molecular fragments formed often have double bonds and other compounds, some of which are very reactive. As a result, it can lead to further *secondary chemical reactions* in which the primary products of pyrolytic decomposition continue to react. Favourable conditions for this situation are high temperatures of over 500 °C, high pressures and/or long residence times [36]. In the secondary reaction, Cracking and Recombination mechanisms can take place [37]. During cracking, the breaking of the bonds of volatile components creates molecules with a low molecular weight [38], in contrast, the recombination leads to a combination of volatile compounds into molecules with a higher molecular weight, which can also be volatile [39] [40]. Under certain circumstances, the secondary mechanism can lead to the formation of secondary coal, especially on the hot surface of the pyrolysis coke that has already formed [37] [41] [42]. If the residence time is long enough, homogeneous gas phase reactions and heterogeneous reactions with the solid residual carbon take place. The coke acts as a catalyst for the conversion of oils and vapours into gases [27] [43].

So, generally speaking, pyrolysis is an endothermic process with occasional exothermic phases, which means that, due to kinetic reasons, heat must be supplied in a technical implementation [49], [50]. The gasification reactions already taking place during the pyrolytic decomposition can be divided into heterogeneous gas-solid reactions and homogeneous gas-gas reactions [44] [45] [13].

The relevant heterogeneous reactions are:

Water gas reaction $C + H_2O \leftrightarrows CO + H_2$ $\Delta H_r^0 = + 131{,}0\,kJ/mol$

Boudard balance $C + CO_2 \leftrightarrows 2CO$ $\Delta H_r^0 = + 172{,}0\,kJ/mol$

Hydrogenative gasification $C + 2H_2 \leftrightarrows CH_4$ $\Delta H_r^0 = -74{,}8\,kJ/mol$

Homogeneous reactions:

Water gas shift reaction $CO + H_2O \leftrightarrows CO_2 + H_2$ $\Delta H_r^0 = - 41{,}2\,kJ/mol$

Steam reforming $CH_4 + H_2O \leftrightarrows CO + 3H_2$ $\Delta H_r^0 = + 206{,}2\,kJ/mol$

Hydrocarbon reforming $C_mH_n + {}_mH_2O \leftrightarrows {}_mCO + ({}_m + {}_{2n})H_2$ $\Delta H_r^0 > 0\,kJ/mol$

Equations 2.1 list of heterogenous and homogenous reactions

Table 2.1 shows the three most important pyrolysis processes and their characteristic parameters in comparison. Depending on the heating rate, there are three main categories of pyrolysis: Slow, Intermediate and Fast Pyrolysis [52]. The flash Pyrolysis can be classified as rapid pyrolysis. In addition to the heating rate, the temperature in the reaction zone and the reaction time has the greatest influence on the product quality and composition [15], [53], [54]. Other factors are the particle size, the alkali content, the pressure and the temperature of the pre-treatment [55] - [59]. The slow and medium-fast pyrolysis takes place at very low to low heating rates and long residence times, which lead to an increased formation of carbon [60], [61]. In contrast, rapid pyrolysis is characterized by a higher heating rate with a shorter residence time at the same time.

Pyrolysis process	**Dwell time (Steam) [s]**	**Heating rate [°C / s]**	**Temperature [°C]**	**Particle size [mm]**	**Products [% By weight (DM)]**
Slow Pyrolysis	450-1800	0.1 - 1	350-400	5-50	K: 25-35% Fl: 20 - 50% Gas: 20 - 50%
Intermediate Pyrolysis	10-30	3-8	350-450	1-5	K: 30 - 40% Fl: 35 - 45% Gas: 22-32%
Fast Pyrolysis	0.5-10	10-200	550-750	< 1	K: 29-34% Fl: 46 - 53% Gas: 11-15%
Flash Pyrolysis	< 0.5	> 1000	1050-1150	< 0.2	K: 20-32% Fl: 46 - 51% Gas: 15-22%

Abbreviations: K=char and Fl=liquid * (* bio-oil: mixture of oil and water)

Table 2.1: Characterization of pyrolysis processes. Types of pyrolysis processes, typical Process conditions as well as product yield and composition (based on the dry matter (DM)). Based on [13] [46] [47].

Flash pyrolysis, on the other hand, is characterized by the highest heating rate and the shortest residence time, which leads to a very high yield of bio-oil [46]. The heating rate is of enormous importance in the pyrolysis of biomass with regard to the composition and type of end products [48] [49] [50]. High heating rates reduce the limitations in heat and mass transfer, increase the proportion of volatile components and minimize the time available for undesired side reactions (repolymerization, overcracking, etc.) [51] [52]. A combination of a high heating rate and a short dwell time of a few seconds to minutes are significantly more favourable in order to achieve an optimal yield of bio-oil [46]. In contrast, residence times that are too short lead to only partial conversion of biomass due to the limitation of heat transfer at the particle surface. That is why the residence time of the biomass particles should be longer than the residence time of the resulting steam in order to achieve a higher conversion of biomass and yield of bio-oil [53].

The pyrolysis temperature also influences the yield of bio-oil and its composition [46]. In general, the maximum recovery of the liquid phase is in the temperature range from 400 to 550 ° C [48] [51] [54]. If temperatures of more than 600 °C are exceeded, secondary decomposition can take place, which increases the product gas yield at the expense of the yield of bio-oil and biochar [48]. If the temperature is higher than 700 °

C, the carbon content increases in the form of polycyclic aromatic hydrocarbons in bio-oil [51]. The size of the biomass particles has a direct influence on the heating rate and the release of aerosols and ultimately the product distribution [55]. Very small particles enable aerosols formed to be expelled quickly and the pyrolysis vapours generated do not have to diffuse through the spaces between the cells in order to escape [56] [57]. The limitation of the mass flow increases with increasing particle size [55]. Depending on the pyrolysis process, suitable areas of application can be derived from this [45].

2.2.1. **Slow pyrolysis**

The main goal of slow pyrolysis is to obtain a solid carbon-rich product (pyrolysis coke) with a total content of 30% [13] [36] [58]. The process is characterized by a very low heating rate (< 1 °C/s), a low pyrolysis temperature (300-550 °C) and a long dwell time (5-30 min or sometimes up to 25-35 h) [59] [60]. Slow pyrolysis can also be subdivided in torrefaction (230-300 °C) and Carbonation (approx. 400 °C). Torrefaction is a process used to pretreat biomass in order to increase the energy density, reduce the O / C and H / C ratio and reduce hygroscopicity. The carbonization is distinguished by a very long residence time of several days, which means that there is sufficient time for the conversion of condensable vapours to carbon and non-condensable gases [13].

2.2.2. **Fast pyrolysis**

Fast pyrolysis aims to produce pyrolysis oil: it requires rapid heating, a short dwell time and rapid and efficient cooling of the process gases [61] [62], so as to achieve a high heating rate, the biomass should have a small particle size in order to reduce the limitations of heat and material transport [63]. The short reaction time is intended to minimize secondary reactions and additional gas formation [62] [64]. The heat and material transport as well as the chemical reaction kinetics are decisive due to the short reaction time [65]. The reaction time is less than two seconds for the gas phase [13] and the temperature in the reaction zone should be around 500 °C and in the vapour phase around 400 - 500 °C. After cooling and condensation, a dark brown liquid forms, the calorific value of this is approximately half the calorific value of diesel [13] [31]. The mass fraction of the bio-oil can be 50-75% by weight (DM) [29] [66]. However, the higher the ash content in the biomass, the lower the yield of pyrolysis oil and its calorific value due to the presence of catalytically active minerals [67] [68] [69] [70].

Various reactor types are conceivable for high-speed pyrolysis. A faster heat transfer is achieved with solid-solid contact in contrast to heating with gas, which is why all reactors are heated by direct contact of the biomass with a hot solid (sand or the reactor wall). The general advantages of this process include the low technical complexity, operation at atmospheric pressure, relatively easy to handle liquid main product, low production costs, high thermal efficiency and low use of fossil fuels and consequently almost CO_2 neutral fuel [71]. From the overall energy balance of biomass, rapid pyrolysis oil contains 60 - 70% of the original energy content of the starting material [72]. There are still some unsolved problems for energetic use in engines and turbines because it has relatively low calorific value (16-19 MJ/kg) (due to the presence of high oxygen and water content) [29] [73] and some issue related to oxygen and other chemically active compounds [61] [74] [75] [45].

2.2.3. **Flash pyrolysis**

Differently from fast method, the main feature of flash pyrolysis is the really high heating rate of up to 1000-2500 °C / s and the formation of bio-oil as the main product [66]. This process temperature is between 400 and 1000 ° C and the residence time is 0.1 to 0.5 s. During this action, the heat and mass transfer processes, along with the chemical reaction kinetics, are of great importance. Precise control of the parameters is necessary for optimal process management, on one side, this requires a sufficiently high temperature of the biomass particles for the reaction and, on the other hand, a minimization of the residence time at low temperatures, which otherwise lead to coke formation. To achieve these goals, small particles, which are also present in the fluidized bed, can be used [31].

2.2.4. **Intermediate pyrolysis**

In terms of the reaction conditions and the product composition, Intermediate pyrolysis is in between slow pyrolysis and fast pyrolysis [29] and the aim is also to obtain a good liquid energy source. Typical operating parameters are a temperature of 400 to 500 °C, a heating rate between 200 and 300 K / min and a residence time of 10 to 25 minutes for the solid [29]. Unlike to the solid, the vapour phase usually has a shorter residence time (2-4 s) in the reactor and should be cooled down quickly to avoid subsequent reactions. The intermediate pyrolysis is particularly suitable for a largely balanced production of bio-oil and biochar with the highest possible product quality [76]

[77]. The particle size can be a few mm to a few cm and the water content up to 40%. This offers the possibility of reducing costs for the preparation and treatment of the biomass [45]. In addition, a wide range of biomass can be used, including those with a high ash content.

Since the secondary reactions are much more controlled due to the moderate heating rate, the formation of high molecular tar is significantly reduced and the pyrolysis oil has a lower viscosity [45] [59] [78] [79]. Furthermore, the oxygen and water content can be significantly lower compared to the starting material [80], producing a calorific value of the bio-oil obtained which is quite similar to diesel fuel or biodiesel. Compared to rapid pyrolysis, the yield of pyrolysis oil in intermediate pyrolysis is lower, but the composition of the bio-oil has better properties due to the chemical composition [81]. Since the acid, oxygen and water content are lower, fractional distillation and mixing with conventional fuels is possible: the intermediate pyrolysis oil has a significantly higher potential for use as a biofuel [45] [81]. A special feature of biochar obtained is the brittle texture and the low level of moisture, as it contains less tar and therefore less toxic compounds [59]. In this way, the biochar is suitable for subsequent gasification or used as a fertilizer [59]. This form of pyrolysis of biomass has been researched and continuously developed for over two decades [82]. One of the most important technology is the thermocatalytic reforming (TCR®).

2.3. Pyrolysis products

The products of pyrolysis are *pyrolysis coke, pyrolysis oil and pyrolysis gas*. The yield, composition and quality of the products are mainly dependent on the process conditions and the input material [28] [65]. The secondary reactions and thus the yield of products (gas and vapour phase) depend on the time-temperature curve. The most influencing elements on the product composition are temperature and heating rate. The corresponding relationships are shown in Figure 2.2.

The proportion of gaseous products is higher at a high heating rate in contrast to the low heating rate and the proportion of solid pyrolysis products is correspondingly lower. The reason for this is the limited reaction time for the chemical reactions to take place during the pyrolytic decomposition at a high heating rate [28]. The proportion of liquid pyrolysis products decreases with increasing temperature, whereas the proportion of gas increases. This is due to the thermal cleavage of long-chain organic molecules, which occurs in increasing temperature.

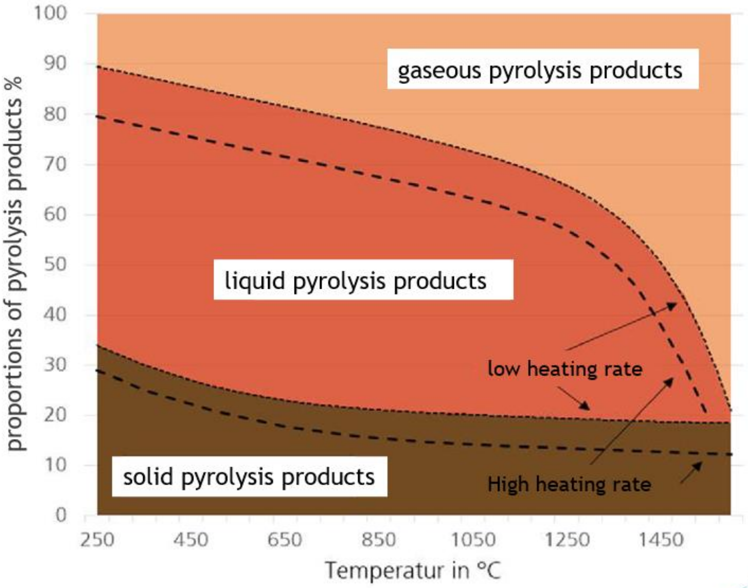


Figure 2.2: Composition of the pyrolysis products with different parameters. Depending on different heating rates and temperatures using the example of wood. Translated from [28]

2.3.1. **Pyrolysis char**

Pyrolysis char is the solid residue from thermochemical conversion and contains carbon and mineral ash [28]. Depending on the temperature, there is a different structure for the residue: up to 300 °C the char has a fibrous structure similar to that of the feedstock; and above 400 °C a crystalline structure is already formed as for graphite from [28]. The pyrolysis char acts as a catalyst for the steam cracking, that is why rapid and effective separation from the steam is necessary [65]. Otherwise, there is the possibility of increased char formation, especially if alkali metals are present [41] [83]. A low temperature, low heating rate and long residence times are necessary for the major formation of char [28]. Possible areas of application for the pyrolysis char obtained are (i) energetic, (ii) industrial, (iii) ground-related and agricultural Application as well as in (iv) Animal feeding, for example co-incineration, gasification, reducing agent in metallurgy and adsorbent [84]. The biochar already has a porous structure as a result of the degassing during the pyrolytic decomposition, which is why it can be used as an adsorbent without prior activation [85]. Furthermore, the carbonate fraction can also be mixed with earth or sand and results in black earth, which serves as a soil improver [86]. The advantages are high fertility, nutrients and humus content and high-water storage capacity [87] [88] [89]. Since most of the original minerals in the biomass remain in the pyrolysis coke, a positive side effect is the storage of CO_2 in the ground, bringing a long-term CO_2-Sequestration and a negative CO_2 Balance is possible [90].

2.3.2. **Pyrolysis oil**

Pyrolysis oil is a complex mixture of hydrocarbon compounds, which can also contain water as well as carbon and ash particles [28]. There are several different organic compounds in pyrolysis oil: acids, alcohols, aromatics, ethers, esters, ketones, aldehydes, phenols, furans, sugars and nitrogenous or multifunctional compounds [74] [91]. The molar mass of the individual compounds is in a range from 18 (water) to more than 5,000 g/mol (pyrolytic lignin) and on average 370 - 1,000 g/mol [91]. In addition, there is an aqueous phase in the oil phase. As a result of the acidic compounds present, the pH value is relatively low (2.5-3.5) [59]. Pyrolysis oil is typically dark brown colour, is fluid and has a pungent or smoky odour [91].

A summary of the relevant physicochemical properties of fast pyrolysis oil from wood and light heating oil as a comparison oil is shown in Table 2.2. Compared to the feedstock, the pyrolysis oil has a lower carbon content because part of the original carbon is contained in the pyrolysis coke [28]. The elemental composition of pyrolysis oil is more similar to the feedstock and thus differs significantly from petroleum [92] [93]. This is also the reason for the significantly higher oxygen content [94]. The typical water content is in the range from 20 to 25% and is completely miscible in bio-oil in this range [59] [95]. If the water content is greater than 40% by weight, there is a risk of phase separation into a water phase and a heavy tar-like mass (high-molecular: lignin). For that purpose, the raw material should contain less than 10% water [50] [96] [97]. Lower water content is advantageous for the transport costs, energy density, stability and acid content of the pyrolysis oil [17]. Most of the water-soluble compounds in oil originate from cellulose and hemicellulose. As a result, pyrolysis oil has a calorific value of around 18 MJ/kg, which is significantly lower than that of conventional heating oil with 42±1 MJ/kg [59].

Parameter	Unit	Light heating oil	Fast pyrolysis oil	Intermediate pyrolysis oil
Carbon (C)	Wt%	90	50-60	75,1
Hydrogen (H)	Wt%	10	7-8	7,6
Nitrogen (N)	Wt%	-	< 0.5	4,9
Oxygen (O)	Wt%	0.01	35 - 40	10,6
Sulfur (S)	Wt%	0.18	< 0.5	1,6
Water content	Wt%	0.025	20-30	<2
ash	Wt%	0.01	< 0.3	0,6
Particles	Wt%	-	< 1	
calorific value	MJ / kg	42.8	13-18	34,4
Density (15 °C)	kg / m^3	830	1100-1300	
Viscosity (40 °C)	mm^2/ s	6	15 - 40	
Flash point	°C	70	40-110	
pH value	-	-	2-3	
Acid number	mg KOH / g	-	70-100	27,7
Distillability	-	distillable	not distillable	

Table 2.2: Comparison of the physicochemical properties of oils. presentation of the Differences between rapid pyrolysis oil made from wood and light heating oil. In arrival based on [75] [98] [99].

The high proportion of reactive oxygen-containing and volatile compounds means that the pyrolysis oil, in addition to its low calorific value, has also a relatively low chemical and thermal stability, especially compared to fossil fuels [74]. During storage, the volatile constituents can evaporate, oxygen can be adsorbed and thereby promote possible polymerisation reactions and lead to phase separation (“aging”) and an increase in viscosity [74] [100]. The oil viscosity depends on the water content and the proportion of volatile components and the storage time, which is why it can vary widely. Furthermore, the pyrolysis oil has a high viscosity and low volatility, a corrosive effect and is not miscible with less polar hydrocarbons [59] [101]. Due to the high polarity, pyrolysis oils are only compatible with other polar compounds such as alcohols. For that purpose, tanks made of stainless steel must be installed for the storage of pyrolysis oil, which are resistant to corrosive attack by bio-oil [73] [92] [95]. An improvement in the storage stability can be achieved if the bio-oil has lower ash and/or water content [102]. Further improvements in the stability can be achieved by removing very volatile compounds and adding a small amount of alcohol [103] [104] [105]. Fast pyrolysis oils cannot be distilled, as reactive compounds polymerize at temperatures below 100 °C and decompose at temperatures above 100 °C [61] [73].

After the extraction, pyrolysis oil can be used energetically and chemically, the possible field of application are: (i) extraction of electricity, heat generation and fuels, (ii) manufacture of chemicals and (iii) preliminary products conceivable for industrial application [17] [31]. However, the oxygen content, the acid number and the concentration of reactive compounds severely limit the applicability [17] [106], that is why all water and organically bound oxygen must be removed for co-processing of pyrolysis oil [17] [73]. Without an effective pretreatment and refinement, pyrolysis oil cannot be used as a substitute for crude oil. The easiest way to use it as a fuel is to add it to diesel, which may require the addition of additives. Problems with the use of pyrolysis oil in diesel engines are the coking of the injection system and deposits in the combustion chamber as a result of the thermally unstable connections and the corrosion of the fuel-conducting components by the acids present. The high water content also has a negative effect on ignition delay and particle formation. The chemical compounds derived from pyrolysis oil can be used in the chemical and food industries to produce resins, fertilizers, flavours, adhesives and acetic acids [17] [31] [73].

The higher amount of liquid fraction produced in fast pyrolysis cannot justify the low quality of oil compared to slower pyrolysis process. In contrast to fast pyrolysis, where only fine raw material can be used to enable the fast heat transfer, intermediate pyrolysis is able to handle larger biomass pieces due to lower heat transfer rates, and also the moisture content can be more than three times higher. Since the secondary reactions are much more controlled due to the moderate heating rate, the formation of high molecular tar is significantly reduced, and the pyrolysis oil has a lower viscosity. Furthermore, a higher calorific value and the presence of fewer oxo-components will give a better economic value and easier industrial handling than the fast pyrolysis oil. This means producing a better-quality oil ready for further chemical applications, such as hydrotreatment, or direct use. In Chapter 2.5 specific case of intermediate pyrolysis is analysed: thermo-catalytic reforming (TCR®) technology which provides advantages compared to established fast pyrolysis technologies regarding the quality of the oil [31] [73] [80] [45] [107]

2.3.3. **Pyrolysis gas**

Pyrolysis gas is a mixture of carbon monoxide (CO) and carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), short-chain hydrocarbons (C_xH_y) and other gases which are gaseous under ambient conditions [28] [91] the calorific value is about 17 MJ / kg [17]. A very high temperature, high heating rate and long residence time should be ensured for gasification [28]. Depending on the application, a more or less expensive gas cleaning is required to remove particles from the gas. For simple direct combustion in power plants or for heating the pyrolysis reactor, this can usually be completely dispensed. In the case of electricity generation (gas engine or turbine), more complex gas cleaning is necessary, which increases further if the pyrolysis gas is to be used in a fuel cell or as synthesis gas. If the proportion of hydrogen in the pyrolysis gas is sufficiently high, the recovery of pure hydrogen by means of pressure swing adsorption could be worthwhile [108].

2.4 Biomass and Sewage sludge: Input materials for thermochemical conversion

Biomass

In principle, all carbon-containing substances can be used as feedstock for thermochemical conversion, in fact to protect global resources and climate, biomass seems to be the most suitable, because it saves fossil fuels, which are becoming increasingly rare, and no more carbon dioxide is released than was previously absorbed by the plants (carbon neutrality). Here, however, the focus should be more on unused waste and residues in order to avoid competition between energy and food crops. In a narrower sense, biomass combines all-natural substances with an organic origin and thus carbon-containing matter. This includes biomass “the naturally living phyto and zoo masses (plants and animals), the resulting residues (e.g. animal excrement), dead (but not yet fossilized) phyto and zoo masses (e.g. straw) and, in a broader sense, all substances, which have arisen or are incurred, for example, through a technical conversion and/or material use (e.g. black liquor, paper and cellulose, slaughterhouse waste, organic household waste, vegetable oil, alcohol) [109]. Also, unrecognized substances such as sewage sludge, animal by-products and paper products are considered as biomass. According to the EU directive2009/28 / EC Biomass includes not only the biodegradable part of waste, products and residues from agriculture but also the biodegradable part from industry and households in the form of waste [110].

It is estimated that there are $3.5 \cdot 10^{12}$ tons dry matter on the continents, about half of which is living or dead biomass [111]. Nowadays the big competition of biomass for energy use is split into the great advantage that it can be stored but also the ethical food issue. A large part of the biogenic residues and waste is already being used for energy or material, so the need for a suitable disposal option is rather low. This situation could open the possibility for more efficient utilisation of unused biomass. The three most common elements in solid biomass are carbon (C), hydrogen (H) and oxygen (O), which together make up more than 90% by weight of the total organic mass (see Table 2.3) [36]. In general, biomass consists of cellulose (50-70 wt.%), Hemicellulose (10- 40% wt.%) and lignin (10-30% wt.%) [41].

	C [Wt% (DM)]	**H [Wt% (DM)]**	**O [Wt% (DM)]**
Cellulose	43.3-44.6	5.6-7.1	48.2-49.5
Hemicellulose	39.9-46.7	5.4-6.1	4.2-6.2
Lignin	51.2-67.4	4.2-6.2	47.4 - 54.0

Table 2.3: Elemental analysis of the biomass components. Mass fractions of carbon (C), Hydrogen (H) and oxygen (O) for the main components of lignocellulosic biomass; based on dry matter (DM) (based on [36])

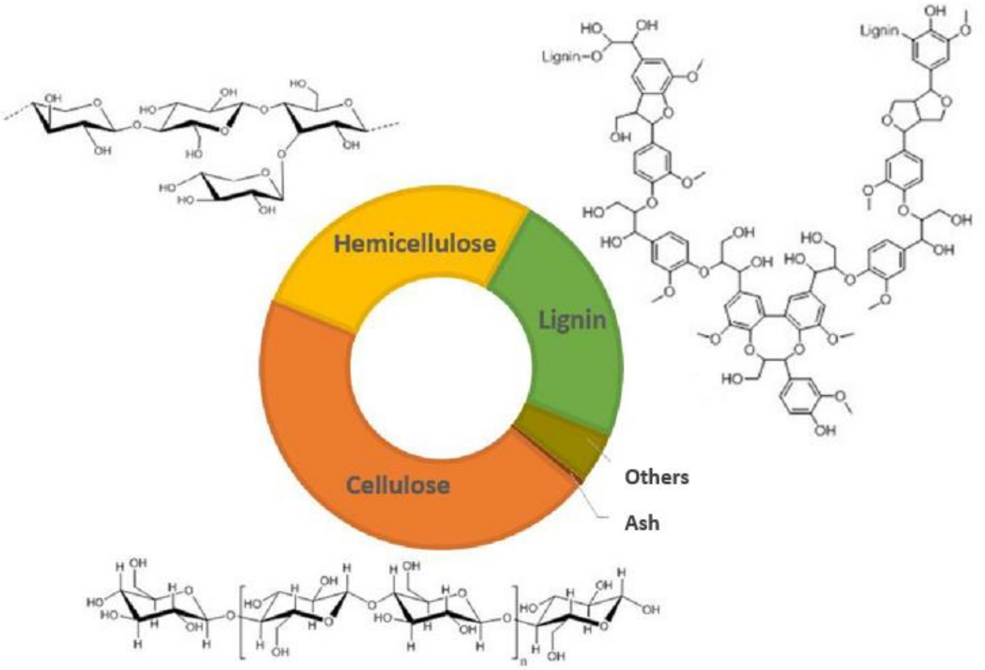


Figure 2.3 Typical composition of biomass, from [112]

Cellulose is a crystalline glucose polymer. The cellulose is built up by linking D-glucose molecules in a 1,4 β-Glycosidic bond and has a degree of polymerization of 6,000 to 14,000. A hydrogen bridge bond is formed through which can form fibrils, and this leads to high tensile strength of the material. This results in the specific stability of the cell walls. Thermal decomposition occurs mainly at 315-400 °C [113] [16] [46].

Hemicellulose is an amorphous polymer consisting of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose) and sugar acids [113]. In contrast to cellulose, hemicellulose is not chemically homogeneous, and the degree of polymerization is significantly lower, 100 to 200. Hemicellulose mainly decomposes at 220-315 °C [113] [16] [46]

Lignin is a large polyaromatic compound with a complex three-dimensional structure, which gives the biomass its rigidity [96]. The formation takes place via a radical polymerization with phenyl propane derivatives as monomers. This formation mechanism leads to a chemically extremely heterogeneous macromolecule. The mechanical strength of the cell walls is increased by the intercalation of lignin between the cellulose microfibrils. As a result of the high carbon content of lignin, the biomass has a high energy content and, in general, lignin is difficult to biodegrade [113]. This process is difficult to get over a wide temperature range of 160-900 °C, with a high proportion of solid residues (~40% by weight) remains. [16] [46].
In addition to the high carbon content, biomass also has a high oxygen content. The remaining portion can be made up of a large number of diverse elements: nitrogen, potassium, calcium, silicon, magnesium, chlorine, phosphorus, sulphur, sodium, iron, manganese, zinc, boron, copper, molybdenum and cobalt [169]. Based on this, the calorific value or gross calorific value can be calculated approximately with empirical correlation from Channiwala and Parikih [114]

Sewage sludge

Sewage sludge is known as the residue that occurs in sewage treatment plants after the mechanical-biological or chemical treatment of the wastewater. Sewage sludge is classified by European Commission as " *a mud-like residue resulting from wastewater treatment. Sewage sludge contains heavy metals and pathogens such as viruses and bacteria. It also contains valuable organic matter and nutrients such as nitrogen and* *phosphorus, and can therefore be very useful as a fertilizer or soil improver*" [115]. Landfilling, thermal, biological, chemical and physical processes are available for subsequent disposal or recycling. In a modern wastewater treatment plant, the wastewater is typically treated in three main stages: the mechanical wastewater treatment (Primary sludge), biological treatment (Secondary sludge / activated sludge) and chemical cleaning (Tertiary sludge). The sludge is most frequently collected and stored together.

Wastewater treatment starts off with mechanical water purification. Substances larger than 5-20 mm and mineral solids are retained by a rake and the sand trap. Subsequently, floating substances are removed in the grease trap and in the primary settling tank, solids are sedimented and cleared into a funnel for further thickening. The primary sludge is produced at this point and for the subsequent biological treatment, the biodegradable pollutants are fed into the aeration tank. The required oxygen is introduced, and the bacteria recirculate via the return sludge: In this way, the bacteria can decompose the pollutants under aerobic conditions and multiply. Subsequently, in the secondary clarifier, the activated sludge is separated from the treated wastewater by sedimentation. The part that corresponds to the growth of microorganisms as a result of the elimination of pollutants, is fed to the sludge treatment as secondary sludge. In the thickener, all sludge produced is collected and thickened to reduce the volume. The decomposable organic substances are decomposed in biogas under anaerobic conditions. There should be a final chemical cleaning of the wastewater using some precipitants and this precipitation can occur through the use of Iron phosphates or aluminium salts [116].

After completion of the Sludge treatment, the sludge can be recycled or treated further, digested sludge, however, has a high-water content of 90-95%. An energy self-sufficient incineration of sewage sludge is only possible from a calorific value of approx. 4.5MJ / kg or a water content of less than 50% by weight. For thermal recycling, the water content is therefore reduced to less than 15% by weight through a drying process [186]. After drying, this results in a calorific value of around 17MJ / kg for raw sludge and around 11MJ / kg for stabilized sewage sludge, which in turn depends on the ash content [117] [118].

Table 2.4 shows the most important properties and parameters as well as the chemical composition of sewage sludge. The loss of ignition indicates the proportion of organic substances in the dry matter and it is important for determining the energetic potential. Sewage sludge consists mainly of organic substances. The ash content is relatively high due to inorganic components [119] and depending on the process and origin, sewage sludge can contain several nutrients such as potassium, phosphorus and nitrogen. Compared to biomass waste and wood-based biomass, the carbon content is relatively low, while the nitrogen content is relatively high [120] [121]. On the other hand, heavy metals can accumulate during wastewater treatment, however, an excessive heavy metal concentration leads to an inhibition of the anaerobic process and, in the case of soil-related applications, to an accumulation of pollutants in the soil. Other critical organic compounds are the polychlorinated dibenzodioxins and furans (PCDD / F), perfluorinated surfactants (PTF), polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAHs).

Material	**Unit**	**Range of values**	**Material**	**Unit**	**Range of values**
pH value		7.7	copper	mg/kg (raw)	300-350
Dry matter	Wt%	30.5	manganese	mg/kg (raw)	600-1500
Loss on ignition	%	45 - 80	nickel	mg/kg (raw)	30-35
water	% By weight (raw)	65-75	selenium	mg/kg (raw)	44317
ash	% By weight (raw)	30-50	Thallium	mg/kg (raw)	0.2-0.5
calorific value	MJ / kg (raw)	44531	Vanadium	mg/kg (raw)	10-100
carbon	Wt .-%	33-50	mercury	mg/kg (raw)	0.3 - 2.5
oxygen	Wt .-%	44105	zinc	mg/kg (raw)	100-300
hydrogen	Wt .-%	44289	tin	mg/kg (raw)	30-80
nitrogen	Wt .-%	44349	AOX	mg kg DM	200-400
sulfur	Wt .-%	0.5 - 1.5	PCDD / F	ng/kg TE	5-100
fluorine	% By weight (raw)	approx. 0.01	PCB6	mg/kg DM	0.01-0.02
chlorine	% By weight (raw)	0.05-0.5	PAK	mg/kg DM	18264
phosphorus	g/kg (raw)	20121	molybdenum	g/kg DM	3.9
antimony	mg/kg (raw)	11079	cobalt	g/kg DM	6.53
arsenic	mg/kg (raw)	11049	Calcium	g/kg DM	71
lead	mg/kg (raw)	70-100	potassium	g/kg DM	2.63
cadmium	mg/kg (raw)	1.5-4.5	magnesium	g/kg DM	9.17
chrome	mg/kg (raw)	50-80			

Table 2.4: Properties and chemical composition of sewage sludge. On the basis at [117] [122] [123][174], [191], [192]. Abbreviations: AOX = adsorbable organically bound halogens; PAH = polycyclic aromatic hydrocarbons; PCB = polychlorinated biphenyls; PCDD / PCDF = polychlorinated dibenzodioxins / furans; raw = reference to the original substance in the delivery condition; DM = dry matter; TE = toxicity equivalent; waf = free of water and ash

Landfilling of sewage sludge decreased sharply in the 1990s and has been banned in this form since 2005 [124]. Since then, untreated waste has no longer been allowed to be dumped without further actions [117], then landfilling has been completely prohibited since the adoption of Directive 2008/98 / EC [125]. At the same time, agricultural utilization rose sharply and has been falling continuously since the end of the landfill. This led to a larger proportion of sewage sludge that is thermally recycled. Soil-related sewage sludge recycling is only permitted if the limit values are complied with. In many cases, however, the soils are already saturated with nutrients through the intensive use of mineral fertilizers, which means that further fertilizer addition is not advisable. In 2017 Germany scenario, the proportion of thermal sewage sludge recycling was already around 70% and the co-incineration and mono-incineration make up the majority of this. In addition, thermochemical processes such as gasification and pyrolysis are permitted [126]. Overall, the aim of the EU regulations is to avoid, minimize, recycle or thermally utilize the amount of sewage sludge [127] [128]. This results in increasing demand in Germany for further systems and processes for the thermal utilization of accumulating sewage sludge.

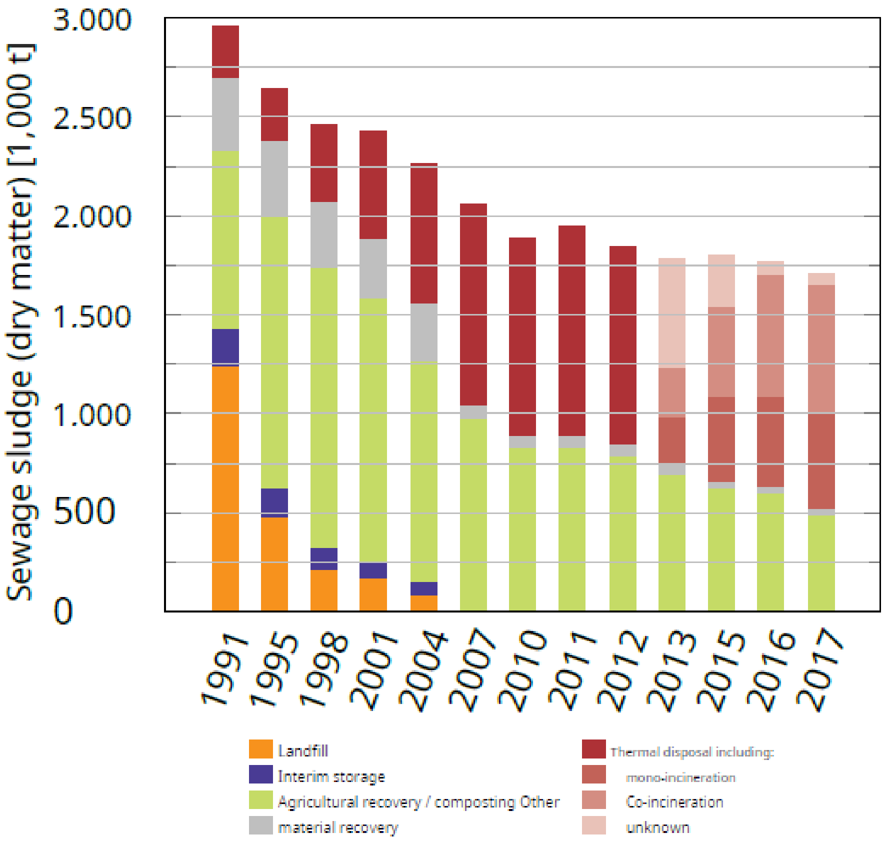


Figure 2.4: Amount accumulated of sewage sludge and its recycling or disposal in Germany. Based on [124]

2.5 TCR® technology: thermocatalytic reforming

Fraunhofer UMSICHT research institute developed a thermo-catalytic reforming process (TCR®) which is a two-stage thermochemical process for converting biomass into energetically and materially usable products, consisting of a screw reactor and reformer. The central processes are the intermediate pyrolysis and the catalytic reforming [129] [130]. A corresponding schematic representation of the process is shown in Figure 2.5. As input materials for the TCR® Process, various substances have already been used successfully: digestate, paper sludge, sewage sludge, wood shavings, olive residues and municipal solid waste [131] [132] [133] [134]. In principle, all biomass and residues are suitable for this process, provided that their structure is suitable for transport by a screw conveyor inside the reactor (such as pellets, wood chips or granules) [129] [130]. For economic utilization, the biomass should have a calorific value of more than 8 MJ / kg and a water content of less than 20% by weight [121] [133]. In contrast to fast pyrolysis, the requirements for the feedstock are significantly lower. Furthermore, the lower heating rate compared to rapid pyrolysis enables the use of particles with a size of up to 50 mm [135].

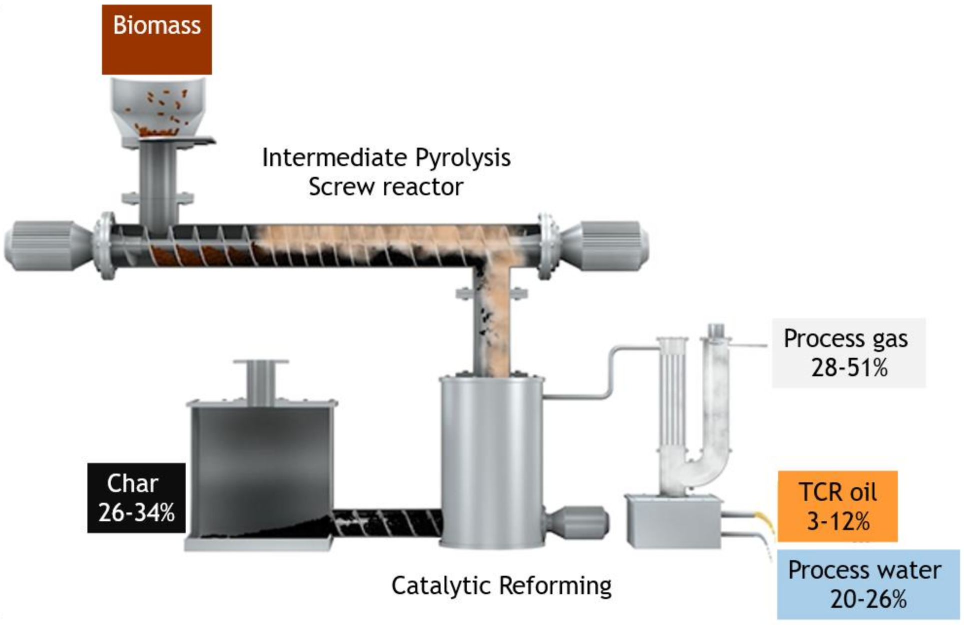


Figure 2.5: Schematic representation of the TCR®-Procedure: it’s evident the two-stage process where biomass reacts initially through an intermediate pyrolysis in the screw reactor, secondly goes to catalytic reformer to upgrade the products quality. Based on [136] [137].

In the first stage, the intermediate pyrolysis takes place at standard pressure and temperature from 350 to 450 °C with a low heating rate of 1 to 20K/s [138] [139] [140]. As a rule, the solids residence time is up to 10 minutes, whereas the process gas formed leaves the reactor after 2 - 10 s [81] while the solids residence time depends on the feed of the feedstock and decreases with a higher feed rate [135]. The first stage is preceded by the loading area and the preconditioning zone, in which the feedstock is fed in anoxic condition and then preheated to 150 °C in order to dry the material [141]. The air exclusion is achieved by a gas-tight storage container or a nitrogen-flushed lock system. In the area of the first pyrolysis zone, there are mixing elements that cause a continuous mixing between the preconditioned and carbonized materials. In addition, the freshly formed carbonate serves as a carbon-based catalyst during the start-up process for cracking, decarbonylation and decarboxylation reactions of the large-molecular and oxygen-containing hydrocarbons and organic acids: these reactions are of great importance for product quality.

In the second stage takes place catalytic cracking or catalytic reforming of the gas and vapour phases: temperature range of 500 to 750 °C is the most suitable [135] [138] [139] [142]. The catalyst used is the carbon fraction (carbonate) formed in the intermediate pyrolysis reactor; this is collected in a heated fixed-bed reactor (post-reformer) and is passed through the gas and vapor phases [141]. In addition to the heterogeneous reactions previously described in the pyrolysis reactor, here a decarboxylation of organic acids takes place, leading to a drastically decrease of the total acid number (TAN) close to zero. Due to the increase of the temperature inside the post reformer, heating the char to around 600 to 700 °C, a further cleavage of C-OX, C-SX and C-NX bonds occurs; this leads to the formation of a very un-polar oil with resulting low water content. The most important reaction inside the post reformer is the saturation of reactive compounds in the TCR vapours by hydrogen: hydrogen is generated on the surface of the hot char by the heterogenous water gas shift reaction. When the in-situ hydrogen gets contact with reactive sides of TCR-vapour compounds, it spontaneous reacts with these centres to saturate them and by this deactivates the reactive sites. This leads to a non-reactive and thereby thermal stable oil. Investigations by *Neumann et al.* have shown that this reforming process is of the greatest importance for product quality [132] [133], in fact the higher the reforming temperature, the higher the gas yield, while the liquid and solids yield decreases [135] and the reactions that take place increase the carbon content and reduce the oxygen in the pyrolysis oil. *Schmitt et al.* have operated the TCR®-Process in a test series with and without downstream reforming and found that the acid number of 23.7 mgKOH / g could be reduced to 5.1 mgKOH / g [135]. In reforming reactions tar formation is almost completely suppressed due to the low heating rate and the draining [133]. Overall, the quality of the pyrolysis oil is improved, which reduces the effort required for further preparation and processing [132] [143]. Both the screw reactor and the reformer are externally heated with electric current at the TCR®-2 (Laboratory scale) and TCR®-30 (Pilot plant scale) with a processing capacity of 2 or 30 kg feedstock per hour [144] [78] [135]. In contrast to this, in the TCR ®-300 (Demonstration scale) and TCR ®-500 take place the external heating thermally, using flue gas from a combustion chamber [144].

Conclusively, the product is separated into solid, liquid and gaseous components. The separation of the non-condensable gases from the condensable vapours is achieved by cooling to about 273 K, which means that liquid can be condensed and separated directly. The liquid phase, in turn, is made up of process water (Hs ≈ 2,4 MJ/kg) and an organic phase and can be further separated due to the non-polarity of the oil and the different densities [155]. Moreover pyrolysis oil has a lower density of 960 kg / m^3 compared to process water (at 288 K) and thus collects on the surface [135] [145].

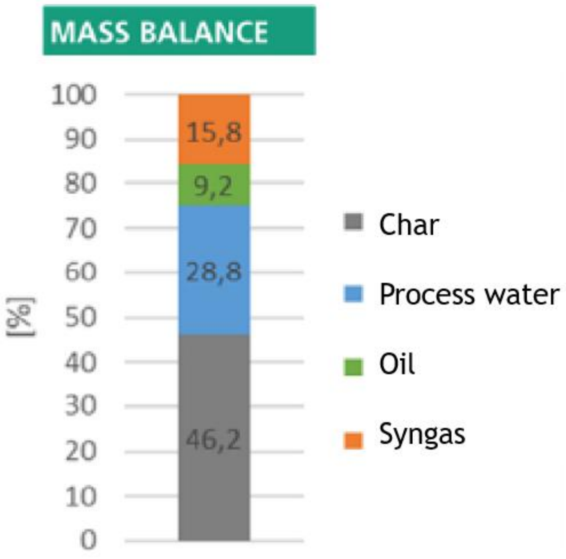


Figure 2.6: TCR®-Products mass balance made from sewage sludge [144]

Bio-oil (3-12% by weight) is the desirable product of the TCR® Process and is a dark brown organic liquid that is very similar in colour to fast pyrolysis oil [135] [146]. The comparison of the chemical and physical properties of TCR® Bio-Oil compared to fast pyrolysis oil and biodiesel is shown in Table 2.5 The high carbon and low oxygen content, which are responsible for the higher calorific value of TCR® Bio-Oil are striking (Hs < 35,6 MJ/kg) compared to rapid pyrolysis oil (Hs ≈ 16-29 MJ/kg) [73] [121] [147]. The resulting calorific value is also dependent on the equipment used as raw material, it reaches the highest value for substrates such as sewage sludge or digestate. It is therefore more similar to biodiesel than to fast pyrolysis oil, due to the low oxygen content and high calorific value [135].

In addition, the low oxygen content has a beneficial effect on the acid number. For the most part, the oxygen-containing compounds are organic acids that cause increased corrosion in the pipes and containers. As a result, the TCR®-Oil through the low oxygen content can be regarded as free of organic acids, which means that storage costs are lower [135]. Furthermore, the water content is also comparatively low, which enables miscibility with ethanol, biodiesel, vegetable oils, gasoline, diesel and crude oil due to a similar polarity [78] [120] [133]. A special feature of the TCR® Bio-oil is the high storage stability and thermal stability, which enables atmospheric distillation without polymerization [82] [121] [148] [149]. The ability to be distilled and miscible enables further processing in conventional refineries oil industry [135] and due to the properties of the oil is possible to direct energetic use as fuel in boilers, combustion chambers or combined heat and power plants. In whatever manner, further processing is necessary for use in conventional diesel and gasoline engines. Catalytic hydrogenation of the TCR® Bio-oil can take place, the oil obtained can be fractionated into standardized petrol (EN228) and diesel fuel (EN590) [78] [150].

Parameter	Unit	TCR® Bio-oil	Fast Pyrolysis oil	Biodiesel
Carbon (C)	Wt .-%	77.4	54.2	77.2
Hydrogen (H)	Wt .-%	7.7	6.9	13.2
Nitrogen (N)	Wt .-%	9.6	0	0.1
Sulfur (S)	Wt .-%	0.8	0	< 0.1
Oxygen (O) [a]	Wt .-%	4.5	38.9	9.4
Water content	% By weight (DS)	1.7	12.8	< 0.1
Ash	% By weight (DS)	< 0.05	0.4	< 0.1
Calorific value [b]	MJ / kg	35.6	20.1	39.3
Acid number [b]	mg KOH / g	4.6	111-200	2

Table 2.5: Chemical and physical properties of TCR®- organic oil, rapid pyrolysis oil and biodiesel. The TCR®-Bioil was obtained from sewage sludge at a reformer temperature of 973K and the rapid pyrolysis oil from wood. On the basis [151] [152] [153] [154]. a Calculation by means of difference; b Based on the dry matter (DS)

Biochar is also produced (26-34% by weight), which consists mainly of carbon and ash [135]. Its proportion of product decreases with increasing reformer temperature due to the release of volatile compounds [41] [155] [132] [156]. The TCR® Biochar has a very low hydrogen (0,17 < H : C < 0,21) and oxygen percentage (0,01 < O : C < 0,02), whereby the O: C ratio provides an indication of the stability of the biochar in the earth [135]. Coal with an O: C ratio between 0.2 and 0.6 has a half-life of more than 1000 years [157]. For this reason, the stability is comparable to hard coal and anthracite coal, which makes it particularly suitable for CO_2 Storage [158]. In addition, the calorific value of TCR® Biochar from sewage sludge as a feedstock (Hi= 8,2 MJ/kg), is between that of raw lignite (Hi = 8 MJ/kg) and hard coal (Hi = 27 MJ/kg) [135] [159]. The TCR® Biochar can be used as fuel or carbon storage because of its large surface area as activated charcoal.

Both the yield and the composition of permanent gases (28-51% by weight) depend on the reformer temperature and the chemical reactions that take place. The basic gas composition is shown in Table 2.6. The proportion of hydrogen in the process gas is heavily dependent on the reformer temperature, high proportion of hydrogen is formed with temperatures of over 1273 K; with 753 K the proportion is less than 10% by volume [160] [161]. *Neumann et al.* achieved, for the gas mixture, a hydrogen content of about 45 Vol % and corresponding calorific value of 18.8MJ/kg with sewage sludge as feedstock and a reformer temperature of 973 K [142]. In general, the calorific value of the TCR® Gas is between 13 and 18 MJ / m^3 [162] [144], as a consequence of the relatively high calorific value, this can be burned directly [135]. The driving force for the hydrogen formation are the water gas shift reaction, the methane reforming at 973 K and the gasification of long-chain hydrocarbons [142]. The comparatively high hydrogen content (< 50% by volume) can be separated from the rest of the gas (e.g. PSA, pressure swing adsorption) and used for processing the bio-oil [135] [121]. From a temperature of 1023K in the reformer, the TCR® process supplies sufficient hydrogen for the complete hydrogenation of the TCR® bio-oil formed [163].

TCR®-Gas	**H_2**	**CO**	**CO_2**	**CH_4**	**CxHy**
Volume fraction %	38 ± 3	8 ± 2	30 ± 3	14 ± 2	3 ± 1

Table 2.6: Composition of the TCR®-Gas with sewage sludge as feedstock. [162]

2.6 Scrubbing theory

As said in the previous chapter thermochemical process produce solid, liquid, and gaseous products. Because of the presence of impurities and many hetero atoms in the starting raw material fed, the syngas produced may contain different pollutants which cause some environmental issue and process system degradation. For this reason, a gas control system is necessary to better treat the entire end of life of the product.

A scrubber is a waste gas treatment system where a gas stream is brought into intensive contact with a liquid, with the aim of allowing certain gaseous components to pass from the gas to the liquid. Scrubbers can be employed as an emission-limiting technique for many gaseous emissions. [164] [165] [166] [167]

In chemistry, absorption is a physical or chemical process in which atoms, molecules or ions enter some bulk phase – liquid or solid material. This is a different process from adsorption, since molecules undergoing absorption are taken up by the volume, not by the surface (as in the case for adsorption). During the process of scrubbing or absorption there is a transfer of components from the gas phase to the liquid phase. The level of gaseous components that can pass to the liquid phase is determined by the ability of these components to dissolve in the liquid. Henry's Law is applicable to the solubility of gases in liquids, for low concentrations and components with a partial pressure < 1 atm:

$$P = H \cdot X$$

Equation 2.2: Henry's law; p = partial pressure (Pa) H = Henry constant (Pa) x = mole fraction

The equilibrium concentration in the vapour phase, which corresponds to a certain concentration in the liquid phase, is determined by the temperature; the higher the temperature in the liquid phase, the higher the equilibrium concentration in the vapour phase. Thus a reduction in temperature has a favourable effect on the yield.
It is possible to increase the load by adding chemicals to the washing liquid, which help to convert absorbed components: organic liquids, chemicals, micro-organisms.
The concentration of polluted substances in out-going gas streams can never become lower than that permitted by the equilibrium between the gas phase and the scrubbing liquid.
The liquid-gas ratio (L/G) in a scrubber is the relationship between the scrubbing liquid flow rate and the gas stream flow rate. For dimensioning purposes, and to evaluate the workings of a scrubber, it is important to know how much liquid is required per m³ to realise the required residual emission.

From a practical point of view, a scrubber consists of three parts: An absorption section (**A**), a droplet collector (**B**) and a recirculation tank with pump (**C**). It can be clearly seen in figure 2.7 [168] [169] [170] [171]

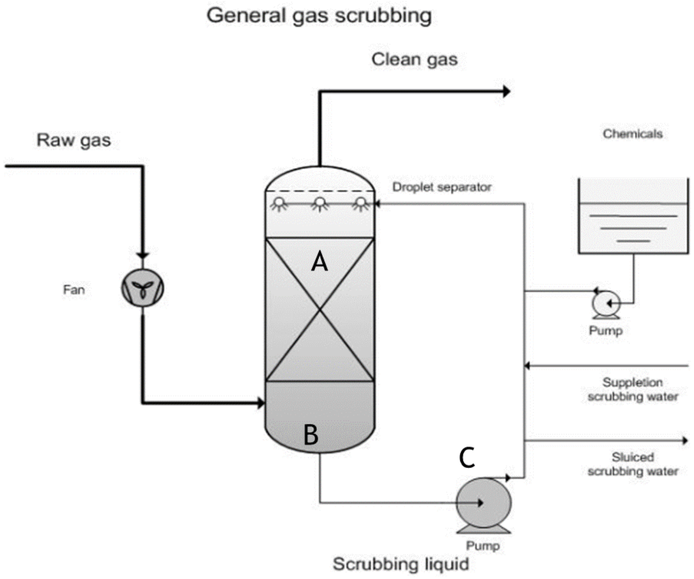


Figure 2.7: shows absorption section (A), a droplet collector (B) and a recirculation tank with pump (C).

The different types of scrubbing technologies can be distinguished in terms of the flow direction of the gas in relation to the liquid.

1. Counter-flow scrubbing: the scrubbing liquid and the raw gas flow through the scrubber in opposite directions. The main advantage of counter-flow scrubbing is that the cleaner the gas becomes, the lower the pollutant concentration in the scrubbing liquid becomes - whereby the driving force is maintained throughout the column.
2. Co-flow scrubbers: the gas and liquid stream flow in the same direction. The scrubbing efficiency of co-flow scrubbers is lower compared with counter-flow scrubbers. However, the advantage they offer is that they are suited to high gas and liquid loads. Co-current scrubbers have a more compact construction and are normally considered when limited space is available and a lower yield is acceptable.
3. Cross-flow scrubbers: the gas and the liquid move across one another. For vapour-like components, the liquid will normally flow in a downward direction and gases will flow horizontally. In dust scrubbing, the sprayers will be horizontal to the gas flow. This type of scrubber is more compact than a counter-current scrubber, if one works with a multi-stage set-up, and uses less electricity.

Another method to distinguish gas scrubbers is by the design of the scrubbing section:

Gas scrubbers without built-in device:

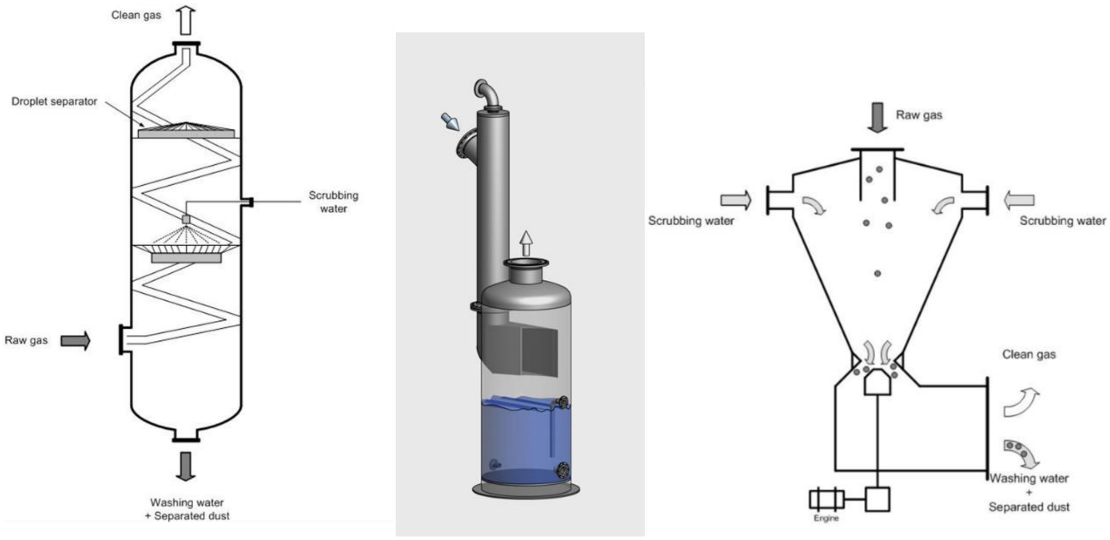
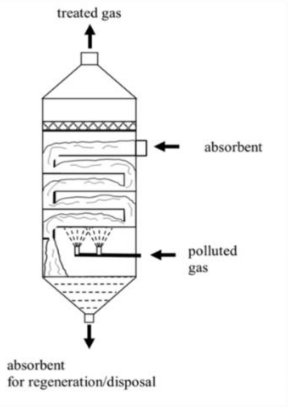


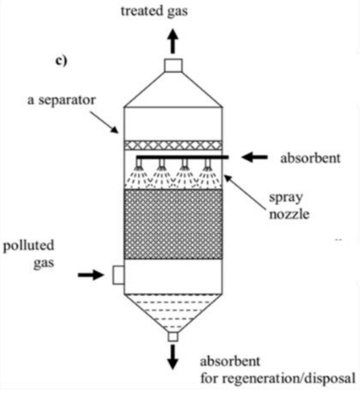
Figure 2.8 Scrubber without built-in system: spray tower system, jet scrubber, venturi scrubber

- Spray towers: In spray towers the water is dispersed in fine droplets, normally via sprayers at the top of the scrubber, while the gas is fed from underneath – thus in counter-flow. Set-up is also possible in co-flow or cross-flow formats, and those can be also used as a dust scrubber.
- Jet scrubbers: At the top of the jet scrubber a washing liquid is injected through special thrust nozzles and finely dispersed to produce a maximum gas/liquid exchange surface, causing drops with a high speed with respect to the gas flow. Due to the big input of energy, the jet scrubber can collect and transport the gases autonomously. This injector effect allows the purification of exhaust gases without generating a pressure loss on the gas side, therefore, no mechanical fan is typically required to suck and transport the gas.
- Venturi scrubber: A venturi scrubber consists of a converging section, a throat (the narrowest part of the venturi tube) and a diffuser. The gas flows through the venturi tube and reaches top speed in the throat section. Thereafter, the gas passes into the diffuser where the speed of the gas drops once again. The liquid is added to the gas flow either in the throat section or prior to it. Intensive mixing takes place between the gas and the liquid in the throat section of the venturi tube. Due to the high speed realised by the gas and liquid, the water is broken down into fine water droplets. Can also be used as a dust scrubber.

Generally speaking, if gas flow contains a lot of solid particles or other components that could lead to cake-forming and blockage, scrubbers without built-in devices are more suitable because less sensitive to these. Anyhow, it is always necessary to consider the type of solution treated in the scrubber and adapt the best technology to clean it and avoid long maintenance periods.

Gas scrubbers with built-in device (bulk packing):





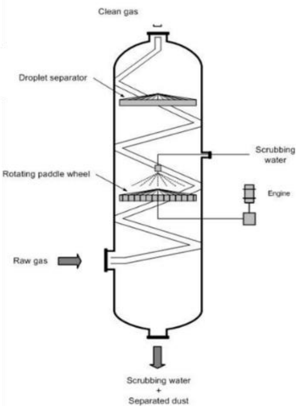


Figure 2.9 Scrubber with built-in system: plate column, packed column and rotation scrubber systems

- Plate column: A plate column is a column that is divided into segments by perforated plates. The perforations have been designed in a way that forces the raw gas to bubble through a sealed fluid layer on the plates, which is where absorption takes place.
- Packed columns: Scrubbers with packed columns are filled with structured or unstructured packing material. This material has a high specific surface area, which means a large phase interface is created between the gas and the liquid and the scrubbing liquid flows downwards in a thin film over the packing material, while the gas flows upwards through the remaining free space. In scrubbers with packed columns, the liquid and the gas do not disperse into one another. Because of the multi-functionality of packing material inside the system, this type of scrubber is really adapted for absorption applications.
- Rotation scrubber: In rotation scrubbers, a fast-rotating spray, breaks the scrubbing liquid down into small droplets. Whereby a large contact area is created between scrubbing agent and gas. As a result of the rotating sprayer, dust particles are forced to the sides of the scrubber and separated. Rotation scrubbers are primarily used as dust scrubbers.

In summary scrubber systems present many advantages for gas purification process: broad applicability, high removal yield (till 99%), compact installation and easy maintenance, the technology used is relatively simple, they can be used to cool hot gas flow. On the other hand, some disadvantages must be considered: the wasted liquid must be treated, the use of liquid reagents represent an economic cost, susceptibility to frost, if also dust is simultaneously collected, drainage is necessary, packing material could possibly be susceptible to blockage by dust (> 10 mg/m^3) and fat. For these reasons every process needs to be previously considered and tested in order to achieve the desired goal and not having gas related issues.

2.7 Specific case: H_2S gas scrubbing

Bioenergy recovery from biomass resources may be achieved via the employment of several biomass conversion pathways. TCR® technology represents an efficient way to obtain valuable products from initial wasted biomass. Focusing only on the TCR®

Gas product obtained, because of its properties and average composition, it can be compared to general biogas treatment, even if the final composition will depend on the raw material used during the thermocatalytic conversion.

The treatment of biogas is a widely discussed and studied topic, for this reason, these already known technologies can be adapted to the TCR® process by integrating with the appropriate systems and necessary knowledge. [172] [173] [174] [175] The biogas product is typically composed of carbon dioxide (CO_2) and biomethane (CH_4), which represent the main percentage fractions, but also carbon monoxide (CO), ammonia (NH_3) and other light hydrocarbon residues. However, the degradation of sulphur containing organics, like proteins, and the reduction of anionic species, like SO_4^{2-}, will generate hydrogen sulphide (H_2S), which is a toxic gas even at low concentration. High H_2S concentration in biogas is undesirable, since there is a risk of H_2S release (during biogas collection and transfer) which may lead to pulmonary oedema in humans at concentrations higher than ~400 mg/m^3 (≈ 0.029% v/v). Furthermore, the utilisation of biogas containing H_2S as a biofuel for combined heat and power generation also has the potential of leading to the corrosion of engines, rapid degradation of engine lube oil, and poisoning mechanical systems/reactors. The combustion of biogas containing H_2S also leads to the formation of sulphur dioxide (SO_2), via the reaction presented in Equation:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

Equation 2.3: sulphide oxide formation

SO_2 is a precursor for acid rains formation that is responsible for several negative impacts on the environment, such as the destruction of agricultural vegetation and pollution of the surrounding aquatic environment. It is also possible for the formation of H_2SO_4, which is a strongly corrosive acid that may be formed when H_2S reacts with water, leading to corrosive effects on equipment. It is therefore necessary to ensure that the H_2S content in biogas is minimised, thus limiting the occurrence of the negative effects discussed above. Indeed, the European committee of standards specifies that the preferred biogas product for use as biofuel should have a H_2S concentration of <20 mg/m^3 (≈ 0.0015% v/v).

The behavior of H_2S in liquid solution is highlighted in equations 2.4: the formation of soluble sulphides (HS^-) in the solution will release a proton (H^+) leading to acidic conditions.

$$H_2S \leftrightarrows H^+ + HS^-$$

Equation 2.4: dissolution of hydrogen sulphide

The concentrations of the species of HS^- and H_2S in the aqueous phase are determined using the Henderson–Hasselbach, relationship

$\mathrm{Log}_{10}\,[HS^-]/[H_2S] = pH + \mathrm{Log}_{10}Ka$ Ka first ionisation constant of H_2S 9.1×10^{-8}

Equation 2.5: Henderson–Hasselbach relation

It is clear that the concentrations of H_2S and HS^- within the system are in mutation depending on the pH value that the same system has, as shown in Figure 2.10.

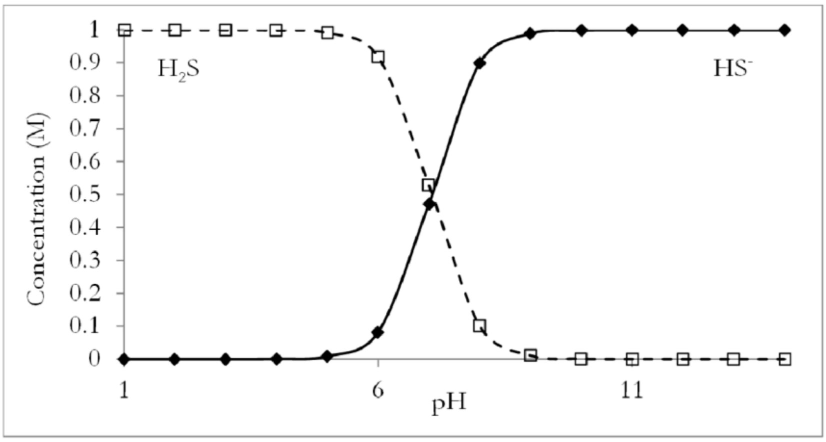


Figure 2.10: Illustrating the variation of concentrations of dissolved hydrogen sulphide (H_2S) and bisulfide (HS^-) in an aqueous solution with pH. [173]

Because of the negative features of hydrogen sulphide gas present in the TCR products, it requires an important gas treatment in order to reduce the possible emissions or presence in the system. For this purpose, desulfurization processes can be divided into: biological, chemical and adsorptive processes. [176] [177] [178] [179]

In biological desulphurisation, sulphur bacteria (thiobacillus) are settled at a certain point on the gas path from the fermenter to the gas utilization or further processing. If small amounts of air are added (between 2 and 5% of the amount of gas produced daily), these bacteria oxidize the hydrogen sulphide (H, S) using the oxygen in the air to form elementary sulphur and sulphate. Due to the air admixture, the biogas has an increased nitrogen and possibly oxygen content and therefore the methane content required for further processing of the biogas into bio-methane may not be achieved.

Chemical desulfurization includes the precipitation of H_2S with iron salts such as iron chloride $FeCl_2$ or iron sulphate $FeSO_4$, alternatively iron hydroxide $Fe(OH)_3$ or iron oxide Fe_2O_3.

$FeCl_2 + H_2S \leftrightharpoons FeS + 2HCl$

$2Fe(OH)_3 + 3H_2S \leftrightharpoons 2 FeS + S + H_2O$

$Fe_2O_3 + 3H_2S \leftrightharpoons 2FeS + S + 3H_2O$

Equation 2.6: Chemical desulfurization

The respective iron compounds are added to the fermenter: hydrogen sulphide is converted into iron (II) sulphide (FeS) and sulphur (S) in the fermentation tank, as shown in equations. The water-insoluble iron (II) sulphide and the elemental sulphur are then discharged. This type of dosing desulphurisation approach for sulphite precipitation using salts of Fe^{2+} and Fe^{3+} constitutes an easy approach that can be readily retrofitted to existing plants, such that handling and monitoring concerns are minimal. However, while the method is clearly straightforward, the employment of chemicals to aid sulphide precipitation suggests a constant dosing requirement if the desulphurisation process is to be sustained. The need therefore arises for the introduction of auxiliary equipment, such as pumps, to maintain a chemical supply, thus increasing the number of unit operations. Many studies for large system are required to be processed, in fact a possible limitation to the utilisation iron salts for sulphide removal is the risk of system clogging due to the accumulation of precipitated metallic sulphides along the piping line, very good byproduct for second life use, but not for the maintenance of the system itself.

In "classic" absorptive desulfurization, the gas is passed through a column filled with an alkaline medium (e.g. NaOH). When using sodium hydroxide (NaOH), as an example, the hydrogen sulphide reacts to sodium hydrogen sulphide (NaHS), which can then be separated. Regular addition of the alkaline medium is necessary to maintain the process.

Adsorptive desulfurization. A higher level of de-attenuation can be achieved by using impregnated or doped activated carbon. The doping can be done with potassium iodide, potassium carbonate or potassium permanganate. In such a method, the activated carbon is fixed in a container and from the raw flows through biogas. The hydrogen sulphide contained is adsorbed on the impregnated or doped activated carbon and is there through a catalytic reaction (Oxidation) converted. Regeneration of the activated carbon used is in principle possible, but relatively expensive. Therefore, the use of activated carbons is only for fine desulphurisation.

Nowadays different purification reactors or system can be easily installed to eliminate the presence of H_2S; the most classical methods have been overtaken by new “green” one, however sometimes is possible to combine two technologies and having good compromise. At the end of every possibility, the efficiency and final economic cost will weigh the most. In order to give a qualitative overview of the possible purification approaches it is shown in figure 2.11 the comparison between different methods and their economical sustainability.

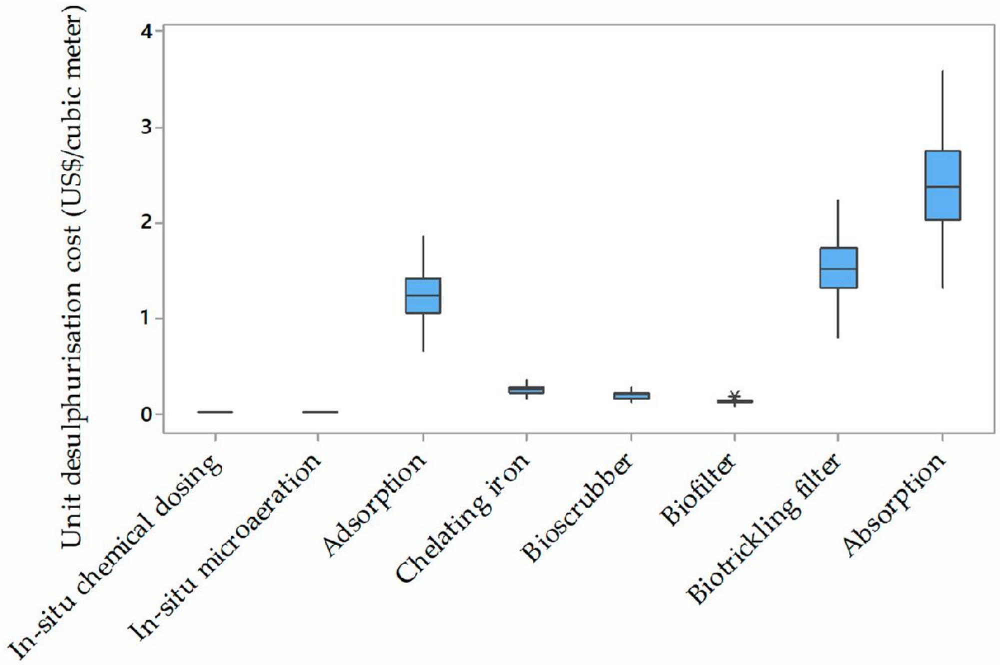


Figure 2.11: the unit costs for different desulphurisation technologies, [173]

The unit desulphurisation cost associated with in-situ chemical dosing (CD, using **$FeCl_2$**) and microaeration (MA) approaches are estimated to be the cheapest. The low unit desulphurisation of CD is consistent with a previous study where reduced capital, maintenance, and repair costs were identified as significant advantages of the CD approach compared to other ‘post-digestion’ biogas scrubbing desulphurisation approaches. It must however be emphasised that the introduction of chemicals into the reactor to minimise H_2S formation may also present negative effects on microbial activity, leading to diminishing biogas yields. In addition to possible challenges of diminished microbial activities due to the introduction of chemicals to the digester, there may be additional environmental costs associated with the disposal of the resulting sludge containing Fe^{2+} and Fe^{3+} compounds in surrounding land. Although iron (i.e., Fe^{2+} and Fe^{3+}) constitutes an essential nutrient for plants, excessive amounts in soil may have toxic effects on plants due to its accumulation within plant cells. The higher cost of the MA desulphurisation method compared to the CD method may be due to the additional cost associated with the purchase of auxiliary technologies, such as pumps for oxygen and air supply.

The figure 2.11 also shows that the *traditional* absorption desulphurisation strategy using **NaOH** constitutes the most expensive desulphurisation strategy, which is about 10 times the cost of H_2S absorption using the chelating iron. This high cost may explain why this approach is nowadays rarely employed as a viable desulphurisation strategy. In addition to the high cost of traditional absorbers using NaOH, a high technical requirement is necessary to handle the caustic (NaOH) solution and manage associated secondary pollution challenges, since NaOH is typically not regenerated from its Na_2S and NaHS reaction products. A comparison of the unit desulphurisation costs using biotrickling filters (BTFs), biofilters (BFs) and bioscrubbers (BS) shows that the BF system is the cheapest desulphurisation strategy. This observation is not unexpected since BF presents a simple design, composed of a fixed bed, equipped with cheap bedding materials and easily acquired microbes.

As far as the treatment of gases in the TCR® system is concerned, trying to obtain the most effective and economical result at the same time, the chemical dosing reagent strategy with $FeCl_2$ adapted to a usual absorption reactor would seem to be compatible. Specifically, the liquid reagent would also be useful for purifying ammonia residues present in the TCR® gas and easy to handle for daily operations. The reactor with scrubber function would have more compact dimensions than a conventional digester with attached microbiota and nutrients to manage.

Scrubbing reaction description:

When hydrogen sulfide (H_2S) goes into solution in water, a hydronium ion (H_3O^+) and hydrogen sulfide ion (HS^-) are formed. The sulfur is precipitated by consecutive reaction with iron(II) chloride ($FeCl_2$), in which solid iron(II) sulfide (FeS) precipitates and hydrogen chloride (HCl) is formed. [173] [180] [181]

$$H_2S + H_2O \leftrightarrows H_3O^+ + HS^-$$

$$FeCl_2 + H_3O^+ + HS^- \rightarrow FeS\downarrow + 2HCl + H_2O$$

Equation 2.7: Scrubbing reaction of hydrogen sulphide with $FeCl_2$

Since ammonia is also present in the gas flow leaving the TCR® process together with hydrogen sulphide, it is advisable to specify the scrubbing of this second component. Ammonia (NH_3) acts as a base and reacts with water to form hydroxide ions (OH^-) and Ammonium (NH_4^+). Neutralization can be achieved by the presence of an acid such as hydrochloric acid which is formed during the sulphur precipitation. As products of the neutralization of the acid and base form ammonium chloride and water. [250]

$$NH_3 + H_2O \leftrightarrows NH_4 + OH^-$$

$$NH_4^+ + OH^- + H_3O^+ Cl^- \leftrightarrows NH_4 + Cl^- + 2H_2O$$

Equation 2.8: scrubbing reaction of ammonia with $FeCl_2$

According to the Principle of Le Chatelier a alkaline pH value is favourable for the solution of hydrogen sulphide in water, whereas an acidic pH value is effective for ammonia.

2.8 Environmental background: CO_2 contribution and LCA study on TCR® 500

The IPCC's Sixth Assessment report finds that global warming of 1.5°C and 2°C will be exceeded during the 21st century unless deep reductions in carbon dioxide (CO_2) and other greenhouse gas (GHG) emissions occur in the coming decades. Following the inexorable climate change underway and all the technical-political treaties that are promulgated by entire nations, today the sustainability of a product and respect for the environment must go hand in hand with the evolution of technologies. [182]

In recent years, TCR® technology has been subjected to various sustainability studies to verify the effective positive contribution in terms of CO_{2eq} emissions and further analyses of its integrated LCA cycle (still in progress)

CO_2 process balance**:** [183]

It is often said the simplified assumption that when energy is generated from biomass or products no more carbon dioxide can be released than was previously withdrawn from the atmosphere during plant growth (through photosynthesis). On closer inspection, however, it quickly becomes apparent that various influences, including the mechanical effort involved in plant cultivation and harvesting, plant fertilization and the application of protective agents, biomass transport and various downstream processing or conditioning steps were not taken into account. A deeper and internal inspection provided by Fraunhofer researchers shows a holistic view, following the ordinance on requirements for sustainable production of biofuels (Biokraft- NachV). All these aspects which require energy and consequently also go hand in hand with GHG emissions are taken into account, from the first step to the final use.

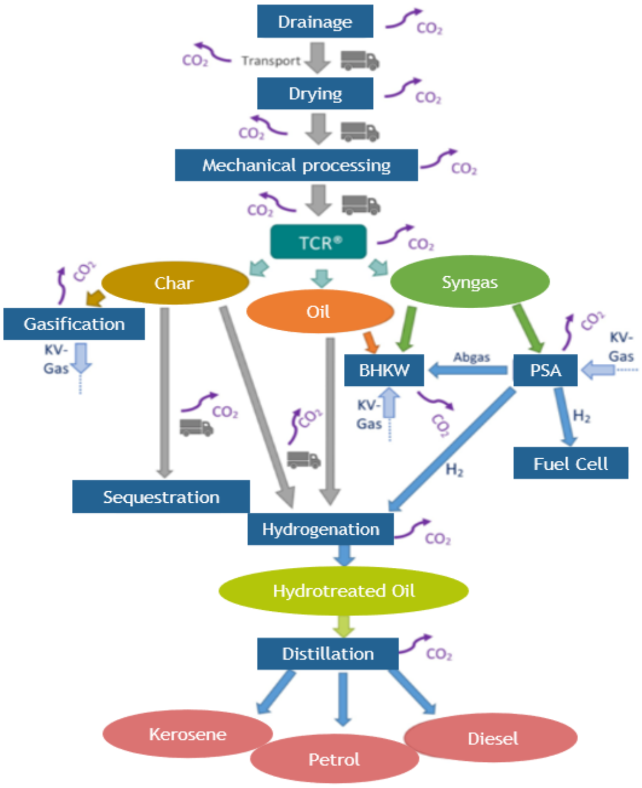


Figure 2.12: Example of possible CO_2 emission road

Depending on the scenario hypothesized, the greenhouse gas reduction potentials of at least 60% are achieved by TCR®-Fuels, compared to conventional fuels required from 2018 according to Biokraft-NachV. Due to the high savings potential of more than 90%, mainly due to carbon sequestration provided by biochar storage capacity, the fuels produced using this process offer the best prerequisites for establishing themselves on the market in the long term. TCR® Product offers a long time alternative to a wide variety of petroleum products and TCR®-Technology shows the potential to make an important contribution to environmentally friendly fuel production, while at the same time conserving resources through the use of residual and waste materials.

LCA tosynfuel [184] [185] [186] [187]

The International Energy Agency (IEA) Bioenergy Task 42 defines biorefining “the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and/or materials) and bioenergy (biofuels, power and/or heat)” (IEA 2017). The emerging advanced biorefineries based on more sustainably-derived bio-mass feedstocks and cleaner thermochemical and biological conversion technologies promise to be a more sustainable and environmentally benign system than the conventional biorefineries (IEA, 2009).

The application of Life Cycle Assessment (LCA) to advanced biorefineries appears fundamental to assess their environmental performances and measure the overcoming of limitations shown by conventional biorefineries.

External experts from the University of Bologna are evaluating the environmental performances and sustainability of current sewage sludge management (incineration, landfilling, agricultural use) and comparing it with the innovative solutions investigated in TCR technology to produce biofuel. Specifically, the sustainability of the TCR®-PSA-HDO integrated system is being analysed by means of LCA according to ISO 14040 and ISO 14044 and calculation of Greenhouse gases (GHG) emission savings according to Renewable Energy Directive (RED). The system boundaries analysed include the entire life cycle of the biofuel from source to usage, which considers sewage sludge collection, biofuel production by TCR®-PSA-HDO, and the distribution and use phases of the biofuel.

The Greenhouse Gases Emission of biofuel produced by the TCR®-PSA-HDO integrated system is evaluated and compared with conventional fuel (diesel and gasoline). The results are encouraging in accordance with the sustainability objectives defined by the Renewable Energy Directive, in particular with respect to some impact categories such as Climate Change, Acidification, Freshwater Eutrophication and Ionizing Radiation, Ozone Depletion and Photochemical

The results of these studies show that sludges have the potential to become a renewable energy source thanks to the use of new thermochemical technologies, such as pyrolysis followed by a reforming stage using biochar as catalyst. A net energy production of about 2 MJ per kg of dry, ash-free, sludge can be obtained by directly processing the sludge. Such a processing configuration shows avoided GHG emissions of about 0.5 kg CO_{2eq} per kg of dry, ash free, sludge. The reduction in waste volume and weight obtained by the process is substantial, which helps operators to save gate fees. Moreover, the very high temperature of the pyrolytic process guarantees the sanitation of the sludge and the decomposition of harmful pharmaceutical and other molecules.

3 Materials and method:

3.1 ToSynFuel plant: integrated TCR®+PSA+HDO

ToSynFuel Project, financially supported by the EU funding program Horizon 2020, is characterized by the presence of TCR®-500 which reproduces the thermochemical conversion of sewage sludge with a nominal capacity of 500 kg/h. The aim is to demonstrate the feasibility of an integrated process consisting of central elements of thermocatalytic reforming (TCR®), hydrogen production using pressure swing adsorption (PSA) and hydrodeoxygenation (HDO) with fully automated operation of 7000Bh / a [188] [121] [189] [134] [143] [162].

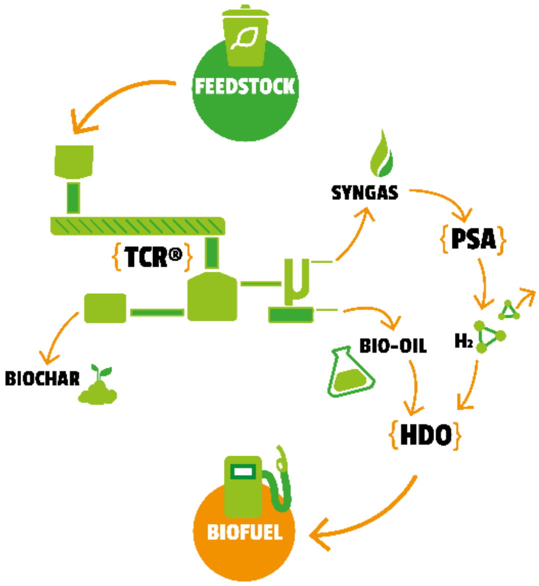


Figure 3.1: To-Syn-fuel process scheme.

The corresponding representation of the overall process plant is shown in Figure 3.2. In detail, the process consists of the (1) Entry system, (2) Screw reactor, (3) Post reformer, (4) the Gas treatment, (5) the Combustion chamber, (6) the Coal store together, (7) Pressure swing absorption and (8) Hydrodeoxygenation.

Figure 3.1 shows the schematic idea of the integrated approach

Figure 3.2 Representation of Tosynfuel project plant, placed in Hohenburg. Fraunhofer Umsicht property

The TCR®-500 is a thermally heated plant to convert 500 kg/h of dried biomass into high-quality products named TCR® bio-oil (approx. 50 L/h), TCR®-syngas (approx. 100 Nm³/h), and TCR® carbonisate (approx. 250 kg/h).

The main chemical reactions of TCR®-500 happen in the two reactors stages, which is composed of the auger reactor (2) and the post reformer (3). In order to give the calorific energy required, the combustion chamber is present (5) with a heat gas distributor. The product gas train (4), where the gas is treated in order to obtain as much as possible clean hydrogen eliminating pollutants, consists of a hot gas cleaning system, a condensation stage, and a scrubber. The starting feeding system (1) feeds the TCR® plant with sewage sludge and a char extraction system (6*) removes the carbonisate outside the plant.

Concerning these last two components, the feeding system (1) feeds the auger reactor with dried sewage sludge (water content approx. 10 – 15%). Here a chain conveyer transports the biomass from a feed storage to a sluice system that ensures that the TCR®-500 plant stays inertised. Downstream of the sluice system a calibrated dosing screw feeds the auger reactor with 500 kg/h of the dried sewage sludge. After the post reformer the char extraction screw (6*) with a jacket and inner tube cooling system transports outside into storage silos the carbonisate to a chain conveyer and cools the char to temperatures lower than 90 °C.

The first reactor stage, the green auger itself (2), is approx. 8.6 m long, has a diameter of 0.76 m and operates with a rotational speed of 4 – 5 rpm. These features lead to an intermediate pyrolysis process, whit a retention time of 8 – 10 min where the feedstock is heated to approx. 450 °C and converted into char and vapours.

The second reactor stage is the so-called post reformer (3) that heats up the char and vapours to approximately 650 °C and the catalytic reforming takes place. This is the key step for the production of better-quality oil, than a traditional fast pyrolisis or just an intermediate one. Here the solid char operates as a catalyst, which leads to high hydrogen content of up to 40 Vol.-% in the TCR®-syngas. Furthermore, the tar production issues within the product gas treatment system are avoided because of the cracking of long hydrocarbon chains due to the high temperatures. Instead meeting the requirements for biofuels and good storage features, the reduction of acids in the gas stream leads to low total acid numbers (TAN) of the TCR® bio-oil.

The post reformer and the auger reactor are heated up by the combustion chamber (5) which burns propane and the resulting flue gas with approximately 900 °C provides the heat for the system. A flue gas distributer distributes the flue gas to the post reformer and the auger reactor in a way that both components are operating at set temperatures.

Concerning the treatment of gases (4) produced in the system, after the post reformer, a two-stage hot gas cleaning system is present that removes dust from the vapours. The first stage is a multi-cyclone that removes coarse particles. At the second-stage, two parallel-operated ceramic fiber bag filters clean the gas from fine particles. Thank to this "twin system" is possible to switch the vapour flow to the second filter If one of the filters is fully loaded with dust. The recovery of the first filter is possible due to a jet stream cleaning with nitrogen.

The dust-free vapors then flow through a gas cooler that reduces the gas temperature to approx. 20 – 35 °C letting the separation of the TCR® bio-oil and process water from the TCR®-syngas. The liquid fraction (bio-oil and water) is divided thanks to a gravimetric separator.

Then a wet scrubber system cleans the syngas from H_2S and NH_3 with an iron chloride solution: here the H_2S is removed to protect the components downstream the TCR®-500 from corrosion, instead the NH_3 is removed to reduce NO_x emission at combustion process of the TCR® syngas.

The final stage of the TCR®-500 is an electrostatic precipitator (ESP) to remove aerosols from the gas stream.

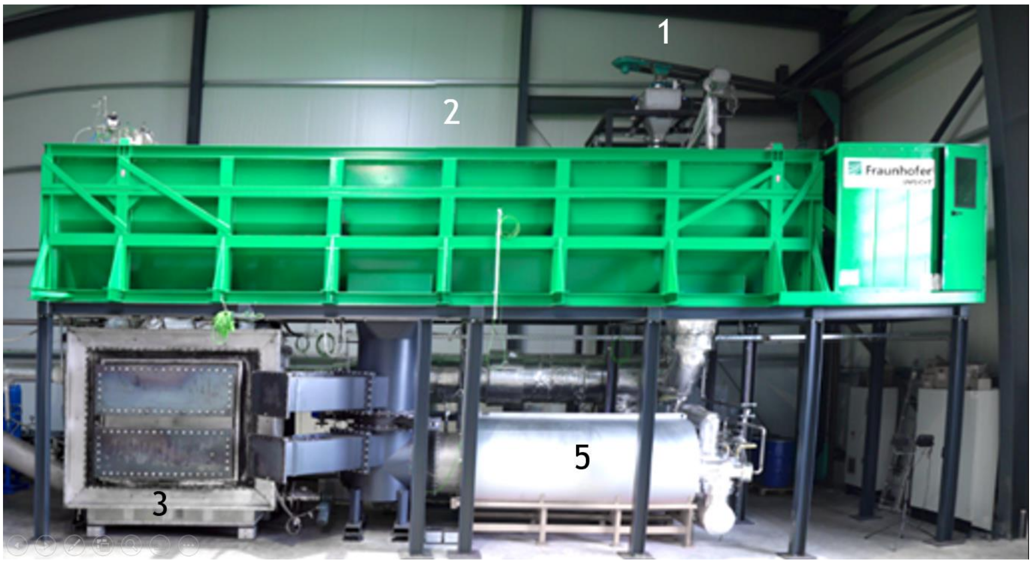


Figure 3.3: the first stage of the TCR process with feeding system (1), auger reactor (2), post reformer (3) and the combustion chamber (5). Fraunhofer Umsicht property

After the gas phase has been cleaned, it is compressed, and the hydrogen contained is then separated using pressure swing adsorption (PSA) with a system provided by HyGear (7). The remaining residual gas mass flow is used in a combined heat and power unit (CHP) to generate thermal and electrical energy. In the end, the organic crude oil and the high-purity hydrogen are then brought together into the Hydrodeoxygenation reactor (HDO) (8) in order to reduce the oxygen content and improve the oil quality. The hydrogenation step is required since the TCR® bio-oil has more heteroatoms, like N, O, S, then the allowed amount for DIN-Fuel. The hydrogenated oil goes through a strip column to remove the undesired by-products from the processed oil. Fuels such as standard-compliant diesel and petrol can be obtained from the TCR bio-oil processed in this way. For this purpose, a fractional distillation of the bio-oil could be implemented and integrated at a later point in the project.

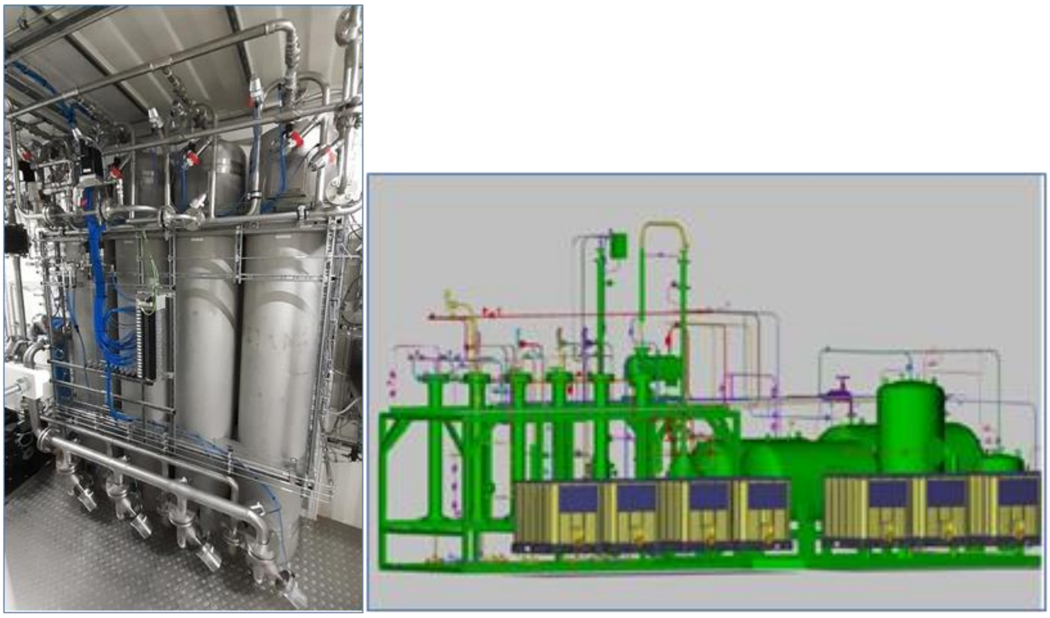


Figure 3.4 The PSA unit (7) on the left and the schematic HDO stage (8)

3.2 Gas Scrubber

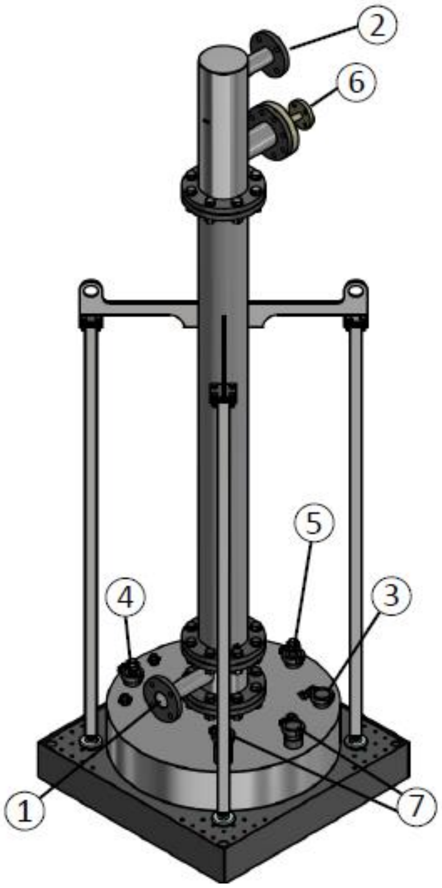


Figure 3.5: Three-dimensional representation of the gas scrubber.

Scrubber technical feauters:

The total height of the gas scrubber is 3007 mm on a footbase of 900 mm x 900 mm, the central pipe section has an inner diameter of 162.3 mm, in which the Pall®-Rings 25 bulk with a specific surface area of 220 m^2/ m^3 are located [190]. This results in a volume of 0.036 m^3 and an effective surface of 7.92 m^2 for the bulk. Their task is to increase the surface area for the mass transfer between the liquid and gaseous phase and the dwell time. The reservoir below, with an inner diameter of 794 mm and a height of 161 mm, has a capacity of less than 79.7 L. Normally, the incoming TCR®-Gas has a temperature of less than 40 °C and an overpressure of 50 mbar following the gas cooling and the cold electrostatic precipitator.

Raw gas inlet flange is highlighted in figure 3.5 by number (1). The gas flows through the gas scrubber from bottom to top and leaves the scrubber at flange (2). The washing solution is continuously circulated. Therefore, it is pumped out of the reservoir (5) upwards and enters the scrubber at flange (6). It is distributed above the bulk for better and constant wettening of the packing.

In order to hold bulk in position, there is a multibeam support grate at the bottom and a hold-down grate at the top of the packing. Droplet discharge is minimized using a droplet separator with a fine fabric structure. The washing solution then drips downwards, against the direction of flow of the gas. Due to the large surface area and the long residence time, both phases are in intensive exchange and both hydrogen sulfide and ammonia are washed out.

In addition to the scrubbing agent (3) tap water is supplied to the reservoir to dilute it for better pH control. The reacted washing solution (4) is then pumped out and disposed of. There are two capacitive level sensors (7) (UWT Level Control Capanivo CN 8100) installed to the reservoir. One them as a high- and the other as a low-level switch. The individual pumps, in particular the suction pump, are controlled as a function of this: the operating conditions of the scrubber must be between the minimum and maximum level signalled by the two sensors. If the upper level sensor registers an increase of the volume, the suction pump is activated; otherwise if an insufficient volume is present inside the reservoir, more liquid is introduced. A pH sensor is located inside the hose line for the circulation of the washing liquid, which is used for the correct setting of the mixing ratio.

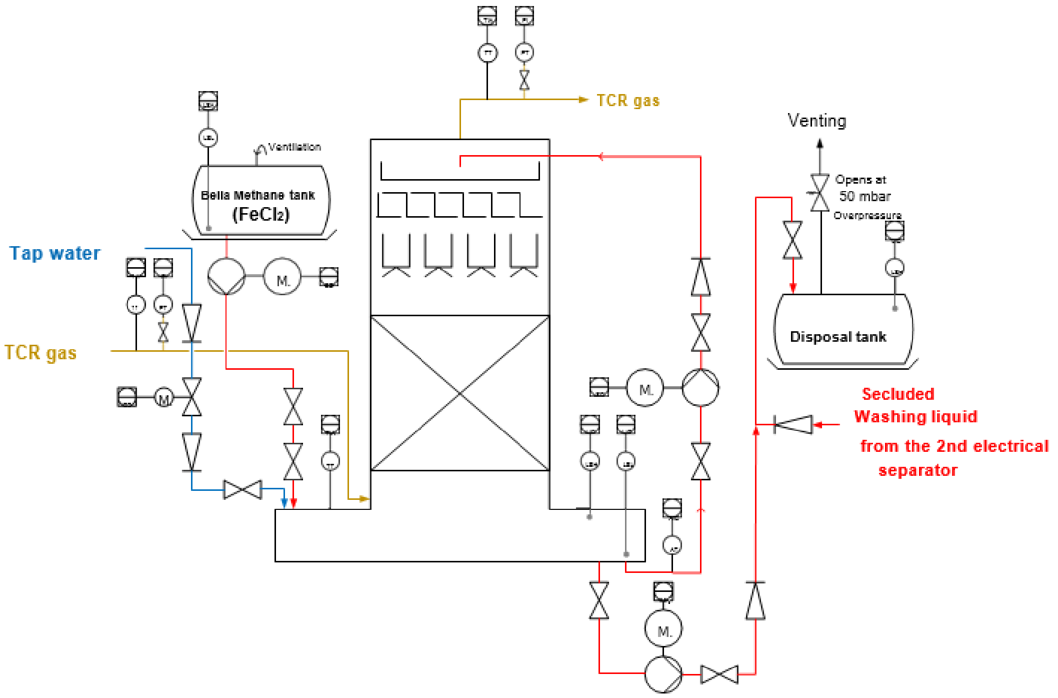


Figure 3.6 Original scheme of Scrubber system installed in to syn fuel project, [191]

Scrubbing conditions:

The incoming gas volume flow ($\dot{m} \approx 100$ kg/h, $\rho = 1$kg/m^3) has an expected content of 2% by volume hydrogen sulfide (H_2S) and in order to avoid corrosion of metal surfaces and to protect the downstream gas compressor this content must be reduced [167]: the final target for the reduction is less than 1000 ppm. Hydrogen sulfide forms because sulfur atoms are present in the feedstock, which react with the hydrogen formed during the thermochemical conversion and can reach a proportion of 100 ppm to 3.5% by volume [172] [192]. For this purpose, a gas washer (see Figure 3.6) is provided between the two electrostatic precipitators. The corresponding flow diagram is shown in Figure 3.7. Its main function is to reduce the Hydrogen sulfide content in the product gas, in addition, also the ammonia content (NH_3) is reduced. In order to achieve this, the product Donau Bellamethane classic from Donau Chemie AG is used as washing liquid, which consists of: 25 to 50% by weight of iron(II) chloride ($FeCl_2$), a density of at least 1.33 g / cm^3 [193] [194], green colour and pH value between 1 and 2. In general, iron salts (Fe^{2+} and Fe^{3+}) are especially suitable for the precipitation of sulfur that's why is mainly used in biogas production for desulphurisation and suppression of the release of ammonia [195].

For more detail informations of scrubbing reactions can be referred to chapter 2.7 equations 2.7 and 2.8

3.3 Component testing and system modification (upgrades)

In this part of the thesis, we will focus on the materials used and component testing done during the commissioning of gas scrubber. They have been done because is necessary to obtain extensive knowledge on the chemicals and the mechanical behaviour of the system, in order to manage them properly**.** It is important to say that the next considerations and some of these first analytical checks have been collected by previous researcher who was working on the commissioning of the scrubber, made explicit when necessary (*). The following chapter 4 concludes the previous tests and results on the gas scrubbing unit of the TCR®-500 system. The previous tests and results are used as a basis and continued by this thesis.

Washing liquid Donau bellamethane classic:

As shown in figure 2.10 of chapter 2.7 the opposite behaviour of NH_3 and H_2S scrubbing condition belongs to the Le Chatelier principle. For this reason, it is important to perfectly know the features of the scrubbing reagent $FeCl_2$ and its behaviour in the liquid environment, because an acidic characteristic of itself would lead to better cleaning of ammonia, instead, an alkali one would be suitable for hydrogen sulphide. That is why a good compromise is necessary in order to scrub both reagents with a high efficiency.

According to the manufacturer the rough range of active component ($FeCl_2$) is between 25 and 50% by weight, its molality should be approx. 5±0,3 mol/kg, the acidity around $pH < 2$ with a pKs value of 9.50. The method used to estimate the actual concentration is a Titration.

A concentration of 1 M of sodium hydroxide is used. The determination of the unknown concentration of the sample solution ($FeCl_2$) is carried out using the added volume of the standard solution (NaOH) up to the equivalence point. To carry out the experiment, bellamethane (10 ml) is diluted with distilled water in a 100 ml volumetric flask so that a mixing ratio of 1:10 is obtained, then a 25 ml of bellamethane is added to a 100 ml beaker including a stirring magnet, placed on a magnetic stirrer. The pH electrode (VWRpH10) is then fixed on a stand and completely immersed in the beaker.

The very low pH of the scrubbing liquid is unsuitable for the intended operation of the gas scrubber, since the equilibrium is very much on the side of the gaseous hydrogen sulphide (equation 2.4 of H_2S and HS^- equilibrium figure 2.10). According to the manufacturer's information, a pH value between 5.5 and 7 is suitable for the simultaneous binding of ammonia and hydrogen sulphide. In order to achieve this pH value, it is advisable to dilute with water during all the process.

Accordingly, a series of dilutions of the washing liquid with water should take place at the beginning in order to determine the necessary dilution ratio for filling the reservoir with water and washing liquid. For this purpose, a defined volume of bellamethane demineralized water is added until a total volume of 20 ml is reached. Depending on the dilution, the pH value is measured with a pH electrode. The experimental setup is similar to that of titration.

$$FeCl_2(s) \leftrightarrows Fe^{2+}(aq) + 2Cl^{-}(aq) \quad \text{in aqueous solution}$$

Equation 3.1: Bellamethane dissolution

Determination of volumes and pump performance*

In the reservoir of the gas scrubber there are two level sensors for which the corresponding level should be precisely determined. For this purpose, a defined volume of tap water is supplied from an intermediate container with the dosing pump. As soon as the corresponding level sensor starts, the supply is interrupted and the level in the reservoir is calculated from the difference between the volume supplied and the remaining volume in the intermediate container.

Concerning the delivery rate of pumps installed in the scrubber, it results from the difference of volume dropped and the time required. The pumps installed are: dosing pump ($FeCl_2$), suction pump (magnetic centrifugal AM30-PPF / AT), peristatic pump 620U (temporary re-circulation pump) and tap water pump. According to the manufacturer's specifications, the dosing pump [196] can operate at maximum delivery pressure with a stroke volume of 21.7ml /stroke and a maximum stroke frequency of 120 min^{-1} Pumping 156 l / h. The size AM30-PPF / AT magnetic centrifugal pump can deliver a maximum of 80 l / min, at a delivery height of 3 m it is about 63 l / min [197]. The 620U peristaltic pump can deliver up to 626 l / h [198].

The quantitative behaviour of different pumps installed in the system were calculated using an empty bucket placed over a mass balance. After having been flowed the water for a while, just to eliminate the delay-air time issue, the specific amount of water moved in the bucket by the pumps was weighted for a specific period (considering 1 g/L density of tap water). In real operation, a deviation can occur because of differences in density and viscosity compared to the medium to be conveyed, it’s important also not forget the position and hightide of pumps itself.

From figure 3.7 can be seen the position of pH sonde [199] in the connecting pipes of scrubber system: the signed positions represent the pipes connection for circulation pump (U), suction pump (A) and dosing bellamethane pump (D).

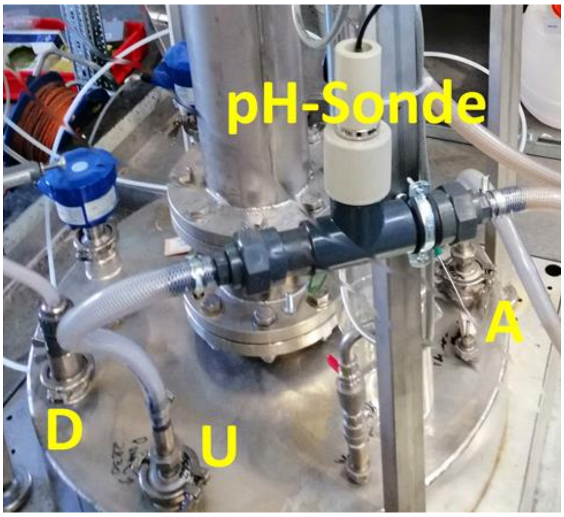


Figure 3.7: Addition locations for bellamethane and the positions of the circulation suction and pH probe. In detail the positions for the dosing (D), suction (A), circulation (U) pumps inlet and the pH Probe. The digital display of the pH probe is located above the image section.

Necessary modifications of the gas scrubber for commissioning*

Before the gas scrubber can be put into operation, the gas supply and discharge must be ensured. In the context of the test series, however, the upstream and downstream components cannot be used, as they are not able to provide the necessary gas mixture and unnecessary contamination of the following stage should be prevented. An artificial mixture of nitrogen, ammonia and hydrogen sulphide is generated to provide the product gas for testing the scrubber performance. The associated experimental setup is shown in Figure 3.8 The TCR®-500 already has a nitrogen supply, consisting of a compressed air compressor (MA SB 15-10, MEGA AIR), dehumidifier (RDP 100, MEGA AIR) for compressed air preparation and a nitrogen generator (N-GEN 25, Omega Air GmbH).

Both ammonia (ammonia 5.0, Linde GmbH) and hydrogen sulphide (hydrogen sulphide 2.5, Linde GmbH) are made available via gas bottles (50 L) with purity of over 99.999 or 99.5% by volume [200].

To achieve a constant and a sufficiently high nitrogen volume flow, is also used 5.0 bundle (Linde GmbH) with 12 x 50 L gas bottles connected to the nitrogen line. To determine the volume flow, flow meters are connected downstream for each individual component. For all gas components except nitrogen, a pressure reducer is installed after the outlet, which is used for fine control of the volume flow. Due to the high-pressure losses in the long hose lines and the frequent changes in cross-section, there is no throttling to compensate for the nitrogen supply. The diaphragm pressure reducer

C 106/1 (Linde GmbH) is used for ammonia and the line pressure regulator LE51-6-300-10 PVDF (Rießner-Gase GmbH) is used for hydrogen sulphide. To determine the volume flow, flow meters are connected downstream for each individual component. The measuring principle is based on a change in the area between the float and the conical tube, which changes the flow resistance. As soon as the weight and buoyancy are identical, the flow can be read on the scale. The flow meters are from Systech Systemtechnik GmbH (ammonia, hydrogen sulphide) and Bailey- Fischer & Porter. Similar to the pressure reducers, a mounting plate is also made at this point.

All components of the gas train are connected with fabric hoses (with nitrogen up to the entry into the flow meter) and polyamide hoses (ammonia, hydrogen sulphide).

To ensure the artificial gas mixture to the scrubber, a temporary flange is welded to a tube with three connections for the gases and a fourth connection is present for pressure monitoring. In order to increase the dwell time and the mixing of the gases two metal sheets are welded inside the tube-flange so that the direct flow is prevented. The temporary gas outflow from the scrubber is provided by a polyurethane spiral hose open at the end that goes outside the plant. A connection for a pressure gauge is also installed.

For the uptake of gas sample analysis another pipe screw connection including a ball valve is set in the outflow flange.

In order to verify the tightness of all the system, pressure test of the gas scrubber can be done providing an overpressure of 100 mbar, then the pressure change over time is recorded. This should be in the range of 2 to 4 mbar / min, otherwise the leakage point must be found and sealed.

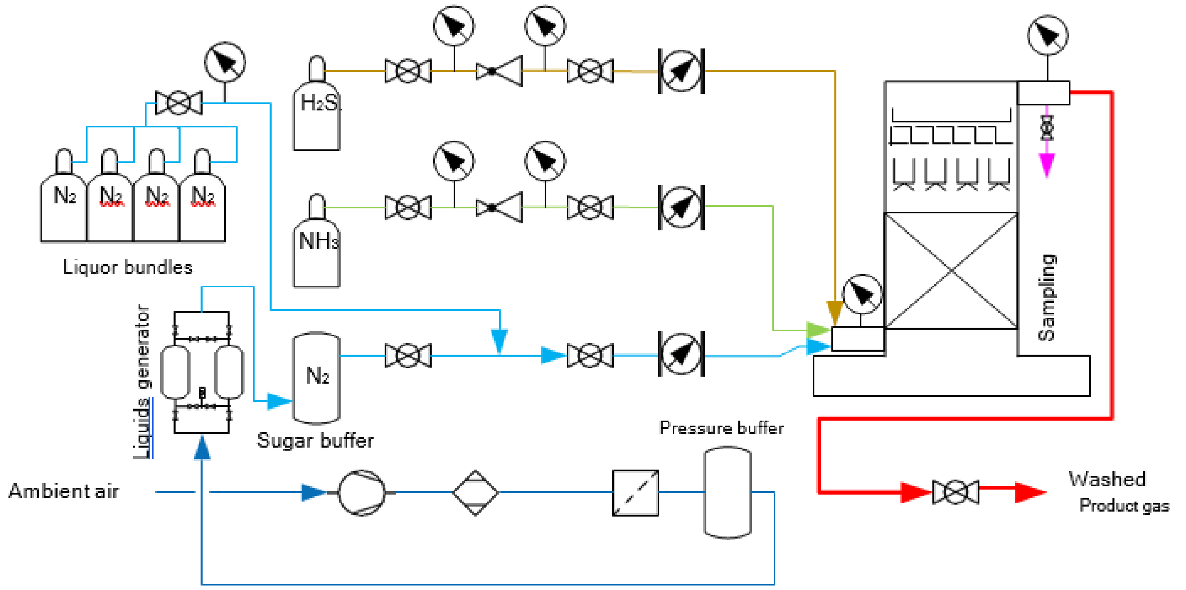


Figure 3.8: Schematic representation of the experimental setup for testing the gas scrubber, from [191]

Setting parameters for the product gas supply

The gas composition for commissioning depends on the actual product gas composition, the limitations of the nitrogen supply and the operating limits of the flow meters. The aim is therefore to get by with the existing system and to increase the total nitrogen volume flow by temporarily adding a nitrogen bundle. Almost atmospheric pressure (50 mbar) is assumed for the nitrogen flow meter and the gas mixing tube. Table 3.1 lists the relevant characteristics and assumptions as well as the expected composition with regard to the gas components ammonia and hydrogen sulphide on the basis of initial measurements: the volume proportions should be 2.0% for hydrogen sulphide and 3.0% by volume for ammonia. The conversion and density calculations are carried out using the thermal equation of state of ideal gases. The calculated standard volume flows are used for the simulated product gas (see Table 3.2), since approximately the same volume flow is aimed for during commissioning. As an inert gas component, the nitrogen volume flow is intended to replace the remaining components of the product gas.

	$\dot{m}$ [kg / h]	$\dot{V}$ [m^3/h]	ρ [kg / m^3]	ω [-]	φ [-]	$\dot{V}n$ [m^3/h]
Product gas	**100**	100	**1.00**	1	1.00	93.37
H_2S	2.84	2.00	1.42	0.028	**0.02**	1.87
NH_3	2.13	3.00	0.71	0.021	**0.03**	2.80

Table 3.1: Composition and characteristics of the TCR®-500 product gases. For the calculations apply for the state variables of the product gas an assumption of T = 303,15 K and p = 1,05 bar. The physical standard condition is marked net through Tn = 273,15K, pn = 1,01325bar. The other assumptions are highlighted.

φ target [-]		**$\dot{V}n$ target** [m^3/h]	**P actual** [mbar]	**ϑactual** [°C]	**$\dot{V}n_{actual}$** [m^3/h]	**φ actual** [-]	**value 1** [-]	**φ actual** [-]	**value 2** [-]
N_2	**95**	88.70		**10**	43,48	0.90	100%[1]	0,95	40[2] m^3/h
H_2S	**0.02**	1.87	**50**	**20**	2.05	0.04	35 l / min	0,02	13,3 l/min
NH_3	**0.03**	2.80		**20**	2.93	0.06	50 l / min	0,03	20 l/min

Table 3.2: Composition and characteristics of the simulated gas test. The assumptions made are highlighted

1 calculation based 2% and 3% H_2S and NH_3 for max volume flow TCR® gas

2 calculation based on 2% and 3% H_2S and NH_3 for limited commissioning volume flow of 40 m^3/h

Series of experiments to determine the performance of the gas scrubber

In the first step, the reservoir is filled with tap water and the necessary volume of bellamethane to set the desired pH value until the upper level is reached with the circulating pump running. The filling level remains constant over the entire duration of the experiment. Only nitrogen is supplied while the reservoir is being filled, and the subsequent fine adjustment is carried out with the pH probe. The desired test gas mixture (table 3.2) can then be supplied during the fine adjustment. As soon as the desired pH value is reached, the addition of bellamethane / tap water and the suction of the washing liquid must be stopped and the counter pressure increased. This allows a gas sampling bag to be filled with the washed test gas at the sampling point when the ball valve is open. At the moment the gas sampling bag is completely filled, the associated pH value is recorded and the back pressure is minimized. The volume fractions can be analysed immediately on site using Dräger short-term tubes.

In order to determine the optimal operating point could be useful to start working in a discontinuous mode, so that best pH condition, dilution factor and reagent concentration can be discovered. After then the strategy for adding and sucking off the washing liquid is varied in order to achieve a continuous process.

The theoretically necessary bellamethane volume flow is calculated on the basis of reaction equation 2.7 and the result of the titration, since the focus is on the leaching of hydrogen sulphide. The number of strokes required then follows from the volume flow and the stroke volume of the dosing pump. In addition, this value can be multiplied by a safety factor.

$$\dot{V}_{BellaMethan} = \frac{\dot{n}_{FeCl_2}}{c_{FeCl_2}} = \frac{\dot{n}_{H_2S}}{c_{FeCl_2}} = \frac{\dot{m}_{H_2S}}{M_{H_2S} \cdot c_{FeCl_2}}$$

Equation 3.2 volume flow required of bellamethane

c = Mole concentration [mol / m^3] ṁ = Mass flow [kg / s] M = Molar mass [kg / mol] ṅ = Material flow rate [mol / s] V̇ = Volume flow [m^3/ s]

Specifically, in different pH ranges (from 5 to 8) the washing performance at different delivery rates of the circulation pump (from 200 to 600 l / h) can be determined in a discontinuous process. Starting from the associated optimal operating point, the strategy for adding and sucking off the washing liquid is varied in order to achieve a continuous process. The pumps can be operated at different times or at the same time. The starting value for the necessary volume flow of bellamethane is calculated depending on the determination of the concentration of iron (II) chloride and the stoichiometric conversion. Building on this, the volume flow is gradually increased and the possible pH changes recorded.

Finally, the optimal strategy for the water supply is developed on the basis of the knowledge gained. In detail, there is a parallel and sequential addition, variation of the distribution of the volume flow between bellamethane and tap water and adaptation of the suction strategy.

The general approach to activate the gas cleaning scrubber test is:

- Set previously the gas mixture (without circulating)
- Set the circulation pump, fill the tank with bellamethane + water until the upper level is reached, adjusting the pH value if necessary, remembering the dilution of $FeCl_2$ in water or discharging some amount of it
- Start the nitrogen supply in parallel (0.5 bar, ~ 35%) and note the value
- Start the ammonia and hydrogen sulphide gas flow
- Adjust the test gas mixture shortly before the desired pH value is reached
- Turn off the suction pump
- As soon as the wanted pH value is reached, increase the back pressure to fill the gas bag in the upper flange
- Note the starting and ending pH values and on the gas bag
- Local analysis with short-term Dräger tubes, for an immediate result
- If possible and relevant, analyse gas bag content in the laboratory GC

3.4 Analytics

Dräger short-term tubes

Dräger short-term tubes are used to quickly measure the instantaneous concentration of a specific gas and are calibrated for the respective chemical compound, this gas is supplied manually via the accuro-pump. Depending on the gas and the concentration, the measurement takes a few seconds to a few minutes, here the volume fraction can then be read off directly based on the scale and as a result of a color change in connection with the reaction that has taken place. The possible measuring range for hydrogen sulfide is 100 to 2000 ppm and 0.2 to 7% by volume with a standard deviation of ± 5-10%. The reaction principle is based on the sulfur bond with lead or copper cations. In contrast, the measuring range for ammonia is 5 to 600 ppm and 0.5 to 10% by volume with a standard deviation of ± 10-15%. Ammonia reacts with a pH indicator (bromophenol blue) to form a blue reaction product. [201] [202] [203] [204] [205].

Figure 3.9 shows a H_2S concentration test in the Dräger tube

4 **Tests and experimental results**

This chapter will show chronologically all the experimental tests and verifications necessary to make the scrubber operative inside the plant.

The first commissioning operations carried out will be reported, as described in the previous chapter necessary to have sufficient know-how, and then the upgrades developed to solve the difficulties faced during the cleaning of the simulated TCR® gases.

4.1 Previous work

4.1.1 **Dilution of $FeCl_2$**

As bellamethane is a strong acidic solution, it is important to know its behaviour in an aqueous solution trying to reproduce the reservoir system of scrubber. The results of the dilution series of the washing liquid (Donau bellamethane classic) with demineralized water are summarized in Figure 4.1. From them the qualitative interpretation of bellamethane behaviour in water solution can be collected.

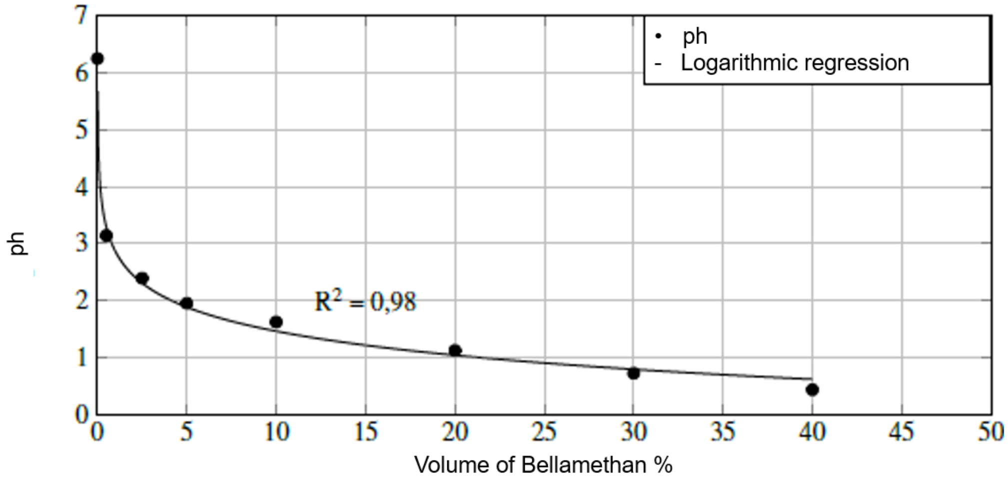


Figure 4.1: Dilution series of bellamethane (BM) with demineralized water. [191]

4.1.2 **Pumps and Scrubber capacity test**

The volumes present in the scrubber are: Lower level sensor 42.7L (53.6%), Upper level sensor 62.3 L (78.2%), total reservoir capacity 79.7 L.

Unfortunately, the lower filling level sensor cannot confirm that the reservoir has been completely suctioned off, since it is positioned too high up.

- Tap water pump: the maximum flow rate was 27.98 l/min. This means that the completely empty reservoir can be filled up to the upper level sensor within 133 seconds.
- Dosing pump ($FeCl_2$): The maximum volume flow was 2.6 L/min and thus exactly matches the manufacturer's specifications at maximum delivery pressure, which is 21.6 ml/stroke, for 120 strokes every minute.
- The suction pump (magnetic centrifugal AM30-PPF / AT) can operate at 100% power, the only parameter that can be set in the control panel is the on-off time of operation, with a flow rate of 17 L/min
- Peristatic pump 620U (temporary re-circulation pump): The maximum measured volume flow was 642 l / min and the value can be easily read on the digital display.

Figure 4.2 shows the different uptake rate of the pumps installed in the scrubber:

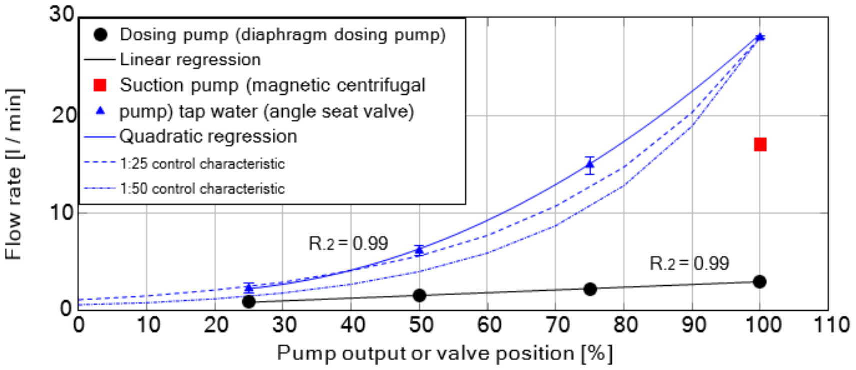


Figure 4.2: Characteristic curves of the pumps and the tap water connection of the gas scrubber picture [191]

4.2 Estimation of bellamethane reagent content

In order to estimate the concentration of $FeCl_2$ present in bellamethane solution, a titration was used. The solutions prepared are: NaOH 1M, and 10 ml bellamethane diluted in 90 ml distilled water. During the titration, the smallest possible amount of NaOH solution (0.025 ml) was added per measuring point in order to estimate the position of the equivalence point. The pH value of the sample solution at the beginning of the titration was round 2.4 and was therefore insignificant different than the dilution series. During the titration the following two reactions could occur:

$HCl + NaOH \leftrightarrows H_2O + NaCl$

$FeCl_2 + 2NaOH \leftrightarrows Fe(OH)_2 + NaCl$

Equation 4.1: titration of bellamethane with sodium hydroxide

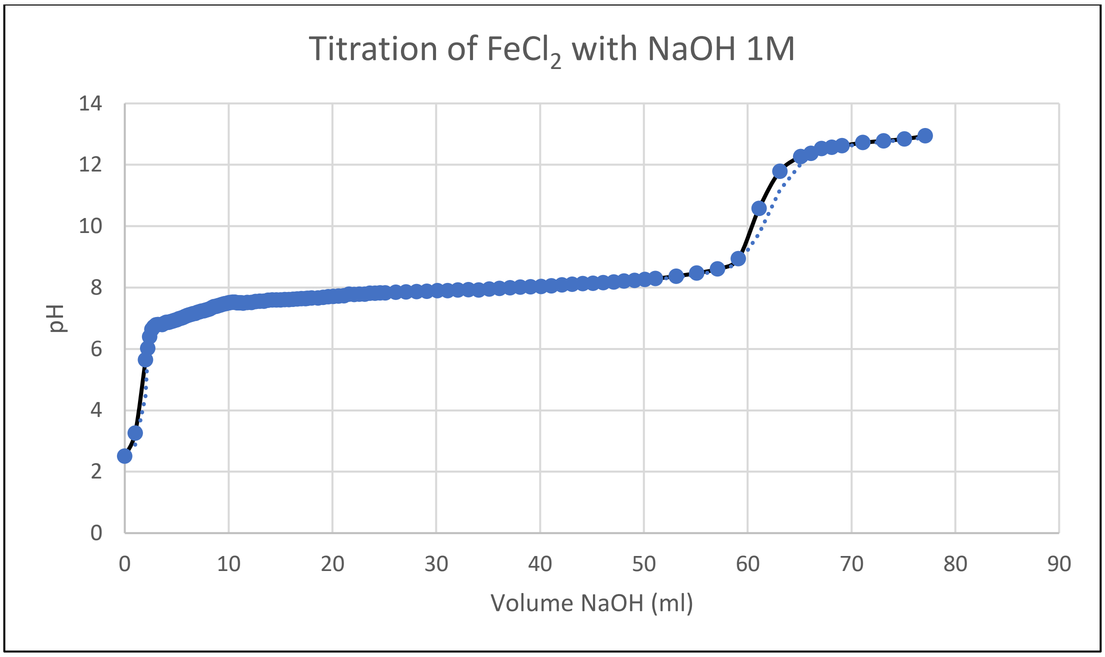


Figure 4.3: Titration of 10-fold diluted bellamethane with 1 molar sodium hydroxide solution

In the plateau at ca. pH 8 the Fe^{2+} ions are consumed by the OH^- ions, mainly forming $Fe(OH)_2$ compounds which precipitate forming a green solid. This consideration is supposed following the qualitative and color evolution of titration compared to Pourbaix diagram for iron [206]. The concentration of $FeCl_2$ was estimated from the volume of NaOH consumed, $C_{FeCl_2} = 3.02$ mol/L. The actual percentage of ferrous chloride in the washing liquid is 29% by weight and is therefore in the lower range of the manufacturer's specifications. However it should be remarked that the presence of oxygen during the titration may lead to the oxidation of Fe^{2+} to Fe^{3+} with the formation of FeOOH, Fe_2O_3 or $Fe(OH)_3$ leading to an estimation in excess of iron concentration and not too precise measurement. Consequently, the necessary volume flow of bellamethane for the leaching of hydrogen sulphide can be calculated with these results using equation 3.2. At this point, hydrochloric acid is not taken into account in the calculation due to its low content. Assuming a complete stoichiometric reaction, this results in a necessary bellamethane volume flow of 441 ml / min for the test gas of H_2S. Since the iron concentration in solution has possible estimation errors, during scrubbing operations we always worked with a stoichiometric excess of washing reagent (> 0.5 l / min), considering the lower percentage value indicated by the manufacturer, i.e 25%.

	MM (g/mol)	**density (kg/dm3)**	**pH**	**%**	**mol/L**	**Gas flow**	**m^3/h**	**L/min**	**m^3/h**	**L/min**
$FeCl_2$ titr.	126,75	1,32	0,7	29%	**3.02**			**0,441**		**0,177**
H_2S	34	1,36				2%	2	33,33	0,8	13,33
NH_3	17,03	0,73				3%	3	50	1,2	20
FeS	87,85							7,03 **kg/h**		2,8 **kg/h**
Tot gas (m^3/h)							100		40	

Table 4.1: stoichiometric calculation for bellamethane reaction

4.3 Gas scrubber activity tests and optimisation

In this part of the thesis all the chronological tests done will be reported in order to verify the optimal scrubber condition for TCR® gas flow cleaning, the operations and upgrades added in the system to make it more efficient. As said before, an integration gas system was added in order to simulate the H_2S, NH_3 and N_2 supply required.
The general approach to activate the gas cleaning scrubber is present in chapter 3.3, but from here after there will be specified every specific approach set during the tests.

4.3.1 **First experimental approach**:

The commissioning parameters previously calculated have been set in the washing system:

- max recirculation rate of peristatic pump 626 l/h,
- $\dot{V}$ N_2 = 14.45 m^3/h,
- $\dot{V}$ NH_3 = 1.47 m^3/h (8.82% by volume),
- $\dot{V}$ H_2S = 0.73 m^3/h (4.38% by volume)

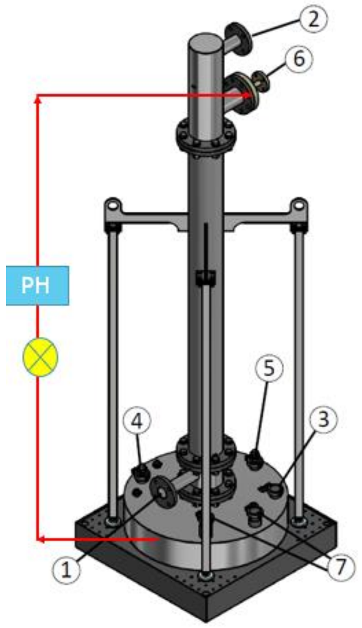


Figure 4.4: First experimental scrubber setup

The test was conducted with the total gas flow lower than the parameters calculated previously, simulating a high percentage of hydrogen sulphide (0.73 m^3/h) and ammonia (1.47 m^3/h), but not overcoming the maximum limit of nitrogen supply.

The recirculation established in the scrubber was at the maximum level of the peristaltic pump in order to facilitate the homogenisation of bellamethane in the liquid fraction and allow a better scrubbing condition in the absorption reaction between liquid and gas. An excess of bellamethane solution was added during the scrubbing process.

As can see in table 4.2 the first test at pH of 5.5 presents a low concentration of H_2S (500 ppm) and it is similar for ammonia (> 600 ppm), however, this last one cannot be measured more accurately because the test overcomes the limit of the drager tube. Following the other tests, increasing the pH, a low concentration of ammonia is registered (round 5) indicating a better cleaning efficiency. Concerning hydrogen sulphide, high values concentration are registered for test 2 and 4. Instead for its sample number 3 it shows an opposite low result.

It was not possible to collect other tests because some technical issues: the formation of precipitated FeS obstructed the entire scrubber (base, rushing rings, pipes) resulting in a consequent increase in overpressure and an inefficiency of cleaning of the gases, the blocking of the gas sensors-level, and the corrosion of the pH meter. For safety reasons it was necessary to stop the test and check the pressure. These issues are likely responsible of the lack of reproducibility of the results during the gas cleaning.

Test	**1**	**2**	**3**	**4**
pH	5.5	6.1 - 6.2	6.5 - 6.6	7 - 7.1
$FeCl_2$	excess	“	“	“
C H_2S (ppm)	500	>2000	380	1900
C NH_3 (ppm)	>600	<5	<5	40

Table 4.2: first experimental setup for scrubbing reaction, 1%= 10’000 ppm

From the table 4.2 it is evident that the scrubber system is working, i.e. the residual percentage of hydrogen sulphide and ammonia are reduced to a few ppm. However, due to the formation of insoluble dark-solid iron sulphide particles (FeS), this operation cannot be reproduced for a longer test run or in different conditions, this means that first test results, even if quite positive, cannot be considered reproducible. Moreover, the maximum cleaning efficiency of H_2S and NH_3 happens under conditions theoretically disadvantaged for them, which is quite unusual: ideally the H_2S should solubilize and release HS^- ions in a neutral-alkaline solution, however here the best result is achieved with an acidic pH. Same situation happens for ammonia which should be more reacted, and so cleaned away, with acidic condition. Without considering further theoretical problematic in the inefficient gas cleaning process such as, retention time, gas-liquid contact phase, surface area of reaction, temperature…, it is important to focus on the residues produced during the reaction of bellamethane.

The presence of dark solid precipitate in the bed of reservoir clearly states that the reaction between H_2S and $FeCl_2$ is happening, according to the stochiometric reaction the amount of FeS should be around 7 Kg/h (see table 4.1 stoichiometry). This produces a hard condition for the scrubber itself: the accumulation of this pasting sedimentation product blocks the connection, makes dirty all the pipes and pH sensor, moreover the rushing rings inside the column of the scrubber are totally stuck. Rushing rings that should arise the surface area for scrubber system, instead, this leads to a less effective gas-liquid exchange, lowering the reaction conversion but, what it is impossible to avoid, creating an overpressure that obliges the operator to stop all the system process. No more tests can be done, because all the mechanical part are stuck, gas and liquid are blocked and cannot operate correctly.

From figure 4.5 can be seen the pasting condition of rushing rings and the corrosion of pH sensor caused by the high amount of iron sulphide compound produced.

Figure 4.5: The accumulation of FeS in the scrubber column stucking all the rushing rings; the pH probe dirty and corroded by Fe solution.

4.3.2 **Substitution of rushing rings with vertical impeller**

In the second experiment approach the main goal is to achieve the stability of the system avoiding possible overpressure and trying to establish a good cleaning condition so that the scrubber can continuously run without emergency stop. Once cleaned all the scrubber components, the rushing rings inside the column were substituted with a new vertical impeller. This device should avoid blockage caused by the precipitation of FeS in the central column and give enough surface for gas-liquid phase exchange and residence time.

From the figure 4.6 can be seen the dismantle process providing the new vertical impeller in the column of the scrubber.

Figure 4.6: The dismantling process of scrubber with the insertion of new impeller.

After having checked that the impeller itself it is not causing a possible overpressure in the system, the testing procedure of the scrubbing unit was continued. Two sessions were performed with different environment conditions in order to understand the possible features of gas cleaning at different pH values. The conditions are summarized in Table 4.3.

Reaction condition:

- N_2 40 m^3/h,
- H_2S 35 l/min,
- NH_3 50 l/min,
- Recirculation rate 626 l/h

	Day 1 Test 1	Day 2 Test 1	2	3	4	5	6
$FeCl_2$	Excess	0	0.52l/min	“	0	0	1.04l/min
pH	8-8.5	9.38	5.95	6.05	7.5	9.03	4.92
H_2S ppm	200	>2000	>2000	1950	>2000	>2000	800
NH_3 ppm	>600	>600	>600	600	500	>>600	>>600

Table 4.3: second experimental setup for scrubbing reaction

From the table 4.3. it can be observed that in the first day session, a low concentration of hydrogen sulphide (200 ppm) and a high concentration of ammonia (over 600 ppm) are registered with a neutral-basic pH condition. This first result seems to be coherent with theory reaction conditions, for which H_2S is better cleaned in the alkaline regime. No other tests were taken because the NH_3 (over 600 ppm) is left in the gas stream producing a smell and corroding the final outlet valve.

In the second day session a kind of “equilibrium state” for the system was reached: during the scrubbing tests the pH tends to naturally increase with time because in the gas mixture there is more content of NH_3 respect to H_2S, and it solubilizes in the bellamethane-water solution. For this reason, first tests were performed with higher pH than following pH tests. As soon the bellamethane is added (tests 2 and 6), the pH was lowered. It should be noted that if there is not any bellamethane addition, when the gas mixture is flowing the pH tends to naturally increase. Despite the addition of washing solution, in all samples taken the resulting concentration of hydrogen sulphide and ammonia are really high, and sometime also over the limit scale of measure. The only two “good” exceptions are in test number 3 and 6 where, respectively with a neutral pH condition and doubling the washing liquid inflow, some lower concentrations are registered than other tests or at least not overcoming the limit of measure.

Without having successful and reproducible results, the scrubber had to be cleaned again because of FeS formation was accumulated inside the system. Thanks, the presence of new impeller in the cylindrical body of scrubber any blockage was avoided, although FeS was formed and deposited in the reservoir unit. The reason could be found in the high fraction of bellamethane diluted in small amount of fresh water used during scrubbing process, and the small capacity of the reservoir. Further optimisation of the scrubbing unit is required to capture the solid precipitation and avoid the possible sedimentation inside the scrubber.

4.3.3 **Integration with external sedimentation barrel**

As design change is not possible for time reason, some external and temporary upgrades were added to test their effectiveness.

As can be clearly seen in the left part of figure 4.7, a 200 L cylindrical barrel tank was added and connected to the scrubber like an extension of the reservoir capacity. Due to the higher volume of the external sedimentation tank, the flow velocity is decreased significantly. It is planned to use this effect for sedimentation of the FeS outside of the scrubber system. The sedimentation tank is connected to the scrubber by high pressure-resistant pipes and valves. Therefore, as can be seen in figure 4.8, an inlet metal pipe is placed at the bottom of the tank, to ensure radial inflow that causes only minimum of turbulence to the sedimentation of solid particles. The outlet flow is placed in the upper surface of the barrel through a floating system provided by a foaming polymer suspender. Furthermore, a third hole to connect a venting pipe is drilled into the tank.

As can be seen in the figure 4.7, the recirculation now is provided by the peristatic pump (yellow) which connects the outlet of the sedimentation tank to the inlet flange of the scrubber. A magnetic pump (highlighted in green at figure 4.7) connects the outlet suction point of the reservoir to the inlet of the sedimentation tank.

In order to make the flow continuously and with the same regular capacity, a previous test was done, to reach the equilibrium of the two different pumps: 520l/h was found as the optimal recirculation rate to create a steady state between inlet and outlet.

The addition of the barrel is also helpful to stabilize the “jumping” behaviour of the pH meter, because a higher quantity of water provides better and less acidic environment with more bellamethane concentration diluted in it.

Reaction condition:

- Recirculation rate of peristatic pump 520 l/h (yellow),
- Recirculation rate of magnetic pump 1040l/h operating half time (green),
- $\dot{V}$ N_2 = 40 m^3/h,
- $\dot{V}$ NH_3 = 50 l/min,
- $\dot{V}$ H_2S = 35 l/min

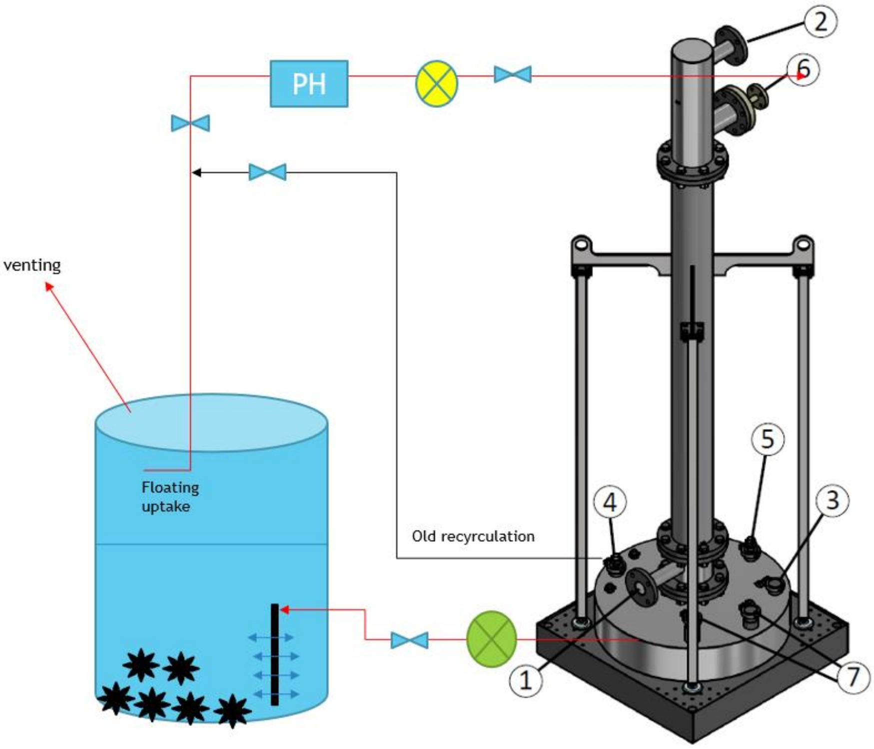


Figure 4.7: third experimental scrubber setup with new 200L barrel (left cylindric part) and recirculation installation.

Figure 4.8: system for radial inflow (right picture) and floating outflow pipes in the sedimentation barrel

	Test 1	**2**	**Test 3**	**4**	**Test 5**	**6**	**Test 7**	**8**
pH	2,4	5,5	7,7	7,6	7,1	7,1	6,3	6,5
Time (min)	0	4’	0	4’	0	4’	0-1’	3’ 30’’
$FeCl_2$	excess	“	“	“	“	“	“	“
NH_3 ppm	60	60	-	-	-	-	< 5	0
H_2S ppm	-	-	>2000	>2000	>2000	>2000	>2000	0,50%
Condition	Only NH_3		Only H_2S		Only H_2S		H_2S NH_3	

Table 4.4: Third experimental setup for scrubbing reaction

From table 4.4 we can see the results of third experimental scrubber setup: A longer test run than with previous setup was performed, it lasted overall 2h with a continuous recirculation of the liquid. The approach adopted was to test the single gas cleaning behaviour with a short-time reaction inside the scrubber, recirculating the liquid inside the scrubber for all the time and understanding if better conditions were provided by new barrel integration. Same reagent conditions (excess, 0.5 l/min) were adopted: time zero from the addition of bellamethane to time x was tested to check the cleaning capacity of the system.

This procedure was repeated in 4 steps: the first one with only NH_3 flow (test 1-2), second and third one with only H_2S (test 3-4 and 5-6), the fourth one with both gases (test 7-8). Passing from step to different step, every time the gas flows were stopped and let only the liquid recirculation flow, so that a kind of “Batch” gas approach would have been tested.

From the table 4.4 it becomes clear that the experiment can be considered only half successful, because only one gas was scrubbed away: ammonia was well cleaned in both cases, alone or in the gas mixture, i.e. every single test shows a low concentration of residual gas (from 60 to 5 ppm). Hydrogen sulphide instead revealed to be really hard to get rid of, alone itself and with ammonia, every test from 3 to 8 present a high concentration result (over 2000 ppm).

The pH behaviour registered is coherent with mixture flow in the system also with the new external tank addition: pH dropped with the addition of $FeCl_2$, rised up with flow of NH_3, and then decreased again with addition of H_2S.

Concerning the external sedimentation process in the barrel, the precipitation of solid particles in the bottom part of the tank and a quite clean water solution in the surface were evident.

A further test was run to understand the condition inside the 200L tank changing the recirculation rate from 150 to 600 l/h, and visualising the difference in turbulence due to the time passing every 20 minutes. From the results obtained it can be stated that time passing/aging is affecting the final result in sedimentation efficiency rising the recirculation inside the barrel. However, the surface of the barrel, where it is up taken the liquid for the scrubber, remains quite clean. This seems to be enough satisfying for further test with this new installation, not only for the sedimentation process itself, but also because the pH inside the system is rather stabilized by the high amount of water that can solubilize bellamethane.

Concerning the suction pump placed in the outflow of the scrubber, this is not operating sufficiently well, leaving some FeS inside the reservoir and making dirty the level-sensor: this obliges the operator to clean every time the system controllers and at least flush away the reservoir with some fresh tap water.

Until now it can be stated that:

- There is a lack of reproducibility of good concentration results in the tests: the final low concentration for NH_3 shows that is cleaned away, probably also due to the addition of the external barrel with high amount of water. Instead H_2S shows high final concentration, sometimes also over the limit scale of analytical instrument (2000 ppm), which means that is not properly scrubbed.
- FeS solid particles deposition is problematic inside the reservoir: it is necessary to find a way to remove it better because many kg/h of FeS are produced. Another quantitative test should be necessary to understand if external sedimentation tank is sufficient to trap the solid particles.
- Design of the scrubber: difficult to self-clean. Modification/upgrade in the reservoir design could help the outflow of solid particles
- pH sensor and level indicator are suffering the reaction condition: need to be often cleaned. A modification is necessary to do easy maintenance.

- Reagent bellamethane is very acidic, which is no good for HS^- ion scrubbing condition: evaluating a basic reagent or buffer to keep stable the pH would be necessary for different improvement.
- Temporary installation of new system: evaluate for long lifetime and process application
- Scrubber produces high byproduct quantity, is necessary an evaluation for long run continuous mode process when will be integrated in the TCR plant.
- The artificial gas mixture is not considering other possible reagents inside the scrubber: in the real situation the presence of other gas such as CO_2 could produce other solid particles.

Considering the gas-liquid phase exchange efficiency and following the Henry law, some parameters that could improve the cleaning reaction are: i) temperature because lowering it would improve the solubility in the liquid; ii) pressure; iii) residence time; iv) higher surface area in the scrubber for a better mass transfer; and v) changing the cleaning reagent. All these parameters cannot be changed or controlled easily for the actual system (mechanical issue, space availability, system addition), that is why pH parameter will be the most important one to control and test, trying to create the best environment for H_2S solubilization.

According to this consideration and the previous statements, the next upgrades will follow: filtration system, bypass creation and sample taking, decrease the gasses flow, washing liquid directly in the tank, some basic reagent.

4.3.4 **Filter addition, IBC tank installation and**

As shown in the figure 4.10, a new IBC 1000 L tank was added in the scrubber system to help the sedimentation and the future workers operations. Because of the new higher position of the tank and the related pipes connection installation, new calculation of liquid flow by pumps was checked, re-equilibrating all the system recirculation (510 l/min). From these it seems that the new installation is trapping the majority of solid particle in bottom part, avoiding also the typical “jumping” behaviour of the pH meter. To prevent the dirty deposition and make it possible to clean it when necessary, the pH meter, a bypass system and a first BWT Bolero filter was added before it. This new filter removes particles with diameter of more than 10 micrometres. Unfortunately, the filter can only be used for short test runs, because it is blocked quite easily leading to higher pressures in all the pipelines and connection until they are not tight anymore. A second type of filter was then installed. This membrane filter can be replaced easily while operation of the scrubber because of the installed bypass.

In order to prove the possibility of H_2S cleaning through our system, a lower gas flow mixture was fed.

Figure 4.9: Before and after bolero filter workout; the new filter installed

Reaction procedure condition:

- Start liquid recirculation from scrubber to tank and from tank to scrubber: 510L/h
- open nitrogen gas flow: N_2 40 m^3/h
- make it run: 1 hour (only 20' with gas flow)
- open NH_3 and then H_2S:
  NH_3 is < 20 L/min
  H_2S 4 L/min (4 L/min means 0,6% concentration so 6000 ppm)

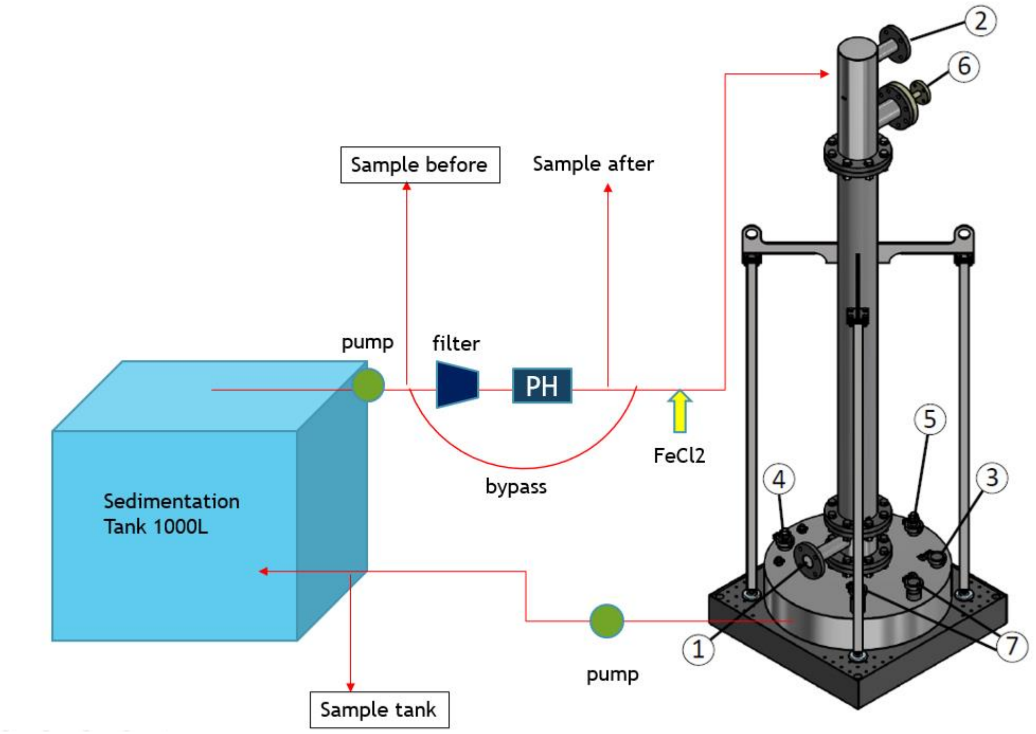


Figure 4.10: Fourth experimental scrubber setup

The approach adopted is the following: first gas sample was taken without $FeCl_2$ inserted, which means that system is cleaning only with previous tank liquid, this is basically water, previous liquid cleaned from scrubber, some residual of bellamethane, solid particles precipitated and free ions. Then $FeCl_2$ started to flow at 20%, this means feeding 0,5 L/min of $FeCl_2$. From stochiometric reaction this value is to be considered an amount in excess respect to the necessary quantity to compensate H_2S and NH_3 scrubbing. Successively the following samples were taken with $FeCl_2$ flow on and flow off, so that we can test the scrubbing capacity of residual washing liquid reagent left in the system. In the end it is important to check the sedimentation process in the tank and the filtering capacity taking some sample before and after it.

In order to prove the reproducibility of our scrubber data, a second test was immediately performed after it under the same conditions and approach.

Test RUN 1	***1***	***starting FeCl2***	***2***	***3***	***stop FeCl2***	***4***	***5***
pH	6.90		6.95	6.93		6.91	6.91
Time (s)	0’’	1’’	2’	5’	5’ 01’’	7’	10’
H_2S ppm	100 ppm		650	400		150	100
NH_3 ppm	5 ppm		5	5		-	-
$FeCl_2$	0 %		20 % (0,5L/min)	20 %		0 %	0 %

Table 4.5: Fourth experimental setup for scrubbing reaction

Test RUN 2	***1***	***starting FeCl2***	***2***	***3***	***stop FeCl2***	***4***	***5***	***6***
pH	6.99		7.01	7.04		7.04	7.04	7.06
Time (s)	0	1’’	3’	5’	5’ 01’’	7’	11’	20’
H_2S ppm	40 ppm		1000	800		10	150	160
NH_3 ppm								5 ppm
$FeCl_2$	0%		20%	20%		0%	0%	0%
Considering 6000 ppm concentration of H_2S								
Scrubbing efficiency:	*99%*		*84%*	*87%*		*99.99%*	*97.5%*	*97.5%*

Table 4.6: Reproduction of fourth experimental setup for scrubbing reaction

From the two tables we can clearly see that lowering the gas mixture inflow, H_2S and NH_3 can be cleaned, sometimes completely, and the overall efficiency is rather good, justified by the low concentration of residual gas registered. For samples 2 and 3 of both test run, as soon bellamethane is added, the cleaning efficiency dropped only for H_2S; even if the scope of bellamethane is to react and better scrub the gas mixture. This strange behaviour could be explained because adding $FeCl_2$ in the inlet position, right before the entrance in the scrubber, keeps low the pH creating an acidic local environment: following the dilution series, more or less 6% solution of $FeCl_2$ will produce a pH of 2,5, not permitting the total dissociation of H_2S in HS^-. This can also explain the better result obtained in the following samples (4, 5 and 6) after 5 minutes as soon the bellamethane addition is stopped; the residual concentration of gas is rather eliminated to hundred ppm. The reason must be found in the iron ions present in the solution which is recirculated, but differently from previous samples it has a neutral pH.

Concerning ammonia concentration, it is always cleaned away and the results obtained are next to zero concentration. The reason must be found in the higher amount of freshwater recirculated which allows the solubilisation of ammonia, as matter of the fact the pH is always slowly increasing because of the production of ammonium product. Moreover, the HCl present as a product of H_2S reacted, will consume the NH_3 present and not solubilized.

From the scrubbing reactions we know that the higher amount of NH_3 than H_2S in the gas mixture increases the pH slowly. Changing the artificial gas mixture composition will produce a different environment and if necessary, also producing an equilibrium in the pH solution for which it can stay stable. Moreover, pH is also kept stable by the big amount of water in the tank itself, avoiding the problematic sudden changes in scrubbing condition due to the addition of bellamethane. For further optimisation, based on pH environment for scrubbing efficiency, it should be important to understand the amount of NH_3 will be cleaned out for the future operating plant in the previous cleaning gas step: the previous cooler system, should produce 4% of NH_3. From this result a better bellamethane addition and operating scrubber pH could be reached.

Figure 4.11 The new upgrades filter in the system: before and after the scrubbing activity the filter itself turns to black and dirty condition

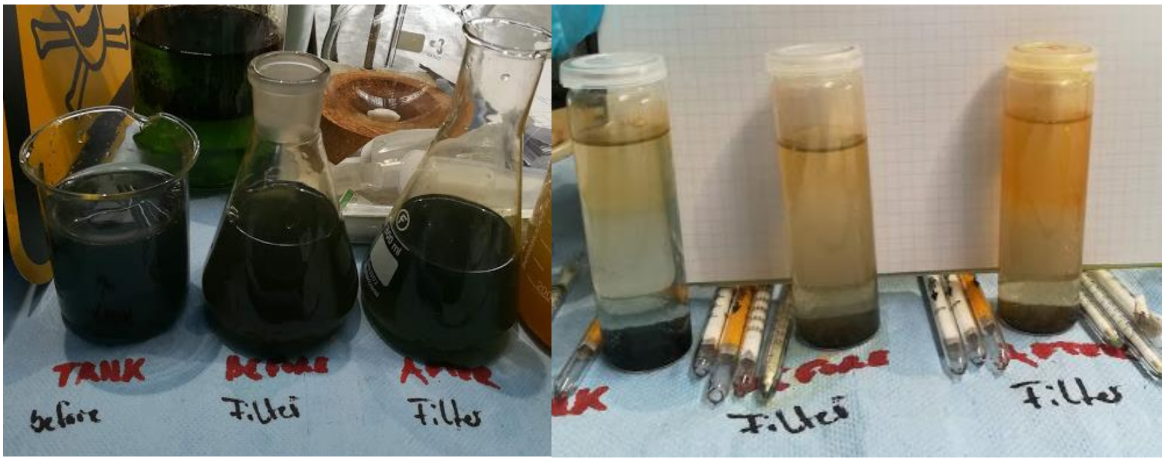


Figure 4.12 The samples collected: before sedimentation tank, before filter and after filter. The second one represents the same samples after a while occurring the sedimentation.

Figure 4.13 The collected sample inside the reservoir, very dirty

After 30’ of test run the filter turned to black colour, but no problem of overpressure happened. The difference between before and after sample can be seen in the figure 4.11.

Concerning the sedimentation process and solid particles, some qualitative tests of different recirculating liquid were taken in different position of the system. The three samples are taken respectively in these positions: before the IBC tank, before the new filter and after the filter. The main difference that can be outlined is the presence of smaller particulate present in sample after the filter, differently no other important result to highlight. Another sample was taken directly from the reservoir, during the cleaning operation as shown in the figure 4.13 the presence of precipitate and foaming agent is really evident and could be problematic for longer test run.

The qualitative interpretation showed that filter is limiting the contamination of solid particle in the pH meter and so in the scrubber. However, the overall scrubber test run lasted 2 h and sedimentation tank was quite “agitated” inside after it, that is why from the figure 4.12 can be seen not so much difference between before and after filtration samples. Nevertheless, the sedimentation goal of tank seemed having work enough, and this is promising for longer test run. But reservoir is really dirty in its bottom part: without any design improvement it is necessary to flush out manually the solid residuals.

From here after in order to improve the scrubbing efficiency it necessary to evaluate:

- The reproducibility of tests with the increase of gas flow rate to a more real simulation (Test 2% H_2S for 40 m^3/h and 100 m^3/h (worst scenario))
- The value of pH to more basic condition, if better scrubbing results can be obtained for hydrogen sulphide
- The feeding position of $FeCl_2$ directly inside the tank and test what happens to pH and ions behaviour
- Verify new possible reagents

4.3.5 **Small scale-laboratory approach**

A small scale-laboratory test was set in order to investigate doubts and hypothesis from previous experiments, the behaviour of bellamethane, test its scrubbing efficiency changing the pH and other environment parameters in detail.

A laboratory gas washer was set so that the washing capacity of different solution have been tested. The Duran [207] glass gas washer presents a filter disk that increases the effectiveness of the absorption through the distribution of gases in liquids inside the bottles. The feeding system was similar to scrubber test, the main difference was the specific control of gas mixture inlet provided by a more sensible flow meter only for H_2S gas (ml/min). Due to the small capacity of gas washer it is necessary to set small gas flow, otherwise powerful bubbling and hard foaming condition could occur, for this reason firstly a blank test was done. In the figure 4.14 the gas washing system operating only with water can be seen.

Figure 4.14: Gas washer system with the inflow of gas mixture on the right and the outflow of cleaned gas on the left part.

The approach adopted to test the gas washing efficiency was: preparing the washing solution desired to be tested, start the nitrogen flow inside the gas washer, then open also the hydrogen sulphide gas flow, wait 2 minute in order to create an homogeneous gas flow and letting react with washing solution, uptake in the outflow a sample for the residual gas concentration test.

Here in table 4.7 are summarized the solution tested and their behavior

		Starting condition			**Scrubbed mixture**	
N°	**Solution**	**pH**	**Flow rate**	**H_2S ml/min**	**pH**	**H_2S ppm**
1	Pure Bellamethane	-2	10	100		no result
2	Diluted Bellamethane 2,5%	2,2	5	50	2	>2000
3	Wastewater liquid from IBC tank	5,79	5	50	3,9	>2000
4	Solution NaOH 0.1M	12,7	5	50	7,9	3000
5	Anoxic solution of 100 ml $FeCl_2$ + 20 ml NaOH 1M	4,7	5	50	2,4	1600

Table 4.7 The different solutions tested and the result acquired from them

From the table it can be distinguished different solution used to test the scrubbing efficiency for hydrogen sulphide gas flow.

In the first experiment, a solution of pure bellamethane was tested but no results were obtained because of the formation of foam which led to the over pressurization of glass system. However, the change in colour of solution inside the bottle led us to say that reaction is occurring, because some black solid small particles are formed making dirty the solution: formation of FeS.

In the second experiment bellamethane diluted solution, decreasing the gas flow, the issue of the foam is limited, but not completely avoided. The production of FeS is always occurring, however no consistent result was noted, maybe due to low sensibility of drager column measure.

For the third solution experiment the gas washer system was upgraded to decrease the foaming issue and to collect properly all the outflow gasses: two gas washers were set in series, connected with a rubber pipe, so that the first one could work properly with no problem of foaming and the second one could collect and then analyse the clean gas from liquid fraction. As soon as the gas flow is started, solution got darker and some precipitate appeared, but what is more important is that pH decreased by H_2S solubilisation very fast, stopping its scrubbing capacity. The scrubbing solution and the environment must be kept stable and possibly neutral, otherwise the protonic release will create an acid solution, not suitable for H_2S scrubbing efficiency.

Figure 4.15 The doubling system of gas washer and the dark solid particle formation of FeS

Fourth sodium hydroxide solution 0.1M was tested.

Reaction: $2NaOH + H_2S \rightarrow Na_2S + 2H_2O$

This is a classical method for caustic scrubbing, usually doubling the system with a second NaClO washing liquid. 150 ml of sodium hydroxide was inserted, which means more or less 0.015 mol present in the gas washer, considering the stoichiometric reaction with H_2S fed with 50ml/min (0.0019 mol/min), the scrubbing agent should be enough. Unfortunately, despite the excess of NaOH and the ideally pH value, this washing liquid was not able to clean H_2S sufficiently leaving a concentration of 3000 ppm residual gas.

Final test was performed with ideal anoxic solution of bellamethane and some NaOH to increase the pH: the result obtained of 1600 ppm concentration, demonstrates that the experimental approach was correctly set and had worked. Bellamethane washing solution ideally could work but if we do not provide enough basic condition the scrubbing efficiency will decrease. However, NaOH does not work in order to increase and stabilize pH value, because it produces quite immediately precipitation also in anoxic preparation condition. The precipitates which could form are $Fe(OH)_2$, $Fe(OH)_3$ and other oxides, these can cause different problematic blocking the pipes and over pressurizing the system.

Concluding the results from small scale-laboratory tests it becomes clear that:

- pH is very important for good H_2S scrubbing efficiency. It has to be approximately 7 in order to have HS^- ions
- It is necessary to have some ions which reacts with HS^- (no pure water itself coming from the IBC tank)
- NaOH itself cannot ensure sufficient gas cleaning
- Some reagents are necessary to keep the pH value stable, although H_2S will decrease pH very fast. During operation condition, the NH_3 is helpful for this purpose, but depends on how much NH_3 will remain after the previous gas cooling stage.
- $FeCl_2$ seems to have a limit in scrubbing system

4.3.6 **Scale up of scrubbing test**

In the last part of the work, the scale up of the scrubber was tested: following previous results, same condition and upgrades installed were adopted, the only change occurred was the position of bellamethane input which was placed directly in the IBC tank, so that would not create an acidic washing solution and not lowering immediately the pH, keeping it quite neutral. In order to verify the cleaning efficiency for higher flow rate, also the gas mixture has been changed to a scale more comparable to actual reaction conditions: 2.5 times lower to real TCR® 500 gas flow, which means 2% H_2S and 4% NH_3 for 40 m^3/h total gas mixture.

Reaction condition:

- 30’ run reactor: same condition and working procedure like previous time test.
- recirculation rate 510 L/h
- N2 40m^3/h
- H_2S 2% → 13.3 L/min
- NH_3 4% → 26.6 L/min

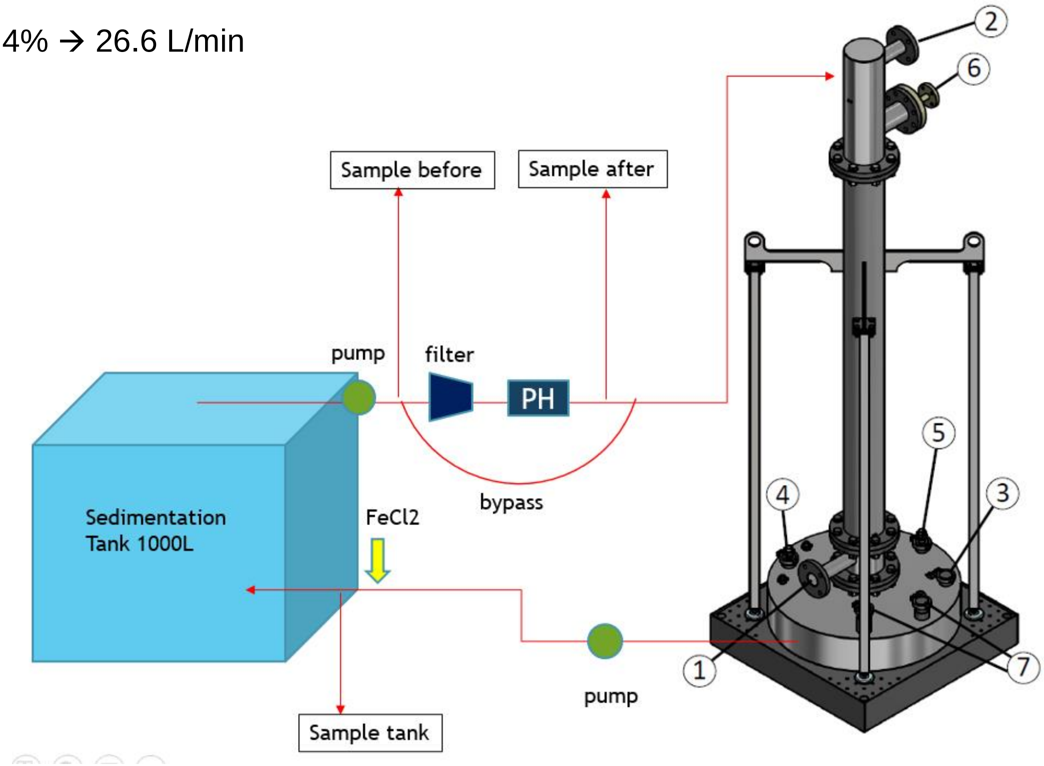


Figure 4.16: Fifth experimental scrubber setup

The gas mixture flow is set % in accordance with nitrogen max flow which is 40m^3/h, i.e. 666 l/min (100% if gas mixture)

Test RUN 1	***1***	***starting FeCl$_2$***	***2***	***3***	***4***	***stop FeCl$_2$***	***5***	***6***
pH	7.10		7.12	7.09	7.10		7.10	7.09
Time *(min)*	0’’	01’’	3’	5’	10’	10’01’’	15’	20’
H_2S ppm	450		1600	950	950		750	1200
NH_3 ppm	0		1	/	/		/	1
FeCl$_2$	0 %		20 % (0,5L/min)	20 %	20 %		0 %	0 %
Temp. *(°C)*	21.2		21.3	21.6	21.7		21.8	21.7
Scrubbing efficiency	Waiting H_2S		92 %	95 %	95 %		96 %	94 %

Table 4.8: Fifth experimental setup for scrubbing reaction

Reproduction of same experiment approach test

Test RUN 2	***1***	***starting FeCl$_2$***	***2***	***3***	***4***	***stop FeCl$_2$***	***5***	***6***
pH	7.07		7.17	7.22	7.25		7.27	7.27
Time *(min)*	0’’	01’’	3’	5’	10’	10’01’’	15’	20’
H_2S ppm	1200		700	1100	500		900	1600
NH_3 ppm	1		1	/	/		< 5	
FeCl$_2$	0 %		20 % (0,5L/min)	20 %	20 %		0 %	0 %
Temp. *(°C)*	22°C		22.1	22.2	22.1		22.1	22.2
Scrubbing efficiency	Same as last test sample		96.5 %	95 %	97.5 %		95.5%	91.5%

Table 4.9: Reproduction of fifth experimental setup for scrubbing reaction 1%= 10’000 ppm

Efficiency considered 2% over 40m^3 N_2 → 2% is 20.000 ppm concentration → result / 20.000

1ppm of H_2S = 1,42 mg/m3

Considering the results obtained in the two tables 4.8 and 4.9 the main goal of reproducibility of the results is reached. Even though the results are not perfectly identical, but there is a qualitative similarity that rise up the confidence on the experimental approach and the know how reached for future operation of the plant. The same timing and approach were adopted when collecting the scrubber results: from time zero was recirculated the gas mixture and washing liquid in the scrubber, then started the bellamethane addition, after 10 minutes stopped the bellamethane inflow and continuously recirculated the scrubber till 20 minutes overall. Qualitatively speaking, it can be seen how the efficiency of gas cleaning is positively subject to the addition of $FeCl_2$. In fact, with the passage of time, the collected data shows low concentrations of residual gases. The first sample, without any washing reagent added, seems to be well cleaned; maybe this is due to the previous unreacted bellamethane present in the IBC tank from the previous test or just the time delay during gas diffusion. As soon as the bellamethane is added the following samples show better cleaning of H_2S and NH_3 due to the low concentration in the gas samples taken. These value ideally could represent the maximum cleaning capacity of scrubber, reaching its limit (residual concentration H_2S 500-1000 ppm). The scrubbing condition also occurs when the inflow of the reagent itself inside the IBC tank is stopped after 10 minutes, the reason must be found in its residual presence inside the system liquid solution. However, the cleaning capacity of the system is limited to the residual presence of the same reagent inside the recirculated liquid, which collapses in the final result after 10 minutes of non-dosing bellamethane. We have to say that overall the scrubbing efficiency for H_2S obtained is quite satisfying, since the results show efficiency of more than 90%, and up to 97,5%. Compared to previous session test in chapter 4.3.4, the upscale of scrubber gas mixture with a factor of 3 produces results that are not deviating significantly. The new feeding point for $FeCl_2$ produced a better environment for scrubbing condition and pH stability. As matter of the fact, the pH value took advantage because no jumping was shown in the display of the pH sensor during $FeCl_2$ addition. But most important, even growing with a factor of 3 the H_2S and NH_3 concentration did not decrease the final washing efficiency.

The final consideration on the NH_3 cleaning efficiency can be seen in the tables: ammonia is always cleaned away, with a total efficiency of close to 99.99 %. The reason must be found: in the reaction of ammonia with the presence of HCl in bellamethane; the HCl produced by reaction of $FeCl_2$ with H_2S; and the amount of water in the IBC tank provides a useful environment that allows NH_3 solubilization. The set percentage of ammonia keeps stable the pH during all the scrubbing test contrasting the acidic reagent feature, moreover, it is affirmable that even if ammonia would react with bellamethane, the presence of water would push the ammonia forming complex of $Fe(H_2O)_6{}^{2+}$ and not $Fe(NH_3)_6{}^{2+}$. It is important to remember that NH_3 solubilize in water, its solubility is 517 g/L at 293 K, which means using an excess of 15L/h of fresh water inside the scrubber will be useful for our scope

The next step would be to test:

- Increase time of $FeCl_2$ addition or increase $FeCl_2$ concentration
- Increase H_2S to worse scenario (2% of 100 m^3/h N_2), similar to TCR® 500 real gas flow
- Increasing the pH if would lead to a better scrubbing efficient of H_2S

Due to the finishing of available time and the upcoming hot-test of the complete TCR® 500 plant, no further scale up scrubber tests have been done. A good know in terms of recirculation, concentration of bellamethane necessary, best pH environment condition and a system that is working quite efficiently with not stuck condition have been reached within this thesis.

5 Discussion

5.1 Discussion of the results

The work performed in this master thesis has led to a series of results dealing with both engineering and chemical aspects of the scrubbing of hydrogen sulphide and ammonia gas, simulating the TCR® gas production. In this section they will be discussed.

The results gained during the commissioning of the scrubber revealed that a pump flow of 510 l/h is the most suitable for suction in and out the washing liquid recirculated between the scrubber and its external tank. These two flows must be set equally otherwise disequilibrium and dry condition inside the scrubber could occur. The bellamethane addition thorough dosing pump should follow 20% of its power, this coincides with the amount necessary to neutralize the hydrogen sulphide gas flow with a safety factor of 0.5 l/min, discovered thank to a previous analytical estimation.

Concerning the activity of the chemical absorption process inside the scrubber, the first results gained were not possible to reproduce because an intense accumulation of FeS in the central column was discovered. For this reason, the installation of a vertical impeller let the system work properly, eliminating its over pressurization. Despite the over pressure is decreased, the results obtained show no good cleaning efficiencies for both H_2S and NH_3 (> 2000 and> 600 ppm). Moreover, the system continued to suffer from the accumulation of solid material formed during the scrubbing reactions. To solve this situation, a tank with some freshwater was installed, with the aim of facilitating the sedimentation of FeS outside the scrubber. This upgrade not only gave better results for cleaning the scrubber components but also improved pH stability of the washing liquid and reduced residual ammonia concentrations (<5 ppm).

Further improvements have been added to the system: a filter positioned before the pH-meter probe to try to keep it as clean as possible, a bypass near it for emergency maintenance, and even more voluminous external tank to facilitate sedimentation and have more washing liquid available where to solubilize the bellamethane. Small-scale chemical investigations analysed the cleaning behaviour of hydrogen sulphide through different washing solutions and the pH of reactions. It has been obtained that a neutral pH is necessary to have good washing efficiency, and the only available way to increase the basicity of bellamethane is to dilute it in freshwater, as the addition of other alkaline compounds (NaOH) causes its precipitation or does not work.

All these upgrades made it possible for the system to work continuously, without having to discharge or interrupt the tests during the commissioning work.

In this way it was proceeded to check the scrubber washing efficiency by initially setting a low-speed gas mixture flow (H_2S 0.6% and NH_3 4%): the best result obtained has a residual concentration of H_2S around 100 ppm and complete cleaning ammonia. Then the H_2S was increased by a factor of 3, reproducing the likely conditions of the gas mix exiting from the TCR® plant. The result showed that the ammonia is completely cleaned and solubilized within the system (<5 ppm), the hydrogen sulphide is cleaned up to an efficiency of 95% (around 1000 ppm). This final result is reproducible and promising for the start-up of the system in real conditions.

In conclusion, evaluating the scrubber test results, a pH value in the neutral range is favourable for the absorption of the hydrogen sulphide in the washing liquid, whereas a lower pH value should be present for better absorption of ammonia. Both considerations can be validated also by theoretical reactions. Hydrogen sulphide requires neutral-basic conditions to produce the HS^- ions which can react with $FeCl_2$ washing reagent. Ammonia, a basic reactant, can react directly with hydrochloric acid present in bellamethane solution, but also with the HCl produced during hydrogen sulphide cleaning reaction. Moreover, ammonia has a high solubilization degree in atmospheric and average temperature water conditions, as a matter of fact, the majority of results had a positive effect on the ammonia scrubbing effect. A final cleaning success was obtained (NH_3: > 99,9%; H_2S: > 95%).

It is important to remember that a lower gas flow mixture (factor 2.5) than the real TCR® gas ideal flow was set, but always respecting the ideal percentage of gas concentration (2% H_2S and 3-4% NH_3). This produced good scrubbing results but also feasible operating conditions with the system installed, moreover longer residence time than the real volume flow in the gas scrubber was established. This last condition has a positive effect on the binding of the gases, so, a change in the gas composition and an increase in the volume flow would presumably lead to a deterioration in the cleaning effect due to a lower mass transfer. For this reason, once the best cleaning conditions have been found, further series of tests should be carried out reproducing the real

TCR® gas flow mixture, using the last setup of scrubber installed which provides continuous cleaning process inside the plant.

5.2 **Future work**

Nowadays TCR 500 plant is already running and achieving its goal, because of time issues it was not possible to install a new scrubber or strongly modify the actual one. Therefore, it is used as ammonia scrubber only and secure the downstream components from corrosion by drying the TCR-gas. Since it is not a long-term solution, further mechanical upgrades are suggested:

1. First of all, an integration in reservoir design would be necessary to avoid iron sulphide sedimentation and trapping inside the scrubber. For this purpose, as can be seen in figure 5.1, the installation of a bigger reservoir with a central cone in the basement would help the suction and recirculation of liquid outside the scrubber, facilitating the separation of solid particles from the washing liquid or other manual cleaning operations. Moreover, to support the external sedimentation process, better separation of solid particles from liquid could be provided with downstream filters addition, and maybe twining the system. For the design of these sedimentation tanks, the necessary investigations should be carried out to determine the influencing factors (particle density, density and dynamic viscosity of the liquid, etc.) for the sedimentation speed.
2. In order to achieve an increased resistance of the packing of the bed to soiling and deposits, packing could be tested with an enamel coating. Otherwise there is a risk of cleaning operations that are often necessary.

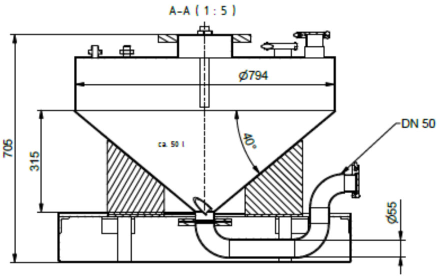


Figure 5.1 shows the possible scrubber design modification in order to better pump out the solid particles from the scrubber unit.

3. Under certain circumstances, based on these initial results, a second gas scrubber would be suitable for series or parallel connections with the existing gas scrubber. In this way, a stepped gas scrubbing could be achieved with coarse and fine activity, differently, one of the two systems could be extensively serviced while at the same time "ensuring" the gas cleaning through a redundant design. In addition, the resident time could be increased by increasing the volume, which could compensate for the possible issue with the higher gas flow in normal TCR® operation. However, this would only double it, whereas the product gas volume flow would be 2.5 times higher. If this measure is not sufficient, the diameter and the height of the central column section could be increased. In this way, the specific surface area can also be increased in parallel for a more effective mass transfer. With a combination of series or parallel connections, both advantages can be achieved, however, this increases the space requirement, costs, control, and regulation effort. On the other hand, through an identical design, synergy effects can be exploited.
4. Another possibility to increase the scrubbing efficiency could be the cooling down of the gas flow: during scrubbing operation, the increase of temperature was registered due to gas-liquid phase exchange. Lowering the overall system temperature could provide better environmental conditions for gas solubility according to Henry law (Heat of neutralization ΔH^0_r = -57,3 kJ/mol). Its potential importance also depends on the temperature development in long-term operation and the throughput of washing liquid, with about 7170 kJ / h being released through the neutralization of ammonia.
5. The last consideration that could be done is in the washing reagent itself: bellamethane is suitable for the gas-liquid reaction both with ammonia and hydrogen sulphide, moreover the byproduct obtained in the sedimentation tank liquid has a second life, so an economical value, for the public wastewater treatment plant. Although these pros of $FeCl_2$ washing liquid, doubling the system could open the new considerations for different potential scrubbing reagents, which are already available in the market. Anyway, further investigations are required.

In any case, safety measures should also be worked out and implemented in the event of inadequate gas cleaning. That is why a bypass pipe to the flare was installed during experimental research for exceptional situations, otherwise activated carbon filter or iron oxide pellets would be added as an additional adsorbent.

5.3 **Automation of the process**

Finally, all the scrubbing processes have to be automatized following the know-how and experience gained during the tests, so that a continuous operation mode can be established:

- Controlling the washing liquid concentration necessary for stochiometric reactions or at least using a safety factor (based on the titration or other analytical methods).
- Calibrating the pH probe once a week and controlling its wellbeing, what is possible due to the installation of a bypass.
- Checking all pumps efficiency and correct recirculation thorough the installation of singular flow meters to monitor possible blockage or unusual deviation to target value.
- Automation of emergency bypass line to the flare in order to protect the following system components in case of insufficient gas scrubbing.

For the next future works, if the suggested additions are followed, it is possible to establish a hypothetical approach for the use of the scrubber and its automation:
Set equal flow for the pumps used in the scrubber inlet and outlet.
Upon the arrival of the bellamethane reagent, estimate its concentration and calculate the stoichiometric quantity that must react with the gases leaving the TCR system. Once the quantity has been established, set the time dosage of the reagent with a controlling factor (in excess); the ideal situation would be to be able to dynamically control the concentrations of the incoming gases and calculate the stoichiometric quantity necessary for the gases to be eliminated minute by minute, also having a double control at the exit of the scrubber. (Theoretically necessary 30 L/h of bellamethane for 2% H_2S max gas flow)
Turn on the scrubber pumps homogenizing the solutions recirculated inside it between the scrubber and the IBC tank. (it is important to have equal flows for a balanced recirculation and to start with 500L of freshwater)

Check the pH of the solution by verifying its neutrality, in case it is too acid it should be diluted with freshwater or change the external tank with a new one, discarding the old washing liquid. Only then the entering gas flow can be started.

According to the values estimated and obtained from the tests, an addition of 10 L of freshwater every hour is necessary to solubilize the ammonia in it. If this quantity is respected and no other interventions are necessary, the volumes of liquids involved should be sufficient for about 20 hours of work, after which it is necessary to replace the external tank with a new one.

Continuous maintenance of the components and control of the various systems installed is important, in this regard it would be necessary to adapt the systems installed with digital alarms to indicate the anomalies present and automatically modify the parameters to be set. Otherwise, the emergency system has to be activated.

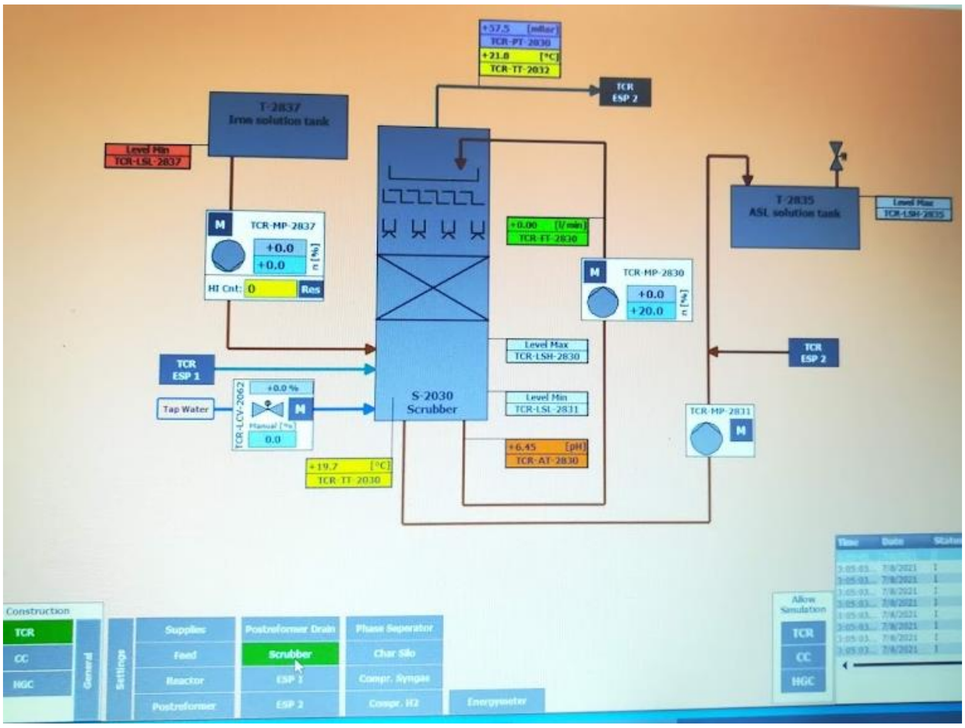


Figure 5.2 automation of scrubber

6 Conclusion

This thesis shows the optimization and commissioning work for the cleaning of hydrogen sulphide and ammonia gases through the use of a wet scrubber.

In this regard, the chemical composition of the washing liquid was examined and the individual components were calibrated and put into operation.

The scrubber could ideally work as the hypothetical reactions show; however a number of complications have required further consideration and modification: the overpressure caused by the entrapment of the solid phase in the bulk of the scrubber has been solved by adding an impeller in place of the rushing rings; the same solid byproduct formed during cleaning was partially eliminated by adding an external sedimentation tank and a filter; better control of the pH of the system was possible through the greater solubilization of the washing reagent with an external tank connected; the optimization of all these practices has also led to an overall reproducibility of the tests and final results.

Thanks to the modifications and upgrades installed through an experimental cause-and-effect method, the functional tests of the gas scrubber showed an overall good cleaning effect both in relation to the proportion of hydrogen sulphide and ammonia. The overall cleaning efficiency of 99.9% and 95% for ammonia and hydrogen sulphide respectively was achieved in continuous preliminary mode.

However, these promising results are only intended for a simulated and not real gas mixture. Before starting the scrubber integrated into the TCR® system with a true continuous gas flow, further improvements are needed and suggested.

From all the acquired knowledge, recommendations for the operational and automation strategy for the system, but also suggestions for optimizing the washing efficiency were developed.

7 References

[1] *World population http://www.umrechnung.org/weltbevoelkerung-aktuelle-momentane.htm.*

[2] *Hoorneweg, Daniel and Bhada-Tata, Perinaz. What a Waste - A Global Review of Solid Waste Management. Urban development series knowledge papers 2012.*

[3] *WWF. World Wide Fund For Nature http://www.wwf.ca/?21901/Earths-resources-depleted-for-2016..*

[4] *Brüggemann, Michael, et al. Climate change in the media. Hamburg climate report - knowledge about ckimate, climate change and effects i Hamburg and norhern Germany,* 2018.

[5] *The daily mirror. Paris Climate Agreement - Only three are not included: Syria, Nicaragua and the USA,* 2017.

[6] *Climate KiIC https://www.climate-kic.org/news/new-ipcc-report-reveals-urgent-need-for-climate-innovation/.*

[7] *G. Lalude, „Importance of Oil to the Global Community,“ Global Journal of Human-Social Science,* 2015.

[8] *R. Rathmann, A. Szklo und R. Schaeffer, „Land use competition for production of food and liquid biofuels: an analysis of the arguments in the current debate",* Renewable energy, 2010.

[9] *T. Bhaskar, B. Bhavya, R. Singh, D. V. Naik et al., „Thermochemical Conversion of biomass to biofue",* Elsevier, 2011.

[10] *A. Hornung, A. Apfelbacher, R. Daschner, N. Jäger et al., „To-Syn-Fuel: Turning sewage sludge into fuels and hydroge" 26th european biomass conference and exhibition.*

[11] *R. Daschner, A. Apfelbacher und A. Hornung, „Thermo-Catalytic Reforming (TCR®) in demonstration scale - experiences from scale up" 27th european biomass conference and exhibition,* 2019.

[12] *SM Kohan, "Basic Principles of Thermochemical Conversion," in Biomass Conversion Processes for Energy and Fuels, SS Sofer and OR Zaborsky, eds., Boston, MA: Springer US, 1981, pp. 145-172..*

[13] *M. Pande and AN Bhaskarwar, "Biomass Conversion to Energy," in Biomass conversion,.*

[14] *A. Demirbaş, "Biomass resource facilities and biomass conversion processing for fuels and chemicals," Energy Conversion and Management, Vol. 42, No. 11, pp. 1357-1378, 2001..*

[15] *SW Banks and AV Bridgwater, "Catalytic fast pyrolysis for improved liquid quality," in Handbook of Biofuels Production, Rafael Luque, Carol Sze Ki Lin, Karen Wilson and James Clark, eds., Elsevier, 2016, pp. 391–405..*

[16] *RK Maurya, AR Patel, P. Sarkar, H. Singh et al., "Biomass, Its Potential and Applications," in Biorefining of Biomass to Biofuels, S. Kumar and RK Sani, eds., Cham: Springer International Publishing, 2018, pp. 25–52..*

[17] *T. Bhaskar, B. Bhavya, R. Singh, DV Naik et al., "Thermochemical Conversion of Biomass to Biofuels," in Biofuels, Elsevier, 2011, pp. 51-77..*

[18] *A. Williams, JM Jones, L. Ma and M. Pourkashanian, "Pollutants from the combustion of solid biomass fuels," Progress in Energy and Combustion Science, Vol. 38, no. 2,.*

[19] *M. Hakkı, T. Salan, E. Altuntaş and E. Karaoğul, "Liquefaction Processes of Biomass for the Production of Valuable Chemicals and Biofuels: A Review," 2013..*

[20] *E. Chornet and RP Overend, "Biomass Liquefaction: An Overview," in Fundamentals of Thermochemical Biomass Conversion, RP Overend, TA Milne and LK Mudge, eds., Dordrecht: Springer Netherlands, 1985, pp. 967-1002..*

[21] *European Union Renewable Energy Centers Agency, The future for renewable energy: Prospects and directions. London: James & James Science Publishers, 1996..*

[22] *PK Swain, LM Das and SN Naik, "Biomass to liquid: A prospective challenge to research and development in the 21st century," Renewable and Sustainable Energy Reviews, Vol. 15, No. 9, pp. 4917-4933, 2011..*

[23] *P. Manara and A. Zabaniotou, "Towards sewage sludge based biofuels via thermochemical conversion - A review," Renewable and Sustainable Energy Reviews, Vol. 16, No. 5,.*

[24] *X. Luo, T. Wu, K. Shi, M. Song et al., "Biomass Gasification: An Overview of Technological Barriers and Socio-Environmental Impact," in Gasification for low- grade feedstock, Y. Yun, ed., InTech, 2018, pp. 1–17..*

[25] *B. de Caprariis, P. de Filippis, M. Scarsella, A. Petrullo et al., "Biomass Gasification and Tar Reforming in a Two-stage Reactor," Energy Procedia, Vol. 61, pp. 1071-1074, 2014..*

[26] *A. Ray and A. Anumakonda, "Production of Green Liquid Hydrocarbon Fuels," in.*

[27] *V. Wilk, H. Hofbauer and M. Kaltschmitt, "Thermo-chemical conversion processes," in Energy aus biomasse, M. Kaltschmitt, H. Hartmann and H. Hofbauer, eds., Berlin.*

[28] *V. Wilk, H. Hofbauer and M. Kaltschmitt, "Thermo-chemical conversion processes," in Energy aus biomasse, M. Kaltschmitt, H. Hartmann and H. Hofbauer, eds., Berlin, Heidelberg: Springer Vieweg, 2016, pp. 646–683..*

[29] *P. Quicker, A. Kruse, K. Weber and D. Blöhse, "Thermochemical Processes for the Production of Biomass Carbonisates," in Biochar, P. Quicker and K. Weber, eds., Wiesbaden: Springer Fachmedien Wiesbaden, 2016, pp. 15–82..*

[30] *RH Venderbosch and W. Prins, "Fast pyrolysis technology development," Biofuels, Bioproducts and Biorefining, Vol. 4, No. 2, pp. 178-208, 2010..*

[31] *MN Uddin, K. Techato, J. Taweekun, M. Mofijur et al., "An Overview of Recent Developments in Biomass Pyrolysis Technologies," Energies, Vol. 11, No. 11, p. 3115, 2018..*

[32] *AM Azeez, D. Meier and J. Odermatt, "Temperature dependence of fast pyrolysis volatile products from European and African biomasses," Journal of Analytical and Applied Pyrolysis, Vol. 90, No. 2, pp. 81-92, 2011..*

[33] *TE McGrath, W. Chan and MR Hajaligol, "Low temperature mechanism for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of cellulose," Journal of Analytical and Applied Pyrolysis, Vol. 66, No. 1-2, pp. 51-70, 2003..*

[34] *J. Scheirs, G. Camino and W. Tumiatti, "Overview of water evolution during the thermal degradation of cellulose," European Polymer Journal, Vol. 37, No. 5, pp. 933-942, 2001..*

[35] *M. van de Velden, J. Baeyens, A. Brems, B. Janssens et al., "Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction," Renewable Energy, Vol. 35, no. 1, Pp. 232-242, 2010..*

[36] *D. Christ, M. Scherzinger, U. Neuling and M. Kaltschmitt, "Thermochemical Conversion of Solid Biofuels: Processes and Techniques," in Energy from Organic Materials (Biomass),.*

[37] *L. Wei, S. Xu, L. Zhang, H. Zhang et al., "Characteristics of fast pyrolysis of biomass in a free fall reactor," Fuel Processing Technology, Vol. 87, No. 10, pp. 863-871, 2006..*

[38] *RJ Evans and TA Milne, "Molecular characterization of the pyrolysis of biomass,".*

[39] *T. Hosoya, H. Kawamoto and S. Saka, "Pyrolysis behaviors of wood and its constituent polymers at gasification temperature," Journal of Analytical and Applied Pyrolysis, Vol. 78, No. 2, pp. 328-336, 2007..*

[40] *P. Morf, P. Hasler and T. Nussbaumer, "Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips," Fuel, Vol. 81, No. 7, Pp. 843-853, 2002..*

[41] *MJ Antal and M. Grønli, "The Art, Science, and Technology of Charcoal Production,".*

[42] *D. Neves, H. Thunman, A. Matos, L. Tarelho et al., "Characterization and prediction of biomass pyrolysis products," Progress in Energy and Combustion Science, Vol. 37, no. 5, Pp. 611-630, 2011..*

[43] *ML Boroson, JB Howard, JP Longwell and WA Peters, "Heterogeneous cracking of wood pyrolysis tars over fresh wood char surfaces," Energy & Fuels, Vol. 3, No. 6, Pp. 735-740, 1989..*

[44] *S. Dasappa, "Thermochemical Conversion of Biomass," in Transformation of Biomass,.*

[45] *A. Hornung, "Pyrolysis," in Transformation of Biomass, A. Hornung, eds., Hoboken: Wiley, 2014, pp. 99-112..*

[46] *J. Fermoso, P. Pizarro, JM Coronado and DP Serrano, "Transportation Biofuels via the Pyrolysis Pathway: Status and Prospects," in Energy from Organic Materials (Biomass),.*

[47] *P. Mohanty, KK Pant and R. Mittal, "Hydrogen generation from biomass materials: challenges and opportunities," Wiley Interdisciplinary Reviews: Energy and Environment, Vol. 4, No. 2, pp. 139–155, 2015..*

[48] *T. Kan, V. Strezov and TJ Evans, "Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters," Renewable and Sustainable Energy Reviews, Vol. 57, pp. 1126–1140, 2016.*

[49] *S. Yaman, "Pyrolysis of biomass to produce fuels and chemical feedstocks," Energy Conversion and Management, Vol. 45, No. 5, pp. 651-671, 2004..*

[50] *D. Mohan, CU Pittman and PH Steele, "Pyrolysis of Wood / Biomass for Bio-oil: A Critical Review," Energy & Fuels, Vol. 20, No. 3, pp. 848-889, 2006..*

[51] *J. Akhtar and N. Saidina Amin, "A review on operating parameters for optimum liquid oil yield in biomass pyrolysis," Renewable and Sustainable Energy Reviews, Vol. 16, No. 7, pp. 5101-5109, 2012..*

[52] *V. Strezov, B. Moghtaderi and JA Lucas, "Thermal study of decomposition of selected biomass samples," Journal of Thermal Analysis and Calorimetry, Vol. 72, No. 3, p. 1041– 1048, 2003..*

[53] *DS Scott, P. Majerski, J. Piskorz and D. Radlein, "A second look at fast pyrolysis of biomass.*

[54] *H. Hernando, S. Jiménez-Sánchez, J. Fermoso, P. Pizarro et al., "Assessing biomass catalytic pyrolysis in terms of deoxygenation pathways and energy yields for the efficient production of advanced biofuels," Catalysis Science & Technology, Vol. 6, No.*

[55] *JA Garcia-Nunez, MR Pelaez-Samaniego, ME Garcia-Perez, I. Fonts et al., "Historical Developments of Pyrolysis Reactors: A Review," Energy & Fuels, Vol. 31, No. 6,.*

[56] *RJM Westerhof, HS Nygård, WPM van Swaaij, SRA Kersten et al., "Effect of Particle Geometry and Microstructure on Fast Pyrolysis of Beech Wood," Energy & Fuels, Vol. 26, No. 4, pp. 2274-2280, 2012..*

[57] *S. Zhou, M. Garcia-Perez, B. Pecha, AG McDonald et al., "Effect of particle size on the composition of lignin derived oligomers obtained by fast pyrolysis of beech wood," Fuel, Vol. 125, pp. 15-19, 2014.*

[58] *AV Bridgwater, P. Carson and M. Coulson, "A comparison of fast and slow pyrolysis liquids from mallee," International Journal of Global Energy Issues, Vol. 27, No. 2, p. 204, 2007..*

[59] *KK Pant and P. Mohanty, "Biomass, Conversion Routes and Products - An Overview," in.*

[60] *P. Roy and G. Dias, "Prospects for pyrolysis technologies in the bioenergy sector: A review," Renewable and Sustainable Energy Reviews, Vol. 77, pp. 59-69, 2017.*

[61] *AV Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," Biomass and Bioenergy, Vol. 38, pp. 68-94, 2012..*

[62] *AV Bridgwater, D. Meier and D. Radlein, "An overview of fast pyrolysis of biomass,".*

[63] *CU Jensen, J. Hoffmann and LA Rosendahl, "Co-processing potential of HTL biocrude at petroleum refineries. Part 2: A parametric hydrotreating study, "Fuel, Born 165,.*

[64] *M. Kaltschmitt, "Biomass as Renewable Source of Energy: Possible Conversion Routes," in Energy from Organic Materials (Biomass), M. Kaltschmitt, ed., New York, NY: Springer New York, 2019, pp. 353–389..*

[65] *AV Bridgwater, "Pyrolysis of Solid Biomass: Basics, Processes and Products," in Energy from Organic Materials (Biomass), M. Kaltschmitt, ed., New York, NY: Springer New York, 2019, pp. 1221-1250..*

[66] *TYA Fahmy, Y. Fahmy, F. Mobarak, M. El-Sakhawy et al., "Biomass pyrolysis: past, present, and future," Environment, Development and Sustainability, Vol. 22, No. 1, Pp. 17–32, 2020.*

[67] *N. Tröger, D. Richter and R. Stahl, "Effect of feedstock composition on product yields and energy recovery rates of fast pyrolysis products from different straw types," Journal of Analytical and Applied Pyrolysis, Vol. 100, pp. 158-165, 2013..*

[68] *A. Funke, M. Tomasi Morgano, N. Dahmen and H. Leibold, "Experimental comparison of two bench scale units for fast and intermediate pyrolysis," Journal of Analytical and Applied Pyrolysis, Vol. 124, pp. 504-514, 2017..*

[69] *J. Lehmann, J. Gaunt and M. Rondon, "Bio-char Sequestration in Terrestrial Ecosystems.*

[70] *ZA Mayer, A. Apfelbacher and A. Hornung, "A comparative study on the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char," Journal of Analytical and Applied Pyrolysis, Vol. 96, pp. 196-202, 2012..*

[71] *A. Oasmaa, E. Kuoppala, S. Gust, and Y. Solantausta, "Fast Pyrolysis of Forestry Residue..*

[72] *A. Oasmaa, C. Peacocke, S. Gust, D. Meier et al., "Norms and Standards for Pyrolysis Liquids. End-User Requirements and Specifications, "Energy & Fuels, Vol. 19, No. 5, Pp. 2155-2163, 2005..*

[73] *S. Czernik and AV Bridgwater, "Overview of Applications of Biomass Fast Pyrolysis Oil,".*

[74] *A. Oasmaa and C. Peacocke, "Properties and fuel use of biomass-derived fast pyrolysis liquids - A guide," VTT Journal, 2010..*

[75] *A. Oasmaa, B. van de Beld, P. Saari, DC Elliott et al., "Norms, Standards, and Legislation for Fast Pyrolysis Bio-oils from Lignocellulosic Biomass," Energy & Fuels, Vol. 29, No. 4, pp. 2471–2484, 2015..*

[76] *S. Brick and S. Lyutse, Biochar: Assessing the Promise and Risks to Guide US Policy, Natural Resources Defense Council, ed., New York, 2010..*

[77] *M. Calonaci, R. Grana, E. Barker Hemings, G. Bozzano et al., "Comprehensive Kinetic Modeling Study of Bio-oil Formation from Fast Pyrolysis of Biomass," Energy & Fuels, Vol. 24, No. 10, pp. 5727-5734, 2010..*

[78] *A. Hornung, A. Apfelbacher, J. Neumann, N. Jäger et al., "Combined Heat and Power Generation from Solid Biomass derived Bioliquids and Syngas by TCR®-Upgrade of TCR-Liquids by Hydrodeoxygenation, "24th European Biomass Conference and Exhibition, Ed..*

[79] *A. Hornung, A. Apfelbacher and S. Sagi, "Intermediate pyrolysis: A sustainable biomassto-energy concept - Biothermal valorisation of biomass (BtVB) process," Journal of Scientific & Industrial Research, Vol. 70, pp. 664-667, 2011.*

[80] *Y. Yang, JG Brammer, M. Ouadi, J. Samanya et al., "Characterization of waste derived intermediate pyrolysis oils for use as diesel engine fuels," Fuel, Vol. 103, pp. 247-257, 2013..*

[81] *A. Hornung, "Intermediate pyrolysis of biomass," in Biomass Combustion Science, Technology and Engineering, Elsevier, 2013, pp. 172-186..*

[82] *N. Jäger, J. Neumann, A. Apfelbacher, R. Daschner et al., "Two decades of intermediate pyrolysis: A major step towards CHP applicable bio-oils," 25th European Biomass Conference and Exhibition, ed., Stockholm, 2017 , Pp. 1194-1197..*

[83] *S. Vitolo, B. Bresci, M. Seggiani and M. Gallo, "Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behavior of the catalyst when used in repeated upgrading – regenerating cycles,"Fuel, Vol. 80, No. 1, pp. 17-26, 2001..*

[84] *AK Kurchania, "Biomass Energy," in Biomass conversion, C. Baskar, S. Baskar and RS Dhillon, ed., Berlin, Heidelberg: Springer Berlin Heidelberg, 2012, pp. 91–122..*

[85] *M. Ahmad, AU Rajapaksha, JE Lim, M. Zhang et al., "Biochar as a sorbent for contaminant management in soil and water: a review," Chemosphere, Vol. 99, pp. 19–33,.*

[86] *A. Hornung, A. Apfelbacher and S. Sagi, "Intermediate pyrolysis: A sustainable biomassto-energy concept - Biothermal valorisation of biomass (BtVB) process," Journal of Scientific & Industrial Research, Vol. 70, pp. 664-667, 2011..*

[87] *B. Glaser, L. Haumaier, G. Guggenberger and W. Zech, "The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics," Natural Sciences, Vol. 88, No. 1, pp. 37-41, 2001.*

[88] *B. Glaser, J. Lehmann and W. Zech, "Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review," Biology and Fertility of Soils, Vol. 35, No. 4, pp. 219-230, 2002..*

[89] *B. Glaser and JJ Birk, "State of the scientific knowledge on properties and genesis of Anthropogenic Dark Earths in Central Amazonia (terra preta de Índio)," Geochimica et Cosmochimica Acta, Vol. 82, pp. 39-51, 2012..*

[90] *A. Hornung, F. Stenzel and J. Grunwald, "Biochar — just a black matter is not enough,".*

[91] *AA Boateng, Pyrolysis of Biomass for Fuels and Chemicals. Elsevier, 2020..*

[92] *MF Demirbas, "Biorefineries for biofuel upgrading: A critical review," Applied Energy, Vol. 86, S151-S161, 2009.*

[93] *A. Demirbas, "Biofuels securing the planet's future energy needs," Energy Conversion and Management, Vol. 50, No. 9, pp. 2239-2249, 2009..*

[94] *JP Diebold, RJ Evans, BE Levie, TA Milne et al., Low pressure upgrading of primary oils from biomass: Annual report, 1 January 1986–31 December 1986.*

[95] *MK Karmakar, J. Mandal, S. Haldar and PK Chatterjee, "Investigation of fuel gas generation in a pilot scale fluidized bed autothermal gasifier using rice husk," Fuel, Vol. 111, pp. 584-591, 2013..*

[96] *SN Naik, VV Goud, PK Rout and AK Dalai, "Production of first and second generation biofuels: A comprehensive review," Renewable and Sustainable Energy Reviews, Vol. 14, No. 2, pp. 578-597, 2010..*

[97] *P. Mohanty, KK Pant, SN Naik, LM Das et al., "Fuel production from biomass: Indian perspective for pyrolysis oil," Journal of Scientific & Industrial Research, No. 70,.*

[98] *A. Oasmaa, B. van de Beld, P. Saari, DC Elliott et al., "Update on standardization of fast pyrolysis bio-oils from lignocellulosic biomass," IEA Bioenergy Task 34 PyNe 37,.*

[99] *J. Lehto, A. Oasmaa, Y. Solantausta, M. Kytö et al., Fuel oil quality and combustion of fast pyrolysis bio-oils, Espoo, 2018..*

[100] *A. Oasmaa, J. Korhonen and E. Kuoppala, "An Approach for Stability Measurement of Wood-Based Fast Pyrolysis Bio-Oils," Energy & Fuels, Vol. 25, No. 7, pp. 3307-3313, 2011..*

[101] *T. Stoikos, "Upgrading of Biomass Pyrolysis Liquids to High-Value Chemicals and Fuel Additives," in Biomass Pyrolysis Liquids Upgrading and Utilization, AV Bridgwater and G. Grassi, eds., Dordrecht: Springer Netherlands, 1991, pp. 227-241.*

[102] *A. Demirbas, "Progress and recent trends in biofuels," Progress in Energy and Combustion Science, Vol. 33, No. 1, pp. 1-18, 2007..*

[103] *JP Diebold and S. Czernik, "Additives To Lower and Stabilize the Viscosity of Pyrolysis Oils during Storage," Energy & Fuels, Vol. 11, No. 5, pp. 1081-1091, 1997..*

[104] *A. Oasmaa, E. Kuoppala, J.-F. Selin, S. Gust et al., "Fast Pyrolysis of Forestry Residue and Pine. 4. Improvement of the Product Quality by Solvent Addition, "Energy & Fuels, Vol. 18, No. 5, pp. 1578-1583, 2004.*

[105] *A. Oasmaa and E. Kuoppala, "Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel, "Energy & Fuels, Vol. 17, No. 4, pp. 1075-1084, 2003..*

[106] *S. Czernik, DK Johnson and S. Black, "Stability of wood fast pyrolysis oil," Biomass and Bioenergy, Vol. 7, No. 1-6, pp. 187-192, 1994..*

[107] *X Hornung, A., Apfelbacher, A. and Sagi, S. (2011) Intermediate pyrolysis: a sustainable biomassto-energy concept – biothermal valorization of biomass BtVB process. Journal of Scientific & Industrial Research, 70, 664–667..*

[108] *S. Steiert, J. Brellochs and M. Specht, "Subproject V: Process simulation AER gasification,".*

[109] *K. Bloche-Daub, H. Hartmann, H. Hofbauer, M. Kaltschmitt et al., “Introduction and Objectives,” in Energy aus biomasse, M. Kaltschmitt, H. Hartmann and H. Hofbauer, eds., Berlin, Heidelberg: Springer Vieweg, 2016, pp. 1–76..*

[110] *The European Parliament and the Council of the European Union, DIRECTIVE 2009/28 / EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of April 23, 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealin.*

[111] *I. Lewandowski and C. Wilhelm, “Biomasse Development,” in Energy aus biomasse, M. Kaltschmitt, H. Hartmann and H. Hofbauer, eds., Berlin, Heidelberg: Springer Vieweg, 2016, pp. 77–123..*

[112] *Akash, Bilal. Thermochemical Depolymerization of Biomass. ELSEVIER. pp 827-834, 2015,52.*

[113] *H. Yang, R. Yan, H. Chen, DH Lee et al., "Characteristics of hemicellulose, cellulose and lignin pyrolysis," Fuel, Vol. 86, No. 12-13, pp. 1781-1788, 2007..*

[114] *SA Channiwala and PP Parikh, "A unified correlation for estimating HHV of solid, liquid and gaseous fuels," Fuel, Vol. 81, No. 8, pp. 1051-1063, 2002..*

[115] *European Commission, sewage sludge definition, https://ec.europa.eu/environment/topics/waste-and-recycling/sewage-sludge_en.*

[116] *J. Werther and T. Ogada, "Sewage sludge combustion," Progress in Energy and Combustion Science, Vol. 25, No. 1, pp. 55-116, 1999..*

[117] *A. Roskosch and P. Heidecke. "Sewage sludge disposal in the Federal Republic of Germany." Federal Environment Agency, ed. (2018)..*

[118] *S. Werle and RK Wilk, "A review of methods for the thermal utilization of sewage sludge: The Polish perspective," Renewable Energy, Vol. 35, No. 9, pp. 1914-1919, 2010..*

[119] *B. Wiechmann, C. Dienemann, C. Kabbe, S. Brandt et al., Sewage sludge management in Germany, Federal Environment Agency, ed., Dessau-Roßlau, 2015..*

[120] *N. Jäger, R. Conti, J. Neumann, A. Apfelbacher et al., "Thermo-Catalytic Reforming of Woody Biomass," Energy & Fuels, Vol. 30, No. 10, pp. 7923-7929, 2016..*

[121] *R. Conti, N. Jäger, J. Neumann, A. Apfelbacher et al., "Thermocatalytic Reforming of Biomass Waste Streams," Energy Technology, Vol. 5, No. 1, pp. 104–110, 2017..*

[122] *J. Oliva, A. Bernhardt, H. Reisinger, M. Domenig et al., Sewage sludge: materials for waste management, Klagenfurt, Vienna, 2009..*

[123] *Thermal treatment of sewage sludge: co-incineration in power plants, May 2012. Hennef (Sieg): German Association for Water Management, Sewage and Waste, 2012, Bd. M 387..*

[124] *BDEW Federal Association of Energy and Water Management e. V, ed.,Wastewater data Germany: structural data on wastewater disposal, Berlin, 2019..*

[125] *The European Parliament and the Council of the European Union, DIRECTIVE.*

[126] *Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Ordinance on the reorganization of sewage sludge recycling..*

[127] *The Council of the European Communities, DIRECTIVE OF THE COUNCIL of 21. May 1991 on urban waste water treatment (91/271 / EEC): 91/271 / EEC..*

[128] *The Commission of the European Communities, DIRECTIVE 98/15 / EC OF THE COM-MISSION of February 27, 1998 amending Council Directive 91/271 / EEC in connection with certain requirements set out in Annex I: 98/15 / EC..*

[129] *A. Hornung, A. Apfelbacher, M. Quadi and J. Neumann, "Pyrolysis oil and processes for its production," DE102015108552A1, 2015..*

[130] *S. Binder, M. Jakuttis, A. Apfelbacher and A. Hornung, "Plant and process for the thermocatalytic treatment of material and pyrolysis oil produced with it," WO2015158732A1, 2015.*

[131] *N. Jäger, R. Conti, J. Neumann, A. Apfelbacher et al., "Thermo-Catalytic Reforming of Woody Biomass," Energy & Fuels, Vol. 30, No. 10, pp. 7923-7929, 2016..*

[132] *J. Neumann, S. Binder, A. Apfelbacher, JR Gasson et al., "Production and characterization of a new quality pyrolysis oil, char and syngas from digestate - Introducing the thermo- catalytic reforming process," Journal of Analytical and Applied Pyroly.*

[133] *J. Neumann, J. Meyer, M. Ouadi, A. Apfelbacher et al., "The conversion of anaerobic digestion waste into biofuels via a novel Thermo-Catalytic Reforming process," Waste management (New York, NY), Vol. 47, No. Pt A, pp. 141–148, 2016..*

[134] *M. Ouadi, N. Jaeger, C. Greenhalf, J. Santos et al., "Thermo-Catalytic Reforming of municipal solid waste," Waste management (New York, NY), Vol. 68, pp. 198–206, 2017..*

[135] *N. Schmitt, A. Apfelbacher, N. Jäger, R. Daschner et al., "Thermo-chemical conversion of biomass and upgrading to biofuel: The Thermo-Catalytic Reforming process - A review," Biofuels, Bioproducts and Biorefining, Vol. 13, No. 3, pp. 822-837, 2019..*

[136] *R. Daschner, J. Grunwald, A. Apfelbacher and A. Hornung, Drop-in biofuels from biogenic waste streams via the thermo-catalytic reforming process, Fraunhofer UMSICHT, ed., Sulzbach-Rosenberg..*

[137] *Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT Branch Sulzbach-Rosenberg, Ed., The biobattery: Thermo-Catalytic Reforming TCR®,.*

[138] *S. Binder, M. Jakuttis, A. Apfelbacher and A. Hornung, "System and method for thermocatalytic treatment of material and pyrolsis oil produced therewith," WO2015158732A1,.*

[139] *J. Neumann, N. Schmitt, N. Jäger, R. Conti et al., "Hydrodeoxygenation of bio-oils from thermo-catalytic reforming - high energy efficient route to renewable gasoline and diesel," 24th European Biomass Conference and Exhibition, ed ., Amsterdam, 201.*

[140] *A. Hornung, A. Apfelbacher, R. Daschner, N. Jäger et al., "EN-fuels from solid waste biomass by thermo-catalytic reforming," Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes, ed., 2019..*

[141] *J. Neumann, "Production of renewable fuels from biogenic residues by thermochemical conversion and refining as well as their motor application," Dissertation, Oberhausen, 2019..*

[142] *J. Neumann, N. Schmitt, N. Jäger, R. Conti et al., Conversion of Residual Biomass in a Thermo-Catalytic Reforming Plant - an Experimental Investigation of Sewage Sludge.*

[143] *J. Neumann, N. Jäger, A. Apfelbacher, R. Daschner et al., "Upgraded biofuel from residue biomass by Thermo-Catalytic Reforming and hydrodeoxygenation," Biomass and Bioenergy, Vol. 89, pp. 91–97, 2016..*

[144] *R. Daschner, A. Apfelbacher and A. Hornung, "Thermo-Catalytic Reforming (TCR®).*

[145] *J. Neumann, A. Hornung, A. Apfelbacher and R. Daschner, "Pyrolysis of Residual Biomass via Thermo-Catalytic Reforming - Experimental Investigation of Sewage Sludge," 25th European Biomass Conference and Exhibition, ed., Stockholm, 2017, p. 949–.*

[146] *Q. Lu, W.-Z. Li and X.-F. Zhu, "Overview of fuel properties of biomass fast pyrolysis oils,".*

[147] *K. Raveendran and A. Ganesh, "Heating value of biomass and biomass pyrolysis products," Fuel, Vol. 75, No. 15, pp. 1715-1720, 1996..*

[148] *GW Mushrush and JG Speight, Petroleum products: Instability and incompatibility. Washington DC: Taylor & Francis, 1995..*

[149] *N. Schmitt and A. Hornung, "Hydrotreating of bio-oil from Thermo-Catalytic Reforming.*

[150] *N. Schmitt, A. Apfelbacher and A. Hornung, Thermo-catalytic reforming and hydrotreating: Production of fuels and chemicals from biogenic residues, Straubing, 2017.*

[151] *R. Conti, N. Jäger, J. Neumann, A. Apfelbacher et al., "Thermocatalytic Reforming of Biomass Waste Streams," Energy Technology, Vol. 5, No. 1, pp. 104–110, 2017..*

[152] *DC Elliott, TR Hart, GG Neuenschwander, LJ Rotness et al., "Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products,".*

[153] *CE Greenhalf, DJ Nowakowski, AB Harms, JO Titiloye et al., "A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products,".*

[154] *AK Hossain, M. Ouadi, SU Siddiqui, Y. Yang et al., "Experimental investigation of performance, emission and combustion characteristics of an indirect injection multicylinder CI engine fueled by blends of de-inking sludge pyrolysis oil with biodiesel.*

[155] *K. Crombie, O. Mašek, SP Sohi, P. Brownsort et al., "The effect of pyrolysis conditions on biochar stability as determined by three methods," GCB Bioenergy, Vol. 5, No. 2,.*

[156] *IF Titiladunayo, AG McDonald and OP Fapetu, "Effect of Temperature on Biochar Product Yield from Selected Lignocellulosic Biomass in a Pyrolysis Process," Waste and Biomass Valorization, Vol. 3, No. 3, pp. 311-318, 2012.*

[157] *H. Zhang, P. Voroney and G. Price, "Biochar effects on soil organic carbon storage," in Biochar, Y.-S. Ok, SM Uchimiya, SX Chang and N. Bolan, eds., Boca Raton, London and New York: CRC Press Taylor & Francis Group, 2016, pp. 325–356..*

[158] *S. van Loo and J. Koppejan, The handbook of biomass combustion and co-firing. London and Sterling, VA: Earthscan, 2007..*

[159] *J. Weber, "Energy carriers," in Stoves and fireplaces, M. Herrmann and J. Weber, eds., Berlin and Vienna et al.: Beuth, 2011, pp. 25–72..*

[160] *M. Blanco Lopez, C. Blanco, A. Martinez-Alonso and J. Tascon, "Composition of gases released during olive stones pyrolysis," Journal of Analytical and Applied Pyrolysis, Vol. 65, No. 2, pp. 313-322, 2002..*

[161] *A. Dominguez, JA Menendez, Y. Fernandez, JJ Pis et al., "Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas," Journal of Analytical and Applied Pyrolysis, Vol. 79, No. 1-2, pp. 128-135, 2007..*

[162] *A. Hornung, A. Apfelbacher, R. Daschner, N. Jäger et al., "To-Syn-Fuel: Turning sewage sludge into fuels and hydrogen," 26th European Biomass Conference and Exhibition, ed., Copenhagen, 2018, p 1035-1038..*

[163] *N. Schmitt, A. Apfelbacher and A. Hornung, "Thermo-Catalytic Reforming as Basement for a Novel Biorefining Route to Produce Chemicals and Fuels," 26th European Biomass Conference and Exhibition, ed., Copenhagen, 2018, pp. 935-939 ..*

[164] *BOOK Coulson & Richardson_s Chemical Engineering. Vol. 6_ Chemical Engineering Design_ 4th Ed.*

[165] *PERFORMANCE EVALUATION OF WET SCRUBBER SYSTEM FOR INDUSTRIAL AIR POLLUTION CONTROL Bashir Ahmed Danzomo, Momoh-Jimoh E. Salami, Sani Jibrin, Md. R. Khan, and Iskandar M. Nor 2012.*

[166] *Wet Scrubbers ByKenneth C. Schifftner, Howard E. Hesketh Edition2nd Edition First Published1996.*

[167] *PJ Woolcock and RC Brown, "A review of cleaning technologies for biomass-derived syngas," Biomass and Bioenergy, Vol. 52, pp. 54–84, 2013..*

[168] *https://emis.vito.be/en/bat/tools-overview/sheets/gas-scrubbing-general.*

[169] *https://sensorex.com/wet-scrubbers/.*

[170] *https://www.deloachindustries.com/blog/hydrogen-sulfide-scrubber.*

[171] *https://marinecue.it/riduzione-delle-emissioni-inquinanti-navali-lo-scrubber/18872/.*

[172] *RP Gupta, BS Turk, JW Portzer and DC Cicero, "Desulfurization of syngas in a transport reactor," Environmental Progress, Vol. 20, No. 3, pp. 187-195, 2001..*

[173] *OV Okoro and Z. Sun, "Desulphurization of Biogas: A Systematic Qualitative and Economic-Based Quantitative Review of Alternative Strategies," ChemEngineering, Vol. 3, No. 3, p. 76, 2019..*

[174] *Advanced Technologies for Desulphurisation of Coke Oven Gas.*

[175] *Caustic Scrubber Designs for H2S Removal from Refinery Gas Streams. Mamrosh, D.L., K.E. McIntush, K. Fisher Trimeric Corporation 2014.*

[176] *Weichgrebe Kapitel 6: Biogas (Zusammensetzung, Nutzung und Aufbereitung).*

[177] *GASAUFBEREITIJNG UND VERWERTUNGSMÖGLICHkEITEN.*

[178] M. K. H. H. H. Hofbauer, Energie aus Biomasse Grundlagen, Techniken und Verfahren Editors (view affiliations), 2016.

[179] *Water Scrubbing for Removal of Hydrogen Sulfide (H2S) Inbiogas from Hog Farms Cheng-Chang Lien1*, Jeng-Lian Lin1, Ching-Hua Ting2 2014.*

[180] *Absorption of Hydrogen Sulfide into Aqueous Ferric Chloride SolutionsSatoru Asai, Hidemi Nakamura, Hideaki Aikawa 1997.*

[181] *Operational Characteristics of Effective Removal of H2S and NH3 Waste Gases by Activated CarbonBiofilter Ying-Chien Chung , Yu-Yen Lin & Ching-Ping Tseng, 21 Feb 2012.*

[182] *Ippc report https://www.climate-kic.org/news/new-ipcc-report-reveals-urgent-need-for-climate-innovation/.*

[183] *Neidel Johannes master thesis “Evaluation of a plant concept for fuel production by thermochemical Conversion of sewage sludge” 2018.*

[184] *Tosynfuel Turning sewage sludge into fuels and hydrogen Issue 3 / October 2020 Filippo Baioli, University of Bologna, reported To-Syn-Fuel LCA preliminary results at Ecomondo 2019. Credit: ETA-Florence Renewable Energies..*

[185] *Life Cycle Assessment of TCR-PSA-HDO integrated system to produce biofuels from sewage sludge . Filippo Baioli, Diego Marazza, Andrea Contin, Luciano Vogli, Roberto Porcelli, Serena Righi . University of Bologna.*

[186] *Serena Righi paper 5. Life cycle assessments of waste-based biorefineries - A critical review.*

[187] *Diego Marazza aStefano Macrelli , Mirta D’Angeli , Serena Righi , Andreas Hornung, Andrea Contin “Greenhouse gas savings and energy balance of sewage sludge treated through an enhanced intermediate pyrolysis screw reactor combined with a reforming process.*

[188] *To-Syn-Fuel, The demonstration of waste biomass to synthetic fuels and green hydrogen: Map and quantification of all inputs and outputs for TCR 300 and integrated TCR / PSA / HDO plant, Sulzbach-Rosenberg, 2018..*

[189] *Thermo-Catalytic Reforming (TCR®): a Platform Technology to Contribute Present Energy, Environmental and Resource Challenges. Jäger, N., Conti, R., Neumann, J., Apfelbacher, A., Daschner, R., Binder, S., Hornung, A. 24th European Biomass Conference.*

[190] *UNITED FILLER FABRIKEN GmbH & Co. KG. "Plastic packing: Physical parameters: Plastic packing." (Undated), [Online]. Accessible under:https:// www.vff.com/de/produkte/fuellkoerper/kunststoffe.*

[191] *Benjamin Ott, master thesis "Generation of green energy and products from residues - commissioning and optimization of a demonstrator for thermo-chemical conversion" 2021.*

[192] *A. Bassani, G. Bozzano, C. Pirola, E. Ranzi et al., "Low Impact Methanol Production from Sulfur Rich Coal Gasification," Energy Procedia, Vol. 105, pp. 4519-4524, 2017..*

[193] *Donau Chemie AG, Safety data sheet: Donau Bellamethan classic, Vienna, 2020. Donau.*

[194] *Chemie AG, Danube Bellamethane classic, Vienna, 2018. Donau Chemie AG, Donau.*

[195] *Bellamethane: Product family, Vienna, 2014..*

[196] *Lutz-Jesco GmbH, Motor-driven diaphragm metering pump: MEMDOS L: Operating instructions, Wedemark, 2020..*

[197] *Wolfgang Wussow Pumpen-Filter-Technik GmbH, AM magnetic centrifugal pumps, Hildesheim.*

[198] *Watson-Marlow Pumps Group, Watson-Marlow 620UN / 620U, 620SN / 620S pumps, Falmouth, 2005..*

[199] *JUMO GmbH & Co. KG, publisher, JUMO AQUIS 500 pH: transmitter / controller for pH value, redox, voltage and NH3 (ammonia) concentration Type 202560: B 202560.0, Fulda, 2017..*

[200] *Linde GmbH, Ammonia 5.0, Pullach, 2008. Linde GmbH, Hydrogen sulfide 2.5,.*

[201] *Dräger Safety AG & Co. KGaA, Hydrogen sulfide 0.2% / A (CH 28101): Dräger tubes®, Lübeck, 2001.*

[202] *Dräger Safety AG & Co. KGaA, Hydrogen sulfide 100 / a (CH 29 101): Dräger tubes®, Lübeck, 2015..*

[203] *Dräger Safety AG & Co. KGaA, Ammonia 0.5% / a (CH 31901): Dräger-Tubes®,.*

[204] *Dräger Safety AG & Co. KGaA, Ammonia 5 / a (CH20501): Dräger-Tubes®, Lübeck, 2010..*

[205] *Dräger Safety AG & Co. KGaA, Manual for Dräger tubes® and MicroTubes, Lübeck, 2021..*

[206] *https://www.substech.com/dokuwiki/lib/exe/detail.php?id=pourbaix_diagrams&cache=cache &media=pourbaix_diagram.png.*

[207] *Duran Gas Washer 09_technical_information.*

[208] *https://emis.vito.be/en/bat/tools-overview/sheets/gas-scrubbing-general.*

[209] *https://sensorex.com/wet-scrubbers/.*

[210] *N. Schmitt, A. Apfelbacher, N. Jäger, R. Daschner et al., "Thermo-chemical conversion of biomass and upgrading to biofuel: The Thermo-Catalytic Reforming process - A review," Biofuels, Bioproducts and Biorefining, Vol. 13, No. 3, pp. 822-837, 2019..*

[211] *RJM Westerhof, HS Nygård, WPM van Swaaij, SRA Kersten et al., "Effect of Particle Geometry and Microstructure on Fast Pyrolysis of Beech Wood," Energy & Fuels, Vol. 26, No. 4, pp. 2274-2280, 2012..*