Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.

Diplomarbeit

Development of an industrial catalytic filter for tar reforming

ausgeführt an den Universitäten
KTH Royal Institute of Technology
Technische Universität Wien

zum Zwecke der Erlangung des akademischen Grades eines Diplom-Ingenieurs

unter der Betreuung von
Univ.Prof.i.R. Dipl.-Ing. Dr.techn. Hermann Hofbauer
Assist. Prof. Efthymios Kantarelis

eingereicht an der Technischen Universität Wien
Fakultät für Maschinenwesen und Betriebswissenschaften

durch

Harald Scharfetter

11741232
Färberau 13a
5550 Radstadt

26. November 2020

Unterschrift StudentIn

Abstract

The wide spectrum of end-use applications makes gasification a process with great potential to exploit biomass as a renewable and sustainable energy source. Biomass gasification is in direct competition to conventional energy technologies, which makes constant development and optimization of the technology inevitable in order to compete against the huge volume of oil and coal industries. The formation of heavy hydrocarbons during the gasification states a big problem of the process. Complex cleaning systems to remove impurities from the product gas are required to fulfill criteria for following process steps. In this study, a concept for a hot-gas filtration with an integrated catalytic structure is elaborated. Merging two operations, namely filtration and catalytic reforming, enables an efficient use of process temperatures and leads to an overall increase of the process efficiency. Two methods are developed to deposit a nickel based catalyst onto a commercial low density filter. A $Ni/MgAl_2O_4$ catalyst is prepared via a sol-gel route. One approach to generate a catalytic filter is by direct treatment of the filter body with the prepared sol-gel and calcination of the filter candle. A catalytic slurry is used for coating of the filter candle in a second method. Results show improved properties for the catalytic filter that is prepared by the sol-gel method, as contact time between the catalytic sites and the gaseous compounds is improved due to the distribution of the catalytic material over the whole cross-section of the filter. Light hydrocarbons and methane are broken down up to 50 % during the experimental tests. Naphtalene is converted up to 80 % at temperatures in the range of 750-800 °C. The efficiency for the conversion of hydrocarbons is largely influenced by the temperature inside the filtration-unit. Additives to the filter bodies for an improved mechanical stability have no significant effect on the catalytic activity, but are critical when running tests with a real product gas, due to the formation of a filter cake. The concept of a catalytic hot-gas filtration shows positive aspects, additional tests at temperatures exceeding 800 °C are required to determine the performance of the catalyst and gain further information about the improvement of the overall process efficiency.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Acknowledgements

I am very grateful for the opportunity to realize this work within the division of Process Technology at KTH Royal Institute of Technology and want to thank everybody that contributed to it. I would like to express my gratitude to my supervisor Efthymios Kantarelis for his extensive support and mentoring throughout the project.
I want to thank Prof. Klas Engvall and Christer Rosén for their support and the hours they put in on the installation of the experimental setup.
I want to thank Prof. Hermann Hofbauer for supervising the thesis at Technical University of Vienna and am grateful for his editorial comments.
Finally, I owe more than thanks to my family for their support and encouragement throughout my life.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Contents

I Theoretical background

1 Introduction **2**
- 1.1 Motivation of the work . . . 2
- 1.2 Scope of the work . . . 2

2 Biomass gasification **4**
- 2.1 Fundamentals of gasification . . . 4
- 2.2 Technology & processes . . . 5
  - 2.2.1 Types of gasifier . . . 6
  - 2.2.2 Gasifying agents & product gas . . . 9
- 2.3 Outlook on biomass gasification . . . 10

3 Tar in biomass gasification **12**
- 3.1 Definition of tar . . . 12
- 3.2 Problems of tar formation . . . 12
- 3.3 Formation of tar in biomass gasification systems . . . 13
- 3.4 Methods for tar removal and reforming . . . 15
  - 3.4.1 Primary methods . . . 15
  - 3.4.2 Secondary methods . . . 17

4 Hot-gas filtration in biomass gasification **20**
- 4.1 Theoretical background on hot-gas filtration . . . 20
- 4.2 Concept of catalytic hot-gas filtration . . . 21
  - 4.2.1 Process description . . . 21
  - 4.2.2 Advantages & drawbacks . . . 22
  - 4.2.3 State of the art in catalytic hot-gas filtration . . . 23

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

II Experimental work

5 Aim & content of the study **26**

6 Materials & methods **27**

6.1 Catalytic hot-gas filter 27

6.1.1 Hot-gas filter 27

6.1.2 Catalyst & sol-gel preparation 28

6.1.3 Catalytic coating of the filter 29

6.1.4 Catalyst characterization 31

6.2 Experimental set-up 32

6.2.1 Filtration unit 32

6.2.2 Gas analysis & tar sampling 33

6.2.3 Simulated product gas 34

6.3 Experimental design 36

7 Results & discussion **39**

7.1 Characterization of the catalytic filter 39

7.1.1 XRD 39

7.1.2 BET 40

7.1.3 SEM 41

7.1.4 Coating technique 43

7.2 Experimental runs 44

7.2.1 Thermal effects on the reforming of hydrocarbons 44

7.2.2 Catalytic effects on the reforming of hydrocarbons 46

8 Conclusion **54**

9 Outlook **56**

List of Figures **v**

List of Tables **vi**

References **vii**

Appendix

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.

Part I

Theoretical background

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

1 Introduction

1.1 Motivation of the work

Over the past years, green and sustainable energy systems have been focused strongly, as they represent the inevitable trend towards environmentally friendly technologies that protect natural resources and minimize negative impacts on our planet. The effects of global warming and the unbroken rise of greenhouse gas emissions seem to have ultimately reached policy makers. Green technologies are on the advance, however, as they compete against conventional energy technologies, namely oil and coal, the development of competitive processes states a tough challenge. With a rising awareness for climate change, biomass based energy production became a promising technology. In addition to power and heat, gasification of biomass enables the production of a wide spectrum of valuable products, applicable in various end-use applications. Production of hydrogen for fuel-cell technologies or FT-fuels for the transportation sector are two possible fields of application. Biomass is available almost everywhere and in all kinds, ranging from crops to industrial residues and waste streams. This variety makes biomass suitable for the decentralized production of energy, adapted to the available resources. However, the direct competition with large oil refineries, requires constant development of the technology. Process optimization and minimization of costs is essential for commercial biomass gasification plants.

1.2 Scope of the work

In this thesis, reforming of hydrocarbons in the product gas by the concept of a catalytic hot-gas filtration is investigated. The thesis is divided into two main parts. A brief introduction about biomass gasification, its technologies and essential theoretical information about biomass based processes are described in the first part. Different gasifying technologies, reactor types and the main challenges that come along with gasification of biomass are discussed. Furthermore, the formation of tar during gasification and the problems that arise due to tar formation are elaborated. The focus is then put on cleaning systems and operations downstream of the gasifier that are required for

the production of clean synthesis gas. The removal of impurities and reforming of hydrocarbons is described in detail, as it is one of the main challenges of biomass gasification and utilization of the product gas. Furthermore, the concept of a catalytic hot-gas filtration for the reforming of hydrocarbons is elaborated. The fundamentals for both operations, filtration and catalytic conversion of hydrocarbons, are described separately and eventually the positive aspects of the merging of the two operations into a single one are discussed.

The second part discusses the experimental studies that are performed in this project. The focus of the project is put on the development of a catalytic filter that is used for the reforming of tar products in a hot-gas filtration. The chosen approach and experimental structure is described in detail. A major part of the experimental study is the preparation of the catalytic filter bodies. Two different methods are developed to coat the filter bodies with a catalytic material. Characterization of the prepared catalyst, as well as the filter structures enable an evaluation of the applied methods. Furthermore, the catalytic filter bodies are tested in an experimental set-up to determine the efficiency to break down tar products. The work concludes with an evaluation of both, the methods for the catalytic coating and the efficiency of the catalytic filtration for tar reforming. Finally, an outlook on biomass gasification and its possible role in the future is given.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.

2 Biomass gasification

2.1 Fundamentals of gasification

Gasification describes the thermochemical conversion of a liquid or solid fuel into a caloric product gas. A gasifying agent is used for an understoichiometric oxidation of a carbon based feedstock and its conversion into a product gas, also named producer gas. While overstoichiometric conditions in combustion processes lead to exothermic reactions and full oxidation of the fuel to CO_2 and H_2O, gasification requires additional energy. One way to provide energy for the endothermic gasification reactions is by partial oxidation of the biomass feedstock, termed autothermal gasification. The second technology is allothermal gasification. The required heat is transferred to the gasifier via an external energy source, for example overheated steam or heated bed material. Several process steps are required to convert raw biomass into a product gas or even a synthesis gas that is then used in various applications. Product gas with a low calorific value, mainly due to high concentrations of nitrogen, is suitable for combined heat and power generation, syngas mainly consisting of CO and H_2 and free of impurities, is used for synthesis processes of chemicals, bio-fuels, or for fuel-cell applications. Biomass is fed into the gasifier, heated up and dried at temperatures around 100 °C in a first step. At temperatures around 300 °C to 600 °C, organic structures of the biomass are thermally decomposed during pyrolysis. The carbon content of the solid biomass residue rises during the pyrolysis, leading to the formation of solid carbon char. In a third step at temperatures above 700 °C, the char reacts with the gasifying agent and compounds of the product gas in several homogeneous gas phase and heterogeneous reactions. The temperature depends largely on the type of gasifier. Equations 2.1 - 2.8 describe the main gas/solid and gas-phase reactions that occur during gasification of a carbon fuel.[1]

Combustion reactions

$$C_{(s)} + O_2 \longleftrightarrow CO_2 \qquad \Delta H = -394\,\mathrm{kJ/mol} \tag{2.1}$$

$$C_{(s)} + 1/2\,O_2 \longleftrightarrow CO \qquad \Delta H = -111\,\mathrm{kJ/mol} \tag{2.2}$$

Boudouard reaction

$$C_{(s)} + CO_2 \longleftrightarrow 2\,CO \qquad \Delta H = +172\,\mathrm{kJ/mol} \tag{2.3}$$

Water gas reaction	$C_{(s)} + H_2O \longleftrightarrow CO + H_2$	$\Delta H = +131\,\mathrm{kJ/mol}$	(2.4)
Water gas shift reaction	$CO + H_2O \longleftrightarrow CO_2 + H_2$	$\Delta H = -41\,\mathrm{kJ/mol}$	(2.5)
Methanation	$CO + 3\,H_2 \longleftrightarrow CH_4 + H_2O$	$\Delta H = -206\,\mathrm{kJ/mol}$	(2.6)
	$CO_2 + 4\,H_2 \longleftrightarrow CH_4 + 2H_2O$	$\Delta H = -164\,\mathrm{kJ/mol}$	(2.7)
Steam reforming	$CH_4 + H_2O \longleftrightarrow CO + 3\,H_2$	$\Delta H = +206\,\mathrm{kJ/mol}$	(2.8)
Tar reforming	$C_nH_m + nH_2O \longleftrightarrow nCO + (n+m/2)H_2$		(2.9)

The main compounds of the product gas are CO, H_2, CH_4 and CO_2. If air is used as gasifying agent, the concentration of N_2 in the product gas is high. Various parameters affect the composition of the product gas and the concentration of specific gaseous compounds and impurities. Depending on the final application, different gasifying technologies are common and downstream treatment of the gas is usually required to remove pollutants and meet quality criteria. A reaction scheme for a biomass gasification is shown in Figure 2.1. It illustrates the main steps of the process, drying, pyrolysis and gasification of the char together with the corresponding reactions. Simultaneously to the formation of char and its gasification, tar is formed mainly from volatiles inside the gasifier. Extensive focus is put on the treatment of the organic and aromatic products, as tar formation has a significant influence on the process efficiency and reliability. A detailed description about tar formation and problems caused by tar formation can be found in Section 3.

2.2 Technology & processes

Gasification technologies have been investigated since the 19th century and are well studied, especially pyrolysis and gasification of coal and corresponding industrial applications. Gasification of coal and biomass are based on the same principle, due to differences in biomass compositions, some process steps have to be modified and adapted for biomass

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

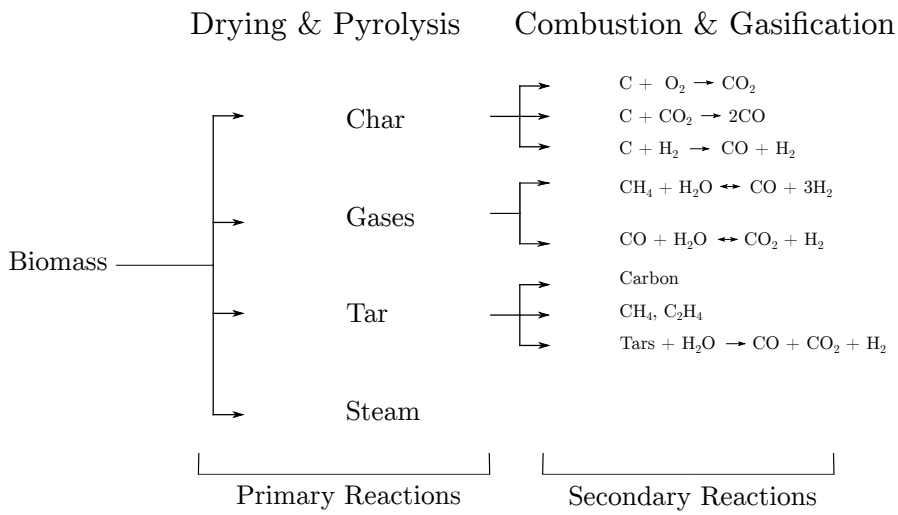


Figure 2.1: Reaction scheme of the gasification process[2]

gasification compared to gasification technologies using coal as feedstock. As the handling of biomass differ from coal, pretreatment steps, such as drying and sizing of the biomass before gasification, are required. Pollutants and impurities vary from coal and therefore suitable cleaning technologies have to be developed. Various kinds of biomass feedstock are available for gasification, ranging from crops, wooden residues to waste streams from industrial plants. The diversity within the feedstock requires versatile technologies and processes, suitable for the available biomass sources and the targeted end-use of the gas.[1]

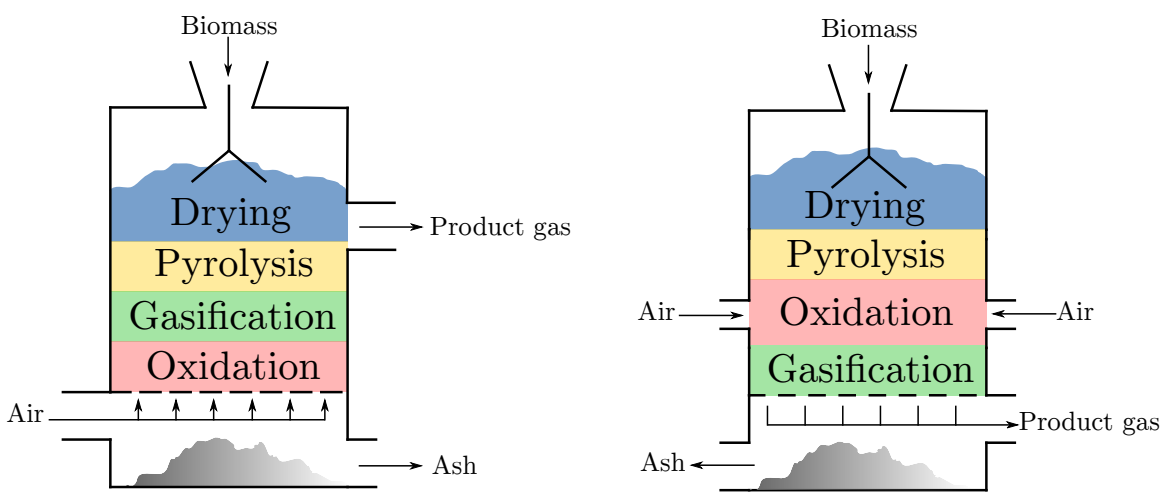
2.2.1 Types of gasifier

For the gasification of biomass, different types of gasifier, mainly classified based on the gas-solid contacting mode and the gasifying agent, are common. Three types of gasifiers are field tested, fixed or moving bed gasifiers, fluidized bed gasifiers and entrained flow gasifiers, with each type further subdivided into very specific reactor designs.[3]

Fixed bed gasifiers state the oldest type of gasifier. The biomass is fed into the reactor from the top or the side. The solid fuel moves downwards the reactor, due to the degradation of the solid fuel inside the gasifier, giving the technology the name "moving bed gasifier". Different designs of fixed bed gasifiers have been studied, classified by the inlet and outlet of the gasifying agent. Figure 2.2 shows schemes of up- and downdraft

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

fixed bed gasifiers with the four reaction zones of the process. For updraft gasifiers (Fig. 2.2a), the gasifying agent enters at the bottom of the reactor and streams upwards in counter-current flow to the biomass. The generated product gas streams upwards the gasifier and leaves the reactor through an outlet at the top. Updraft gasifiers are among the simplest types of reactors for gasification. The counter-current flow of the gasifying medium enables a good utilisation of the combustion heat from the oxidation zone, however, mixing and heat exchange within the solid fixed bed are rather poor, leading to a non-uniform distribution of temperature and gas composition over the cross-section of the gasifier. Another type are downdraft gasifiers. The main advantage of downdraft (Fig. 2.2b) over updraft gasifiers is the significant reduction of tar concentrations in the product gas. The gasifying agent enters the reactor at a higher level compared to updraft gasifiers, usually from the side of the reactor. Oxidation and reduction zones are swapped compared to the updraft technology, causing the product gas to flow through a bed of high temperature char. The contact of the product gas with the hot char leads to the decomposition of tars. Within the subtypes of fixed bed gasifiers different designs are found, each model with specific characteristics and qualities.[3]



(a) Updraft gasifier (b) Downdraft gasifier

Figure 2.2: Types of fixed bed gasifier with four reaction zones

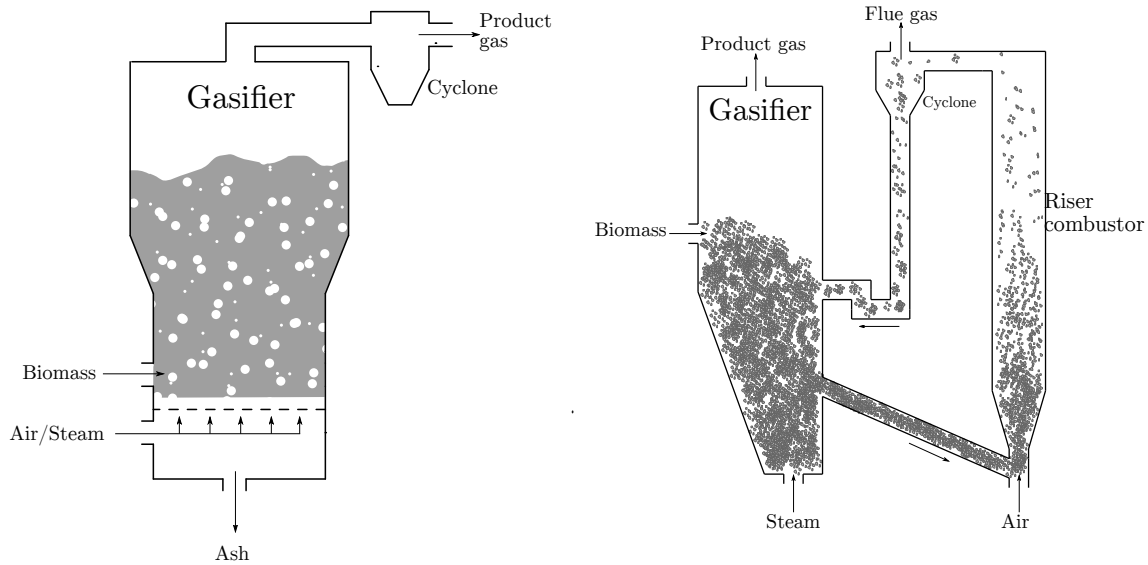
Fluidized bed gasifiers consist of bed material, that is swirled up (fluidized) through the stream of a gasifying agent. Depending on the size of the bed material and the velocity of the gas medium, the intensity of the fluidization is controlled. Common gasifying agents for fluidized bed gasification are oxygen, air or steam. Compared to fixed bed gasifiers, the particle size of the biomass feed is reduced. There are a few specifics

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

about fluidized bed gasifiers, making this technology very popular for the gasification of biomass. An inert bed material which consists of silica sand or catalytic active minerals is used to get smooth fluidization. It is heated up and enables an excellent temperature distribution throughout the gasifier and a nearly uniform temperature inside the reactor. The different thermo-chemical conversion reactions happen simultaneously, leading to a shorter residence time compared to fixed bed gasifiers. Furthermore, very good gas/solid mixing inside the bed makes the technology stable and insensitive against varying feed compositions. The required energy for the endothermic process is provided either through a partial oxidation inside the fluidized bed or through an external source. The bed material is used for an uniform distribution of the thermal energy inside the reactor.[4]

Mainly two different types of fluidized bed gasifiers are classified. The most common technology, widely used for medium-sized units, is a bubbling fluidized bed gasifier. A bubbling fluidized bed is formed by a low velocity of the gas that is streaming into the gasifier. The low velocity leads to the formation of ascending gas bubbles inside the reactor, only little amounts of bed material are discharged with the product gas stream. Circulating fluidized bed gasifiers are operated at higher fluidization velocities (3.5-5.5 m/s) compared to a bubbling bed (0.5-1.0 m/s). Due to high velocity, bed material is entrained and has to be returned to the bed. The contact between bed material and product gas is improved, resulting in a higher conversion efficiency due to better heat and mass transfer inside the gasifier. For the production of a high quality product gas and in order to fulfil quality specifications, the combinations of fluidized beds are applied. In a dual fluidized-bed, combustion and gasification are performed in separate units, connected by the circulating bed material. Exothermic reactions in a riser heat up the bed material that is transferred to the gasifier. Inside the gasifier the heated bed material provides the energy for the endothermic reactions. This leads to a high quality product gas without nitrogen that can be upgraded to synthesis applications. Figure 2.3 shows the schemes of two fluidized bed gasifiers. The bubbling fluidized bed in Figure 2.3a is operated at low fluidization velocities. No bed material is discharged and a cyclone is used only for the removal of char particles and particulates from the product gas stream. Figure 2.3b shows a dual fluidized bed gasification, the bed material is circulated through two connected reactors. The required heat is provided through combustion in a riser and transferred to the gasifier through the circulating bed material. While steam is used as gasifying agent, air is used for the combustion inside the riser, generating a high quality product gas, as well as conventional flue gas.[3]

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



(a) Bubbling fluidized bed

(b) Dual bed circulating fluidized bed

Figure 2.3: Fluidized bed gasifier concepts (adapted from [3])

The third type of gasification reactors are entrained flow gasifiers, mainly used for the gasification of coal in large scale plants and for gasifications with a liquid or slurry feed. Entrained flow gasifiers are co-current plug-flow reactors, operated at temperatures exceeding 1000 °C. High temperatures inside the reactor enable a fast gasification and allow very short residence times. The fuel enters the reactor as a fine powder or slurry together with the gasifying agent. Very high conversion of carbon is realised at this high temperatures, as well as the production of a nearly tar-free product gas. Low amounts of methane make the product gas suitable for further synthesis processes. [3]

For the gasification of biomass, entrained flow reactors are of minor importance, mainly because of the demands on the feed. For entrained flow gasifier, solid fuels need to be existent as fine ground powder. Sizing of biomass is difficult to realize, due to the high moisture content and the fibrous structure. The complex technology of entrained flow gasifiers and the high temperatures inside the reactors, makes the gasifier type suitable for large-scale plants in the oil and coal sector. [4]

2.2.2 Gasifying agents & product gas

The end-use application of the product gas has an essential influence on the parameters of the gasification process and strongly defines the technologies and methods that

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

are considered. The selection of a suitable gasifying medium for the thermo-chemical conversion of the solid fuel is of high importance, as it has a strong influence on the composition and quality of the product gas. Common gasifying agents are air, steam, O_2 and CO_2. Gasification with air as gasifying medium produces a product gas of low calorific value, limiting the application to gas turbines and combustion boilers for power and heat generation. Using oxygen as gasifying agent, a product gas of high calorific value is generated, that fulfils the criteria for several applications. Product gas streams rich in CO and H_2 are used for hydrogen production processes, fuel cell applications or synthesis of chemicals and bio-fuels. The combination of gasifying agents with reactor types is common, Table 2.1 shows typical compositions of product gas streams for specific gasification models, including fixed bed, fluidized bed and entrained flow gasifiers.[5]

Table 2.1: Typical composition of product gases from biomass gasification[4]

	H_2 [vol.%]	CO [vol.%]	CO_2 [vol.%]	CH_4 [vol.%]	N_2 [vol.%]
Fixed bed gasification with air	11-20	12-19	10-15	2-5	45-60
Fluidized bed gasification with steam	35-40	22-25	20-25	9-11	<1
Entrained flow gasification with oxygen	29-35	35-44	17-22	<1	3-9

For the end-use in fuel cells or chemical synthesis processes, the product gas needs to be upgraded and pollutants and impurities removed. In addition, the concentrations of particular compounds in the gas stream have to be adjusted to make the gas usable for further process steps. Depending on the followed application, the ratio of CO/H_2 is adjusted using water-gas shift reactor units. Typical ratios of CO/H_2 needed for the production of gaseous or liquid fuels from syngas are 1/1,1/2, or even 1/3.[4]

2.3 Outlook on biomass gasification

Gasification of biomass, especially biomass from waste streams and residues, represent a promising and sustainable technology for the future to exploit the potential of biomass as a sustainable energy source. A variety of end products can be generated from biomass, making it an alternative to processes based on fossil fuels. Biomass as feedstock is CO_2

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

neutral, resulting in a small carbon footprint of the processes. An important aspect of biomass gasification is its decentralized operation. Gasifiers and further processing units have to be positioned close to the available biomass sources to avoid long transportation routes and minimize costs. It is preferable to use waste streams and biomass residues for the gasification, as their costs are lower compared to more valuable biomass sources, such as wood and specific crops.

However, further improvement of gasifier and downstream cleaning and upgrading equipment is required to be able to compete with fossil based products. The scale of gasifier units is small compared to units processing coal and other fossil fuels, making gas cleaning and conditioning systems more expensive. Raw biomass contains high amounts of problematic compounds and require specific treatment. Therefore, new technologies and further research is of high importance to improve temperature management, make downstream equipment more durable and increase the overall efficiency of the gasification and downstream operations.[5]

The variety of biomass gasification makes the process suitable for a wide range of applications. However, change of surrounding conditions, different feedstock or variable end products require specific process conditions. Biomass gasification is defined largely by local conditions. Availability as well as type of feedstock and size of the plant have significant influence on the process. Gasification plants need to be adjusted to available resources, making it impossible to pick one perfect gasification concept. Continuous development of the current systems and technologies is required to be able to choose suitable gasification concepts for the available sources and operate a plant commercially.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

3 Tar in biomass gasification

3.1 Definition of tar

Tar products and their formation during biomass gasification is often titled the Achilles' heel of the process[6]. One would think that there was a uniform definition for tar, as it represents one of the major challenges in the process of biomass gasification. For a long time, tar products were imprecisely described as organic molecules that condensate under specific operating conditions. Still today different definitions of tar are found. One of the most common definitions is: The organics produced under thermal or partial oxidation regimes of any organic material, that are generally assumed to be largely aromatic and have a higher molecular weight than Benzene (78,11 g/mol)[6]. However, the definition describes the organic compounds insufficiently and lacks information about their formation. A further classification into primary, secondary and tertiary tars gives more detailed information about the composition of these compounds and the conditions under which different kinds of tar are formed. A good understanding of tar products and the formation mechanisms is important to develop methods to reduce tar concentrations in the product gas and break down the formed compounds to light hydrocarbons.

3.2 Problems of tar formation

Regardless of the definition, the removal, conversion, or destruction of tar is one of the main challenges that needs to be solved to develop commercial biomass gasification technologies. The main problem of tar is the condensation at temperatures below 300 °C and the formation of complex, solid structures that lead to clogging of downstream pipes, valves and instruments. Metal corrosion of the plant is a consequence of condensation of tar, leading to a significant decrease in efficiency of the gasification plant and to rising costs due to bigger stress on the equipments.[7]

As long as in gaseous phase, tars are not problematic for pipes and plant equipment, but cooling of the gas stream in downstream process units lead to condensation of tar products. While internal combustion gas engines are more tolerant against contamination,

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

gas turbines and other applications require low tar concentrations, some applications even a tar-free syngas. The emerging of new technologies and applications effects the demands on the product gas, for example the usage in fuel cells or chemical synthesis processes. Tar concentrations in the product gas are strongly affected by the gasifying technology and process parameters. It has to be noted that the problematic aspect of tar is not about the concentration, but mainly about the composition and properties of the tar products. This again emphasizes the need for an uniform categorisation and good understanding of the mechanism behind their formation. Table 3.1 shows the categorisation of tar into five classes according to ECN (Energy research Center of the Netherlands). Tar compounds are classified based on their behaviour in downstream equipment.[8]

Table 3.1: Classification of tars according to ECN[9]

	Class name & properties	Representative compounds
Class 1	GC-undetectable	Determined by subtracting the GC-detectable tar fraction from total gravimetric tar
Class 2	Heterocyclic aromatics	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
Class 3	Light aromatics, light hydrocarbons with single ring	Toluene, ethylbenzene, xylenes, styrene
Class 4	Light PAH compounds, 2-3 ring compounds, condense at low temperature and low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
Class 5	Heavy PAH compounds, larger than 3-ring, condense at high-temperatures at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

3.3 Formation of tar in biomass gasification systems

The formation of tar during the gasification of biomass is a complex process, depending strongly on the reaction conditions. The three constituents of biomass, cellulose, hemicellulose and lignin are broken down to primary tar at temperatures around 200-500 °C mainly during pyrolysis of the biomass. Above 500 °C primary tar is converted to secondary tar that consists of phenolic and olefinic compounds. Further increase in temperature up to 800 °C causes the formation of tertiary tars. Tertiary tars are divided

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

into alkyl-tertiary products, including methylderivates of aromatics, like toluene or indene and condensed tertiary products, polyaromatic hydrocarbons without oxygen substituents, such as benzene, naphtalene or pyrene. Figure 3.1 shows the formation of primary tars, deriving mostly from lignin to secondary and furthermore tertiary tars. The increase in temperature leads to secondary reactions and the conversion of oxygenated tar compounds to light hydrocarbons, aromatics and olefins and eventually to the formation of tertiary products, mainly larger polycyclic aromatic hydrocarbons (PAHs).[6]

While primary and to a certain extend secondary tar products are broken down to lighter compounds at gasification temperatures around 700-800 °C, tertiary tars require temperatures above 1200 °C for a thermal conversion (cracking) to light hydrocarbons.[10]

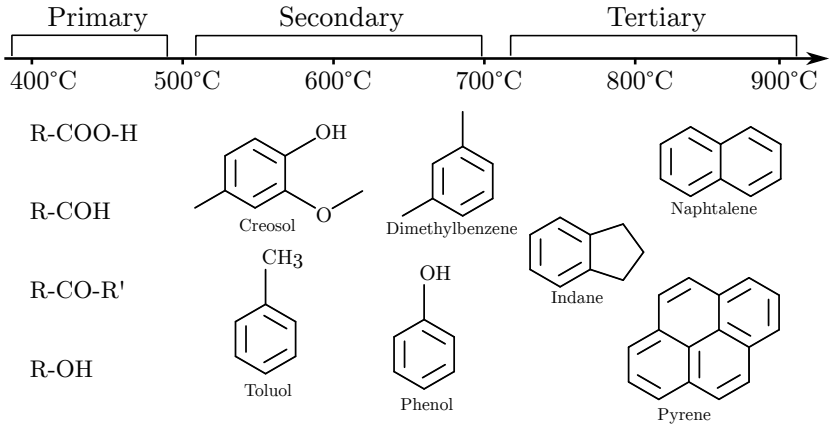


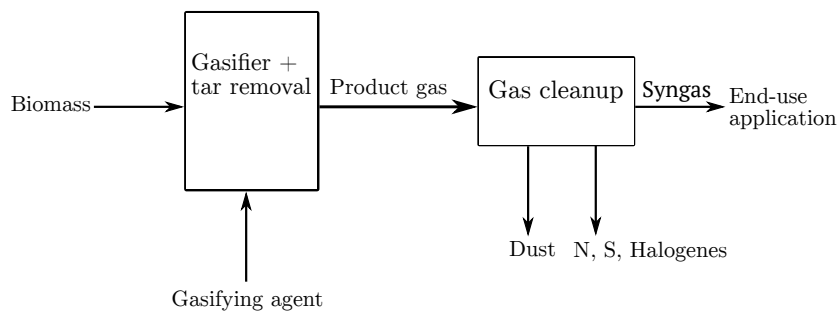
Figure 3.1: Temperature dependent formation scheme and characteristic tar products[11]

Process parameters of the gasification have an important influence on the formation of tars. The strong temperature dependence of tar formation leads to a wide range of tar concentrations in the product gas depending on the chosen gasifier type. Updraft gasifiers are generally considered to generate the highest tar concentration in the product gas ($\approx 100\,\mathrm{g/Nm^3}$), downdraft gasifiers produce relatively low amounts of tar ($\approx 1\,\mathrm{g/Nm^3}$) and fluidised bed gasifiers are somewhere between these two fixed bed gasifier types ($\approx 10\,\mathrm{g/Nm^3}$). Updraft gasifiers produce mainly primary tars, with some degree of secondary character, while tars from downdraft gasifiers are largely tertiary. Fluidized bed gasifiers produce a variety of secondary and tertiary tars. The biomass feed has little influence on the nature of the formed tar[6]. An almost tar free product gas is generated in entrained-flow gasifiers because of the operation at high temperatures.[12]

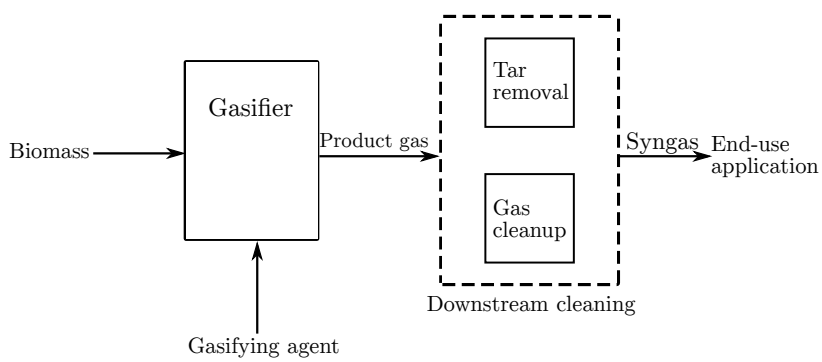
Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

3.4 Methods for tar removal and reforming

Systems and approaches for removal and reforming of tar from the product gas are divided into two categories, depending on the position within the overall process. Primary methods are considered all measures as well as operational parameters inside the gasifier that aim towards a tar-free product gas. Applications placed downstream of the gasifier are considered secondary methods for tar removal. Figure 3.2 shows the principle of primary and secondary tar reforming. The ideal primary concept leads to a nearly tar-free product gas and eliminates the need for further secondary methods.[13]



(a) Scheme of primary tar removal & gas cleaning



(b) Scheme of secondary tar removal & gas cleaning

Figure 3.2: Principle for tar removal[14]

3.4.1 Primary methods

Primary methods for the minimization of tar include all measures that are taken to prevent the formation of tar and break down tar into simple compounds inside the gasifier. This measures are mostly characterized by the design and operation of the gasifier. As the methods are implemented inside the gasifying atmosphere, they usually

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

have an impact on the product gas and influence the formation of other gaseous products. Primary methods are therefore divided into three groups, the selection of fitting operating conditions, the use of bed additives or catalysts inside the gasifier and the design of the gasifier itself.[14]

Operating conditions

The main factors for low concentrations of tar in the product gas are the operating conditions of the gasifier. Besides the formation of tars, it is also an essential parameter for the composition of the product gas and therefore of high importance. Temperature, pressure and gasifying medium describe the most important parameters for an efficient gasification. The temperature conditions inside the gasifier do not just influence the amount of tar that is formed, but also the composition. It is reported, that at temperatures above 850 °C, tar concentrations go down significantly. At high temperatures the composition of tar shifts from oxygen-containing components towards aromatic species without substituent groups, such as naphtalene or benzene. With operating conditions strongly affecting the composition of the product gas, controlling tar formation with operational parameters is limited.[14]

Additives inside the gasifier

Another method to reduce tar concentrations is by adding additives to the bed. Different materials with catalytic properties are added to the gasifying atmosphere, often positively influencing the composition of the product gas towards higher heating values. The added materials must fulfil a few requirements. In addition to the reforming of hydrocarbons in the presence of the gasifying agent, the material needs to have a selectivity for the product gas, a high resistance against coke formation and should be available relatively cheap, as formation of char and ashes might lead to a continuous discharge of the material. Successful tests have been performed using limestone and dolomite as bed material in a fluidized bed gasifier, resulting in a decrease of tar concentrations, as well as a significant improvement of the quality of the product gas[15]. Another material used is olivine, a mineral containing magnesium, iron oxide and silica. Olivine is a cheap alternative to other more expensive additives due to its high availability. Positive effects on tar removal in a fluidized bed gasifier have been reported[16]. Another material that is easily available is char, as it is produced during the gasification. It could serve as catalyst for the primary reduction of tar during gasification, however, further research on its catalytic performance inside the gasifier is required.[14]

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Gasifier design

The design of the reactor is the third aspect that is considered for primary tar removal. Different gasifier types have an essential influence on the calorific value and the composition of the product gas, but also on the formation of tar during gasification. Several attempts have been made to modify gasifiers for a cleaner product gas. Secondary air injection into the gasifier decreases tar concentration due to the increase in temperature inside the reactor's freeboard. Separating pyrolysis and gasification zones, termed two-stage gasifier, leads to a cleaner product gas with lower tar concentrations. Several aspects in the design of gasifiers are promising for lower tar concentrations, however, the low tar concentrations that are required for several end-use applications make secondary treatment of the gas stream inevitable in most cases.[14]

3.4.2 Secondary methods

Although primary systems for tar removal are considered ideal, limitations such as their influence on the product gas, complex gasifier designs and narrow operating windows, make secondary treatment methods important. Different secondary treatment systems are established, that can be operated without primary treatment and achieve high conversions. These systems are installed downstream as separate units resulting in additional operations and a more complex process. Secondary treatment is divided in mechanical/physical, thermal and catalytic methods. While mechanical and physical treatment removes tar products and particles from the product gas, thermal and catalytic systems break down the problematic products to light compounds in cracking and reforming reactions.[8]

Mechanical & physical methods

Different operations are established for the removal of tars using mechanical or physical effects. The processes are divided in dry and wet gas cleaning systems. Dry gas cleaning systems are usually positioned before the cooling of the product gas. Different filter types, cyclones or rotating particle separators are used for a removal of particulates at temperatures above 500 °C. The efficiencies of these systems are often not good enough, requiring additional treatment of the gas stream. Wet gas cleaning systems are positioned after cooling of the product gas, when tar droplets are formed in the gas stream due to their condensation at temperatures below 300 °C. Temperatures in wet-gas cleaning systems are around 20 to 60 °C. Different kinds of scrubber are common systems for an efficient removal of the condensed tars from the gas stream. In

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

addition to tar removal, scrubbers reduce the concentrations of various pollutants in the product gas and remove particulates efficiently. Spray towers, Venturi scrubber or packed bed scrubber are widely used. The liquids in the apparatus range from pure water to oil-water emulsions and organic liquids. However, aside from good tar removal with wet scrubbers, operating costs of the systems are quite high, mainly because of the need to regenerate the liquid[8].

Thermal treatment

Thermal cracking is a process that is well established in the refinery of crude oil and describes the cracking of complex aromatic compounds at approximately 600 °C for an adjustment of the boiling range. High temperatures are required to break down the complex formations to hydrogen and carbon monoxide, causing this method to be very energy intensive. Biomass derived tars are very hard to crack just by thermal treatment alone, requiring longer residence times of the gas or adding of air/oxygen for a partial oxidation in the converter. Thermal conversion of tar starts at temperatures above 700 °C, however, for better conversions of the aromatic compounds higher temperatures are necessary.[8]

Catalytic tar reforming

The high energy demand for the thermal treatment of tar is counteracted by adding catalytic structures to the downstream operations. A variety of catalysts is used to convert aromatic compounds at lower temperatures compared to thermal cracking. In addition to the reforming of tars, catalytic treatment is used for the compositional adjustment and conditioning of the product gas. The general requirements for a good catalyst, besides the ability to break down tar, are resistance against deactivation, selectivity for the product gas to guarantee the targeted composition of the gas for its end-use application, easy regeneration of the catalyst and good availability of the material. Catalytic reforming is mainly performed downstream in fixed bed reactors that consist of a vessel or tubes filled with the catalytic material.[17]

A simple classification of catalysts used in secondary treatment systems divides them into metal and non-metal catalysts. A non-metal and natural catalyst is dolomite. Dolomite shows a significant reduction of tars, that is improved when calcining the mineral. However, dolomite is a rather soft mineral, limiting its application. The main advantage of natural catalysts is their low price compared to metal based catalysts.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

However, higher conversion is often achieved by using metal catalysts. All sorts of metals have been tested for their ability to reform tar products, with nickel being one of the most established metals. Different support materials are used to optimize the catalyst's behaviour by providing high surface areas and a good distribution of the catalytically active sites. Support materials also improve the stability of the catalyst and decrease deactivation effects due to coking. The support material is essential for the catalytic activity due to its influence on the surface area and pore structure. Various different metal catalysts have been investigated, a lot of them showing promising results in terms of reforming of hydrocarbons. Most of the research so far was performed in rather small scale lab-tests, making it difficult to review the feasibility of the tests.[8]

So far, nickel based catalysts are state of the technology, as they show good results for tar removal and are available relatively cheap. Further difficulties with the catalyst that have to be considered are the sensitivity of the catalyst to poisoning and coking. High amounts of impurities in the product gas, such as sulphur based compounds, may lead to poisoning of the catalyst and significant decreases in the efficiency due to the blockage of the catalytic centres. Besides poisoning of the catalytic sites, coking of the catalyst is another effect that has a negative effect on the performance. Deposition of a layer of solid carbon leads to the blocking of the active sites of the nickel catalyst. The rate of deactivation of the catalyst due to coking depends largely on the formation speed of solid carbon, that is significantly influenced by the temperature. A way to counteract coking is by the selection of a suitable support material for the catalyst. Porous support structures with small pore sizes not only increase the available surface for the conversion reactions, but also positively influence the sensitivity against coking. Furthermore, strong acidic sites favour coking effects, making $MgAl_2O_4$ a suitable support material for nickel based catalyst due to its basic properties.[18]

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

4 Hot-gas filtration in biomass gasification

4.1 Theoretical background on hot-gas filtration

Hot-gas filtration has gained a lot of attention in several technical fields over the last years. Increase in process efficiencies, fulfilling of emission levels, or higher demands for end-use applications are criteria that drive forward reliable and efficient gas cleaning systems. Hot-gas filtration starts at temperatures around 260 °C, but is mainly performed at higher temperatures. Removal of particulates following a biomass gasification with a hot-gas filter prevents condensation of tars. Besides biomass gasification, hot-gas filter units are operated in many industrial sectors, including coal combustion and pyrolysis, steel and metal industry, glass industry or cement industry.[19]

High temperature filtration leads to special demands on the filter elements. In addition to the thermal resistance of the medium at operating temperatures, appropriate mechanical stability of the filter body is required. Furthermore, chemical stability against the gaseous compounds of the product gas is needed. H_2S, HCl, NH_3, Cl_2, H_2O, are common pollutants in the product gas stream. Ceramic filters are well established types for hot gas filtration. Low density ceramics show a high porosity and big surface areas inside the filter structure, however, their mechanical stability is low due to the loose structure, resulting in a higher risk of breakage of the filter candles. High density ceramic filters show a better mechanical stability and very good long time behaviour. An alternative to ceramic filters are metal filters. Depending on the material, these filters are operated over a wide temperature range. Filter candles are the most common structure used for the process. Filter cake is formed on the outside of the candle and is easily removed by back-blowing or mechanical impulses. The filtrated and reformed gas stream exits through the inner part of the filter. Another type of filters are low density filter bodies. Due to the low density and the irregular fibrous structure, these filter types are characterized by a lower pressure drop compared to the other types. The mechanical stability of the filter is relatively low, limiting the operation at high space velocities. The filters are made out of inorganic materials, additives are used to improve the mechanical strength of the structures. The high porosity of the material makes the filter type interesting for the deposition a catalytic layer onto it.[19] [20]

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

4.2 Concept of catalytic hot-gas filtration

4.2.1 Process description

The catalytic conversion of tar using a hot gas filter takes advantage of the high temperatures after the gasification. Temperatures inside biomass gasifiers are in the range of 700-1000 °C, depending on the gasifier type, excluding entrained flow gasifiers. Prepared catalytic filters are placed downstream, but close to the gasifier to minimize temperature losses, or in the freeboard of the gasifier. Particulates are removed and tars broken down above their condensation temperature in the catalytic filter, ideally to hydrogen and carbon monoxide. Figure 4.1 demonstrates the concept of the hot-gas cleaning. As temperatures of consecutive operations are in the same range, linking of process steps has a positive influence on the temperature management and the overall efficiency of the process.[19]

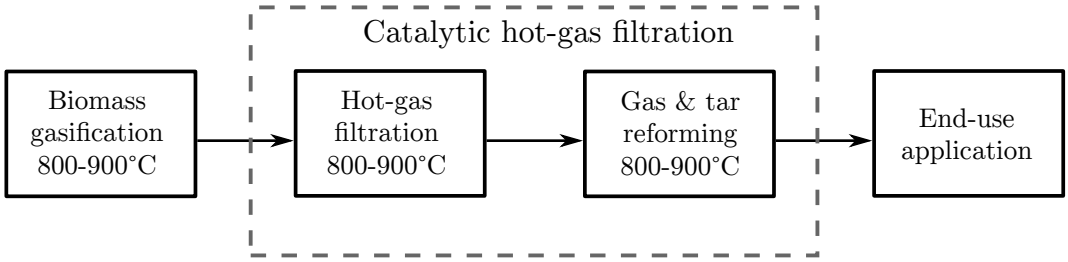


Figure 4.1: Concept scheme of catalytic hot-gas filtration[19]

Figure 4.2 highlights the advantageous sequence of operations. Consecutive processes are operated at similar temperature levels, making heat exchangers and additional heating systems unnecessary. Compared to conventional gas cleaning processes where the gas stream is cooled and heated up again, high temperatures from the gasifier are used efficiently in the following operation.

Catalysts used for the reforming of hydrocarbons are described in Section 3.4.2. The major difference to conventional catalytic reactors is the combination of a filtration process with a catalytic conversion, leading to changes in the required equipment. Different approaches to link the two processes are established. Depositing a catalytic layer onto the filter's surface is a possibility to take advantage of high surface areas of filter structures and gain a high catalytic activity. This method requires an uniform distribution of the catalytic compound over the filter structure and is advantageous for

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

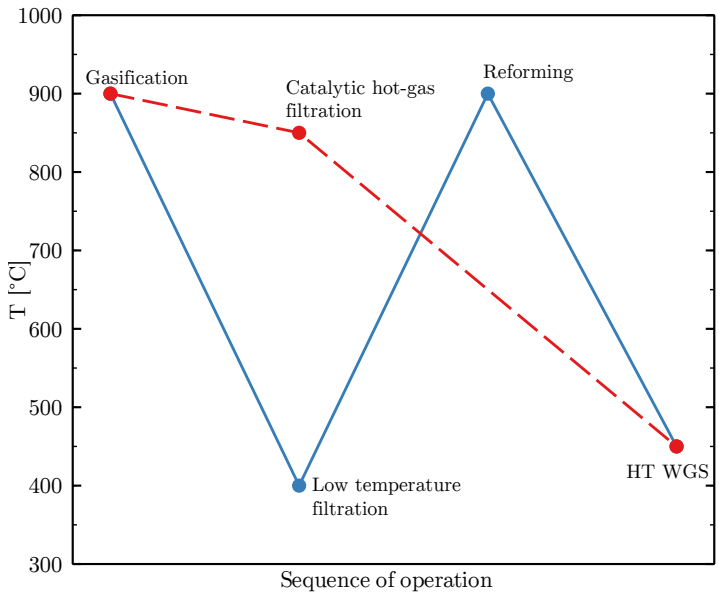


Figure 4.2: Temperature window for optimal consecutive operations

low density filters. In case of filter candles, a different way to include the catalyst is by placing it into the inner volume of the structure. One way to do so is filling it with catalytic grains that are commercially available and provide a high surface area. An alternative way would be the use of a foam that is coated with a catalytic substance and place it in the hollow space. Foams have a very high surface to volume ratio, making them suitable structures for catalytic reactions. Furthermore, the high porosity leads to a decrease in the pressure drop compared to catalytic grains[21]. Metal foams show a very high mechanical and thermal stability and provide a good temperature distribution, making them suitable for high temperature and exotherm processes. A drawback of catalytic active foams or grains is the varying contact time between gas stream and catalyst when using filter units with a certain geometry, such as filter candles. Figure 4.3 shows two different methods for a combination of filtration and catalytic conversion of particulates and tars. The catalyst is either present as packed bed of catalytic grains behind the filter structure, or as thin coating inside the filter's pores.[22]

4.2.2 Advantages & drawbacks

The main advantage of catalytic hot-gas filtration downstream of a biomass gasification is the combination of filtration and catalytic cracking and therefore the merging of two operations into a single one. This enables the design of very compact and space-saving

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

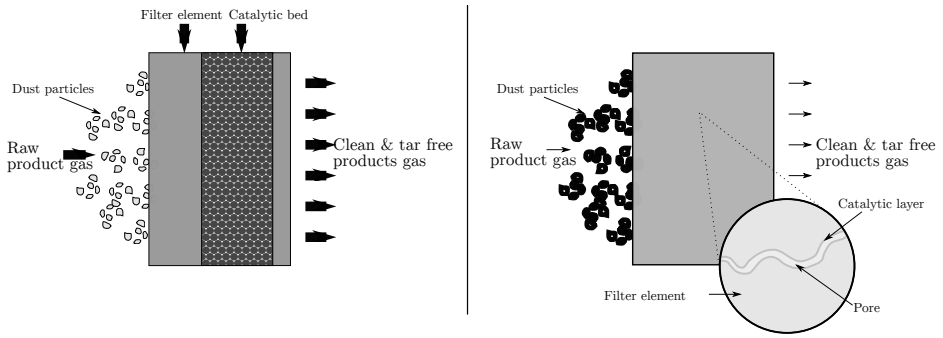


Figure 4.3: Catalytic hot-gas filtration: 2 methods (adapted from[22])

units. Furthermore, improved temperature management has a positive influence on the process efficiency. Placing the filter unit close to the gasifier ensures an optimal usage of the high temperatures of the gas stream after gasification. Attempts to position the filter candles in the freeboard of a fluidized bed gasifier show positive results[23]. While conventional cleaning technologies, such as wet scrubbers, remove condensed tar at low temperatures, hot-gas filtration keeps the temperature of the process at a maximum. Reforming of the aromatic products to lighter products leads to an increase of valuable compounds in the gas, but also prevents waste and recycle streams in the process. Depending on the end-use application of the product gas, conditioning and adjustment of the gas stream is required. Followed operations, such as water-gas shift units, require medium to high temperatures. Therefore the minimization of energy and heat losses is critical for an efficient processing.

The only drawback of the technology are higher investment costs for the catalytic filter unit. The high temperatures lead to an increased demand on the filter unit and its material, as consequence materials and equipment for hot-gas filtration are more expensive. However, higher investment costs in the catalytic filter unit are compensated by reduction of the overall process costs due to the reduced process complexity.[19]

4.2.3 State of the art in catalytic hot-gas filtration

The advantages of catalytic hot-gas filtration, removing and breaking down impurities at high temperatures with an added catalytic phase, are well known. However, the research that has been performed so far is mainly limited to lab-scale studies. Breaking down

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

large hydrocarbons and tar products has been researched in several studies, including all variations of catalysts and filter types. Small filter discs, treated with a catalytic compound, are used in several studies to simulate large filter candles[24], [22]. Simulated product gas, free of pollutants and impurities, is often used in these tests[25]. Especially experiments at temperatures exceeding 800 °C have barely been performed on a bigger scale. Extensive testing on pilot- and industrial-plants is required to transfer results to a bigger scale and test the different approaches under real conditions. Furthermore, tests are necessary to obtain information about the improved temperature management and the increase of the overall efficiency of the process.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.

Part II

Experimental work

5 Aim & content of the study

Gasification describes a process with great potential to exploit biomass as renewable and sustainable energy source with a wide spectrum of possible fields of application. However, bio-fuels or chemicals produced from biomass gasification are in direct competition to fossil based products. As resources and volume of the oil industry are huge compared to biomass based plants, process efficiency and minimization of costs are essential criteria for commercial biomass gasification. A problematic field of biomass gasification is the formation of tar, as these compounds require complex cleaning systems and have negative influence on the process efficiency, causing rising costs and less competitive processes.

In this study a hot-gas filtration with an integrated catalytic phase is performed and investigated to remove particles and break down tar products to light hydrocarbons, ideally to CO and H_2. The focus of the work is put on the coating of a filter structure with a nickel based catalyst, supported with a magnesium spinel. In order to generate an uniform coating of the filter unit and to have a good distribution of the catalytic material over the filter body, different methods are tested and compared. Characterization methods are used to analyse the coating and identify potential weaknesses of each coating technique. Once the filter candles are coated properly with the catalytic material, tests are performed and the efficiency of the coated filter bodies for the removal and reforming of tar is determined. In a first stage tests are performed in the laboratory, using a simulated product gas. Representative tar compounds are injected to the gas stream and the efficiency of the catalytic filter to break down the tar products is determined. Furthermore, the stability of the filter candles and the catalytic coating are evaluated. Previous tests on hot-gas filtration have been performed in a small scale, using representative filter discs for the experiments. The small filter discs are replaced with commercial filter candles and by this, the experimental set-up is scaled up. Tests on the scaled-up unit are carried out to gain further information about catalytic hot-gas filtration. The simulated product gas contains representative tar products, but is free of pollutants and particulates. The efficiency of the process for the reforming of tar products and methane is investigated in the scaled-up set-up. Moving from small-scale lab-tests to experiments on a bigger scale is vital for the development of the concept and upcoming tests that are performed under real conditions on a slipstream of an industrial gasification plant.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

6 Materials & methods

6.1 Catalytic hot-gas filter

6.1.1 Hot-gas filter

The filter candles that are used for the experiments are provided by Tenmat Ltd. and are made out of inorganically bonded granular minerals, the technical data are presented in Table 6.1. Two types of filter candles are used in the experiment that differ in their composition. One type contains inorganic additives for a better mechanical strength, while the second type is free of additional hardener.[20]

Table 6.1: Technical data of the filter candles[20]

Density	450 kg/m^3
Pressure drop	35 mm H_2O at face velocity
Loss of ignition	6.3 % at 70 °C
Filtration efficiency	> 99.99 %
Typical air permeability	8 l/dm^2· min at 200 Pa
Filtration capability	< 1 Particle size (micron)
Emissions	< 1 mg/m^3
Temperature capability	≤ 1000 °C

Figure 6.1 shows a scheme of a filter candle that is used for the experimental tests. The filter candles have an average weight of approximately 200 g without deposited catalyst. The catalytic loading of the filter bodies is set at 10 w.%, resulting in the deposition of roughly 20 g Ni catalyst onto each filter. The gas stream passes through the filter from the outside to the inside of the cylindrical body. Particles are held off by the filter structure, forming a filter cake on the outside of the candle that is removed regularly. Mechanical impulses and back-blowing with a gas stream are conventional techniques to remove the filter cake. The catalyst is deposited uniformly on the inner surface and pores of the filter candle. The even coating of the filter structure ensures an uniform contact time of the gaseous compounds over the whole length of the filter.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

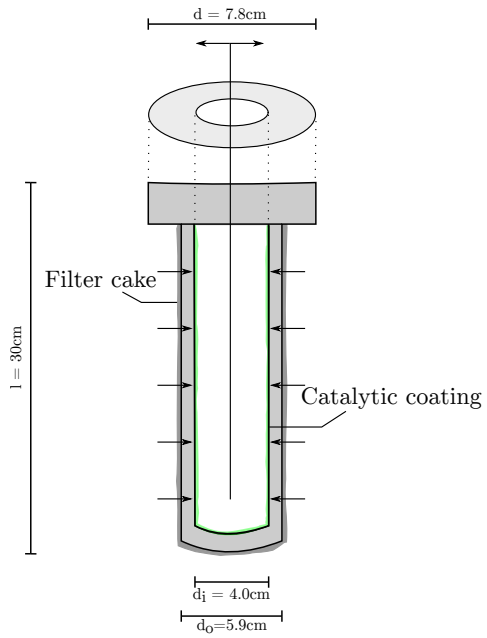


Figure 6.1: Sketch of the filter structure with a catalytic coating on the inner surface

6.1.2 Catalyst & sol-gel preparation

A nickel based catalyst is chosen for the tests, as nickel catalysts are widely used in gas cleaning technologies and tar reforming operations. $MgAl_2O_4$ is used as a support material to improve the quality of the catalyst. The nickel loading of the prepared catalyst is set with 10 w.%. Several methods exist to prepare catalysts from metal precursors, with impregnation or precipitation being well studied techniques. For this project a different method for the preparation of the catalyst is chosen.

The nickel based catalyst is prepared by sol-gel processing. The main basis of the method is the formation of a wet-gel, which consists of a continuous solid network and a surrounding and supporting continuous liquid phase. The gel shows an even distribution of the metal precursors, as it is formed uniformly by the agglomeration of particles from the solution. Wet gels show extremely high porosities, with pores being filled mainly by the initial solvent. The strength of sol-gel methods for the preparation of a supported metal catalyst is the simple formation of a solid from a homogeneous solution. While traditional methods for catalyst preparation are split into two operations, namely the preparation of the support material and the distribution of the catalytic compound over the surface of the support, the sol-gel method merges these two steps into a single one. The viscous gel is then used to deposit a thin catalytic layer onto a solid surface

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

by dip-coating methods. In a second route the sol-gel is further dried and calcined to produce a fine catalytic powder.[26]

For the preparation of the sol-gel the Pechini-Method is chosen, as the production requires only simple lab equipment and low synthesis temperatures. The method is based on trapping precipitated salts in an organic matrix and used for applying thin films or for the preparation of a homogeneous oxide powder[27]. Appropriate amounts of metal nitrates, $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, are dissolved in deionized water. Citric acid is added to the solution as a chelating agent in a molar ratio of 1:1[28]. The liquid is constantly stirred with a magnetic stirrer and heated up to 80 °C. The solution is kept at this temperature over night. Due to the continuous evaporation, a homogeneous sol-gel is formed that is further used for the coating of the filter bodies.[29]

6.1.3 Catalytic coating of the filter

The capability of the filter to remove tar from the gas stream and generate a tar-free syngas is largely influenced by the catalytic layer on the filter element. Non-uniform coating leads to an insufficient tar removal, as parts of the gas pass the filter unit without contact to the catalytic sites. Two different approaches are chosen to ensure a good coating of the filter. The two techniques differ fundamentally from each other, especially the deposition of the catalyst onto the solid surface is different. For both methods the appropriate amount of catalyst is prepared using sol-gel processing as described in Section 6.1.2 to obtain a catalytic loading of the filter candles of 10 w.% is targeted.

One approach to deposit a catalytic layer onto the surface of the filter and its pores is by directly using the light viscous sol-gel. This method is very suitable, as the precursors for the catalyst and the support material are present in a homogeneous gel. To coat the filter structure, the prepared sol-gel is filled into the inner volume of the filter candle. The filter body is moved and spun, until the sol-gel is well distributed over the whole inner surface of the filter candle and no excess gel is present. By this technique catalytic material infiltrates into the filter's pores. The filter is dried in an oven for 48 h at a temperature of 60 °C. Drying of the filter structure is performed at moderate temperatures to avoid any redistribution of the catalytic material. Afterwards the catalytic filter is calcined for 4 h at 850 °C. Coating, drying and calcination of the filter candle are repeated until the targeted loading of 10 w.% is reached.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

The second method to coat the inner surface of the filter candle is by preparing a catalytic slurry. Therefore, a solid catalyst is prepared in a first step. The sol-gel is constantly heated and stirred until a very viscous gel is formed. The gel is dried for 48 h at 90 °C and calcined for 4 h at 850 °C. After calcination the catalyst has a light green color. The catalyst is milled for 48 h in a ball mill to get a fine catalytic powder. The powder is solved in ethanol and mixed with a cellulose based organic binder to improve the adhesion of the catalytic material to the surface of the filter. The solution is poured into the inner volume of the filter and the filter is moved and spun to enable an uniform distribution of the catalyst. The filter is dried at room temperature until the ethanol is evaporated and calcined again at 500 °C for 4 h to improve the adhesion of the catalyst to the solid surface.

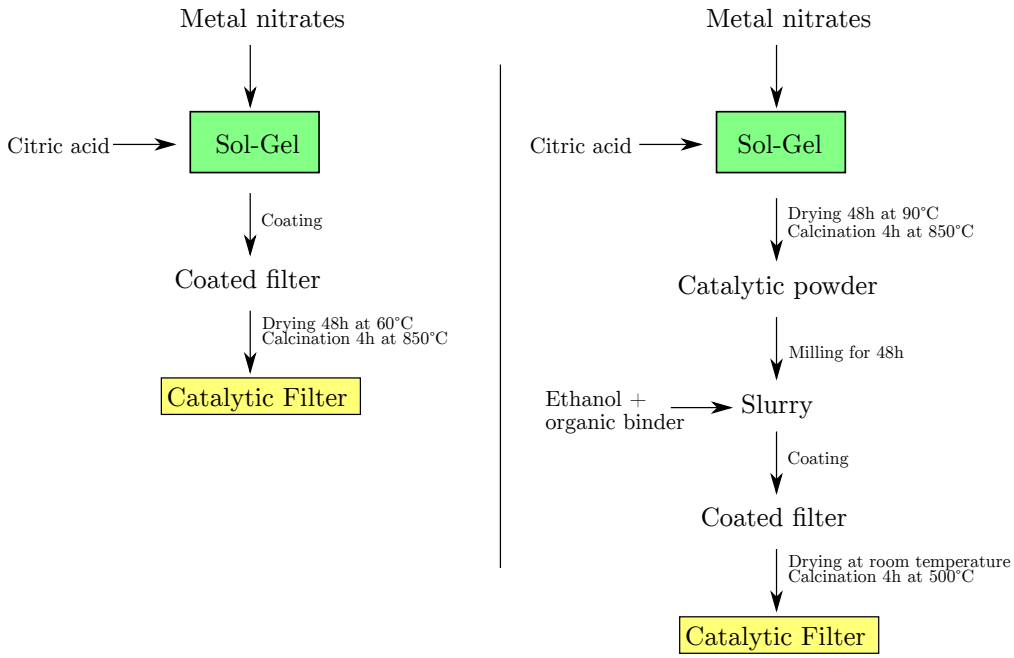


Figure 6.2: Different methods for the coating of a filter body

Figure 6.2 shows schemes of the two methods that are used to coat the filters with the catalytic material. Coating the filter with the sol-gel reduces the number of steps and states a simpler method. However, as the gel infiltrates into the pores of the filter, the evaluation of the coating and characterization of the catalyst is more difficult. Coating the filter with a catalytic slurry results in the formation of a thin catalytic layer on the inside of the filter candle. For both methods a sol-gel is prepared using the corresponding metal salts and citric acid. After drying of the wet-gel, calcination at high temperatures is essential, as the dried gel still contains significant amounts organic residues that have

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

to be oxidized[26]. Besides burning of the residual organics, temperatures up to 850 °C are required to form the highly porous Mg-spinel.

6.1.4 Catalyst characterization

The quality of the catalytic coating and the catalyst itself is determined by characterization instruments. X-ray diffraction (XRD) is used to identify the crystalline phases and obtain information about particle sizes. The instrument consists of a stationary X-ray source and a movable detector that scans the intensity of the diffracted radiation as a function of the angle between incoming and diffracted beams, generating information about the crystalline phases that are present in the solid catalyst[30]. It is used to check the quality of the catalyst's structure, especially of the support material. The generated plots are used to identify present structures and evaluate the formation of support material and the catalytic phase. Furthermore, it provides essential information about the required temperatures for a successful formation of the porous Mg-spinel. The characterization is performed on a Siemens D5000, in the range of 10 to 90 ° and an interval of 0.02 ° for 4 s.

One of the most fundamental parameters in heterogeneous catalysis is the specific surface area of a solid catalyst that is available for the adsorption of gaseous compounds. As reactions occur on the surface of the solids, maximum values for the specific surface area are targeted. Small particle sizes and highly porous structures are favoured for solid catalysts to reach good conversions. BET (Brunauer Emmet Teller) analysis is used to determine the specific surface area of a sample by physical adsorption of gases on the solid phase and the calculation of the amount of adsorbate gas corresponding to a monomolecular layer on the surface[31]. The results of the BET analysis of the nickel catalyst are compared to different samples of nickel catalysts to evaluate the preparation of the catalyst by sol-gel processing. The comparison with samples from conventional preparation methods, such as impregnation and precipitation techniques, enables an exact assessment of the catalyst. Furthermore, characterizations of prepared Mg-spinel as well as aged and reduced catalyst samples are performed to determine the structural changes to the catalyst.

For a visualization of the structures of the catalytic filter elements, a SEM (scanning electron microscope) is used. It is one of the most versatile instruments for analysing and characterization of structures in the fields of material science, chemistry, biology and

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

polymer science. Compared to a light microscope, the resolution of a SEM is improved by two orders of magnitude by replacing the light source with a high-energy electron beam. Information about the morphology, phases, chemical composition and crystallography are obtained, due to the interaction of the electron beam with the sample[32]. Samples of the catalytic filter candles are taken and analysed by SEM to image the catalyst on the filter material and the distribution of the catalytic active phase. Especially for the filter bodies that are coated by the sol-gel technique, SEM is a helpful tool to obtain information about the distribution of the catalyst within the filter material, as the catalytic coating is not directly visible compared to the slurry coating technique. Analysing samples of the filters after the test also provides information about the stability of the catalyst itself and about its tolerance against pollutants in the gaseous phase.

6.2 Experimental set-up

6.2.1 Filtration unit

The tests are performed on a filtration unit that is attached to a product gas stream. A sketch of the set-up is shown in Figure 6.3. The filter candle is placed inside the reactor. The gas stream and the filtration unit is heated up to 850 °C using heating-cables and heating-tapes to set the operating conditions for a hot-gas filtration. To avoid condensation of tar in the product gas stream, temperatures are kept above 300 °C throughout the whole set-up. The product gas leaves the filtration unit at the top and is analysed. Ashes and other particulates that do not pass the filter are collected at the bottom of the unit and disposed afterwards. The filtration unit is either attached to a stream of simulated product gas in the laboratory or to a side stream of a biomass gasifier. For a continuous control and accurate monitoring of the hot-gas filtration, temperature measurements are placed at specific positions of the experimental set-up. The pressure difference between inlet and outlet is monitored to obtain information about the pressure drop due to the possible formation of a filter cake or coking on the filter. Sampling points are installed at the in- and outlet to ensure representative tar sampling. Furthermore, a small side stream before and after the filtration unit is used for the analysis of the gas composition.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

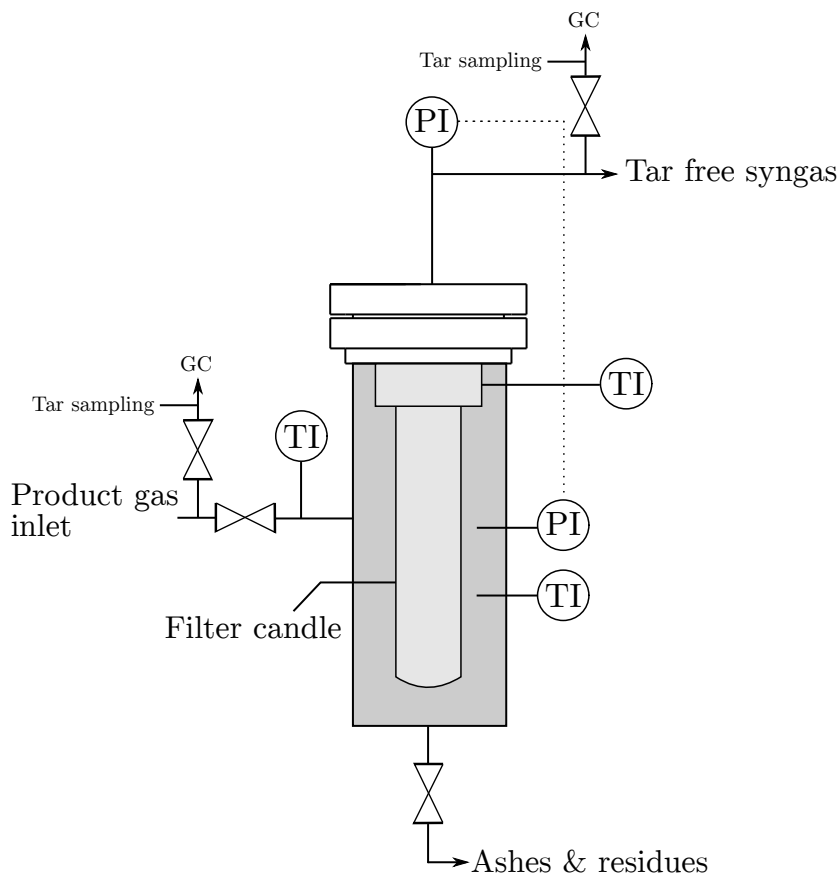


Figure 6.3: Sketch of the experimental set-up

6.2.2 Gas analysis & tar sampling

The composition of the product gas stream is continuously analysed and recorded using a micro gas-chromatograph(GC). Bypassing the experimental unit with a side stream before the inlet enables an exact analysis of the untreated product gas. The device used for the analysis of the gas is a C2V-200 micro GC, gas samples are taken every three minutes during the whole experimental runs. At the start of each run, the gas composition at the inlet is analysed several times (three to five measurements), before switching to the side stream at the outlet. The gas composition at the inlet is analysed again at the end of every run.

Tar samples are taken on a regular base before and after the catalytic filtration, the regular interval chosen is two hours. In order to get optimal and representative samples, the sampling points are positioned close to in- and outlet of the unit. The composition and concentration of the tar compounds are analysed by a solid-phase adsorption method

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

(SPA). The principle of SPA is based on trapping tar vapours and condensation on a solid phase[11]. The samples are then analysed by a gas-chromatograph and the conversion of tar products is determined.

6.2.3 Simulated product gas

First tests of the catalytic hot-gas filtration for tar reforming are performed in the laboratory. Therefore, an appropriate and representative simulated product gas has to be generated. The composition of this gas is of high importance, as it has to be similar and comparable to the product gas of real biomass gasification processes. In addition to the right concentration of gaseous compounds, representative tars have to be injected to the gas stream. The selected product gas composition is listed in Table 6.2. Toluene and naphtalene are chosen as representative tar compounds in the gas stream. Both organic formations are present in product gas under real conditions, with naphtalene being a problematic tar compound, due to its stability and difficulty to crack. The composition of the product gas is comparable to a gasification process using air as gasifying agent. The nitrogen concentration in the gas stream is relatively high, H_2O content low compared to steam gasification. In general the product gas is of low calorific value, because of the high concentration of nitrogen.

Table 6.2: Targeted composition of the simulated product gas

H_2	CO	CO_2	CH_4	N_2	H_2O
7 vol%	12 vol%	11 vol%	3 vol%	44 vol%	23 vol%

Figure 6.4 shows the flow scheme and instruments that are installed to generate the product gas. Appropriate volumetric flows for the gas compounds are set using mass flow controllers. H_2O is added to the gas stream via a bubbling vessel. In a final step, toluene and naphtalene are injected to the gas stream. Using a high pressure pump, tar products are accurately added to the stream in a liquid phase. In the heated mixing chamber, the temperature of the gas stream is increased to 400-500 °C, causing the vaporization of the tar compounds. In order to keep the tar products gaseous, the temperature of the gas stream is kept above 300 °C in the following equipment.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

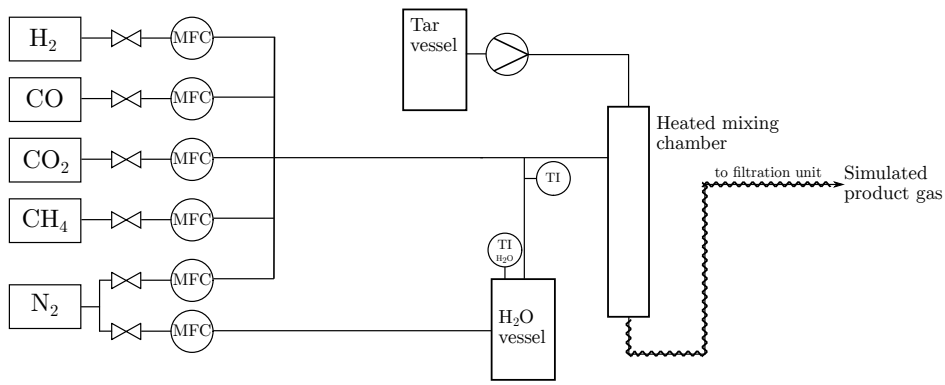


Figure 6.4: Preparation of the simulated product gas

For a precise regulation of the H_2O concentration in the gas stream, the bubbling vessel is placed in a heated oil bath. Nitrogen streaming through the vessel is saturated with H_2O. The required temperature to reach the targeted H_2O concentration in the gas stream is calculated using Equation 6.1 and 6.2, with the saturation pressure p_s and the absolute pressure p in mmHg and the temperature T in °C. The unit for the volumetric flow $\dot{V}$ is Nl/min. The corresponding values for the Antoine coefficients for water are stated in Table 6.3. Furthermore, a temperature indicator close to the mixing point of the saturated nitrogen and the remaining gas compounds ensure an accurate calculation of the H_2O concentration in the product gas.

$$\frac{p_s}{p} = \frac{\dot{V}_{H_2O} + \dot{V}_{N_2}}{\dot{V}_{H_2O}} \tag{6.1}$$

$$\log p_s = A - \frac{B}{C + T} \tag{6.2}$$

Table 6.3: Antoine coefficients for water[33]

A	B	C
8.07131	730.63	233.426

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

The temperature in the oil bath is set at 70.6 °C to reach the targeted concentration of H_2O in the gas stream. However, when analyzing the nitrogen stream at the outlet of the bubbling vessel, a relative humidity of approximately 50 % is measured. The nitrogen stream is not saturated with water, therefore the actual concentration of steam in the product gas is lower than the targeted 23 %. The final composition of the gas is listed in Table 6.4 and is used for the calculations in the upcoming sections.

Table 6.4: Final composition of the simulated product gas

H_2	CO	CO_2	CH_4	N_2	H_2O
8.2 vol%	14.1 vol%	12.9 vol%	3.5 vol%	51.3 vol%	**10.0 vol%**

6.3 Experimental design

The main goal of the experimental study is to determine the influence of different parameters on the reforming of light and heavy hydrocarbons. Extensive focus is put on the reforming of methane and tar products in order to determine the catalytic quality of the prepared filter bodies. The design of the experimental runs and the settings are listed in Table 6.5. The two types, filters with and without additional hardener, are marked with "H" and "no H". Tests with untreated filter candles are required to determine thermal effects on the reforming of the tar products. Catalytic filter candles were prepared with the techniques described in Section 6.1.3 for both types of filter.

The tests were originally set to be run at 800-900 °C to simulate a hot-gas filtration with typical temperatures downstream of a biomass gasifier. Temperatures downstream of a gasification unit are usually in the range of 800-900 °C, therefore, operating a filtration unit in this temperature range is reasonable in order to reach high conversions of hydrocarbons. Due to technical difficulties with the heating system, the temperature at the inlet of the unit was set at 800 °C for the first four tests. After a malfunction of the main heater during the fourth test, the remaining tests were performed with different heaters, resulting in temperatures at the inlet below 800 °C. Conversion and efficiencies that are determined in the following sections will be related to the process temperature of the particular test run. In addition, all data collected from the experimental tests is included in the appendix to ensure a full documentation of the experimental results.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Table 6.5: Experimental design

Experiment	Filter	Catalytic coating	Duration	Nominal tar
#1	CS1255F - H[1]	Blank filter	6 h	5 g/Nm^3
#2	CS1255F no H	Sol-gel	12 h	5 g/Nm^3
#3	CS1255F no H	Slurry	12 h	5 g/Nm^3
#4	CS1255F - H	Slurry	12 h	5 g/Nm^3
#5	CS1255F no H	Blank filter	4 h	5 g/Nm^3
#6	CS1255F - H	Sol-gel	12 h	5 g/Nm^3
#7	CS1255F - H	Blank filter	6 h	5 g/Nm^3
#8	CS1255F no H	Slurry	12 h	5 g/Nm^3

[1] H: inorganic additives (hardener)

The flow rate of the product gas was set at 10 Nl/min, resulting in a filtration velocity of approximately 2 cm/s. The duration of the tests varied for the blank and catalytic filter. The duration of the catalytic tests was set with 12 h to obtain information about the long term stability of the catalyst and monitor the performance over time. Before the runs with catalytic filter bodies, pretreatment of the catalytic filter was required in order to activate the catalytic phase and thermally treat the catalyst at high temperatures. After placing the filter candle, the filtration unit was heated up, reduction of NiO starts at 350 °C. The set-up was then heated up to 550-600 °C to achieve a full reduction of the nickel oxide and expose the catalytic sites. In a second step, the reduced catalyst was pretreated with a mixture of nitrogen, hydrogen and steam. The ratio of H_2/H_2O was set to 10. Usually ageing is performed at higher temperatures than the actual test to ensure an adequate thermal stress on the catalyst. As it was not possible to reach temperatures beyond 820 °C with the installed set-up, ageing was performed at the same temperatures as the actual tests for 5 h.

The concentration of the tar products, consisting of toluene and naphtalene, was set at 5 g/Nm^3. Naphtalene was dissolved in toluene and the solution was fed to the gas stream. This turned out to be challenging, as naphtalene becomes solid at room temperature when it exceeds saturation. Therefore, toluene had to be added to the tar-solution to enable a continuous execution of one run, resulting in varying compositions of the tar-solution during the tests. But not just adding tar to the gas stream, also taking representative samples from the gas stream turned out to be a challenge. As the filtration was run at atmospheric pressure, sampling the tar products at in- and outlet was difficult.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

The samples are not analysed right after taking them. This resulted in several unusable samples, especially for the two runs performed with sol-gel filter bodies, tar sampling did not work properly. However, it was tried to interpret the remaining tests as exact as possible and draw conclusions from these test on the efficiency of the different filter bodies and the whole catalytic filtration.

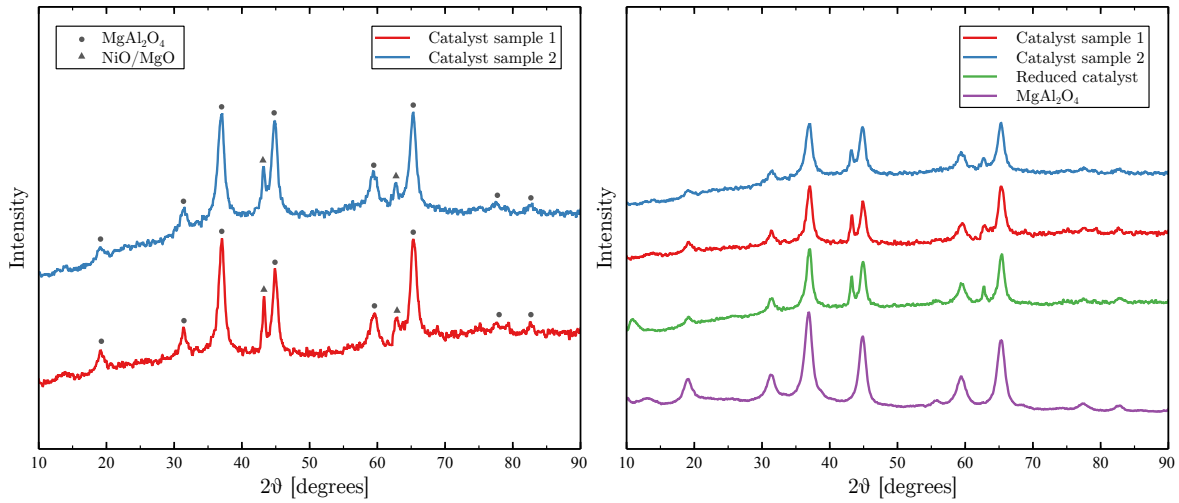
Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

7 Results & discussion

7.1 Characterization of the catalytic filter

7.1.1 XRD

To screen the synthesized structures, XRD characterization is performed for different samples of the Ni/$MgAl_2O_4$ catalyst. Figure 7.1 shows the generated graphs from the XRD characterization. In Figure 7.1a the XRD data of two samples of the prepared catalyst is plotted. Figure 7.1b shows a sample of reduced catalyst and synthesized Mg-spinel in addition to the two catalyst samples. For all samples, distinctive peaks for $MgAl_2O_4$ are identified, that match accurately with the peaks from the synthesized Mg-spinel. Therefore, calcination for 4 hours at a temperature of 850 °C is sufficient to generate the highly porous support structure for the catalytic active nickel compound. Peaks for NiO are not allocated exactly, as MgO forms its peaks at the same angles. Comparing the samples of fresh catalyst with the reduced catalyst shows minor differences in the plots, with peaks for nickel oxide still visible. Therefore, the presence of MgO is likely.



(a) Ni/$MgAl_2O_4$ catalyst synthesized via a sol-gel route (b) Fresh & reduced catalyst plus synthesized Mg spinel

Figure 7.1: XRD of Ni/$MgAl_2O_4$ catalyst

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

In addition to the XRD measurement, TPO/R (temperature programmed oxidation/reduction) of the catalyst was performed to gain further information about the composition of the catalytic structure. The reduction was performed in a temperature range from 300-800 °C. The measurement shows that the catalyst contains a reducible structure. Therefore the presence of Ni is proven, since MgO is not reduced in this temperature range. Most likely the catalyst consists of a mix of NiO and MgO that is distributed over the $MgAl_2O_4$ support. It is difficult to determine the cause of the formation of magnesium oxide. As the structure has catalytic properties, its formation is not a serious problem. In return to the formation of MgO, small amounts of $NiAl_2O_4$ could be formed during the calcination.

7.1.2 BET

Characterization of the specific surface area of the catalyst is performed with a sample of fresh catalyst and a reduced and aged sample. Furthermore, the total volume and the average pore size of the powder are determined. Table 7.1 shows the results of the characterization. The fresh catalyst that was prepared by the sol-gel method has a specific surface area of 67.20 m^2/g. This value is compared with other samples of $Ni/MgAl_2O_4$ catalysts. The specific surface area for $Ni/MgAl_2O_4$ ranges from 30 m^2/g up to 101 m^2/g affected strongly by the preparation technique[25], [34]. The prepared catalyst fits well in this range, having a big specific surface area and a relatively small average pore size. Compared to the catalyst synthesized on a commercial Mg-spinel by wet-impregnation, the specific surface area has been more than doubled by the preparation via the sol-gel route. Furthermore, the values show that the partial formation of $NiAl_2O_4$ has no negative effect on the support material. After reducing and ageing the catalyst, the specific surface area decreases by approximately 30 %. Sintering effects lead to the closing of small pores and hence to an increase of the average pore size of the catalyst. A reduction of approximately 30 % of the specific surface area is within the range for typical ageing effects.

Table 7.1: BET analysis of fresh and aged $Ni/MgAl_2O_4$ catalyst samples

Parameter	$Catalyst_{fresh}$	$Catalyst_{used}$
BET surface area	$67.20 \pm 0.53\,m^2/g$	$45.97 \pm 0.20\,m^2/g$
Pore volume	$0.086\,cm^3/g$	$0.092\,cm^3/g$
Average pore size	5.10 nm	7.99 nm

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

7.1.3 SEM

SEM images are made from both slurry and sol-gel coated filter. While for the slurry coated filter bodies the thickness and composition of the catalytic layer are of interest, the imaging of the sol-gel filter is used to obtain information about the distribution of the catalyst over the cross section. Figure 7.2a shows very well the coating of the filter body with the catalyst. The layer is approximately 250 µm thick. The composition of the layer in the marked square is shown in Table 7.2. The image shows an uniform deposition of the catalytic material on the inner surface of the filter candle. The nickel concentration matches well with the targeted loading of 10 w.%. Furthermore, the fibrous structure of the filter material is clearly visible. In Figure 7.2b a sol-gel coated filter is shown. Spherical formations that do not contain any catalytic structures are identified. As the catalyst is less concentrated in the sol-gel filter compared to the layer in Figure 7.2a, the atomic composition in square 2 and 3 differ strongly to the first sample.

(a) Slurry coated filter candle (b) Sol-gel coated filter candle

Figure 7.2: SEM of catalytic filters

Table 7.2: Atomic composition of the catalytic filters (Fig. 7.2)

Sample [w.%]	O	Na	**Mg**	**Al**	Si	K	Ca	Fe	**Ni**
1L	36.12		**15.93**	**36.03**	0.23		0.15		**11.54**
2-1	49.06	0.40	**1.53**	**3.32**	29.02	0.18	15.59	0.07	**0.84**
2-2	36.45	0.12	**3.92**	**10.06**	16.61	0.06	29.23	0.44	**3.11**
2-3	39.67	0.17	**2.98**	**6.56**	17.54	0.07	28.57	0.54	**3.90**

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

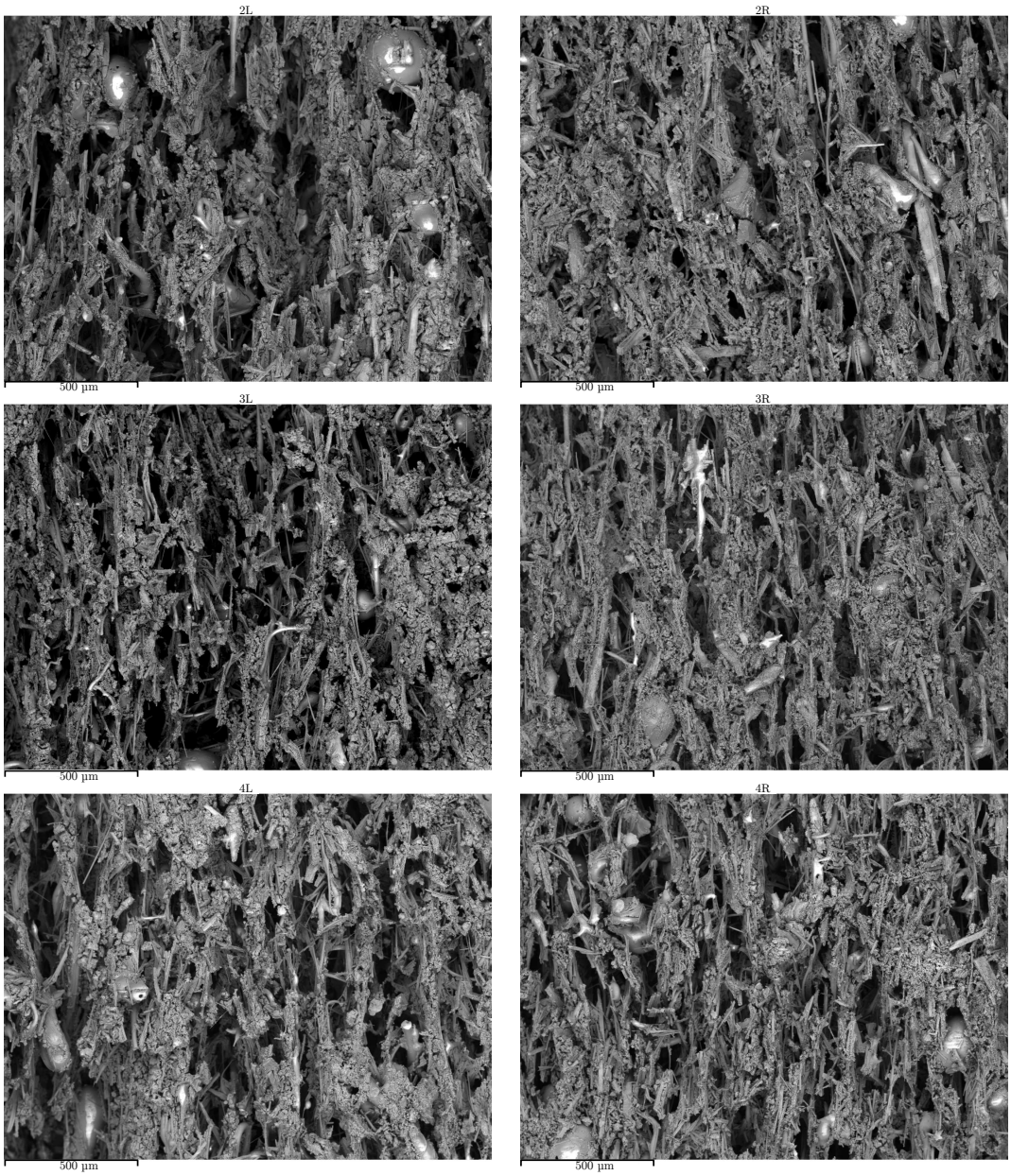


Figure 7.3: SEM of sol-gel coated filter candle

Figure 7.3 shows images of a sol-gel coated filter. Three samples are taken at different heights of the filter, samples marked with L are taken from the inside, samples marked with R from the outside of the filter bodies. As in Figure 7.2, spherical formations are identified. It has to be analysed how these formations are formed and whether they affect the mechanical properties of the filter body. The atomic composition of the shown images is stated in Table 7.3. The concentration of the catalytic compounds, alumina, magnesium and nickel, is significantly higher at the samples marked with L. The sol-gel

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Table 7.3: Atomic composition of the catalytic filter (Fig. 7.3)

Sample [w.%]	O	Na	**Mg**	**Al**	Si	Ca	Fe	**Ni**	Total
2L	39.04	0.22	**4.83**	**10.25**	20.09	17.89	0.37	**7.30**	100.00
2R	41.6	0.30	**2.20**	**4.80**	24.60	23.40	0.40	**2.70**	100.00
3L	38.8	0.20	**5.90**	**12.00**	18.00	16.50	0.30	**8.30**	100.00
3R	41.17	0.33	**2.15**	**4.74**	23.59	24.65	0.51	**2.85**	100.00
4L	40.84	0.24	**3.86**	**8.59**	19.70	21.77	0.24	**4.77**	100.00
4R	42.77	0.38	**1.69**	**3.68**	27.02	21.61	0.42	**2.44**	100.00

is poured into the inner volume of the filter candle, leading to a higher catalytic loading on the inside of the filter structure. The concentration then decreases over the cross section of the filter. Small amounts of catalyst are present on the outside of the filter candle. The distribution of the catalyst over the cross-section is not uniform, however, the catalyst is present within the whole filter material.

7.1.4 Coating technique

The coating of the filter structure differs fundamentally for the two coating methods. While the sol-gel method leads to the distribution of the catalyst over the whole cross section of the filter body, only a thin catalytic layer is generated by coating the filter with a catalytic slurry. Flow rates and space velocity of the filtration may significantly influence the catalytic performance of the different filters, due to the different contact time between the catalytic sites and the gaseous compounds. Taking into account the dimensions of the used filter candles and an average thickness of the slurry coating of 250 µm shows, that for the sol-gel method the catalyst is distributed in a volume that is 100 times bigger compared to the slurry coating technique[35]. However, improvements for the sol-gel method are needed to guarantee an uniform concentration of the catalytic compounds over the whole cross-section of the filter body.

An aspect that is of great importance for filtration operations under real conditions is the pressure drop. All the experimental tests are performed with a simulated product gas, free of any solid particulates. The gas stream from a biomass gasification is full of particulates and solid matter, resulting in the formation of a filter cake on the surface of the filter body and an increase in the pressure drop between in- and outlet. Therefore, a low pressure differential for fresh filter bodies is important to avoid

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

frequent back-blowing at short time intervals. While the catalytically active material is distributed through the whole filter material when coating it directly with a sol-gel, impregnation with a catalytic slurry leads to the placement of an additional solid layer at the inner surface of the filter body. An influence of the coating on the pressure drop has been noticed when monitoring the differential pressure during the tests. As the differential pressure for the slurry coated filters varies a lot, no final conclusion on the effect of the coating method can be made. However, it states an aspect that has to be considered when using this method to deposit a catalytic layer onto a solid filter body.

7.2 Experimental runs

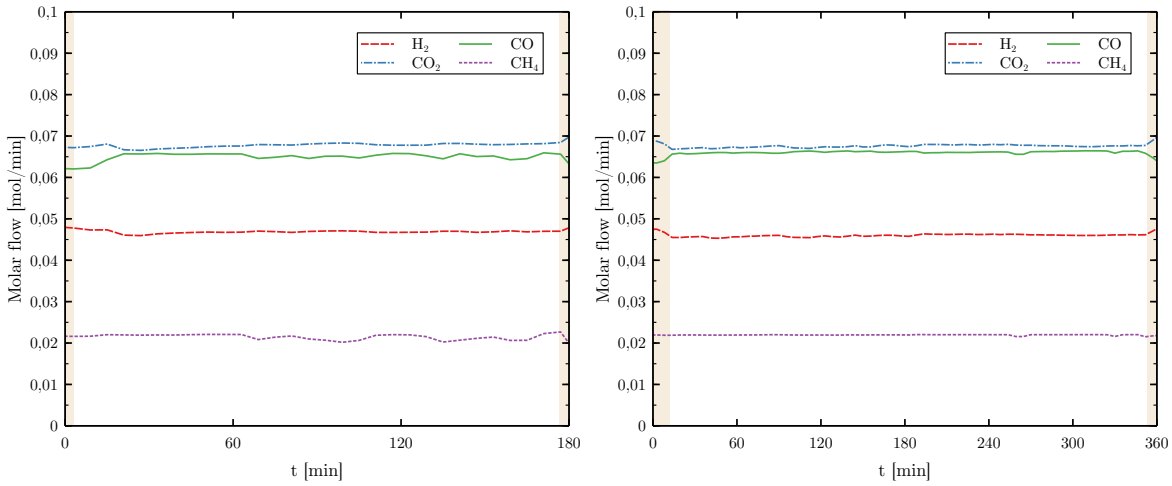
7.2.1 Thermal effects on the reforming of hydrocarbons

At first, results for the filters without any catalytic coating are evaluated. The molar flows of the gaseous compounds in the product gas at in- and outlet give essential information about the reactions that occur inside the filtration unit. In Figure 7.4 the molar flows of two blank tests are plotted. Figure 7.4a shows the collected data from a blank filter candle without additives, Figure 7.4b the data of a filter body containing inorganic hardener for a higher mechanical stability. For each test, the molar composition of the product gas at the inlet was recorded at the start and the end of the run, marked by the shaded sections. Both figures show relatively constant molar flows for all gaseous compounds. CH_4 is unaffected by the blank filter bodies, no reforming of methane is monitored. With temperatures for both tests between 750 °C and 800 °C, no thermal conversion of methane is observed. Besides, the molar flows for the remaining compounds, H_2, CO_2 and CO, differ slightly between in- and outlet.

Slight increase in CO and decrease in CO_2 and H_2 are traced back to the reversed water gas shift reaction (Reaction 7.1). At temperatures above 700 °C, the reversed reaction of the water-gas shift mechanism is favoured, leading to a slight increase of CO at the outlet.

$$CO_2 + H_2 \longleftrightarrow H_2O + CO \tag{7.1}$$

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



(a) #5 Blank filter - no H (b) #7 Blank filter - H

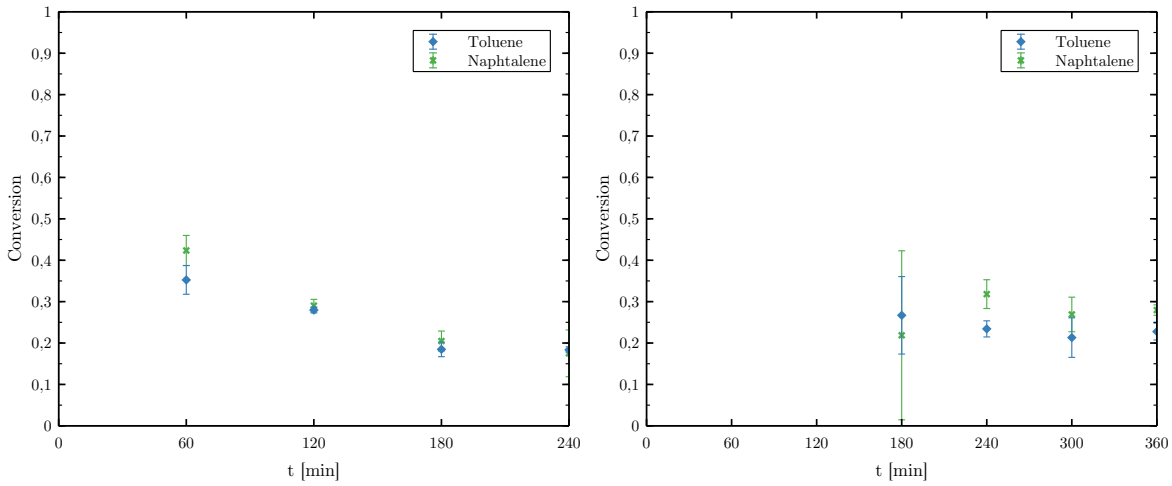
Figure 7.4: Molar flow for blank tests

No reforming of methane is observed during the experimental tests with the blank filters. Operating temperatures in the range of 770-820 °C are not high enough for a thermal decomposition of methane due to the high stability of the molecule. In order to reach higher conversion, catalytic structures are needed.

Furthermore, the conversion of heavy hydrocarbons, namely toluene and naphtalene, is investigated for the two types of filters. Unlike methane, tar products are partially broken down at temperatures around 700-800 °C. Figure 7.5 shows the conversion of toluene and naphtalene for the blank tests #5 and #7. Both types of filter show similar conversion. 20-25 % of the toluene is thermally broken down. Conversion of naphtalene is slightly higher at 20-30 %. Compared to methane, reforming of tar products is more complicated, as high conversion of one tar compound not necessarily means high conversion of tar itself. Heavy tar products form lighter hydrocarbons when broken down. Naphtalene may be broken down efficiently, however, the reforming of the tar compound also causes the formation of lighter products, such as xylene or toluene. Therefore, it is important to identify the different tar products that are present in the gas stream and evaluate their effect on following equipment and operations. Taking into account the total amount of tar at the outlet, tar conversion for the blank filters is around 15 %.

No significant influence of the inorganic additives to the filter on the conversion of hydrocarbons is observed. As the filter material does not appear to have any catalytic properties, additives for a better mechanical stability do not influence reforming reactions.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



(a) #5 Blank - no H (b) #7 Blank - H

Figure 7.5: Tar conversion of the blank filters

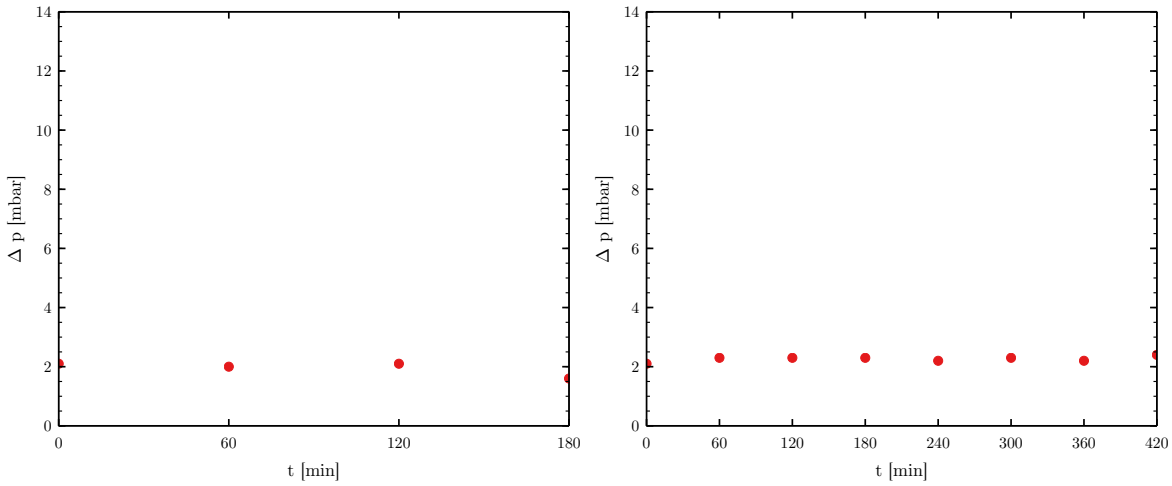
When running a filtration under real-conditions, the filter candles have to be cleaned on a regular base to remove the formed filter cake. Therefore, a certain mechanical stability of the low density filter elements is required to avoid damages on the filters during back-blowing phases. In this investigation the additives are more critical when talking about the pressure drop rather than chemical reactions and conversion of hydrocarbons.

The pressure difference for the experimental test with the blank filters is recorded manually and shown in Figure 7.6. As no solid particulates are present in the product gas, the pressure drop is constant over the whole test. Average pressure drop of 2 mbar is similar to the data provided by the manufacturer of the filter bodies shown in Table 6.1. No significant difference in the pressure drop for filters with and without hardener is detected.

7.2.2 Catalytic effects on the reforming of hydrocarbons

After investigating the thermal effects on the reforming of hydrocarbons, effects and differences of the reforming process are analysed for the experimental tests with catalytic filter bodies. The third, fourth and eighth tests are performed with filter bodies coated with a catalytic slurry. In Figure 7.7 the molar flows of the catalytic filtration with slurry coated filters are shown. As for the blank figures in Section 7.2.1, the molar composition of the product gas at the reactor's inlet is identified at the start and the end of the test runs. The presence of a catalytically active material in the filtration unit

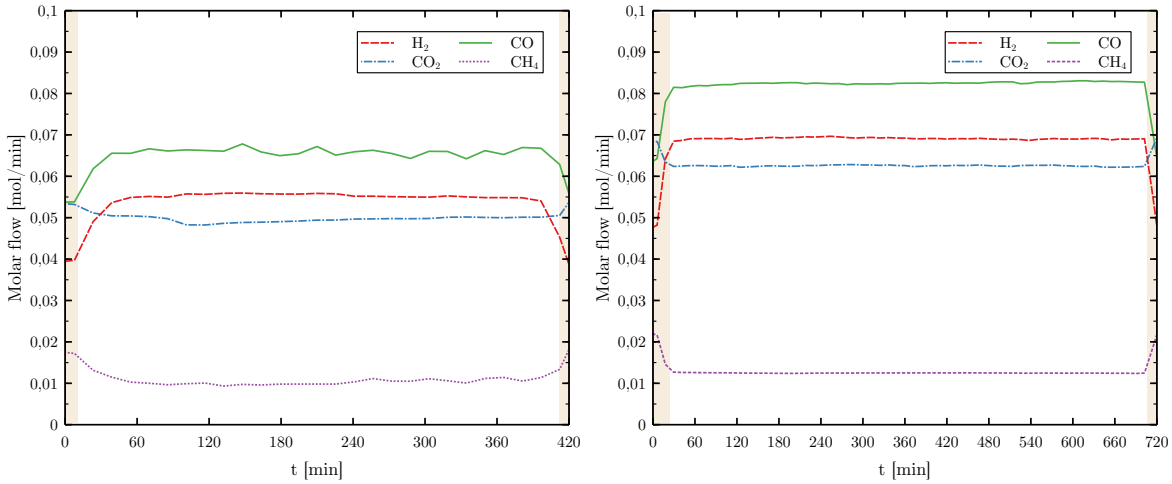
Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



(a) #5 Blank filter - no H (b) #7 Blank filter - H

Figure 7.6: Differential pressure of blank filters

leads to an increase in H_2 and CO at the outlet, while CH_4 and CO_2 are consumed and the concentration at the outlet decreases. In addition to the reversed water gas shift reaction that causes the reduction in CO_2 and H_2 and equimolar increase in CO, CH_4 is reformed according to the steam reforming reaction (Reaction 2.8). The presence of steam in the gas phase leads to the reforming of CH_4 and the production of H_2 and CO.



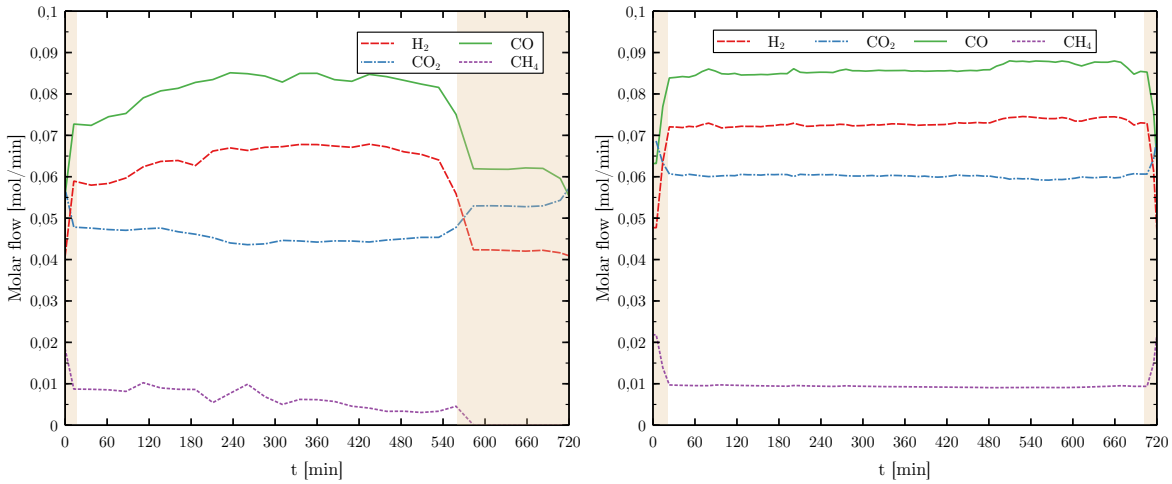
(a) #4 Slurry - H (b) #8 Slurry - no H

Figure 7.7: Molar flow for slurry coated filters

Figure 7.8 shows the molar flow rates for the tests performed with filter units coated by the sol-gel method. The main trend of the four compounds CH_4, CO, CO_2 and H_2

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

is identical to the tests with slurry coated filter bodies. That indicates a successful deposition of catalytic material to the filter structure. Figure 7.8b shows very stable and constant molar flows while the graphs for CO and H_2 in Figure 7.8a drop strongly after 540 min. While running the second test, the CH_4 gas cylinder is emptied. When the supply is stopped, molar flows of H_2 and CO decrease instantly, as the compounds are mainly produced from steam reforming of CH_4. CO_2 increases when no CH_4 is present in the gas phases, most likely because of a change of the equilibrium of the water-gas shift reaction. As no H_2 is produced from CH_4, the equilibrium of the water gas shift reaction shifts towards CO_2 and H_2, resulting in an increase of CO_2.



(a) #2 Sol-gel - no H (b) #6 Sol-gel - H

Figure 7.8: Molar flows for sol-gel coated filters

The experimental runs with catalytic filters show an essential production of CO and H_2, mainly due to steam reforming reactions. Especially for the production of hydrogen, steam reforming states an important reaction, as one mol of methane is converted into three mols of hydrogen. The sharp increase in the molar flow of hydrogen is identified for both coating methods, as well as for both filter types. For the reforming of CH_4 to H_2 and carbon monoxide, the presence of sufficient amounts of steam in the gas phase is essential. Therefore it is of high importance to know the exact amount of H_2O that is present at the inlet.

At temperatures above 700 °C little amounts of CO_2 and H_2 are converted to CO and H_2O following the reversed water gas shift reaction. A decrease of CO_2 is observed during all catalytic tests. The water gas shift reaction is also used to calculate a

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

wet-gas composition after the filtration unit, showing an increase in the concentration of steam up to 11-13 % in the gas phase, most likely due to the reversed water gas shift reaction. The calculated wet-gas composition for all eight tests is attached in the appendix.

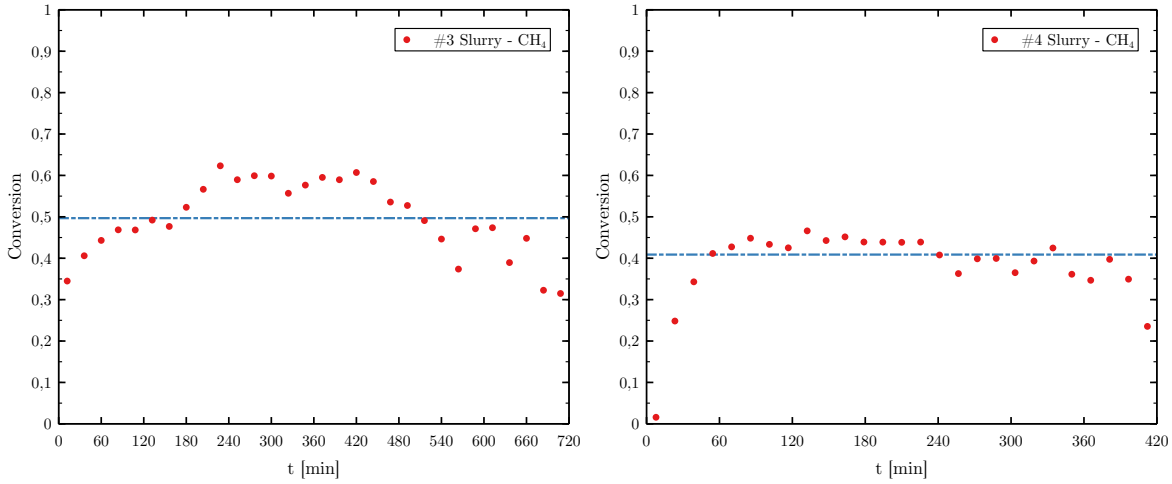
Another mechanism that has to be considered is the dry reforming of methane (Reaction 7.2). The reaction becomes more important at high temperatures close to the Boudouard equilibrium (Reaction 2.3) when CO_2 is partly converted to CO. At temperatures around 770-820 °C dry reforming of methane occurs to a minor extent. The combined reaction of CH_4 and CO_2, two of the most potent green-house gases, makes dry methane reforming an interesting mechanism for the production of syngas. High temperatures and the presence of a catalyst are required, as the reaction is highly endothermic. Rapid deactivation of the catalyst due to carbon deposition, especially at lower temperatures, limit the process' applications so far[36].

$$CH_4 + CO_2 \longleftrightarrow 2H_2 + 2CO \qquad \Delta H = +260.5\,\mathrm{kJ/mol} \tag{7.2}$$

Figure 7.9 shows the conversion of CH_4 with slurry coated catalytic filter bodies. Average conversion of 40 to 50 % of methane are reached by coating the filter candle with a catalytic slurry. The temperature profiles for the two tests are very similar, enabling a direct comparison of the two runs. In Figure 7.9a an average conversion of methane up to 50 % is identified. Although the fourth test was aborted after seven hours, an average conversion of methane around 40 % was recorded before the malfunction of the heating element. Due to the irregular data recording at several points, a direct conclusion on the reforming of methane with and without hardener is difficult to draw. As the filter materials without catalyst do not show any catalytic effect, similar results for both filter types are reasonable.

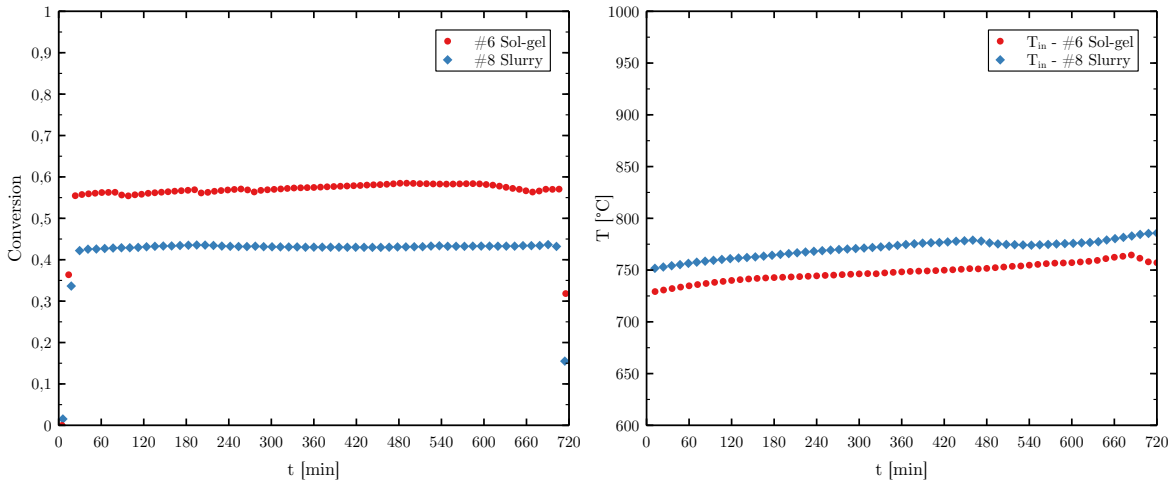
In Figure 7.10a the methane conversion of the sixth and eighth tests are plotted. The sixth test is performed with a filter body that is coated directly with a sol-gel, while the eighth test is run with a slurry coated filter. Although the temperatures at the in- and outlet are slightly higher at the test with the slurry coated filter candle, conversion of methane is clearly higher during the sixth test. Distributing catalytic material throughout the whole filter body leads to a methane conversion up to 60 % while a conversion of roughly 40 % is achieved with the slurry coating. The slurry coating method leads to the formation of a thin catalytic layer, resulting in a short contact time of the

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



(a) #3 Slurry - no H (b) #4 Slurry - H

Figure 7.9: Methane conversion of Test #3 and #4



(a) Methane conversion - slurry vs. sol-gel (b) Temperature profiles of Test #6 and #8

Figure 7.10: Comparison of sol-gel and slurry coated filters for methane reforming

gaseous compounds with the catalytic active centres. The sol-gel technique distributes the catalyst throughout the whole solid filter body, leading to a longer contact time and a higher conversion. No influence of the filter material itself on methane reforming is expected, direct coating of the filter candle with a catalytic sol-gel shows improved properties compared to the deposition with a slurry. Unfortunately, for the test with sol-gel coated filter bodies, no results at temperatures above 800 °C are recorded. 55-60 % methane conversion at a relatively low temperature at around 750 °C is a promising result and shows the potential of the direct treatment of a filter body with a sol-gel.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

In Figure 7.11 the conversion of methane and the two tar compounds, toluene and naphtalene, for the slurry coated filter candles are shown. The effect of the catalytic filter is visible, with conversion of toluene and naphtalene being higher than without catalyst. On average the conversion of toluene is at 75-80 % for run #3 and slightly lower at 65-70 % for run #4. Naphtalene is converted up to 85% during the third test and around 60-65% for the fourth test. The lower conversion of toluene during the eighth test compared to run #3 and #4 is a direct consequence of the increased toluene concentration in the tar-solution. Due to the formation of solid naphtalene, additional toluene is added to the gas stream, leading to higher concentrations of toluene in the product gas and furthermore to a decrease of the toluene conversion. For the sake of completeness, tar conversion of all experiments are attached in the appendix. The challenge of taking representative tar samples is clearly visible, with strongly fluctuating values and defective data.

Table 7.4 and 7.5 show the effective catalytic conversion of tar for the slurry coated filters. Fluctuating conversion of toluene is traced back to changes in the toluene concentration in the tar-solution, but also to the significant influence of the temperature on reforming reactions. The tendency of a higher conversion of naphtalene using filter candles without additional hardener is visible in the graphs, however, due to the limiting number of representative data points, no final conclusion can be drawn.

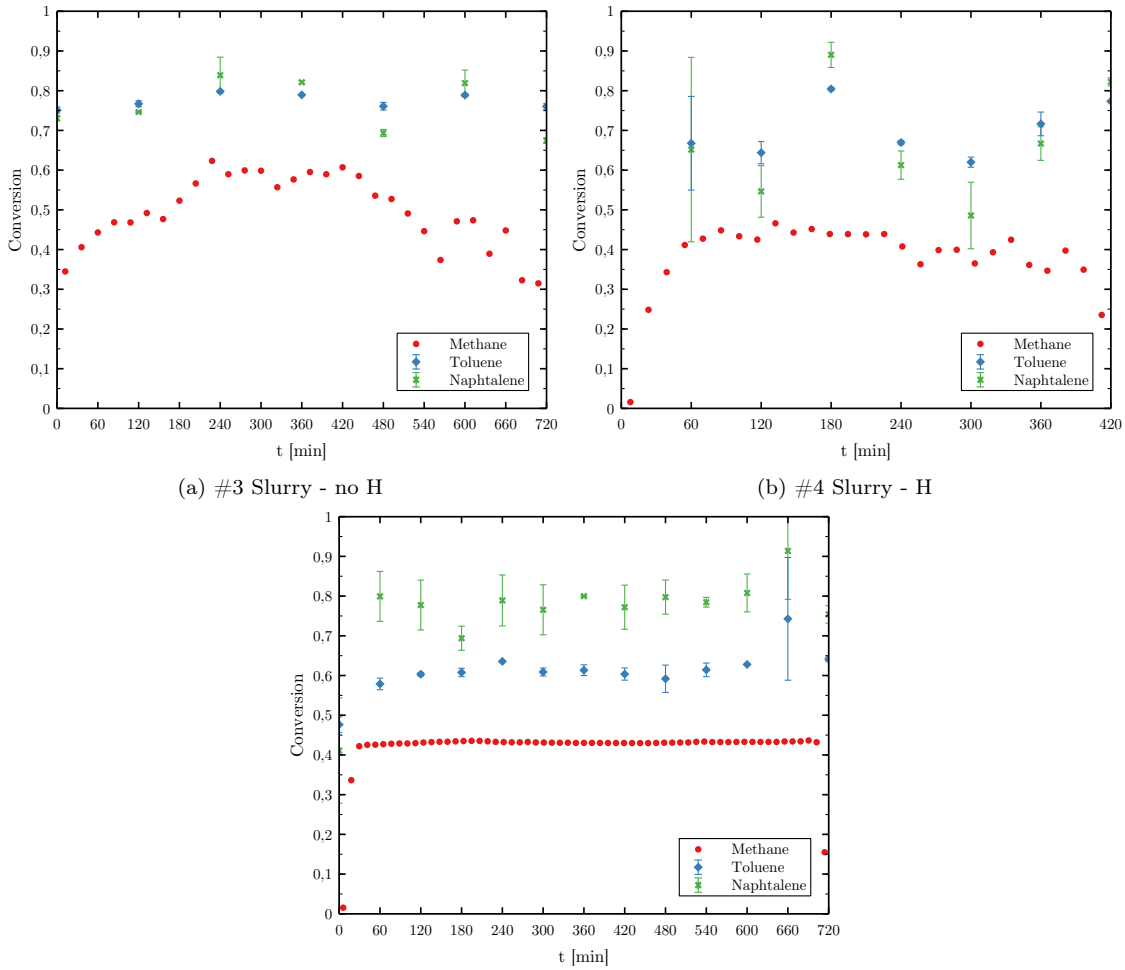
Table 7.4: Thermal and catalytic conversion of toluene

Test Nr.	Thermal conversion [%]	Catalytic conversion [%]	Total conversion [%]
3 slurry - no H	20-25	68-74	75-80
4 slurry - H	20-25	55-61	65-70
8 slurry - no H	20-25	48	60

Table 7.5: Thermal and catalytic conversion of naphtalene

Test Nr.	Thermal conversion [%]	Catalytic conversion [%]	Total conversion [%]
3 slurry - no H	25-30	66-72	75-80
4 slurry - H	25-30	45-52	60-65
8 slurry - no H	25-30	66-72	75-80

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



(a) #3 Slurry - no H

(b) #4 Slurry - H

(c) #8 Slurry - no H

Figure 7.11: Tar reforming of slurry coated filter

In addition to the conversion of toluene and naphtalene, the concentration of total tar products at the in- and outlet is calculated. Table 7.6 shows the tar concentration in the product gas. Again, the rising concentration at the inlet of the set-up is traced back to the adding of toluene to the tar-solution. As tar concentrations for end-use applications are usually defined, it is essential to know the total concentration of tar compounds in the treated gas stream. The total conversion of tar differ from the conversion of toluene and naphtalene due to the formation of lighter tar compounds that are not analysed separately. Little amounts of xylene are formed due to the reforming of naphtalene, but also additional toluene is produced from naphtalene. Total tar conversion of approximately 60 % is reached with the performed experimental tests, showing a significant increase in efficiency compared to the thermal conversion of tar products without a catalytic structure.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

Table 7.6: Total tar concentrations for selected runs

Test Nr.	Tar_{inlet} [g/m^3]	Tar_{outlet} [g/m^3]	Total conversion
3 slurry - no H	5.2 ± 0.69	1.9 ± 0.36	63 %
4 slurry - H	5.2 ± 0.70	1.7 ± 0.58	67 %
5 blank - no H	6.0 ± 0.59	5.2 ± 0.58	13 %
7 blank - H	6.6 ± 0.06	5.3 ± 0.23	20 %
8 slurry - no H	6.8 ± 0.15	2.9 ± 0.54	57 %

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

8 Conclusion

The nickel based catalyst with a $MgAl_2O_4$ support material shows good performance for the reforming of hydrocarbons. Coking is counteracted by the selection of a Mg-spinel, making the catalyst more tolerant against varying product gas compositions. The deposition of the catalytic material onto a low density filter enables the combination of a filtration and a catalytic reforming process at high temperatures, positively affecting the temperature management. Distributing the catalyst over the whole cross-section of the filter body leads to longer contact times between the gaseous compounds and the catalytic sites compared to a single catalytic layer. A positive trend for the sol-gel method is identified, however, due to the limited number of representative tar samples and varying conditions during the experimental runs no final assessment on the coating techniques can be made.

Additional inorganic hardener that was added to the filter material has no significant influence on the performance of the filters concerning the reforming of hydrocarbons. The fibrous filter material shows no catalytic properties. The differential pressure was in the same range for both filter types at approximately 2 mbar for fresh filter candles. Solid matter and particulates in a real product gas lead to the formation of a filter cake on the filter. Mechanical impulses are required to remove the filter cake, therefore the filter type with improved mechanical properties is favoured.

The strong influence of temperature on the reforming of hydrocarbons is reflected in the conversion efficiencies. Conversion of approximately 50 % methane to hydrogen and carbon monoxide is reached with the slurry-coated filters. The eighth test is performed at rather low temperatures compared to the other tests, making the strong influence of the temperature on reforming of hydrocarbons clear. Sol-gel coated filter bodies reach similar conversion of methane, however, the temperature was significantly lower during the sixth test. The catalyst's effects on the reforming of heavy hydrocarbons show a conversion of naphtalene up to 80 %. A tendency for filter bodies without the hardener to break down tar products more efficiently is observed. In addition to the reforming of naphtalene, the conversion of total tar is evaluated. The conversion of total tar is lower compared to the conversion of naphtalene and toluene, as heavy tars are broken down to lighter products such as xylene, toluene and methane. As end-use applications

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

set the tolerable concentration of tar products in the gas, informations about the total concentration of tar and the individual compounds are highly important.

Throughout this project, the complexity of reforming processes, mainly due to the variety of chemical reactions that happen simultaneously inside the reactor, is shown. The investigation to find the optimal process parameters turns out to be a difficult task, as different reactions favour different conditions and are also influenced by the presence of each others reactants. As the composition of product gases varies, it is essential to understand the different reactions and the corresponding operating parameters that are required for a sufficient gas cleaning. Reforming of hydrocarbons is largely influenced by the temperature conditions inside the reactor, therefore, the use of a suitable catalyst is inevitable. Robust catalysts are required to optimize the process and enable a competitive and commercial operation.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

9 Outlook

Although the principles for reforming of hydrocarbons are the same for oil, coal and biomass processes, properties of biomass and differences in the scale of the industries demand constant development of technologies based on biomass feedstock. The merging of filtration and catalytic reforming shows promising aspects to improve the overall efficiency of the process, as thermal energy is used more efficiently. The development of a robust and insensitive catalyst for tar reforming in combination with a low density filter shows good performance. Nickel based catalysts are widely used for reforming of hydrocarbons and show, in combination with a suitable support material, good properties and improved tolerance against deactivation. Depositing catalytic material over the whole cross section of an industrial filter candle lead to a maximization of the contact time and area between gaseous compounds and catalytic active sites. Only few filters were prepared with the sol-gel method, for further tests the preparation technique has to be adjusted to guarantee an uniform and reproducible preparation of catalytic filters. A positive tendency of the sol-gel method is identified. More experiments, especially at temperatures in the range of 850-900 °C, are necessary to check this trend. In addition, more research and experimental tests under real conditions, using product gas that contains further impurities and particulates, are required to gain information about the feasibility of the concept and evaluate the effects on the overall process.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

List of Figures

2.1 Reaction scheme of the gasification process 6
2.2 Types of fixed bed gasifier with four reaction zones 7
2.3 Fluidized bed gasifier concepts 9

3.1 Temperature dependent formation scheme and characteristic tar products 14
3.2 Principle for tar removal 15

4.1 Concept scheme of catalytic hot-gas filtration 21
4.2 Temperature window for optimal consecutive operations 22
4.3 Catalytic hot-gas filtration: 2 methods 23

6.1 Sketch of the filter structure with a catalytic coating on the inner surface 28
6.2 Different methods for the coating of a filter body 30
6.3 Sketch of the experimental set-up 33
6.4 Preparation of the simulated product gas 35

7.1 XRD of $Ni/MgAl_2O_4$ catalyst 39
7.2 SEM of catalytic filters 41
7.3 SEM of sol-gel coated filter candle 42
7.4 Molar flow for blank tests 45
7.5 Tar conversion of the blank filters 46
7.6 Differential pressure of blank filters 47
7.7 Molar flow for slurry coated filters 47
7.8 Molar flows for sol-gel coated filters 48
7.9 Methane conversion of Test #3 and #4 50
7.10 Comparison of sol-gel and slurry coated filters for methane reforming . 50
7.11 Tar reforming of slurry coated filter 52

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

List of Tables

2.1 Typical composition of product gases from biomass gasification 10

3.1 Classification of tars according to ECN 13

6.1 Technical data of the filter candles 27
6.2 Targeted composition of the simulated product gas 34
6.3 Antoine coefficients for water 35
6.4 Final composition of the simulated product gas 36
6.5 Experimental design 37

7.1 BET analysis of fresh and aged $Ni/MgAl_2O_4$ catalyst samples 40
7.2 Atomic composition of the catalytic filters (Fig. 7.2) 41
7.3 Atomic composition of the catalytic filter (Fig. 7.3) 43
7.4 Thermal and catalytic conversion of toluene 51
7.5 Thermal and catalytic conversion of naphtalene 51
7.6 Total tar concentrations for selected runs 53

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

References

[1] Steffen Heidenreich, Michael Müller, and Pier Ugo Foscolo. Fundamental concepts in biomass gasification. In *Advanced Biomass Gasification*, pages 4–10. Elsevier, 2016.

[2] Jacob A. Moulijn, Michiel Makkee, and Annelies E. van Diepen. *Chemical Process Technology*. John Wiley & Sons, 2013.

[3] Prabir Basu. Design of biomass gasifiers. In *Biomass Gasification Design Handbook*, pages 167–228. Elsevier, 2010.

[4] Hermann Hofbauer, Alexander Vogel, Martin Kaltschmitt, and Franziska Müller-Langer. Vergasung. In Martin Kaltschmitt, Hans Hartmann, and Hermann Hofbauer, editors, *Energie aus Biomasse: Grundlagen, Techniken und Verfahren*, pages 599–669. Springer Berlin Heidelberg, Berlin, Heidelberg, 2009.

[5] Klas Engvall, Henrik Kusar, Krister Sjöström, and Lars J. Pettersson. Upgrading of raw gas from biomass and waste gasification: Challenges and opportunities. *Topics in Catalysis*, 54(13-15):949–959, aug 2011.

[6] Thomas A Milne, Robert J Evans, and N Abatzaglou. Biomass gasifier "tars": their nature, formation, and conversion. Technical report, National Renewable Energy Laboratory, Golden, CO (US), 1998.

[7] Chunshan Li and Kenzi Suzuki. Tar property, analysis, reforming mechanism and model for biomass gasification—an overview. *Renewable and Sustainable Energy Reviews*, 13(3):594–604, April 2009.

[8] Samsudin Anis and Z.A. Zainal. Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review. *Renewable and Sustainable Energy Reviews*, 15(5):2355–2377, June 2011.

[9] K Maniatis and A.A.C.M Beenackers. Tar protocols. IEA bioenergy gasification task. *Biomass and Bioenergy*, 18(1):1–4, January 2000.

[10] Jan Fjellerup, Jesper Ahrenfeldt, Ulrik Henriksen, and Benny Gøbel. Formation, decomposition and cracking of biomass tars in gasification. 2005.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

[11] Mozhgan Ahmadi Svensson. *Sampling and Analysis of Tars by Means of Photo Ionisation Detection and Solid Phase Micro Extraction*. PhD thesis, 2013.

[12] Juan J. Hernández, Guadalupe Aranda-Almansa, and Antonio Bula. Gasification of biomass wastes in an entrained flow gasifier: Effect of the particle size and the residence time. *Fuel Processing Technology*, 91(6):681–692, June 2010.

[13] Steffen Heidenreich, Michael Müller, and Pier Ugo Foscolo. Advanced process integration. In *Advanced Biomass Gasification*, pages 18–54. Elsevier, 2016.

[14] Lopamudra Devi, Krzysztof J Ptasinski, and Frans J.J.G Janssen. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy*, 24(2):125–140, February 2003.

[15] Yafei Shen and Kunio Yoshikawa. Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis—a review. *Renewable and Sustainable Energy Reviews*, 21:371–392, May 2013.

[16] Friedrich Kirnbauer, Veronika Wilk, Hannes Kitzler, Stefan Kern, and Hermann Hofbauer. The positive effects of bed material coating on tar reduction in a dual fluidized bed gasifier. *Fuel*, 95:553–562, May 2012.

[17] David Sutton, Brian Kelleher, and Julian R.H. Ross. Review of literature on catalysts for biomass gasification. *Fuel Processing Technology*, 73(3):155–173, November 2001.

[18] Morris D Argyle and Calvin H Bartholomew. Heterogeneous catalyst deactivation and regeneration: a review. *Catalysts*, 5(1):145–269, 2015.

[19] Steffen Heidenreich. Hot gas filtration – a review. *Fuel*, 104:83–94, February 2013.

[20] Tenmat Ltd. Data sheet hot-gas filter. https://www.tenmat.com/high-temperature-materials/hot-gas-filtration/.

[21] J.T Richardson, Y Peng, and D Remue. Properties of ceramic foam catalyst supports: pressure drop. *Applied Catalysis A: General*, 204(1):19–32, nov 2000.

[22] Manfred Nacken, Lina Ma, Steffen Heidenreich, and Gino V. Baron. Performance of a catalytically activated ceramic hot gas filter for catalytic tar removal from biomass gasification gas. *Applied Catalysis B: Environmental*, 88(3-4):292–298, May 2009.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

[23] Sergio Rapagnà, Katia Gallucci, Manuela Di Marcello, Pier Ugo Foscolo, Manfred Nacken, Steffen Heidenreich, and Muriel Matt. First Al_2O_3 based catalytic filter candles operating in the fluidized bed gasifier freeboard. *Fuel*, 97:718–724, jul 2012.

[24] L. Ma, H. Verelst, and G.V. Baron. Integrated high temperature gas cleaning: Tar removal in biomass gasification with a catalytic filter. *Catalysis Today*, 105(3-4):729–734, aug 2005.

[25] Dorothea König. Tar conversion in an integrated catalytic filter. Research project, KTH Royal Institute of Technology, 2018.

[26] Benoît Heinrichs, Stéphanie Lambert, Nathalie Job, and Jean-Paul Pirard. Sol-gel synthesis of supported metals. In *Catalyst Preparation*, pages 177–222. CRC Press, 2016.

[27] George W. Scherer C.Jeffrey Brinker. *Sol-Gel Science*. Elsevier Science Publishing Co Inc, 1990.

[28] Ji-Eun Min, Yun-Jo Lee, Hae-Gu Park, Chundong Zhang, and Ki-Won Jun. Carbon dioxide reforming of methane on ni–mgo–al2o3 catalysts prepared by sol–gel method: Effects of mg/al ratios. *Journal of Industrial and Engineering Chemistry*, 26:375–383, 2015.

[29] Keishi Nishio and Toshio Tsuchiya. Sol-gel processing of thin films with metal salts. In *Handbook of Sol-Gel Science and Technology*, pages 133–154. Springer International Publishing, 2018.

[30] J. W. Niemantsverdriet. *Spectroscopy in Catalysis*. Wiley VCH Verlag GmbH, 2007.

[31] Majid Naderi. Surface area: Brunauer–emmett–teller (bet). In *Progress in Filtration and Separation*, chapter 14, pages 585–608. Academic Press, 2015.

[32] Yi Wang and Vania Petrova. Scanning electron microscopy. In *Nanotechnology Research Methods for Foods and Bioproducts*, pages 103–126. Wiley-Blackwell, feb 2012.

[33] *VDI-Wärmeatlas*. Springer Berlin Heidelberg, 2013.

[34] Zhigang Fan, Kaihang Sun, Ning Rui, Binran Zhao, and Chang jun Liu. Improved activity of $Ni/MgAl_2O_4$ for CO_2 methanation by the plasma decomposition. *Journal of Energy Chemistry*, 24(5):655–659, sep 2015.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

[35] Maxime Georges Philippe Scrive. Catalytic filter for biomass tar steam reforming in gasification applications, 2018.

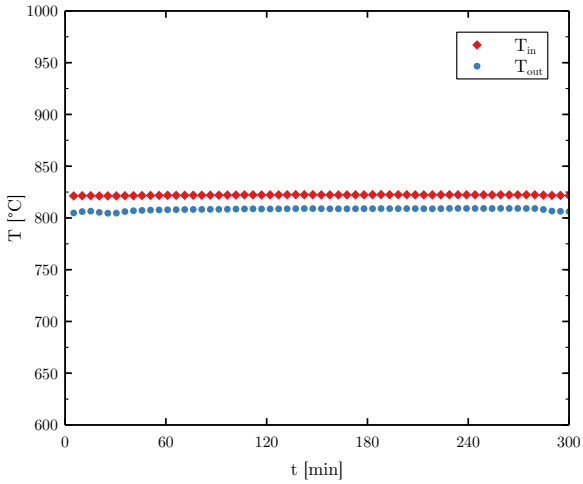
[36] Teddy G. Monroy, Leonila C. Abella, Susan M. Gallardo, and Hirofumi Hinode. Catalytic dry reforming of methane using Ni/MgO-ZrO_2 catalyst. In *Proceedings of the 2nd Annual Gas Processing Symposium*, pages 145–152. Elsevier, 2010.

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

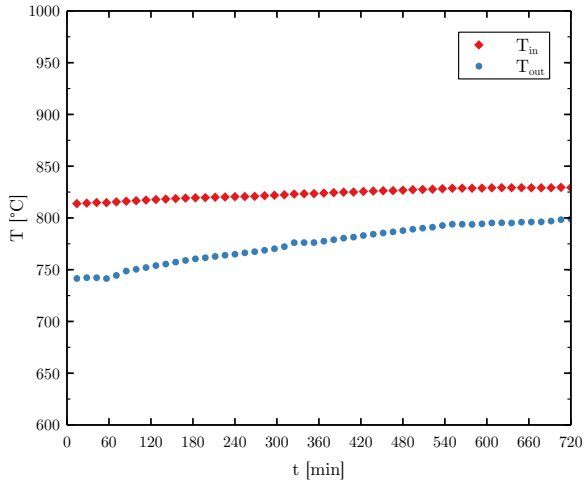
Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.

Appendix

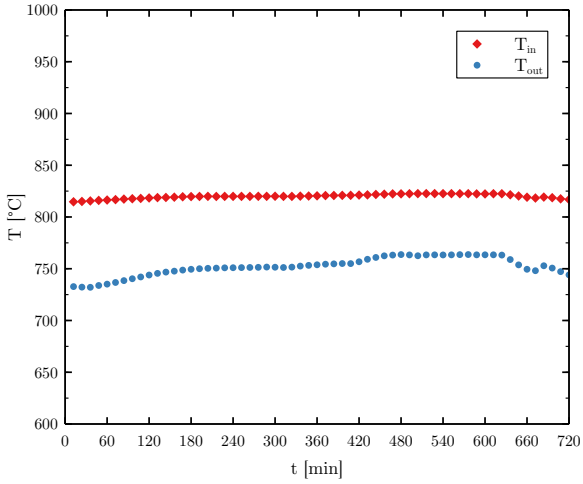
Temperature profiles



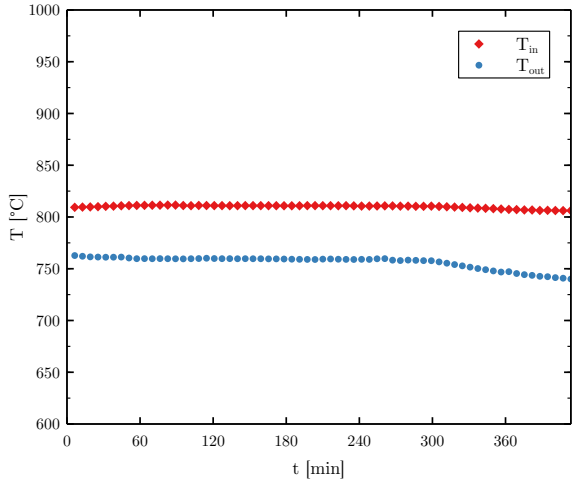
(a) #1 Blank filter - H



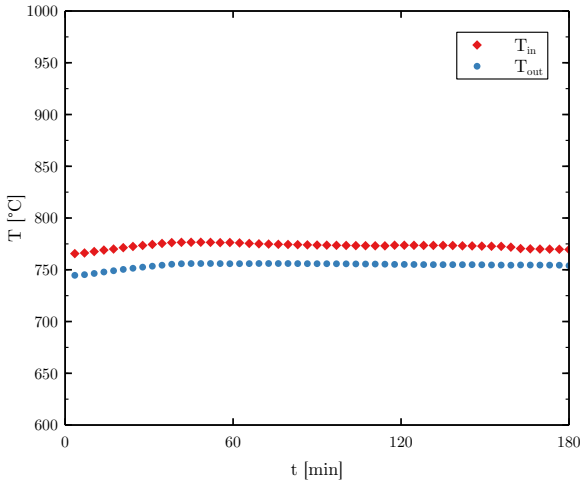
(b) #2 Solgel coating - no H



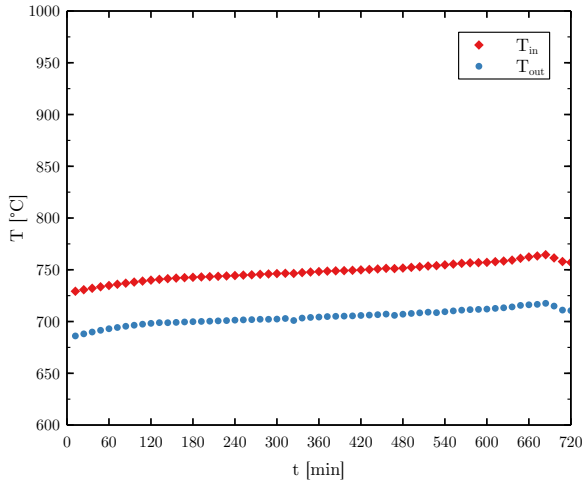
(c) #3 Slurry coating - no H



(d) #4 Slurry coating - H

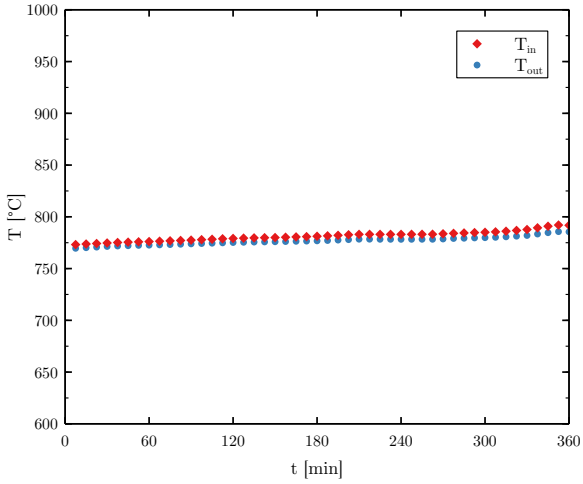


(e) #5 Blank filter - no H

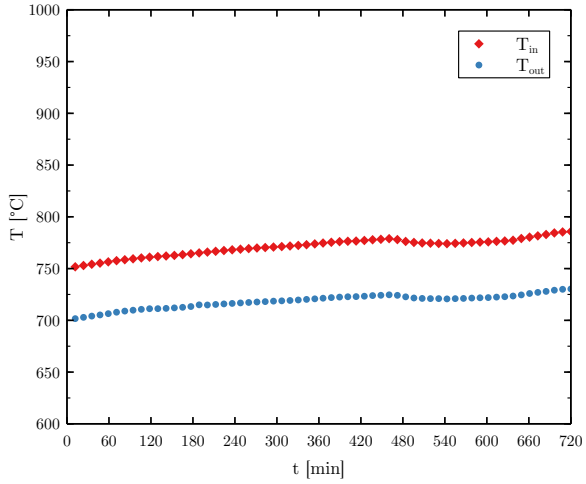


(f) #6 Solgel coating - H

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



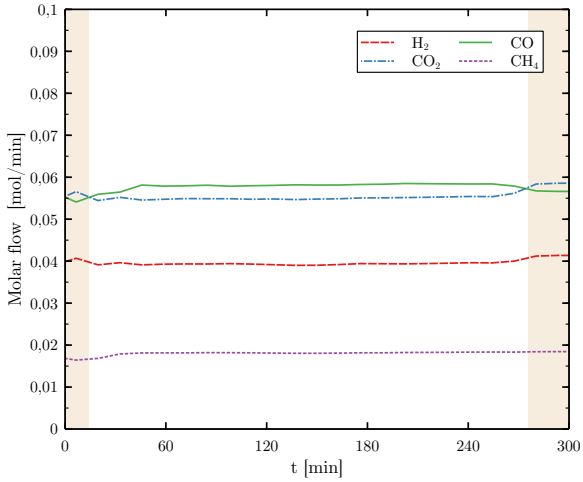
(g) #7 Blank filter - H



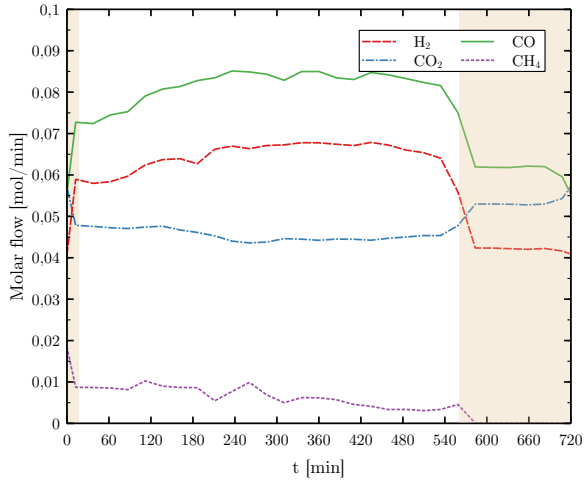
(h) #8 Slurry coating - no H

Figure 9.2: Temperature profile of catalytic filtration

Molar flows

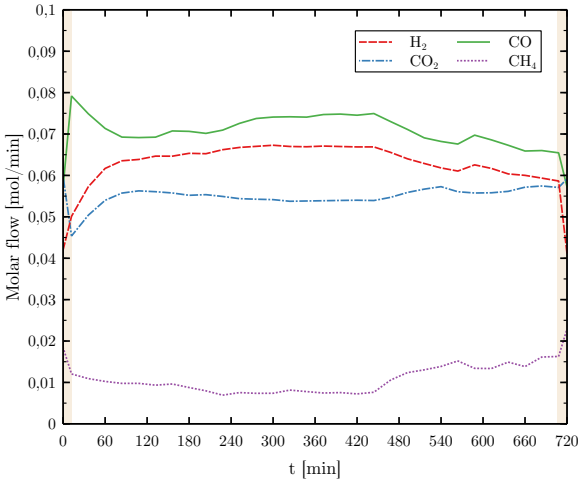


(a) #1 Blank filter - H

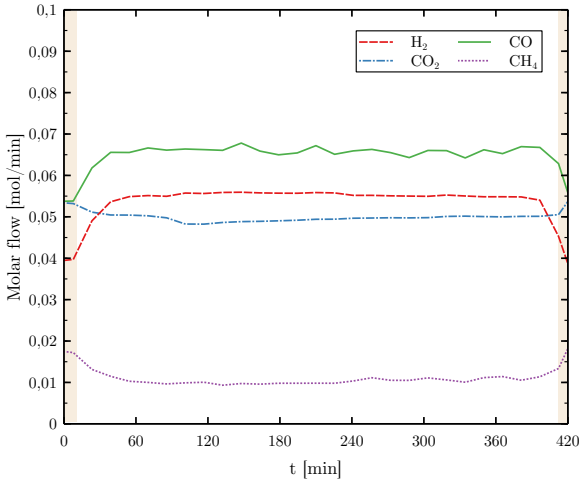


(b) #2 Solgel coating - no H

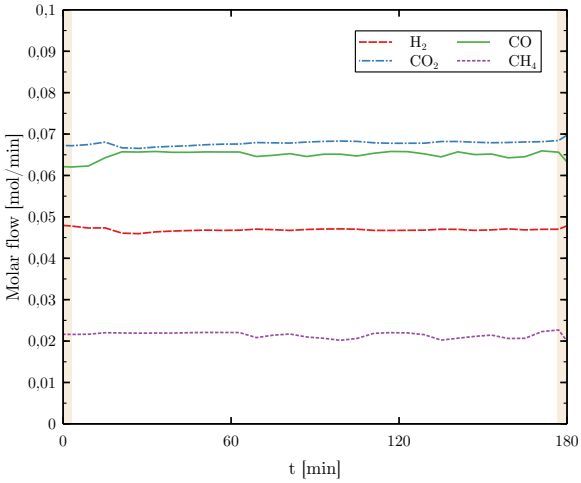
Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.



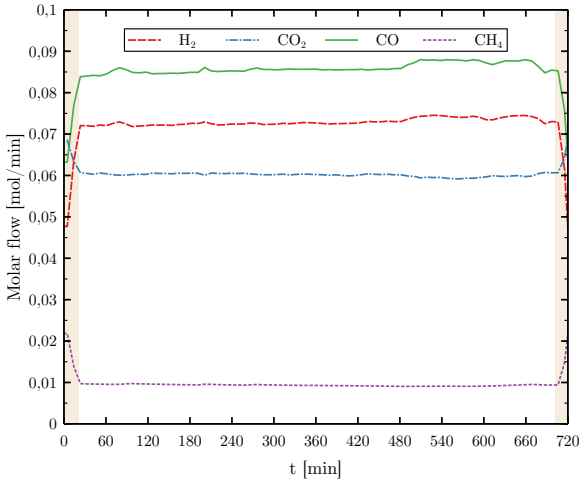
(c) #3 Slurry coating - no H



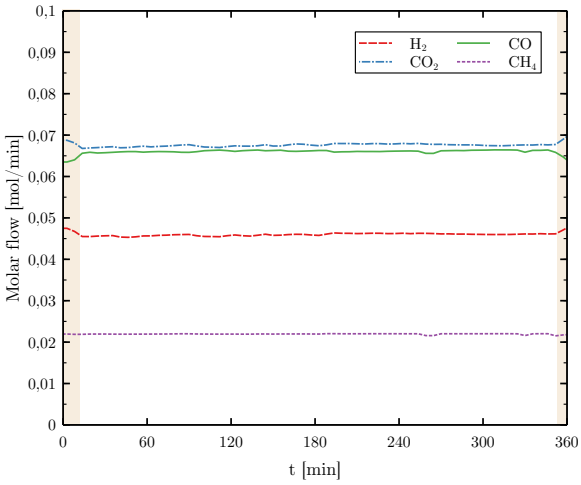
(d) #4 Slurry coating - H



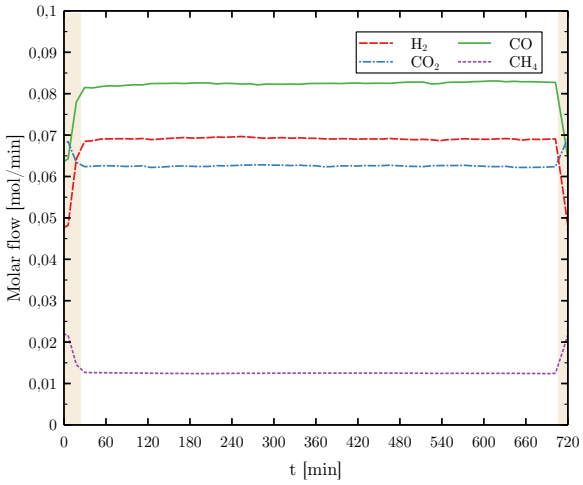
(e) #5 Blank filter - no H



(f) #6 Solgel coating - H



(g) #7 Blank filter - H

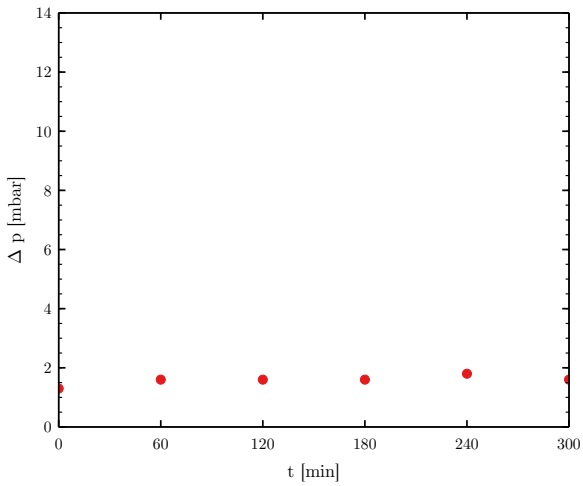


(h) #8 Slurry coating - no H

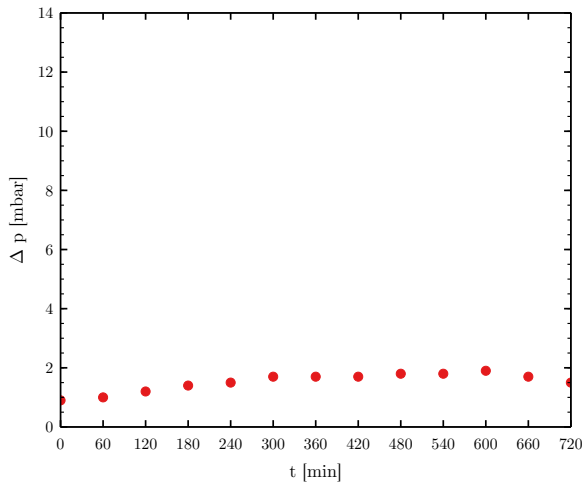
Figure 9.4: Molar flows of the catalytic filtration

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.

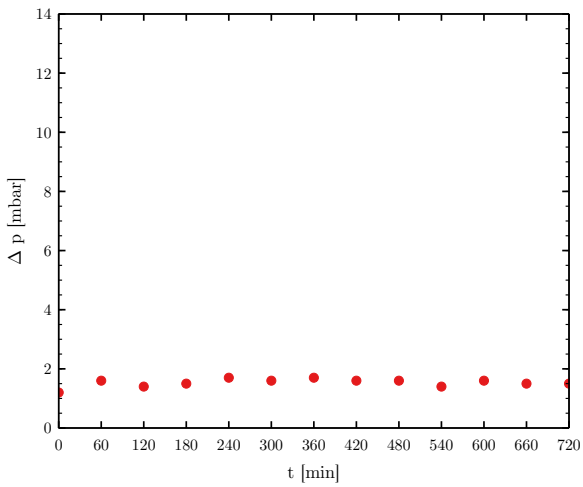
Differential pressure



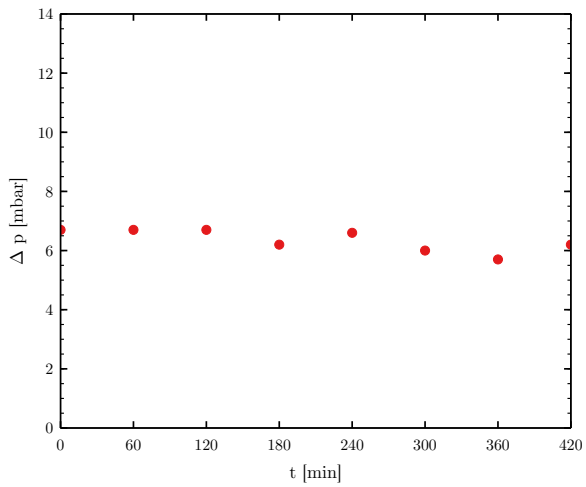
(a) #1 Blank filter - H



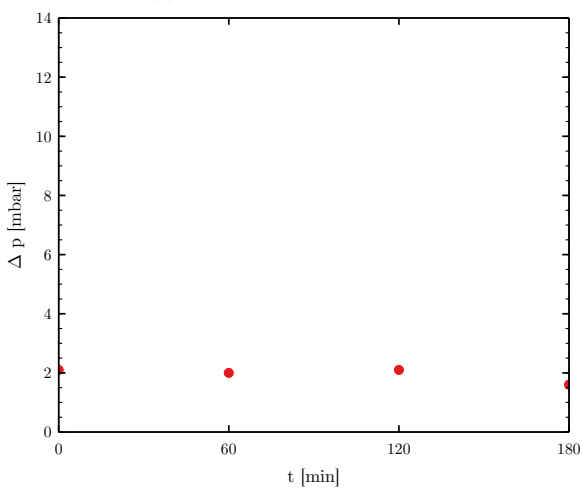
(b) #2 Solgel coating - no H



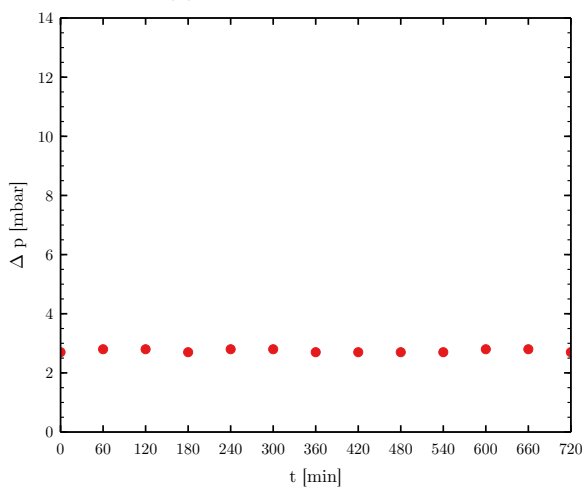
(c) #3 Slurry coating - no H



(d) #4 Slurry coating - H

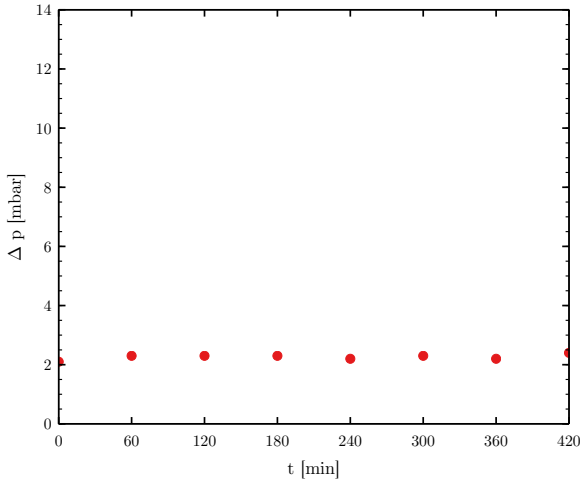


(e) #5 Blank filter - no H

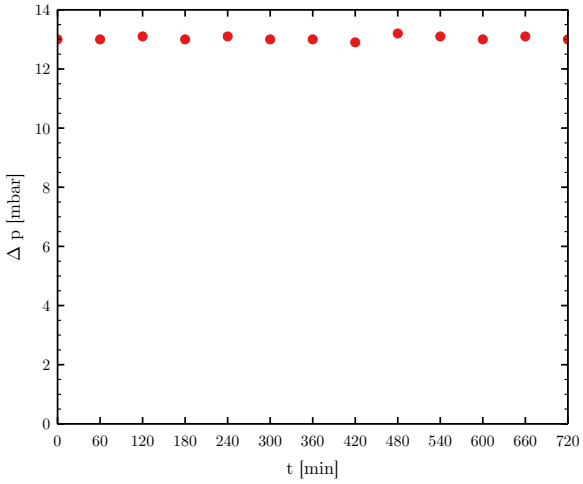


(f) #6 Solgel coating - H

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN



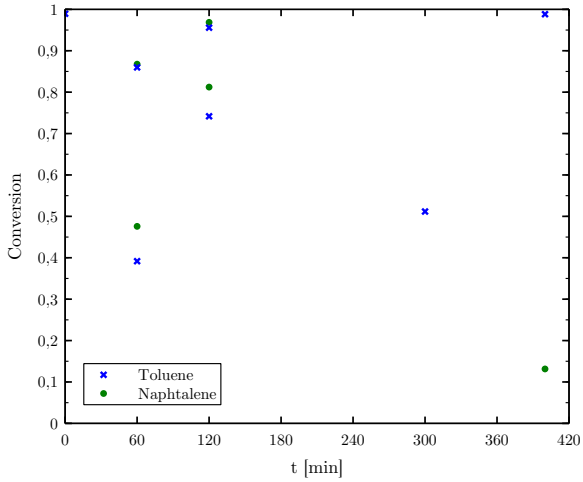
(g) #7 Blank filter - H



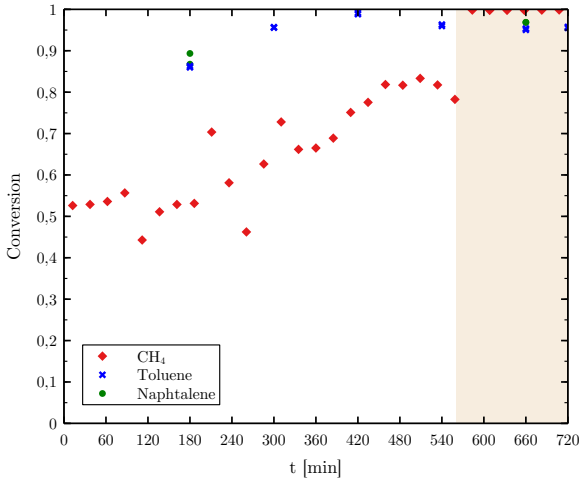
(h) #8 Slurry coating - no H

Figure 9.6: Differential pressure of the catalytic filtration

Conversion of hydrocarbons

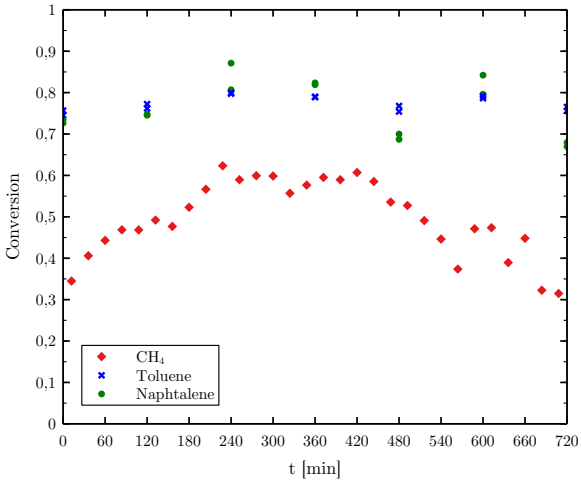


(a) #1 Blank filter - H

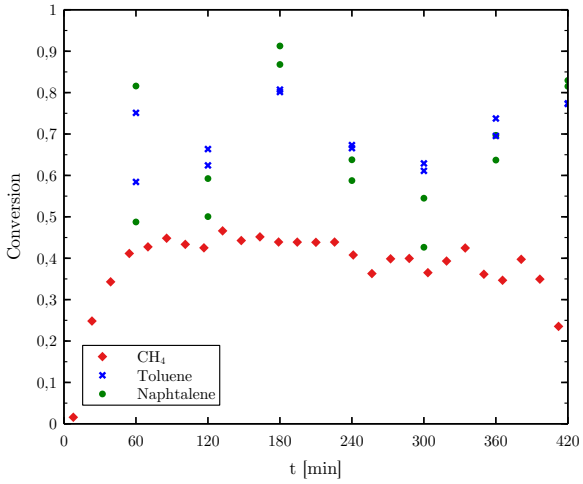


(b) #2 Solgel coating - no H

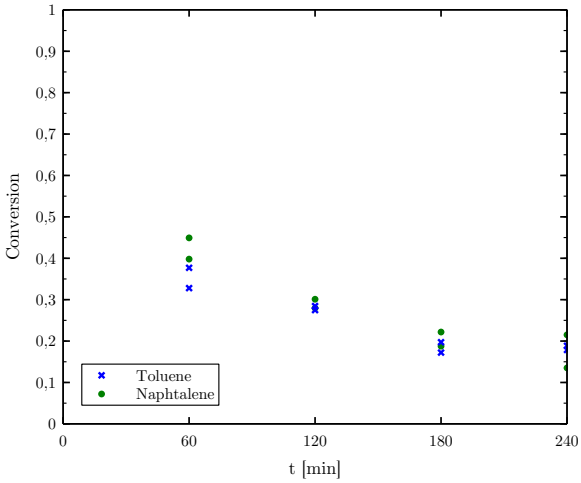
Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.



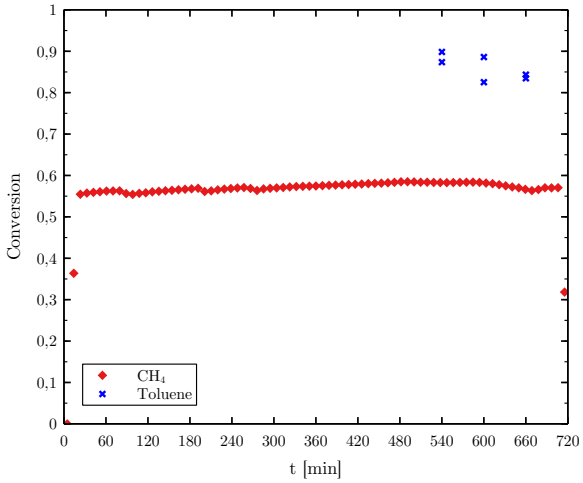
(g) #3 Slurry coating - no H



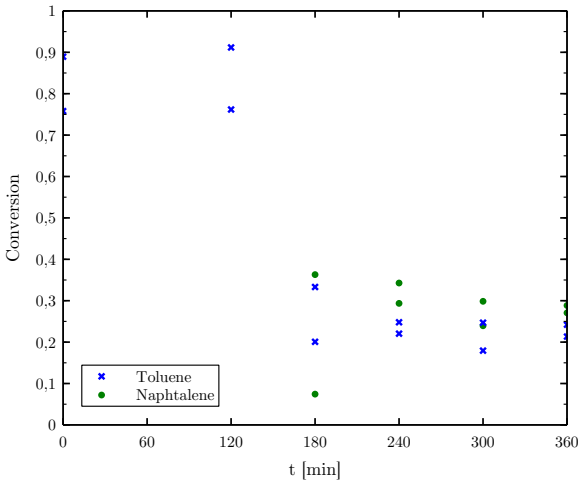
(h) #4 Slurry coating - H



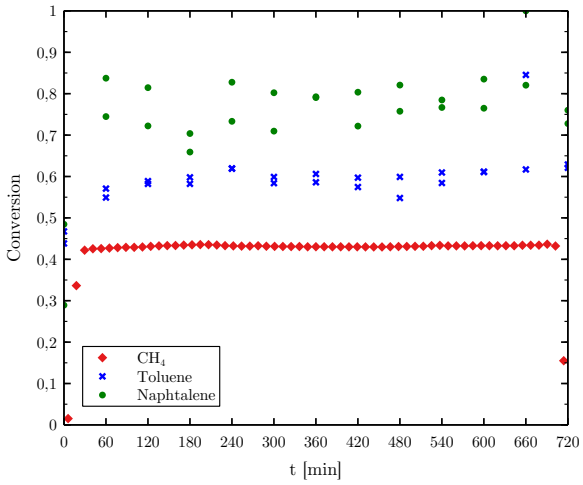
(i) #5 Blank filter - no H



(j) #6 Solgel coating - H



(k) #7 Blank filter - H

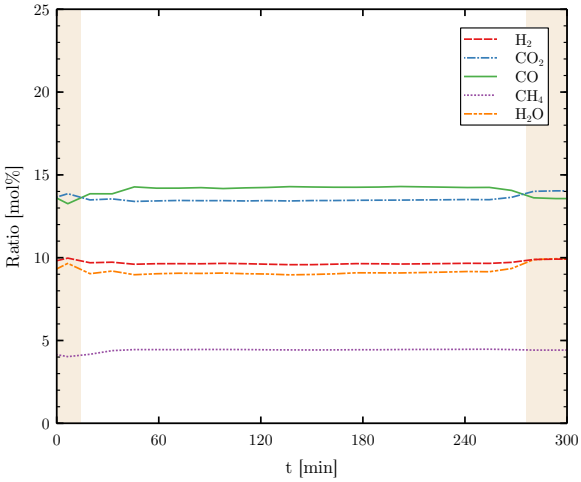


(l) #8 Slurry coating - no H

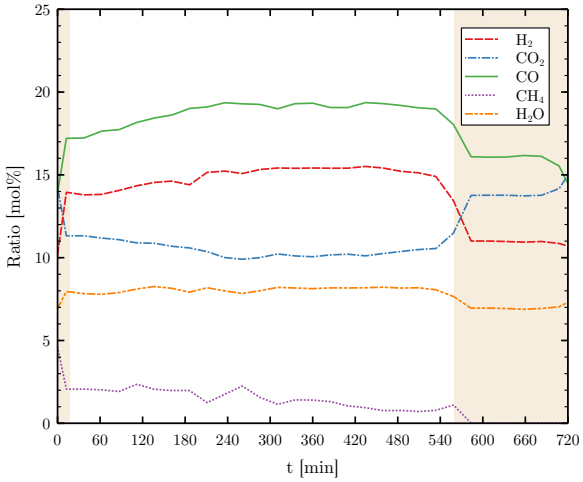
Figure 9.8: Conversion of Methane, Toluene and Naphtalene

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

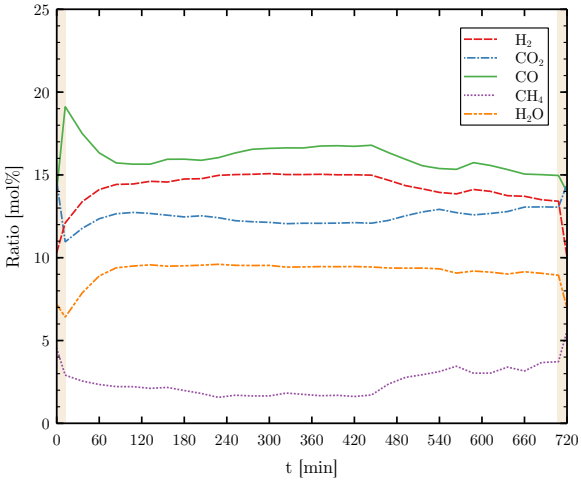
Wet gas composition



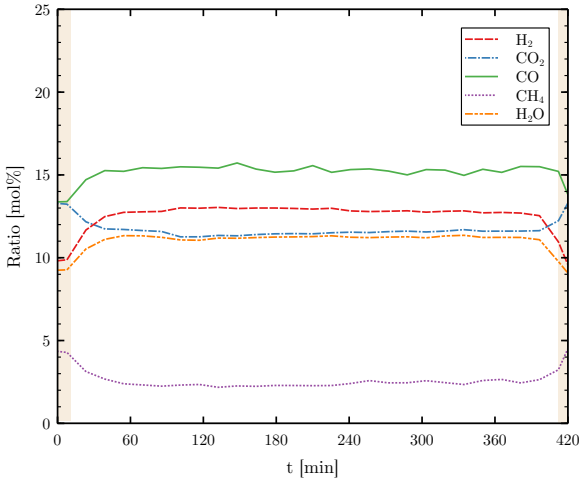
(a) #1 Blank filter - H



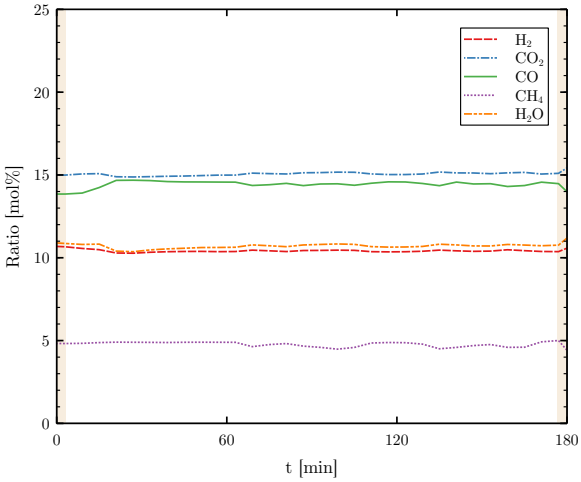
(b) #2 Solgel coating - no H



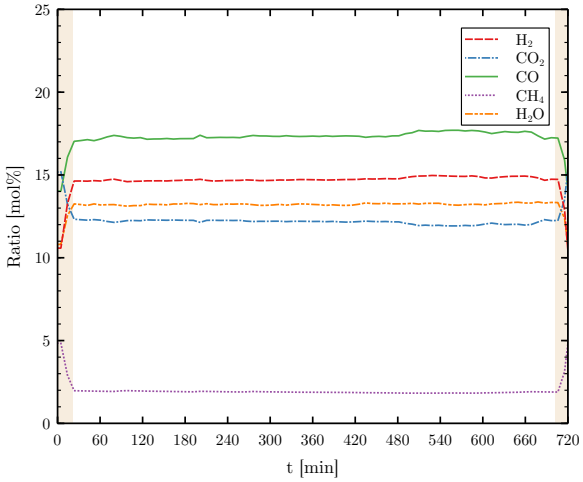
(c) #3 Slurry coating - no H



(d) #4 Slurry coating - H

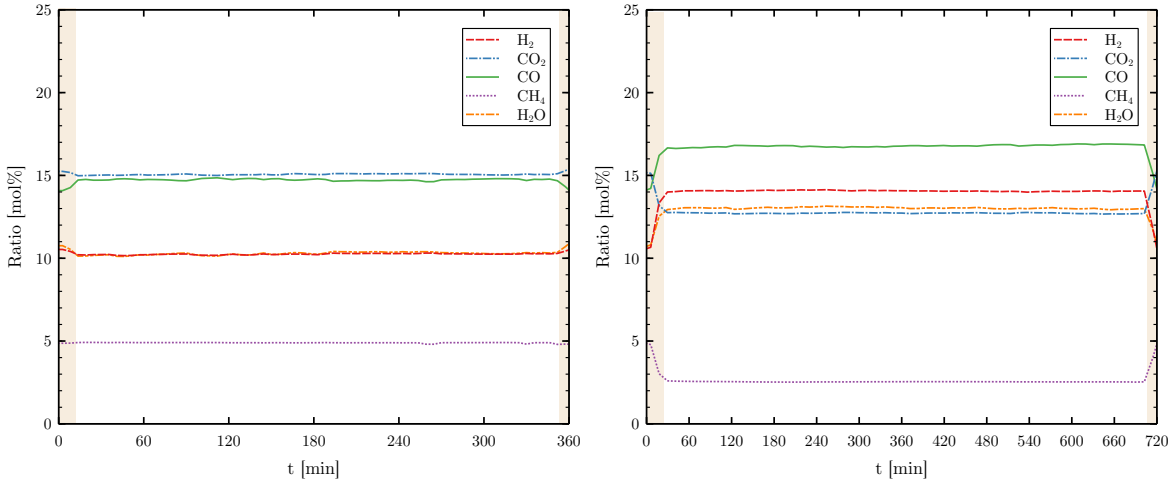


(e) #5 Blank filter - no H



(f) #6 Solgel coating - H

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.
TU Bibliothek Your knowledge hub WIEN

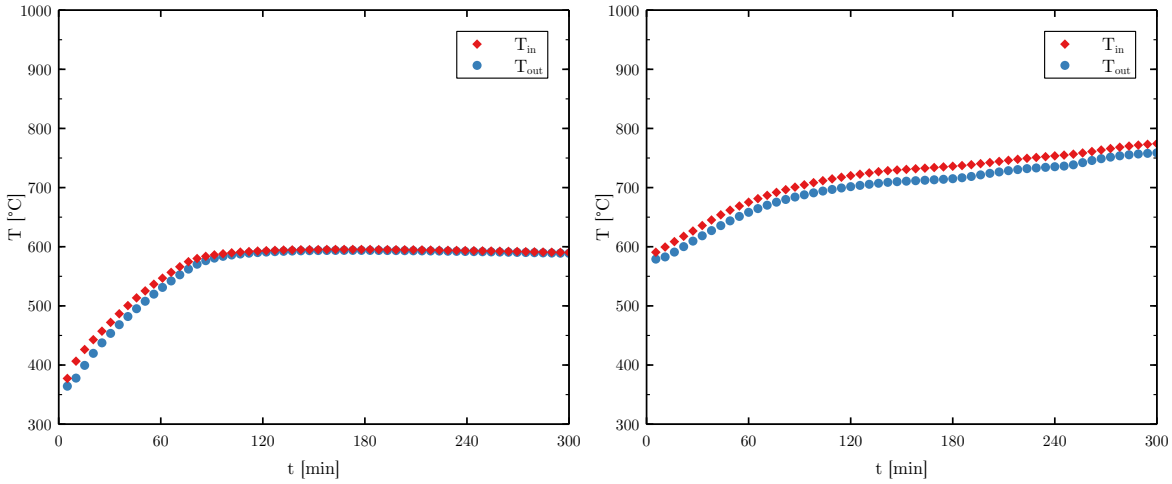


(g) #7 Blank filter - H

(h) #8 Slurry coating - no H

Figure 9.10: Calculated wet gas composition of the product gas after the filtration

Pretreatment of the catalytic filter



(a) Reduction

(b) Ageing

Figure 9.11: Temperature profiles of the pretreatment of a catalytic filter

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar.
The approved original version of this thesis is available in print at TU Wien Bibliothek.