Study of the activity of catalysts for the production of high quality biomass gasification gas – with emphasis on Ni-substituted Ba-hexaaluminates
Abstract

The fossil hydrocarbons are not inexhaustible, and their use is not without impact in our need of energy, fuels and hydrocarbons as building blocks for organic materials. The quest for renewable, environmentally more friendly technologies are in need and woody biomass is a promising candidate, well provided in the boreal parts of the world. To convert the constituents of wood into valuable gaseous products, suitable for the end use required, we need a reliable gasification technology. But to become an industrial application on full scale there are still a few issues to take into account since the presence of contaminants in the process gas will pose several issues, both technical and operational, for instance by corrosion, fouling and catalyst deactivation. Furthermore the downstream applications may have very stringent needs for syngas cleanliness depending on its use. Therefore, the levels of contaminants must be decreased by gas cleanup to fulfil the requirements of the downstream applications.

One of the most prominent problems in biomass gasification is the formation of tars – an organic byproduct in the degradation of larger hydrocarbons. So, tar degrading catalysts are needed in order to avoid tar related operational problems such as fouling but also reduced conversion efficiency. Deactivation of catalysts is generally inevitable, but the process may be slowed or even prevented. Catalysts are often very sensitive to poisonous compounds in the process gas, but also to the harsh conditions in the gasifier, risking problems as coke formation and attrition. Alongside with having to be resistant to any physical and chemical damage, the catalyst also needs to have high selectivity and conversion rate, which would result in a more or less tar-free gas. Commercial tar reforming catalysts of today often contain nickel as the active element, but also often display a moderate to rapid deactivation due to the causes mentioned.
In order to counteract these problems we have tried to introduce a new type of tar decomposing catalyst, with an expected high resistance to poisons, less prone to sintering and a surface less prone to char formation. Substituted hexaaluminates have previously been used in partial oxidation of methane and middle-distillate fuels, high temperature processes often leading to deactivation caused by sintering and coke formation. But this material has showed a good resistance to deactivation, but also a high dispersion of the substituted metal – a property that makes it less receptive to poisons like sulphur.

We have been investigating Ba-Ni-substituted hexaaluminate both in lab-scale and in process-gas from a CFB gasifier and this material has turned out to show very promising qualities as a tar reforming catalyst in biomass gasification. The conversion/degradation of tars is very high and the material has a very good resistance towards both sintering and coke formation. Besides steam-reforming, the activity for methane steam reforming and water-gas-shift has been investigated. BaNi-hexaaluminates has a good water-gas-shift activity, but the methane reforming activity is largely affected by sulphur poisoning.

Future use of biomass for hydrogen and syngas production will need both efficient plants, reduced costs and different application scales for syngas technologies. Catalysis is a key factor for the development in biomass gasification as it is a vital part in advanced reactor designs, in manufacturing different feedstocks and in controlling carbon formation. Hopefully substituted hexaaluminates will become a new concept in the development of tar reforming catalysts.
Acknowledgments

Starting a PhD-education is actually bit overwhelming, I guess specially after a quite long career in chemistry – both in assisting in research work but also as a teacher. Suddenly you find yourself in an (for you) unexplored field of bioenergy technology of which you know more or less nothing. Coming from fields of food technology and analytical chemistry, it was quite a long shot. But it was very, very interesting to get the opportunity to discover the world of bioenergy and dig deeper into the tools of catalysis. Thank you Michael for letting me have this opportunity and for being such a great role model for an enthusiastic researcher and supervisor. I also wish to thank Sune for letting me take part of the Crisgas project. It was the perfect introduction to my own work. I learnt a lot from the WGS-investigations with Jessica, with whom I also had a lot of fun.

Eventually I started my own project, catalysis with a new material – bariumhexaaluminate. Jan, an expert in the field of catalysis and a really practical person in the lab, became my supervisor and during the years he has shown me how to become an even more independent and self-confident researcher. For this I thank you. I would also like to thank Ann-Charlotte for her kind aid as my assisting supervisor during this last year.

In my work I have also had the opportunity to some research collaboration abroad. I would specially like to thank Patricia in Bologna and Martina in Delft/Milan for their generous help and cooperation, and the personnel at TU Delft/Process and Energy for their professional work in the pilot-plant study. We have also had some financing from STEM and BRISK for which I am very grateful. I would also like to thank the collaboration network “Svenskt Förgasningscenter” for letting us joining in.

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I would also like to thank all my friends and coworkers in the bioenergy department – both present and previous. You are all beautiful people and magnificent minds, and I am very lucky to have (or have had) you as colleagues. With you I feel we can make a difference!

Last by not least I would like to thank my wonderful family; Björn, Moa, Ellen and Jack. You are my sanctuary and my asylum 😊 and I love you all very much! And thank you mum and dad for always being so loving and encouraging. You are in my heart.
Content

Abstract ................................................................................................................ 3
Acknowledgments ................................................................................................ 5
Content ................................................................................................................. 7
1. Introduction ...................................................................................................... 9
   1.2 Research aim ........................................................................................... 10
2 Biomass ........................................................................................................... 11
3 Biomass conversion ......................................................................................... 13
4 Gasification ..................................................................................................... 15
   4.1 Chemistry of gasification ........................................................................ 15
   4.2 Gasification technology .......................................................................... 17
      4.2.1 The fixed bed gasifiers .................................................................... 19
      4.2.2 The fluidized bed gasifier ............................................................... 20
5 Tar formation ................................................................................................... 22
6 Cleaning and upgrading in biomass gasification ............................................. 27
   6.1 Particulates .............................................................................................. 29
   6.2 Sulphur .................................................................................................... 30
   6.3 Nitrogen .................................................................................................. 30
   6.4 Chlorine and alkali .................................................................................. 30
   6.5 Tars ......................................................................................................... 31
      6.5.1 Physical separation ......................................................................... 32
      6.5.2 Thermal cracking .......................................................................... 33
      6.5.3 Non-thermal plasmas ...................................................................... 34
      6.5.4 Catalytic cracking ........................................................................... 34
7 Catalytic tar reforming .................................................................................... 35
   7.1 Traditional tar reforming catalysts .......................................................... 37
      7.1.1 Mineral catalysts: ............................................................................ 38
      7.1.2 Synthetic catalysts .......................................................................... 39
   7.2 Research Catalysts/New developments: .................................................. 42
   7.3 Substituted hexaaluminates .................................................................... 43
8 Catalyst deactivation ....................................................................................... 44
   8.1 Thermal degradation and sintering........................................................... 45
8.2 Fouling/Coking .............................................................................................. 46
8.3 Poisoning ....................................................................................................... 47
9 Experimental methods ...................................................................................... 49
  9.1 High temperature water-gas shift step in the production of clean hydrogen rich synthesis gas from gasified biomass ........................................ 49
  9.2 Nickel-substituted bariumhexaaluminates as novel catalysts in steam reforming of tars ......................................................................................... 51
  9.3 Ba-Ni-hexaaluminate as a new catalyst in the steam reforming of tars. Long-term studies on sulphur deactivation and coke formation (manuscript) ......................................................................................... 54
  9.4 Analytical procedures ................................................................................ 55
10 Results and discussion of included work ............................................................ 56
  10.1 Paper I: .................................................................................................... 56
  10.2 Paper II: .................................................................................................. 59
  10.3 Manuscript III: ........................................................................................ 62
11 Conclusions ....................................................................................................... 66
12 Future research .................................................................................................. 68
Author’s contribution to presented papers ............................................................. 69
References ............................................................................................................. 70
1. Introduction

The last decade has been the stage for the most revolutionary development caused by man in Earth’s history. Industrialization has provided an increased wealth for many but has also started an escalating demand for more energy and new raw materials. Many consequences can now be seen on the ecosystems all over the world, as the negative effects of various pollutants and the destruction of habitats become more and more obvious. But, during the last 40 years or so, an environmental consciousness has slowly started to awake, more and more global collaborations have been initiated and the environmental downward spiral has slowly subsided. As IPCC, International panel on climate change, was established in 1988 a scientific focus has been brought on climate changes and their impacts. The fact that the use of fossil carbonaceous raw materials for energy production is one of the main reasons to the anthropologically caused global warming is now an officially approved fact – recognized by most decision makers all over the world.

In Sweden the government has decided as a goal that there will be no net emissions of greenhouse gases by 2050. To reach this goal a lot of adaptations and efforts has to be done in society; such as economizing and saving natural resources and energy and introducing a new and more fuel efficient transportation system. To achieve this aim, new technologies needs to be developed and old technologies modernized and the aim needs to focus on domestic resources. When looking at national renewable energy sources in Sweden we have sun, wind and water – but we also have a lot of biomass. According to Hagström the estimated annual potential amount of dry matter (dm) and corresponding energy from biomass in Sweden would amount to a total (including black liquor) of 32.68 Mt dm or 188.9 TWh, whereas the total energy consumption 2013 summoned up to 375TWh content (E) from selected biomass sources in Sweden.

But as the increased emissions of greenhouse gases are of international concern a lot of efforts must also be taken globally. IEA (International energy agency) maintains that from 1990 to 2012 the CO₂ emissions from fuel
combustion increased by 51%. At the same time IPCC:s latest, fifth, assessment points out that the greenhouse gas emissions needs to be reduced by 40-70% compared to 2010 by mid-century, in order to keep the temperature increase below two degrees. With the aim of stabilizing the level of atmospheric greenhouse gases we need to reduce emissions from energy production and use, but we also need to stabilize greenhouse gas concentrations in the atmosphere. This requires emissions reductions both from energy production and use, but also from transportation, buildings, industrial activities, land use, and human settlements. In the boreal parts of the world there are large potentials for the production of energy and raw materials from woody biomass. Lauri et al (2013) has estimated that in 2050 it would be possible to satisfy 14-18% of the world’s primary energy consumption by woody biomass. These estimations are strongly affected by what scenarios used, and the divergence is due to having both a business-as-usual approach and a more environmentally oriented prediction. At the same time it is important to take into consideration the balance of the lifecycle of GHG and the environmental effects an increased biomass production may have. There will most likely be need for some sustainability criteria in order to have an endurable production of both solid and gaseous biomass derived products.

1.2 Research aim

Being aware of both the prospects but also the challenges in the field of biomass gasification, especially when it comes to the difficulties in producing a product gas with high quality and low impurities, the main objective of this work is to investigate the performance of a new type of tar reducing catalyst. This material was chosen for its expected high sulphur resistance and low tendency for sintering and char formation together with an anticipated high activity for tar reforming.
2 Biomass

There are many definitions of biomass, most of them very similar. IEA defines biomass as follows; “Biomass is any organic, i.e. decomposable, matter derived from plants or animals available on a renewable basis. Biomass includes wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure”. Biomass may be used directly as it is or it may be processed in various ways into solid, liquid or gaseous products. In this context bioenergy can be defined as energy derived from the conversion of biomass. Approximately 10% of the world’s needs for primary energy come from bioenergy and is mainly used for cooking and heating. Historically the use of woody biomass has followed humans, from the early camp fires to today’s modern heating stoves. But the conversion methods has become more and more technically sophisticated as the development of advanced combined heat and power, CHP, and intricate gasification technologies emerges.

Woody biomass mainly consists of three polymeric constituents; cellulose, lignin and hemicellulose and they appear in different rates depending on type of crop. Typically softwood (like pine and spruce) contains approximately 40% cellulose, 30% hemicellulose and 27% lignin. There are also some extractives.
Biofuels are generally classified with a reference to their method of preparation, as they –depending on starting material – may be produced in more than one or two steps. First generation biofuels are prepared directly from biomass and this biomass is often some part of the food chain with important components as starch, fats and sugars. First generation biofuel products may be bioalcohols, biogas or biodiesel. Second generation biofuels rely more on materials like solid waste from municipalities, forestry and agricultural waste. The main used component is cellulose and these fuels are sometimes also called cellulosic fuels. This feedstock is often cheaper and less important for food production and thus has a lower ecological imprint. There are also concepts like third and fourth generation biofuels referring to algae and metabolically engineered algae respectively.

For a more a thorough description on chemical composition in different biomass substrates for gasification, see table 2.
3 Biomass conversion

The translation of biomass resources into more valuable products can be divided into thermochemical and biochemical conversion and extraction. The thermochemical conversion methods include treating the biomass with high temperatures either in an oxygen containing or a non-oxygenic atmosphere to promote structural degradation. There are four main routes; gasification, direct combustion, pyrolysis, and liquefaction; each differing in conditions such as temperature, heating rate, and oxygen level present during the process.

Combustion can be described as the burning of biomass in air. It is being used in many different outputs aimed to convert chemical energy stored in the biomass into heat, mechanical power, or electricity.

Pyrolysis and liquefaction are sometimes mixed up. They are both thermochemical conversion methods where the biomass is converted into mainly liquid products. Liquefaction uses catalysts in order to decompose the feedstock macromolecules into fragmented, lighter hydrocarbons. In pyrolysis catalysts are rarer as the smaller molecules undergo spontaneous homogeneous gas phase reactions into the desired heavier oily compounds. Alterations in operating conditions for the two processes may consist of different parameters such as moisture content in the raw material, oxygen content in the atmosphere, temperature and pressure. For instance hydrothermal liquefaction (HTL) is performed in presence of water at lower temperatures and higher pressures. Bio-oils are thermally unstable and must be upgraded if they are to be used as fuels.

Gasification is a process in which a solid material is converted into, optionally, a gas mixture. The feedstock is heated to high temperatures, producing gases which can undergo chemical reactions to optionally form a synthesis gas. The gasification process follows several steps. First there is a pyrolysis with a vaporization of the volatiles in the feedstock where solid char and ash also are produced. Then the gasification further breaks down the pyrolysis products, aided by the provision of additional heat. Operating
conditions, such as temperature, pressure and steam content, may be altered in different units. The result of the gasification process is a mixture of gases. Biochemical conversion comprises different chemical reactions where microorganisms and/or enzymes alter fermentable feedstock into valuable products. Anaerobic digestion would result in biogas, and in fermentation processes biomass starch is enzymatically degraded into sugars that are converted into ethanol by yeast. This process is followed by distillation in order to achieve usable bioethanol. Physiochemical technologies may also be designated as agrochemical conversion or mechanical extraction. In this process oils are extracted from different oilseed feedstock for direct use or for conversion into biodiesel.

Figure 1: Biomass conversion routes
4 Gasification

Gasification is considered a promising tool for the conversion of woody biomass into gaseous fuels and syngas, but it is a complex technology that is still under development and its reliability and efficiency needs to be proven in order to see a more extended use. One aim must be to develop reliable gasification technologies for large scale applications with high availability and a production of a gas quality that also can meet the standards for synthesis technologies and fuel cells without poisoning the catalysts needed. There are a wide range of reactor set-ups present and the gasifiers may differ in parameters like operational size and pressure, fuel composition and feed method, bed material, flue gas mixture and moisture.

4.1 Chemistry of gasification

Woody biomass consists basically of three types of polymers: cellulose, hemicellulose and lignin. As it is fed into the gasifier the fuel particles transform and undergo different processes. Gasification involves a thermochemical transformation of biomass into a mixture of gases and different by-products. This process contains a series of chemical reactions and some of the main reactions occurring in gasification are listed below in equations 1-14. The gaseous product being formed is optionally a mixture of $\text{H}_2$, $\text{CO}$, $\text{CO}_2$ (so called syngas) and sometimes $\text{CH}_4$, but it also often contains impurities such as nitrogen, sulfur, alkali compounds, some lower hydrocarbons and tars.

The gasification proceeds via a multi-step process; First is the drying and heating of the biomass and this proceeds until approximately 200°C. For gasification, the moisture content should be between 10%-15%. Factors impacting the drying process are particle size, initial moisture content, temperature, relative humidity, and velocity of the surrounding gas. During drying the heat inside the gasifier releases the feed stock moisture as steam
into the gas phase which is evaporated. The next step is pyrolysis, at 150-900°C, which means the breakdown of biomass by heat. This step, sometimes known as devolatilization, is endothermic and it produces mainly volatile substances in the form of gaseous and condensable hydrocarbons, the latter called tars. The actual reaction scheme of pyrolysis of wood would be extremely complex to describe as there are over a hundred intermediate products being formed. As the heating continues the dried wood particles starts to decompose.

The first decomposition step, primary pyrolysis, is when the solid phase is thermally degraded into gases, tar, and char.

The secondary pyrolysis step is the conversion, or the thermal cracking, of tars into gaseous products and char. Cracking reactions may occur in the gas phase as homogeneous reactions or as heterogeneous reactions on fuel particles or char. The remaining nonvolatile material, containing mainly the carbonaceous material, is referred to as char.

The third decomposition step is oxidation or partial combustion. It occurs at temperatures over 700°C and the products from the pyrolysis are partially or completely oxidized in an exothermic reaction that will provide heat for the subsequent gasification reactions.

The last step is the gasification reactions or the reducing reactions. They occur at temperatures over 800°C. Here the hydrocarbons and char formed will react with gasifying agents such as steam or oxygen. The final product mainly includes CO, H₂, CO₂ and CH₄.
Equations 1-14: The main reactions that occur during biomass gasification. Summarized as follows:

**Boudouard reaction:**
\[ C + CO_2 \rightleftharpoons 2CO \quad +172 \text{ kJ/mol} \quad (1) \]

**Steam gasification:**
\[ C + H_2O \rightleftharpoons CO + H_2 \quad +131 \text{ kJ/mol} \quad (2) \]

**Hydrogasification:**
\[ C + 2H_2 \rightleftharpoons CH_4 \quad -74.8 \text{ kJ/mol} \quad (3) \]
\[ C + 0.5O_2 \rightleftharpoons CO \quad -111 \text{ kJ/mol} \quad (4) \]

**Oxidation reactions:**
\[ C + O_2 \rightleftharpoons CO_2 \quad -394 \text{ kJ/mol} \quad (5) \]
\[ CO + 0.5O_2 \rightleftharpoons CO_2 \quad -284 \text{ kJ/mol} \quad (6) \]
\[ CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \quad -803 \text{ kJ/mol} \quad (7) \]
\[ H_2 + 0.5O_2 \rightleftharpoons H_2O \quad -242 \text{ kJ/mol} \quad (8) \]

**Water-gas shift reaction:**
\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \quad -41.2 \text{ kJ/mol} \quad (9) \]

**Methanation reactions:**
\[ 2CO + 2H_2 \rightleftharpoons CH_4 + CO_2 \quad -247 \text{ kJ/mol} \quad (10) \]
\[ CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad -206 \text{ kJ/mol} \quad (11) \]
\[ CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad -165 \text{ kJ/mol} \quad (12) \]

**Steam reforming reactions:**
\[ CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad +206 \text{ kJ/mol} \quad (13) \]
\[ CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2 \quad -36 \text{ kJ/mol} \quad (14) \]

### 4.2 Gasification technology

Gasification is not a new technology. Originally it was developed in the 1800s and was then a process used to make town gas for lighting and cooking. Small scale gasifiers were also used to power internal combustion engine vehicles during fuel shortages in the Second World War. Today, gasifiers that are used on an industrial scale to gasify biomass differ from one another mainly by the mode of contact between feed material and gasifying agent, mode and rate of heat transfer and residence time of fed material into the reaction zone.

Different technological solutions can be implemented in order to obtain different plant configurations; in particular, the mode of contact of the biomass with the gasification agent may be in counter-current, or co-current, or cross flow, and the heat can be transferred from the outside or directly in the reactor using a combustion agent; the residence time can be in the order of hours (static gasifiers, rotary kiln) or min (fluidized bed gasifiers). The gasifying agent is a mixture of steam, air and/or oxygen in different
proportions depending on operating demands. A general input of oxygen or air makes it possible to reach high temperatures without any extra energy input. Air gasification results in a product with low to medium heating values (4–7 MJ/N m), while gasification with oxygen or steam leads to a product with medium heating values (10–14 MJ/N m). If steam is being used, more hydrogen is produced from the methane reforming reaction. This leads to a product stream with higher heating value. Nevertheless, gasification with steam requires higher operating temperatures for the vaporization of water which makes it a more costly alternative. Therefore, it is considered to be more useful to use a mixture of air/steam with a variable inlet ratio in order to better exploit the benefits of each fluidizing gas.

The gasifiers are usually operated at high temperatures, over 800°C, and in order to handle different types of feedstocks and operational demands various types of gasifiers have been developed. They can be categorized into three types; fixed bed, fluidized bed and entrained flow gasifiers. In applications of larger scale the entrained flow or fluidized bed gasification is more employed and in small scale gasification the fixed bed technology is more frequent. It is a common opinion that the updraft gasifiers produce more tars with a high portion of primary tars, fluidized bed gasifiers are intermediate and the tars formed are mainly a mixture of secondary and tertiary tars and the downdraft gasifiers are the cleanest with an almost tertiary tar.

Table 1: Main characteristics for common industrial gasifiers

<table>
<thead>
<tr>
<th>Gasifier</th>
<th>Characteristics</th>
</tr>
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<tbody>
<tr>
<td>Fixed bed</td>
<td>Can handle large and coarse particles</td>
</tr>
<tr>
<td></td>
<td>Release lower temperature gas product</td>
</tr>
<tr>
<td></td>
<td>High particulate content in gas product stream</td>
</tr>
<tr>
<td></td>
<td>High gasifying agent consumption</td>
</tr>
<tr>
<td></td>
<td>Ash is removed as slag or dry</td>
</tr>
<tr>
<td>Fluidized bed</td>
<td>Uniform temperature distribution</td>
</tr>
<tr>
<td></td>
<td>Better gas-solid contact</td>
</tr>
<tr>
<td></td>
<td>High operating temperature (1000-1200°C)</td>
</tr>
<tr>
<td></td>
<td>Low particulate content in the gas stream</td>
</tr>
<tr>
<td></td>
<td>Suitable for feedstocks with low ash fusion temperature</td>
</tr>
<tr>
<td></td>
<td>Ash is removed as slag or dry</td>
</tr>
<tr>
<td>Entrained flow</td>
<td>Need finely divided feed material (&lt;0.1-0.4mm)</td>
</tr>
<tr>
<td></td>
<td>Very high operating temperatures (&gt;1200°C)</td>
</tr>
<tr>
<td></td>
<td>Not suitable for high ash content feedstock</td>
</tr>
<tr>
<td></td>
<td>Very high oxygen demand</td>
</tr>
<tr>
<td></td>
<td>Ash is removed as slag</td>
</tr>
<tr>
<td></td>
<td>Short residence time</td>
</tr>
</tbody>
</table>
Regardless of gasifier type and configuration, their operation results in four common main steps namely drying, pyrolysis/devolatilization, reduction and combustion. In the drying part of the gasifier the fuel is stripped of its moisture content (which may be high for biomass feedstocks). In the following pyrolysis zone volatiles are removed in the form of light hydrocarbons, CO and CO2, but here are also produced some tars. The reduction zone in the gasifier functions as the key process, in which the biomass is fully gasified using oxygen from the air and/or steam to form syngas through a series of endothermic reactions. In the final combustion section, the residual char is burned producing more gaseous products and the necessary heat for the reactions in the reduction zone.

![Diagram](image)

*Fig 2: Typical gasification temperatures for various feedstock and influence of temperature change on some critical factors, as reported by Hallgren*¹²

### 4.2.1 The fixed bed gasifiers

The fixed bed gasifiers are simpler in set-up and operation, which makes them more suitable for small-scale applications in the range of a few hundred kWth. The feedstock is fed from the top, but the inlet gas/air may be fed either from the top, as in a downdraft gasifier (see figure 3 below) or from the bottom of the reactor, as in a downdraft gasifier. The cross-flow gasifier has the intake of gas on the side of the reactor. Due to the altered mixing and flow conditions in each of these set-ups, their final product gases may be very different in terms of temperature and composition, their content of tar and particulates and their thermal efficiency. For example the downdraft gasifier has the advantage of lower tar content as the gas moves along with the fuel through the hot reaction zone."
4.2.2 The fluidized bed gasifier. In this system a bed of fine inert material sits at the gasifier bottom with air, oxygen or steam being blown upwards through the bed. The result is a turbulent mixing of solids and gas and the tumbling action, almost like a bubbling fluid, offers more effective chemical reactions and heat transfer. Biomass is fed through a screw in from the side of the reactor, it mixes with the bed material and gas and subsequently combusts or forms syngas which leaves upwards. This gasifier mainly operates at temperatures below 900°C to avoid ash melting and sticking. The set-up of a fluidized bed can be modified in several ways. For example the bed may be circulated so that a mixture of syngas and particles are carried into a cyclone where the collected material is returned to the gasifier. This is called a circulating fluidized bed, CFBG. There may also be two connected (dual FB) beds, where one is a combustor and the other a gasifier. The char formed in the gasifier is transported into the combustor where it is burnt to generate a heated bed material that is transferred back into the gasifier to provide heat for the gasification reaction. These systems may also be pressurized. In a given fluidized bed gasifier set-up, the operator can alter a number of parameters or input variables to affect the process and its outcome such as biomass properties and feed rate, inlet gas composition or choice of bed material.
4.2.3 **Entrained flow gasifier.** In an entrained flow gasifier a fine powder of biomass is injected or sprayed into the pressurized reactor together with oxygen and/or steam and burns like a pilot flame creating very high temperatures (1200-1500°C). This results in a fast conversion of biomass into a high quality syngas. Ashes formed in these high temperatures melts onto the walls of the gasifier and are collected as molten slag. The figures below shows two different designs for EF gasifiers where the slag being formed is solidified under slightly different conditions.

![Figure 4; Circulating fluidized bed gasifier](image1)

![Figure 5; Entrained flow reactors with different slag formation systems](image2)
5 Tar formation

During gasification the thermochemical processes may produce hundreds or thousands of diverse organic substances, also known as tars. The formation and its outcome are strongly affected by the operating parameters, such as fuel type and processing conditions. As an example, wood as a fuel for gasification has shown to produce larger amounts of tars that also have a greater share of stable aromatic compounds compared to the gasification of coal or peat. Tar formation is considered to be one of the major problems to deal with during biomass gasification. Many tar substances condenses at reduced temperature, thus blocking and fouling onto process equipment such as engine parts, turbines and catalysts. It also signifies a loss of product values from the fuel, as the tar formation reduces the building blocks for valuable (syn-) gases. Several of the tar substances are also considered as harmful, both to health and environment.

Organic substances are produced during gasification under thermal or partial-oxidation regimes. They are generally assumed to be largely aromatic but there is no unique definition. Instead, the diversity in the operational definitions of “tars” usually comes from the variable product gas compositions required for a particular end-use application and how the “tars” are formed, collected and analyzed. According to the IEA Gasification Task meeting it was stated that; “all organics boiling at temperature above that of benzene should be considered as tar”. In this thesis this definition is used. The classification of tars is often connected to their appearance. Primary tars consist mainly of oxygenated compounds that are generated at 400-700°C. Secondary tars contain olefins and phenolic compounds and they are generated at 700-850°C. At 850-1000°C tertiary tars are formed which consist of aromatics, such as PAH:s. Other ways to classify tars may be by their gravimetric properties or by molecular weight.
Gasification generally means a restricted access to the oxygen needed for complete combustion. Tars are formed in a series of intricate gasification reactions and their formation outcome is highly dependent on the gasifying conditions. Due to increased reaction temperature, secondary reactions occur in the gas phase which convert oxygenated tar compounds to light hydrocarbons, aromatics, oxygenates and olefins, subsequently forming higher hydrocarbons and larger PAH in tertiary processes. The tar formation scheme proposed by Elliott is presented below\textsuperscript{17}:

Fig 6: Tar formation scheme as proposed by Elliott, 1988

A more intricate and systematic scheme for biomass conversion, also showing the formation of secondary and tertiary products and the coupling of the products, has been suggested by Evans and Milne\textsuperscript{18} (fig 7)

Figure 7: Scheme for biomass conversion, suggested by Evans and Milne
The biomass composition mainly comprises lignin, cellulose and hemicellulose. Table 2 shows the estimated contents in some types of biomass\textsuperscript{19,20,21}.

Table 2: Approximate analysis of some types of biomass

\textsuperscript{a} Other refers to organic compounds such as starch and inorganics.

<table>
<thead>
<tr>
<th>Type of biomass:</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
<th>Other (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>41</td>
<td>24</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>Hardwood</td>
<td>39</td>
<td>35</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>40</td>
<td>28</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>Rice straw</td>
<td>30</td>
<td>25</td>
<td>12</td>
<td>33</td>
</tr>
<tr>
<td>Bagasse</td>
<td>38</td>
<td>39</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Oak wood</td>
<td>34,5</td>
<td>18,6</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>42,1</td>
<td>17,7</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Birch wood</td>
<td>35,7</td>
<td>25,1</td>
<td>19,3</td>
<td></td>
</tr>
<tr>
<td>Spruce wood</td>
<td>42,1</td>
<td>20,9</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

In dry biomass the lignin fraction normally consists of 20–30 wt% dry of biomass. Lignin is a complex racemic polymer; an example of a typical lignin structure is shown in Fig. 8. The lignin fraction in the biomass are the only aromatic compounds, so it is a potential precursor to PAH:s. Lignin is considered as one of the most difficult to decompose during biomass pyrolysis, and is known to produce non-condensable gases, char and condensable tars at temperatures below 700\textdegree C, and the decomposition takes place in a broad temperature range because of the activity differences in the lignin aromatic ring bonds\textsuperscript{16}.

Woody biomass contains approximately 40% cellulose. Studies have shown that the pyrolysis of cellulose will produce levoglucosan as an intermediate product, which then may be converted to tar compounds. Besides levoglucosan, other primary tar components may also be produced from cellulose pyrolysis\textsuperscript{22}.

Hemicellulose is a complex component of biomass that may contribute to 20-35% of the dry weight. It is interconnected together with cellulose by physical internixing, and is linked to lignin by covalent bonds. In lignocellulosic biomass hemicellulose is the least stable polymer and is not chemically homogeneous. Hemicellulose is the least thermally stable biomass component, so it decomposes faster and at lower temperatures than cellulose and lignin\textsuperscript{23}. 
According to the reaction paths suggested for lignin, cellulose and hemicellulose follows:

The primary process products in biomass gasification consist of cellulose-derived compounds, such as levoglucosan, hydroxyacetaldehyde, and furfurals; analogous hemicellulose-derived products; and lignin-derived methoxyphenols. The products produced in the secondary processes are characterized by phenolics and olefins. In the tertiary processes alkyl tertiary products are formed, including methyl derivatives of aromatics such as methyl acenaphthylene, methylphenalene, toluene, and indene.

Condensed tertiary products are also formed, such as the PAH series without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, and pyrene.

The primary and tertiary products are mutually exclusive. This means that the primary products are destroyed before the tertiary products appear. The tertiary aromatics may be formed from cellulose and lignin, although higher molecular weight aromatics are expected to be formed faster from lignin residues.

Figure 8: Cellulose (right), Hemicellulose and Lignin (left)
Based on their molecular weight, tars are often classified into groups, such as in table 3;

*Table 3: List of tar compounds classified into groups*\(^4\)

<table>
<thead>
<tr>
<th>Tar class</th>
<th>Class name</th>
<th>Property</th>
<th>Representative compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GC-undetectable</td>
<td>Very heavy tars, cannot be detected by GC</td>
<td>Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar</td>
</tr>
<tr>
<td>2</td>
<td>Heterocyclic aromatics</td>
<td>Tars containing hetero atoms; highly water soluble compounds</td>
<td>Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzopental</td>
</tr>
<tr>
<td>3</td>
<td>Light aromatic (1 ring)</td>
<td>Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility</td>
<td>Toluene, ethylbenzene, xylenes, styrene</td>
</tr>
<tr>
<td>4</td>
<td>Light PAH:s (2-3 rings)</td>
<td>2 and 3 rings compounds; condense at low temperature even at very low concentration</td>
<td>Indene, naphthalene, methylnaphthalene, biphenyl,acenaphthalene, fluorene, phenanthrene, anthracene</td>
</tr>
<tr>
<td>5</td>
<td>Heavy PAH:s (4-7 rings)</td>
<td>Larger than 3-ring, these components condense at high-temperatures at low concentrations</td>
<td>Fluoranthene, pyrene, chrysene, perylene, coronene</td>
</tr>
</tbody>
</table>
6 Cleaning and upgrading in biomass gasification

A key aspect to achieve a successful and economically feasible biomass gasification process is to deliver a product gas with high quality. As the end use application may differ, so will the qualities needed. The resulting gasification product gas may be divided into a gas phase and a condensable phase. The gas phase consists of a gas mixture that contains the gases that are incondensable at ambient temperature; generally CO, H₂, CO₂, and possibly some light hydrocarbons such as CH₄. If air is used in the oxidization step as a gasifying carrier, then inert N₂ is present in the gas phase. Minor components are NH₃ and inorganic acid gases (H₂S and HCl and possibly some minor gaseous compounds). The sums of minor components depend on the biomass composition. The amount of syngas may range in 1–3 Nm³/kg on a dry basis, with a LHV between 4 and 15 MJ/Nm³. These values may be greatly influenced by the gasification technology chosen and the operating parameters. Specific considerations are needed for the condensable phase, the tars, since it is made of several organic substances that can, once condensed, be compared to bituminous oil. Selecting the appropriate operating parameters, their proper system design and using the necessary additives and catalysts will reduce the need for a subsequent cleaning of the generated syngas.
Table 4: Typical syngas applications and associated cleaning requirements\textsuperscript{12}

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Application</th>
<th>IC Engine</th>
<th>Gas turbine</th>
<th>Methanol synthesis</th>
<th>FT synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate (Soot, ash, dust, char)</td>
<td>&lt;50 mg/m\textsuperscript{3} (PM10)</td>
<td>&lt;30 mg/m\textsuperscript{3} (PM5)</td>
<td>&lt;0.02 mg/m\textsuperscript{3}</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Tars</td>
<td>&lt;100 mg/m\textsuperscript{3}</td>
<td>&lt;0.1 mg/m\textsuperscript{3}</td>
<td>&lt;0.01 µl/dm\textsuperscript{3}</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Sulphur (H\textsubscript{2}S, COS)</td>
<td>&lt;20 µl/dm\textsuperscript{3}</td>
<td>&lt;1 mg/m\textsuperscript{3}</td>
<td>&lt;0.01 µl/dm\textsuperscript{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen (NH\textsubscript{3}, HCN)</td>
<td>&lt;50 µl/dm\textsuperscript{3}</td>
<td>&lt;0.1 mg/m\textsuperscript{3}</td>
<td>&lt;0.02 µl/dm\textsuperscript{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali</td>
<td>&lt;0.024 µl/dm\textsuperscript{3}</td>
<td>&lt;0.01 µl/dm\textsuperscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halides (primarily HCl)</td>
<td>1 µl/dm\textsuperscript{3}</td>
<td>&lt;0.1 mg/m\textsuperscript{3}</td>
<td>&lt;0.01 µl/dm\textsuperscript{3}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As shown in table 4 the main contaminants in gasification gas include particulates, tars and other inorganics. There are always some species present in the raw syngas that must be removed through gas cleaning. Within the techniques used for gas cleaning these are an increasing selection of old and new methods. Milne has, in 1998, proposed a scheme for various gas cleaning technologies presented in fig 9. In the following part some of the common ones will be briefly introduced.

\textbf{Fig 9: Gas cleaning technologies}\textsuperscript{25}
6.1 Particulates

Particles that are elutriated from a gasifier may have a size span of 1 mm to over 100 mm, and the composition may vary greatly depending on the feedstock composition and process set-up. Fixed bed gasification generally produces less particulates than fluidized beds. The bulk of the particulate matter is composed of inorganic compounds and residual solid carbon from the gasification of biomass, but also bed material or catalysts residues can be elutriated. The inorganic content includes alkali metals (potassium and sodium); alkaline earth metals (mostly calcium); silica (SiO2); and other metals such as iron and magnesium. Minor constituents may be present in trace amounts but primarily when using fossil feedstocks.

Several syngas applications require greater than 99% particulate removal. Common issues with particulate matter are fouling, corrosion and erosion, which cause efficiency and safety concerns if they are not addressed. There is a variety of technologies to remove particulates from gases that can be applied. To remove particulates from synthesis gas the following systems may be used; cyclones, electrostatic filters (ESP), barrier filters and (solvent) scrubbers and the particle separation can be performed at either high temperatures (with cyclones, ceramic filter candles and moving bed filters) or at low temperatures (with scrubbers and wet electrostatic precipitators). Cyclones may be used in a wide temperature range but the separation efficiencies are low. Cyclones are suitable for the initial particle separation step but normally the particle content in the clean gas remains too high. For the removal of particles over 10μm a conventional cyclone can be used, and the material collected may be reintroduced in the gasifier. But, for high temperature particle separation, filters containing ceramic filter candles or moving bed filters are needed as a following treatment to meet the clean gas requirements. As an example, ceramic cross flow candle filters are mostly used for dust removal from hot syngas.

For low temperature particle separation a number of other methods can be considered such as wet electrostatic precipitators, fabric filters and scrubbers. In either of these technologies other impurities also have to be taken into account. For example tar condensation can be a problem when using fabric filters or in scrubbing if water is used as scrubbing liquid. At the same time many of these separating techniques can have several functions for gas cleaning, such as tar removal (e.g. in scrubbers with solvent) or NH3 removal (in case of water scrubbers).
6.2 Sulphur

Sulphur compounds are well known to be corrosive to most metal surfaces and many syngas upgrading catalysts are very sensitive to sulphur in the process gas. Several sulphur cleanup technologies exist and they may be both dry-wet, low–high temperature and physical or chemical. Sulphur removal at high temperatures focuses on either SO₂ or H₂S. Traditionally SO₂ has been the focus compound scrubbed out of the process gas, but with the increasing amount of sulphur sensitive syngas applications the hot removal of H₂S has gained focus. A sulphur adsorption process generally includes three steps; reduction, sulphidation and regeneration. In the first step the solid sorbent (often a metal oxide) is first reduced to be prepared for chemical adsorption. The adsorbent then reacts with sulphur resulting in a metal sulphur compound. The original metal oxide is regained through a reversible reaction, also creating a sulphur oxide to optimally be collected, the sulphur being recovered and used.

6.3 Nitrogen

Nitrogen compounds are present mainly as ammonia, with some hydrogen cyanide formation being possible, and these substances cannot be removed by filtration. Instead they require wet scrubbing with water or other aqueous solutions. The alternative to wet scrubbing would be to leave the N compounds in the gas and use low-NOₓ techniques during combustion, or selective catalytic reduction of the nitrogen oxides in the flue gas.

6.4 Chlorine and alkali

Chlorine content in the biomass is converted mainly into HCl in the gas from the gasifier. The concentration is depending on both the feedstock and gasification conditions. To remove HCl a wet scrubbing technique is often applied, or the chlorine may be absorbed on an active material. Hot gas chlorine cleaning is best performed at 500-550°C and the most common technique is using alkali oxides, active carbon or alumina in fixed beds. Alkali components in the biomass, particularly Na and K compounds, are volatile at high temperatures and they may cause corrosion of ceramic filters and turbine blades. The best way to reduce alkali is to cool the gases to about 500 C to condense the compounds and then remove them by filtering the gas⁵.
### 6.5 Tars

The success of biomass gasification requires a reliable system that can deliver a quality gas product. In addition to the expense of the gasifier, another key contribution to the capital cost and outcome for a gasification project is the need for an adequate tar reformer. One of the decisive questions is often the tar content in the product gas. Figure 10 shows a typical composition of biomass tars but it is worth reminding that this composition is depending both on fuel type and gasification process.

![Fig 10: A typical composition of tars from biomass gasification](image)

The tar dewpoint is the temperature at which the real total partial pressure of tar equals the saturation pressure of tar. But as soon as the actual process temperature is lower than the thermodynamic tar dewpoint, the tar can condense out. The presence of tar can cause operational problems due to possible formation of aerosols, soot formation as a result of repolymerisation but also in case of tar interacting with other contaminants on fine particles. Furthermore, heavy tars may condense on colder surfaces downstream, leading to blockage. The end-use of the gas stream is also an important consideration when deciding which cleanup method to utilize. For more stringent applications such as fuel cells or catalytic conversion processes tar elimination from the product gas is a crucial objective in making gasification an interesting renewable alternative. On the other hand, applications such as combustion may benefit from methods that convert tar to other, less heavier, compounds rather than completely remove them from the gas stream. In this case, converting tars may only provide moderate tar reduction, but by retaining the carbon and hydrogen compounds it maintains the heating value of the gas stream. Conversion methods may also change the gas composition (such as increased carbon dioxide), which may also have a negative effect on the more stringent end applications.
Tar removal technologies can broadly be divided into two methodologies; treatments inside the gasifier, also known as primary methods, and hot gas cleaning after the gasifier, called secondary methods. Primary tar removal methods include a suitable selection of operating parameters, a proper gasifier set-up and the use of suitable bed additives or catalysts during gasification. Secondary tar removal methods include tar cracking, either thermally or catalytically, or mechanical techniques such as using cyclones or electrostatic filters.

For eliminating tars from producer gas four main approaches can be distinguished; physical separation, thermal cracking, non-thermal plasmas and catalytic cracking. The three last-mentioned methods can be regarded as attempting to reach chemical equilibrium for tar cracking reactions by increasing reaction rates\(^{12}\). The approaches may be applied in both primary (in-situ) and/or secondary (post-gasifier) set-ups for tar removal, depending on both the type of gasifier and what is the projected application for the process gas. Primary cleanup measures will be limited to thermal and catalytic cracking, using methods such as high temperatures, oxygen feed replacing air, or different bed materials/additives. The process gas will then achieve a quality sufficient for robust applications such as direct combustion\(^{29,30}\). Secondary cleanup, downstream of the gasifier, may employ any of the four approaches.

Although measures inside the gasifier (primary methods) may be fundamentally more ideal, they have not yet resulted in satisfactorily solutions. Some of the primary methods do result in low tar emissions, but suffer from disadvantages related to, for instance, limits in feedstock flexibility and scale-up, the production of waste streams, a decrease in cold gas efficiency, complex gasifier constructions, and/or a narrow operating window. So, even if primary measures can reduce the tar content considerably, it is foreseen that complete removal is yet not feasible without applying secondary measures\(^{31}\).

### 6.5.1 Physical separation

Many of the physical removal techniques, such as scrubbing and electrostatic precipitation, require lower temperatures in order to operate effectively. However, tar reduction by physical procedures may still occur at higher temperatures by using the partial condensation of the tars. When temperatures fall below 450°C, tars begin to condense and form aerosols within the gas stream that resemble the particulates that can be removed by physical techniques such as ESP and inertial separation devices. But the mechanical separation of tar aerosol droplets would still require partial cooling of the gas stream, which limits the high temperature potential and efficiency of the technique\(^{32}\).
In wet scrubbing of cold gas the selection of the scrubbing solvent is critical in maximizing for the removal efficiency. Water has been used for scrubbing tars from syngas primarily because it is cheaper and the low-weight and oxygenated tar compounds can be readily removed by water scrubbing due to their inherent polarity. But the non-polar, heavy and/or heterocyclic tar compounds have lower removal efficiency. There is also a cost for treating the resulting waste water stream from the scrubber. Instead oil based absorbents are being developed that afford high removal efficiency, particularly for heavy and heterocyclic tar compounds. One of the earliest pilot-scale set-ups of oil-based tar scrubbers was demonstrated at the Energy Research Centre of the Netherlands (ECN) through their OLGA technology, an oil based scrubber that consists of multiple stage scrubbers where a special oil is the scrubbing solvent and this can be regenerated by hot air stripping. There are systems with other adsorbents such as FAME or vegetable oils, all outperforming water as adsorbents but they are still resulting in too high costs and complexity for small scale installations.

6.5.2 Thermal cracking
Thermal cracking methods are using high temperatures to decompose large organic compounds into smaller, non-condensable, gases. The temperatures are generally between 1100 and 1300°C, depending on residence time, with only seconds needed for effective tar reduction at the higher temperatures. This technique is regarded to reduce tar levels by more than a factor of 80 depending on initial tar concentrations.

The high temperatures needed for thermal cracking may be generated in different ways. High temperature gasifiers have a set-up that is designed to promote tar decomposition. The low temperature gasifiers on the other hand are known to produce excessive heavy tars. Tar conversion and reduction in low temperature gasifiers can be achieved by increasing the temperature of the product gas stream by admitting a small amount of air or pure oxygen downstream of the gasifier. Thermal cracking can also be obtained with heat exchangers, indirectly heating the gas stream by using hot surfaces.

Despite the conceptual simplicity of thermal cracking of tar, it has proved difficult and expensive to implement. The cost increases significantly for a more sophisticated high temperature gasification equipment. For thermal cracking methods downstream a gasifier an increased soot production may in turn increase the particulate load on cleanup or processing equipment.
6.5.3 Non-thermal plasmas

Plasmas are reactive atmospheres of free radicals, ions, and other excited molecules created by electrical discharges between two electrodes. The reactive species in the plasma are able to initiate decomposition of tar molecules. Plasmas can be generated by operation at temperatures far exceeding what is possible in gasification (thermal plasmas) or from high energy electron-molecule collisions (non-thermal plasmas). In non-thermal plasmas a high voltage and low amperage is used generating plasmas of several types, including pulsed corona, dielectric barrier discharges, DC corona discharges, RF plasma, and microwave plasma. Plasma can be used for cracking tars at temperatures below the thermal decomposition temperature. Pulsed corona plasma is considered to be one of the most promising of the non-thermal techniques, and reduces tar at optimal temperatures of about 200°C. These technologies have been proven effective in tar reduction, but the cost, energy demand, device lifetime and operational complexities have yet limited their application.

6.5.4 Catalytic cracking

Tar cracking consists of several important reactions (e.g. steam reforming, dry reforming, and partial oxidation), which may occur to different extents depending upon reaction conditions. In catalytic cracking the activation energy is reduced for the chemical tar decomposing reactions, hence lowering the costs associated with the high operating temperature needed for thermal cracking.

The reactor set-up may be primary, secondary or both. There is a variety of tar cracking catalysts and they are classified and referred to in many different ways, for instance based on their chemical mechanism, the operating conditions used, their resistance to different gasifying conditions or their material origin. The catalysts used often suffer from operational challenges that reduce the catalyst activity, typically involving poisoning, carbon deposition, sintering or fragmenting. The catalysts and their challenges will be further explained in the following chapters.
7 Catalytic tar reforming

In heterogeneous catalytic reactions, like tar reforming, the following steps occur;

1. Diffusion of gaseous reactants through the gas film surrounding the catalyst
2. Diffusion of reactants through the pores in the catalyst to the active sites
3. Chemisorption of the reactants on the active sites
4. Reaction between the active site and the reactants
5. Desorption of the gaseous products from the active sites, leaving room for new reactants
6. Diffusion of products through the pores of the catalyst to its surface
7. Product diffusing through the gas film surrounding the catalyst

Step 3-5 are steps that form new compounds, and as the steps are considered to take place in a series, the slowest is the rate-determining, controlling the reaction. The activity of the catalyst is highly dependent on the amount of active sites and the activity level in the sites. Temperature and other reaction conditions may also have an intrinsic effect on the catalytic performance.

Catalysts employed in decomposing unwanted hydrocarbons in gasification gas are responsible both for purification and bringing about a compositional adjustment of the gaseous product. Reaction conditions are modified with the catalyst so to match the gasifier set-up and desired gas composition. The raw gas passing the catalyst may be reformed either with steam, CO₂ or both to produce more CO, H₂ or CH₄. Reforming does not reduce the total chemical energy content of the product gas since heating of the raw gas to the higher temperatures for thermal cracking is not required.
Tar decomposition is a series of complex and simultaneous reaction, and the main ones during catalytic degradation of tars are:

\[
\text{Thermal cracking:} \quad pC_nH_x \rightarrow qC_mH_y + rH_2 \quad (15)
\]
\[
\text{Stream reforming:} \quad C_nH_x + nH_2O \rightarrow (n+x/2)H_2 + nCO \quad (16)
\]
\[
\text{Dry reforming:} \quad C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO \quad (17)
\]
\[
\text{Carbon formation:} \quad C_nH_x \rightarrow nC + (x/2)H_2 \quad (18)
\]
\[
\text{Water gas shift} \quad CO_2 + H_2 \rightarrow CO + H_2O \quad (19)
\]
\[
\text{Boudouard reaction} \quad C + CO_2 \rightarrow 2CO \quad (20)
\]

where \(C_nH_x\) represents tar, and \(C_mH_y\) represents a hydrocarbon with smaller carbon number than \(C_nH_x\). In addition to these reactions, different tars formed may also react with each other in several combinations. Due to these complexities, it becomes difficult to understand the exact behavior of catalytic tar degradation and reforming, and there is no single route\textsuperscript{38}.

Catalytic tar reforming technologies can roughly be divided into two methodologies depending on the position of the catalyst in the gasifier set-up; treatments inside the gasifier, also called primary catalysts that are added directly to the biomass prior to gasification either by wet impregnation or mixing the catalyst with the dry biomass. These catalysts mainly have the aim of decreasing the tar content and have little effect on the conversion of methane and C\textsubscript{2-3} hydrocarbons in the product gas. They operate under the same conditions as the gasifier and generally consist of cheap, disposable materials that usually are non-renewable. The primary catalytic, in-bed, methods are gaining extensive attention as these may have the ability to eliminate or reduce the needs for downstream cleanup, but at the present the so called secondary methods are more common, especially for high purity gas demands.

Hot gas cleaning after the gasifier is operated by so called secondary catalysts that are placed in a secondary reactor, either as a fixed or fluidized bed, downstream from the gasifier. Irrespective of what type of gasifier being used, they can be operated under different conditions than those of the gasification unit. The secondary catalysts are active in reforming hydrocarbons and methane\textsuperscript{39}. The use of a guard bed of an inexpensive catalytic material upstream of a more expensive catalyst reactor bed has been demonstrated to improve the life of the secondary catalysts\textsuperscript{40}. The inexpensive mineral catalyst converts many of the heavy tars, while the expensive catalyst aid in reducing tar concentrations to very low levels in the gas stream.
According to Sutton\textsuperscript{35} a summarization of some criteria for tar reforming catalysts would be:

- 1. The catalysts must be effective in the removal of tars.
- 2. If the desired product is syngas, the catalysts must be capable of reforming methane.
- 3. The catalysts should provide a suitable syngas ratio for the intended process.
- 4. The catalysts should be resistant to deactivation as a result of carbon fouling and sintering.
- 5. The catalysts should be easily regenerated.
- 6. The catalysts should be strong, regarding attrition/abrasion.
- 7. The catalysts should be inexpensive.

Adding steam and/or oxygen to the catalytic reactor may improve the catalytic tar reforming. By the addition of oxygen at 600–700°C the destruction of primary products accelerates and the formation of aromatics is inhibited. If benzene, the major building block in many tars, is being formed it cannot easily be decomposed by oxygen. Adding steam to the catalytic set-up has been reported to produce fewer refractory tars, enhance the formation of phenols, to reduce the concentration of other oxygenates, convert few of the aromatics and produce tars that are easier to reform catalytically\textsuperscript{23}. The addition of steam also enhances the water/gas shift reaction; greater amounts of steam introduced into the system will increase the H\textsubscript{2} and CO\textsubscript{2} concentrations and decrease CO concentration accordingly. This reaction is extremely beneficial for methanol production applications, as methanol production occurs most efficiently when the H\textsubscript{2}/CO ratio is 2. The H\textsubscript{2}/CO ratio for unprocessed producer gas is usually less than 1, and steam addition to a catalytic tar conversion system has demonstrated the ability to adjust the H\textsubscript{2}/CO ratio to levels as high as 13\textsuperscript{41}.

### 7.1 Traditional tar reforming catalysts

Catalysts are reviewed according to the following points: (a) chemical composition, (b) factors of catalytic activity for tar elimination, (c) factors of catalytic deactivation, (e) advantages and disadvantages, and (e) some important results of research on the catalyst. Tar reforming catalysts Abu El-Rub\textsuperscript{40} classifies catalysts by their origin as being mineral or synthetic. This approach will be used in this work as it is both simple and comprehensive. The two classes reflect the basis of their production method.

The mineral catalysts occur naturally and are relatively cheap and are easier to discharge. Examples are calcined rocks like dolomite and magnesite, but also ferrous ores, olivine and clay materials.
Synthetic catalysts are of a large variety, such as fluid catalytic cracking (FCC), alkali or transition metal-based, activated alumina, and char. They are relatively expensive as compared to the mineral catalysts, and also more sensitive to the harsh gasification conditions. Numerous efforts are being made to design synthetic catalysts for decomposing tar and at the same time increase the yield of valuables from the gasification. Modifying catalyst compositions may alter reaction rates, but furthermore increase the attrition resistance of the catalyst. Increasing catalyst durability would improve tolerance for the extreme conditions that often may be the case during high-temperature catalyst regeneration. An overview of the catalysts for tar elimination based on the classification by el-Rub is presented in fig 11.

7.1.1 Mineral catalysts:
Among the minerals the calcined rocks are considered to be the most efficient. They are often used as primary catalysts, but can also be used in guard beds for secondary catalysts. Calcined dolomites are the most widely studied basic solids as additives to the fluidized beds of gasifiers. This mineral is an inexpensive naturally occurring compound with calcium and magnesium with a molar ratio close to 1:1. By calcination at a temperature above 900°C, the carbonate decomposes which in turn results in the mixed oxide CaO-MgO. Dolomite is one of the most frequently used mineral catalysts and has a good
tar reforming activity, but it is prone to attrition resulting in fines in the process gas. This makes it more suitable for secondary reactors. In high-pressure systems the use of dolomite is less suitable as it may become decalcinated at high pressures. Dolomite is deactivated by carbonate formation and at 10 bar it may be needed to operate at a temperature above 920°C.

Olivines are regarded as promising materials for use as catalysts and/or catalyst supports in fluidized bed gasifiers. It is a crystalline magnesium and iron silicate, whose general formula $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ corresponds to a complete solid solution between forsterite $\text{Mg}_2\text{SiO}_4$ and fayalite, $\text{Fe}_2\text{SiO}_4$. It has the advantage of being attrition resistant, making it a suitable material for fluidization. Controlled calcination of olivine increases its mechanical resistance and increases its catalytic activity. Compared to dolomite, olivine is more resistant to attrition, but has less activity, but impregnating olivine with Ni or Fe has proven to largely increase the tar conversion activity in steam gasification.

Clay materials like kaolinite and bentonite are brittle and generally more sensitive to temperatures over 800°C as their porous structure tends to be degraded. Their catalytic activity is mainly due to their silica $(\text{SiO}_2)$ and alumina $(\text{Al}_2\text{O}_3)$ content and typically it is less than that of dolomite. These minerals also promote coking, a reason for reduced activity.

Ferrous metal oxides are minerals that contain appreciable amounts of iron. Various forms of iron compounds are known to catalyze both pyrolysis and tar decomposition but as they are sensitive to hydrogen deficiency there will be a risk of coke formation causing deactivation.

### 7.1.2 Synthetic catalysts

The synthetic tar reforming catalysts are chemically produced and more costly than naturally occurring materials. They are generally sensitive both to agglomeration (alkali metals), coke formation and poisons in the raw gas – problems that attract much attention in developing new catalytic materials. The most well-known group are the nickel containing catalysts and a majority of published literature on high-temperature steam reforming of hydrocarbons and methane concerns commercially available nickel catalysts.

**Transition-metal based**

Transition metal based catalysts are regarded as good catalysts for the reforming of methane and hydrocarbons. Nickel is cheaper and sufficiently active compared to other metals in the group, such as Pt, Ru, and Rh. The general composition of the Ni-based catalysts can be divided into three main...
groups: Elemental Ni, supported Ni, and Ni with promoters. The Ni would represent the active site of the catalyst whereas the support material gives the catalyst mechanical strength and protection against harsh conditions such as attrition and heat. Promoters such as Mg are used to stabilize the Ni crystallite size and K is used to neutralize the support surface acidity and thereby reduce coke deposition on the catalyst surface and enhance catalyst activity\textsuperscript{47}. These catalysts exhibit high activities for tar elimination and gas upgrading in biomass gasification and accelerates steam and dry reforming.

Ni-based catalysts can be deactivated in a number of ways and they can be summarized as: (a) Mechanical deactivation, which normally occurs because of attrition and loss of surface area through crushing. (b) Sintering which causes loss of surface area. (c) Fouling which occurs as a result of coking causing physical blockage of the catalyst surface area. (d) Poisoning which caused by strong chemisorption of gaseous impurities (mainly H\textsubscript{2}S) onto the catalyst active sites\textsuperscript{40}. These deactivation routes will be further presented in the next chapter.

The main advantages of Ni-based catalysts are their capacity to reach more or less complete tar elimination at temperatures of around 900 °C\textsuperscript{48} and also to increase the yields of CO and H\textsubscript{2}\textsuperscript{49}. Their disadvantages would be their rapid deactivation from poisoning and fouling, and also their relatively high price and the need for preconditioning the gas feed before it enters the catalyst bed to avoid rapid deactivation.

**Activated alumina**

Alumina can be activated by heating, which removes hydroxyl groups found in many minerals such as bauxite and aluminum oxide. The resulting compounds can only be approximated as Al\textsubscript{2}O\textsubscript{3} because they usually do not reach equilibrium and may still contain hydroxylated components to some extent. Activated alumina would then rather comprise of a series of non-equilibrium forms of partially hydroxylated aluminum oxides, Al\textsubscript{2}O\textsubscript{3}\textsubscript{12}. The catalytic activity of alumina is explained by the complex mixture of aluminum, oxygen, and hydroxyl ions combining to produce both acid and base sites on the material. It is highly deactivated by coke formation which is one of its main disadvantages. The advantage is that it has a relatively high activity, which is comparable to that of dolomite\textsuperscript{40}

Activated alumina is often used in catalyst formulations because of its high mechanical and thermal stability, as well as a relatively high activity (similar to dolomite).
Alkali-metal carbonates
Alkali metals, mainly K and to a lesser extent Na, exist naturally in biomass. To reduce the tar content, the K/Na-containing ashes can be used as primary or secondary catalysts. They can also be used directly as catalysts in the form of alkali metal carbonates or supported on other materials such as alumina. They are considered as effective catalysts for steam and CO₂ gasification of carbon⁵⁰

Alkali metal catalysts are often added directly to the biomass by dry mixing or wet impregnation. When added like this, the catalyst is almost impossible to recover, due to their volatility at the gasification temperatures, which may raise the costs for the process. It also increases the ash remnants after char gasification, and the disposal of this is expected to become a problem for the technology over the coming years⁴⁵.

FCC catalysts
Zeolites represent a well-defined class of crystalline aluminum silicate minerals whose three-dimensional structures are derived from frameworks of [SiO₄]₄⁻ and [AlO₄]₅⁻ coordination polyhedra ⁵¹. Their acidic (Brönstedt) properties depend on how they are prepared, the form, temperature of dehydration and the Si/Al ratio. The key properties of zeolites are structure, Si/Al ratio, particle size, and nature of the (exchanged) cation. These primary factors affect acidity, thermal stability, and their overall catalytic activity. FCC catalysts are used mainly to perform tar cracking reactions. Their disadvantage and loss of catalytic activity is mainly related to coke formation and sensitivity to substances, like steam, bases and nitrogen compounds that may react with the catalyst acidic sites. The advantages of using FCC catalysts would be their relatively low price and the long experience from using them in FCC units. The major disadvantage would be their rapid deactivation due to coke formation⁴⁰.

FCC catalysts that are used for catalytic tar reforming are often composite catalysts that are made up by one zeolite component and one matrix component consisting of mostly amorphous silica alumina. These catalysts are readily poisoned by substances whose molecules react with their acidic sites. Basic nitrogen compounds and alkaline metals in the feedstock has this poisoning effect⁵².

Char
Char can be defined as the solid residue obtained from pyrolysis by emitting volatile matters including tar and heavy hydrocarbons. Coke, on the other hand, may be defined as the solid carbon produced through the secondary pyrolysis of volatile matters. The definition of coke is clear, but the definition of char may be rather indistinct. In a strict sense the solid carbon is always a mixture of char and coke, but by optimizing pyrolysis conditions the char content may increase. Char may possibly be used by building up a filter cake.
Retaining the tar vapors at high temperature in this filter cake would increase their residence time and enable them to undergo secondary reactions. These reactions, occurring above 400°C have been shown to generate new or add to existing coke and char deposits while decreasing tar.12 Catalytic char may be deactivated by coke formation which in turn will decrease surface area and block the pores in the material. As char can be gasified in the reforming reactions there is also a risk of catalyst loss during gasification.40

7.2 Research Catalysts/New developments:

Most traditional tar reforming catalysts have inconveniences of some type, such as fouling, sintering, abrasion or poisoning. To eliminate or reduce these problems new kinds of catalytic materials are being developed. To avoid sintering problems the active catalyst species can be inserted in the structure of an inert support such as perovskite. To reduce carbon formation and polymerization reactions the catalyst may, at moderate temperatures, contain potassium components.53 By using materials that have strong redox properties is also possible to improve the tar reforming ability of the catalyst. Ceria (CeO2), for example, has a good red-ox reversibility which can be derived from its oxygen storage/release properties.54 Nickel has in some cases been used to enrich natural minerals, creating a hybrid between natural material and artificial catalyst in order to make it more stable than the conventional artificial catalyst. Co-impregnation of, for instance, nickel on a natural catalyst like olivine, dolomite or zeolite is often described in literature and can increase the stability to overcome the carbon deposition, increase the activity for decomposition of tar as well as reducing the cost for the gas-cleaning treatment. Ni-impregnation of calcinated olivine has been described to double the naphthalene conversion.55 By promoting transition metal-based catalysts with various elements one may get a positive effect on catalyst activity, its reducibility and ability to be regenerated, as to its coking resistance. Sometimes promotion also leads to improved mechanical strength and attrition resistance.56 Activated carbons or charcoals are also widely used as catalyst supports for the conversion of tar, not only because the dispersion of metal ions which is improved by their macro- and mesoporous structure, but also due to the facilitated transport of reactant molecules into the internal surfaces of the catalyst. Activated carbon has a high affinity and adsorption selectivity to hydrocarbon compounds such as asphaltenes but also facilitate transport of reactant molecules such as toluene into its internal surfaces.57 Particularly the mesopores of the activated carbons are believed to play a significant part in effective conversion of heavy hydrocarbons into lighter ones, while maintaining a low carbon/coke formation.58
7.3 Substituted hexaaluminates

The general hexaaluminate structure is layered and built by Al-O blocks; four oxide layers thick and has a spinel-like structure. These spinels are separated by mirror planes where large cations are situated that balance the charge of the spinel block. It is assumed that the introduction of a transition metal ion into the hexaaluminate lattice will result in active sites that are well spread and less prone to vaporization, sintering or carbon deposition since it is only the atoms on the surface that are exposed. A replacement of parts of the Al sites in the lattice by transition elements will create ability for oxidation/reduction by the cations in the sites which are believed to be related to the catalytic activity in the crystal. The spinel blocks in the studies presented are materials that contain Ni, a well-investigated active metal in cracking-catalysts. The structural components are Al and O and the mirror plane large cation is substituted for Ba. The general formula in this structure may then be expressed as BaNi$_x$Al$_{12-x}$O$_{19-\delta}$ where $x$ is the substitution level for Ni. Substituted hexaaluminates have not yet been used as catalyst for tar reforming, but have previously been reported as promising candidates for i.e. catalytic combustion, steam reforming of methane and reforming of n-tetradecane.

![Figure 12: Substituted hexaaluminate where Ni would partially be substituting Al](image)
8 Catalyst deactivation

There are many mechanisms of solid catalyst deactivation. According to Argyle, they can be grouped into six intrinsic mechanisms of catalyst decay: (1) thermal degradation, (2) fouling, (3) poisoning, (4) vapor compound formation and/or leaching followed by transport from the catalyst surface or particle, (5) vapor–solid and/or solid–solid reactions, and (6) attrition/crushing. Mechanisms 3, 4 and 5 are chemical by nature, mechanisms 2 and 6 are mechanical while 1 can be regarded as a thermally induced process. Accordingly the general reasons for deactivation may be regarded as chemical, mechanical, and thermal. These six basic mechanisms are briefly defined in Table 5. Sintering, poisoning and fouling are further described in this following chapter.

Table 5: Six mechanisms affecting catalytic activity

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal degradation/Sintering</td>
<td>Thermal or Thermal/Chemical</td>
<td>Thermally induced loss of catalytic surface area, support area and active phase-support reactions</td>
</tr>
<tr>
<td>Fouling</td>
<td>Mechanical</td>
<td>Physical deposition of species from gas/fluid phase onto the catalytic surface and its pores</td>
</tr>
<tr>
<td>Poisoning</td>
<td>Chemical</td>
<td>Strong chemisorption of species on catalytic sites which block active sites</td>
</tr>
<tr>
<td>Vapor formation</td>
<td>Chemical</td>
<td>Reaction of gas with catalyst phase to produce volatiles</td>
</tr>
<tr>
<td>Vapor-vapor and solid-solid reactions</td>
<td>Chemical</td>
<td>Reaction of vapor, support or promoter with catalytic phase to produce inactive phase</td>
</tr>
<tr>
<td>Attrition/Crushing</td>
<td>Mechanical</td>
<td>Loss of catalytic material due to abrasion, loss of internal surface area due to mechanical-induced crushing of the catalyst particle</td>
</tr>
</tbody>
</table>
8.1 Thermal degradation and sintering

Catalyst deactivation induced by high temperatures may either depend on loss or transformation of catalytic surface area, loss of support surface area or chemical conversion of catalytic phase to non-catalytic. The last example is a solid-solid reaction or solid state transformation occurring at high temperatures resulting in a new bulk phase, (and presumably the associated surface phase) which would lead to a decreased activity. These processes may include both metal oxide catalysts and metal-supported catalysts. The two first examples are often referred to as “sintering” and will be further explained below. In addition to a decrease in the surface area, sintering may also lead to a decrease in the pore openings, and ultimately the pores may close completely which would make the active species inaccessible to the reactants.

Sintering can be described a process where small particles grow in size. The driving force for sintering is to minimize the surface energy, which is lesser for large particles than for small. Therefore, small active particles are thermodynamically more unstable and if they are given enough energy they will be susceptible to reorganize to form larger particles. This would result in a decreased surface free energy and a loss of active surface area. Sintering processes usually take place at high reaction temperatures (e.g. >500°C). These thermal deactivation reactions are generally slow but non-reversible, which makes any catalyst preserving method more prone to preventive actions instead of regeneration methods. The sintering rates increase exponentially with temperature; activation energies are on the order of 15–100 kJ/mol. There are some principal parameters that affect the sintering rate; temperature, chemical environment, metal type and metal dispersion, promoters or impurities, support surface area, texture and porosity. The most important parameters are the sintering temperature and the atmosphere over the catalyst. By increasing the temperature a significantly faster sintering process starts. The presence of water in the reaction is also considered to greatly accelerate the sintering process. Hence the combination of very high reactor temperatures and process steam can be expected to cause severe sintering and loss of surface area in many catalyst used in biomass gasification.

Sintering may take place both in supported metal catalysts and in unsupported. In a supported metal catalyst two models are suggested that describe the complex mechanism; In the atomic migration model metal atoms are transported from smaller crystallites across the support surface (or in the gas phase) into the more stable larger crystallites in the material hence causing a general increase in crystallite size in the material and decreasing surface area. In the second model, the crystallite migration model, the crystallites migrate along the support surface to collide and coalesce with each other. Both mechanisms have a number of rate-determining steps, such as metal-particle
spreading on the support, the dissociation and emission of metal atoms or metal-containing molecules from the metal crystallites or the adsorption and trapping of metal atoms or metal-containing molecules on the support surface\textsuperscript{61}. The particle migration mechanism is dominating at lower temperatures while particle coarsening through atomic migration is dominating at high temperatures\textsuperscript{70}

8.2 Fouling/Coking

Coking is an important side reaction in many industrial catalytic processes. Very often, measures to eliminate or depress coke formation are more decisive for the process design than for instance the catalyst activity\textsuperscript{71}. Fouling means a physical or mechanical deposition of species from the gas phase that settles on the catalyst surface. This may result in blockage in both pores and active sites and, in an advanced stage, plugging of the reactor. In biomass gasification the deposition of carbon and coke are the most important examples. The definition of coke and carbon are not completely consistent, but commonly they are defined in relation to their origin. Carbon would then be the product from disproportionation of CO, and char is the product from decomposition or condensation of hydrocarbons on the catalyst surface\textsuperscript{59}. There are a large variety of coke, from high molecular weight formulae to primary carbons as graphite, the form depending on the reaction conditions, catalyst type and how they were aged. It has been suggested\textsuperscript{72} that the catalytic reaction accompanied by char or carbon formation can roughly be regarded as coke-sensitive or coke-insensitive. The coke-insensitive reactions have relatively reactive coke being formed on catalytic active surfaces that are readily removed by gasifying agents as hydrogen. In a coke sensitive catalytic reaction an unreactive coke deposition causes deposition and activity decline. It is also proposed that it is the location and structure of the coke being the most important factors in affecting the catalytic activity, not the amount.

Coke formation cannot be considered a simple one-step transformation of different chemical species. Instead it must be seen as sequence of reaction steps that gradually lead to the formation of coke. The mechanisms for coke formation and the subsequent carbon deposition have some significant differences when comparing metal catalysts with oxide or sulfide catalysts. Bartholomew suggests that for Ni catalysts the rate determining step would be the CO dissociating, leading to the formation of various forms of carbon. Initially as more reactive amorphous adsorbed atomic and polymeric carbons, substances that are over time converted into less reactive, graphitic forms of carbon.
The formation mechanism for coking on oxides and sulphides is believed to be quite complex. It can be regarded as a condensation/polymerization on the catalyst surface starting with olefins/aromatics that through dehydration, polymerization and carbonium-ions intermediates eventually form coke-type structures whose chemical nature is highly dependent on under what conditions they are formed. To minimize coke formation Trimm suggests two approaches; assemble size control, i.e. by controlling the number of sites in an ensemble, it may be possible to minimize coking whilst maintaining steam reforming as coke formation would require an ensemble of surface sites that would be larger than that required for steam reforming. The second approach is based on the idea of preventing the formation of carbide, as it is an essential intermediate in char formation. One method is to add dopants to the catalyst that forms clusters on the catalyst surface and hereby decreases coke formation. Coke deactivation is generally reversible in H₂, steam, CO₂ or O₂.

8.3 Poisoning

Poisoning occurs when the catalytic activity is lost or decreased due to strong chemisorption onto active sites in the catalyst by impurities in the gas stream. Therefore, the term poisoning has operational significance; meaning that whether a species acts as a poison would depend upon its adsorption strength compared to the other species that compete for the same catalytic sites. Upon poisoning the total catalyst activity may be decreased without acting on the selectivity, but often the selectivity is affected since some active sites may be deactivated and some may be, to some extent, unaffected. Multifunctional catalysts, that can at once promote varying chemical transformations, have active sites of different nature and may remain selectivity for certain reactions while others are inhibited. A poison may either have a geometric effect by blocking an active site or it may have a reconstructional effect by modifying the chemical nature or forming new compounds in the active site. A poison may also alter the adsorptivity of other species essentially by an electronic effect or cause.

Raw gas from gasified biomass can contain up to a few hundred ppm of sulfur. An exception is flue gas from gasified black liquor derived from the paper industry which can contain more than 3000 ppm of sulfur. Sulfur is a serious and frequent poison for nickel containing steam reforming catalysts as a sulfur-poisoned nickel catalyst has essentially no activity below 700°C. At reforming conditions it is generally regarded that all sulphur containing compounds in the feed are converted to H₂S and its sulphur atom strongly adsorbs on the nickel surfaces of the catalyst. A compound like H₂S has unshared electron pairs and this may lead to very strong chemisorption on the
metal surface. In reducing conditions the adsorption on the metal is typically dissociative which leaves a reduced sulfur atom that is strongly bonded to the nickel surface. The maximum sulfur uptake in a catalytic reformer is proportional to the available nickel surface area and the shape of the catalyst pellet. Tolerance to H₂S may be critical for tar reforming catalysts because sulfur is difficult to remove at gasification temperatures.

Generally, catalyst poisoning can be either a reversible or an irreversible process. Irrespective of what, the deactivation effects are the same while the poison is adsorbed. Sulphur chemisorption on a nickel catalyst is reversible, and the catalyst may be regenerated i.e. by steam, H₂ and CO at temperatures about 800°C. Sulfur resistance, or the rate of deactivation, can be a function of catalyst properties (such as composition, physical and chemical properties of the support and promoter type) and reaction conditions (specially the temperature and the sulfur concentration). Sulfur tolerance, on the other hand, is independent of the physical properties of the catalysts and is rather an inherent property of the metal. It is mainly a function of the strength of the metal-sulfur bond. As nickel catalysts are considered to be one of the best for catalytic tar treatment, large efforts has been made to try to improve the resistance of the nickel catalyst. One way is to promote it, for example with oxides of Li, K, Ca, and Mg. Another would be to use a regenerable so called sulphur guard in order to reduce H₂S in the gas feed before the catalyst. Modifying the catalyst support and adjusting reaction conditions are also ways to reduce the impact of sulphur poisoning.

Chloride poisoning is especially problematic for Cu/Zn containing LT water-gas shift processes as it is normally present in process gas in non-detectable amounts and forms low-melting chlorides with the catalyst metals. The limits on HCl content to avoid catalyst poisoning are on the order of 1 ppb which is more severe than for H₂S poisoning. But it has been shown that chloride usually is retained by reacting at the inlet of the catalyst bed, with the result that the catalyst can be regarded as partially self-guarding. Organic bases such as ammonia are common poisons for acidic solids, as an example the silica-alumina and zeolites in cracking and hydrocracking reactions. Even small quantities can be harmful in some applications. Besides, to control nitrogen oxide emissions, gas turbines typically needs an ammonia concentrations less than 0.05 ml/l, but less than 0.05 µl/l may still poison some catalysts used to upgrade syngas. Acid gas removal units that are used for sulfur recovery may also have problems unless NH₃ is substantially reduced.
9 Experimental methods

This section gives an overview of the physical conditions in the experiments performed in this research work. Since the aim and set-up is slightly different for the three parts here presented, the experimental part is divided into three accordingly. The analytical procedures are described in a common, finalizing part.

9:1 High temperature water-gas shift step in the production of clean hydrogen rich synthesis gas from gasified biomass

In this investigation a commercial water-gas-shift catalyst is tested in a laboratory set-up. The effects of different parameters impact on the performance of the catalyst are investigated. In the lab test temperature influence of the catalyst activation(test1), long-time stability(test 2) and start-stop experiments (test 3) are made along with poisoning tests by H₂S (test 4), HCl (test 5), and NH₃(test 6) respectively. A test is also made for investigating the performance of two spent catalysts, previously exposed in a CFBG with two different fuels and flows (test 7 and 8).

Set-up
The laboratory set-up consists of a stainless steel reactor with an inner diameter of 10mm inserted in a tube oven and fed with a gas mix. The FeCr-catalyst in its active phase is a magnetite (Fe₃O₄) with Cr as a structural promoter in the form of Cr₂O₃. It has a particle diameter of 0.7-1mm and in the first three experiments both 1ml and 3 ml is investigated. In the poisoning experiments 3ml catalyst is tested and in the study of spent catalyst 1 ml is used. The gas composition in the inlet gas is chosen to try to equal a pressurized CFBG, as this was a part of the CHRISGAS project work. For all experiments the pressure is 100kPa and the volume fractions of gas
components are presented in table 6. For the poisoning experiments H₂S is diluted in N₂. NH₃ and HCl are fed into the system by the water injection in the steam generation unit.

**Table 6: Gas composition for the WGS experiments**

<table>
<thead>
<tr>
<th>(vol%)</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
<th>N₂+poison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>23,8</td>
<td>19,8</td>
<td>23,0</td>
<td>33,4</td>
<td></td>
</tr>
<tr>
<td>Test 2, 3, 7, 8</td>
<td>17,8</td>
<td>14,8</td>
<td>17,3</td>
<td>50,1</td>
<td></td>
</tr>
<tr>
<td>Test 4-6</td>
<td>15,2</td>
<td>12,6</td>
<td>14,8</td>
<td>42,8</td>
<td>14,6</td>
</tr>
</tbody>
</table>

Since the inlet gas already contains a mixture of CO, CO₂, H₂ and water, the conversion of CO or production of CO₂ and H₂ is not a satisfactory description of the state of the gas after the treatment in the integral reactor, without recalculating the new concentrations or partial pressures. Instead the CO₂-ratio (R_{CO₂}) of the total ingoing carbon (CO + CO₂) during the experiments is used:

\[ R_{CO₂} = \frac{CO₂}{CO + CO₂} \]

*Figure 13: Experimental laboratory set-up for WGS experiments*
9.2 Nickel-substituted bariumhexaaluminates as novel catalysts in steam reforming of tars

This work investigates the performance of Ba-Ni-hexaaluminate, BaNi₅Al₁₂₋ₓO₁₉ (BaNi₅HA), as a new catalyst in the steam-reforming of tars. Substituted hexaaluminates are synthesized and characterized. Steam reforming tests are carried out with both a model-substance (1-methylnaphthalene, 1-MNP) and in a slip-stream from a CFB gasifier. The water-gas-shift activity is studied in a lab-scale set-up.

Preparation of bariumhexaaluminate:
The different hexaaluminates are prepared by a co-precipitation method. The resulting gel precipitate is dried overnight at 105°C and then calcinated in air at 1200°C for 14 hours. After calcination the hexaaluminate samples are ground to a fine powder and this material is dispersed with a Böhmite binder with a proportion of 10% catalyst and 90% binder(wt%). This slurry mixture is dried at 120°C over night, calcined at 1200°C for 7 hours and finally crushed and sieved before use. Prior to testing the catalyst is in situ reduced with a stream of the hydrogen-containing process gas.
The α-alumina being used as an inert bed material to reduce the void in the catalytic reactor is crushed Almatis T-162 Tabulated Alumina Balls with a diameter of 1-2 mm and calcined at 1200°C for 7 hours.

Set-up of lab-scale experiments:
In the lab-scale set-up experiments, blank tests are made to investigate the possible activity in pure α-alumina and also the impact high temperature has on the uncatalysed process. In the same set-up the catalysts were furthermore investigated for steam-reforming and water-gas-shift activity. In the blank-test and in the steam reforming experiments, 1-methylnaphthalene (1-MNP) is used as tar model substance. A quartz tubular fixed bed micro reactor is placed in a vertical oven and 10 ml of catalyst with a grain diameter of 0.5-0.71mm was loaded on top of 17 ml α-alumina grains and covered by 17 ml α-alumina to minimize void gas.
In the blank test the reactor contained only α-alumina. A heated gas mixture also containing 1-MNP, is fed to the reactor operated at atmospheric pressure. The temperature is increased stepwise from 600 to 1000°C for a total time of 6 hours. The gas feed is added water for steam generation and pure, liquid 1-MNP.
In the WGS experiments a stainless steel reactor is used, containing 15 ml BaNi₅HA catalyst with the same particle diameter as in the blank experiments and a layer of α-alumina grains in both ends. A gas by-pass can be lead past the reactor in order to measure the composition of the unaffected gas. The gas feed consists of steam, N₂, CO, CO₂, H₂ and CH₄ in various concentrations. In
these experiments the reactor temperature is 300-900°C with a stepwise increase.

**Figure 14:** Experimental set-up for lab-scale experiments of thermal decomposition (blank test), WGS and SR of 1-MNP

**Table 7:** Gas feed concentrations (vol %) for Reforming test, WGS experiments and for Blank test/thermal decomposition experiments, before the addition of 1-MNP (10 g/ Nm³)

<table>
<thead>
<tr>
<th>Test</th>
<th>Blank test</th>
<th>Test WGS</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>CH₄</th>
<th>N₂</th>
<th>H₂O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reforming</td>
<td>1</td>
<td>1</td>
<td>16.7</td>
<td>16.7</td>
<td>16.7</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

**Slip-stream experiments, CFBG TU Delft**

The gasifier in Delft University of Technology is a circulating fluidized bed gasifier that operates on steam-oxygen at atmospheric pressure using 100kW maximal thermal input. The feeding system has an approximate maximum rate of 20kg biomass h⁻¹. The gas cleaning system consists of two high-temperature ceramic fiber tissue candle filters and a Si-SiC ceramic candle filter. The fuel used for gasification in these tests is a pelletized demolition wood fraction. The fluidized bed material is magnesite. For the catalytic tests a stainless steel reactor is placed in a vertical oven. In the tube a volume of 30 cm³ BaNiHA/Böhmite catalyst, with a grain diameter of 0.5-0.71mm, is loaded with a layer of alumina grains at both ends. A slip-steam from the
gasifier gas is fed to the reactor with a GHSV of 2500h⁻¹ based on the active catalyst. The reactor is operated at atmospheric pressure and the activity is studied at 850 and 950°C.

![Figure 15: Experimental set-up for slip-stream experiments at TU Delft](image)

**Table 8: Concentration of wet permanent gases and hydrocarbons in gasifier (vol %).** *Measured, condensed mass. Separate analysis. **As naphthalene, separate analysis*

<table>
<thead>
<tr>
<th></th>
<th>Ni-1-exp</th>
<th>SD_{m}</th>
<th>Ni-2-exp</th>
<th>SD_{m}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_{2}</td>
<td>8.5</td>
<td>0.48</td>
<td>9.7</td>
<td>0.54</td>
</tr>
<tr>
<td>H_{2}O*</td>
<td>57.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{2}</td>
<td>10.3</td>
<td>0.44</td>
<td>11.6</td>
<td>0.18</td>
</tr>
<tr>
<td>CO</td>
<td>4.2</td>
<td>0.26</td>
<td>4.7</td>
<td>0.15</td>
</tr>
<tr>
<td>CO_{2}</td>
<td>17.7</td>
<td>0.61</td>
<td>19.9</td>
<td>0.20</td>
</tr>
<tr>
<td>CH_{4}</td>
<td>2.0</td>
<td>0.11</td>
<td>2.2</td>
<td>0.034</td>
</tr>
<tr>
<td>BTX</td>
<td>1175</td>
<td>72</td>
<td>955</td>
<td>59</td>
</tr>
<tr>
<td>Tars**</td>
<td>260</td>
<td>1</td>
<td>155</td>
<td>1.9</td>
</tr>
</tbody>
</table>
9:3 Ba-Ni-hexaaluminate as a new catalyst in the steam reforming of tars. Long-term studies on sulphur deactivation and coke formation (manuscript)

This work investigates the long-term performance of Ba-Ni-hexaaluminate for the steam-reforming of methane or 1-MNP and the impact on the catalytic activity in the presence of H$_2$S in the feed gas, and the formation of coke during reforming. The tests are made in a laboratory set-up. The catalyst used is a BaNi$_1$Al$_{11}$O$_{19}$, prepared and calcined as before but now mixed with Böhmite binder with a ratio of 90:10. The grain size is 0.7-1mm diameter.

**Experimental set-up**

The reactor is made up by a stainless steel tube in a similar set-up as in the lab-scale test in 9.2. The bed consists of 15 ml catalyst, placed in the middle of the reactor resting on α-alumina in both ends. The gas feed consists of 1-MNP as a tar model, steam, N$_2$, CO, CO$_2$, H$_2$, CH$_4$ and H$_2$S in various concentrations with a total GHSV of 2500h$^{-1}$ based on the active catalyst. The catalytic reactor is placed inside of an oven in a vertical set-up. A gas by-pass can be lead past the reactor in order to measure the composition of the unaffected gas. Reforming tests are made at 850°C and 950°C for about 30h. A H$_2$S-recovery test is also made.

*Table 9: Gas feed concentrations (vol %) for testing H$_2$S poisoning and coke formation*

<table>
<thead>
<tr>
<th></th>
<th>Temp</th>
<th>CO$_2$</th>
<th>CO</th>
<th>H$_2$</th>
<th>H$_2$O</th>
<th>N$_2$</th>
<th>H$_2$S</th>
<th>CH$_4$</th>
</tr>
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<tbody>
<tr>
<td>CH$_4$ ref - Coke formation</td>
<td>850</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>24</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>24</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CH$_4$ ref - H$_2$S</td>
<td>850</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>24</td>
<td>0-300ppm</td>
<td>1</td>
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<tr>
<td></td>
<td>950</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>24</td>
<td>0-300ppm</td>
<td>1</td>
</tr>
<tr>
<td>1-MeNA ref - Coke formation *</td>
<td>850</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>25</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>950</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Me-NA ref - H$_2$S *</td>
<td>850</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>25</td>
<td>0-300ppm</td>
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<td></td>
<td>950</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>50</td>
<td>25</td>
<td>0-300ppm</td>
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</tr>
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9.4 Analytical procedures

Online gas measurements: The components in the produced gas are analyzed on-line by means of GC-FID for the hydrocarbons and micro-GC (TCD) for CO/CO₂/H₂/CH₄. The GC-FID is a Varian CP3800 equipped with heated sample distribution, an on-line injector and a CP-SIL CB8 capillary column. The micro-GC is a Varian CP4900 with a TCD detector and a Poraplot Q column for the determination of CO/CO₂ and a Molsieve 5A PLOT column for H₂. The FTIR-instrument is a Gasmet DX4000.

To further investigate and identify the decomposition products in the 1-MNP cracking experiments in 9.2, gas samples were taken using Tenax TA and analyzed by GCMS (Agilent GC7890/MS5975C). These results were used for identifying heavier major decomposition products.

Catalyst characterization: For the characterization of the catalytic materials several techniques are used, many in cooperation with the university of Bologna; The total metal content was analyzed by means of Atomic Absorption Spectroscopy. Measurements were performed by a Perkin-Elmer AAnalyst 400 Atomic Absorption Spectrometer with the following detection limits: Ba 0.5 ppm, Al 1 ppm and Ni 0.14 ppm. Thermal analysis was carried out by a Netzsch STA 409PC. The heating rate used was 15°C/minute, and the samples were heated in air from ambient temperature to 700°C. Powder X-Ray Diffraction (PXRD) analyses were carried out using a Philips PW1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit (λ = 0.15418 nm). A 2θ range from 10° to 80° was investigated (step size: 0.2°) at a scanning speed of 70°/h. Specific surface area assessment was carried out in a Micromeritics ASAP 2020 instrument. Calcined solids were heated up to 150°C until they reached a pressure of 30 µmHg, then kept 30 min at this temperature and finally heated up to 250°C and maintained so for 30 min. Temperature Programmed Reduction analyses were carried out with a H₂/Ar 5/95 v/v (total flow rate 20 ml/min) gas mixture in the 60-1050°C temperature range and 10°C/min heating in a ThermoQuest CE instruments TPDRO 1100. SEM/EDS analyses were performed by using an EVO 50 Series Instrument (LEO ZEISS) equipped with an INCAEnergy 350 EDS micro analysis system and INCASmartMap to image the spatial variation of elements in a sample (Oxford Instruments Analytical). An accelerating voltage of 20kV was applied with a spectra collection time of 60s. XRF measurements were performed in a PANalytical Axios Advanced WD-XRF (wave length dispersive x-ray fluorescence) Spectrometer equipped with x-ray tube (Rh target), working at 4kW. The pellets to be analyzed (diameter 13mm) were prepared by mixing 0.300g of the sample with 0.100g wax (binder) at 100kN for 120 min.
10 Results and discussion of included papers

10.1 Paper I:

The temperature dependency for the FeCr WGS-catalyst activation was investigated and showed that, for a fast activation of the catalyst the set-up needs a temperature above 350°C (Fig 16).

The long-time experiments were made with 1ml catalyst and 3 ml catalyst respectively and went on for approximately 70h. They showed a slight decrease in activity after about 20h to become relatively stable at 70-75% compared to equilibrium conditions (Fig 17).
The start and stop experiments were made to find out if the shut-downs and restarts in industrial application have any negative effect on the catalyst performance. Three runs for 4h/day are made and the activity is calculated and plotted. It shows a slight initial decrease in activity which might be connected to the initial formation of magnetite in the catalyst.

The three poisoning tests show that there is no large influence from the 150ppm H₂S in the gas feed. HCl, on the other hand, show a rapid deactivation during the first hours with approximately 25% lower CO₂-ratio, which is then stabilizing for the remaining 30h on stream, but is then close to the inlet CO₂-ratio of 45%. NH₃ also deactivates the catalyst but the process is slower and appears to reach a relatively steady state after about 25h and the CO₂-ratio is then about 20% lower than the reference.
When studying the performance of the spent catalysts that had been exposed to product gas from a CFB gasifier, two lab tests were made. In test A the fuel was clean wood and the catalyst was passively exposed for the product gas for 24h with a temperature ranging from 100 to above 350°C. In test B the flow through the catalyst bed was forced to a SV of 3000h\(^{-1}\), but this was in fact decreasing to about 1400h\(^{-1}\) the first day and remained approximately 3000h\(^{-1}\) the second day. This test was made for 15h and the fuel was miscanthus. In test B the CO\(_2\)-ration is low from the start but decreases further to in principle reach the same ratio as the inlet gas.

This study suggests that the FeCr catalyst may indeed be activated in the produced synthesis gas if the temperature is above 350°C. At H\(_2\)S-levels of 0-150ppm it can be used for shifting synthesis gas without affecting the activity, but any presence of poisons like HCl and NH\(_3\) in the process gas must be considered since they seem to have a large impact on the performance on these catalysts. This deactivation, and measures for minimizing HCl and NH\(_3\), needs to be further investigated before FeCr catalysts can be used in large scale gasification in the purpose of producing hydrogen rich synthesis gas.
10.2 Paper II:

To estimate the impact on tar reforming of both using α-alumina as a filling material in the catalyst reactor and the general effect of thermal decomposition of tars, a blank test was carried out both in pure N₂ and in Delft model gas at increasing temperatures. This was compared to a catalytic decomposition on BaNi-hexaaluminate. The results show that there is indeed a thermal effect in the degradation of 1-MNP appearing at temperatures above 800°C, but the extent of conversion is largely increased by the catalyst.

![Figure 21: Thermal/α-alumina catalyzed decomposition (in %) of 1-methylnaphthalene in N₂ (Exp 1) and thermal/α-alumina catalyzed decomposition (%) of 1-methylnaphthalene in Delft model gas (Exp 2) compared to catalytic decomposition with BaNi(1)hexaaluminate (Exp 3).](image)

Steam reforming tests are carried out with both a model-substance (1-methylnaphthalene) and a slip-stream from a circulating fluidized bed gasifier. For the tests in lab scale a catalytic, heated reactor was used. An analysis of the products formed in the decomposition of 1-MNP was done by GCFID, showing the decrease in molecular mass for the compounds formed as the reactor temperature increased. The lift-off for the BaNiHA is estimated to 850°C. As shown in Fig 22 there is a decrease of 1-MNP of about 95% at 900°C.
In the pilot-plant tests a slip-stream of the product gas was passed through a heated catalyst reactor at 850°C and 950°C and the tars were sampled with SPA. Since there was an almost total decomposition of tars, only the 850°C is presented here. Two formulas of catalyst were tested. The catalyst named Ni-1 is a BaNi$_{0.63}$Al$_{11.37}$O$_{19}$ and the Ni-2 catalyst is a BaNi$_{0.88}$Al$_{11.12}$O$_{19}$. The results show that there is a significant effect of the catalyst for facilitating tar steam reforming.
The water-gas-shift activity is studied in a lab-scale set-up. To investigate if the catalyst not only reforms the tars but also shifts the gas towards equilibrium, tests were made with a focus on the composition of permanent gases before and after passing the catalytic reactor. Measured product gas concentrations for the two catalysts are compared to calculated WGS-equilibrium data in HSC software. The results show that the shift reaction approaches equilibrium at temperatures close to 500°C.

Figure 24: WGS study on BaNiHA. CO₂-ratio at different temperatures in experiment 1 with fits. Equilibrium data are calculated in HSC software
10.3 Manuscript III:

Coke formation: To investigate any formation of coke during steam reforming and its impact on the BaNiHA-catalyst performance, two studies were made in a lab-scale set-up under controlled experimental conditions. Gas compositions were set to be similar to actual CFBG conditions according to permanent gases and as a carbon source either methane or 1-methyl naphthalene was used. The different experiments were tested either at 850°C or 950°C and the time span was in the order of 23-29 hours. The spent catalyst samples were characterized to look for indications on coke formation and sintering. These results are still under evaluation and are only sparsely presented here.

The reforming of 1-MNP at 850°C remains at 100% during the test and no formation of coke has been detected either in thermogravimetric analysis, micro Raman or BET. The same applies for the test made at 950°C with 1-MNP.

![Figure 25: Conversion of 1-MNP at 850°C for totally 29h](image)

For the reforming of methane a slight decrease in conversion can eventually be anticipated at 850°C. A linear fitting for this test reveals that the slope is actually within the standard deviation. For 950°C there is a complete CH₄ conversion throughout the test. The characterization analysis by micro-Raman does not imply any coke formation for either of these tests, but the evaluation is still ongoing.
The results suggest that coke formation does not decrease the capacity for the catalyst to assist in decomposing 1-MNP, and also propose good results for CH$_4$ reforming, especially at higher temperatures. This can be explained by the characteristics of BaNiHA: Substitution of Ni atoms into the hexaaluminate lattice, spreading them, seem to restrict the formation of larger Ni clusters prone to coke formation. When this substitution of Ni is coupled with the presence of a larger di-valent metal cation, like barium, in the mirror plane of the hexaaluminate, the result is a catalyst that is both active in reforming and resistant toward carbon deposition. This result is consistent with a CH$_4$-CO$_2$-reforming study made by Gardner et al showing that the total amount of carbon deposited onto the catalyst surface increases with Ni substitution into the lattice, and decreases with increasing Ba/Ni ratio at the surface.

For the H$_2$S-poisoning the long term tests are made with a stepwise increasing H$_2$S concentration, running with 100ppm overnight. If the conversion is unaffected after approximately 23h the H$_2$S concentration is gradually increased to 300ppm in order to stress the BaNiHA-catalyst. In the methane reforming activity tests the catalytic activity ends immediately after adding 20ppm H$_2$S, both at 850 and 950°C. The reforming of 1-MNP is reduced to 60% conversion at 850°C (figure 27).
The conversion remains at 100% throughout the experiment at 950°C even at increasing concentrations of H₂S up to 300ppm (Fig 28). A slight rise in benzene content (fraction 2.7 in the diagram) can be seen as the concentration of H₂S increases. Fraction 12 is 1-MNP and the large peak at 23,3h (and adjacent peaks) is a sampling of reactor by-pass gas, representing the reactor-inlet gas composition used as a control sample.

![Figure 28; Reforming of 1-MNP with H₂S at 950°C. Results by GCFID](image)

In the methane reforming activity tests with H₂S the catalytic activity in BaNiHA ends immediately after adding 20ppm H₂S, both at 850 and 950°C. Even though the reforming of 1-MNP is reduced to 60% conversion at 850°C, it remains at 100% throughout the experiment at 950°C even at increasing concentrations of H₂S up to 300ppm. This suggests both that there are different mechanisms for reforming CH₄ and 1-methylnaphthalene on Ni-substituted bariumhexaaluminates, and that this material is a good candidate as catalyst for steam reforming of tars even in sulphur containing product gas.

A sulphur-recovery test was performed for methane reforming at 950°C, where 20ppm H₂S was injected for 1h and then turned off, repeatedly. Figure 29 (below) shows the performance for the first hours. The sulphur deactivation test shows that there is indeed a catalyst recovery after exposure to H₂S. Repeating the exposure will still imply a high recovery and after standing over-night in a low flow of N₂ at 100°C the catalyst is fully recovered indicating that the sulfur is reversibly adsorbed.
Figure 29: Recovery test for methane reforming in 20ppm H$_2$S at 950°C.
11 Conclusions

**WGS**
Depending of the end-usage of the gasification gas there might be need for shifting the gas. Using a WGS-catalyst may give a considerable increase of hydrogen yield. The trials made here with the FeCr-catalyst shows that it works in a H$_2$S-containing synthesis gas. The catalyst rapidly forms the active magnetite phase in sufficiently high temperatures, and in the presence of H$_2$S it forms the slightly less active form of FeS. The conversion to FeS is depending on various factors, such as temperature, pressure, steam, hydrogen and H$_2$S content in the synthesis gas. At low H$_2$S concentrations it may be assumed that this conversion is only partial and consequently these tests are made with a partially FeS-converted catalyst, which also seem to work. However, the FeCr catalyst is highly sensible to other poisons such as chlorides (HCl) and ammonia (NH$_3$) and it is also plausible that is will be sensitive to others like organic chlorides, amines and cyanides. We therefore see a need for gas cleaning of these substances before the WGS step when using FeCr catalysts.

**Substituted hexaaluminate as a catalyst**
The BaNi-substituted hexaaluminate has shown a good activity as a new catalytic material for tar reforming; both in lab-scale experiments with a tar model substance and in slip-stream test with actual CFBG process gas. It also cracks tar in H$_2$S concentrations up to 300ppm in lab-scale set-up and works in an actual process gas containing both sulphur and other contaminants. Identification of the degradation products from 1-MNP suggests that the degradation is a stepwise break-down.
The results from CH$_4$-reforming tests show that the BaNiHA is very sensitive to sulphur when it comes to decomposing CH$_4$ but is has good resistance to coke formation and in sulphur-free gas it has a high conversion of CH$_4$. The sulphur seems to be reversibly adsorbed, as there is indeed a recovery from sulphur poisoning. These findings suggests that BaNiHA could be a suitable catalyst for converting biomethane from methane rich synthesis gas, but not
for the production of pure synthesis gas if there are sulphur contaminants in the gas to be converted. The BaNiHA also showed a WGS activity. It is a high-temperature WGS catalyst that had a lift-off at above 400°C in the tests performed. This means that the produced syngas should have a composition, besides the CH₄, that is close to the thermodynamic composition at equilibrium.
12 Future research

The results from the tests of BaNiHA so far has shown this material to be a promising candidate for catalytic steam reforming of tars in biomass gasification, but further test can be done. Extended long-time tests in a pilot set-up would be of great interest as the catalyst so far has shown no indications on coke formation. This type of testing would also give an indication on the sensitivity for other poisons in the process gas. Another interesting question to continue working with, in a controlled lab-scale set-up, is why the reforming capacity of CH₄ and 1MNP differs in a sulphur containing gas and what the mechanisms are behind this behavior.

There are also the possibilities of testing other metals in the substitution of hexaaluminates, both the large cations and transition metals, in order to improve the performances of the catalyst. Tests have been made in other applications to synthesize substituted hexaaluminates both with La and Sr instead of Ba, and Mn, Co or Cr instead of Ni.

The hexaaluminate as a material is considered to be a very hard and abrasion resistant substance, something that may imply that it would be suitable as an in-bed catalyst. In order to work as such the Ni would be a problem due to waste handling. But if a less environmentally problematic transition metal would show good properties in a reforming hexaaluminate catalyst the concept would be very interesting and, if a high tar reforming capacity can be achieved, may even eliminate the need for further secondary gas-cleaning steps.
Author’s contribution to presented papers

1. Planned and performed all practical work concerning catalyst performance for WGS in cooperation with main author. Assisted in writing this part.

2. Planned and performed all parts regarding the catalyst and its performance, both lab-scale and pilot testing, and some analysis on the catalyst material. Characterization was mainly made by University of Bologna. Evaluating and writing the main part of the work – cooperation with Bologna on the characterization part.

3. Planned and performed all parts regarding the catalyst and its performance and some analysis on the catalyst material. Characterization was mainly made by University of Bologna. Evaluating and writing the main part of the work – cooperation with Bologna on the characterization part.
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