

Master Thesis

Product Gas Cleaning for Biomass Gasification with Focus on Catalytic Tar Decomposition and Operation of a Downstream Reformer

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unter der Leitung von

Univ.Prof. Dipl.-Ing. Dr.techn. Hermann Hofbauer

unter der Betreuung von

Univ.Prof. Dipl.-Ing. Dr.techn. Christoph Pfeifer

Projektass. Dipl.-Ing. Christoph Varga

Institut für Verfahrenstechnik, Umwelttechnik und technische Biowissenschaften

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Fakultät für Maschinenwesen und Betriebswissenschaften

von

Matthias Kuba

Matrikelnummer: 0727381

Starchantgasse 9

1160 Wien

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Matthias Kuba

Kurzfassung

Die Vergasung von Biomasse ist eine vielversprechende Technologie für die dezentrale Erzeugung von Wärme, Strom und Syntheseprodukten. Systeme zur Biomassevergasung müssen jedoch verbessert werden, um sie gegenüber anderen Kraftwerkstypen konkurrenzfähig zu machen. Die Gasreinigung nimmt hierbei eine Schlüsselrolle ein. Zurzeit wird das Produktgas mittels Filter und Wäscher gereinigt. Da das Produktgas jedoch vor diesen Gasreinigungsschritten gekühlt werden muss, sind diese Systeme nicht energieeffizient.

Diese Arbeit zeigt Optionen zur Heißgasreinigung von Produktgas auf. Die Reduktion von Chlor-, Stickstoff- und Schwefelverbindungen sowie Partikeln und Teeren ist hierbei berücksichtigt. Ein Kapitel befasst sich im Speziellen mit der gegenwärtigen Erforschung von Katalysatoren zur Spaltung von Teeren. Es wurden Versuche an einem dem Vergaser nachgeschalteten Teerreformer an dem Biomassekraftwerk Güssing, Österreich, durchgeführt. Ein Teilstrom des Produktgases wurde von dem Vergaser in den Teerreformer geleitet. In dem Reformer befanden sich zwei Lagen von Monolithen.

Die durchgeführten Tests zeigten vielversprechende Resultate für die weitere Erforschung eines solchen Gasreinigungssystems. Temperatursprünge während der Versuche führten jedoch zu thermischer Beanspruchung der Monolithen. Die Resultate werden präsentiert und diskutiert.

Abstract

Biomass gasification is a promising technology for decentralized generation of heat, power and synthetic products. However, biomass gasification systems have to be improved to make them more competitive. Gas cleaning is one of the key areas in which an improvement has to be achieved. Currently, the product gas is cleaned with cold gas filters and scrubbers. Since the product gas has to be cooled down before gas cleaning, the energy efficiency of these systems decreases.

This thesis reviews hot gas cleaning options to reduce impurities in the product gas. The reduction of chlorine-, nitrogen- and sulfur compounds as well as particles and tars is considered. One chapter will specifically highlight the current research of catalysts for decomposition of tars. Experiments on a downstream tar reformer at the biomass gasification plant in Güssing, Austria, were carried out. A slip stream of product gas from the gasifier was transported into the reformer. Inside the reformer there were two layers of monoliths. The tests showed promising results for further investigations. However, sudden temperature changes during the experiments led to strain of the catalysts. The results are presented and discussed.

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List of Abbreviations and Symbols

Symbol	Meaning
CHP	Combined Heat and Power
DFB	Dual Fluidized Bed
LHV	Lower Heating Value
FIR	Flow Indicating Recorder
FIRC	Flow Indicating Recording Controller
PAHs	Polycyclic aromatic hydrocarbons
ppm	parts per million
ppmv	parts per million by volume
TIRAS	Temperature Indicating Recording Alarming Switch
TIRC	Temperature Indicating Recording Controller
TIRCAS	Temperature Indicating Recording Controlling Alarming Switch
vol%	volume percent
wt%	weight percent

1 Introduction

In the last few decades the generation of power, heat and synthetic products was characterized by the development of large, central power plant systems. The rapid increase of the power demand could only be balanced by the development of large grids with centralistic production systems. Due to the regulated energy market centralistic systems were economically advantageous.

Nowadays, a liberalization of the energy market takes place. Long term investments for the development of large power plant systems become more risky due to the increasing competition with small, regional energy suppliers. These new circumstances benefit the development of smaller, decentralized power plants.

As a consequence of the increasing awareness of the climate change environmentally friendly processes play an ever-increasing role in energy technology. Besides, the limited availability of fossil resources such as oil, coal and natural gas strengthens the development of renewable energy systems.

Biomass gasification counts as one of the most promising technologies for decentralized production of power, heat and/or synthetic products. In Austria more than 50% of the land area is forest. Therefore, the gasification of wood not only provides CO_2 -neutral and renewable energy, but also enhances the creation of value in the region. As a result the dependency on fossil fuel exporters could be minimized.

At the Vienna University of Technology a dual fluidized bed (DFB) gasifier has been developed and was successfully demonstrated in Güssing, Austria. The biomass power plant in Güssing has a fuel input capacity of 8 MW and has an output of 2 MW(el) and 4.5 MW(th).

The product gas has to be cleaned from impurities before it can be used for the production of electricity or synthetic products. Nowadays, gas cleaning is realized by cold gas filters and scrubbers. This is relatively expensive and not very energy efficient because the product gas has to be cooled down before the gas cleaning. Therefore, in present times most researchers focus on hot gas cleaning systems.

This thesis will give a short overview of gasification technologies. It will further explain

which impurities have to be separated from the product gas. The current gas cleaning methods and especially the research on hot gas cleaning done in the last few years will be reviewed in detail. There will be a focus on the catalytic decomposition of tars. Furthermore, experiments on a downstream tar reformer which were carried out at the biomass gasification plant in Güssing will be explained. The results will be presented and discussed.

2 Principles of Biomass Gasification

Gasification is the conversion of solid or liquid feedstock into product gas. In comparison to combustion (a closely related thermochemical process) the feedstock is converted into a secondary energy carrier. Gasification creates a product gas, in which energy is held in chemical bonds. Combustion releases that energy by breaking those bonds (Basu, 2010, p.117).

The gasification process requires a gasifying medium to convert the solid carbon (C) of the biomass into gases. The most important gasifying media are oxygen (O_2), steam (H_2O), hydrogen (H_2), carbon dioxide (CO_2) and air (21% O_2 , 79% N_2). If air is used, the product gas contains high amounts of nitrogen, which does not contribute to its heating value since it is an inert gas (Kaltschmitt et al., 2009, p.600).

The temperatures in biomass gasifiers are usually between $800^\circ C$ and $1200^\circ C$. The product gas is composed of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), methane (CH_4) and light hydrocarbons. During the thermochemical conversion also tars (condensable hydrocarbons) and nitrogen compounds, such as ammonia (NH_3) and hydrogen cyanide (HCN), as well as solid products are formed (Simell, 1997).

Typically, the gasification process includes the following steps, which often overlap since there is not always a sharp boundary between them: drying, thermal decomposition or pyrolysis and char gasification.

First the feedstock is dried at temperatures between $100^\circ C$ and $200^\circ C$ to remove the water bound in the biomass. From $200^\circ C$ to $650^\circ C$ pyrolytic degradation takes place. Pyrolysis is a thermal decomposition process without the addition of an external agent. The products of pyrolysis then react both among themselves and with the gasifying medium. The char produced through pyrolysis also reacts with the gasifying agent. This biomass char is not pure carbon, it also contains hydrocarbon. Therefore in pyrolysis char certain amounts of hydrogen and oxygen can be found (Basu, 2010, p.120).

Figure 1 shows the three main groups of biomass gasifier configurations: fixed bed gasifiers (also called moving bed gasifiers), fluidized bed gasifiers and entrained bed gasifiers. This

commonly used classification is based on the fluid mechanics in the reactor. However, gasifiers also can be categorized regarding the way of providing heat or the pressure ratio in the reactor (atmospheric or increased pressure) (Kaltschmitt et al., 2009, p.602). Heat can be provided either autotherm (internal) or allotherm (external). Autothermal heat supply can be realized by partial combustion of the feedstock in the gasifier. As a consequence, the product gas contains N_2 , which does not contribute to its heating value. Allothermal heat supply can be realized by heat exchanger or by dual fluidized bed systems (further explained in chapter 2.2.3)

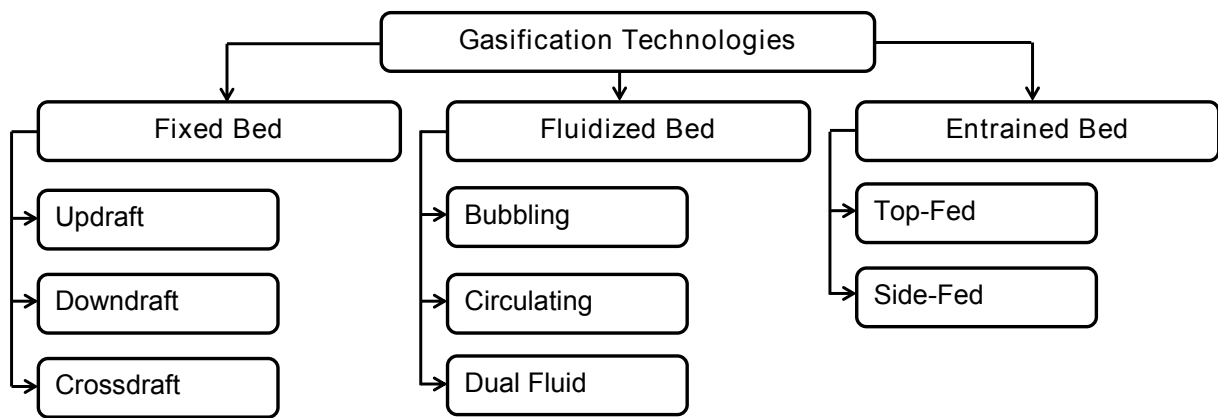


Figure 1: Classification of Gasification Technologies

2.1 Fixed Bed Gasification

In a fixed bed gasifier the feedstock usually is added at the top and moves downwards due to gravity and continuous material degradation. As a consequence, fixed bed gasifiers are also known as moving bed gasifiers (Basu, 2010, p.169). The area in which the gasifying medium is added depends on the type of the fixed bed gasifier (updraft, downdraft or crossdraft gasifier). The gasifying medium reacts with the feedstock and is led through the fixed bed together with the produced gas. As a result, the steps of gasification proceed to a great extend spatially separated. Fixed bed gasifiers can be economically operated in small sizes. For this reason all around the world numerous small-scale fixed bed gasifiers are in use in present times (Kaltschmitt et al., 2009, p.603).

2.1.1 Updraft Gasification

The updraft gasification belongs to the oldest and simplest designs for fixed bed gasifiers. Figure 2 shows the different zones in an updraft gasifier. Usually the feedstock is added into a shaft-shaped reactor from the top and the gasifying agent from the bottom. The feedstock moves downwards whereas the gasifying medium travels upwards. As a result, updraft gasification is also referred to as counter current gasification (Kaltschmitt et al., 2009, p.605). The gasifying medium is added to the reactor through a grill at the bottom. Instantly, it comes into contact with the hot ash (Ruiz et al., 2013). This area is called oxidation zone. Here, the chemical reactions deliver the heat necessary for the gasification process. In this zone there can locally emerge such high temperatures that non decomposable ash components might melt and transform into slag. The heated gas travels upwards into the reduction zone. Here the gasification reactions take place. On its way through the reactor the gas further passes the pyrolysis and the drying zone. The gas temperature decreases on the way up and leaves the gasifier at the top with degrees around $100^{\circ}C - 200^{\circ}C$. Due to the low outlet temperature of the product gas updraft gasifiers achieve high cold-gas efficiency. Another important advantage of this technology is the wide spectrum of possible solid feedstock. Nevertheless, the gas produced through pyrolysis does not pass the hot reduction zone. Therefore it contains high amounts of undesirable tars (Kaltschmitt et al., 2009, p.606).

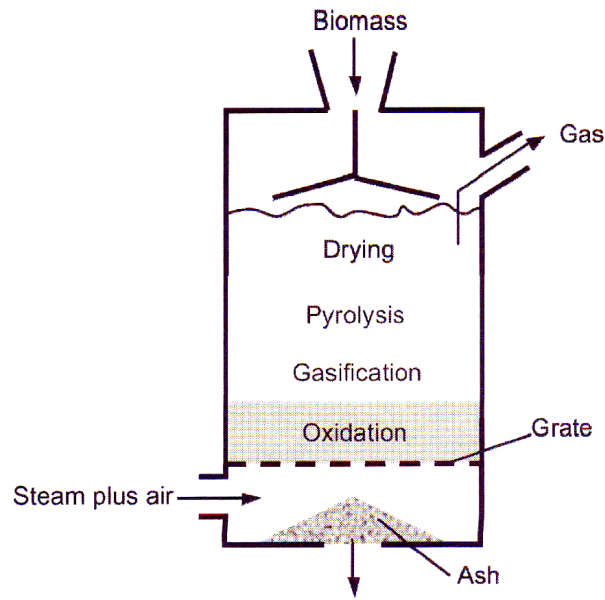


Figure 2: Updraft Gasifier (Basu, 2010, p.171)

2.1.2 Downdraft Gasification

During downdraft gasification the feedstock and the gasifying medium move into the same direction (co-current mode). Here, the pyrolysis gas passes the oxidation zone and then leaves the gasifier at the bottom through a bed of hot ash, as it is shown in figure 3. As a result, downdraft gasifiers have the lowest tar production rate of all gasification systems. Therefore, downdraft gasifiers produce a relatively clean raw gas. This can be advantageous since it reduces the cost of expensive downstream gas cleaning. Furthermore, no pollutive waste is produced. However, due to the high outlet temperature of the product gas ($600 - 800^{\circ}\text{C}$), co-current gasifiers suffer from high heat loss. As a consequence, the conversion efficiency is low compared to counter-current gasifiers (Kaltschmitt et al., 2009, p.606).

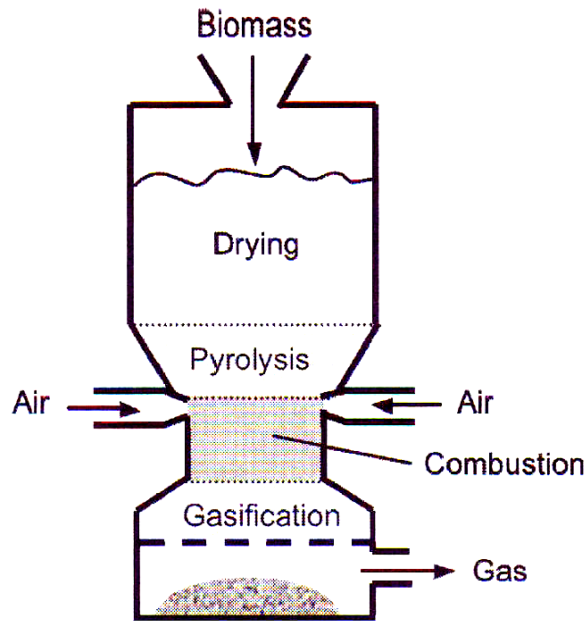


Figure 3: Throated Downdraft Gasifier (Basu, 2010, p.173)

2.1.3 Twin-Fire Gasification

A twin-fire reactor combines the advantages of updraft and downdraft gasification while avoiding the disadvantages of both systems. Air is introduced into the upper part of the gasifier and also from the bottom. Therefore, an additional oxidation zone is established at the bottom. As a result, the gasifier can be divided into two different zones. The upper zone behaves like a downdraft gasifier whereas the lower zone shows the characteristics of an updraft gasifier (Kramreiter et al., 2008).

Typically, the air distribution between the upper and the lower zone is approximately 2:1. Due to the oxidation zone at the bottom of the gasifier the product gas contains a relatively low tar content (Kaltschmitt et al., 2009, p.608).

2.1.4 Crossdraft Gasification

The crossdraft gasifier, as seen in figure 4, is a special type of fixed bed gasifiers. It operates in co-current mode. The fuel is fed from the top and the gasifying agent from the side. The product gas is released opposite to the entry point of the gasifying medium.

Hence, it is also called sidedraft gasification. This type is convenient for small-scale biomass gasification units. It possesses a relatively small reaction zone with minor thermal capacity. Consequently, its response time is very short (Basu, 2010, p.176).

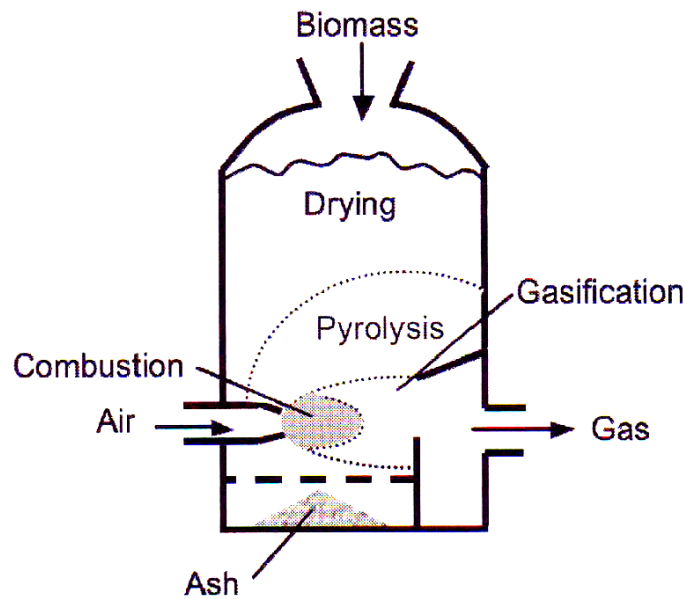


Figure 4: Crossdraft Gasifier (Basu, 2010, p.176)

2.1.5 Staged Gasification

In recent times, numerous new fixed bed gasifiers are so called staged gasifiers. The single process steps - such as pyrolysis, gasification and combustion - are more or less spatially divided. As a consequence, the operating parameters can be adjusted more precisely. Therefore, the product gas contains less tars in comparison to the above mentioned gasification processes (Kaltschmitt et al., 2009, p.608). Staged gasification processes represent a special group within fixed bed gasification.

CHOREN Industries GmbH developed a staged gasification process which was firstly demonstrated in Freiburg, Germany, in 2010. The first process step is a pyrolytic decomposition where the biomass feedstock is thermally cracked. The operating temperatures are between 400°C and 500°C . The products are charcoal and pyrolysis

gas. In a second process step the pyrolysis gas is further oxidised with pure oxygen in a combustion chamber at temperatures above the melting point of the fuel ash. As a consequence, the hydrocarbon-rich pyrolysis gas is converted into a hydrocarbon-free product gas. In a third step the char reacts with the hot product gas from the combustion chamber. Since those reactions are highly endothermic, the product gas is cooled down by more than 500°C (Vogels, 2010).

Another industrial example of a staged gasification process is the Viking gasifier which was developed by the Danish Technical University (DTU) in the 1990s. An 80 kW_{th} gasifier located at the Riso facility, Denmark, was successfully demonstrated since 2002. The biomass feedstock is moved from storage into the gasifier by a screw. The screw is heated indirectly by the outgoing gases from the gasifier and the feedstock is transported into a zone of higher temperature. Therefore, the biomass feedstock is pyrolysed. The products are pyrolysis gas with volatile hydrocarbons and non-volatile char. The char falls into the gasifier at the end of the screw and forms a stationary char bed. The pyrolysis gas is partially oxidised above the char bed due to injection of air. The hot gases then pass through the char bed and function as gasifying medium. By passing through the bed most of the tars are reduced (Brandin et al., 2011).

2.2 Fluidized Bed Gasification

Fluidized bed gasifiers contain fine bed material. Usually the bed material is silica sand or catalytic active minerals. The passage of the gasifying medium at sufficient velocities creates the fluidized state. The feedstock for fluidized bed gasifiers is typically smaller compared to fixed bed gasification. The different thermo-chemical conversion reactions expire parallel. The intensive heat transfer from the bed material to the feed particles minimizes the necessary residence time of the solid feedstock in the gasifier. Usually the solid particles' residence time varies from several seconds to minutes. Fluidized bed systems are effective for biomass gasification since they are able to operate with a wide range of different solid materials (Kaltschmitt et al., 2009, p.609). Inside the gasifier there is excellent gas-solid mixing and nearly temperature uniformity. Thus making fluidized bed gasification relatively insensitive to the quality of the fuel. Furthermore, fuel agglomeration is minimized due to the uniform temperature inside the reactor (Basu, 2010, p.177).

Principally there are three different types of fluidized bed gasifiers: bubbling, circulating and dual fluidized bed gasifiers.

2.2.1 Bubbling Fluidized Bed Gasification

The flow velocity of the gas in bubbling fluidized bed gasifiers is between the minimum fluidization velocity and the terminal velocity for one individual particle of the bed material. As a consequence, the particle discharge of the system is small (Kaltschmitt et al., 2009, p.611).

The average particle diameter of the bed material ranges typically from 0.7 to 1.5 mm. A crucial advantage of bubbling fluidized bed gasifiers is their ability to process a bright variety of fuel qualities. The tar produced is between that of a downdraft and an updraft gasifier (Rauch, 2000).

2.2.2 Circulating Fluidized Bed Gasification

The fluidization velocity is high enough to entrain solids with the product gas. Typically, these entrained particles are then removed by a cyclone and returned to the fluidized bed. The product gas stays longer in contact with the bed material which improves the conversion efficiency of this process (Bolhàr-Nordenkamp, 2004).

Usually the gasifier unit is higher and possesses a smaller diameter compared to bubbling fluidized bed gasifiers. Due to the high fluidization velocities the dust content of the product gas is high. Therefore, dust removal systems have to be installed downstream the gasifier (Rauch, 2000).

2.2.3 Dual Fluidized Bed Gasification

The combination of two fluidized bed systems can lead to a product gas with specific characteristics. Figure 5 shows the concept of such a combination. Here, two fluidized bed reactors are spatially separated. The bed material circulates between them and functions as a heat transporter. In comparison to the gasification processes mentioned above dual fluidized bed systems work with allothermal heat supply. In the combustion reactor the exothermic oxidation heats up the bed material, whereas in the gasification reactor the heat is needed for the endothermic process. The aim of this configuration is to generate medium calorific product gas (Kaltschmitt et al., 2009, p.614).

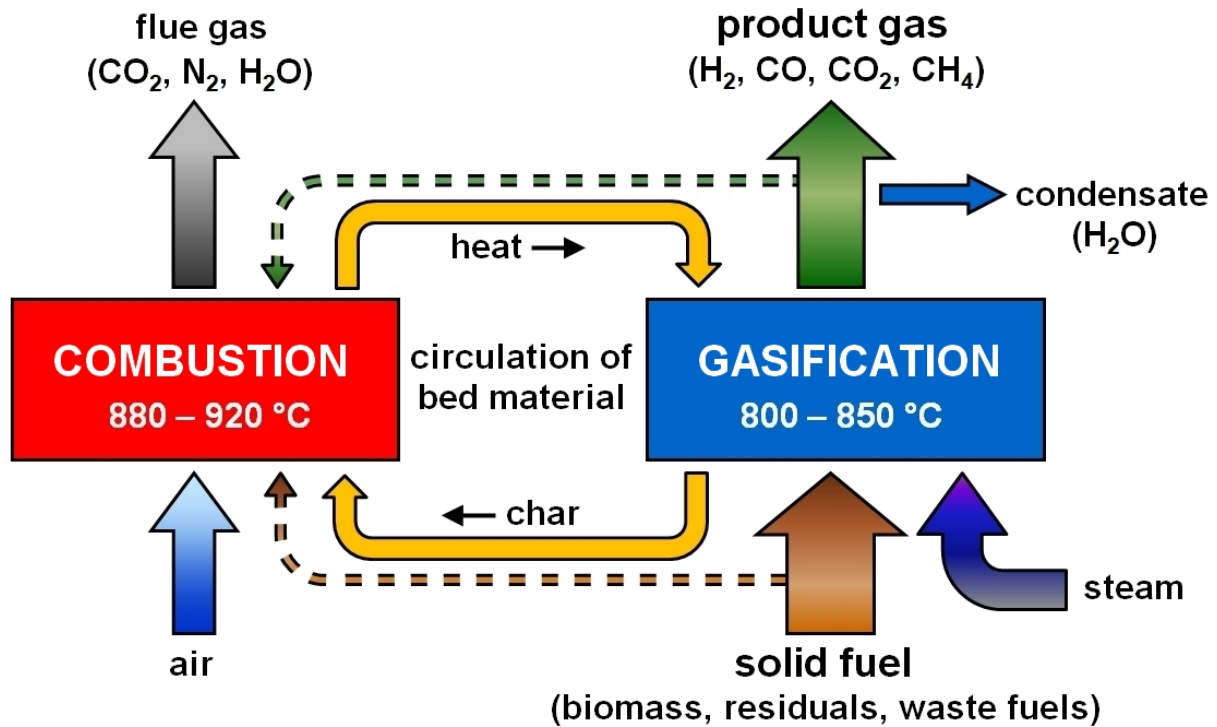


Figure 5: Concept of Dual Fluidized Bed Gasification (Vienna University of Technology)

Figure 6 shows the design of the dual fluidized bed gasifier which is built in Güssing, Austria. The configuration is composed of a bubbling fluidized bed reactor as gasification unit and a circulating fluidized bed reactor as combustion unit. Through a chute at the bottom of the gasification reactor the used bed material is transported into the combustion reactor. Due to the high fluidization velocity the bed material is entrained and travels upwards. A cyclone then collects the heated material. Through a loop seal the bed material is brought back into the gasification reactor. A detailed description of the dual fluidized bed gasifier in Güssing will be given in chapter 5.

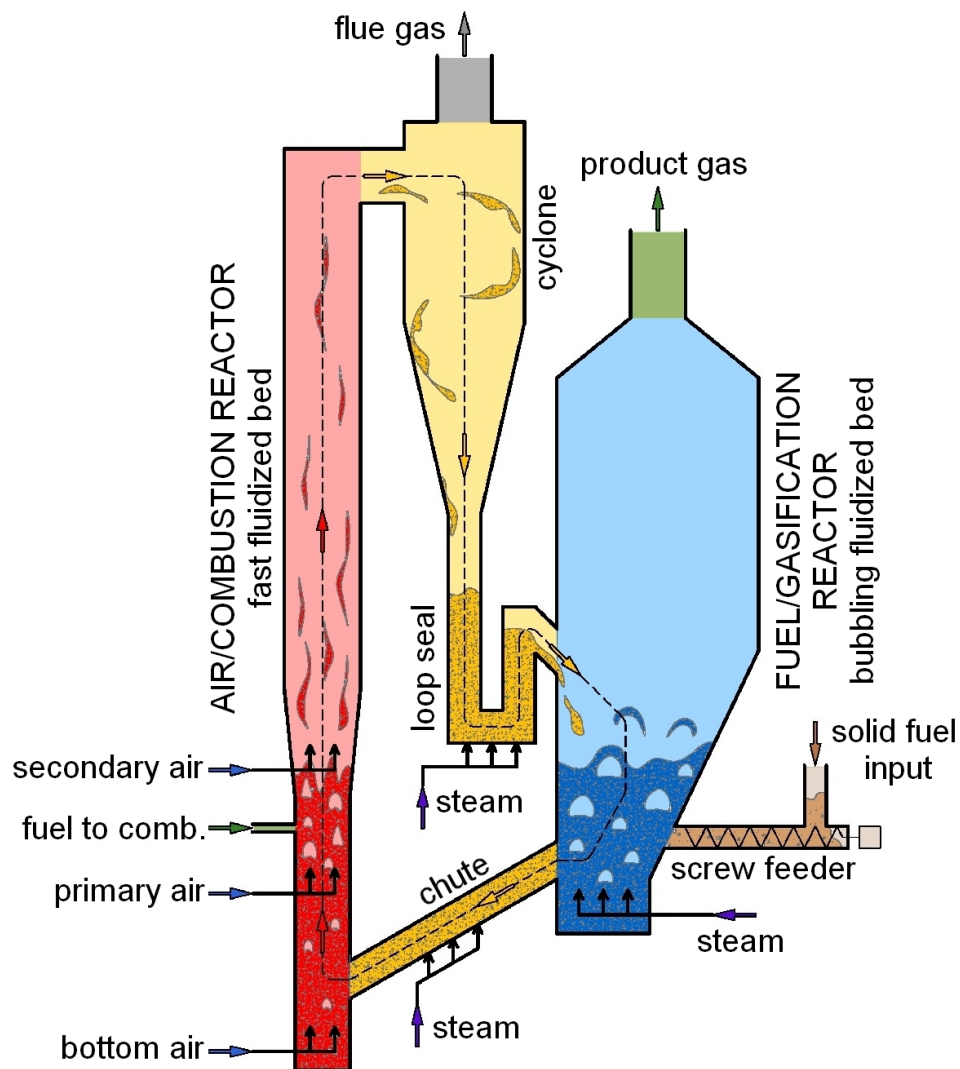


Figure 6: Dual Fluidized Bed Gasifier (designed by Vienna University of Technology)

2.3 Entrained Flow Gasification

Entrained flow gasifiers are co-current plug-flow reactors. The gasification temperature usually well exceeds 1000°C , allowing the generation of a product gas which is basically tar free (Basu, 2010, p.186). The pasty fuel is injected together with the gasifying medium into the gasifier. Almost complete gasification of the fuel takes place. Today, entrained flow gasifiers play a subordinate role in biomass gasification due to the high technical effort of handling the high temperatures (up to 2000°C). Furthermore, the feedstock must be preprocessed before it can be used in entrained flow gasifiers. This technique only comes into question for plants with a very high capacity (Kaltschmitt et al., 2009, p.617).

Nevertheless, beside the production of a tar free product gas, entrained flow gasifiers have advantages such as acceptability of a broad range of feedstock and a high conversion rate of carbon. Furthermore, the product gas contains a low content of methane which is advantageous for synthetic gas production (Basu, 2010, p.186).

Entrained flow gasifiers are mainly divided into two groups: side-fed upflow and top-fed downflow gasifiers.

2.3.1 Side-Fed Entrained Flow Gasification

In side-fed gasifiers the pulverized fuel is added through a set of horizontal nozzles. They are positioned opposite each other in the lower section of the reactor. The fuel and gasifying medium are injected as jets and form a stirred tank reactor. Therefore, side-fed gasifiers stand out because of their high degree of mixing. The product gas travels up and leaves the reactor at the top. Figure 7 shows a schematic of a side-fed entrained flow reactor developed by E-Gas. It was designed for the use of sub-bituminous coal (Basu, 2010, p.187).

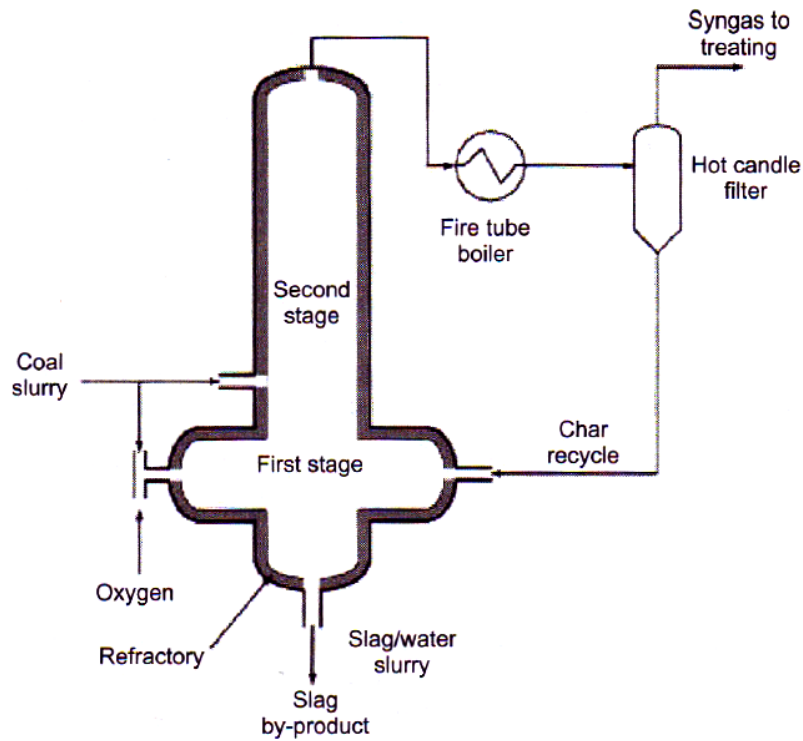


Figure 7: Schematic of a Side-Fed Gasifier (Basu, 2010, p.189)

2.3.2 Top-Fed Entrained Flow Gasification

Pulverized fuel and the gasifying agent are conveyed into a vertical cylindrical reactor vessel. The vessel is similar to a vertical furnace with a downward burner. The fuel and gasifying medium are injected from the top through a jet. Top-fed entrained flow gasifiers are used by GE Energy and Siemens SFG for the gasification of coal. The reactants are injected through a single centrally positioned burner. Figure 8 shows a schematic of a top-fed downflow entrained flow gasifier (Basu, 2010, p.187).

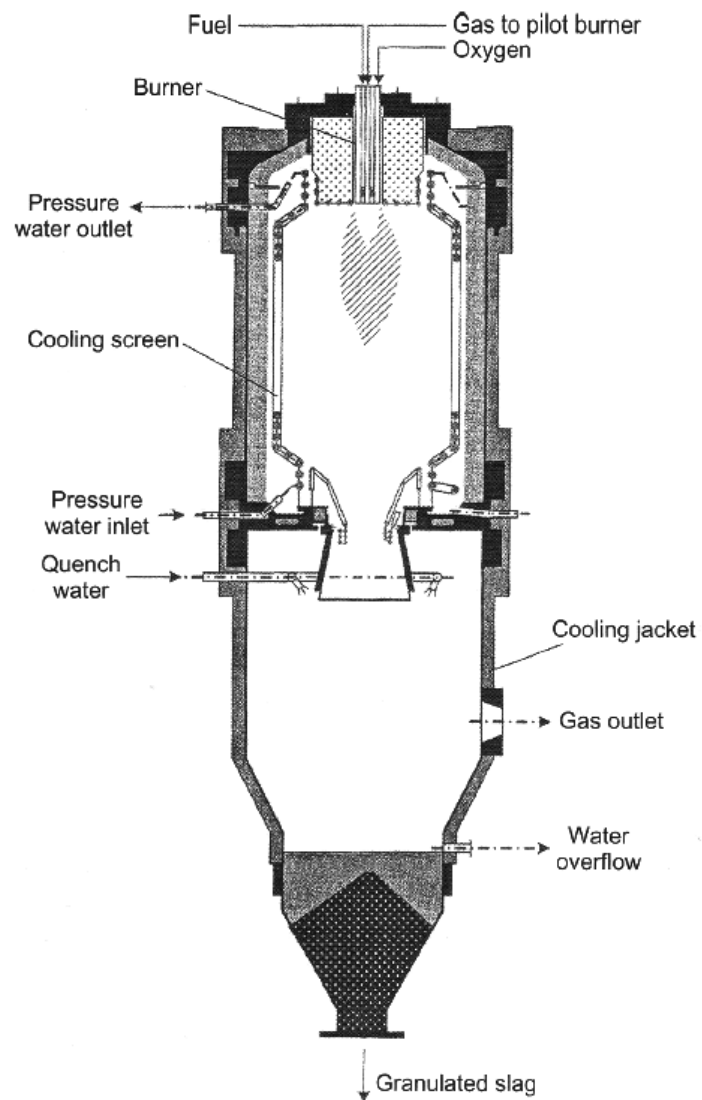


Figure 8: Schematic of a Top-Fed Gasifier (Basu, 2010, p.188)

3 Reduction of Impurities in Product Gas

The major problem regarding the generation of product gas is the amount of contaminants present in it. Figure 9 shows the impurities which have to be removed before the product gas can be used for either heat and power production or synthesis processes. Chlorine-, nitrogen- and sulphur compounds as well as particles and tars have to be removed. The extend of these impurities is highly dependent on the gasification process as well as the feedstock. Table 1 shows a typical product gas composition of a dual fluidized bed (DFB) gasifier. As it can be seen, the product gas contains high amounts of particles and tars. Moreover, contaminates such as H_2S , NH_3 and HCl are also of concern. They are precursors of emission products such as SO_2 and NO_x and possess a corrosive nature. Due to their corrosive nature they would affect downstream plant components. Emission products have to be held at a minimum. Furthermore, emission limit values have to be considered, especially regarding the often very high amounts of nitrogen in biomass.

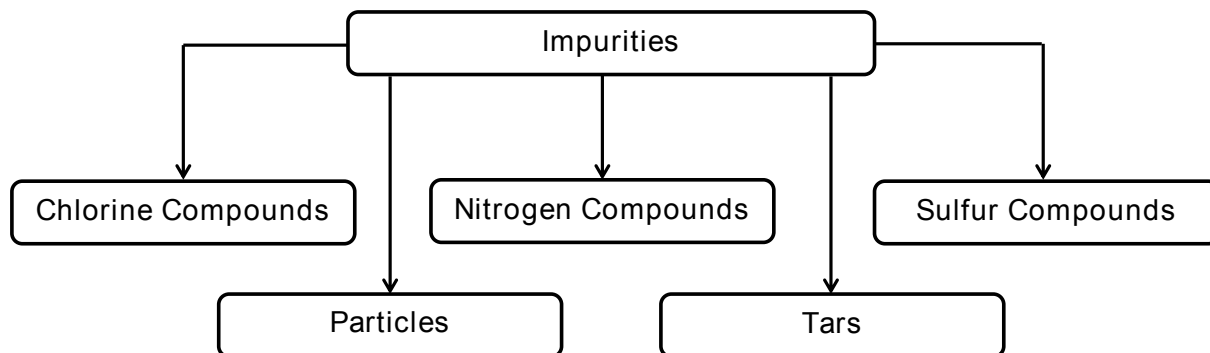


Figure 9: Impurities in Product Gas

Components	Quantities	Units
H_2O	30 - 45	<i>vol%</i>
CH_4	10 - 11	<i>vol%</i> (dry)
C_2H_4	2 - 2.5	<i>vol%</i> (dry)
C_3 fraction	0.5 - 0.7	<i>vol%</i> (dry)
CO	24 - 26	<i>vol%</i> (dry)
CO_2	20 - 22	<i>vol%</i> (dry)
H_2	38 - 40	<i>vol%</i> (dry)
N_2	1.2 - 2.0	<i>vol%</i> (dry)
H_2S	130 - 170	<i>ppmv</i> (dry)
NH_3	1100 - 1700	<i>ppmv</i> (dry)
<i>tar</i>	2 - 5	<i>g/Nm³</i> (dry)
<i>particulates</i>	20 - 30	<i>g/Nm³</i> (dry)
<i>LHV</i>	12.9 - 13.6	<i>MJ/Nm³</i> (dry)

Table 1: Typical Composition of a Product Gas from the DFB Gasification Process before Gas Cleaning (Pröll et al., 2005)

3.1 Chlorine Compounds

The biomass chlorine is mainly converted into hydrogen chloride (HCl). Usually HCl is removed by scrubbers. This technology is well-tested and commercially available (Kaltschmitt et al., 2009, p. 640).

In recent times the research focuses on the reduction of HCl in the hot state of the product gas. Kameda et al. (2008) investigated the potential of magnesium-aluminium oxide ($Mg - Al$ oxide) for the removal of hydrogen chloride (HCl). The experiments were carried out with and without addition of water vapour. Both wet and dry removal of HCl showed satisfying results. At $130^\circ C$ between 75% and 82% of HCl could be removed. The reduction of HCl in case of water vapour addition was attributed to the production of $MgCl_2 \cdot 6H_2O$. The removal of HCl without added water vapour occurred due to the

production of $MgCl_2 \cdot 4H_2O$.

Ohtsuka et al. (2004) stated that *Na*-based sorbents are useful for the removal of *HCl*. They reported that nahcolite (sodium bicarbonate $NaHCO_3$) sorbents mixed with binders can reduce the *HCl* level from 1750 ppm down to less than 1 ppm at 400 – 600°C when using coal-derived flue gas.

Dou et al. (2002) tested the hot gas removal of *HCl* of coal-derived product gas. They used four different sorbents. Three of them were commercially available alkaline and alkaline earth metal compounds ($\sim 8 - 17$ wt%) supported on $\alpha - Al_2O_3$. The fourth sorbent was a self-prepared sorbent. It was composed of alkaline and alkaline earth metal compounds (~ 80 wt%) with binders and texturing agents. The experiments were carried out at 550°C with a space velocity of $3000h^{-1}$. The inlet concentration of *HCl* was 1000 ppm. The allowable *HCl* outlet concentration was less than 1 ppm. Therefore, when the concentration reached 1 ppm, the sorbent was regarded as laden. The experiments showed that all four sorbents can reduce the *HCl* concentration to less than 1 ppm. The self-prepared sorbent showed the best characteristics for *HCl* removal. While the three commercially available sorbents had to be regarded as laden after two to four hours, the self-prepared sorbent lasted almost six hours.

3.2 Nitrogen Compounds

During the gasification process most of the biomass nitrogen is converted into ammonia (NH_3). Additionally, lower amounts of hydrogen cyanide (HCN), isocyanic acid ($HNCO$) and nitrogen oxides (NO_x) are formed. The total amounts of these compounds depend strongly on the nitrogen content in the biomass feedstock. Nitrogen compounds are highly undesirable because they can poison catalysts and they are precursors for NO_x (Torres et al., 2007).

The reduction of nitrogen compounds can be achieved either in the hot or the cold state of the product gas. Currently, nitrogen compounds are separated from the product gas using wet scrubbers (Kaltschmitt et al., 2009, p.639).

Pröll et al. (2005) studied the effectiveness of ammonia removal in the cold gas state

with an organic solvent scrubber. The main goal of such a scrubber is to absorb tars into organic solvents. As a secondary effect water condenses in the scrubber, allowing the removal of nitrogen and sulphur compounds. The NH_3 concentration can be reduced when the operating parameters of the scrubber are adjusted. Nevertheless, the efficiency for NH_3 separation is limited to 50% within the possible operation range. Further gas cleaning units are needed.

In terms of energy efficiency it is advantageous to reduce them in the hot state. There exist two catalytic routes for the removal of NH_3 : decomposition and selective oxidation. The desirable decomposition (1) to N_2 and H_2 does not create additional contaminants in the gas stream.



The reaction is usually catalysed by calcined dolomite, nickel or iron catalysts (Torres et al., 2007).

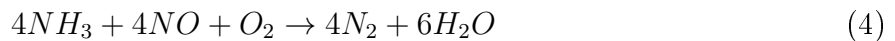
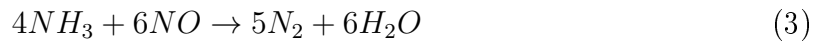
When dolomite catalysts are used as primary catalysts, the amount of ammonia in the product gas increases. This might be because of its high activity for cracking tars. Thus releasing the tar-bound nitrogen which leads to formation of ammonia. Consequently, although dolomite has the ability to decompose ammonia, competing components such as tar can reduce the decomposition activity towards ammonia (Xu et al., 2010).

Corella et al. (2005) tested the effectiveness of nickel monoliths for ammonia elimination. They installed a monolith reactor downstream a bubbling fluidized bed gasifier of 15 cm diameter and 5.2 m height. The nickel monolith, supplied by BASF AG, had a size of 15x15x30cm. The NH_3 conversion varied between 44 and 96.5 vol%. Corella et al. (2005) concluded that nickel monoliths have a similar activity as much cheaper dolomites.

Ohtsuka et al. (2004) investigated the decomposition effectiveness of NH_3 to N_2 with Fe and Ca catalysts loaded on activated carbon. A series of tests were carried out with 2000 ppm NH_3 in He. At 750°C they observed the highest decomposition of almost 100% for 2-6 wt% Fe catalysts. The activity was higher than that of both 6 wt% Ca and even 8 wt% Fe. At a temperature of 850°C complete decomposition could be achieved with all Ca and Fe catalysts.

Tsubouchi et al. (2005) studied limonite rich in $\alpha - FeOOH$ for catalytic NH_3 decomposition. First the $\alpha - FeOOH$ enriched limonite was reduced with H_2 . In this step particles of $\alpha - Fe$ were formed. The highly dispersed Fe then successfully decomposed 2000 ppm NH_3 (diluted with inert gas). Almost 100% decomposition could be achieved at a temperature level of $500^\circ C$ under ambient pressure.

The selective oxidation is realized by controlled addition of an oxidiser. The oxidizer is added to the gasification gas and selectively transforms NH_3 into N_2 . The reactions (2), (3) and (4) show useful oxidisers for this task, namely O_2 , NO or a mixture of them.



The selective oxidation of NH_3 is advantageous compared to decomposition since the reactions proceed in relatively low temperatures ($300 - 600^\circ C$). Nevertheless, the reaction has generic problems. The oxidants can be involved in the undesirable competing reactions (5) – (8).



To avoid these reactions optimal catalysts and conditions still have to be found (Torres et al., 2007).

3.3 Particles

The discharge of particles out of the gasifier is highly dependent on the gasifier type. Fluidized bed gasifiers have a much higher discharge than fixed bed gasifiers. Particles have to be removed from the product gas before it can be further used. Currently, particles

are either removed by cyclones, filters and/or scrubbers. Cyclones are used to separate high amounts of particles from the gas stream. However, since they are not effective for separation of particles smaller than $5\ \mu m$, they are only used as initial cleaner. In comparison, filters can remove small particles ($0.5 - 100\ \mu m$) effectively. Nevertheless, they lead to a rapidly increasing pressure drop. Scrubbers are usually installed for combined removal of particles and tars. Clean gas concentrations of $10 - 20\ mg/m^3$ can be achieved. There is a broad range of different scrubber designs. They are reviewed in detail by Kaltschmitt et al. (2009, p.633). The current methods for particle removal have the disadvantage of low operation temperatures.

Therefore, nowadays most of the research concentrates on hot gas cleaning systems. They are more energy efficient. Heidenreich (2013) reviewed filtration media as well as filter elements at higher temperatures. The collection efficiency of high density ceramic filters is almost 100%. In addition, they also achieve high collection rates for sub-micron particles. Operating temperatures of more than $1000^\circ C$ are possible. In comparison, by the same collection the operating temperature rates of metal filter media are beneath $1000^\circ C$. Preferably hot gas filter elements are installed in the form of candles which are closed at one end. Depending on the material the length ranges from 1 to 3 m with a outer diameter of 60 to 150 mm.

Simeone et al. (2011) tested the performance of a high temperature filter unit containing three ceramic candles. The candles had an outer diameter of 60 mm, 10 mm wall thickness and a length of 1520 mm. During the experiments they varied the temperature between $600^\circ C$ and $800^\circ C$. They successfully operated the candles for more than 50 h.

Stanghelle et al. (2007) investigated granular bed filtration of product gas from the biomass gasification plant in Güssing, Austria. The tests were carried out at a temperature level of $550^\circ C$. The pressure drop over the granular filter was comparable to that of a bag filter. Granular beds can operate with higher filtration velocities than bag filters.

3.4 Sulphur Compounds

Biomass feedstock contains sulphur. The amounts vary depending on which feedstock is used. During the gasification process sulphur is mainly converted into hydrogen sulphide (H_2S). Usually most biomass fuels produce a H_2S concentration of about 100 ppmv when gasified. In addition, lower amounts of carbon disulphide (CS_2), carbonyl sulphide (COS), mercaptanes (CH_3SH and CH_3CH_2SH) and thiophene (C_4H_4S) are formed. For certain applications the tolerable level of sulphur is very low. Thus making deep desulphurization of the product gas necessary. For instance, the allowable sulphur level for ammonia production is lower than 0.1 ppmv (Meng et al., 2010).

Those sulphur compounds are contaminants which cause environmental pollution due to emission of SO_x after burning. Furthermore, severe corrosion of equipment is a consequence. Moreover, sulphur compounds reduce the activity of the majority of catalysts and therefore impair their performance (Itaya et al., 2009).

Dunleavy (2006) stated that sulphur species are poisons for all catalysts with reduced metals as active phase. Therefore, in the following chapters the reduction of sulphur compounds will be reviewed in detail. Figure 10 shows the different possibilities to reduce sulphur compounds.

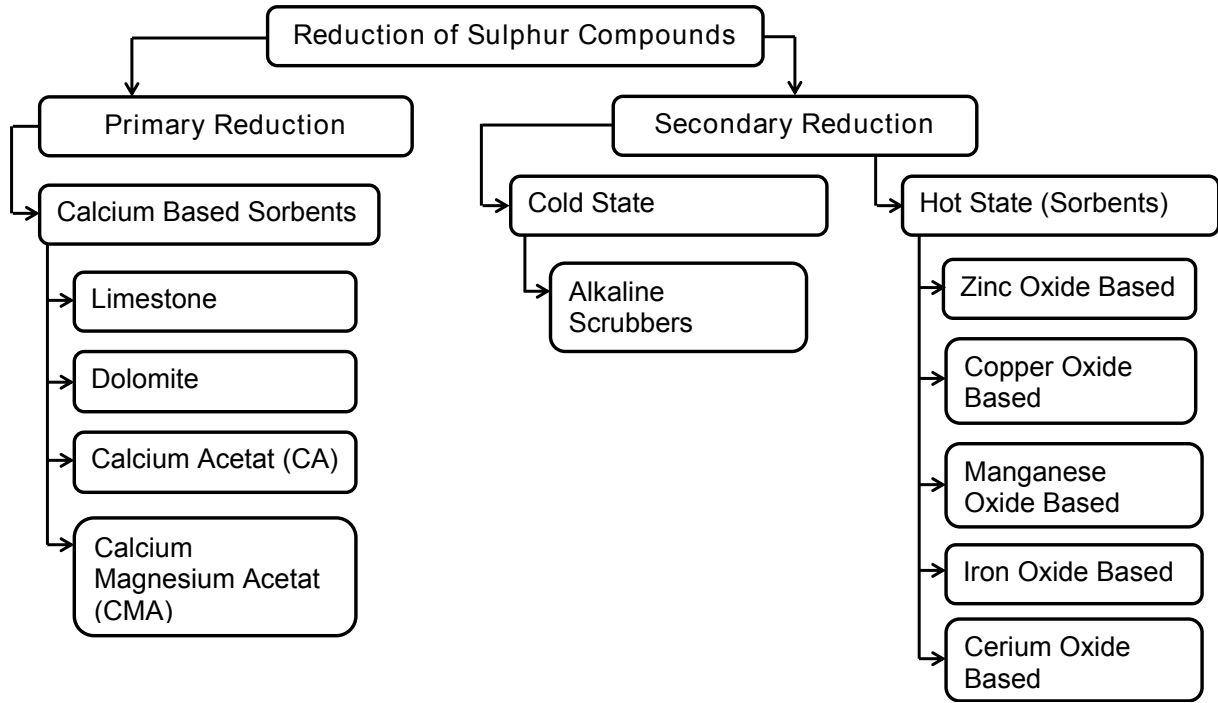


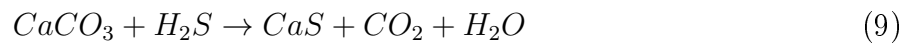
Figure 10: Reduction of Sulphur Compounds

3.4.1 Primary Reduction of Sulphur Compounds

Primary measures to reduce sulphur compounds are advantageous because they are cheap and work continuously.

So far most of the in-bed sulphur reduction has been achieved with calcium-based sorbents. There are naturally occurring sorbents available such as limestone and dolomite. They are most commonly used for sulphur capture since they are easily available and relatively cheap. Sulphidation can proceed either directly or via the calcined sorbents. The following formulas will show the mechanism by the example of limestone and its calcined form calcite, respectively.

Direct sulphidation of limestone:



Calcination of limestone and sulphidation of calcite:



The product CaS is relatively unstable. Therefore, it easily reacts with O_2 :



The product $CaSO_4$ is environmentally friendly and stable. However, $CaSO_4$ can form a layer on the surface of the sorbent. As a result, it reduces the extent of the reaction. The reactions (9), (10) and (11) proceed in an analogous manner for dolomite. Dolomite, however, captures sulphur almost twice as fast as limestone. This is apparent by the difference in the pore matrix between dolomite and limestone (Meng et al., 2010).

The calcination temperature has a significant influence on their ability to capture sulphur. Complete conversion can be achieved above the respective calcination temperature. Below the calcination temperature the capacity of sulphur capture decreases (Meng et al., 2010). Álvarez Rodríguez and Clemente-Jul (2008) investigated the temperature influence on the reduction of sulphur compounds when dolomite sorbent is used. They varied the temperatures from $900^\circ C$ to $950^\circ C$. Almost no influence could be observed when the sorbents are operated above their calcination temperature. Additionally, the reaction rate increases with increasing magnesium to calcium ratio in the sorbent.

Meng et al. (2010) reported that the reaction between limestone and H_2S is inhibited by H_2 and HCl . The latter shows high affection to react with limestone to form $CaCl$. Furthermore, sulphur capture with either limestone or dolomite suffers from chemical attrition which reduces the reaction rate.

Hu et al. (2006) carried out experiments of H_2S capture by limestone in a high-pressure fluidized bed reactor. They used 2 g, 177-250 μm limestone particles (98% $CaCO_3$) and added 4 g, 125-177 μm alumina particles. The alumina particles enhanced the heat transfer between particles and avoided a decrease in the bed temperature because of the endothermic calcination of limestone. They varied the total pressure from 0.3 to 1.0 MPa and held the temperature constant at $949.85^\circ C$. The results showed that the variation of total pressure had no influence on the conversion of CaO in the initial reaction stage. In the middle and final stage the reaction rate decreased with increasing total pressure. After 600 seconds the reaction rate with 1.0 MPa total pressure was about 15% lower than the one with 0.3 MPa.

Commercially available sorbents such as calcium acetate (CA) and calcium magnesium acetate (CMA) show higher efficiency towards sulphur capture. Experiments at 1000°C , 0.8 s residence time and with 5000 ppmv H_2S were carried out testing different natural and commercially available sorbents. CA and CMA had the highest sulphur capture capacity (more than 90%). The lower value in comparison to the above-mentioned complete conversion of H_2S with limestone and dolomite is a consequence of the short residence time. In these experiments the short residence time of 0.8 s had to be chosen to compare the sorbents (Meng et al., 2010).

3.4.2 Secondary Reduction of Sulphur Compounds

Sulphur reduction downstream of the gasifier unit can be achieved either in the cold or the hot state of the product gas. Currently, sulphur compounds are removed with alkaline scrubbers. This technology is well developed. Nevertheless, the removal of sulphur compounds in an alkaline scrubber creates waste water which makes expensive water conditioning necessary (Kaltschmitt et al., 2009, p.636).

Therefore, hot gas desulphuration (HGD) using sorbents for sulphur capture is advantageous and more energy efficient. The sorbents need to be easily regenerable. The research of HDG is mainly focused on metal oxide sorbents. They are either zinc oxide (ZnO), copper oxide (CuO), manganese oxide (MnO), iron oxide (FeO) or cerium oxide (CeO) based.

Among them zinc oxide belongs to the best sorbents due to its good sulphidation thermodynamics. Basically, there are two types of zinc oxide based sorbents: zinc ferrit (ZnFe_2O_4 , ZF) and zinc titanate (ZnTiO_3 , ZT). Three formulations of ZF with different ZnO content (from 28.7 wt% to 34.7 wt%) have been tested for their conversion capacity. All three showed satisfying conversion of H_2S (Meng et al., 2010).

To improve the conversion capacity Ikenaga et al. (2004) prepared ZF in the presence of activated carbon and activated carbon fiber. They were able to reduce H_2S from 4000

ppmv down to less than 1 ppmv. The experiments were carried out at 500°C . Further they could regenerate the activated carbon enriched ZF from ZnS , FeS and $Fe_{1-x}S$. Additionally, they could use it for repeated absorption with only slight decrease in its capacity.

Zinc titanate is attractive for its ability to perform at higher operating temperatures (up to 700°C) (Meng et al., 2010).

Park et al. (2006) achieved a desulphuration from 10,000 ppmv to less than 5 ppmv with a two stage process. The primary stage was a fluidized bed using zinc oxide, natural zeolith, Fe_2O_3 and CaO mixed with an organic binder ethylene glycol as sorbent (weight percentage of 64 : 24 : 9 : 3). The secondary stage was a fixed bed reactor using Al_2O_3 supported zinc oxide and copper oxide in different proportions.

Copper based (CuO) sorbents have been studied intensively due to their high sorption rate under reducing and oxidizing atmospheres (Meng et al., 2010).

Ozaydin et al. (2008) compared the sorption activities of different Copper-Incorporated MCM-41-Type sorbents. They were prepared by one-pot and impregnation procedures. MCM (Mobile Crystalline Materials) are mesoporous materials with silicate structure. They distinguish themselves from other materials because of their regular array of uniform pores. As a result, they possess a high surface area. The H_2S sorption capacity was tested at a temperature level of 500°C . The inlet gas stream contained 1 vol% H_2S and 10 vol% H_2 in helium. Ozaydin et al. (2008) observed high H_2S sorption capacity with sharp breakthrough curves.

Karvan and Atakülb (2008) tested two different types of CuO /mesoporous SBA-15 (Santa Barbara Amorphous) sorbents. They were prepared by the wet impregnation method. The first sorbent contained 21.97 wt% whereas the second sorbent contained 40.2 wt% Cu . The experiments were carried out in the temperature range of 515 to 565°C . The capacity of sulphur capture varied with different Cu contents. After three cycles of sulphidation and regeneration the sorbent with 21.97 wt% Cu was determined to provide a capacity of 0.63g S/100g of sorbent. However, the sorbent with 40. 2wt%

Cu delivered 1.57g S/100g of sorbent.

Manganese oxide (MnO) based sorbents have been studied deeply during the past decade. MnO has been found to be stable at temperatures from $400^{\circ}C$ up to $1000^{\circ}C$ or even higher. Thus allowing MnO based sorbents a great flexibility in sulphidation and regeneration without struggling with loss of sorbent (Meng et al., 2010).

Iron oxide (FeO) based sorbents are not comparable to the above mentioned materials in terms of their desulphuration potential. The desulphuration is lower due to severe sorbent decrepitation caused by reduction. Furthermore, iron carbide which does not possess any desulphuration potential is formed at temperatures higher than $550^{\circ}C$ (Meng et al., 2010).

Sorbents based on cerium oxide (CeO) are much less examined, mainly due to their high cost. Moreover, they possess a low sulphidation equilibrium at higher oxidation states (4+) (Meng et al., 2010).

Yasyerli (2008) investigated the capacity of cerium-manganese mixed oxide sorbents. The tested sorbents contained different molar ratios of Ce/Mn (3/1, 2/2 and 1/3). The authors stated that the desulphuration capacity is significantly enhanced by the addition of manganese into the cerium oxide based sorbent.

3.5 Tars

Up to this day there is no uniform definition of *tar*. Kübel (2007) stated that usually tar is understood to be every substance with a molecular weight larger than benzene (78,1 g/mol). A task force within the European Union worked out a standard for tar sampling and measuring (often referred to as Tar Guideline). It was first published in 2001. In the current version (3.3) tar is defined as follows: "Generic (unspecific) term for entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar" (Neeft et al., 2003).

During gasification tars are primarily produced in the pyrolysis stage. The three main

constituents of biomass, namely cellulose, hemicellulose and lignin, break down into primary tars. Above temperatures of 500°C these primary tars start to recombine into non condensable gases and heavier molecules. They are called secondary tars. At even higher temperatures primary and secondary tars can be destroyed and tertiary tars are produced. Tertiary tars can either be alkyl tertiary products or condensed tertiary aromatics. Alkyl tertiary products include methylacenaphthylene, methylnaphthalene, toluene and indene. Condensed tertiary aromatics are mainly polynuclear aromatic hydrocarbons (PAHs) such as benzene, naphthalene, acenaphthylene and pyrene (Basu, 2010, p.100). Among them naphthalene is usually used as tar model compound for experiments in laboratory scale. Representative primary tars are for example phenol and creosol (Kübel, 2007).

Figure 11 shows the different measures to reduce tars.

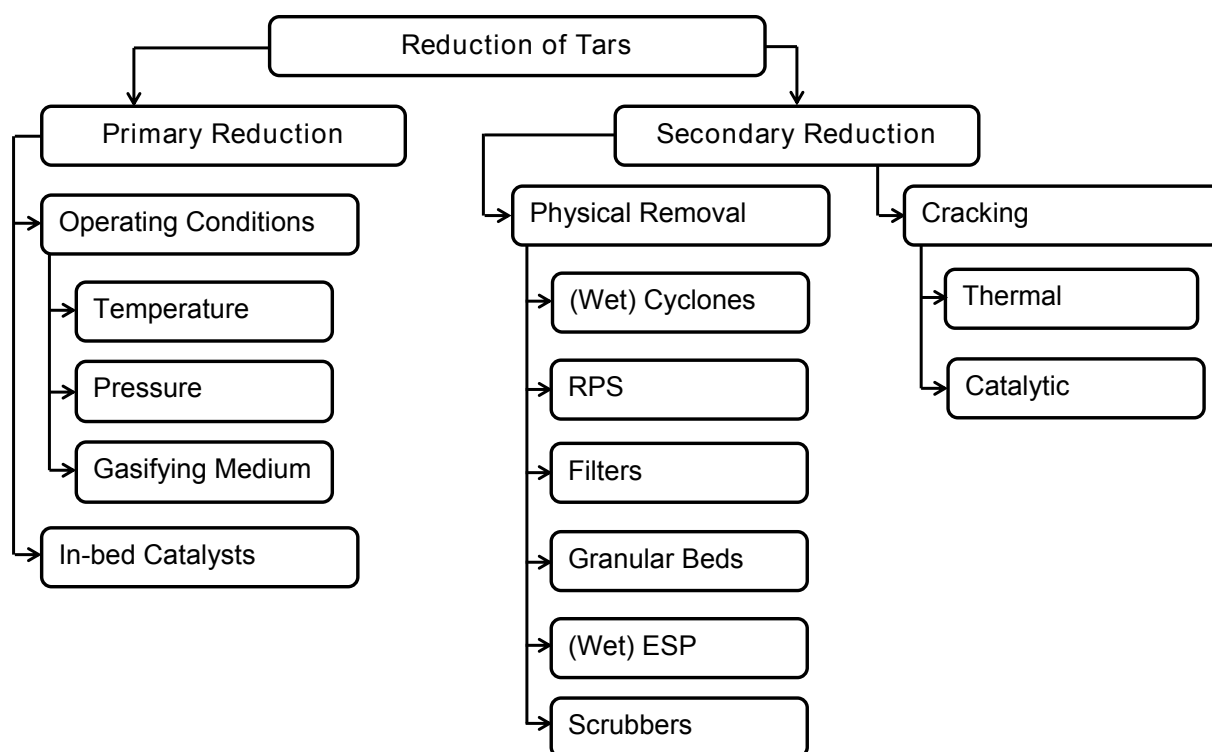


Figure 11: Reduction of Tars

3.5.1 Primary Reduction of Tars

Tar reduction can be realized either in-situ (primary reduction) or downstream of the gasifier (secondary reduction). In-situ tar elimination lessens the tar production inside the gasifier. Its major problem is the interference with the process inside the gasifier. In-situ tar reduction can be achieved by either modifications of the operation conditions (temperature, pressure and gasifying medium) or the usage of catalytic bed material. Therefore, primary measures influence the product gas quality (Basu, 2010, p.103).

The operating conditions play a significant role in the gasification process regarding tar formation. To convert high amounts of the biomass carbon while at the same time obtaining a product gas with low tar content, temperatures above 800°C are necessary. Increasing temperature leads to a decrease of the total number of tar species. Besides influencing the amount of tar being formed, temperature further affects the tar composition. Oxygen-containing compounds (e.g. phenol and cresol) can only be found in minimal amounts at temperatures above 800°C . Moreover, only above 850°C degradation of polyaromatic hydrocarbons (PAHs) can be achieved (Devi et al., 2003).

Increasing the steam pressure leads to a significant decrease of tars. However, the amount of polyaromatic hydrocarbons (PAHs) increases and the thermal efficiency decreases (Knight, 2000).

Furthermore, depending on the gasifying medium used, there is a difference in tar formation. Gil et al. (1999) have shown that the yield of tar using steam as gasifying agent is higher than that of using a combination of steam and air. Further, they stated that air as gasifying medium produces the lowest amounts of tar.

A reduction of tar can also be achieved by adding catalysts into the gasifier. Suitable catalysts for primary conversion of tars are reviewed in chapter 4.

Kirnbauer et al. (2012) investigated the effects of bed material coating on tar reduction. They compared fresh olivine as a reference and used olivine from an industrial gasification plant. The olivine generates a calcium-rich layer as a consequence of the interaction with biomass ash and additives. This layer enhances the water-gasshift reaction and therefore leads to an increase of hydrogen and carbon dioxide in the product gas. On the contrary,

the carbon monoxide content decreases.

3.5.2 Secondary Reduction of Tars

Unlike the concept of in-situ tar reduction downstream applications do not interfere with the process. However, they are more expensive than primary measures. The methods of secondary tar reduction are physical removal and cracking. Essentially, there are two types of cracking: catalytic and thermal.

Physical removal of tar can be either achieved by dry or wet methods. Dry methods might be cyclones, condi-cyclones, rotating particle separators (RPS), filters, granular beds and electrostatic precipitators (ESP). Wet methods might be scrubbers, spray towers, wet electrostatic precipitators and wet cyclones.

Cyclones are useful to remove particles with a diameter above 10 μm . The laden gas spirals round a vertical cylinder creating centrifugal forces. The particles are thrown to the walls of the cylinder. Since they cannot remove tar droplets smaller than that they only appear in combination with further cleaning devices. Based on the same principle are condi-cyclones, but they combine the cyclone principle with a Laval nozzle. The gas, which expands adiabatically through the nozzle, reaches supersonic speed. This leads to a decrease of the temperature so that the water and tar compounds condensate (Pfeifer, 2005).

A new development in gas cleaning devices using centrifugal forces is the rotating particle separator (RPS). A RPS uses a rotating cylinder placed inside a cyclone, which can be operated either with constant or variable rotation speed. This modification of an ordinary cyclone improves the separation ability of tar from the product gas, nevertheless further reduction of tar is still necessary. Hence, an additional tar removal unit downstream of a RPS has to be installed (Hasler and Nussbaumer, 1999). For a RPS tar separation varies between 30% to 70 % (Anis and Zainal, 2011). Rabou et al. (2009) observed a decrease of tar content from 8 g/Nm^3 to 4.5 g/Nm^3 .

Filters are physical barriers holding particulates and tar back while allowing the clean

gas through. They can be applied as candle or fabric filters. Candle filters are mostly ceramic. Thus making them useful at high temperatures (up to 900°C). The raw dust-laden product gas flows through the porous ceramic candle filter from the outside to the inside. The restrained particulates are collected on the surface of the candle forming a solid layer called filter cake. This layer increases the filtration efficiency. Since the pressure drop increases with growing filter cake, dedusting using periodical pulses of nitrogen is necessary (Basu, 2010, p.113). Tar reduction of 75.6% to 97.9% was observed by de Jong et al. (2003) during their experiments with two kinds of ceramic filters (quartz and glass fibre).

Fabric filters can only operate at lower temperatures (under 300°C). Since certain tars condensate at such low temperatures they can adhere on the fabric (Pfeifer, 2005).

Another concept using filtration to separate particulates and tar from the product gas are granular beds. Most commonly used materials are sand, activated carbon and sawdust. Those filtering beds can be used at high temperatures (1000°C). Especially for removing tars adsorption, as a secondary collection mechanism, is important. At room temperature activated carbon loadings up to 80 wt% have been observed (Hasler and Nussbaumer, 1999).

The use of sand bed filters also proved to be suitable to remove tars. A reduction of tar level of 50-97% can be achieved by such sand bed filters (Anis and Zainal, 2011).

Pathak et al. (2007) also observed a tar reduction above 90% using sand bed filters. A significant limit of performance in tar reduction of all granular beds is the inability to easily clean them. Tar accumulation on the surface leads to plugging and failure of the filter system (Anis and Zainal, 2011).

Electrostatic precipitators (ESP) use high voltage fields to charge and separate particles and tar droplets. The collected solid particles can be removed mechanically, however liquid like tars have to be washed out by a water film (wet ESP) (Basu, 2010, p.114). In Harboore, Denmark, ESPs installed downstream the gasification units have achieved 40-70% tar removal (Han and Kim, 2008).

Wet gas cleaning systems are widely applied in gasification plants due to their high

performance. Scrubbers are the most often used wet gas cleaning units for tar removal (Han and Kim, 2008). Wet scrubbers use water scrubbing to condense tars from the product gas. Tar levels can be reduced to 20-40 mg/m^3 , depending on the type of scrubber is used. The most commonly used wet scrubbers are packed column scrubbers (spray tower), packed bed scrubbers, impingement scrubbers and venturi scrubbers. Among them spray towers have the lowest efficiency. However, they are also the simplest and cheapest of the different types of scrubbers (Anis and Zainal, 2011).

Bhave et al. (2008) developed and evaluated a gas cleaning and cooling system using a wet packed bed scrubber. The unit is suited for small size gasifier-engine systems. They stated that the tar and dust content of the outlet gas is below 150 mg/Nm^3 as long as the content in the inlet gas is below 600 mg/Nm^3 .

According to Anis and Zainal (2011) for impingement scrubbers the overall efficiency for tar removal is about 70%. The efficiency can be increased by creating a cascade of at least three impingement scrubbers by connecting them in series. As a result, tar reduction of 95% or higher is possible.

Shen and Yoshikawa (2013) investigated several kinds of scrubbing liquids, such as water, diesel fuel, biodiesel fuel and vegetable oil. They stated that water could reduce the gravimetric tar down to 9.1 g/m^3 . Their experiments showed gravimetric tar levels of 32 g/m^3 for diesel fuel, 20 g/m^3 for biodiesel fuel and 5 g/m^3 for vegetable oil as scrubbing liquid.

In 2001 the energy research centre of the Netherlands (ECN) developed a scrubbing method called OLGA (dutch acronym for oil based gas washer). They chose an approach that did not concentrate on the tar content but on the behaviour of the tar. The product gas stream was defined as tar free when it was free of tar related problems. The concept is explained in detail by Boerrigter et al. (2005).

Cracking is a chemical conversion of tar into gases such as H_2 and CO . Contrary to most concepts of physical removal the tar is converted at the hot state of the product gas. It can be achieved either in a thermal or a catalytic way (Basu, 2010, p.116). There

are also methods combining both thermal and catalytic cracking.

Thermal cracking is mostly applied in fluidized bed gasifiers due to the high outlet temperature of the product gas. In order to do this, partial oxidation through secondary addition of air has to be initiated. As a result, the heating value of the product gas decreases (Kaltschmitt et al., 2009, p.638). Another way of reaching sufficiently high temperatures is the direct contact of the product gas with a hot surface. Since the surface has to be independently heated this method leads to an overall efficiency decrease. Thermal cracking occurs at temperatures from 700 - 1250°C. Phenol, for example, is relatively stable at 700°C (only 6.3 wt% conversion). At 800°C more than 97 wt% and at 900°C more than 98 wt% of phenol is converted (Anis and Zainal, 2011).

Phuphuakrat et al. (2010) observed a reduction of gravimetric tar by thermal cracking of 78% at 800°C. Gravimetric tar is defined as the evaporation residue at given and standard conditions (temperature, pressure, duration).

Tars can further be decomposed catalytically downstream the gasifier unit. There are different approaches to realize secondary catalytic tar conversion. Aravind and de Jong (2012) describe tar cracking or reforming in separate beds of natural or synthetic catalysts. Pfeifer and Hofbauer (2007) developed a monolithic tar reformer. Commercial monolithic catalysts with honeycomb structure were tested with real product gas from an industrial dual fluidized bed gasifier. Anis and Zainal (2011) have reported that catalytic filters are an efficient way to reduce tar in the product gas. Those ceramic candle filters have a catalytic coating on their surface, thus allowing them to combine both physical removal and catalytic cracking of tars. As a result, high performances for converting benzene and naphthalene were found.

Catalytic filter candles were also investigated by Nacken et al. (2012). They found naphthalene conversion of 90% at 800°C in the presence of H_2S . The experiments were carried out at laboratory scale.

Tars from biomass gasification can be effectively converted by catalytic reforming. The high-molecular-weight hydrocarbons are reformed with steam which is already present in the product gas.

The following chapter will examine suitable catalysts and their performance regarding hot gas conversion of tars.

3.6 Summary and Outlook

The main issue regarding the usage of product gas is the reduction of contaminants. Chlorine-, nitrogen- and sulphur compounds as well as particles and tars have to be removed. Nowadays, industrial plants usually possess a combination of filters and scrubbers. The product gas has to be cooled down before it can enter those gas cleaning units. Filters separate the majority of particles from the gas stream. Scrubbers can remove chlorine-, nitrogen- and sulphur compounds as well as tars, depending on which scrubbing liquid is used. Common liquids are water, diesel fuels and vegetable oil.

Due to energy efficiency reasons most of the research focuses on hot gas cleaning methods. For the reduction of chlorine compounds Na -based sorbents show promising results. Furthermore, investigations with sorbents composed of alkali- and alkali-earth metal compounds supported on $\alpha - Al_2O_3$ showed high potential for the reduction of chlorine compounds.

Hot gas removal of nitrogen compounds (mainly NH_3) can be achieved either by decomposition or selective oxidation. The decomposition reaction is usually catalysed by calcined dolomites, nickel or iron catalysts. The selective oxidation is initialized by controlled addition of an oxidiser, such as O_2 , NO or a mixture of them. However, there are a number of undesirable competing reactions which cannot be fully controlled yet.

Particles can be effectively removed by high density ceramic filters in the hot state of the product gas. Temperatures of more than $1000^\circ C$ are possible.

Sulphur compounds can be removed either in-bed or downstream of the gasifier. The primary reduction is advantageous because it is cheaper and works continuously. Natural occurring catalysts for in-bed reduction, such as limestone and dolomite, are easily available. Commercial sorbents such as calcium acetate (CA) and calcium magnesium acetate (CMA) show higher sulphur capture efficiency. Since they are synthetically produced, they are more expensive. Secondary reduction can be achieved by a broad

spectrum of different sorbents. Zinc oxide (ZnO) and copper oxide (CuO) based sorbents are among the most promising candidates for downstream reduction of sulphur compounds.

Tars can also be removed by both primary and secondary measures. Adjusting the operating conditions (temperature, pressure and gasifying medium) or the design of the gasifier can result in a significant decrease of the amount of tars in the product gas. The secondary reduction can be realized by a broad spectrum of different cleaning devices. Physically by cyclones, rotating particle separators (RPS), filters, granular beds, electrostatic precipitators (ESP) and scrubbers. Chemically tars can be converted by cracking them either in a thermal or in a catalytic way. The decomposition is advantageous because the undesirable tars are converted into useful gases.

Future investigations could bring a significant improvement in primary gas cleaning methods. There is still a great potential for in-bed reduction of impurities. As a result downstream applications could be reduced which would lead to a decrease in the operating costs. Thus, making the biomass gasification process more economically competitive. Nevertheless, depending on the use of the product gas (heat, power, synthesis) further gas cleaning could still be necessary. Hot gas cleaning methods will replace the current gas cleaning devices due to energy efficiency reasons.

4 Catalysts for Hot Gas Conversion of Tars

This chapter presents an overview of the research on catalysts for hot gas conversion of tar that has been carried out by various groups during the last decade. It further examines their performance as well as their limits of performance. Most of the work presented has only been performed in laboratory scale. Thus showing that catalytic hot gas cleaning is still not state of the art in biomass gasification processes.

Hot gas cleaning by means of catalytic tar reforming is attractive due to the low additional energy input. Furthermore, no tarry waste streams are produced since the tars are transformed into useful gases. There are basically four main problems regarding deactivation of catalysts: poisoning, fouling, coking and thermal degradation of tar reforming catalysts (Aravind and de Jong, 2012).

Poisoning occurs as a consequence of chemisorption (chemical adsorption) of impurities on the active components of the catalysts. Typically, sulphur compounds (mainly H_2S but also carbonyl sulfide COS , thiophenes and thiols) are responsible for poisoning effects. Fouling is the deposition of particles onto the surface of the catalyst. As a result, the surface of the catalyst is coated and therefore deactivated. Coking is a combination of poisoning and fouling. Some carbonaceous components can deposit physically on the surface of the catalyst while others are chemisorbed. Thermal degradation is the consequence of numerous factors. One of the main factors is sintering. It occurs at high temperatures (above $770^\circ C$) due to crystallite growth (Kaltschmitt et al., 2009, p.628).

Figure 12 shows the classification of catalysts which is further used. Catalysts for tar reduction can be divided into two main groups, naturally occurring and synthetically produced catalysts.

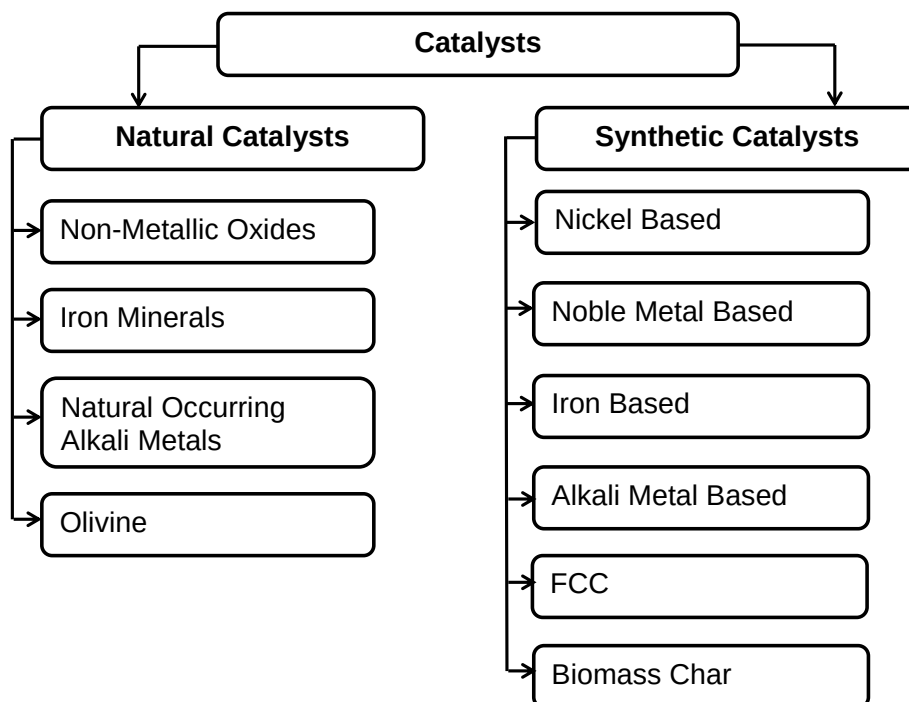


Figure 12: Catalysts for Decomposition of Tars

4.1 Natural Catalysts

Catalysts available in nature are usually cheaper because they can be used directly; no chemical treatment is necessary.

4.1.1 Non-Metallic Oxides

The majority of the published work of non-metallic oxides concerns calcined rocks. In this group calcites (CaO), magnesites (MgO) and calcined dolomites have shown catalytic activity for tar elimination. The uncalcined form of calcite is called limestone ($CaCO_3$), that of magnesium carbonate ($MgCO_3$). The chemical formula of dolomite in its uncalcined state is $CaCO_3 \cdot MgCO_3$ (El-Rub et al., 2004).

Dolomite is a cheap catalyst and has the ability to significantly reduce tars in the product gas. Therefore a plethora of investigations has been conducted. Devi, Ptasinski, Janssen, van Paasen, Bergman and Kiel (2005) tested the conversion of polyaromatic hydrocarbons (PAHs) in a secondary fixed-bed reactor filled with sand. They observed 90% conversion

of PAHs when 17 wt% pre-calcined dolomite was added to the sand.

El-Rub et al. (2004) reported tar conversion of up to 95%. Further, they stated that the problem with dolomite is its fragility. Since dolomite is soft, it easily suffers from erosion. Hence, it is not suitable in fluidized bed gasification. Consequently, these catalysts are more advantageous in downstream gas cleaning units, where attrition is avoided.

Simell et al. (1992) published a classification of these catalysts according to their CaO/MgO ratio. They distinguished four groups:

- Dolomite (CaO/MgO : 1.5)
- Calcitic dolomite (CaO/MgO : 1.5 - 4)
- Dolomitic limestone (CaO/MgO : 4 - 50)
- Limestone ($CaO/MgO > 50$)

The activity towards tar conversion ascends with increasing CaO/MgO ratio. An effective way of further improving the activity is decreasing the grain size of the catalysts. As a result the active surface increases (El-Rub et al., 2004).

The catalytic activity of calcined dolomites is sensitive to CO_2 pressure. The CO_2 partial pressure must remain below the equilibrium pressure for dolomite decomposition to maintain the catalytic activity (Richardson et al., 2012).

It was observed that dolomite modified by mixing it with Fe_2O_3 powders led to a slight increase in tar conversion (Xu et al., 2010).

4.1.2 Iron Minerals

The iron minerals hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite ($HFeO_2$), siderite ($FeCO_3$), ilmenite ($FeTiO_3$) and pyrite (FeS_2) are the main sources of iron. They can be grouped into oxides, carbonates and sulphides depending on their chemical compositions. Hematite, magnetite, goethite and ilmenite are oxides, whereas siderite is a carbonate and pyrite a sulphide (El-Rub et al., 2004).

Nordgreen et al. (2006) reported that iron in metallic state possesses catalytic ability towards tar conversion. In contrast, they observed that the iron oxides FeO (wustite),

Fe_2O_4 and Fe_3O_4 do not show any catalytic activity at all. If metallic iron is used as an in-situ catalyst during the gasification process, the product gas is not able to transform the iron from its metallic state to its first oxide (wustite FeO). The product gas does not possess enough oxidising power for the transformation. Hence, metallic iron is an effective catalyst for primary tar reduction. At temperature levels of $900^\circ C$ the authors observed almost 100% tar breakdown.

4.1.3 Natural Occurring Alkali Metals

Some alkali metals exist naturally in biomass. These naturally occurring alkali metals are mainly potassium (K) and sodium (Na) (Turn et al., 2000). Their salts are present in the ashes of plants. Those ashes can be used either in-situ or downstream the gasifier as catalysts to reduce the tar content in the product gas (El-Rub et al., 2004).

Pfeifer (2005) stated that using the ashes as primary tar reduction catalysts inside the gasifier (where they are produced) can lead to an economic benefit. However, agglomeration effects easily cause a significant loss of activity.

According to Sutton et al. (2001) alkali metals can be added directly to the biomass. This can be achieved by dry mixing or wet impregnation. As a consequence, the alkali metals are difficult to recover. Hence, this procedure leads to an increase of the alkali metal content in the ash. Further the authors reported that alkali metals reduce the tar as well as the methane content of the product gas when added directly to the biomass.

4.1.4 Olivine

Olivine represents a special category within the group of natural catalysts. It is a magnesium iron silicate ($(Mg, Fe)_2SiO_4$). Its density ranges from 2500 - 2900 kg/m^3 which is similar to that of sand (Basu, 2010, p.108).

Ising (2002) reported that olivine has promising tar reducing qualities. Due to its high resistance against attrition it has a great potential as in-bed catalyst for fluidized bed gasifiers. Furthermore olivine is sufficiently available and therefore cheap in comparison to other primary catalysts.

Rauch et al. (2004) reported that iron plays an important role in the activity of olivine. They stated the hypothesis that free iron oxides outside of the olivine structure are of importance in the activity. Furthermore, olivine contains calcium which also influences the tar reduction.

Therefore, it can be inferred that olivine could also be categorized into a new group of naturally occurring supported metallic oxides.

According to Devi, Craje, Thüne, Ptasinski and Janssen (2005) calcination of olivine significantly improves the tar conversion. The free iron oxide content increases during calcination. The exact link between calcination and formation of free iron oxides has yet to be found. The authors tested the increase of tar conversion with increasing calcination time. They compared calcination times of 1 hour, 5 hours, 10 hours and 20 hours. Olivine which was pre-calcined for 1 hour showed a naphthalene conversion of 62%. Increasing the calcination time up to 5 hours led to an increase of the conversion up to 69 %. After 10 hours of calcination time they observed the optimal conversion of more than 80 % of naphthalene. They stated that the calcination time of 10 hours might be an optimum since an increase up to 20 hours did not improve the conversion.

Olivine is attrition resistant due to its hardness and therefore suitable as an in-bed catalyst. The catalytic activity of olivine can also be improved by impregnating it with additional iron species. Fe/olivine catalysts with 20 wt% of Fe show similar catalytic activity as Ni/olivine catalysts containing around 3.8 wt% of Ni. As a result Ni could be replaced by a metal less toxic for the environment (Richardson et al., 2012).

4.2 Synthetic Catalysts

Synthetically produced catalysts are usually more expensive than naturally occurring catalysts due to cost intensive chemical procedures and materials. Usually synthetic catalysts consist of a support, the transition metal as an active component and optionally promoters. Catalyst supports are typically solid materials with a large surface area (e.g. alumina or silica based materials), giving the catalyst mechanical strength. Promoters enhance the ability of the catalyst to operate under severe conditions (El-Rub et al., 2004).

4.2.1 Nickel Based Synthetic Catalysts

From the literature published on supported transition metal catalysts the majority of the work is about nickel (Ni) (Sutton et al., 2001). Nickel is a promising candidate for a catalytically active component because of its relatively low price (e.g. nickel supported on alumina) compared to other transition metals (Wang et al., 2010).

El-Rub et al. (2004) stated that nickel based catalysts are 8 - 10 times more active than dolomite. Therefore, they are widely used in commercial gasification plants.

Sutton et al. (2001) reported that using nickel catalysts at temperatures over 740°C the hydrogen and carbon monoxide content in the product gas increases while the content of hydrocarbons and methane decreases. On the contrary, at lower temperatures the thermodynamics enhance methanation.

Deactivation of catalysts is an important issue. Nickel, despite of its high activity regarding tar reforming, easily struggles with deactivation due to fouling, coking and sulphur poisoning (Sutton et al., 2001). Deactivation caused by fouling or coking usually is reversible and therefore the activity of the catalyst can be restored by regeneration with air and/or steam (Pfeifer, 2005). Sulphur poisoning on the other hand can lead to permanent deactivation of the catalyst. The irreversible deactivation is caused by strong absorption of sulphur compounds. Sulphur may cause poisoning effects even at low concentrations because of its ability to form strong metal-sulphur bonds (Dunleavy, 2006).

Furthermore, nickel catalysts are not very effective as primary catalysts because of the

severe coke formation inside the gasifier (Xu et al., 2010).

Corella et al. (2004) tested full-size 15 x 15 x 30 cm nickel-based monolith catalysts regarding their effectiveness for tar elimination. They used mixtures of pine wood chips and residue from olive oil production as biomass feedstock. The biomass feedstock was entered into a small scale fluidized bed gasifier. The monoliths were positioned downstream the gasifier. At the front of the monoliths the temperatures ranged from 820°C to 956°C. The monolithic nickel-based catalysts showed moderate activity, but they were able to operate with gas containing particulates. As a consequence hot filters could be avoided.

4.2.2 Noble Metal Based Synthetic Catalysts

In recent times noble metals, such as ruthenium (Ru), rhodium (Rh), palladium (Pd), Iridium (Ir) and/or platinum (Pt) have been increasingly tested as active components. Rönkkönen, Simell, Niemelä and Krause (2011) investigated the performance of different noble metals on modified zirconia support ($m - ZrO_2$) in comparison to a benchmark $Ni/m - ZrO_2$ catalyst. Pt and Pd as active components have proven to be efficient oxidation catalysts. Rh and Ni on the other hand showed great reforming activity. At the selected set point (900°C) only $Rh/m - ZrO_2$ achieved complete conversion of naphthalene and toluene (used as biomass tar model compounds).

Rönkkönen et al. (2010) reported that at temperatures from 850°C to 900°C the order of activity was $Rh \approx Ni > Pd > Ir > Ru > Pt$.

Regarding deactivation of the catalyst noble metals (especially Rh) might be an alternative solution, since Rönkkönen, Simell, Niemelä and Krause (2011) reported lower extend of carbon deposition in comparison to Ni . Further Rönkkönen, Simell, Reinikainen, Niemelä and Krause (2011) observed a high resistance towards sulphur poisoning at high temperatures (above 800°C) when using Rh -catalysts. Only at temperatures below 700°C sulphur strongly poisoned the Rh -catalyst.

Ammendola et al. (2010) tested an alumina supported $Rh - LaCoO_3$ catalyst in a fixed bed reactor system. They investigated the effect of rhodium load in the range of 0.1-

(2010). The surface area of the $Fe - Al$ catalyst decreased with an increase of the Fe content. At the same time the catalytic activity increased. For the $Fe - Zr$ catalyst on the other hand they observed an increase both of the surface and the catalytic activity.

4.2.4 Alkali Metal Based Synthetic Catalysts

Alkali metals, such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) or francium (Fr), can be used as active components on a support such as alumina. Furthermore, they act as promoters in cracking the cellulose chains during thermal degradation of woody biomass (El-Rub et al., 2004).

Alkali metal based synthetic catalysts can reduce methane in the product gas. The problem is that it is very difficult to recover them once they have been used (Basu, 2010, p.108).

Synthetic catalysts based on alkali metals are seldom used for commercial plants, since their catalytic activity is lower than that of dolomite. Since dolomite is much cheaper and more easily available, alkali metal based catalysts are economically not competitive (El-Rub et al., 2004).

4.2.5 Biomass Char

Biomass char represents a special category within the group of synthetic catalysts. The synthetic production process occurs naturally inside the gasifier and therefore biomass char is cheap compared to other synthetic catalysts. Thus making it an attractive alternative for in bed-tar conversion (El-Rub et al., 2008).

Brandt et al. (2000) observed almost complete tar conversion ($< 15 \text{ mg/Nm}^3$) during their experiments with a two stage gasifier using char as catalyst.

El-Rub et al. (2008) compared biomass char to conventional catalysts like nickel-based catalysts, dolomite and olivine. They also compared the performance of biomass char to non-catalytic silica sand proving its activity. Using naphthalene as tar model compound they observed higher conversion with biomass char (94.4%) compared to dolomite (61%) and olivine (55%). Thus making biomass char the most active among the low cost material

catalysts. Only nickel-based catalysts achieved higher conversion of almost 100%. One of the major advantages of using biomass char as a catalyst is the continuous activation by steam and CO_2 content in the product gas (El-Rub et al., 2008).

4.3 Summary and Outlook

The most promising development in hot gas cleaning is the catalytic decomposition of tars. The undesirable tars are not removed but transformed into useful gases. There exist a number of catalysts suitable for decomposition of tars. They are classified into naturally occurring and synthetically produced catalysts. Natural catalysts can be grouped into non-metallic oxides, iron minerals, alkali metals and olivine. Among the naturally available catalysts olivine has been investigated intensively in the past few years. Due to its relatively high attrition resistance it is suitable as an in-bed catalyst. The catalytic activity can be enhanced by impregnating it with additional active components such as iron.

The majority of the work published on synthetic catalysts is about nickel (Ni). Nickel based catalysts are more catalytically active compared to natural occurring catalysts. However, it easily struggles from deactivation due to fouling, coking and sulphur poisoning. Noble metal based catalysts - such as ruthenium (Ru), rhodium (Rh), palladium (Pd), etc. - are promising candidates for tar decomposition. They possess a comparable activity to nickel and have a higher resistance towards sulphur poisoning. However, noble metal based catalysts are more expensive. A special category within the group of synthetic catalysts represents biomass char. Since the synthetic production process occurs naturally inside the gasifier, they are cheap compared to other synthetic catalysts. However, only few research has been done on biomass char as a tar decomposition catalyst so far.

Future investigations could concentrate on testing suitable in-bed catalysts. Naturally occurring catalysts will play an important role due to their low price. For further gas cleaning highly active catalysts for downstream devices will be necessary. Noble metal catalysts may be suitable. However, deeper knowledge of their operation performance in industrial scale has yet to be gained.

5 Experiments at the CHP Plant Güssing

The following chapter will describe the basic concept of the combined heat and power (CHP) plant in Güssing, Austria. Further, it will present the experiments carried out at a slip stream reactor installed at the CHP plant. The slip stream reactor is used as a testing device for catalytic gas cleaning downstream the gasifier. Nevertheless, it was operated with catalytically inactive material. The experiments show the operating conditions under which such a product gas cleaning device has to perform without the influence of chemical reactions inside.

5.1 Description of the CHP Plant Güssing

Figure 13 shows the basic flow sheet of the CHP plant Güssing. Wood chips are transported into a metering bin from a daily hopper. Then they are fed into the fluidized bed reactor by screw feeders.

The centrepiece of the CHP plant is a dual fluidized bed gasifier. It consists of a gasification and a combustion zone. In the gasification zone the biomass is fluidized with steam. Therefore, a nitrogen free product gas can be generated. The combustion zone on the other hand is fluidized with air and delivers the heat which is necessary for the gasification process via the circulating bed material. The heat of the flue gas from the combustion is used to preheat the air (combustion zone) and superheat the steam (gasification zone). Surplus heat which is not needed for the process is delivered to the district heating grid.

The product gas then has to be cooled in a water cooler from 850°C - 900°C down to 160°C - 180°C . The first gas cleaning device is a fabric filter to separate particles and a part of the tars from the product gas stream. The particles are returned into the combustion unit. The product gas then passes through a scrubber. The remaining tars are washed out by methyl ester of rapeseed (RME), which is an organic solvent. Once the solvent is saturated with tar it is vaporized and added into the combustion unit.

The outlet temperature of the scrubber is around 40°C . This temperature level is necessary for the gas engine where electricity and heat are produced. Alternatively, the

product gas can be burned in a boiler to produce heat.

The fuel power of the CHP plant is $8MW_{fuel,input}$. The electrical output is 2 MW and the thermal output is 4.5 MW.

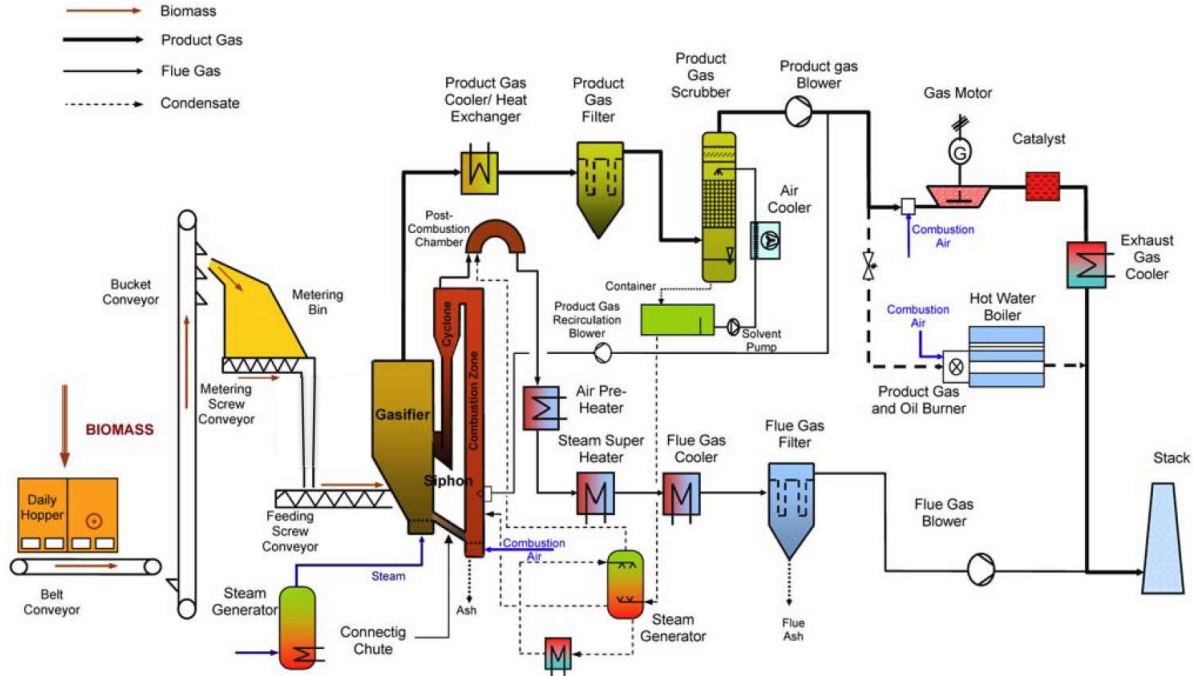


Figure 13: Flow Sheet of the CHP Plant Güssing (Vienna University of Technology)

5.2 Description of the Reformer

Figure 26 (in the appendix) shows the design of the slip stream reformer installed downstream of the gasifier at the CHP plant in Güssing. It possesses a height of 2.75 m and a diameter of 0.85 m. The product gas flows downwards through the reactor. The reactor can be divided into two zones, each with the room for four monolithic catalysts. The monoliths are 150 mm x 150 mm x 300 mm. The first zone has a circular inlet section which changes into a rectangular shape in the section of the also rectangular catalysts. Figure 14 shows the first layer of monoliths. Each layer of monoliths can be trace heated by electrical heating elements. Hence, the temperature decrease caused by the heat loss endothermic reforming reactions can be counterbalanced.

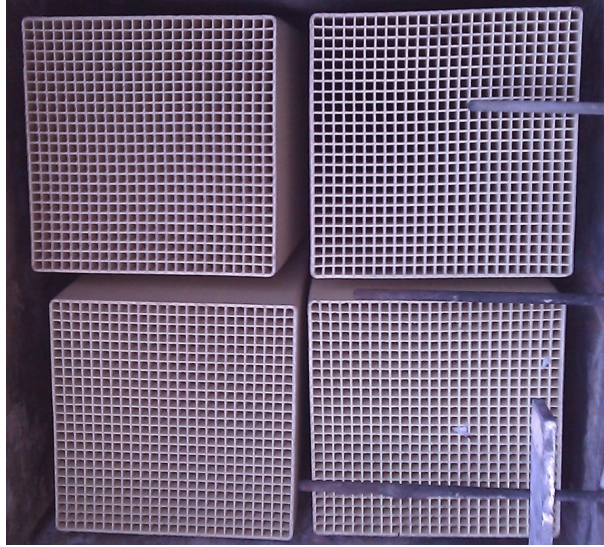


Figure 14: Positioning of the Monoliths

Figure 15 shows the visualisation of the controlling system for the reformer and all the measuring modules. The controlling system is a programmable logic controller (PLC). During the experiments the reformer has to shut down and restart safely in an automatic mode when the gasifier fails in operation.

The reformer is made of steel. The heat insulation is realized through ceramic fibre blankets on the inner side of the vessel. Measurement devices on the outside of the reactor are used for temperature, pressure and differential pressure. Furthermore there are nozzles for nitrogen pulse jets for the removal of dust and for regeneration (through oxidation with air) of coke deposition. The same nozzles which are used for regeneration can be used for partial combustion of the product gas. In table 2 seven of the sampling devices and nozzles are explained. These sampling devices and nozzles can also be seen in figure 15. The measured parameters are investigated in detail in the following chapters. A slip stream (about $100 \text{ Nm}^3/\text{h}$) of the product gas leaves the gasification unit and enters the catalytic tar reformer. While passing through the two layers of monoliths the product gas cools down. After the second layer of monoliths the gas is reinjected to the main product gas stream using a steam jet compressor to overcome the pressure drop from the reactor and the piping.

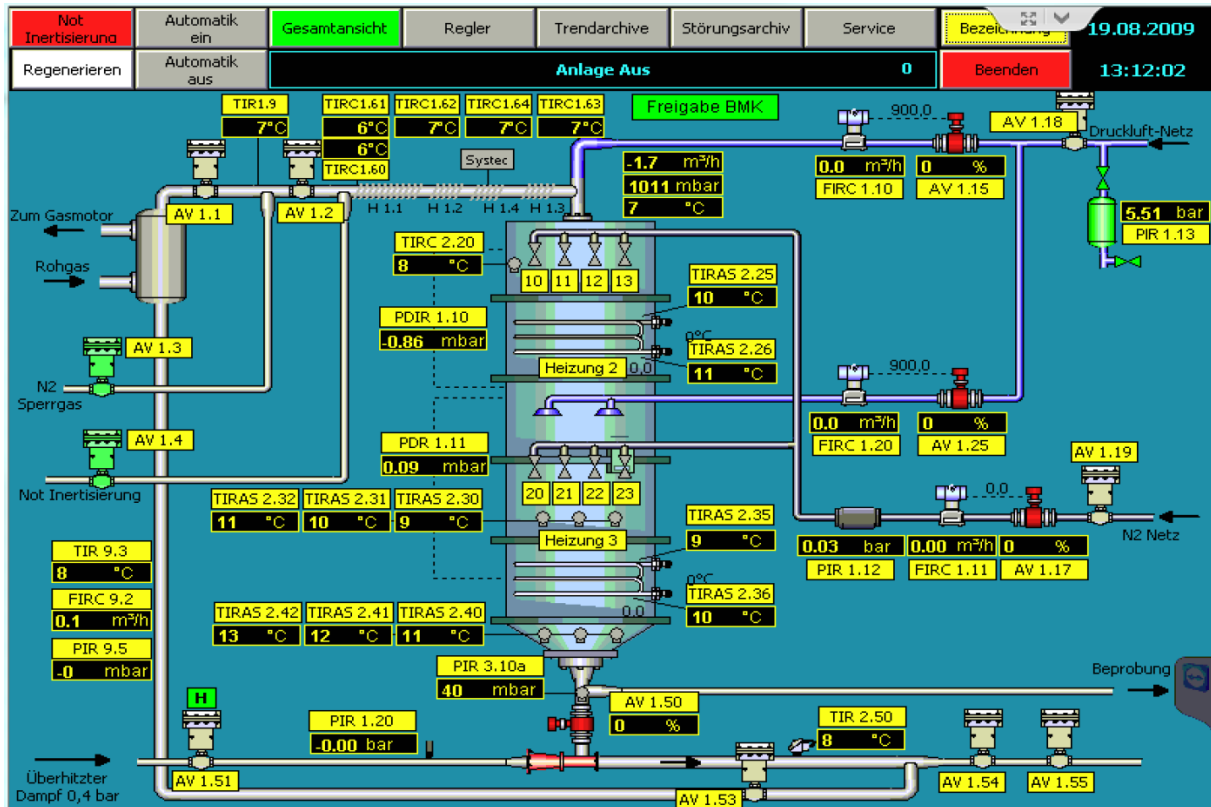


Figure 15: Visualisation

Name	Purpose
FIRC_1_10	Addition of air into the inlet section of the reactor
FIRC_1_20	Addition of air above the second layer of monoliths
FIRC_1_11	Addition of nitrogen above respectively below the first layer of monoliths
TIRC_1_63	Temperature element near the trace heating of the pipe coming from the gasifier freeboard
TIRC_2_20	Temperature element above the first layer of monoliths
TIRCAS_2_30	Temperature element above the second layer of monoliths
TIRAS_2_40	Temperature element below the second layer of monoliths

Table 2: Measurement Devices

5.3 Experiments with Non-Catalytic Honeycombs

A slip stream (100 Nm^3) of product gas was taken from the freeboard of the gasifier and fed into the reformer. Heat traces prevented the product gas from cooling down before entering into the reformer. There were non-catalytic honeycomb monoliths installed inside the gasifier. Therefore, no catalytic tar reducing reactions took place. However, it is likely that thermal cracking reaction have occurred.

5.3.1 First Experiment

Table 3 shows the procedure of the first experiment. The sections can further be seen in figure 16.

The heat up (section 1) was realized without product gas. Nitrogen was warmed up by trace heating and fed into the reformer. The temperature at the top of the reactor (TIRC_2_20) was approximately 535°C . The temperature TIRCAS_2_30 was approximately 438°C and the temperature TIRAS_2_40 approximately 365°C .

The trace heating was then adjusted to higher capacity, which led to an increase of the temperature level (section 2).

As a result, the sudden temperature change - caused by addition of product gas (section 3) - was reduced. The operating time with product gas of the first experiment was 21 hours. The operating temperatures inside the reformer were the following: TIRC_2_20 was held at 780°C , TIRCAS_2_30 at 740°C and TIRAS_2_40 at 720°C .

The reformer automatically interrupted the addition of product gas as a consequence of a shutdown of the gasifier (section 4). The product gas was replaced by nitrogen to ensure a minimal temperature change inside the reformer. When the gasifier continued its operation the nitrogen was replaced by product gas (section 5).

The shutdown (section 6) was also realized by addition of nitrogen to ensure that no combustible product gas was left inside the reformer.

The detailed procedure of the first experiment can be seen in table 6 in the appendix.

Section	Date	Time	State	Medium
1	24.10.2012	15:40	Heat up	Nitrogen
2	29.10.2012	14:42	Additional heat up	Product gas
3	30.10.2012	14:47	Normal operation	Product gas
4	31.10.2012	03:25	Gasifier shutdown	Nitrogen
5	31.10.2012	04:04	Normal operation	Product gas
6	31.10.2012	11:51	Shutdown	Nitrogen

Table 3: Procedure of the First Experiment

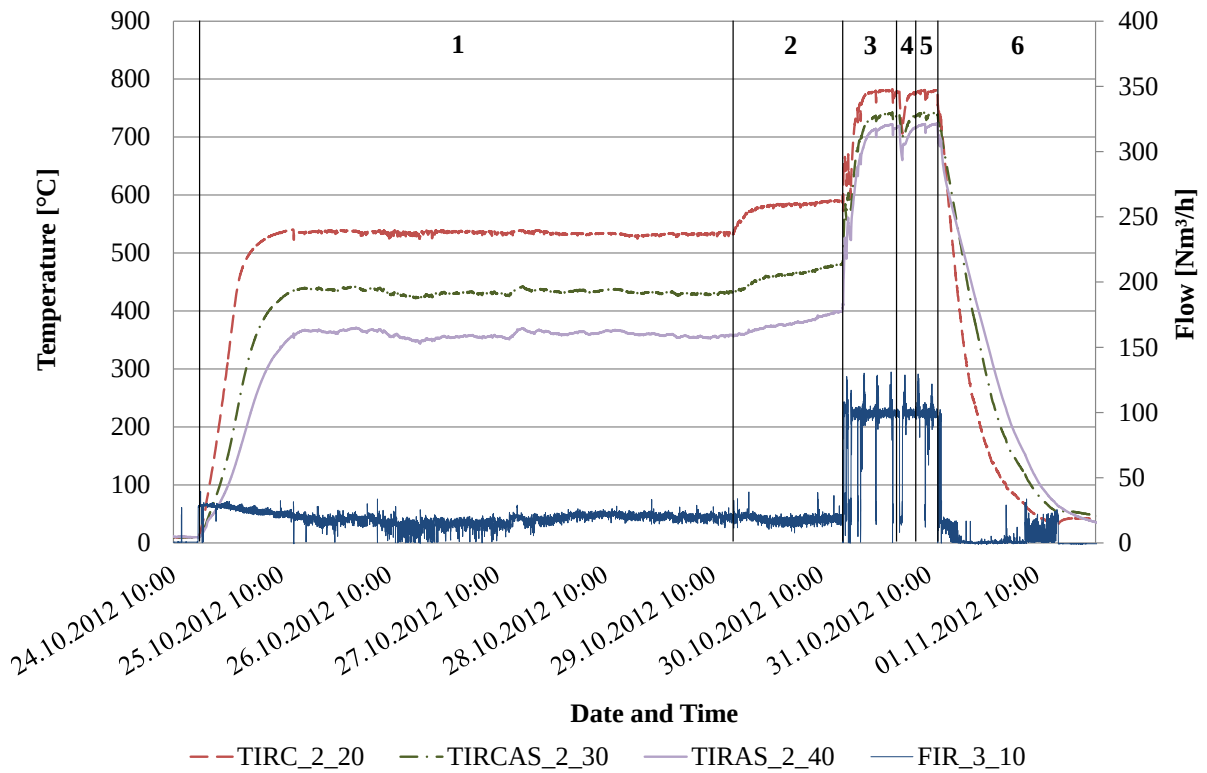


Figure 16: Sections of the First Experiment

Figure 17 shows the adjustment of the trace heating measured by the temperature element TIRC_1_63. The temperature level of TIRC_2_20 could be raised by 50°C , TIRCAS_2_30 by 30°C and TIRAS_2_40 by 20°C . The temperature was still slowly increasing. Therefore, it can be assumed that slightly higher temperatures can be achieved.

TIRC_1_63 shows a constant fluctuation of the temperature. This is due to the functionality of the programmable logic controller (PLC). The desired temperature is defined. The PLC then regulates the realization.

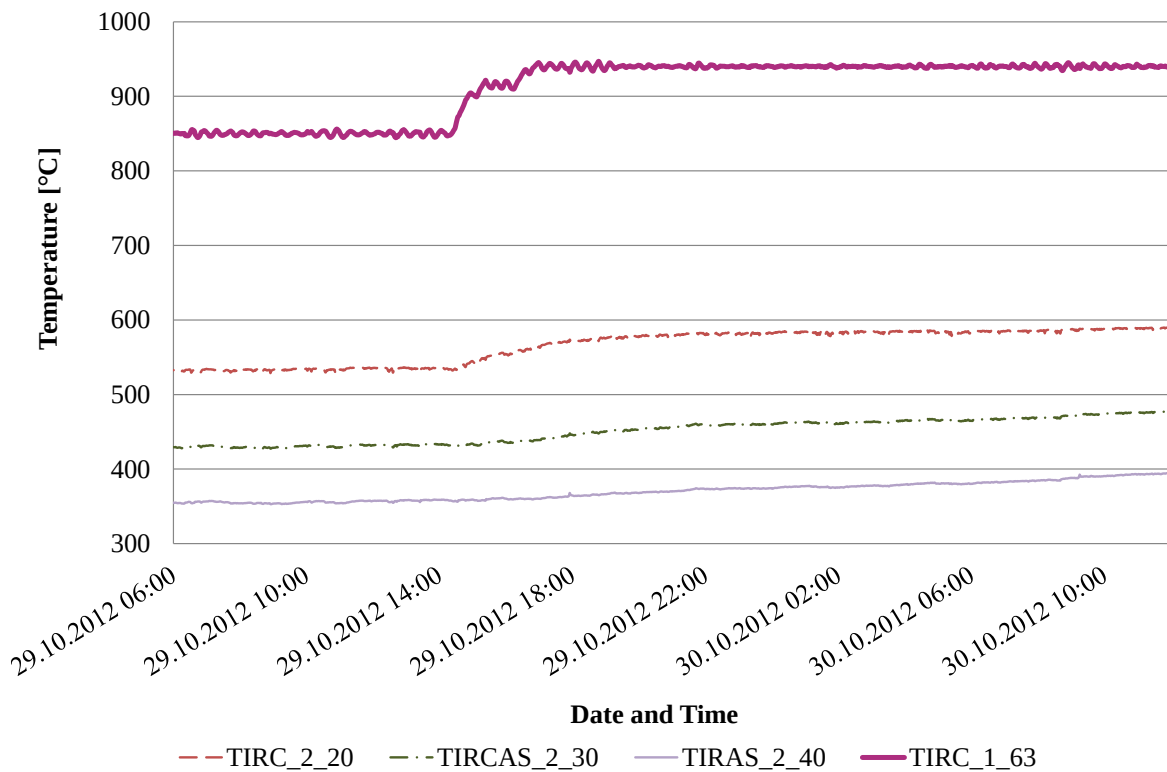


Figure 17: Adjustment of Heat Traces

5.3.2 Second Experiment

In comparison to the first experiment the operating time with product gas of the second experiment was 172 hours. Table 4 and figure 18 show the procedure of the second experiment.

Analogous to the first experiment the heat up to similar temperatures was realized by addition of nitrogen. During the operating time when product gas was fed into the reformer, there were three gasifier shutdowns (sections 3, 5 and 7). The procedure as described above was the same for all three of them. The experiments were characterized by constant temperature levels. TIRC_2_20 was held at 780°C , TIRCAS_2_30 at 744°C and TIRAS_2_40 at 728°C .

Table 7 in the appendix shows the detailed procedure of the second experiment.

Section	Date	Time	State	Medium
1	02.11.2012	20:50	Heat up	Nitrogen
2	06.11.2012	12:52	Normal operation	Product gas
3	07.11.2012	15:49	Gasifier shutdown	Nitrogen
4	06.11.2012	17:23	Normal operation	Product gas
5	08.11.2012	10:51	Gasifier shutdown	Nitrogen
6	08.11.2012	12:58	Normal operation	Product gas
7	10.11.2012	13:10	Gasifier shutdown	Nitrogen
8	10.11.2012	18:58	Normal operation	Product gas
9	13.11.2012	19:24	Shutdown	Nitrogen

Table 4: Procedure of the Second Experiment

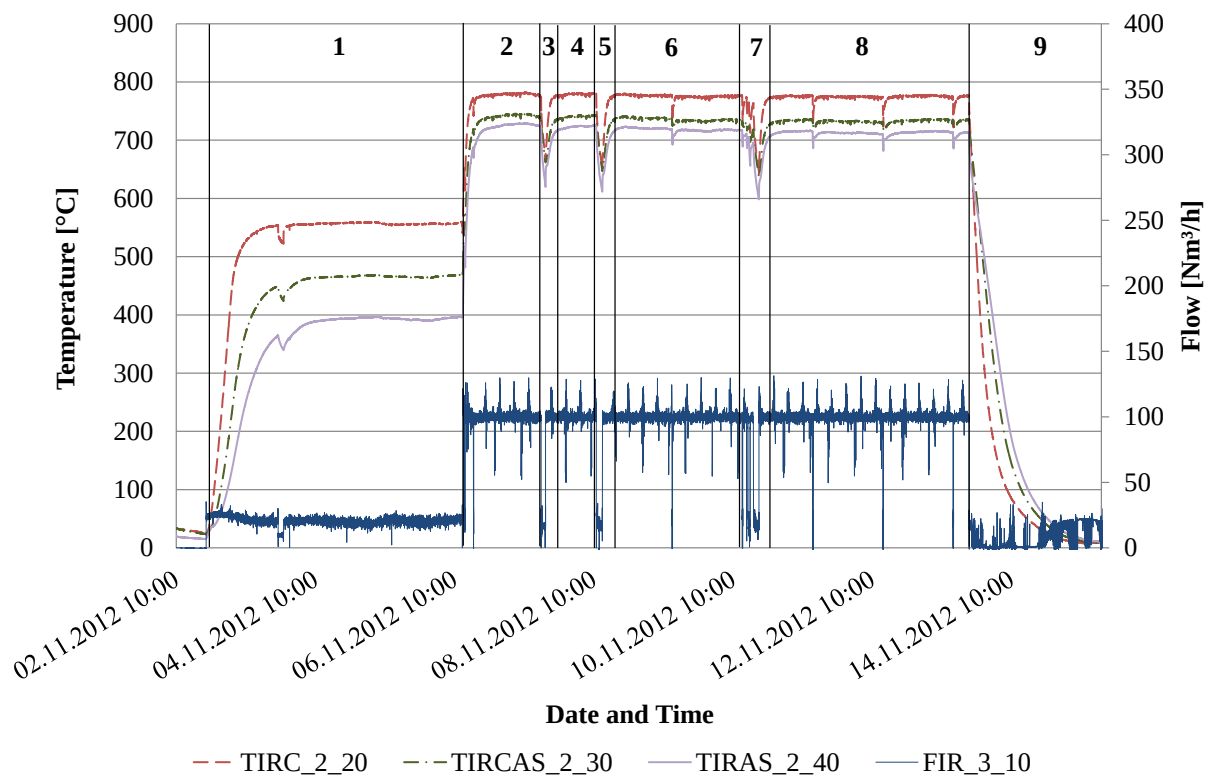


Figure 18: Sections of the Second Experiment

Figure 19 shows the correlation between the addition of air due to regeneration and the sudden temperature change as its consequence. Every 24 hours a regeneration cycle took place. It simulated the regeneration of catalysts inside the reformer. First, the addition of product gas was interrupted. Then nitrogen was fed into the reformer to displace the remaining product gas. The regeneration itself was realized by addition of air at the top of the reformer. The air was diluted with nitrogen which was added through four nozzles above the first layer of monoliths.

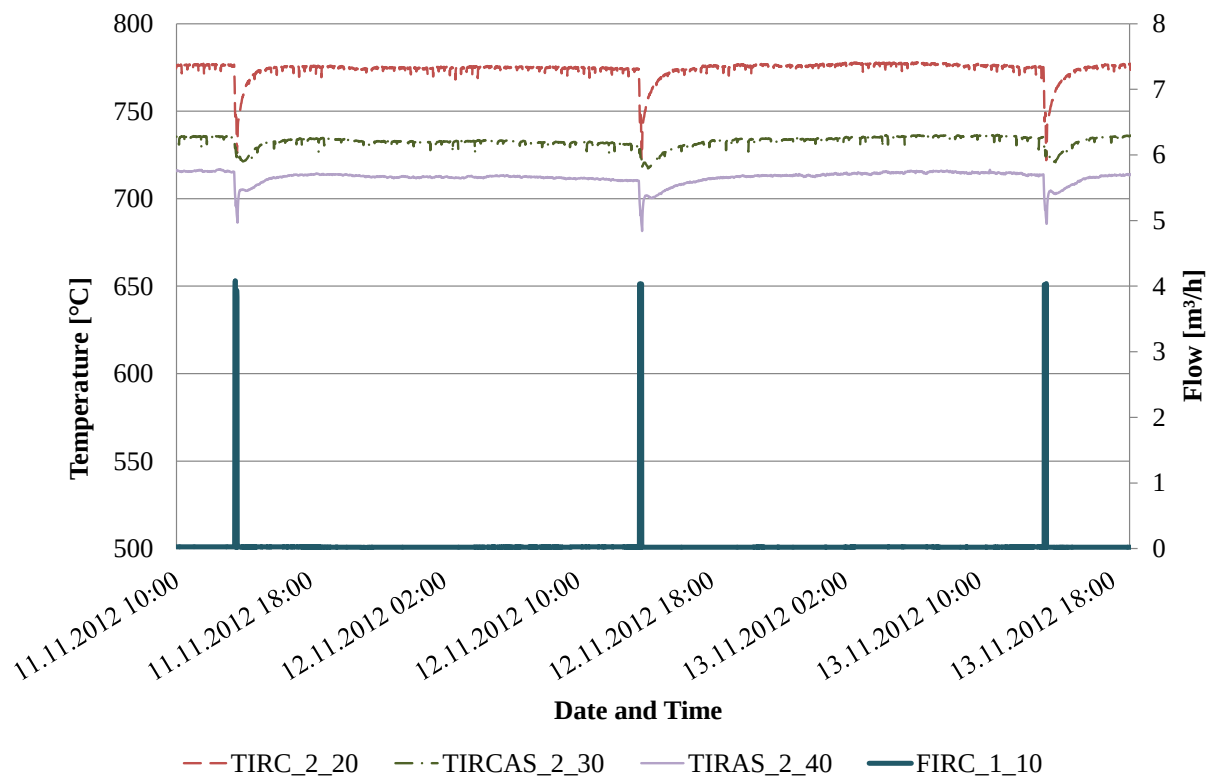


Figure 19: Regeneration

Figure 20 shows a single regeneration cycle. It can be separated into two phases. Those two phases proceeded within less than ten minutes. Each of them consisted of addition of air and nitrogen. As a result a decrease of the temperature inside the reformer could be observed. In each phase twice as much nitrogen as air was added.

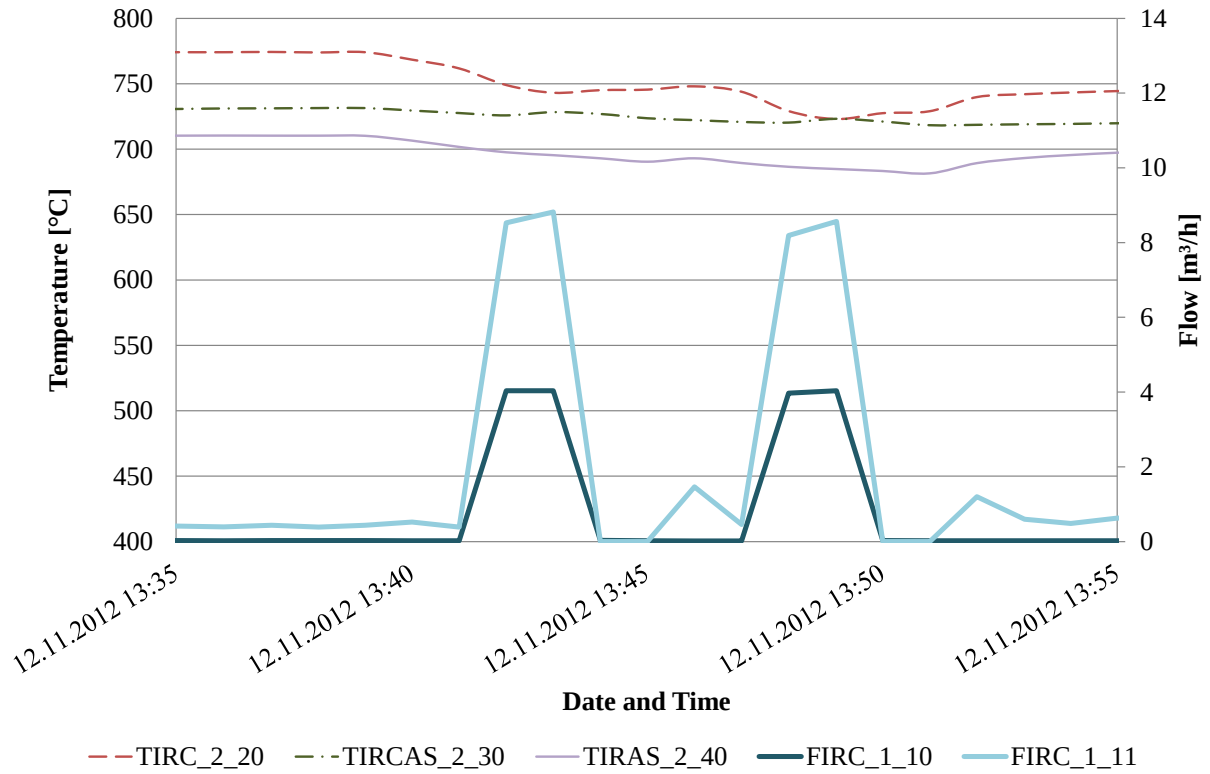


Figure 20: Regeneration Cycle

5.3.3 Third Experiment

The operating time with product gas of the third experiment was 260 hours. Table 5 and figure 21 show the procedure of the third experiment. After the addition of product gas one of the trace heating devices broke which resulted in a decrease of temperature (section 2). TIRC_2_20 could reach 757°C , TIRCAS_2_30 723°C and TIRAS_2_40 703°C .

During the experiment there was one severe and one short shutdown of the gasifier (sections 3 and 5). The severe shutdown was caused by three consecutive gasifier shutdowns and resulted in a temperature change of approximately 200°C inside the reformer. At the time of the second shutdown another trace heating device broke. Therefore, TIRC_2_20 was further reduced to 755°C , TIRCAS_2_30 to 720°C and TIRAS_2_40 to 694°C .

Section 7 shows partial combustion of the product gas. Air was added into the reformer through nozzles above the second layer of monoliths. The experimental data of the partial combustion will be investigated in detail below.

The detailed procedure of the third experiment is shown in table 7 in the appendix.

Section	Date	Time	State	Medium
1	16.11.2012	18:03	Heat up	Nitrogen
2	19.11.2012	12:10	Normal operation	Product gas
3	22.11.2012	10:09	Gasifier shutdown	Nitrogen
4	23.11.2012	01:14	Normal operation	Product gas
5	27.11.2012	10:33	Gasifier shutdown	Nitrogen
6	27.11.2012	14:31	Normal operation	Product gas
7	28.11.2012	15:49	Partial combustion of the product gas	Product gas
8	30.11.2012	11:07	Shutdown	Nitrogen

Table 5: Procedure of the Third Experiment

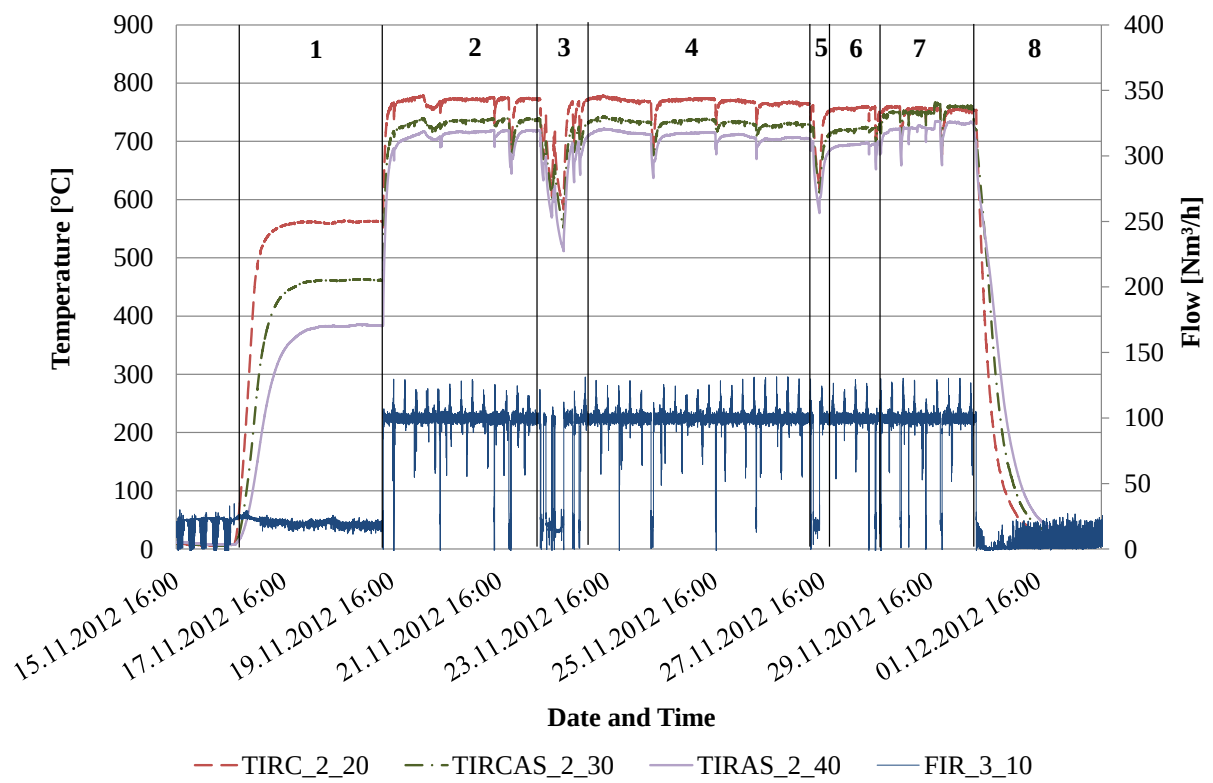


Figure 21: Sections of the Third Experiment

Figure 22 shows the coherence between nitrogen pulse jets and sudden change of temperature inside the reformer. Every ten minutes a nitrogen pulse jet is introduced to displace dust from the monoliths. Through each of the eight nozzles nitrogen can be pulsed into the reformer. Four of them are placed above the first and four above the second layer of monoliths. Every ten minutes cold nitrogen is added through one of these nozzles. The addition of nitrogen alternates between the two layers. As a consequence, every ten minutes there is a temperature decrease (TIRC_2_20 or TIRCAS_2_30) of $5 - 8^{\circ}\text{C}$.

Contrary to the data seen in figure 22 there is no difference of the amount of nitrogen added into the reformer. The values of the measured parameters were logged every minute, but the nitrogen pulse jets did not occur exactly every ten minutes. There was a delay of a few seconds. Therefore, a small mistake in the data of figure 22 has to be heeded.

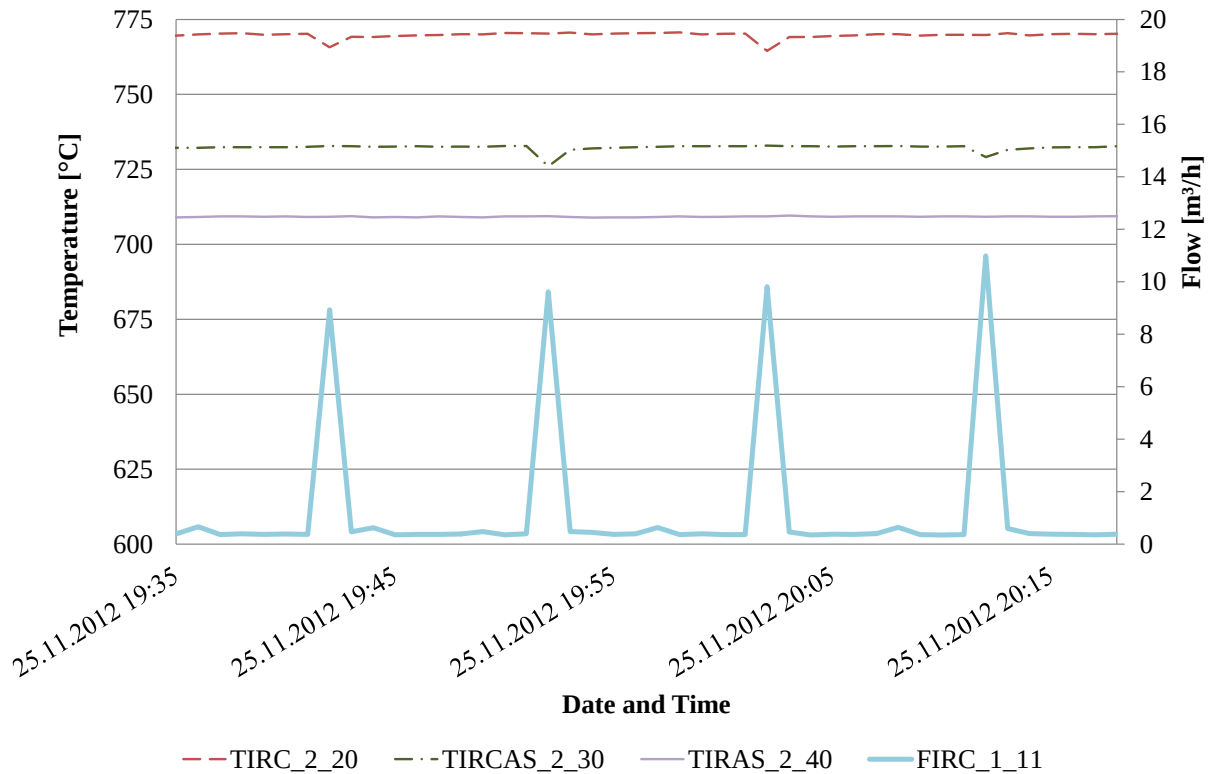


Figure 22: Nitrogen Pulse Jets

Figure 23 shows the correlation between partial combustion of product gas and the temperature level inside the reformer. The partial combustion was initiated by addition of air through nozzles above the second layer of monoliths. The addition of about 2 m^3 air led to an increase of the temperature in the lower section of the reformer. TIRCAS_2_30 was raised to 750°C and TIRAS_2_40 to 720°C .

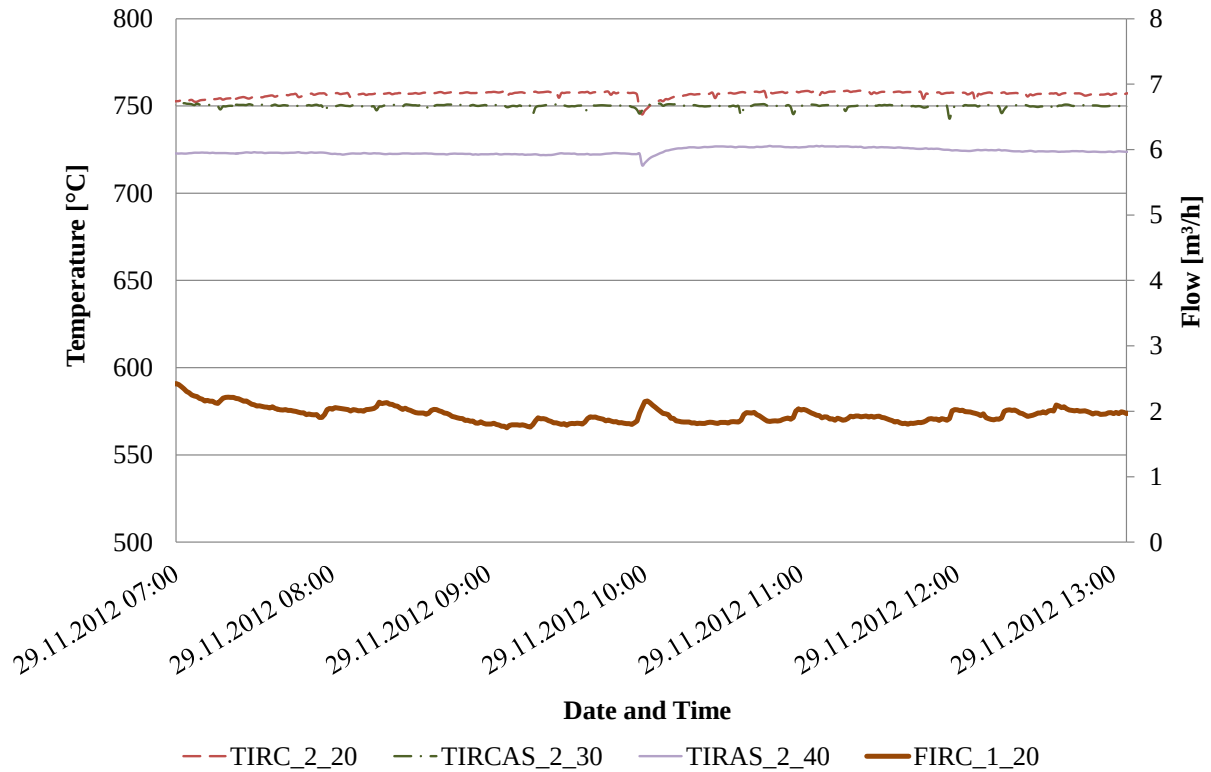


Figure 23: Partial Combustion with $\sim 2 \text{ m}^3$ of Air

Figure 24 shows the addition of 3.5 - 4 m^3 of air. As a consequence the temperature in the lower section of the reformer was further raised. TIRCAS_2_30 was raised to 760°C. Therefore the temperature level above the second layer of monoliths was higher than above the first layer. TIRAS_2_40 was increased to 730°C. The temperature levels in the reformer were consistent during the partial combustion.

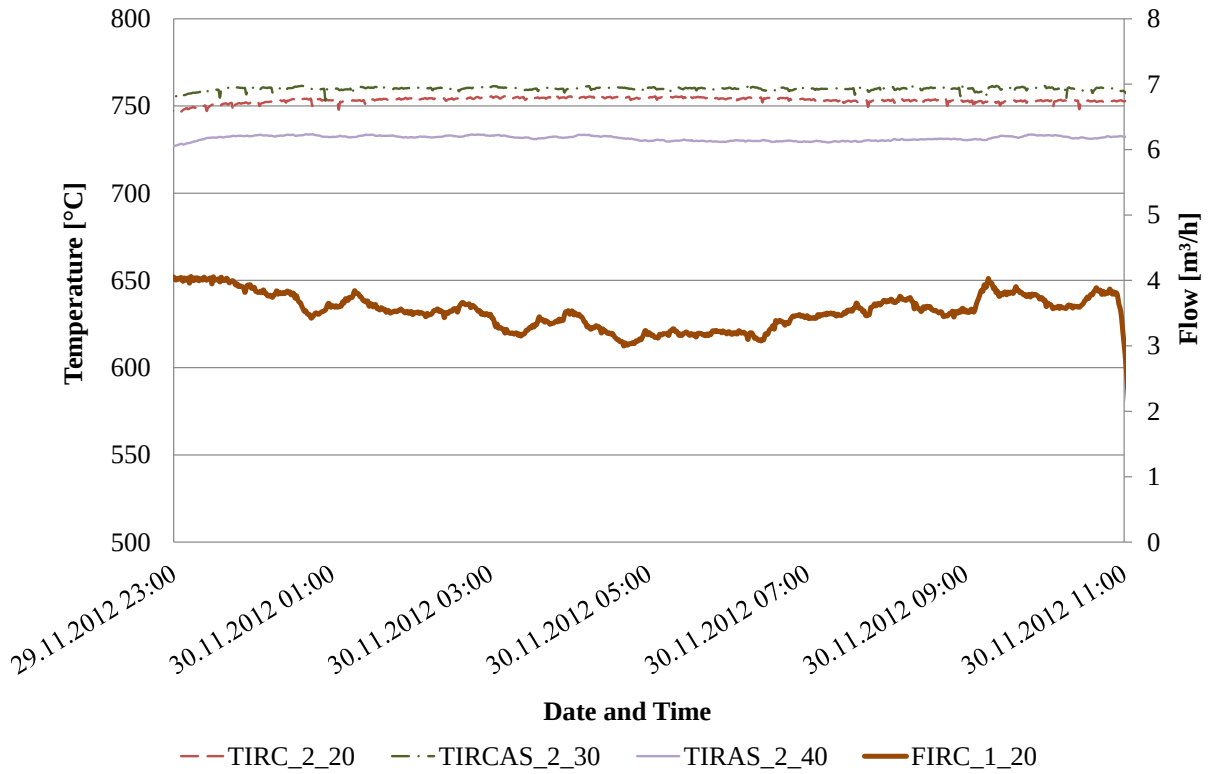


Figure 24: Partial Combustion with $\sim 4 m^3$ of Air

Figure 25 shows a comparison of the average temperatures TIRC_2_20, TIRCAS_2_30 and TIRAS_2_40 during partial combustion. Since the air was added into the reformer above the second layer of monoliths, the temperature at the gas inlet section (TIRC_2_20) was consistent. The temperatures TIRCAS_2_30 and TIRAS_2_40 increased equally. As it can be seen, the temperature difference between the gas inlet section (TIRC_2_20) and the gas outlet section (TIRAS_2_40) can be counterbalanced to a certain extend.

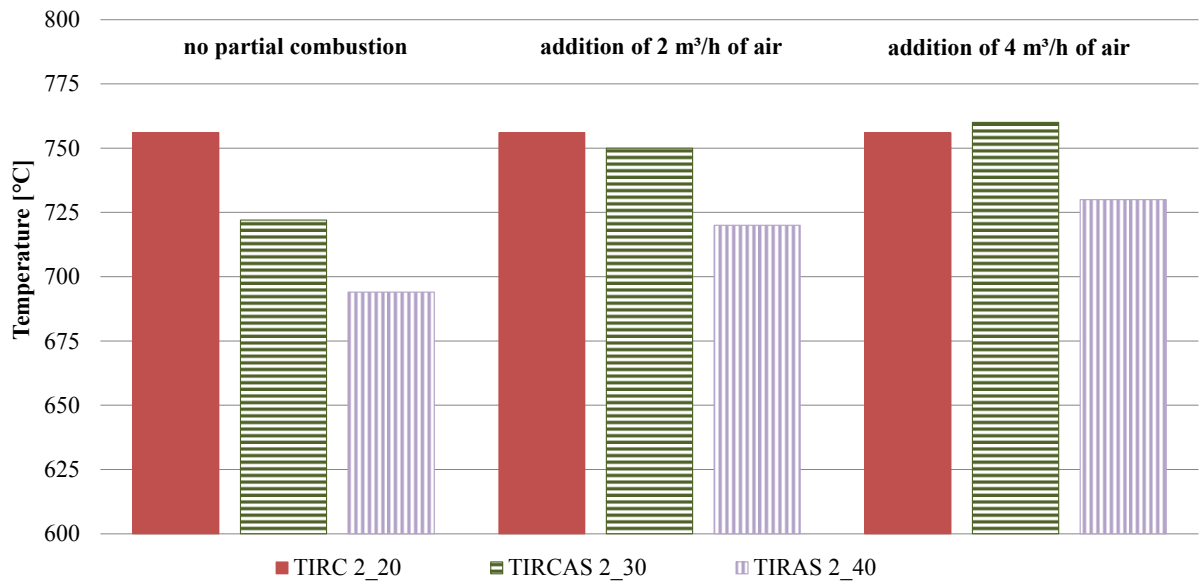


Figure 25: Average Temperatures during Partial Combustion

5.4 Results

During the first experiment only 21 hours of operation time with product gas were realized. The focus lay on optimising the heat up of the reformer and ensure stable conditions in case of gasifier shutdowns.

Preheating the reformer with nitrogen leads to a significant decrease of the sudden temperature change when product gas is added. Sudden temperature changes cause thermal stress of the monoliths. The higher the temperature change the higher is the risk of overstraining the material of the monoliths which leads to fraction. A reformer of the design described above can be slowly heated up to an inlet temperature (TIRC_2_20) of 590°C . This can be seen in figure 17.

Furthermore, the temperature loss due to gasifier shutdowns can be reduced by the automatic addition of nitrogen. Nevertheless, due to a significant difference in the amount of gas passing through the reformer, the temperature difference can still be a problem. The temperature loss depends on the lengths of the gasifier shutdown. Consequently, short shutdowns do not cause problematic thermal strain. However, longer shutdowns may be critical regarding the thermal resistance of the monoliths.

The second experiment lasted for a time span of 172 hours with stable conditions. Figure 19 shows the sudden temperature change inside the reformer due to regeneration. At the top of the reformer (TIRC_2_20) a temperature loss of 100°C was measured. Figure 20 shows that this temperature loss occurs within ten minutes. Thermal strain caused by such a rapid decrease of temperature may be critical. Again, the sudden temperature change was caused by the difference of the amount of gas flowing through the reformer but further by the fact that the air and the nitrogen were cold when they were added. Therefore, a preheating system for air and nitrogen should be considered for future investigations.

Another problematic issue regarding the regeneration of the monoliths is the local generation of heat. The oxygen from air added into the reformer reacts with carbon which accumulates in form of fly ash and dust on the monoliths. Since the oxidation

reaction is exothermic, the heat generation is locally very high. As a result the monoliths suffer from severe tension due to a high temperature difference between the top and the bottom. As a consequence the lifetime of the monoliths is drastically shortened. Therefore, it would be advantageous to remove the dust before it comes into contact with the monoliths. Due to energy efficiency reasons the dust would have to be removed in the hot state of the product gas. That could either be realized by hot gas filters or a heated cyclone. If the product gas was freed from dust and fly ash, the catalytic monoliths would not suffer from additional strain.

The duration of third experiment was 260 hours. Due to the failure of two trace heating devices the temperature level was significantly lower compared to the first and second experiment.

Figure 22 shows the temperature loss inside the reformer due to nitrogen pulse jets. Those temperature changes are considerable small and therefore do not cause severe thermal stress of the monoliths. Further the dilution of the product gas caused by addition of nitrogen is very small. Those pulse jets displace dust and fly ash from the monoliths by forcing them through the channels of the monoliths. This is necessary to keep active sites of catalytic monoliths free so that they can trigger the reforming reactions.

Partial combustion of product gas leads to an adjustment of the temperature levels in the reactor. Figure 23 shows similar temperature levels above the first and above the second layer of monoliths. The temperature difference is less than 10°C . However, addition of only 2 m^3 of air still leaves a temperature difference of almost 30°C between the top (TIRC_2_20) and the bottom (TIRAS_2_40) of the reformer.

By increasing the amount of air fed into the reformer, the temperature at the bottom of the reformer (TIRAS_2_40) raises to a similar level. Figure 24 and 25 show that almost complete temperature uniformity can be realized throughout the whole reformer by adding $3.5 - 4\text{ m}^3$ of air. Further increasing the amount of air might lead to a degradation of the efficiency of the process due to loss of valuable product gas.

This uniformity of the temperature levels inside the reformer is essential since most commercial catalysts only work at high temperatures. If the temperature fell below a certain value, the catalysts would drastically lose their activity. Therefore, the second layer of monoliths would suffer from a temperature loss across the reformer. Partial combustion of product gas can ensure the operation of both layers of catalytic monoliths.

6 Conclusion

Biomass gasification is a promising technology for decentralized production of heat, power and synthetic products. Hot gas cleaning can make the process more energy efficient and therefore economically competitive.

In the near future chlorine compounds could be separated from the product gas by either *Na*-based sorbents or alkaline and alkaline earth metal compounds supported on $\alpha\text{-Al}_2\text{O}_3$. Nitrogen compounds could be reduced by decomposition or selective oxidation. For the separation of particles high density ceramic filters in the form of candles could achieve high collection efficiencies.

Sulphur compounds, which are critical regarding their ability to poison catalysts, could either be reduced inside or downstream the gasifier. In-bed reduction of sulphur compounds could be realized by calcium based sorbents such as limestone or dolomite. Other than that, commercial catalysts like calcium acetate (CA) or calcium magnesium acetate (CMA) could be an effective alternative since they possess higher efficiency towards sulphur capture. Downstream of the gasifier metal oxide sorbents, especially zinc oxide, copper oxide or manganese oxide based, could be used for conditioning of the product gas.

The focus of tar reduction lies on catalytic decomposition. Tars could be transformed into useful gases instead of separated into a tarry waste stream which has to be considered. There are numerous catalysts which are suitable for decomposing tars. Nevertheless, most of the research only has been done in laboratory scale so far.

Downstream reforming of tars, as it has been tested at the biomass gasification plant in Güssing, shows promising results. However, the strain of the catalysts caused by necessary regeneration of dust and fly ash is still a serious problem. Future experiments could concentrate on the reforming of tars in a product gas freed of particles.

A combination of primary and secondary measures to reduce impurities in the product gas could lead to a significant increase of the competitiveness of biomass gasification systems.

7 Appendix and References

Date	Time	State	Medium	T_2_20 [°C]	T_2_30 [°C]	T_2_40 [°C]
24.10.2012	15:40	Heat up	Nitrogen	535	438	366
29.10.2012	14:42	Additional heat up	Product gas	585	465	381
30.10.2012	14:47	Normal operation	Product gas	780	740	720
31.10.2012	03:25	Gasifier shutdown	Nitrogen	718	701	670
31.10.2012	04:04	Normal operation	Product gas	780	740	720
31.10.2012	11:51	Shut down	Nitrogen	31	30	18

Table 6: Detailed Procedure of the First Experiment

Date	Time	State	Medium	T_2_20 [°C]	T_2_30 [°C]	T_2_40 [°C]
02.11.2012	20:50	Heat up	Nitrogen	555	464	390
06.11.2012	12:52	Normal operation	Product gas	780	748	728
07.11.2012	15:49	Gasifier shutdown	Nitrogen	662	643	620
06.11.2012	17:23	Normal operation	Product gas	780	744	728
08.11.2012	10:51	Gasifier shutdown	Nitrogen	654	643	619
08.11.2012	12:58	Normal operation	Product gas	780	744	728
10.11.2012	13:10	Gasifier shutdown	Nitrogen	638	634	598
10.11.2012	18:58	Normal operation	Product gas	780	744	728
13.11.2012	19:24	Shut down	Nitrogen	9	10	11

Table 7: Detailed Procedure of the Second Experiment

Date	Time	State	Medium	T_2_20 [°C]	T_2_30 [°C]	T_2_40 [°C]
16.11.2012	18:03	Heat up	Nitrogen	561	460	380
19.11.2012	12:10	Normal operation	Product gas	773	736	716
22.11.2012	10:09	Gasifier shutdown	Nitrogen	582	554	518
23.11.2012	01:14	Normal operation	Product gas	773	736	716
27.11.2012	10:33	Gasifier shutdown	Nitrogen	624	617	580
27.11.2012	14:31	Normal operation	Product gas	757	722	694
28.11.2012	15:49	Partial combustion with 2 m^3/h of air	Product gas	758	750	720
29.11.2012	16:49	Partial combustion with 4 m^3/h of air	Product gas	755	760	730
30.11.2012	11:07	Shut down	Nitrogen	12	12	13

Table 8: Detailed Procedure of the Third Experiment

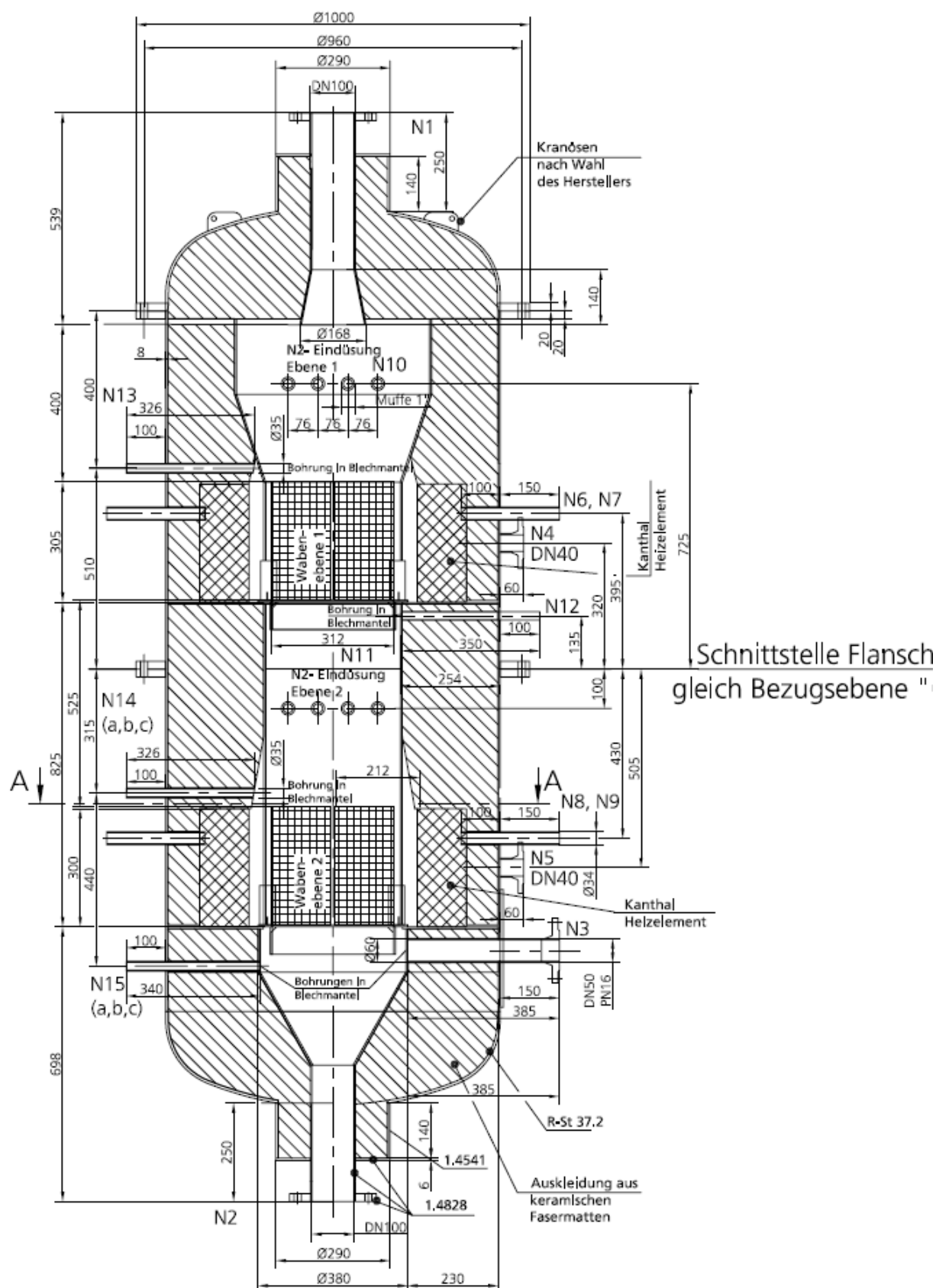


Figure 26: Technical Drawing of the Reformer (by Fraunhofer UMSICHT in 2005)

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