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## Abstract

The effectiveness of three different catalysts regarding tar cracking and decomposition of syngas deriving biomass gasification in a fluidized bed has been investigated in this study. The catalysts that were tested were iron based, and commercially available nickel based and precious metal catalysts in order to compare their ability to decrease the amount of tar in the product gas. The catalysts were tested in different temperatures and residence times. The reference operating conditions were 800°C and a space velocity of 6500 1/h. The nickel based catalysts were proved to be the most effective by achieving conversion of ~99%, precious metal ~97% and iron based catalysts ~40%. The contribution of the thermal destruction was evident for the iron based catalysts; when the temperature was raised to the highest point (860°C) the conversion rose to ~70%. The blank experiment indicated that the contribution of the temperature is ~12% of conversion. For the iron based catalysts, some compounds such as naphthalene increased in the product gas, which indicates the stability of its molecule. However, when the temperature got higher, the only compound that didn't decrease was biphenyl. The iron and nickel based catalysts were stable, and no sign of deactivation was observed during the tests. As for the precious metal catalysts, the CH<sub>4</sub> in the product gas after the catalytic bed was initially ~0%, but gradually rose to ~5% and stabilized at this value. This could possibly indicate deactivation of the catalyst in the beginning, but it reached stability soon and remained in stable state during the whole experiment. The characterization of the iron based catalysts was realized before and after the tests to define the influence of the steam reforming on its surface (X-Ray Diffraction, BET surface measurement, SEM). The BET measurement of the iron material revealed that the active sites of the catalysts were reduced after its use, although that didn't affect its effectiveness regarding tar decomposition. The iron based catalysts need optimization in their structure. The particles were fine and soft, so they were blown away during the experiment. Possible evolution of their material could achieve higher tar conversion, particle strength and render them a feasible material for in situ use.

**Key Words:** Iron based catalysts, nickel based catalysts, precious metal catalysts, tar removal, biomass gasification

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## List of Abbreviations

<b>BET</b>	Brunauer, Emmett, Telle measurement
<b>BFB</b>	Bubbling Fluidized Bed
<b>CFB</b>	Circulating Fluidized Bed
<b>e.g.</b>	exempli gratia
<b>ER</b>	Equivalence Ratio
<b>FT</b>	Fischer-Tropsch
<b>GC/FID</b>	Gas Chromatographer/ Flame Ionization Detector
<b>ICE</b>	Internal Combustion Engine
<b>IGCC</b>	Integrated Gasification Combined Cycle
<b>LHV</b>	Lower Heating Value
<b>PAH</b>	Poly-Aromatic Hydrocarbons
<b>Redox</b>	Reduction-Oxidation
<b>SEM</b>	Scanning Electron Microscopy
<b>SNG</b>	Synthetic Natural Gas
<b>SPA</b>	Solid Phase Adsorption
<b>SV</b>	Space Velocity
<b>Syngas</b>	Syntheis Gas
<b>TGA</b>	Thermo-Gravimetric Analysis
<b>TPD</b>	Temperature Programmed Desorption
<b>TPO</b>	Temperature Programmed Oxidation
<b>TPR</b>	Temperature Programmed Reduction
<b>UV</b>	Ultra Violet
<b>VOC</b>	Volatile Organic Compounds

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<b>vol %</b>	Volume percent
<b>waf</b>	Water ash free
<b>WGSR</b>	Water Gas Shift Reaction
<b>WHSV</b>	Weight Hourly Space Velocity
<b>wt %</b>	Weight percent
<b>XRD</b>	X-Ray Diffraction

## Notation

$\Delta H$	[Kj/mol]	Enthalpy (or Heat) of Vaporization
$T$	[s]	Residence Time
$C^*$	[-]	Number of atoms of carbon in hydrocarbons
$D$	[-]	Metal Dispersion
$dp$	[mm]	Particle Diameter
$dp$	[mbar]	Pressure Drop
$F$	[-]	Mole fraction of each component in the product gas
$K_{app,tar}$	[mTb,wet <sup>3</sup> /kgh]	Apparent kinetic constant for tar elimination
$LHV$	[Kj/Kg]	Lower Heating Value
$M$	[-]	Molar density of gas
$M_M$	[g/mol]	Molar mass of the noble metal
$M_N$	[mol/h]	Molar feed rate of carbon to the reactor
$P$	[bar]	Pressure
$Q$	[mTb,wet <sup>3</sup> /h]	Gas flow rate at the inlet of the catalytic bed
$Q$	[1/h]	Volumetric flow rate of gas
$QV_N$	[kg/h]	Gas Flow
$S/B$	[-]	Steam/Biomass ratio
$S_t$	[mol/mol]	Stoichiometric Ratio
$SV$	[1/h]	Space Velocity
$T$	[°C]	Temperature
$T$	[-]	Fraction of tar (or tar model compound) that reacted
$T_b$	[°C]	Temperature in the center of the catalytic bed
$t_{spc}$	[kgh/mTb,wet <sup>3</sup> ]	Critical space time

<b>t<sub>o</sub></b>	[kgh/mTb, wet <sup>3</sup> ]	Space Time [W/Q]
<b>V<sub>cat</sub></b>	[L]	Volume of the Catalyst
<b>V<sub>x</sub></b>	[cm <sup>3</sup> /g <sub>gas</sub> ]	Irreversible H <sub>2</sub> uptake
<b>W</b>	[kg]	Weight of Catalyst
<b>W/mb</b>	[h]	Catalyst weight/ biomass flow rate ratio
<b>WHSV</b>	[1/h]	Amount of fed/mass of catalyst in the reactor ratio
<b>wt%</b>	[g/g <sub>cat</sub> ]	Loading
<b>X<sub>tar</sub></b>	[-]	Conversion of tar





## 1 Introduction

The depletion of global fossil fuels resources has been a major concern for the world recently. In order not to run out of energy supplies it is essential to focus on the research of alternative systems for combined heat and power production. Biomass, as in all organic materials that are originated from plants, has high potentials for both industrialized and developing countries. Thus, biomass gasification has been proved as an appealing alternative option towards the fuels that have been used for the past decades. In addition, the concern for the climate change is another reason why the interest in this technology has been increased recently. Currently, the greenhouse gas emissions (60% CO<sub>2</sub>, 20% CH<sub>4</sub>, 20% N<sub>2</sub>O) are estimated around 26.6 CO<sub>2</sub> Gt /year and it is possible that they reach the value of 40.4 Gt CO<sub>2</sub>/ year by 2030.

The use of biomass deriving fuel gas is a CO<sub>2</sub> neutral source of renewable fuel as it consumes the same amount of CO<sub>2</sub> from the atmosphere during growth as it is released during combustion. Hence, if it can be widely applied the greenhouse gas emissions will be considerably decreased. Specifically, it has been reported that if this technology gets mature enough for wide application the CO<sub>2</sub> emissions will decrease 50-80% by 2050. At the moment, 8.5% (5.6 EJ/year) of energy consumption derives from biomass (including MSW) in Europe and also contributes 10-15% (45EJ/year) in the total world energy use. The estimated potential for the use of biomass can reach almost 50% of the demanded energy by 2050 in the best case scenario (Demirbas,2009).

However, the commercial breakthrough of this potential source of energy is still not achieved. There are still some drawbacks that render its application difficult. The syngas that is produced during the gasification of biomass contains apart from the desired combustible components (CO, H<sub>2</sub> and CH<sub>4</sub>) impurities such as particulates, soot, ash, sulfur species, ammonia and trace quantities that need to be removed in order to obtain high quality fuel gas. Particulates removal has been already achieved significantly, as the available technologies are quite efficient. As for the sulfur species and the trace quantities with the use of appropriate sorbents, very high quality product gas can be obtained. Hence, the bottleneck of this technology is the removal of the higher hydrocarbons (usually characterized as tar) that condense on the colder parts of the plant and cause plugging and corrosion. Therefore, gas cleaning is a crucial step that needs to be applied in order to have the quality of syngas required for the downstream applications that also affects the optimized design and operation of the biomass gasifier.

Considerable efforts have been made the past twenty years in order to come up with an efficient technology to completely get rid of tar compounds. Cold cleanup methods seem to be quite efficient but the heating value of the gas fuel is substantially diminished and a waste stream created is difficult to dispose. As a result, hot gas cleaning seems to be more appropriate in order to maintain the quality of the product gas. Also, high temperature clean-up can give both tar and ammonia-free syngas. The use of catalysts for tar destruction and decomposition is a very promising technology. Many types have been tested so far such as dolomite, limestone, olivine etc. that are inexpensive but not that efficient. It has been proved, though that one type of catalysts, nickel based, can give completely tar-free gas. However, these ones have other disadvantages such as the fact that they can't be used in situ, due to their rapid deactivation mostly from carbon deposition. So the use of a second catalytic bed increases a lot the cost of the facility. Iron based catalysts have dragged the attention recently as they are not toxic; they are naturally abundant and cheap. They are not that efficient compared to nickel catalysts but they can be used in situ as they are not easily deactivated by carbon. The fact that they can be used inside the gasifier makes them quite attractive as an alternative technology, but their effectiveness needs to be increased in order to use them in large scale facilities. As a third option, precious metal catalysts seem quite appealing in terms of effectiveness, whereas their main disadvantage is their high cost.

## 1.1 Motivation

Power generation technology based on the gasification of biomass is a field growing rapidly nowadays. A lot of research is being done in all the process steps that are involved in the production of electricity from this source. The three basic areas that are being worked on are the gasification reactor and its optimization to achieve gas of a higher heating value as high as possible, the gas cleaning to remove the impurities that could possibly damage the engine, and of course the downstream application of the product gas. The tars that are produced from biomass gasification are considered the toughest and most serious problem that has still not been overcome. The main problems caused from tar is the fact that they crack in the pore of the filters forming coke and plugging them, they condense on the cold spots plugging the lines, all of which are serious operating inconveniences. Hence, it is obvious that this problem should be solved in order to achieve at some point mass electricity production from the biomass.

The objective of this diploma thesis is to experimentally define and compare the effectiveness of three types of catalysts for tar decomposition. The iron based, nickel based and precious metal catalysts were tested in the same operating conditions in order to have a reference point to compare their results. The effectiveness of the nickel based catalysts is already well known, but precious metal and iron based catalysts are not thoroughly investigated. The results of the iron based catalysts have not been very promising so far, so there is still a lot of research to be done. The main point is about the optimization of the structure of the catalysts which should contain the adequate amount of iron combined with the correct support and promoter to result to the highest tar conversion. As for the precious metal catalysts, their main disadvantage is their high cost, but it would be interesting to test them in long time on stream. If they don't deactivate and they can last long enough, probably their high cost would be compensated.

Therefore, in this work these types of catalysts were tested at different operating conditions to gain information under which circumstances they could probably work the best. The main focus is drawn onto the iron based catalysts as they have high potentials, mostly because they can be used in situ because it is said that they don't deactivate by carbon deposition. Part of this work was also to investigate the resistance of iron catalysts to deactivate and if so, to what extent. Hence different temperatures and residence times were applied during the tests. To define the influence of the conversion on the catalyst surface, measurements were conducted before and after the experiment to define the differences and maybe come to a conclusion regarding its possible deactivation.

As the most widely tested catalysts are the Nickel based catalysts, a series of experiments were conducted in order to compare their effectiveness and their potentials with the iron based ones. Their high effectiveness in tar conversion is well known so far but also the fact they rapidly deactivate cannot make them an appealing solution for tar decomposition. Precious metal catalysts were also tested to identify their effectiveness and to conclude whether they are comparable with the results obtained from nickel based. With this procedure remarkable information could possibly be gained for the comparison of the iron based catalysts with the nickel based and the precious metal catalysts regarding tar decomposition.

Of course, not only the decomposition of the tar is important but also the quality of the product gas. Thus, the gas composition was on line measured during the whole time of the procedure to see how the different operating conditions of the catalytic bed and the catalytic material itself can affect the syngas. From the results obtained from the measurement, the Lower Heating Value of the product gas was calculated in every case to compare the influence on each catalyst.

As a last part of this work, the thermal decomposition of the hydrocarbons was defined by a blank test with an empty catalyst reactor to investigate the percentage of the conversion that occurs due to thermal cracking.

## 1.2 Tasks

The present master thesis basically focuses on the thermal and catalytic decomposition of tars. Due to the lack of information regarding Iron based catalysts it is essential to draw the attention onto them as they seem to be very promising. Thus, the aim of this work was to test Iron based catalyst manufactured by the University of Bologna at different operating conditions and with different pretreatment methods. The information gained at the end of this experimental work can give a clearer picture of the potential and the efficiency of these catalysts to obtain tar-free gas that can be used on downstream applications.

To achieve this objective, the first step was mainly about literature investigation for iron, nickel based and precious metal catalysts. It was very useful to know beforehand which operating conditions were likely to affect the most the tar decomposition. Also, information was gained on what should the catalysts be consisted of and in what extent the amount of metal they contain that could optimize or not the results. From the literature investigation it turned out that an important factor for the obtained result is also the pretreatment of the catalyst and it can actually play an important role in the catalytic tar cracking.

In the already existing studies both deriving gas from the gasifier and syngas with a tar model compound were used. But it was chosen for this work to use real gas from the gasifier, so the results could be more realistic. Most of the iron based catalysts used either  $\text{Al}_2\text{O}_3$  (Anis,2011) or olivine (Virginie,2012) as a support and Cu (Noichi,2010) or Mg (Polychronopoulou,2006) as a promoter. All the above mentioned types had fairly good results, therefore the catalyst that are tested here which have  $\text{Al}_2\text{O}_3$  as support and Mg as a promoter and are expected to have sufficient effectiveness. For the choice of the operating conditions, it is worth testing three different temperature points and 3 different space velocity values. Mostly the temperature range that is usually applied is 700-850°C, so the three set points chosen were to be 750,800,860°C to obtain comparable results to the existing literature. As for the space velocity the range is 7500-8000 1/h, which is considered quite high as the residence time decreases a lot. In this work the aim was to test for the iron based catalysts four set points 6500, 8500, 10000 1/h to clearly distinguish the different results between them. As for the nickel based and the precious metal catalysts the temperature was chosen to be constant 800°C and the two space velocities tested were 6500 and 10000 1/h. The reference temperature was chosen to be 800°C as the iron based catalysts, on which the interest is mainly focused, are supposed to be able to be used in situ, and this is the temperature inside a fluidized bed.

After the first series of experiment with the above mentioned measuring points, it was decided to run a second phase of experiment in order to investigate whether a lower space velocity would give significantly better results of tar decomposition. So the iron based catalyst was tested at 800°C and ~4500 1/h, to go to the lowest space velocity as possible. Prior to this second phase the previously used catalyst was flushed with a mixture of  $\text{H}_2/\text{N}_2$  (10%/90%) to check whether there was carbon deposition on the catalyst's surface or not. The reduction procedure was repeated; as the forming gas passed over the catalyst, the  $\text{H}_2$  value was monitored and no changes of its content were observed. This indicates that the iron based catalyst was still in reduced state. Finally, a blank test was conducted to evaluate the contribution of the thermal cracking to the tar decomposition.

### 1.3 Structure of the work

Chapter two includes a general overview regarding biomass gasification, why it is worth research and what are the potentials for the future. Also, the main gasifiers are being mentioned along with the advantages and disadvantages of each technology. The reason why a fluidized bed was used during the experiment is also explained. The basic and most commonly used gas cleaning methods are presented and the step of the procedure in which that they can be applied. Hot gas cleaning is the most appropriate one and it is explained why it is the most profitable. It is essential to state also the main types of gas impurities and which are the ones that are most prominent to damage the engine in downstream applications. Sulfur is considered as very dangerous species so the commonly used chemical solutions for its depletion are mentioned. As tar decomposition is the main focus of this thesis there is a whole analytical part in this chapter regarding higher hydrocarbons. Which of them are defined as tar and with which mechanisms they can be catalytically destructed. The tar removal methods are presented in details, along with comments for the advantages and disadvantages of every one of them. Of course, the operating parameters such as the temperature and pressure at which the gasification is realized play an important role to the final quantity of the produced tar. As for catalysts, the chemical mechanisms with which they act are explained.

In chapter three, the main catalyst, Nickel based, that has been widely tested for the past 20 years is presented here. The most important promoters and supports that have been tested and their effectiveness are explained. This part is very important for their comparison with the iron based catalysts as the pretreatment and the basic structure of these two kinds of catalysts is similar. The advantages and disadvantages of this catalyst have been described by many writers. The basic problem of this type of catalyst is its rapid deactivation, so all the possible deactivation reasons are mentioned in detail at this point. Eventually, there are methods to overcome the deactivation of the nickel catalysts, especially regarding sulfur poisoning but they are not adequate. It is concluded that because of the strong inconveniences of nickel based catalysts it is essential to focus and research on a different type that could be more appropriate to achieve the desired result.

In chapter four, the work is focusing on the presentation and description of the iron based catalysts. It is evident that they don't easily deactivate as the nickel based ones, but according to most experimental researches made they don't have such high potential in tar destruction. The reason why there are so promising is the fact that they can be used in situ, mixed with the bed material, so there is no need for the construction of catalytic test rig. As a result, there should be a lot of research done not only regarding the operating conditions of the gasifier and catalyst bed, but also in the structure and the composition of the catalysts. As the main experiment that were conducted in this work involved iron based catalysts, an analytical presentation of the measurements that take place before and after the use of the catalyst for its evaluation is made. It is evident that depending on the pretreatment the results obtained can be better or worse.

In chapter five, a theoretical review is done regarding precious metal catalysts. The results from prior investigations are presented, their potentials for the future along with their advantages and disadvantages.

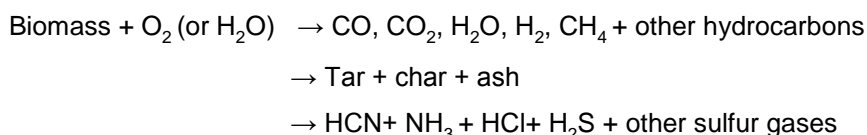
In chapter six, the experimental facility is described. The basic procedure that was followed is explained in details according to the literature investigation, and it is justified why it was chosen.

In chapter seven, the final results of all the experiments are presented. It was agreed to conduct a series of experiments involving iron based, nickel based and precious metals catalysts in order to jump into conclusions for their potentials and to compare their results. Also, it was important to investigate not only the impact of the catalyst on the tar destruction but also on the composition of the product gas and how this changed with the use of different catalysts. The yield of the product gas varies depending on different operating parameters and the catalyst used. With this general overview, it easier to understand which type of catalyst is more appropriate in different downstream applications and why.

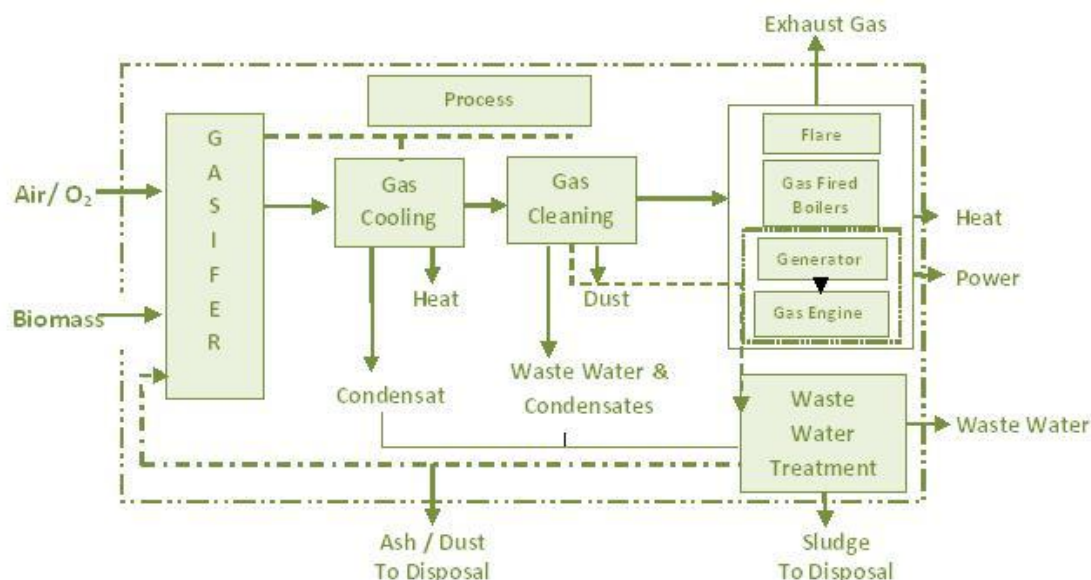
## 2 Biomass Gasification

Biomass Gasification is a thermo-chemical conversion in which carbonaceous materials are effectively and economically converted through partial oxidation into a gaseous fuel mixture of low or medium calorific value, with the use of a gasifying medium (Boyle,1996), (Wang,2008). It is an efficient and environmentally friendly method for production of electricity, heat or synthetic gas.

The process occurs with the interaction of hot steam (H<sub>2</sub>O) or oxygen (air) with the solid fuel in the gasifier. The oxidant could also be carbon dioxide or a mixture of the above (Ahmed,2009). Steam gasification involves endothermic reactions, so an external source of heat has to be provided in order for the gasification process to occur (auto-thermal procedure). When pure oxygen is used as a gasification medium the necessary heat is provided through the exothermic reactions that take place inside the gasifier (allo-thermal procedure). For the completion of the gasification processes high operating temperatures are demanded. The operational pressure inside the gasifier ranges from a little above the atmospheric pressure to an elevated one in the presence of steam, air/oxygen (Mondal,2011). As the feedstock enters the gasifier due to high temperatures the volatiles are firstly released from the heated solid, leaving volatilized hydrocarbons and char (Boyle,1996), (Mondal,2011). These two components undergo reactions with the oxidant matter resulting in the product gas, a mixture of combustible components (mainly carbon monoxide, hydrogen, methane, higher hydrocarbons and condensable tars) together with carbon dioxide and water.



A graphic scheme of the whole procedure during biomass gasification and the downstream applications in the product markets can be seen in Figure 1 (<http://www.biozio.com/pro/gas/gas.html>).



**Figure 1: Biomass Gasification**

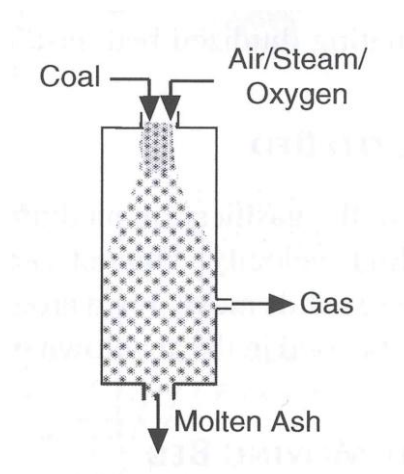
<http://www.biozio.com/pro/gas/gas.html>

## 2.1 Gasifiers and Applications

The gasification systems that are used for these procedures are divided into four types depending on how the gasification medium and the fuel contact each other (Basu,2006).

### Entrained Bed

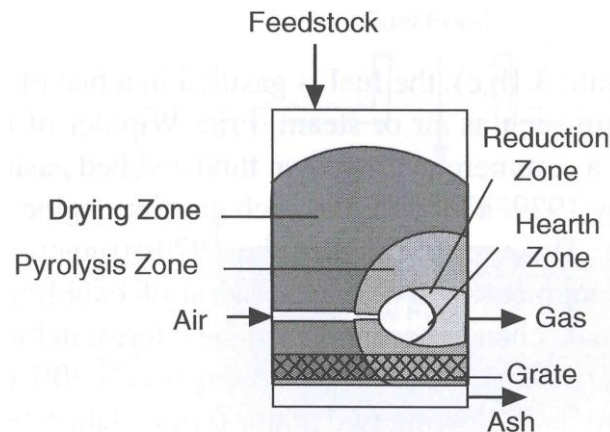
Pulverized fuel particles are gasified by a stream of oxygen (or air) and steam, Figure 2. It cannot be used for the gasification of biomass as it requires very fine particles (80-100  $\mu\text{m}$ ) but it has high capacities (>100MWe).



**Figure 2:** Entrained flow bed (Basu,2010)

### Fixed or Moving Bed

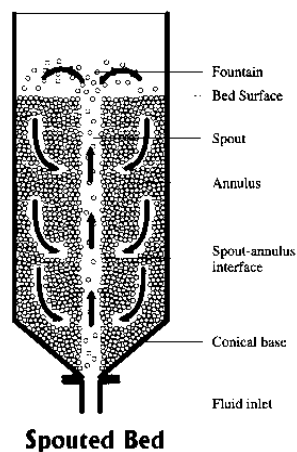
The gasification medium flows through the reactor and comes in contact with the solid fuel particles, Figure 3. Depending in the direction of the gas stream and the solid flow they are divided into updraft (or co-current), downdraft (or counter current) and cross draft (or cross current). The downdraft type is the most appropriate for biomass gasification but it has the small capacities (>1.5 MWe).



**Figure 3:** Fixed or moving bed (Basu,2010)

### Spouted Bed

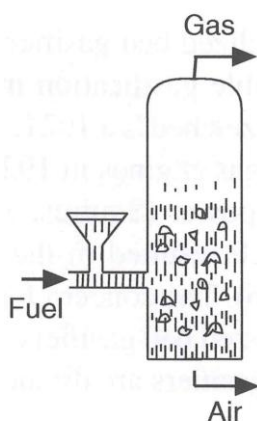
It is a fluid bed in which the gasification medium pierces through a thick bed of relatively coarse particles at high velocity, Figure 4.



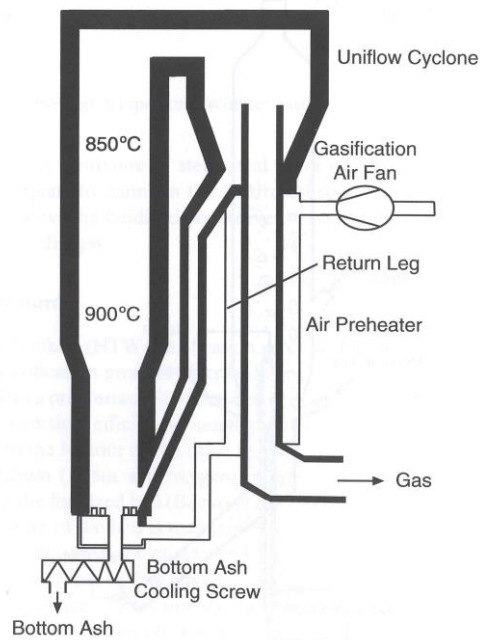
**Figure 4:** Spouted bed (Basu,2010)

### Fluidized Bed

The fuel is gasified in a bed of small particles that are fluidized by a suitable gasification medium. This type of gasifier can be divided into two groups; Bubbling Fluidized Bed (BFB), Figure 5 and Circulating Bubbling Fluidized Bed (CFB), Figure 6. This gasifier is the most appropriate for biomass gasification as it achieves excellent heat and mass transfer between the gas and the solid phases with the best temperature distributions. Its main advantage is that the biomass particles are uniformly surrounded by the fluidized material so the gasification is taking place uniformly too and the maximum potential is achieved. The conversion of the feedstock takes place in the bed but small conversion in gas continues also in the freeboard.



**Figure 5:** Bubbling Fluidized bed (Basu,2010)



**Figure 6:** Circulating Fluidized bed (Basu,2010)

The main applications of the product gas in the energy industry are (Boyle,1996), (Mondal,2011):

- Electricity from Integrated Gasification Combined Cycle (IGCC)
- Liquid fuels production as substitutes for petroleum products
- Hydrogen production for fuel cells
- Synthetic Natural Gas (SNG) production
- Chemicals production

The heating value and quality of the produced synthetic gas (syngas) depends on the gasification system used, the gasifying agent, the operational conditions (temperature at which gasification takes place, residence time, size of feedstock) and the quality control technologies (Wang,2008).

The upper limits in tar and particulates depending on application downstream the gasifier can be seen in the following Table 1 (Milne,1998).

**Table 1:** Upper limits of biomass gas tar and particulates (Milne,1998)

Application	Particulates (g/Nm <sup>3</sup> )	Tar (g/Nm <sup>3</sup> )
Direct combustion	No limit specified	No limit specified
Syngas production	0,02	0,01
Ga turbine	0,1-120	0,05-5
IC engine	30	5-100
Pipeline Transport		5-500 (for compressors)
Fuel cells		<1,0



## 2.2 Gas Cleaning

The product gas not only consists CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O but also includes gas impurities such as particulates, unwanted inorganic compounds (H<sub>2</sub>S, HCL, NH<sub>3</sub>, HCN etc), heavy hydrocarbons (tars), alkali, halogen species and unburned char. The nature of these contaminants depends on the gasification process and the type of biomass feedstock (Mondal,2011).

Use of syngas as a fuel for internal combustion engines, gas turbines and fuel cells for heat and power generation depends mainly on cleaning technologies used to remove particulate dust and condensable tar in the syngas. Therefore, gas purification is essential for the efficient use of product gas to downstream applications (Wang,2008).

As a first step, particulate cleaning is important due to the emission limit requirement for the application of syngas to downstream technologies. It is necessary also, as the removal of particles facilitates the purification of the gas for the rest unwanted compositions. Particulates can be removed with the use of various technologies depending on the required temperature of the following gas cleaning system to be applied.

Gas Cleaning can broadly be divided into two categories: primary methods applied inside the gasifier for tar reduction and gas cleaning downstream the gasification. The upper limits of dust (or particulates) content of the gas are 50 mg/Nm<sup>3</sup> (Bhave,2008).

The first can be achieved with the appropriate choice of the operational parameters regarding the ratio of the gasifier agent to the carbonaceous feedstock, the equivalence ratio (ER), use of a proper bed additive, temperature at which the gasification takes place, the gasifying agent and of course a proper gasifier design (Devi,2003).

As for gas cleaning downstream the gasification, the main categories which derive according to the operating temperatures are: Wet or cold gas cleaning (T<200°C), warm gas cleaning (T=200-500°C) which avoids great loss of useful heat and overwhelms the drawbacks from vapor condensation and hot gas cleaning (T>500°C) (Sharma,2010).

The wet or cold gas cleaning technology is consisted of the use of cyclones, wet electrostatic precipitators (unattractive due to high cost), wet scrubbers, fabric filters, sand bed filters and beds packed with sorbents. These technologies are known as “wet” processes because the condensable substances, which are in gaseous form at high temperatures, are found in liquid form at room temperature (Villot,2012). This process is known to produce gas with very low tar, ammonia and particulates content. When syngas is about to be used for power generation through internal combustion engines or for thermal applications it is necessary to cool biomass-based product gas to ambient temperature and clean it of tar and particulates before it can be used as a fuel. Therefore the technology mostly used with 100% availability factor is wet packed bed scrubber based system (Sharma,2010).

By this system, the hot gas passes upward through the packing material, which is usually dry sand (Mukunda,1994), while the water is uniformly distributed above the packed bed and flows downward in counter-current flow. These units are able to cool gas from 300° C down to just above the water inlet temperature. It has been reported that high collection efficiencies for both particles and heavy tars increase with the augmentation of the wet packed bed height as the available contact area as well as the residence time are increased. This method allows cooling and cleaning of the gas in one compact vertical toner at low pressure drop and low cost (Bhave,2008).

However, the most important drawback of this technology is the fact that cooling syngas and reheating it to produce biofuels causes great energy loss and lowers its heating value (Leibold,2008). In addition, it produces water sludge, which is a hazardous material and difficult to dispose. Also, very small particles (0.1-2µm) are difficult to collect as water vapor and tar can condense on them. A major hurdle of this technology is also the large quantity of waste water (Bhave,2008).

As a result it is essential to focus on hot gas cleaning techniques because the product gas is really hot, due to the high temperature at which gasification is completed (above 700°C) and it is obvious that if gas purification is applied in lower temperatures this results in high energetic losses and decrease of the overall thermodynamic cycle efficiency. This reduction of the gas temperature near the ambient temperature results in loss of thermal efficiency for subsequent power generation pur-

poses. It is important to state the requirement to maintain the gas temperature above acid dew points. Hence, hot gas cleaning is the most appropriate method to maintain the desired temperatures. This system could improve energy efficiency and lower operational costs for high temperature applications of the product gas such as H<sub>2</sub> production (by the shift reaction), use in combined cycle systems and power generation by a fuel cell (Mondal,2011), (Wang,2008).

## 2.3 Hot Gas Cleaning

The temperature at which the gas cleaning takes place depends on the technology that is being used and of course the requirements of the downstream application of the product gas.

Principal Gas Impurities (Kohl,1997):

- 1) Hydrogen Sulfide
- 2) Carbon Dioxide
- 3) Water Vapor
- 4) Sulfur dioxide
- 5) Nitrogen oxides
- 6) Volatile Organic Compounds (VOCs)
- 7) Volatile Chlorine Compounds (e.g. HCl, Cl<sub>2</sub>)
- 8) Volatile fluorine compounds (e.g. HF, SiF<sub>4</sub>)
- 9) Basic Nitrogen compounds
- 10) Carbon Monoxide
- 11) Carbonyl Sulfide
- 12) Carbon Disulfide
- 13) Organic sulfur compounds
- 14) Hydrogen cyanide

Generally, to achieve removal of vapor-phase impurities from hot gas streams five main procedures exist. Mostly used procedures are the absorption into a liquid and the adsorption on a solid. The firsts consist of the transfer of a gas phase component to a liquid phase, which is soluble. The latter involves the selective concentration of one or more components of a gas at the surface of a micro porous solid. In this case the adsorbent can be released (desorbed) by raising the temperature or by reducing the partial pressure of the component in the gas phase. Alternative methods are permeation through a membrane, chemical conversion to other compounds and condensation (Kohl,1997).

The possible procedures which are being used in order to achieve clean gas are various. The order in which the impurities are being removed plays an important role. For biomass gasification the basic traces that should be removed are sulfur compounds, alkali species, halogens, nitrogen species, metal traces, particulates and tar. In order to minimize the number of separation stages the following procedure is suggested (Sharma,2010). First the halides and alkalis are being separated from the raw gas via a sorbent then desulfurization occurs, particulates removal is followed and finally catalytic tar decomposition which leads to a clean syngas. In most experimental facilities though, the particulates removal is prior to the separation of the various traces from the syngas and tar removal is the final stage. In the case physical removal of tar can be achieved as the tar condenses on the particulates surface. It is essential to operate this procedure at high temperatures (800-900 °C), otherwise tar condensation on particulate surfaces can result into gas cleaning equipment plugging and fouling problems. The acceptable availability is 95-99% (Sharma,2010). The most widely used mechanical technologies are cyclones, bag filters, and electrostatic precipitators and baffle filter (Wang,2008).

However, if this order is applied it is possible that coke, which is formed due to thermal tar cracking, plugs the filter and decreases its efficiency. For this reason the use of monolith catalysts, honeycomb structures is an appealing alternative as they can operate with particulate containing gas. Hence, tar is firstly removed and then the particulates are being filtered (Corella,2004). These

types of catalysts, though, are not very efficient are expensive so further investigation needs to be done.

As for the sulfur removal the following procedures are the most common (Kohl,1997):

#### Sulfur Scavenging

*Iron Oxide:* Most widely used process is Iron Oxide adsorbent. The iron oxide captures the H<sub>2</sub>S by forming Iron sulfide. It is possible to regenerate the iron by adding air to oxidize sulfide to elemental sulfur. Operating temperature of iron Oxide sponge is 20-50°C



*Zinc Oxide:* It can be used as an adsorbent to form zinc sulfide. Its main advantage is that it is stable and can be useful for hot synthesis gas streams.

The sorbents for the removal of traces of H<sub>2</sub>S are cylindrical extrudates of 3-4mm in diameter and 4-8mm in length. The maximum sulfur loading is 30-40 lb sulfur/ 100 lb sorbent and usually beds are designed to last over a year. The operating temperature is 200-400°C.



## 2.4 Catalytic Tar Destruction

### 2.4.1 Tar Definition

'Tar' is defined by Milne and Evans (Milne,1998) as the organic compounds produced under thermal or partial-oxidation regimes (gasification) of any organic material that condense under operating conditions of boilers, transfer lines, ICE and inlet devices and are considered as largely aromatic. As tar are considered all the hydrocarbons with molecular weight larger than that of benzene. However, in some studies benzene is excluded and not taken in consideration as a tar molecule, whereas in other cases it can be used as tar model compound for the examination of the effectiveness of a catalyst.

The classification of Tar is based on the behavior of the tar compounds in downstream process. The characterization of "tars" as primary, secondary, and tertiary is a first step in classifying these materials and relating the composition of "tars" with formation conditions (2004).

*Class 1:* Components of tar that are the primary pyrolysis products and are virtually absent above 800°C. They can't be detected with a GC and are close to the composition of the biomass itself.

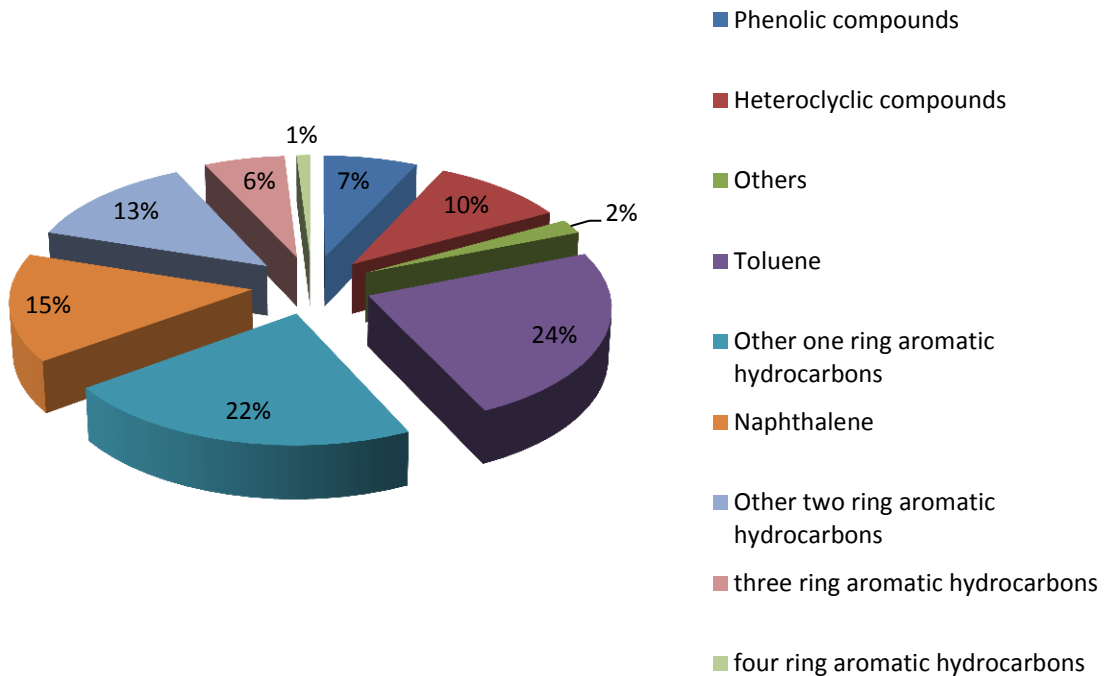
*Class 2:* Aromatic compounds with hetero atoms (oxygen and nitrogen) that have high solubility and are present in 500-1000°C with a maximum peak at 750°C. They are the decomposition of primary tars.

*Class 3:* Light aromatics, toluene, xylene, styrene which do not contribute into tar related problems and are present at 650-1000°C with a maximum peak at 900°C.

*Class 4:* Light polyaromatics such as naphthalene, acenaphthylene, anthracene and pyrene are present above 750°C. They are contained of 2-3 aromatic rings and condense when the gas is cooled down. For processes above 1000°C naphthalene is the primary component.

*Class 5:* Heavy polyaromatic tars that are produced either by the decomposition of heavy large class 1 compounds or from lighter tar compounds due to growth reactions or pyrolytic aromatic hydrocarbons. They contain 4-7 aromatic rings.

A typical composition of the biomass deriving tar is presented in Figure 7 (Coll,2001).



**Figure 7:** Typical compositions of biomass tar (Coll,2001)

#### 2.4.2 Tar Composition, Maturation and Removal

Tar formation is mainly the transition of the primary products to phenolic compounds and to aromatic hydrocarbons as a function of process temperature (Milne,1998).

Mixed Oxygenates (400°C) → Phenolic Ethers (500°C) → Alkyl Phenolics (600°C) → Heterocyclic Ethers (700°C) → PAHs (800°C) → Larger PAHs (900°C)

Once particulates and impurities are removed from the raw gas, tar decomposition should be the final step for achieving clean gas. The tar destruction occurs in high temperatures, so that the condensation of the tar is prevented. Hence the tar dew point which is the temperature, at which the real total partial pressure of tar equals the saturation pressure of tar, influences the operating conditions. Once the actual process temperature passes the thermodynamic tar dew point, tar can condense out. It doesn't mean that condensation will always occur (Contributions ECN Biomass to the '2nd World conference and technology exhibition on Biomass for Energy, Industry and Climate Protection' 2004).

The methods used should be efficient, economically feasible and of course should not affect useful gaseous products.

To achieve tar removal there are basically two approaches:

1. In the gasifier (primary methods)
2. Tar treatment from the product gas (secondary methods)

Mechanical and Physical Methods of tar elimination:

These methods are used for the simultaneous elimination of tar and particles from the product gas. Dry gas cleaning: it is applied prior to gas cooling where temperature is greater than 200°C and partly below 500°C after gas cooling (Wang,2008). Usually, a heat exchanger cools the gas from 850-900°C to 160-180°C and then a fabric filter is used to separate particles and some tars from the product gas. The residuals can be returned into the combustion zone in the gasifier (Villot,2012).

Wet gas cleaning: After gas is cooled down, typically at temperatures about 20-60°C by using a wet scrubber. The wet scrubber liquid is saturated with tar and the condensate is vaporized and fed for thermal disposal into the combustion zone (Villot,2012).

Tar is then present as vapor but it can be removed from the gas as liquid droplets following condensation so it can be removed as tar condenses on the particulates.

In-Gasifier Bed material

In the fluidized bed gasifiers the use of solid additives as bed materials is common due to their catalytic effect during the gasification procedure. There is a big variety of additives which differ in structure and surface area. The most widely used are raw dolomites, raw olivine sintered olivine and nickel on olivine (Corella,2004).

- Raw Olivine ((Mg,Fe)<sub>2</sub>SiO<sub>4</sub>): It is known for its great mechanical strength even at high temperatures, so it reacts better in fluidized bed environment than dolomite (Abu El-Rub,2004). It also has the ability to decrease the tar content from 43 g/ Nm<sup>3</sup> with sand to 2.4 g/Nm<sup>3</sup>. It has been reported that olivine is resistant to attrition and of course is low priced (Courson,2000).
- Sintered Olivine (Corella,2004): It is also hard so the most important advantage is that it does not generate many particulates in the gasification gas. But it does not have actually any significant activity in tar elimination due to the absence of internal surface area.
- Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>): It is a calcium magnesium ore and is known for its high tar conversion, around 95%, it can decrease the tar content of the tar from 43 g/ Nm<sup>3</sup> with sand to 0.6 g/Nm<sup>3</sup> (Courson,2000). According to Simell et al. CaO in dolomite is responsible for its high activity in tar conversion. So it is commonly used as a guard bed prior to the catalyst bed. It can be used in situ which is cheap but less effective, or downstream the gasifier in a secondary reactor which results in higher costs but in higher tar reduction also (Abu El-Rub,2004).

The use of dolomite increases the hydrogen content and the H<sub>2</sub>/CO ratio which favors the tar cracking and reforming (Xu,2010). Unfortunately, dolomite erodes a lot so it must be fed continuously in amounts of around 3 wt% of the total biomass flow rate (Corella,2004). Also its friability is high and it disintegrates into fines. In comparison to olivine dolomite is fragile at high temperatures. Another problem is that the chlorine content in biomass may react with calcium oxide to give calcium chloride which can cause the consumption of the catalyst (Nordgreen,2006). When it is integrated on Ni-catalysts it enhances sintering at high temperatures and encourages coke formation (Zhang,2007).

- Calcinated Dolomites: During calcination the carbonate mineral is being decomposed, eliminating CO<sub>2</sub> to form MgO-CaO. They are inexpensive and disposable and can be used both in situ and in secondary fixed bed, downstream the gasifier. However, the calcination reduces the surface area and makes them more friable. In addition, it loses its activity under conditions where CO<sub>2</sub> partial pressure is greater than the equilibrium decomposition pressure of dolomite. Because it is not very robust, prone to attrition and erodes it can't be used for fluidized bed reactors (Dayton,2002).

### 2.4.3 Catalysts for cracking and decomposition of tars

Tar elimination mainly occurs due to a series of reactions during which tar reacts with steam or carbon dioxide (dry reforming) and forms lower carbon species that are not considered tars. Catalysts can be applied in situ or in a separate reactor downstream the gasifier.

### Thermo-catalytic cracking

The raw gas is maintained at high temperatures and the tar molecules cracked to lighter gases, refractory tars (condensable tar and char) and steam. Basically there are three groups of catalysts that have been researched in terms of their efficiency in catalytic tar destruction. Alkali metals, non-metallic oxides and supported metallic oxides. The use of the alkali metals mainly enhances the gasification reaction and it is used in situ, whereas the other two groups catalysts tar decomposition (Dayton,2002).

Many catalysts have been tested during the past twenty years. Steam and dry reforming reactions are catalyzed by group VIII metals. Among them, Nickel based catalysts have been mostly researched due to their high efficiency in thermal cracking and reforming and are widely used in the industry (Sutton,2001).

The catalysts for steam reforming of light hydrocarbons (methane-reformers) are less active and selective towards CO than the catalysts for heavy hydrocarbons (naptha-reformers) (Aznar,1998). It has been concluded by scientists that the conversion of methane and benzene only starts after all the naphthalene is converted. Also the methane decomposition seems markedly slower than the aromatic hydrocarbon decomposition (Rönkkönen,2011b).

Regarding toluene conversion it has been reported that it is higher than that of benzene because it has less stable chemical structure. Its conversion is also increased by the increase of time (Zhang,2007).

### Hydrocarbons Steam Reforming Mechanism

First methane and other hydrocarbons are separately adsorbed onto a metal site where metal-catalyzed dehydrogenation process occurs. Water is also adsorbed onto the support hydroxylating the surface. At an appropriate temperature the OH radicals migrate to the metal sites so the hydrocarbons are oxidized by steam until all the carbon atoms are converted to CO or CO<sub>2</sub> and H<sub>2</sub> is given up (Dayton,2002).



The reaction is endothermic  $\Delta H=927 \text{ KJ/mol}>0$ .

This procedure can be enhanced by the increase of temperature and/or with the use of a catalyst so the reaction rates can be increased.

During the steam gasification, analysis on the inner and outer part of the catalyst has shown that the ions in the catalysts migrate to the carbon layer and are deposited over the catalyst surface. The procedure includes endothermic reactions that take place on the catalyst's surface which are all summarized in Table 2. Possible reactions of hydrocarbons in gas clean-up with toluene as model hydrocarbon and equilibrium reactions of the main gas components.

**Table 2:** Basic tar cracking reactions (Rönkkönen,2011b, Xu,2010)

Reaction	Equation		$\Delta h_{900} \text{ } ^\circ\text{C}$ (kJ mol <sup>-1</sup> )
Steam reforming	$C_7H_8+7 H_2O \rightarrow 7CO+11H_2$	(6)	927
	$C_7H_8+14 H_2O \rightarrow 7CO_2+18H_2$	(7)	695
Steam dealkylation	$C_7H_8+H_2O \rightarrow C_6H_6+CO+2H_2$	(8)	1159
	$C_7H_8+2H_2O \rightarrow C_6H_6+CO_2+3H_2$	(9)	1291
Hydrocracking	$C_7H_8+10H_2 \leftrightarrow 7CH_4$	(10)	-653
Hydrodealkylation	$C_7H_8+H_2 \leftrightarrow C_6H_6+CH_4$	(11)	-54
Dry reforming	$C_7H_8+7CO_2 \rightarrow 14CO+4 H_2$	(12)	1159
	$C_7H_8+11CO_2 \rightarrow 18CO+4 H_2O$	(13)	1291
Thermal cracking	$C_7H_8 \leftrightarrow 7C+4 H_2$	(14)	-23
Carbon formation	$C_7H_8 \leftrightarrow 7C+4 H_2$	(15)	-23

Partial oxidation	$C_7H_8+5,5O_2 \rightarrow 7CO+4 H_2O$	(16)	-1810
Oxidation	$2 CO+O_2 \rightarrow 2 CO_2$	(17)	-564
	$2 H_2+O_2 \rightarrow 2 H_2O$	(18)	-498
	$C_7H_8+9 O_2 \rightarrow 7 CO_2+4 H_2O$	(19)	-3783
Water–Gas shift	$CO+ H_2O \leftrightarrow CO_2+H_2$	(20)	-41,98
Methanation	$CO+3 H_2 \leftrightarrow CH_4+ H_2O$	(21)	-227
	$C+2 H_2 \leftrightarrow CH_4$	(22)	+74,90
Water gas	$C+ H_2O \leftrightarrow CO+ H_2$	(23)	-131,38
	$C+2 H_2O \leftrightarrow CO_2+ 2H_2$	(24)	103
Boudouard	$CO_2+C \leftrightarrow 2 CO$	(25)	-172,58
Ammonia synthesis	$N_2+3 H_2 \leftrightarrow 2 NH_3$	(26)	-112

The above reactions that take place during tar cracking and reforming are affected by several factors such as the operating temperature, the amount of oxygen and steam that is added etc.

#### 2.4.4.1 Influence of Different Parameters

##### *Temperature*

According to Le Chatelier's "reaction equilibrium will move to oppose the constraints placed upon it". So if a system in equilibrium experiences a change in concentration, temperature, volume or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established. So, higher temperatures favor the reactants in exothermic reactions or the products in endothermic reactions. Therefore, as long as steam reforming is an endothermic reaction with the raise of temperature the equilibrium is shifted towards the conversion of tars to compensate this change and the forward of the reactants is favored. As a result, the formation of light hydrocarbons, and the elimination of coke is observed. Methanation occurs due to two different possible reactions (17) and (18). The dominant one is (17) which and reaches equilibrium faster. As it is an exothermic reaction, it can be concluded that methanation is favored at lower temperatures. In addition, hydrogen yield is improved by 6-11 vol% on dry basis at high temperatures and light hydrocarbons formation is decreased (Zhang,2007). It is important to mention that of course the temperature of the reactor containing the catalyst depends on the catalyst formulation (Elliott,1993).

##### *Pressure*

The changes of pressure are attributable to the changes in volume so its change affects the reactions proportionally to Le Chatelier's principles. It causes the reaction to shift to the side with the fewer moles gas.

##### *Space Velocity-Residence Time ( $\tau$ )*

As the space velocity increases the conversion of tars is decreased due to the less residence time inside the catalyst bed and it affects the gas composition (Zhang,2007). As the space time increases the reactions in the catalytic reformer have a greater opportunity to proceed and the system tends toward equilibrium. Therefore, there is a critical space time  $t_{spc}$  at which the tar yield is reduced to <2 g/kg and benzene and naphthalene are essentially eliminated. But it decreases linearly as the temperature increases. If a space time of an actual system exceeds the critical value, the effectiveness of the catalytic procedure is obviously decreased because if the space time is longer, then larger catalysts are required (Kinoshita,1995).

Residence time, also is a value that indicates how many and to what extent, consecutive reactions can take place at a certain temperature. Increase of the residence time enhances the ammonia formation.

*Role of oxygen*

For temperatures above 800°C hydrocarbon decomposition mainly occurs via steam reforming and/or steam dealkylation reactions.

For temperatures below 800°C oxidation is the main tar decomposition reaction. It creates heat for the endothermic reforming reactions causing the overall reaction to somewhat resemble autothermal reforming (Rönkkönen,2011b).

*Influence of H<sub>2</sub>O content*

The amount of steam, which is used as the gasifying agent, has a great influence on the procedure of tar elimination. When tar elimination occurs mainly to steam reforming reactions then becomes a reactant. It also determines the H<sub>2</sub>O/C\* ratio so it influences the coke deposition and H<sub>2</sub>O removal from the catalyst's surface (Corella,2004). C\* is the number of atoms of carbon in hydrocarbons that react with the steam in the fuel. If H<sub>2</sub>O is added it is able to gasify the accumulate coke/carbon off the catalyst's surface (Xu,2010). But if the content of steam is very high then the heating value of the product gas is decreased, hence high moisture content is not desired (Corella,2004). It has also been reported that it affects the formation of bulk nickel sulfide (Hepola,1997a).

Once the tars, methane and light hydrocarbons have been converted, the water-gas shift reaction largely determines the final gas composition. This is also another reason why the amount of vapor introduced into the reactor is important (Elliott,1993).

*Catalyst Weight/Biomass flow rate ratio (W/mb) (Garcia, 1998)*

As W/mb increases the yield of total gas increases too and diminishes the liquid yield ( $\uparrow$ H<sub>2</sub>, CO  $\uparrow$  and  $\downarrow$  CO<sub>2</sub>,  $\downarrow$ CH<sub>4</sub>, $\downarrow$  C<sub>2</sub>) Also it was reported that for a given W/mb ratio, H<sub>2</sub> and CO yields decrease with the increase of the reaction time, while the yields of CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub> increase. For a W/mb ratio higher than 0.4 h, the initial yields of several gases do not vary significantly and the experimental gas composition of pyrolysis at 650 and 700 °C is very close to thermodynamic equilibrium.

*WHSV: moisture-free feed rate/weight of catalyst in the bed after activation (1/h)*

This value determines the amount of biomass fed to the reactor, divided by the mass of catalyst in the catalytic reactor (He,2009).

WHSV= (Charge feed weight per hour/ Cat weight loaded in the reactor)

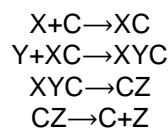
WHSV indicates the gas residence time in the catalytic gasification reactor, lower WHSV value means longer gas residence time, which can promote tar adsorbing and improve the catalytic cracking of hydrocarbon and the elimination of tar.

**2.4.4.2 How do catalysts work**

Catalysis is a process during which the rate of the chemical reaction is either increased or decreased. The catalysis can be either homogeneous or heterogeneous depending on the phase of the two components that come into contact. In heterogeneous catalysis the catalyst is usually solid and the reactants are either gases or liquids. A catalyst is not consumed in the reaction, unlike the different reactants that participate in the chemical reaction (Ross, 2012).

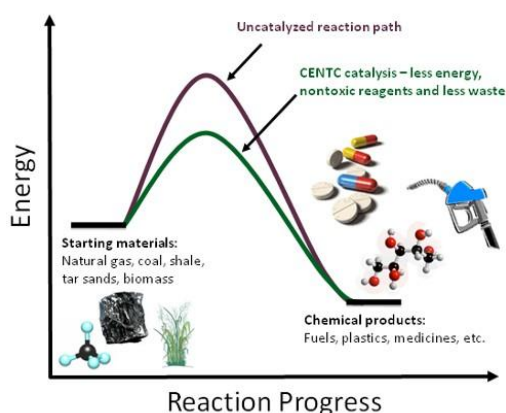
Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst.

Below the typical reactions that take place during catalysis are presented, where C represents the catalyst, X and Y are reactants, and Z is the product of the reaction of X and Y:





The following scheme, Figure 8, describes how catalyst can speed up a certain chemical procedure.



**Figure 8:** Catalyst contribution in reaction progress

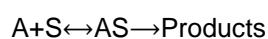
<http://depts.washington.edu/centc/>

As raw gas passes over the catalyst's surface, the tar molecules are broken down to lighter gases and soot either due to steam reforming or dry reforming with carbon dioxide or both to produce additional carbon monoxide and hydrogen (Sutton, 2001).

There are three basic mechanisms for heterogeneous catalytic conversion.

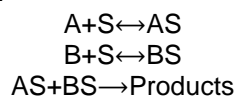
#### *Surface reactions*

Consider reactions in which at least one of the steps of the reaction mechanism is the adsorption of one or more reactants onto a surface. The simplest surface reaction is a simple decomposition in which the reactant A gets adsorbed on the Surface S directly to form the products P, as seen below:

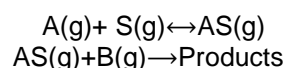


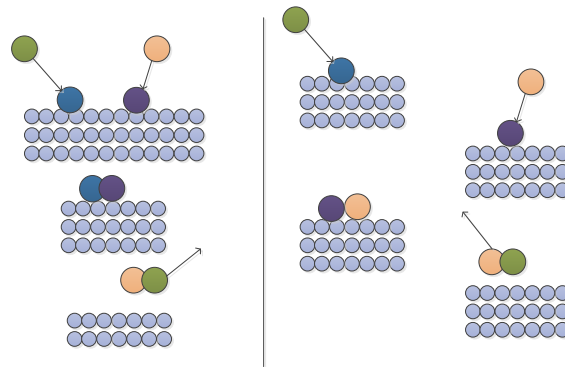
*Bimolecular reactions*, a schematic explanation of the reactions is shown below, Figure 9.

- Langmuir-Hinshelwood theory proposes that at gas/solid interface the reactions are a combination of two elementary steps: an equilibrium between adsorbed reactant species and those in the gas phase followed by kinetically controlled reaction on the surface involving adsorbed species (White, 1990).



- Eley-Rideal mechanism proposes here that one reactant attacks the chemisorbed species without itself becoming chemisorbed (White, 1990).





**Figure 9:** Langmuir-Hinshelwood and Eley-Rideal mechanism

#### *The Mars-Van Krevelen Mechanism*

This mechanism is used to describe the kinetics of reactions such as selective oxidation of hydrocarbons and it is more applied for the hydrodesulfurization and NO<sub>x</sub> removal.

Because steam reforming is a highly endothermic reaction the maximum conversion is achieved with high temperature and low pressure and high steam-to-hydrocarbon ratio. Their basic advantage is that their use does not reduce the heating value of the gas. The Mars-van Krevelen mechanism is based on the idea that adsorption of one molecule occurs on top of another molecule which had previously been adsorbed (Ross, 2012).

The tar decomposition is significantly affected by the presence of methane due to the catalytic reforming reactions (Hepola,1997b). The basic processes in which they are used are hydrogenation reactions, steam reforming (production of H<sub>2</sub> or syngas), and methanation (Sehested,2006).

#### 2.4.4.3 State of the art

The basic criteria that a catalyst should fulfill to commercially feasible are listed below (Sutton,2001), (Courson,2000), (Hepola,1997b):

1. Effectiveness in the removal of tars
2. Capability of reforming methane
3. Should provide a suitable syngas ratio depending on the desired application
4. Resistance to deactivation due to carbon deposition, sintering and sulfur poisoning
5. Easily regenerated
6. Resistance to mechanical stresses
7. Inexpensive
8. Compatible with the continuous oxidation and reduction cycles
9. The catalyst life time is also a basic factor that can control the viability of the whole process

*Groups of Catalysts that have been tested for tar elimination so far (Abu El-Rub,2004):*

-Fluid catalytic Cracking Catalysts

-Alkali metals are less active for carbon conversion and hard to recover (Xu,2010).They are mixed directly into the biomass as it is fed into the gasifier and the char formation is enhanced (Dayton,2002).

-Calcinated Rocks (dolomites, olivine etc.)

-Olivine

-Clay Minerals

-Char

-Activated Alumina

-Metal Based (Nickel and precious metals)

-Ferrous metal Oxides

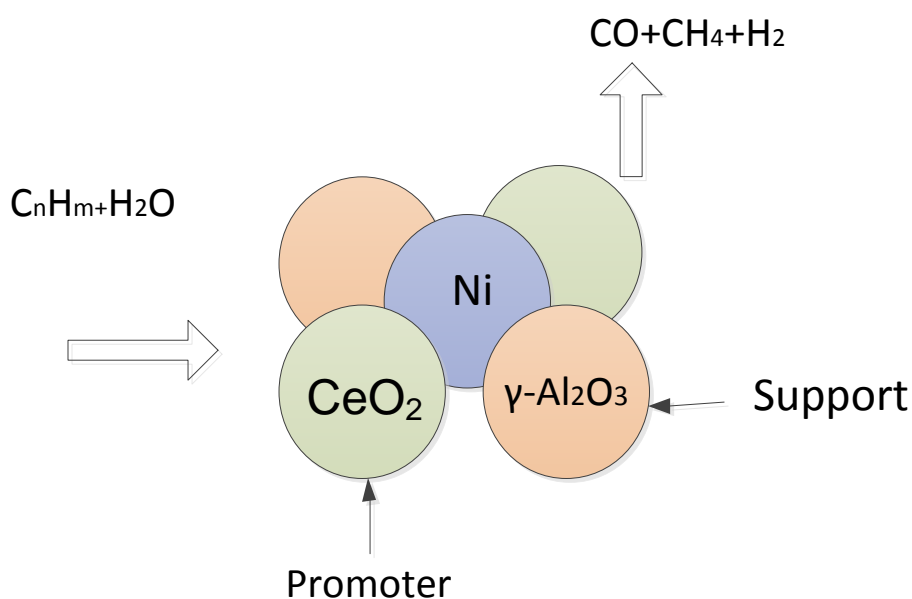
### 3 Nickel Based catalysts

#### Introduction:

The most commonly preferred for the reforming of methane and hydrocarbons.

General Composition of Ni-based Catalysts, which is shown schematically below, Figure 10:

- Ni element which is considered as the active site of the catalyst
- Support to give mechanical strength and protection
- Promoter to ensure the economical operations (Mg, alkali metals such as potassium).



**Figure 10:** Composition of Ni-based catalysts

Although in some studies it was reported that the Ni content of the catalyst affects the decomposition of the hydrocarbons. The catalyst A1 containing ~13 wt % Ni was more effective (90%) than the catalyst B which contained ~2 wt% Ni (Hepola,1997a). In other the contradictory result was concluded, all olivine impregnated catalysts resulted in similar tar decomposition (~76%) although the Ni content was different (3 or 6 wt% Ni) (Zhang,2007). It is important to mention that in both cases synthetic gas was used with toluene as a tar model compound.

*Supports* protect the catalyst from sintering and carbon deposition if a strong nickel-support interaction exists initially, as they provide a high surface area.

The most commonly tested supports for steam reforming are:

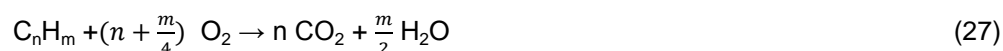
- Zirconia based which is active in tar decomposition and has a minor tendency towards coking and deactivation by sulfur. However, it has moderate effect on ammonia decomposition and a low activity regarding lower hydrocarbons (Rönkkönen,2011b).
- Olivine ( $(Mg, Fe)_2SiO_4$ ) contains iron so the stabilization of Ni is enhanced. The hardness, density and basicity of the catalyst are compatible with the gasification environment. It also accelerates the reaction of steam with absorbed gaseous species. Olivine is has natural characteristics, such as hardness, density and basicity, that could be combined with high effectiveness of nickel to obtain a very promising catalyst (Zhang,2007). In some tests it

- even showed good ageing behavior, at least 260h at 800 °C and no sintering of nickel particles or carbon deposition was evident (Zhang,2007), (Courson,2000).
- iii. a-alumina supports are the most commonly used supports because they are cheap and sufficiently active (Abu El-Rub,2004). But they are not stable and deactivate easily (Pfeifer,2008). A-alumina supports have a favorable surface area, provide mechanical strength and its surface chemistry allows dispersion of metal phases. These supports accumulate coke and enhance the catalytic activity (Richardson,1997).
  - iv. Dolomite when used as a support has very good efficiency; it is capable of 97% tar removal at 750°C (Świerczyński,2007), (Swierczynski,2008). Also it was reported that almost complete tar conversion can occur at 650 °C (Wang,2004).
  - v. Calcium Oxide (CaO) is a well-known catalyst support used for both dry and steam reforming (Pfeifer,2008).

*Promoters* are known for their ability to increase the activity and/or stability of the catalyst. They can also affect its reducibility, regenerability and coke resistance (Anis,2011).

- i. Potassium (K) has been reported to enhance significantly the Ni-based catalysts activity (Arauzo,1997). They also affect the neutralization of the support surface acidity and reduce the coke deposition on the catalyst (Abu El-Rub,2004).
- ii. Magnesium (Mg) reinforces the stabilization of the Ni crystallite size (Abu El-Rub,2004) and improves the resistance to attrition but increases the coke production (Arauzo,1997).
- iii. Cerium Oxide CeO<sub>2</sub> is very effective in preventing carbon deposition. As the surface of the available O<sub>2</sub> content is higher due to the increased crystal oxygen on the catalyst surface the redox reaction is being favored during steam reforming. It adsorbs water and dissociates it resulting in –O and –OH transferring to the nickel and reacting with carbon on the catalysts surface to form CO or CO<sub>2</sub> (Zhang,2007).
- iv. Calcium Oxide (CaO) is also used as a promoter to reduce carbon deposition (Anis,2011).
- v. Chromium (Cr) it is mostly known for its ability to inhibit the encapsulation of nickel crystallites by inactive carbon filaments. It also increases the number of active nickel sites and has a significant effect on the surface metal dispersion and pore dimensions (Bangala,1998).

Generally, the containment of oxygen in the support or the promoter can have a very positive effect in tar reforming due to the occurrence of the reduction-oxidation (Redox) Eq. (27); all chemical reactions in which atoms have their oxidation state changed.



#### Characteristics of Ni-based catalysts:

##### *Advantages:*

They are 8-10 times more active than other commonly used catalysts, such as calcinated dolomites. It has been reported that complete tar elimination is achieved for catalytic reaction around 900°C and they are also capable of increasing the yields of either of CO and H<sub>2</sub>O by the water-shift reaction (Abu El-Rub,2004). According to Le Chatelier's principle, when the temperature increases the equilibrium shifts towards CO/H<sub>2</sub>O, whereas when it decreases, the equilibrium shifts towards H<sub>2</sub>/CO<sub>2</sub> production. Methane formation reaction is favored in lower temperatures (Anis,2011) and reverse ammonia conversion reaction occurs too (Dayton,2002). As a result they can be extensively used for high-temperature steam reforming reactions of hydrocarbons and ammonia (Hepola,1997b).

**Disadvantages:**

The main problem that renders these catalysts difficult to be used widely is that they are easily deactivated if they are used repeatedly in high temperature. Used nickel catalysts are toxic, so their disposal is a potential environmental problem (Dayton,2002).

One of the most important reasons for their deactivation is fouling due to physical blockage by coke. They can also be easily poisoned by sulfur compound for operating temperatures below 900 °C. Sintering at high temperatures is also a common, which reduces the catalyst activity (Rönkkönen,2011b).

Regarding mechanical deactivation, attrition causes the loss of the active surface area through crushing. Besides, they are expensive, so long lifetime is required (Abu El-Rub,2004), (Pfeifer,2008). Therefore their use is not recommended for in-situ use because Ni-based catalysts become quickly deactivated, as coke built up is more rapid inside the gasifier.

Types of Ni-based Catalysts (Corella,2004):

- a) Commercial particulate-shaped catalysts (rings, spheres, pellets, extrudates) that require particulate-free fuel gas.
- b) Un-commercialized monoliths (honeycomb structure) that have been not studied thoroughly.

Further investigation would be interesting as it has been reported that can operate with fuel gas containing particulates, avoiding the use of filters, though they are noted very active, have a high cost and their technology is difficult. They also have to operate in adiabatic form (Rönkkönen,2011b).

The most practical catalyst structure should probably be a honeycomb monolith catalyst. In this type the pore diffusion resistances are much smaller than in the pellet catalysts. Additional Characteristics of Ni-catalysts are proved through tests, such as the fact that all the components of the gas utilize the same active nickel sites on the catalyst surface. Also it has been reported that the pressure drop is lower for shapes with internal holes (Hepola,1997a).

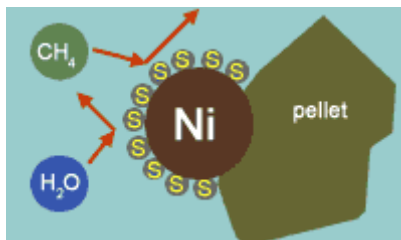
According to some tests that were realized (Aznar,1993) the particle size of the catalyst gas also affects slightly its effectiveness. As the diameter of the particle decreased, less tar yield and more gas yield were obtained in the outlet gas due to a slight diffusion control for  $d_p > 1.6$  mm. In addition, with the increase of particle size more carbon is being deposited (Rönkkönen,2011b).

**3.1 Deactivation Causes of Ni-based Catalysts**

The activity of a catalyst is very crucial in order to be widely applied in the industry. Three are the most common reason which causes low activity.

**3.1.1 Sulfur poisoning**

Sulfur is adsorbed on the surface and the steam reforming reactions can no longer occur so the catalyst is deactivated, as seen below in Figure 11. Sulfur may cause significant deactivation even at very low concentrations, due to the formation of strong metal-S bonds.



**Figure 11:** Sulfur poisoning of Ni-based catalysts  
<http://resources.schoolscience.co.uk/JohnsonMatthey/page21.htm>



The content of sulfur adsorbed on the catalyst surface depends on temperature, pressure,  $H_2S$  concentration in the gas and the catalyst type (Hepola,1997a).

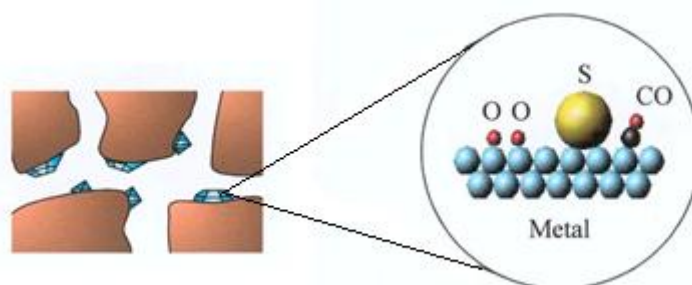
Regarding the catalyst type, sulfur adsorption capacity depends on the nickel surface area, the shape of the catalyst pellet.

During the poisoning the bed temperature decreases considerably because steam decomposition is an endothermic reaction and then after poisoning it is increased again. Therefore, poisoning can be indicated by the determination of the increase of the temperature (10-40 °C) at the top of the catalyst bed.

In addition, higher hydrocarbons, although they have larger molecular sites than methane, their conversion is less affected by sulfur poisoning than that of methane. The methane content is larger than the tar content in overall so the need of active nickel sites is higher. According to some tests homogenous Ni-Catalysts are affected less by sulfur.

Bulk nickel sulfide may also form in special cases. When bulk nickel is formed, toluene decomposition decreases because the  $H_2$  component from the  $H_2S$  species interacts with the unsaturated hydrocarbons to give hydrogenated species. Also the concentration of sulfur seems almost the same at all parts of the bed at this state (Hepola,1997a).

Sulfur formation is evident inside the pores of the catalyst as seen in Figure 12 (Lassi,2003):



**Figure 12:** Sulfur formation (Lassi,2003)

Effect of the different processes parameters on sulfur poisoning:

**Temperature:** Based on thermodynamics, sulfur formation is an exothermic reaction. Thus, according to Le Chatelier's principle at lower temperatures the reaction towards sulfur poisoning of the catalyst surface is favored. So, the higher the temperature the lower the sulfur poisoning effect. It is recommended for catalysts to operate at  $>900^{\circ}C$ . At these conditions no decline in decomposition activity is reported (Hepola,1997b). At temperatures  $>900^{\circ}C$  the amount of sulfur adsorbed forms an irreversible monolayer on the catalysts surface. For temperatures  $<900^{\circ}C$  a multilayer of sulfur form is composed. Higher temperatures increase not only the reaction rates but also the mass transfer; therefore the decrease of sulfur adsorption is favored. Sulfur is adsorbed on the catalyst area at low temperatures because the reaction of sulfur poisoning is exothermic and the products are favored based on thermodynamics principles. It has been reported that a poisoned nickel catalyst has no activity below  $700^{\circ}C$  (Hepola,1997a).

**Pressure:** The higher the pressure the more severe is the impact of the sulfur poisoning because the contact time of the gas with the catalyst is increased and the phenomenon is enhanced. Also, the sulfur diffusion phenomena of sulfur species are more evident. Therefore, it is usually preferable for the catalysts to operate at atmospheric pressure or at slight overpressure.

**Operating Conditions:** As described above the optimum conditions for the operation of Nickel based Catalysts are high temperature and low pressure. These conditions result in carbon-free and sulfide free operation of the catalyst. The outlet gas has low concentration of  $H_2S$  and increased concentration of hydrogen and carbon dioxide due to the  $H_2O$  and/or  $CO_2$  reforming of hydrocarbons and the water-gas shift reaction. It has been reported that as pressure raises the toluene and methane conversion is decreased but the opposite effected is being observed regarding ammonia due to the different mechanism of reforming (Hepola,1997a).

### Compensation of sulfur poisoning effect

One of the most important parameters that affect sulfur poisoning is the space velocity. So with the proper selection during the process the effect could be eliminated. Alternatively, a desulfurization process of the feed prior to the reaction over the catalyst is recommended. A commonly used procedure is the conversion of H<sub>2</sub>S into metal sulfides by the addition of ZnO which is the universal sulfur adsorption material in modern desulfurization units for cylindrical pellets (Aasberg-Petersen,2011).

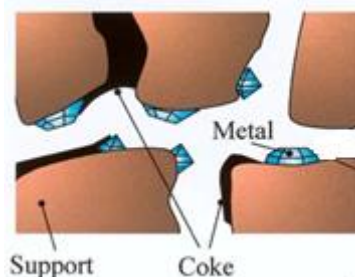


This conversion occurs in the temperature range of 315-530°C which produces SO<sub>2</sub> during regeneration through oxidation at 590-680°C (Mondal,2011).

It has also been reported by many researches that the use of guard bed of dolomite before the gas enters the catalyst bead could really decrease the concentration of sulfur in the gas feed (Sutton,2001).

### 3.1.2 Carbon Formation

There is not a single chemical mechanism regarding carbon formation. The coke deposition depends on the nature and the surface of the catalyst, Figure 13, (Lassi,2003), the operating conditions which affect the reactions that occur and the composition of the feed. Especially, with the increase of pressure the carbon formation is enhanced (Hepola,1997b).



**Figure 13:** Carbon formation (Lassi,2003)

The carbon can either react with water or form products such as H<sub>2</sub>, CO<sub>2</sub> or CO. or pass through series of steps leading to carbon deposition (Zhang,2007). Coke formation is the main deactivation reason of catalysts (Pfeifer,2008). Three main carbon types exist: pyrolytic, encapsulating and whisker carbon (Sehested,2006).

*Pyrolytic:* When the catalyst's activity is decreased, higher hydrocarbons don't decompose and so they are exposed to higher temperatures and form this type of carbon (Sehested,2006). It can be avoided through proper design of the catalyst (Aasberg-Petersen,2011).

*Encapsulating carbon (gum):* This type of carbon is formed during the reforming of heavy hydrocarbon feeds with a high content of aromatic compounds. It consists of a thin CH<sub>x</sub> film or of a few layers of graphite in between the nickel particles (Sehested,2006). The formation of this type is enhanced by low temperatures and the high final boiling point of the hydrocarbon mixture. Therefore after pressurized tests it was reported that a dense layer of encapsulating carbon was formed (Hepola,1997a).

*Whisker:* It is considered as the most destructive form of carbon. It is formed because of the reaction of hydrocarbons or CO of the nickel particle on the one side of the catalyst and the nucleation of graphite carbon as a carbon whisker on the other side.

A correlation between carbon formation and small concentrations of H<sub>2</sub>S has been reported indicating that small amounts of sulfur enhanced the carbon formation compared to higher amounts, dur-



ing pressurized tests. It is possible that sulfur modifies the diffusion characteristics of carbon species through the catalyst particles (Hepola,1997a).

So sulfur can have beneficial effects on the activity of the catalyst, this is why sulfur compounds are needed in the feed. The catalysts are being passivated for carbon-free steam reforming of methane. Therefore, formation of whisker carbon is being avoided. Above certain sulfur coverage (70-80%) this type of carbon is not formed at all (Hepola,1997b).

Treatment of coke formation is essential. It has been reported that the increase of temperature  $\sim 900^{\circ}\text{C}$  at the catalyst bed could decrease the coke formation about 25%. Addition of magnesium in the catalyst has a positive effect too and of course pretreatment of the catalyst is obviously necessary (Pfeifer,2008). Also as nickel content increases the carbon deposition increases too (Świerczyński,2007). However, if coke is formed on the catalyst surface there could be applied procedures for its removal. Cleaning with oxygen-steam mixtures and nitrogen pulses has positive effects as it frees the catalyst both from dust and coke. Therefore, some sintering remains but there are no losses of nickel due to volatilization (Pfeifer,2008).

### 3.1.3 Sintering

It is described as the augmentation of the size of small particles, Figure 14 (Lassi,2003). This results in reduction of the total surface energy. The two basic mechanisms for metal particle growth are either the particle migration (entire crystallites migrate over the support) or the Ostwald ripening (atom migration or vapor transport) (Sehested,2006). It has been observed that sintering is enhanced at higher temperatures at which the sintering mechanism changes from particle migration to atom migration.

It is obvious that sintering influences the two other catalytic challenges and of course it decreases the catalyst's activity.



**Figure 14:** Particles sintering (Lassi,2003)

## 3.2 Regeneration

One regularly used process is simply the increase of temperature, which is in respect to toluene and methane conversion. Hepola et al. raised the temperature at  $900^{\circ}\text{C}$  and the activity of the catalyst regained rapidly especially in respect to methane and toluene conversion. The multilayer of sulfur which is formed at temperatures below  $900^{\circ}\text{C}$  could be desorbed from the catalyst in sulfur free hydrogen containing atmosphere, but the monolayer remains. For atmospheric tests the regeneration desorption occurs in the same temperature as the one of the formation of sulfide/bulk sulfide desorption  $\sim 650^{\circ}\text{C}$  due to polysulfides. The main part of the sulfur is quickly desorbed around  $400\text{-}700^{\circ}\text{C}$ . Also it has been reported that the ammonia decomposition performance is not completely regained which indicates the irreversible sulfur adsorption (Hepola,1997a).

Another procedure suggested described as the controlled exposure of the catalyst to oxygen in a very low  $\text{O}_2$  partial pressure or to species that dissociate to oxygen. It has been reported that exposure to  $\text{O}_2$  at  $600^{\circ}\text{C}$  gave fresh value catalyst but sintering and carbon were still obvious. However, 70% of saturation at sulfur coverage could efficiently be eliminated while the steam reforming reaction still proceeds (Sutton,2001).

In another experiment carbon deposition was completely removed by heating the used catalyst at  $600^{\circ}\text{C}$  in air for 5h to remove the deposited carbon as carbon dioxide. The same group also tried to regenerate the catalysts by putting them on hydrogen stream for 5h or heating the catalyst in an

argon flow that contained 45 vol% vapors but none of these procedures had as good results as the first one. What was interesting was the fact that the activity of the regenerated catalysts decreased more rapidly with the gasification time due to sintering (Yamaguchi,1986). Regeneration is considered as the removal of carbon deposits could also be achieved by putting the catalyst into H<sub>2</sub>O or CO<sub>2</sub> stream (Wang,1998).

This procedure was followed also by Arauzo et al. (Arauzo,1997). They put the catalysts on stream of H<sub>2</sub>O or CO<sub>2</sub> or mixtures of both and achieved complete gasification of secondary coke and soot that was deposited on the catalyst surface. This method was tested into different states regarding the catalytic reforming.

In the first test the regeneration was made once the run of the experiment was finished, so a slow combustion in situ at 500 °C was realized. The catalyst regained its original color and it appeared completely clean of coke. In the second test the regeneration was made during the run of the experiment by using different gasifying mediums like small amount of oxygen (0.25 L/min of air) and low sand/catalyst ratio was chosen in order to emphasize on the effect of coke gasification. The catalyst regained similar activity to the fresh catalyst but there was a small loss of activity by attrition.

### 3.3 Reduction of the Ni-based catalysts

It has been reported that the reduction procedure affects significantly the poisoning of the catalyst due to sulfur (Hepola,1997a). Therefore it has a clear effect on the catalyst activity and life (Sutton,2001), (Pfeifer,2008). According to tests made by M.P. Aznar et al. it was concluded that when catalysts are previously reduced the conversion of tars by steam reforming is higher (Aznar,1993). Temperature control during these procedures is important in order to eliminate an exothermally generated over-temperature condition that could possibly damage the catalyst (Elliott,1993).

The usual procedures are:

- a) Reduction can be performed by using only the synthetic gas mixture, which is flown on the catalyst. Then a slow reduction procedure is performed with a (50%-50%) N<sub>2</sub>/H<sub>2</sub> mixture over 12-16 hours at the heating rate of 50 °C/h to determine whether the synthetic gas had any effect on the sulfur poisoning of the catalyst (Hepola,1997a), (Hepola,1997b).
- b) Zhang et al. (Zhang,2007) reduced the catalysts at 700°C, with a flowing mixture of (50%-50%) N<sub>2</sub>/H<sub>2</sub> for 2.5 hours at a flow rate 80ml/min. For each test there were filled 0.5 ml of 20 and 30 mesh particle size catalysts into the reactor.
- c) The sample catalyst is heated up under a constant flow of He (20ml/min) and then reduced at a constant flow of for hydrogen for 1 hour at 850 °C (10 ml/min).When the demanding reaction temperature is reached the catalyst is charged with steam and toluene (Pfeifer,2008).
- d) Activation in situ. In the catalytic bed with a flow of hydrogen at 450°C for 2 h followed by 1 hour at 750 °C (Aznar,1993).
- e) The catalyst is placed inside the reactor to be purged with nitrogen and pressurized with hydrogen to about 1 MPa. Then it is heated slowly to the reduction temperature (300-400°C). Finally it is subjected at 700°C in H<sub>2</sub> stream for at least 3 hours, usually overnight (Elliott,1993).
- f) The simplest process would be to put the catalyst in hydrogen stream for at least 4 hours at 700°C (Yamaguchi,1986).
- g) By heating the catalyst and keeping it at 900°C for 1h in (50%-50%) N<sub>2</sub>/H<sub>2</sub> mixture (Simell,1997).
- h) Under the reactants gas mixture for 30 minutes at 750 °C (Świerczyński,2007).

### 3.4 Procedures for definition the catalyst sites and characterization

- *Reduction is applied in situ* at 500°C for 3 hours, under flowing H<sub>2</sub>. Then the reduced samples are being evacuated at 350°C for 2 hours before measuring the total H<sub>2</sub> chemisorption isotherms for the determination of the active nickel surface area. The samples are later evacuated at 30°C for ½ hour and a second isotherm of chemisorption is measured (Rönkkönen,2011b).
- *Performance of hydrogen chemisorption measurement.* The catalyst sample is being reduced under a flow of dry Ar/H<sub>2</sub> following temperature programmed procedure from 20 to 900°C. Then the bed is cooled in pure argon atmosphere so the hydrogen can be absorbed into the catalyst at steady flow of 70% Ar/30% H<sub>2</sub> at temperature about 25°C. To determine the nickel surface area the temperature is again raised to 500°C (20 °C/min) in Ar atmosphere to desorb the adsorbed hydrogen from the catalyst (Hepola,1997a), (Hepola,1997b).
- *Temperature Programmed Reduction* is another procedure used. 200 mg of catalyst sample is filled in a U-shaped quartz tube and passed through the reactor a reductive gas mixture ( $H_2 = 0,12 \frac{NL}{h}$  and  $Ar = 3 \frac{NL}{h}$ ) which was heated from room temperature to 915°C with a slope of 15 °C/min. The sample is then kept at 910 °C until baseline stabilization is achieved so that a thermal conductivity detector can analyze the effluent gas after a water trap for the quantification of hydrogen consumption (Abu El-Rub,2004).
- *Measurement of H<sub>2</sub> chemisorption* at room temperature. Hydrogen is flown on the catalyst at high pressure range 5-50 mmHg until adsorption equilibrium is registered. Then the volume adsorbed is determined by extrapolating the linear part of the isotherm at zero pressure (Courson,2000).

#### *Test procedure:*

Usually real gas from a gasifier is not possible to be tested. Therefore, the acceptable tar model compound is toluene which is introduced to the synthetic gas mixture (Hepola,1997b). Naphthalene could be an alternative model compound but its usage causes problems often due to crystallization. When catalysts are tested in laboratory conditions they are crushed and sieved, whereas when they are tested in pilot-industrial applications they are applied in their original size (Pfeifer,2008).

#### *Determination of the effectiveness of Nickel based catalyst:*

Before evaluating the effectiveness of a catalyst it is important to perform blank tests to the gasifier to define the percentage of the tar decomposition that is being achieved due to the catalyst itself and not due to the high temperatures that exist in the gasifier.

Subsequently, there are various methods to determine the conversion efficiency.

The most common measurement techniques constitute tar sampling either with tar protocol or by SPA measurement.

The formula that has being used by Zhang et al. (Zhang,2007) to calculate the conversion effec-

tiveness of the catalyst is 
$$\frac{100Q(F_{CO}+F_{CO_2}+F_{CH_4})}{M \times N_C}$$

Q: volumetric flow rate of gas (1/h)

F: mole fraction of each component in the product gas

Nc: molar feed rate of carbon to the reactor (mol/h)

M: molar density of the gas

### 3.5 Pretreatment to reduce tendency towards coke formation

The reactor is heated up under constant flow of  $N_2$  (750NI/h). The activation of the catalyst is achieved by flushing hydrogen for 1-2h (400 NI/h  $N_2$  + 350 NI/h  $H_2$ ). After the reduction steam treatment is being applied (750 NI/h  $N_2$  +0.6 l/h  $H_2O$ ) so the active sites of the catalyst are occupied by water. This procedure reduces the initial activity of the catalyst but the tendency towards coke formation is reduced. With the increase of time on steam (approximately 2h) the catalyst regains its activity and its selectivity towards CO (Pfeifer,2008).

### 3.6 Calcination of Ni catalysts

It has been reported that calcinated Nickel catalysts are highly effective (95% methane conversion with dry reforming) in tar decomposition and have long lifetime feasibility (no sintering and little carbon deposition <1 wt % at 800°C for at least 260h) (Courson,2000). C. Courson et al. tested olivine Nickel catalysts at different calcination temperatures. These catalysts were prepared by wet impregnation of natural olivine as a support onto the nickel catalyst. Therefore the calcination temperature plays an important role in the final effectiveness of a catalyst. The best adapted calcination temperature seems to be at 1100°C. No parasite crystalline was observed, the olivine phase was maintained as the only crystalline. More grains were formed and the presence of iron containing particle and no interaction with olivine structure was evident, which enhanced the strength of the catalyst. They tested the catalysts both in steam and dry reforming, but the latter procedure proved to be more effective. Less coke was formed with dry reforming of tar, whereas with steam reforming carbon content tended to increase versus water concentration in the inlet gas mixture. In another research the catalysts were calcinated in air atmosphere with low heating rate at 750°C final temperature for 3 hours (Garcia,1998).

## 4 Iron Based Catalysts

### Introduction:

Although nickel based catalysts are the ones that have been most widely studied the past 20 years, due to their disadvantages researchers have turned towards alternative catalyst investigation in order to achieve sufficient tar cracking and reforming. Development of iron based catalysts seems to have gained a lot of attention as it is a promising technology for the decrease of the tar content in the product gas, while catalyzing the water gas shift reaction also. One of their basic advantages is that they can be applied in situ as they are not so prominent to be deactivated by carbon deposition, compared to nickel catalysts. This is very important as the use of a second reactor to place the catalyst increases a lot the cost of a facility (Virginie,2010b). In addition, they are cheaper and the disposal of used iron catalysts is not toxic, as it is in the case of nickel based catalysts (Azhar Uddin,2008). Of course they can be regenerated and iron is naturally abundant (Virginie,2010b), which makes their use appealing.

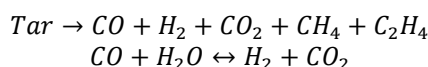
However, Ni catalysts have much higher reforming abilities for hydrocarbons decomposition than metallic Fe catalysts due to the high ability of these catalysts to decompose the C-H and C-C bonds on their metallic surface. So, iron catalysts need to be much more investigated (Guan,2012). So far, many different types of Fe-based catalysts have been studied. Most commonly, researches focus on the impregnation of iron onto olivine or onto a support that seems to enhance the activity of the catalyst. These types of catalysts are quite effective (65% conversion at 850 °C), inexpensive, non-toxic and have a good ageing behavior. They can also act as an oxygen carrier that transfers oxygen from the combustor to the gasifier to burn volatile compounds (Virginie,2012).

### 4.1 Mechanism of biomass tar decomposition over Fe-based catalysts

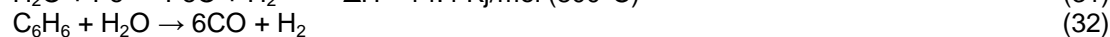
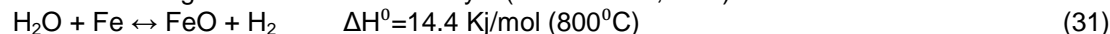
There are three basic catalytic methods for the use of Fe-based catalysts. The most common one is the impregnation of iron on a bed material (usually olivine) for in situ use. Alternatively the catalytic material can be used in the freeboard of the gasifier or it can be placed in a secondary reactor (Nordgreen,2012).

Ferrous materials are able to catalyze the reactions of the main components of the fuel gas (H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O) pyrolysis and tar decomposition. They can also decompose NH<sub>3</sub> and HCN efficiently (Simell,1992).

The mechanism of tar reforming includes the decomposition of tar over the iron based catalyst followed by Water Gas Shift Reaction (Azhar Uddin,2008), (Noichi,2010).

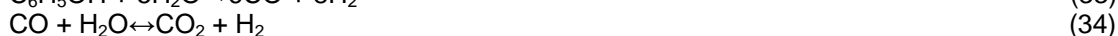


Steam reforming over a Fe-Based catalyst (Sarvaramini,2012):



Phenol was used as a tar model compound for decomposition over Fe catalysts to describe the mechanism of tar cracking. The phenol is adsorbed separately on the iron oxide surface to form surface phenoxy species. The derived hydrocarbon fragments from the phenoxy adsorbed species are oxidized by labile, -O and/or -OH species of support via a back spillover process and by -OH groups residing on iron oxide surfaces to form H<sub>2</sub>, CO, CO<sub>2</sub> and WGSR (Virginie,2010b).

Steam reforming of phenol:



Real gas has not been very commonly used in order to investigate the effectiveness of the iron catalyst. Synthetic gas is more likely used, so a tar model compound is injected inside the reactor to imitate real gas conditions. Two are the mostly used tar model compounds; toluene or naphthalene.

Steam reforming of toluene:



Steam reforming of 1-methyl naphthalene:



Tar conversion depends on the ratio of the reductive gases ( $\text{H}_2$  and  $\text{CO}$ ) to the oxidative gases ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ). The result of tar decomposition depends on the temperature, the catalyst material and the oxygen potential (Nordgreen,2012). The more active the material, the lower the temperature at which the best results are obtained as the tar is decomposed sufficiently (Simell,1992).

The activation of tar molecules is accomplished either in the gas phase or via chemisorption on the catalyst surface (Min,2011). In the first case, the volatiles produced from biomass pyrolysis contain abundant radicals that react with tar molecules to form activated tar fragments. Thus, H- and  $\text{CH}_3$ -radicals are abstracted in the gas phase. In the second case, the procedure depends on the temperature. At higher temperatures, the steam reforms the gas or/and the coke that is deposited on the catalyst surface. At lower temperatures, the coke yields are higher due to low reactivity of steam. Hence, tar fragments combine together easily on the surface of the catalyst to form coke which is difficult to gasify at low temperatures.

## 4.2 Catalyst Deactivation

The main reason for catalyst deactivation is attrition and of course carbon deposition. Also due to physical changes such as sintering, phase changes and component volatilization (Nordgreen,2012). The main problem is that once coke is deposited on a catalyst's surface the reforming of large aromatic compounds is difficult as there are less vacant continuous active sites (Min,2011).

### 4.2.1 Carbon deposition



Andrzej Machocki mainly focused his research on the formation of carbonaceous deposit and its effect on carbon monoxide hydrogenation on iron-based catalysts. He tested Iron-Cobalt catalyst and Iron catalysts promoted with potassium (K) and concluded that carbon deposition occurs regardless the ratio Fe/Co. Also the deposition doesn't depend on the initial metallic phase composition, the particle size or on the amounts and quality of metal carbides. Temperature and  $\text{H}_2/\text{H}_2\text{O}$  ratio though play an important role in carbon deposition (Sarvaramini,2012). At  $800^\circ\text{C}$  though, as  $\text{H}_2/\text{H}_2\text{O}$  ratio increases the coke formation is enhanced and at  $720^\circ\text{C}$  the deposition decreased slowly with the increase of the ratio. As for Fe/olivine catalysts, carbon formation is relatively low and after  $750^\circ\text{C}$  no carbon deposition is evident (Virginie,2012). The carbon deposition also increases with the increase of Fe amount in the catalyst (Polychronopoulou,2006).

Also, it has been reported that coke is less active in dry  $\text{CO}/\text{CO}_2$  reforming conditions.

The fundamental properties of coke depositions are the amount, the type and the location of the coke on the catalyst which depend on the operating conditions, catalyst type and feed composition (Le Minh,1997).

Measurement of Carbon Deposition:

The amount of carbon deposition could be measured by the quantification of the oxidation products that are observed by temperature programmed oxidation (TPO) by MS (Virginie,2010b), (Polychronopoulou,2006) and (Di Felice,2011). With this technique it is possible to determine the carbon deposition stability depending on the carbon oxidation temperature.

Temperature Programmed Desorption should be always applied prior to TPO. A typical procedure desorption with helium at up to 900°C (15°C/min) then cooled, an oxidizing gas mixture of 10% oxygen in helium (total flow 50mL/min) passed through the catalyst heated up to 1000°C (15°C/min) (Polychronopoulou,2006).

Another method would be by weighting the catalyst before and after the experiments. The validity of the method could be confirmed by blank experiments without feeding them with biomass (Min,2011).

A factor that could be calculated for carbon deposition is (Di Felice,2011):

$$\frac{g \text{ carbon deposited}}{g \text{ catalyst} \cdot g T \text{ reacted}}$$

T: is the fraction of tar (or tar model compound) that reacted.

Removal of Carbon off the catalyst surface:

As this is the major reason for catalyst deactivation many researchers have tried to evolve methods for its removal so the catalyst is practically regenerated and doesn't have to be disposed. Carbon formed can be removed from the catalyst surface if it is oxidized in high presence of water concentration in the combustion zone (Virginie,2010b), (Virginie,2012), (Min,2011). Alternatively, carbon can be removed by burning off in situ the coke deposited on the catalyst surface (Sarvarmini,2012).

It has been though elsewhere reported that carbonaceous materials could not be removed by any procedure, especially at low temperatures (Zhao,2002).

#### 4.2.2 Attrition

Attrition resistance was studied by Zhao et al. (Zhao,2002). They tested several iron catalysts with different Fe content and incorporated binder SiO<sub>2</sub> during catalyst preparation and then calcinated them at 300° for 5 hours. The Fe catalyst containing 9.1 wt% iron was the one that showed the greater attrition resistance. Attrition was measured by X-Ray Diffraction (XRD). It is interesting though to state that the concentration of SiO<sub>2</sub> added plays an important role, as its content is increased, the chemical attrition decreased. Same group reported that spray drying of the catalyst during preparation improves also the attrition resistance without affecting the activity of the catalyst. They also figured out the different characteristics of the catalyst that could affect its resistance in attrition. The most critical aspect of the particle properties is the catalyst particle density which affects significantly the final attrition performance. Attrition phenomena generally contribute in iron loss of about 32% in the first 12 hours of test and 17% for 12-48 hours of test, regarding Fe/olivine catalysts (Virginie,2012).

#### Morphology of Catalysts:

It is important to investigate how the catalyst surface changes in reference to the deactivation reasons. Pore volume does not change with the use of the catalyst but a decrease of the surface area is evident due to coke deposition. In contrary, the particle size was almost the same before and after the use of the catalyst (Zhao,2002).

### 4.3 Iron state

Iron can be found on the catalyst surface basically in two phases: metallic iron state or Iron oxide. Hence, it is essential to identify which of the phases is more prominent to achieve better results regarding decomposition of tar.

Iron is potentially effective in different oxidation states. It is reported though, that metallic iron is more appropriate for aromatic hydrocarbon destruction, so the iron state influences the efficiency of the catalyst (Virginie,2010b). Of course the oxidation state of the catalyst material has an influence on the tar content and gas composition of the outlet gas (Nordgreen,2012).

#### *Iron Oxide Catalysts:*

Iron oxides are chemical compounds composed of iron and oxygen. The main oxides of Iron are iron (III) oxide or ferric oxide which is an inorganic compound referred as hematite with the formula  $\text{Fe}_2\text{O}_3$ , iron(II) oxide ( $\text{FeO}$ ) referred as wüstite which is rare and iron(II,III) oxide ( $\text{Fe}_3\text{O}_4$ ) which also occurs naturally as the mineral magnetite. Hematite ( $\text{Fe}_2\text{O}_3$ ) is often obtained in polymorphs such as  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$ .

The use of Iron Oxide catalysts affects the composition of the gaseous products in biomass decomposition (higher hydrogen and carbon dioxide yields but lower carbon monoxide yields) (Azhar Uddin,2008).

The formation of different Iron oxides depends on the temperature. It has been reported (Virginie,2010b) that in the range of 350-500°C  $\text{Fe}_2\text{O}_3$  is reformed to  $\text{Fe}_3\text{O}_4$  and in the range of 500-900°C  $\text{Fe}_3\text{O}_4$  is reformed to  $\alpha$ -Fe.



In studies for Fe/olivine catalysts (Virginie,2010a) it was concluded, via Mössbauer spectroscopy, that in the temperature range of 400-1100°C Fe(II) is extracted from the olivine structure and is oxidized to form "free" Fe(III) oxides. In the temperature range 1100-1400°C Fe (III) is less present as a few parts of the iron reintegrate the olivine structure as Fe (III). This state of iron increases as the calcination time increases too.

In some studies (Virginie,2012), a balance between the phases  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  was observed due to the Redox equation.



According to Nordgreen et al. (Nordgreen,2006), the iron oxides  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  could not accomplish any catalytic activity. They just achieved initially the oxidation of the tars but this tendency declined as steady state was reached.

#### *Metallic Iron State:*

Pure metallic iron material has the highest capacity for tar reduction than iron oxides, so low activity is obtained in tar decomposition for high oxygen content in the catalyst (Nemanova,2011). Pure metallic iron state is mainly responsible for the C-C and C-H bond breakdown. The catalytic ability is very high, so low tar contents are achieved in the product gas (Polychronopoulou,2006).The magnetite ( $\text{Fe}_3\text{O}_4$ ) is reduced to Iron oxide ( $\text{FeO}$ ) (a mineral form of iron (II) oxide) in the catalyst bed (Simell,1992). In these experiments the highest reduction was achieved for almost oxygen free material (60% conversion). A catalyst in its metallic state generally has a better cracking capacity in comparison to the oxidized state (80% naphthalene conversion at 850°C and 60% capacity in total tar conversion) (Nordgreen,2012). Their effect is enhanced when higher temperatures occur in the catalytic bed and with higher equivalence ratio (Nordgreen,2006).

Iron, in its metallic state shows better catalytic activity than its oxide form more likely because the active sites for the reforming of the volatiles and tar are larger (Guan,2012).

In tests regarding the effectiveness of ilmenite in tar decomposition (Min,2011) it was reported that pre reduced catalysts had slighter higher activity than those who were untreated which indicates that the reduced forms of the iron containing species have higher activity than iron oxides.



The percentage of the metallic iron that is available after reduction can be determined from the hydrogen consumption given from the TPR profiles and compared to that of the support (Virginie,2010a).

#### Ellingham Lines:

Ellingham Lines, as presented in Figure 15, is a graph showing the temperature dependence of the stability for compounds. They are used to determine the different iron oxides in relation to the oxygen potential and temperature in the product gas. The diagrams are useful in predicting the conditions under which a metal ore will be reduced to metal. The Ellingham lines indicate the temperature range at which the carbon monoxide will act as a reducing agent. The logarithmic quotient of the partial pressure of  $\text{CO}_2$  and  $\text{CO}$  is referred to as the oxygen potential. According to this diagram, there is only a small window at which the iron is kept to its metallic state (Nordgreen,2012). The oxygen potential in the product gas varies sharply between metallic iron and its oxides (Nordgreen,2006).

The standard Gibbs reactions of formation of various oxides of iron are:



Every point in an Ellingham diagram represents a unique thermodynamic state (combination of temperature and partial pressure of oxygen). Any point is a pair of values of  $T$  and  $RT \ln p(\text{O}_2)$  and substitution of the value of  $T$  into the value of  $RT \ln p(\text{O}_2)$  gives the corresponding value of the partial pressure of oxygen.

A gaseous atmosphere containing oxygen gas in equilibrium with carbon thus contains both  $\text{CO}$  and  $\text{CO}_2$ , but the different thermodynamic stabilities of two gases causes the ratio  $p(\text{CO})/p(\text{CO}_2)$  in the gas in equilibrium with carbon to be a significant function of temperature. At lower temperatures  $\text{CO}_2$  is more stable than  $\text{CO}$  and hence the gas in equilibrium with carbon is predominantly  $\text{CO}_2$ . The composition of the gas mixture in equilibrium with pure carbon (at unit activity) is determined by the equilibrium  $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ .

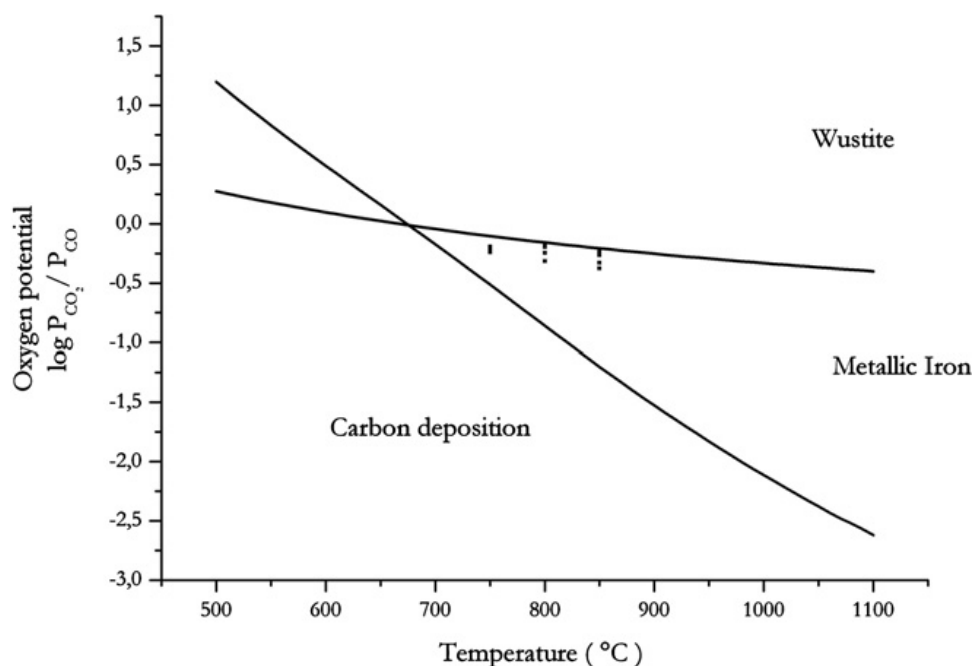


Figure 15: Ellingham lines (Nordgreen,2012)

Through the graph it is possible to estimate the risk for carbon deposition on the catalyst surface depending on the composition of the gas, as the line which represents the Boudouar reaction is also included (Nordgreen,2006).

#### 4.4 Amount of iron in the catalyst

Regarding this parameter the opinions are contradictory, probably depending on the support of the iron based catalyst. It was reported (Virginie,2010b) that the catalyst with 20 wt% iron/olivine had greater efficiency (95% conversion) than the catalyst containing 10 wt% iron/olivine (90% toluene conversion). But the catalyst containing 10 wt% iron/olivine showed higher stability (average conversion of 90% for 30 hours). As for Fe-Alumina and Fe-Zirconia catalysts the activity of the catalyst increases with the increase of iron (Noichi,2010). Elsewhere, it was reported that sintered iron ores and pelletized iron ores had very low activity in tar decomposition despite their high iron content (Simell,1992). For the identification of the optimum amount of iron in a catalyst measurements were conducted for the conversion of toluene for different iron contents, 1-5-10-20 wt% (Di Felice,2011). It was conducted that increasing the percentage of iron does not necessary result in improvement of toluene conversion. Catalysts containing smaller amounts of iron (1 or 5 wt. %) were more active than catalysts with bigger iron amounts. In these studies the reactivity order was 5 % < 1% < 10~10% Fe. There is an optimum Fe loading in 1-10 wt % range for best results towards catalytic tar reduction (Polychronopoulou,2006).

These differences could be justified by the fact that synthetic gas with different tar model compounds is used for investigation in most studies while real gas has only been used in one case (Simell,1992). It is necessary that more experiments are being run with use of real gas from gasifier to obtain more accurate results.

#### 4.5 Enhancement of catalyst effectiveness

Use of supports:

Iron catalysts supported by alumina or zirconia were tested (Noichi,2010) in order to figure out their activity for naphthalene cracking used as a model compound. Generally the two different types of catalysts had similar results at steady state conditions. For the al-Fe catalysts it was reported that their activity was increased with the increase of iron and in this case compound oxides were formed, whereas the surface area decreased. As for Zr-Fe catalysts both surface area and catalytic activity increased with the increase of iron content. The support's chemical composition influences the rate of steam reforming of phenol towards H<sub>2</sub> formation (Polychronopoulou,2006).

The addition of Al<sub>2</sub>O<sub>3</sub> as a support improves significantly the activity of the catalyst, the surface areas and the CH<sub>4</sub> production. But when a big content of a-alumina is added, the activity for WGSR was decreased. This fact does not affect, though, the tar decomposition as it was proved that the active sites for WGSR are different of those for tar cracking. This was concluded by the run of cycle continuous cycles. As the number of cycles increased the decomposition of tar was constant whereas the WGSR activity decreased (Azhar Uddin,2008).

The addition of Zirconia results in the formation of iron oxide phase and aluminum ferrite phase, which are highly active.

Use of promoters:

It has been reported that the addition of copper increases the activity of Fe-Alumina catalysts for naphthalene reforming as is dispersed evenly in the compound oxides to prevent deactivation (Noichi,2010). Also the reduction of iron is facilitated, the surface decrease is prevented so less sintering is observed and the activity remains unchanged compared to the catalysts without copper additions. However, the conversion of naphthalene was higher at lower Cu loading (1 wt %). Copper does not play the role of a promoter because its addition does not result in formation of compound oxides or ferrites (Fe<sub>2</sub>O<sub>3</sub>).

## 4.6 Catalysts characterization

Generally the morphology and structure of the catalysts does not change after the tests (Virginie,2010b), (Virginie,2012).

- X-Ray Diffraction:

Determination of the different phase compositions of the Fe catalysts tested before and after activation is achieved through XRD using Cu-K $\alpha$  radiation. The major crystalline constituent of the calcinated catalyst is hematite (Fe<sub>2</sub>O<sub>3</sub>) which is converted into Fe<sub>3</sub>O<sub>4</sub> by O<sub>2</sub> during the exposure of the catalyst in air in the course of XRD analysis (Azhar Uddin,2008), (Virginie,2010b). It has been reported that differently activated catalysts result in different Fe-phase catalysts (Zhao,2002). XRD can also be used to measure attrition. It is interesting also to identify the crystalline phases of the samples before and after calcination, if it applied (Sarvaramini,2012). For Fe/olivine catalyst structure it was reported that the olivine structure was maintained after iron impregnation and thermal treatment (Virginie,2010a). Characterization after tests showed that the magnetite phase (Fe<sub>3</sub>O<sub>4</sub>) is mainly evident and Fe+2 are higher than Fe+3 due to reduction. But the most important conclusion is that iron is maintained in its metallic phase.

- Micromeritics Automated System:

The catalyst's effectiveness is based on its ability to absorb gas molecules on its surface, so the measurement of its available surface area is essential. The BET (Brunauer, Emmett, Teller) gas adsorption technique is a standard procedure used to measure the surface areas and the pore volumes of finely divided solids. The procedure involves the adsorption of nitrogen on the catalyst surface, usually at the temperature of liquid nitrogen (77 K) (Azhar Uddin,2008), (Zhao,2002), (Nemanova,2011), (Nordgreen,2012), (Polychronopoulou,2006). The basic principal is the multi-layer physisorption in which less strongly adsorbed layers tend to develop on top of the initially-adsorbed monolayer, so vapor is condensed on a surface to form a liquid layer. The temperatures at which BET takes place are not far from the boiling point of the corresponding liquid (Ross, 2012), (Campbell,1988).

The key feature in the characterization of the surface is the collision theory which describes the "equilibrium" rate of adsorption=rate of desorption (White,1990). The specific adsorption capacities, Va/cm<sup>3</sup>, is given as a function of the pressure of nitrogen gas (expressed in terms of the fraction of the standard pressure, p/p) (Campbell,1988).

The procedure involves that the samples are previously degassed under vacuum at 100° C for 1 hour and then at 300° C for 3 hours (Azhar Uddin,2008) or degassed at 110 ° C for ½ hour before measurement (Nemanova,2011) or at 400°C under vacuum (P= 1,3x10<sup>-3</sup> mbar) overnight (Polychronopoulou,2006) or even degassed under vacuum at 250 °C overnight (Virginie,2010b). It is also very important to state that it has been reported that though three catalysts tested (Nemanova,2011) had very large differences in surface area; they presented similar ability in tar decomposition at 850 °C.

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

- Scanning Electron Microscopy (SEM):

This measurement allows the determination of the physical texture and the morphology of the catalyst (Zhao,2002). Through this procedure useful information can be obtained on the form of the micro pores. The resolution though, is not very high (about 5 nm) so information on atomic scale is impossible to be extracted (Ross, 2012).

- Microtrack Laser:

This method is used to determine the particle size of a catalyst before and after it is used (Zhao,2002).

- Mercury Porosimetry:

A procedure to determine the pore volume distribution (particle mass divided by its volume) and skeletal density (particle mass divided by its volume excluding all open pores) (Zhao,2002). The principal of this technique is to relate the force necessary to 'intrude' a nonwetting liquid, such as

mercury, to the average radius of the pores which are filled. The number of these pores is related to the volume of mercury to fill pores of a certain average diameter (White,1990).

- Determination of the active sites of the catalysts:

By putting the catalyst under a flow of 3,85 vol% of H<sub>2</sub> in argon (total flow 52 mL /min) with a temperature raise from room temperature to 900°C (15°C/min) and determined by temperature programmed reduction (Virginie,2010b).

- Mössbauer studies:

This method is used for the determination of the iron oxidation state after steam reforming with Fe<sub>2+</sub>/Fe<sub>3+</sub> ratio depending on the support's chemical composition (Polychronopoulou,2006).

The ratio of H<sub>2</sub>/inert gas may vary (H<sub>2</sub> 20%-N<sub>2</sub> 80%) or the rate of the increase of temperature (7°C/min) (Noichi,2010). Especially after activation of the catalyst under H<sub>2</sub> flow it is essential to determine the active sites by H<sub>2</sub> chemisorption (Polychronopoulou,2006). The Mössbauer spectra measurements in some studies (Virginie,2010b) were carried out in transmission mode with <sup>57</sup>Co diffused into an Rh matrix as a source moving with constant acceleration. The spectrometer (Wissel) was calibrated by means of a -Fe foil standard, and the isomer shift was expressed with respect to this standard at 293 K.

- Quantification of tar yields via UV-fluorescence spectroscopy to semi-quantify the extent of reforming of aromatic ring systems (Min,2011). The fluorescence intensity is multiplied by the tar yield to display the fluorescence intensity on the basis of "per gram biomass".

## 4.7 Activation of Iron-based Catalysts

There are three basic activation methods of Fe- catalysts, under H<sub>2</sub>, CO or syngas. Rong Zhao et al. (Zhao,2002) applied all these three methods as pretreatment for Fe catalysts and reported the different iron phases that resulted. Before applying the activation gas in all cases there was a general procedure held which involved heating the catalysts under atmospheric pressure to 280° C (1°C/min) and kept them at this temperature for 12 hours. Then the catalysts were cooled down to room temperature under He flow (50 cm<sup>3</sup>/min). Finally, passivation was achieved as the catalysts were under 5% O<sub>2</sub> in He flow (50 cm<sup>3</sup>/min) flow rate. Passivation results in a thin layer (less than 1-2 mm) of Fe oxide that prevents the bulk of the catalysts particles from further oxidation. Reduction has to be applied prior to calcination, if it is applied (Polychronopoulou,2006).

### *Activation under H<sub>2</sub> flow:*

It involves the reduction of catalyst under a flow H<sub>2</sub> in an inert gas such Argon or Nitrogen. The Fe<sub>2</sub>O<sub>3</sub> was reduced to FeO and then further to α-Fe or carburized to various carbides (mostly magnetite) with a flow rate 350 cm<sup>3</sup>/min. Reduction under hydrogen flow reduces the iron oxidation state providing more active sites for tar cracking (Sarvaramini,2012). In a study (Guan,2012) the catalyst was put under H<sub>2</sub> flow for ½ hour at 650°C which was enough to achieve the desired oxidation state of the catalyst.

Another procedure was proposed by Polychronopoulou (Polychronopoulou,2006).Reduction of Iron based catalysts under 20% H<sub>2</sub>/He flow at 400°C for 4 hours that can fully reduce the Fe metal on the surface in Fe with respect to the total Fe in the sample for the various supported Fe catalysts. Following, the catalyst has to be heated to 600°C in He flow to desorb any H<sub>2</sub> that might have been spilled over the support, then cooled in He flow to 200°C and finally the feed has to be switched to 2% H<sub>2</sub>/He gas mixture for 30 minutes until the catalyst is cooled to room temperature and left for 15 minutes. The aim is to detect no H<sub>2</sub> with the MS when the He flow is switched in the end. When the reduction is achieved the catalyst sample is heated up again up to 700°C to apply Temperature Programmed Desorption (TPD) experiment and determine the fraction of Fe on the catalyst surface (µmol Fe s/ µmol Fe). It is important to state that when reduction was applied the catalyst was more stable, so initial reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>/Fe is suggested.

To achieve the reduction of the oxide to the elemental state it is important to apply reduction in situ, in the catalytic reactors. The catalyst is placed in the reactor and a stream of H<sub>2</sub> (9 dm<sup>3</sup>/min of nitrogen with 40% hydrogen) passes through the catalyst at 800°C for 4 hours (Nordgreen,2006).

Reduction is concluded when the gas composition of the outlet gas equals the inlet gas composition.

*Activation under CO flow:*

Reduction to magnetite (flow rate 185 cm<sup>3</sup>/min) and with the increase of the flow (375 cm<sup>3</sup>/min) more X-carbide (Fe<sub>5</sub>C<sub>2</sub>) was evident.

*Activation under syngas flow:*

Reduction to magnetite and  $\epsilon$ -carbide (Fe<sub>2</sub>, 2C) and H<sub>2</sub>/CO= 2/3 under flow rate (375 cm<sup>3</sup>/min). The general conclusion that derived from these experiments was that though the physical strength of the differently activated catalysts was different, the surfaces were all relatively smooth. All in all, the Fe phase composition in the catalyst highly depends on the gas phase composition, the temperature, the pressure and space velocity of pretreatment gas.

## 4.8 Influence of difference parameters

*H<sub>2</sub>O presence in the gasifier:*

The evolution of volatile matter and the decomposition of tar are affected by the presence of H<sub>2</sub>O, but reactions of H<sub>2</sub>O that are prominent to happen don't occur in all temperatures. In the temperature range 200°-500°C it is not possible to activate the H<sub>2</sub>O reaction with biomass. Around 600°C it is not high enough to activate the H<sub>2</sub>O tar reduction. This is the reason why high temperatures must be applied to achieve the desired reactions (Azhar Uddin,2008). The more the concentration of vapor in the reactor the more biomass tar is converted into tar.

As Hydrogen yield increases, in the inlet gas the decomposition of tar increases too (Sarvaramini,2012). So the Hydrogen/Water ratio affects the optimal conditions in which the catalytic activity of toluene conversion occurs (Virginie,2010b). Hydrogen compensates the pronounced oxidative character due to the presence of water, so the catalyst is kept in its metallic form which is the reforming active metal (Virginie,2010a).The optimum biomass to vapor ratio has been found 1.5/1 for 750-850°C (Virginie,2010b), (Sarvaramini,2012). At this ratio toluene conversion was increased from 85% to 95% at a given temperature for the same conditions over a Fe/olivine catalyst (Virginie,2010a).

By increasing the steam concentration, the number of available active sites for tar decomposition decrease as the metallic iron is oxidized, according to the equations for steam reforming. However, coke deposition is decreased by increasing H<sub>2</sub>O (Sarvaramini,2012).Hence, increase of steam/biomass ratio decreases the CO volume percentage, while the yields of H<sub>2</sub> and CO<sub>2</sub> increase (enhancement of WGS), but has very little effect in tar reduction (Virginie,2012).

To determine the role of steam Min et al. (Min,2011) used two steam injection methods continues and pulsed (every 20s, 40s, 60s) application. The tar yield was lower after the steam reforming with continuous steam injection because the activated fragments would be continuously reformed into gas on the ilmenite's surface at high temperatures. With the absence of sufficient steam accumulation and further condensation of coke was exhibited. Therefore, external steam addition has little effect on the thermal cracking and reforming of tar in the gas phase.

*Addition of Oxygen in the gasifier:*

Achieves the activation of smaller aromatic systems and polymerizes them into larger aromatic compounds. Therefore coke formation is enhanced (Min,2011). Also the concentration of radicals is increased and the production of PAHs also.

*Temperature in the gasifier and the catalyst reactor:*

As it is obvious, higher gasification temperatures result in lower tar yield with the increase of temperature. The tar content in the product gas derives from the gasifier. The increase of the gasification temperature also changes the oxygen potential in the product gas so the catalyst is transformed from its metallic state to the iron oxide, wüstite (FeO) (Nordgreen,2012).

The gas composition depends strongly on temperature. Hence it is possible that, at a high temperature, the high activity materials catalyze mainly the water-gas reaction (Simell,1992).



As for the temperatures in the catalytic bed, the tar removal is enhanced from 750°C to 850 °C (Virginie,2012) and coke removal from the catalyst's surface is possible.

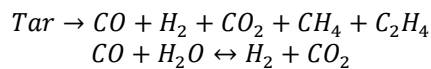
At low temperatures, the adsorbed and activated aromatic ring systems polymerize to form coke on the surface of the catalyst due to the low reactivity of steam and the high thermal stability of the aromatic ring systems (Min,2011).

The iron oxidation state depends on the temperature (Virginie,2010a).

#### *Effect of space velocity:*

Space Velocity affects the gasification of biomass tar. To study the effect of residence time it is possible to conduct experiments comparing the results of total tar content obtained from a catalyst to those for an inert material (Simell,1992). Regarding iron oxide catalysts, as the SV decreases the yield of H<sub>2</sub> and CO<sub>2</sub> increases whereas the yield of CO decreases. Because the lower the SV is more time is given to the reactions to occur. When ferron dolomite was studied regarding the effect of space velocity, it was concluded that when residence time was extended from 0.1 s to 0.3 s the amount of PAHs was reduced.

Tar is decomposed over the iron oxide catalyst and the CO produced from tar is catalytically converted to H<sub>2</sub> and CO<sub>2</sub> via WGSR (Azhar Uddin,2008).



#### *Cyclic Use of Iron Catalyst:*

To determine the stability of the catalyst it can be repeatedly used without regeneration. In a research (Azhar Uddin,2008) it was reported that with the increase of cycle number the yield of hydrogen and carbon dioxide decreased but the yield of carbon monoxide increased and the CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> yields were constant. In addition the surface area of the catalyst decreased too.

#### *Calcination of Fe-based Catalysts:*

Calcination is a thermal treatment process, in presence of air applied, to ores and other solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. It can occur into different temperatures and the main constituent of the catalyst is usually hematite (Zhao,2002). It has been reported that the more active materials are best calcinated materials (Simell,1992).

Mirella Virginie et al. (Virginie,2010b) calcinated Fe/olivine catalysts at different temperatures (400°C, 900°C, 1000°C, 1100°C 1400°C) with different concentrations in iron. It seems according to this research that the best results were obtained for 10 wt. % Fe/Olivine and calcination at 1000°C, achieving 91% conversion of toluene which was used as tar model. The same authors suggested elsewhere (Virginie,2010a) that calcination needs to be performed at 1000°C to prevent free iron oxides from the olivine surface. It is the best compromise between the amount of metallic iron available after reduction and the lower energy required for calcination. Hence, the iron particles are maintained and the absence of agglomeration is possible so the active sites during steam reforming are enough.

To determine the calcination temperature and time Thermo gravimetric Analysis can be used. During the procedure samples of 3g were kept in N<sub>2</sub> atmosphere and heated up from room temperature 20°C to 900°C (15 °C/min). Then they were kept at this high temperature until the weight of the sample was constant (approximately 70 min). CO<sub>2</sub> content on the samples was calculated from the obtained weight loss. It was concluded that the calcinated residues of the carbonate rocks were higher than those obtained by Thermo Gravimetric Analysis (TGA) (Simell,1992).

In those studies the calcination was conducted in situ at 900°C for 1 ½ hours.

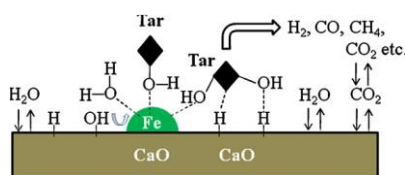
Therefore, many similar procedures are being applied in order to achieve calcination. The calcination of catalysts can be achieved under an air flow rate of 200 mL/min for 2 h at 900 °C (Sarvarmini,2012). Elsewhere, calcination of catalysts was applied in 20%O<sub>2</sub>/He at 800°C for 2 hours before storage and further uses (Polychronopoulou,2006). For iron catalysts with CaO or MgO used as a support were calcinated at 900°C for 4 hours at a 3°C/min heating rate to give (CaMg)O, CaO

and MgO (Di Felice,2011). Alternatively calcination can be applied in air at 700°C for 1 hour (Azhar Uddin,2008).

#### *Calcinated Scallop Shell:*

An interesting alternative that was studied (Guan,2012) involved the wet impregnation of 2.5 wt % iron on calcinated scallop shell, a material with porous structure that can recycled and is appropriate for tar decomposition via steam reforming, as seen in

Figure 16 . Catalytic activity was observed only after a period of reactions, which indicates that in the beginning the metal oxides were reduced to their metallic forms by the syngas, which was initially produced from the pyrolysis of biomass. The catalysts obtained at 800 °C calcination temperature were chosen for the steam reforming of tar, as they exhibited the best results.



**Figure 16:** Mechanism of decomposition of tar on a calcinated scallop shell (Guan,2012)

## 4.9 Thermal Procedures for Catalyst Characterization

*Analyses performed before the use of the catalysts:*

**Temperature Programmed Desorption (TPD)** is a method to describe the energy of sorption, as in the desorbed molecules from a surface when the surface temperature is increased. Usually catalysts are subjected to thermal procedures prior to their use. When the iron catalysts comprise calcium or magnesium oxides they can easily absorb steam and CO<sub>2</sub> from air, as molecules come in contact with a surface, minimizing their energy by forming a chemical bond with the surface. Therefore, during thermal treatments it is likely that they desorb these compounds causing error in the data that is about to be obtained. Hence, TPD has to be applied in order to remove the presorbed CO<sub>2</sub> and H<sub>2</sub>O from their surface (Di Felice,2011). The apparatus used for this procedure is usually a thermal gravimetric apparatus. A high flow of inert gas, usually Helium (total flow 50ml/min), is established over the shallow bed of sample and the temperature is increased at fixed rate. Typical, rates are 15°C/min or 15°C/min and the sample is heated up to 900-1000° C. Then the sample is cooled down and the procedure is being repeated for several times at different programming rates. The amount of gas desorbed is recorded versus the sample temperature and the characterization of the strength of the sorbent-surface bond is also possible (Polychronopoulou,2006), (White,1990).

**Temperature-programmed reduction (TPR)** is a technique for the characterization of solid materials and is often used in the field of heterogeneous catalysis to find the most efficient reduction conditions. According to the procedure followed by Polychronopoulou et al. (Polychronopoulou,2006) the initially oxidized catalyst sample is placed in a container (U-tube) and is submitted to a programmed temperature rise ( 30 °C /min) while a reducing gas mixture is flows over it. This sample vessel is positioned in a furnace with temperature control equipment. To remove the present air, the container is filled with an inert gas (nitrogen, argon or helium). Flow controllers are used to add hydrogen (2 vol% H<sub>2</sub>/He with a flow rate 50 NmL/min). The composition of the gaseous mixture is measured at the exit of the sample container with appropriate detectors (thermal conductivity detector, mass spectrometer) so the quantification and determination of H<sub>2</sub> consumption is possible. The sample in the oven is heated up to 900°C. If a reduction takes place at a certain temperature, hydrogen is consumed. The most accurate way of measuring the reduction is by measuring the vapor content in the outlet of the catalyst. This is due to the fact that in the inlet concentration of water is zero, so any increase can be measured more accurately.

According to Virginie et al. (Virginie,2010a) there are two reduction zones for Fe/olivine catalysts. The first occurs in the temperature range 335-515°C (for a calcinated catalyst 400-900°C) at which the iron oxides are reduced to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is the easily reduced to Fe. In the second zone, 605-790°C, iron oxides of the olivine support are reduced at 660°C in Fe<sub>3</sub>O<sub>4</sub> or in iron spinel in the structure MgFe<sub>2</sub>O<sub>4</sub>.

The procedure that can alternatively be followed is the placement of 50 mg catalyst in a container under a reductive mixture of 10% H<sub>2</sub> in Argon. The catalyst is heated from room temperature to 900°C at a rate of 15°C/min. The reduction is indicated by the return of H<sub>2</sub> concentration to a baseline (Di Felice,2011).

Elsewhere (Virginie,2010b), 50mg of sample, was flushed under a flow of 3.85 vol% of hydrogen in argon (total flow of 52mLmin<sup>-1</sup>). The temperature was increased at a rate of 15 °Cmin<sup>-1</sup> from room temperature to 900 °C.

A small amount of catalysts sample was placed in a platinum basket and a mixture of H<sub>2</sub> (20%)–N<sub>2</sub> was flowed at rate of 200 cc-STP/min into the TGA chamber at room temperature until the entire interior was replaced with H<sub>2</sub>–N<sub>2</sub> gas mixture. After the H<sub>2</sub>–N<sub>2</sub> flow was confirmed, the sample was heated at a rate of 7 °C/min up to 900 °C to obtain the TPR spectrum. Then the rates of weight loss due to reduction of the metal oxides were calculated from the TGA data for sample weight against time and temperature (Noichi,2010).

*Analyses performed after the use of the catalysts:*

**Temperature Programmed Oxidation (TPO)** is a procedure applied in order to detect the presence of the various oxidizable species (carbon forms). The amount of carbon deposited on the various catalysts which is oxidized during the analysis is detected from the amount of carbon-containing products (CO and CO<sub>2</sub>).

Mainly the identification is realized by the continuously monitoring of CO and CO<sub>2</sub> that evolve from the oxidation of the carbon. Maximum three peaks can be obtained from the carbon dioxide evolution and the one from the carbon monoxide in the TPO spectra. The smallest peak of CO<sub>2</sub> indicates highly reactive coke or coke in the vicinity of trace metals. The two high peaks of CO<sub>2</sub> are evident at higher temperatures and are due to competing coke oxidation mechanisms.

For the realization of the procedure the experimental facility needed involves a flow reactor surrounded by a thermostatically controlled furnace. The used catalyst is placed in the center of the furnace, in a boat. Temperature linear program is being applied from 200 to 1000°C at 5 or 10 °C/min while controlled flow of oxygen (0,939 ±0,019 % in nitrogen) passes through the sample to burn off the layer of coke. The O<sub>2</sub> is in low partial pressure in order to avoid heat release during oxidation or secondary reactions, such as CO oxidation. The CO and CO<sub>2</sub> produced are converted to methane over a ruthenium catalyst at 300°C and monitored via a dual FID. The 1<sup>st</sup> FID is monitoring the CO and CO<sub>2</sub> that derive from the reactor. The 2<sup>nd</sup> FID measures the CO by absorbing the CO<sub>2</sub> onto an ascarite adsorbent before the conversion to CH<sub>4</sub>.

The units of the rate of CO and CO<sub>2</sub> evolution are calculated from the calibrated FID signal:

$$\text{CO and CO}_2 \text{ rate } [\mu\text{mol}/(\text{g of catalyst}) \text{ } ^\circ\text{C}] = \frac{2 \times P_{\text{FID}} \times \dot{m} \times 60}{R \times 273 \text{ K} \times W_{\text{cat}} \times \beta}$$

R: gas constant

β: heating rate °C/min

This analysis was performed on 50mg of after test samples. After a temperature programmed desorption is realized the sample is cooled and returns to baseline. Then an oxidizing gas mixture of 10% oxygen in helium (total flow of 50mLmin<sup>-1</sup>) passes through the catalyst. The temperature is increased with a rate of 15 °Cmin<sup>-1</sup> from room temperature to 1000 °C followed by a step of 30 min to assure a return to baseline (Virginie,2010b).



## 5 Precious Metal Catalysts

Recently an alternative type of catalyst has gained the attention, the precious metal catalysts. They are mostly known for their use in gas clean-up for subsequent Fischer-Tropsch (FT) synthesis of biofuels. Hence, they could be an appropriate solution for hot gas cleaning of the product gas for various downstream applications. The precious metal catalysts that have been investigated so far are Platinum (Pt), Rhodium (Rh), Palladium nitrates (Pd) and Ruthenium nitrosylminitrates (Ru) (Rönkkönen,2010), (Rönkkönen,2011b). In some studies their ability for tar conversion was tested for syngas deriving from cedar wood gasification (Tomishige,2004). The order of their activity at 550°C was Rh>Pd>Pt>Ni=Ru. The CeO<sub>2</sub> was used as a support and SiO<sub>2</sub> was used as a promoter. Elsewhere, they were supported on modified Zirconium (m- ZrO<sub>2</sub>) to compare their results with Ni/m- ZrO<sub>2</sub> commercial nickel catalysts. In all these investigations (Rönkkönen,2010), (Rönkkönen,2011b), (Rönkkönen,2011a) synthetic sulfur containing gas mixture was used and toluene and naphthalene were used as tar model compounds. In the first phase (Rönkkönen,2010); all the catalysts were tested in the following operating conditions; temperature range 600-900°C and atmospheric pressure. The activity order was Rh=Ni>Pd>Ru>Pt. For the catalyst with the best performance (Rh/ m- ZrO<sub>2</sub>), the stability of the catalysts was tested after 10 h on stream at 800°C. The catalysts were in sulfur containing environment of 100 ppm, and their carbon tolerance was investigated as well.

### *Preparation:*

They were prepared by incipient wetness impregnation under a vacuum; they aged overnight and then dried under a vacuum for 2 hours. All the catalysts were calcinated in air at 800°C for 1 hour. The loading of the metal for the precious metal catalysts was ~0.5 wt% and for the nickel catalyst 5 wt% (Rönkkönen,2010), (Rönkkönen,2011b; Rönkkönen,2011a).

### *Measurements:*

To determine the dispersions of metal on the surface of the m- ZrO<sub>2</sub>, a chemisorption measurement of H<sub>2</sub> was performed (Rönkkönen,2011b) at 30°C to minimize the H<sub>2</sub> spillover on the support. All the catalysts were firstly reduced at 500°C for 3 hours under flowing hydrogen. The Ru catalyst especially, was reduced at 300°C to avoid the formation of volatile Ru compounds. Then, all the samples were evacuated at 350°C for 2 hours before measuring the total H<sub>2</sub> chemisorption isotherms. Finally they were evacuated again at 30°C for ½ hour and a second isotherm of chemisorption was measured.

The metal dispersion was calculated according to the Eq. (48), assuming 2:1 stoichiometry between the metal surface and the adsorbed hydrogen.

$$D = \frac{V_X - S_t M_M}{V_M \text{wt}\%} \cdot 100\% \quad (48)$$

The  $V_X$  is the irreversible H<sub>2</sub> uptake [cm<sup>3</sup>/g<sub>cat</sub>],  $V_m$  is 22.41 [dm<sup>3</sup>/mol],  $S_t$  is the stoichiometric ratio [mol/mol],  $M_M$  is the molar mass of the noble metal [g/mol] and wt% is the metal loading of the catalyst [g/g<sub>cat</sub>].

### *Conversion:*

Oxidation reactions are the main reason for tar decomposition below 800°C, as they create heat for the endothermic reforming reactions causing overall the reaction to somewhat resemble to auto-thermal reforming. For temperatures 800-900°C, dealkylation reactions are the most dominant (Rönkkönen,2011b).

The activity below 800°C for the Rh catalyst was; in a sulfur containing environment the conversion of toluene and naphthalene was ~80%, whereas without sulfur the conversion reached almost 100% conversion. Respectively for the Pt catalyst the in non- sulfur containing environment was for the two model compounds ~50%, whereas with sulfur it was a lot lower (~20%) (Tomishige,2004).

The effectiveness of the catalysts for the decomposition of different compounds was ethylene>methane>ammonia (Rönkkönen,2011b). Hence, they are more effective in decomposing higher hydrocarbons. It was observed though, that this decomposition is evident at high temperatures mainly 800-900°C. The amount of benzene though, after the catalytic bed increased, for Pd, Ru and Pt use of catalysts (Rönkkönen,2010), but at the temperatures from 600 to 800°C, but at 900°C it decreased. The gas composition had the less amount of benzene with the use of Rh catalyst at 900°C (300 mg/m<sup>3</sup>N) (Rönkkönen,2011b).

#### *Deactivation:*

The main reasons for deactivation of the precious metal catalysts are sulfur poisoning, coke formation and particle size growth. However, the decrease of their performance is evident after long hours on stream. After 6 hours on stream the catalysts started to show a decrease in their activity due to sulfur poisoning. So they were flushed overnight with N<sub>2</sub>, to restore their performance and after that the tar conversion was even higher than before (Rönkkönen,2010).

As for the coke formation, after the 10 hours stability test Pd was the catalyst with very clear carbon deposition on its surface. The catalysts showed deactivation due to coke in the following order Pd>Ru>Rh>Pt= none. It is evident that the Rh shows quite good tolerance to carbon deposition (Rönkkönen,2011b).

#### *Results:*

Generally, the precious metal catalysts are more tolerant to sulfur poisoning compared to nickel based catalysts which rapidly deactivate at temperatures below 900 °C (Rönkkönen,2011b)The most promising catalyst for adequate tar conversion was Rh/m- ZrO<sub>2</sub>, above 800°C (Rönkkönen,2010), (Rönkkönen,2011b), (Rönkkönen,2011a). However, the only catalyst that had the ability to decompose ammonia in sulfur containing environment was Ru/m- ZrO<sub>2</sub>. The Pt and Pd catalysts showed similar activity over 95% for very high temperatures, but below 900 °C the Pt catalyst was less effective than Pd in decomposition of naphthalene, toluene and aromatic hydrocarbons. The minimum conversion occurred at 800 °C and it was 50% for the Pd and 25% for the Pt catalyst (Rönkkönen,2011b). In addition, Rh, Ru,Ni had very low conversion below 800°C, but the total hydrocarbon conversion for 900°C was 98%, 70% and 91% respectively.

The metal loading may slightly influence the activity of the catalyst (Rönkkönen,2011b). Increasing the amount of Rh from 0.5 to 5wt% did not improve its performance (Rönkkönen,2011a). The most promising amount proved to be 0.5wt% metal loading. However, the particle size of the metal may have a more severe influence on the activity of the catalyst particularly at low time on stream. It may influence also the formation of carbon.

Although the sulfur content poisoned the active site of the catalysts, a promoting effect of its presence was observed regarding naphthalene oxidation. At low temperatures (600-700 °C) the addition of sulfur selectively enhances the conversion of naphthalene for the Pt catalyst but it poisons the Rh one.

The conversion increases with the increase of temperature in all catalysts. Metal additions of modified zirconium for temperatures <850°C showed a negative effect on the activity of the support (Rönkkönen,2010).

During the first phase of tests (Rönkkönen,2010) it was concluded that the Rh/ m- ZrO<sub>2</sub>, was the catalyst that showed the higher tar conversion and its effectiveness was comparable to the nickel based catalyst. In (Tomishige,2004), the Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalyst showed the higher tolerance against carbon deposition and sulfur.

#### *Stability:*

The catalyst with the best performance (Rh) was tested 10 hours on stream at 800 °C (Rönkkönen,2010; Rönkkönen,2011b). Its ability was decreased mainly due to sulfur poisoning, coke formation and particle size growth. But still its performance remained high enough.

*Bimetallic catalyst:*

As the Rh catalyst was proved to be the most prominent and Pt showed the greater carbon deposition resistance in (Rönkkönen,2011a) a Pt-Rh noble metal system was built up to compare its effectiveness with a nickel based commercial catalyst. The bimetallic Pt/Rh/m- ZrO<sub>2</sub> is less active than the monometallic Rh/ m- ZrO<sub>2</sub> catalyst in a 100 ppm H<sub>2</sub>S containing environment.

All in all, regarding the precious metal catalysts, the Rh/m- ZrO<sub>2</sub> was the most promising and was tested independently at . The results showed that these catalysts produce very low tar content gas which high efficiency power production in engine. Plus the product gas by using oxygen blown fluidized gasification is appropriate for biofuel production. The problems main disadvantages of this catalyst are the sulfur poisoning, the coke deposition and the particle growth size. Still, they show much higher resistance compared to the nickel based catalysts. According to the investigation in (Rönkkönen,2011a) a proposal for future tests would be to check the effectiveness of the Rh catalyst at 800 °C, with a space velocity of 3400 1/h, and pressure 1-10 bar. With this low space velocity, it may achieve even higher hydrocarbons decomposition.

## 6 Experiments

### 6.1 Experimental Facility

#### Gasifier:

The experimental set-up at the Technische Universität München, as shown in Figure 18 is consisted of the following parts: (i) a gasifier vessel with internal diameter 154mm, length 1500 mm, (ii) a biomass feeder which feeds into the bottom of the gasifier wood pellets, (iii) a steam providing section with a steam flow, (iv) a gas measurement and sampling section, (v) temperature control section.

The reactor which produced the gas, with which the catalysts were tested, is an allothermal fluidized bed gasifier constructed out of high temperature resistance steel (German material number 1.4841). It is heated up electrically to 800°C and metal heat pipes transport the heat inside the bed. Steam was used as a fluidizing medium. The steam of 150 °C was produced by a steam generator and was supplied to the gasifier at the bottom. The steam to biomass ratio (S/B) is 1.0 .

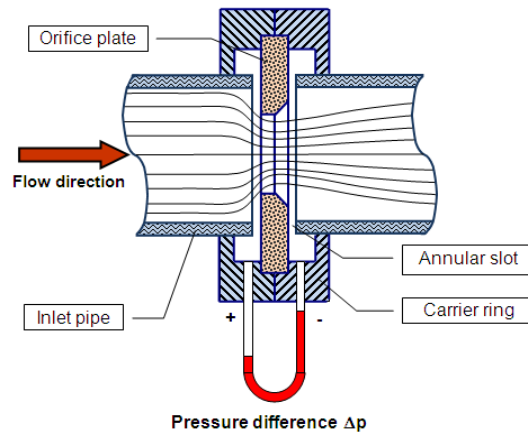
The mass flow was measured by steam mass flow meter.

The produced gas flow exits the reactor at the top of the gasifier. Then, it passes through a cyclone (~400°C) and then through a ceramic candle filter (~340°C) which are placed right after the gasifier to achieve particulates removal. The particulates free gas is driven to the catalyst test rig via transfer lines which are heated up to ~320°C to avoid tar condensation.

The volume flow is being calculated by an orifice plate. The device,

Figure 17, is placed right after the catalyst test rig and it uses the Bernoulli principle to describe the relation between the pressure and the velocity of the gas.

The space velocity is calculated as  $SV = \frac{QV_N}{V_{catalyst}}$ .



**Figure 17 : Orifice Plate**

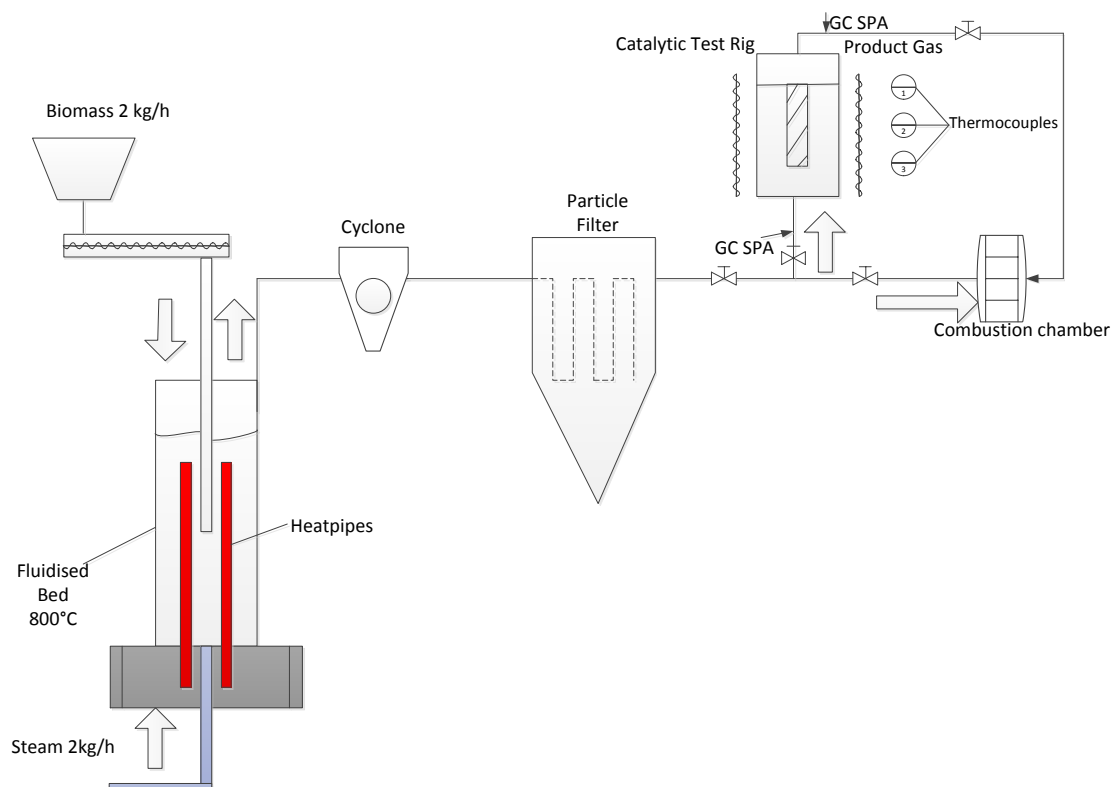
[http://en.wikipedia.org/wiki/Orifice\\_plate](http://en.wikipedia.org/wiki/Orifice_plate) (wikipedia 2012)

#### Feed Materials:

As bed material ~15-17 kg of olivine was used and the height of the bed was ~ 700 mm. As biomass feedstock wood pellets were used which are commercially available under the trading name Agrol and are a blend of ~80% spruce and ~20% pine. The biomass throughput for the reactor was experimentally determined. The proximate and ultimate analysis (Vario Macro CHNS analyzer) of the pellets can be seen in Table 3. The volatile content is relatively high and the pellets have low moisture and ash content.

**Table 3:** Biomass feedstock elemental and proximate analysis in [wt %]

C waf	H waf	N waf	S waf	O waf
49,9	6,8	0,1	0,1	43,2
Water	Ash db	Volatile db	Fix C db	
4,8	0,1	85,6	14,3	

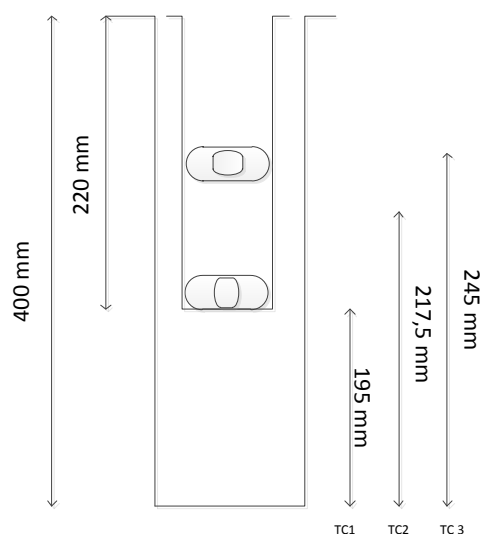
**Figure 18:** Overview of the facility**Catalytic Test Rig:**

The catalyst reactor can be seen in Figure 19. The catalyst is placed in a tube (inner diameter 2-5 cm) which contains a grid at the bottom and the top to ensure that the fine particles of the catalyst are not swept away by the gas during the experiment. The dimensions of the test rig can be seen in detail in Table 4.

**Table 4:** Dimensional details of the bed

Height of the test rig	Height of the tube	Height of the bed
400 mm	220 mm	75 mm

The heating inside the catalyst bed is monitored by three thermocouples placed at the bottom, the middle and the top of the bed. Hence, an overview of the temperatures inside the bed is achieved. The measurements indicated that the temperature was uniform inside the bed during the whole experiment.



**Figure 19 : Catalyst Bed**

## 6.2 Catalysts

In this work three types of catalysts were tested. The main interest was drawn to iron based catalysts for the reasons explained previously. It was interesting though to compare the tar conversion results to commercially available nickel based and precious metal catalysts.

### *Catalysts Preparation:*

The Iron based catalyst that was used for the tests was manufactured by the University of Bologna, Italy. The catalyst is supported by  $\text{Al}_2\text{O}_3$  (16 wt%) and Mg (68 wt %) was used as a promoter on the iron (16 wt %). The commercially available nickel based catalysts were prepared by the manufacturer. Precious metal catalysts were prepared by the supplier too. The amount of catalyst that was used for all the experiments was 40 mL.

### *Characterization Techniques*

The BET technique (NOVA 4000e surface and pore analyzer, Quantachrome Instruments) was used to determine the surface area of the catalyst before and after the tests. The results were obtained through the following procedure; nitrogen at the temperature of liquid nitrogen (77 K) was used to examine the ability of the adsorption of the molecules on the solid surface. Prior to the procedure the samples were degassed at 110°C for ½ hour. Sample of ~3,5 g was used.

The determination of the different phase compositions of the Fe catalyst (crystalline constituents) and the structure of the catalyst before and after the tests was observed by X-Ray diffraction using Cu-Ra radiation.

Temperature Programmed Reduction (TPR) analyses were carried out with a  $\text{H}_2/\text{N}_2$  (10%/90%) gas mixture. The sample was heated up from room temperature to 900°C with a heating range of ~7°C/min during the whole procedure.

## 6.3 Experiments

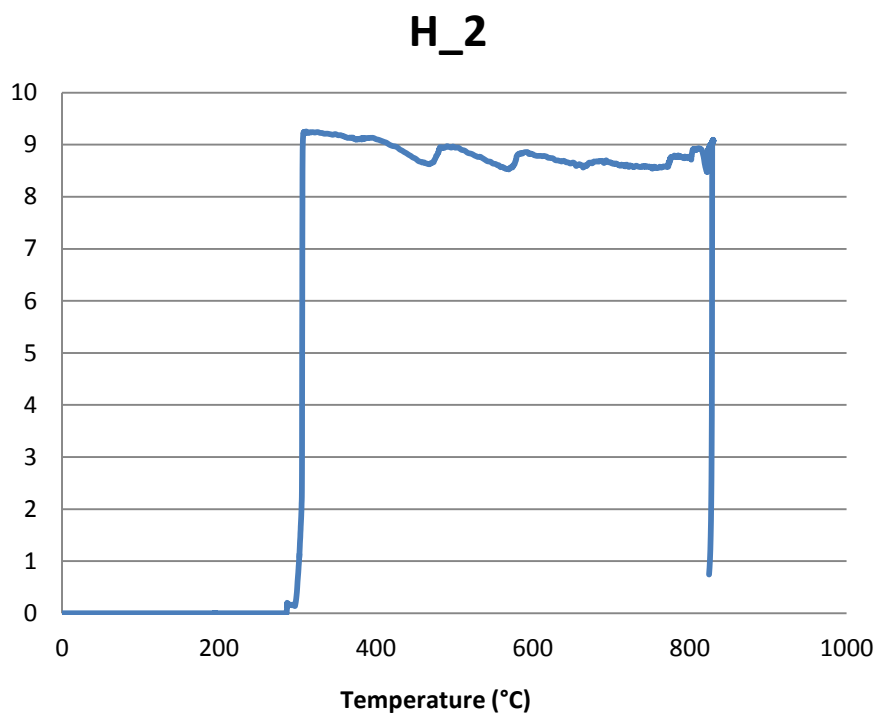
In the first series of experiments the iron based catalysts were tested in different operating conditions. As a second step a blank test was conducted with an empty catalyst reactor in order to define the percentage of tar conversion due to thermal cracking. And finally the nickel based and the precious metal catalysts were tested in comparable operating conditions.

### 6.3.1 Experimental Procedure

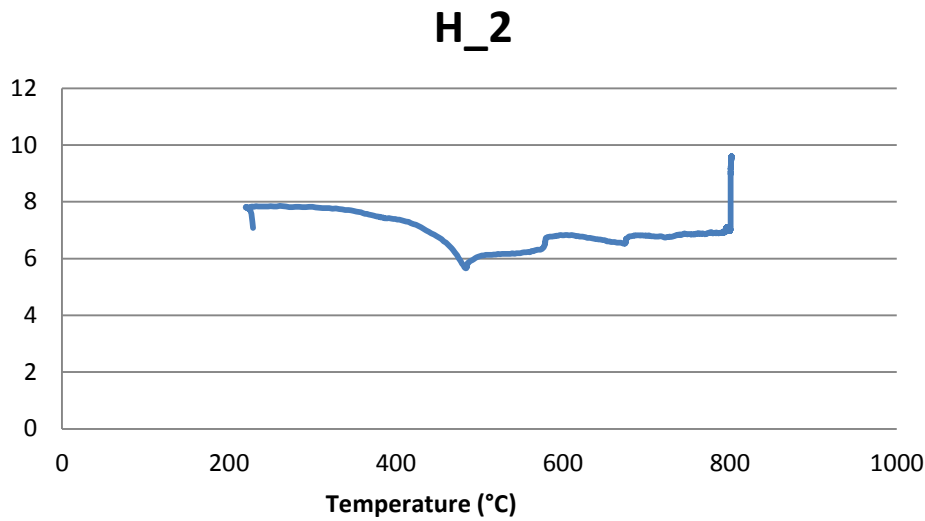
The two most important parameters that affect the tar conversion in a catalyst bed are the temperature at which the catalyst operates and the residence time of the gas inside the bed. Therefore the study for the iron based catalysts was made at three different temperatures 750°C, 800°C and 860°C to see how the behavior of the catalyst changes with the increase of the temperature. For these series of experiments the space velocity was ~6500 1/h. In a second phase the temperature was maintained at 800°C and the pressure drop varied at the values of 0.45 mbar, 0.9 mbar, 1.5 mbar, and 2.0 mbar to determine the tar conversion as the space velocity varied. The reason why the temperature of 800°C was chosen in the second phase is because of the future intention for the iron based catalysts is to use them in situ as they don't get easily deactivated by coke deposition. Before each tar sampling the gas was left running through the catalyst bed for ~1 ½ hours to achieve stable gas composition.

For the Nickel and the precious metal catalysts temperature of 800°C was kept as constant and the space velocity was chosen for pressure drop 0.9 mbar and 2 mbar to have comparable operating conditions with the iron based catalysts. In order to define the influence of the space velocity to the gas composition for nickel catalysts, the dp was raised to 3.0mbar and 4.0mbar. As for the precious metal catalysts, there was a sampling point of gas composition at dp=0.45 mbar.

All the catalysts were reduced 24 h prior to the experiments with a mixture of H<sub>2</sub>/N<sub>2</sub> (10%/90%). They were flushed with the forming gas while the temperature was being raised from room temperature to 800°C. As for the iron and nickel catalysts, the H<sub>2</sub> was reduced in the beginning as it reacted with the oxygen from the catalyst's surface. When the amount of H<sub>2</sub> started to rise again, then reduction of the catalyst was assumed. It is probable that the precious metal catalysts were not in oxidizing state at the first place. However, the reduction procedure was applied for all the three types to have one single pre-treatment procedure. In the following Figure 20 and Figure 21 the change of the monitored amount of H<sub>2</sub>, as a function of temperature is presented for both the iron and nickel catalysts respectively.



**Figure 20:** Reduction of Iron based catalyst



**Figure 21:** Reduction of Nickel based catalyst

The reactor was loaded with biomass and it started being heated up at 450°C under N<sub>2</sub> flow, while good fluidization of the bed material with steam was achieved. Prior to the catalyst tests the gasifier was operated for ~2 hours to ensure stable operating conditions. In the beginning the product gas bypassed the catalytic test rig and was driven directly in the combustion chamber until steady state gas composition was reached. For the experiments of the iron based catalysts the temperature was raised at 750°C with dp=0.9 mbar and after an hour at these conditions with the gas passing through the catalyst, two tar samples were taken before and after the catalyst test rig. This procedure was repeated for all the different operating conditions that were about to be tested. The set point of dp=0.9 mbar and 800°C was tested twice to compare the tar measurements to the values obtained at the same point about two hours earlier. Finally, the pressure drop reached the lowest point dp=0.45 mbar. The effectiveness of the catalysts was tested in sulfur and chlorine containing environment. The operating conditions at which the samples were taken are presented in the following Table 5.

The two additional gas compositions sampling points for the nickel based catalysts were ~12500 1/h for dp=3 mbar and ~14500 1/h for dp=4 mbar.

All the calculations were made for 40mL amount of catalyst. However, after the experiments with the iron based catalysts. A protective grid was placed on top of the catalyst amount inside the bed, to prevent the larger particles to be blown away, but for the finer ones it was impossible to avoid it. It is not known if the particles were blown away all at once in the beginning of the experiment or they were linearly decreased.

**Table 5:** Different operating conditions of sampling points for iron based catalysts

Sampling Points	Temperature (°C)	Pressure Drop (mbar)	Space Velocity (1/h)
1	750	0,9	6500
2	800	0,9	6500
3	860	0,9	6500
4	800	0,45	4500
5	800	1,5	8500
6	800	2	10000



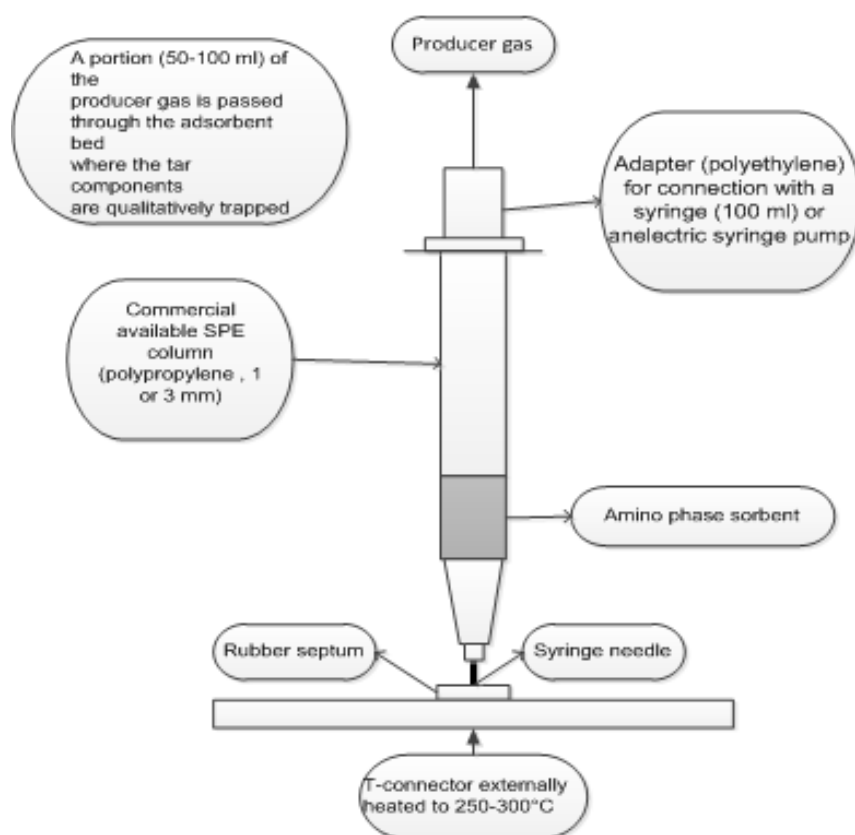
### 6.3.2 Tar Sampling Method-Solid Phase Adsorption (SPA)

The correct evaluation of the effectiveness of a catalyst depends strongly on the method that is used for tar sampling. The more accurate the sampling procedure is, the more realistic the results obtained are. Two off line methods are the most commonly used for tar sampling and analysis; the first one is the conventional cold trapping technique in solvent-filled impingers followed by liquid injection. The second one involves the use of multi-bed solid-phase-adsorbent (SPA), in which the gas is adsorbed on the surface of the material and it was initially developed by the Royal Institute of Technology in Sweden.

In the present work the SPA method was chosen for tar sampling, instead of the cold trapping technique, due to its numerous advantages. The fact that no solvent is required makes the sampling device very convenient and accurate sampling can be achieved without condensation. So it is simpler in use and maintenance. Also, the detection levels for hydrocarbons are higher, plus it is a time-saving method. Not only the preparation procedure is very short (less than one minute to connect the SPA tube to the sampling line) but also the sampling time is much less (1 sample/min) whereas the other method is time consuming (1 sample/hour) (Dufour,2007).

The procedure involves the following steps. A needle is fixed on the tip of a SPA column containing 100 mg of amino phase and a gastight syringe (100mL) is placed to the head of the column. Tar samples were taken by inserting the syringe into the heated lines before and after the catalyst test rig bed via silicon septum. A 100 mL sample was collected in ~1 min as the product gas was in slight overpressure and pushed out the column of the syringe. Then the column was disconnected and covered airtight until the GC-FID analysis.

The sample has to be eluted in a solvent prior to its injection in the detector. Dichloromethane was selected by the European Commission joint meeting in Brussels, spring 1998, as the solvent that would be used for all aspects of the method and was adopted as European and US standard (Abatzoglou,2000). The method can be seen in Figure 22 (Ziad Abu El-Rub, 2008).



**Figure 22:** SPA sampling method (Ziad Abu El-Rub 2008)

### 6.3.3 Gas analysis in GC-FID

After the sample is obtained, the quantification of tar is made in Gas Chromatographer-Flame Ionization Detector (GC-FID); Agilent Type 7890A. The amount obtained by sampling has to be a representative amount for the chromatographic analysis, so the determination of the concentration of the organic contaminants is facilitated. The calibration was made in-house. The eluted sample is injected into the GC at 250°C via a rubber septum, with hydrogen used as a gas carrier. The compounds are identified by the retention time which depends on the physical and chemical characteristics of the sample. The size of the spectral peak is proportional to the amount of the substance that reaches the detector in the GC instrument. The only disadvantage of this method is that because for *o*-xylol and styrol have similar retention times and the identification can be wrong. The error value of the device used in this work is  $\pm 7\%$ .

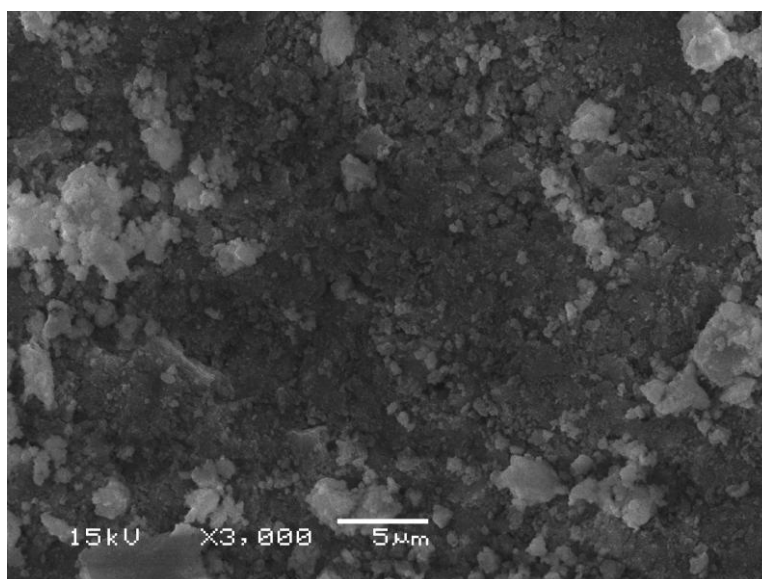
## 7 Results and Discussion

### 7.1 Iron based Catalyst Characterization

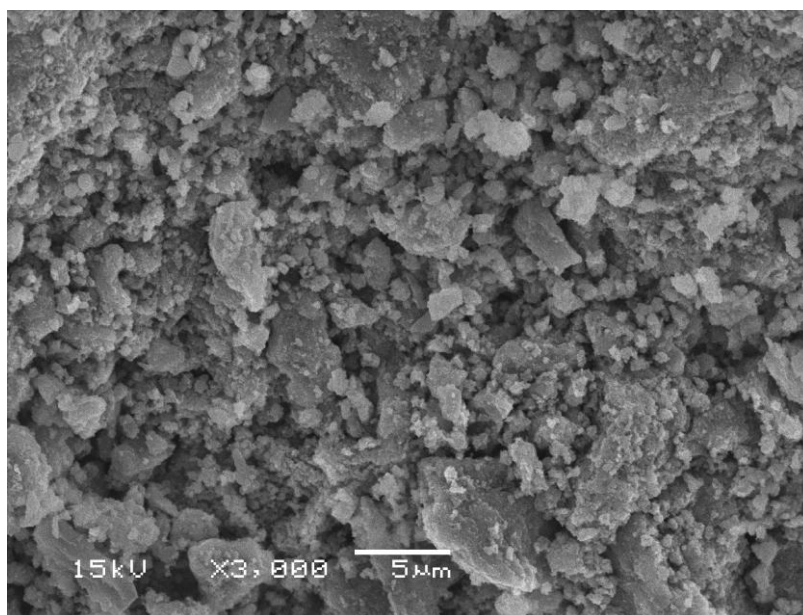
BET surface depends mainly on the amount of the support that is impregnated on the iron based catalyst. The catalyst in this study contains 16 wt% of  $\text{Al}_2\text{O}_3$ . Generally, Addition of alumina improves significantly the surface area, but the WGSR is decreased (Azhar Uddin,2008),(Noichi,2010). Hence, according to these studies the surface of the catalyst is expected ~ 40  $\text{m}^2/\text{g}$  and the obtained results indicated a surface area of 45.1  $\text{m}^2/\text{g}$ . The active surface area of the catalyst was measured after the tests and the result obtained was 15.6  $\text{m}^2/\text{g}$ . This indicates a significant decrease of the potential surface for reaction with the tar. According to the results from (Azhar Uddin,2008),in some cases the active surface area was also decreases more than 50% after the use of the catalyst.

X-ray diffraction (XRD) patterns were recorded with PHILIPS X'Pert Pro System with a Cu-K $\alpha$  radiation of  $\lambda=0.154056$  nm (45kV, 40mA) and step size 0,017° (40 sec/step). The measurements were acquired both for the fresh and used catalyst in order to determine the influence of the reduction and the interaction of the hydrocarbons with its crystallites. The measurements indicated that the Magnetite ( $\text{Fe}_3\text{O}_4$ ) is much more intense in the fresh catalyst. Iron oxide ( $\text{FeO}$ ), aluminum oxide ( $\text{Al}_2\text{O}$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ) are the main crystallites of the used catalyst. This is expected as after the use, the catalyst is more reduced iron state and it is more active.

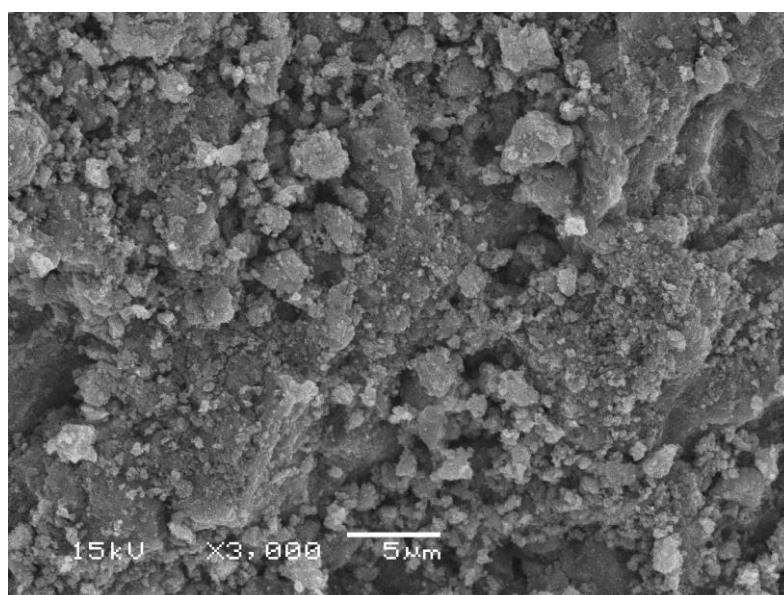
Scanning Electron Microscope was used to scan the fresh and used iron based catalyst. The used catalyst was observed to have grey and black particles, so with the microscope analysis, the point was to investigate whether this difference could be evident. In the following Figure 23: SEM image of Fresh catalyst Figure 24 and Figure 25 are presented the results from the measurements. From this measurement, the particle size growth is evident, and this could lead to possible deactivation. Still in these tests, the growth of the particles didn't affect the catalyst's performance.



**Figure 23:** SEM image of Fresh catalyst



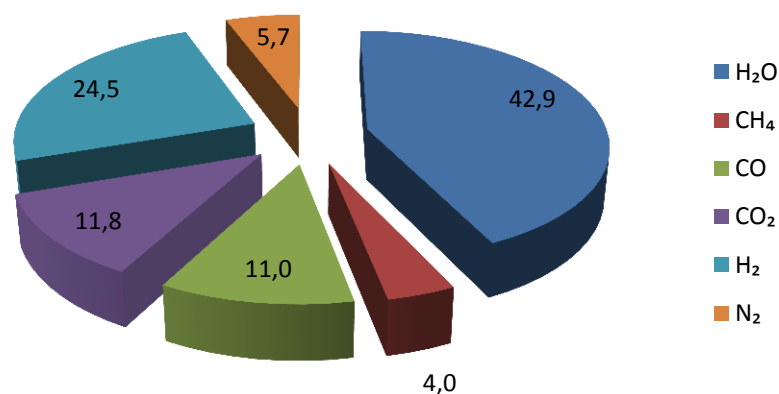
**Figure 24:** SEM image of Used Catalyst, grey particles



**Figure 25:** SEM of Used Catalyst, black particles

## 7.2 Sampling and Gas Analysis

The product gas was online monitored in order to determine its composition at different operating conditions. The sampling point was after the catalyst bed, in order to have a clear picture of how it is affected by the presence of the catalyst. With the results of these measurements further values were calculated to define the potentials of the syngas. The compounds that were measured were CO, CH<sub>4</sub> and H<sub>2</sub> which constitute the fuel of the product gas and of course the CO<sub>2</sub> and the water content. The gas yield before the throughput of the gas in the catalyst bed can be seen below Figure 26. After the decomposition of the tar inside the catalyst bed the composition changes significantly.



**Figure 26:** Gas composition before catalyst test rig

Dry product gas Lower Heating Value (LHV) was calculated for the different operating conditions. The results can be seen below in Table 6, Table 7 and Table 8. For the iron based catalysts, it can be seen that as the temperature increases the heating value increases too, whereas as the space velocity increases the heating value decreases. This is expected as the temperature and the residence time of the gas in the catalyst are two essential factors that define the value of the product gas. The higher the activity of the reactions that take place the higher the richness of the gas composition in H<sub>2</sub>, CH<sub>4</sub>, and CO. For the iron based catalysts, the highest heating value of the gas is obtained at 860°C and SV=6584 1/h. But this value is very close to the one obtained for 800°C and SV=4488 1/h, which is important as these catalysts are supposed to be used in situ where the maximum temperature reached is 800°C. For the nickel based catalysts, the LHV is slightly affected by the changes in the SV. These catalysts were sufficiently active in all the different operating conditions, so the differences in the residence time didn't affect a lot the gas composition. For the precious metal catalysts the influence of the SV is not very evident either. The LHV of these two catalysts don't differ a lot but the product gas in their presence has significantly higher heating value compared to the iron ones.

To calculate the LHV first the wet concentration of every compound was found with the following equation

$$\text{wet concentration} = \text{dry concentration} \times \frac{100\% - \text{Vol \% H}_2\text{O}}{100\%}$$

Then taking into consideration the molar mass of every compound and its heating value the LHV was calculated, and the results can be seen below. It is obvious that although the operating conditions vary significantly the heating value of the gas didn't range a lot, because the composition of the gas was affected enough by the presence of the catalyst.

**Table 6:** LHV dependency on operational parameters for Iron based catalysts

Gas LHV (KJ/Kg)	Space Velocity (1/h)	Temperature (°C)
7652	4500	800
7486	6500	750
7546	6500	800
7750	6500	860
7434	8500	800
7200	10000	800

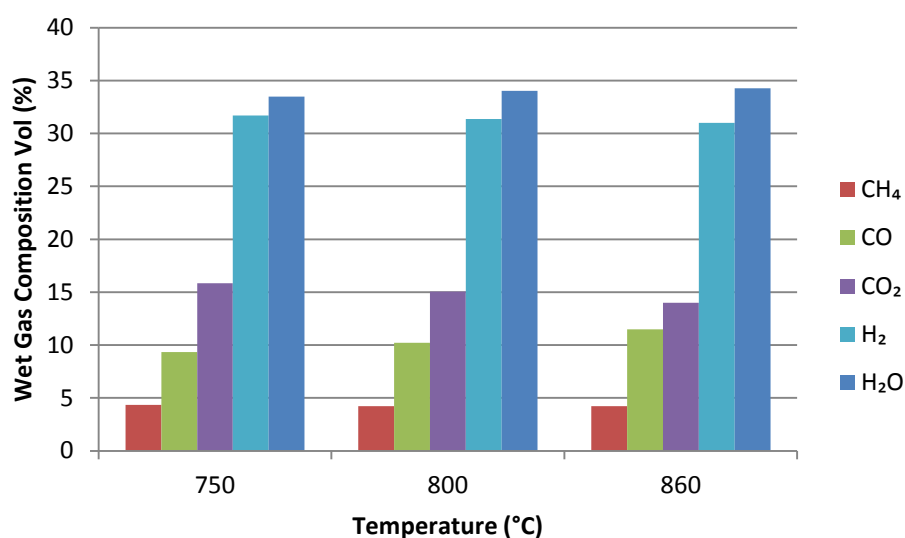
**Table 7:** LHV dependency on operational parameters for Nickel based catalyst at 800°C

Gas LHV (KJ/Kg)	Space Velocity (1/h)
8159	6500
8161	10000
8228	12500
8188	14500

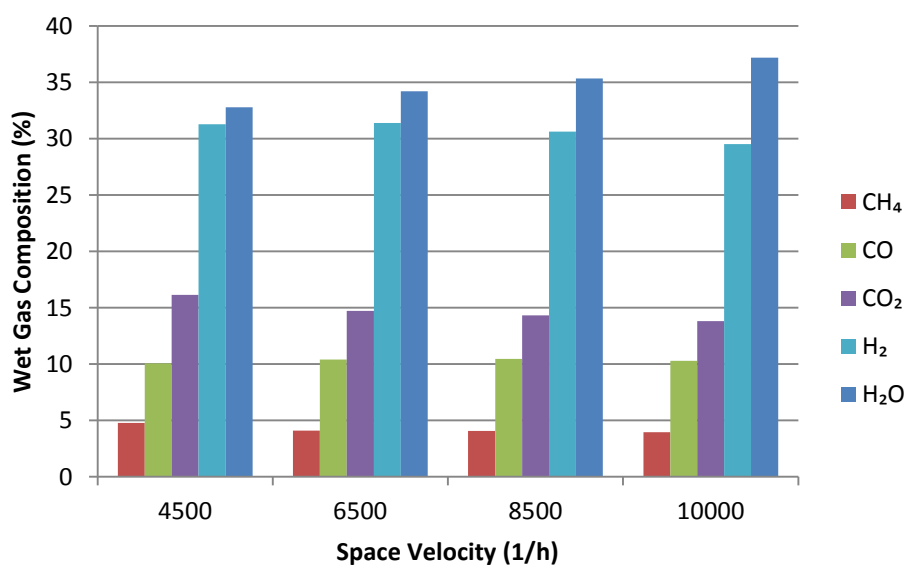
**Table 8:** LHV dependency on operational parameters for precious metal catalysts at 800°C

Gas LHV (KJ/Kg)	Space Velocity (1/h)
8248	4500
7546	6500
7750	10000

In the following Figure 27 and Figure 28 the gas composition in the presence of iron based catalysts is presented. It is easily concluded that Le Chatelier's principle affects a lot the result of the product gas. The  $\text{CO}_2$  is decreased both with the raise of temperature and the decrease of the residence time. In comparison,  $\text{CO}$  increases in both cases and  $\text{CH}_4$  and  $\text{H}_2$  are stable. There is a wide range of equations that either consume or produce these components. However, the mechanism of their occurrence and the exact influence of each one of these equations are not exactly known, but probably the water gas shift reaction is the most dominate. The fact that the  $\text{H}_2\text{O}$  value decreases compared to the one obtained before the catalyst indicates that it is consumed for steam reforming of tar.

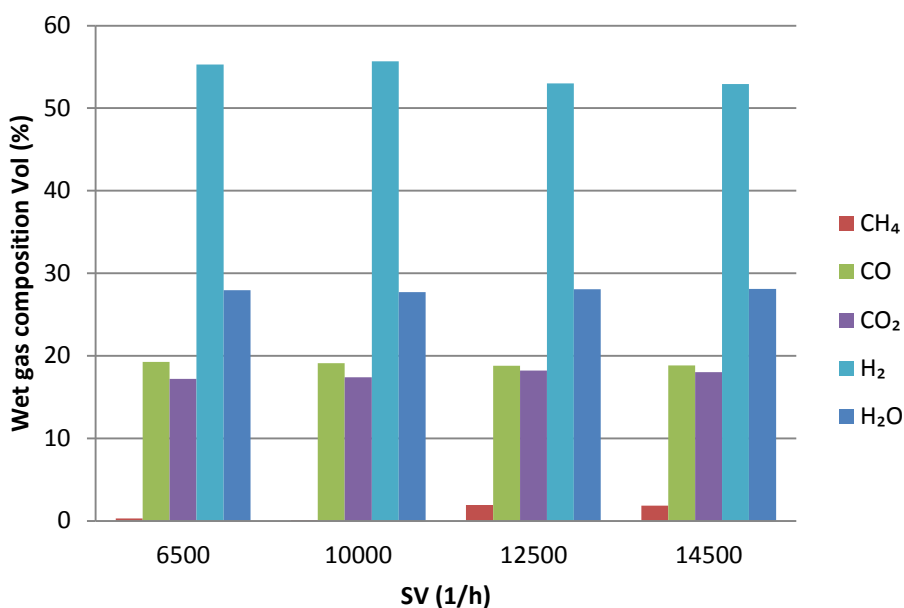


**Figure27:** Iron catalyst-Wet gas composition-Temperature dependence



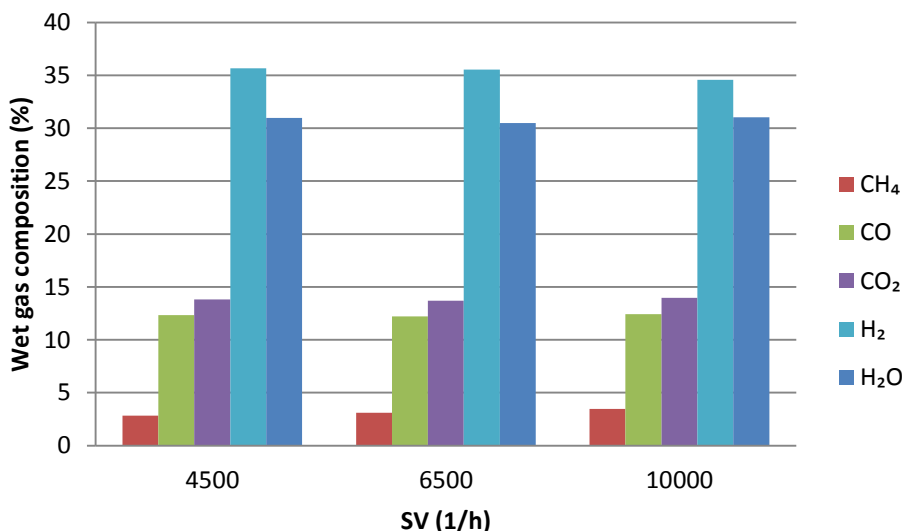
**Figure28:** Iron catalyst-Wet gas composition-SV dependence

As the tar conversion was higher with the use of nickel based catalysts we can see a significant difference in the gas composition in Figure 29. Hydrocarbons are apparently fully converted, so CH<sub>4</sub> is almost zero and the CO value is increased. As a result of the water-gas shift reaction and methane reforming, the production of H<sub>2</sub> is much higher as well as the value of CO<sub>2</sub>. Of course steam is a lot lower (~27.5%) in the gas composition after the catalyst the before the bed (~43%), due to the steam reforming. It also clear that as the residence time decreases, the catalyst works better, but still in all the operating conditions it efficient enough.



**Figure 29:** Nickel catalyst-Wet gas Composition-SV dependence

The precious metal catalyst also had higher tar conversion than the iron based catalyst but lower than the nickel one, the gas composition can be seen in Figure 30. CH<sub>4</sub> is low, not as low as with the nickel catalyst, but it is evident that the hydrocarbons are significantly converted. Steam is ~30%, much lower than the value in the gas composition before the catalyst which indicates high steam reforming action. The CO<sub>2</sub> and CO values are lower for this catalyst, which indicates a not so high activity of the equations. H<sub>2</sub> is ~35%, as it is for the iron based catalyst. The best results are obtained for the lowest space velocity, but the different results between the various operating conditions are not significant.

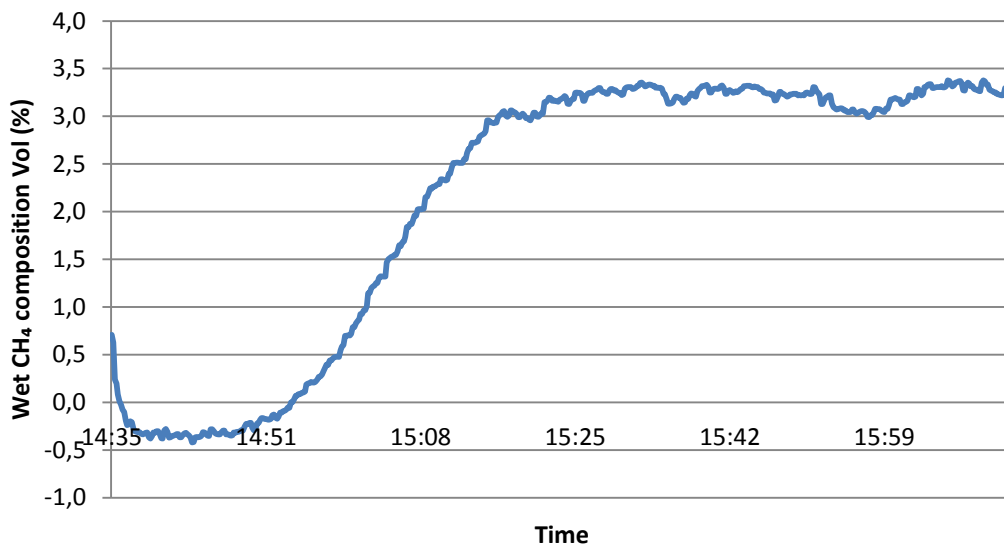


**Figure 30:** Precious metal catalyst-Wet gas composition-SV dependence

It is interesting at this point to mention the behavior of the precious metal catalysts regarding CH<sub>4</sub> conversion. In Figure 31, it can be seen that the product gas started running through the catalyst bed, the methane of the gas composition was zero for a short amount of time. But then it started rising, which in the first place could probably be interpreted as deactivation of the catalyst. However,



er, the value of CH<sub>4</sub> stabilized after a while, which indicated efficient steam reforming. It is probable that the catalyst is semi- deactivated very fast but then it becomes stable and it can work long-term. Either way the value of the methane at dp=0.9 and T=800°C is significantly lower than the value obtained from the iron based catalysts at the same conditions.



**Figure 27:** Change of wet gas composition of CH<sub>4</sub> with time

### 7.3 Tar Analysis

The Table 9 presents the classification of tars. Class 1 one tars can't be detected by the GC/FID.

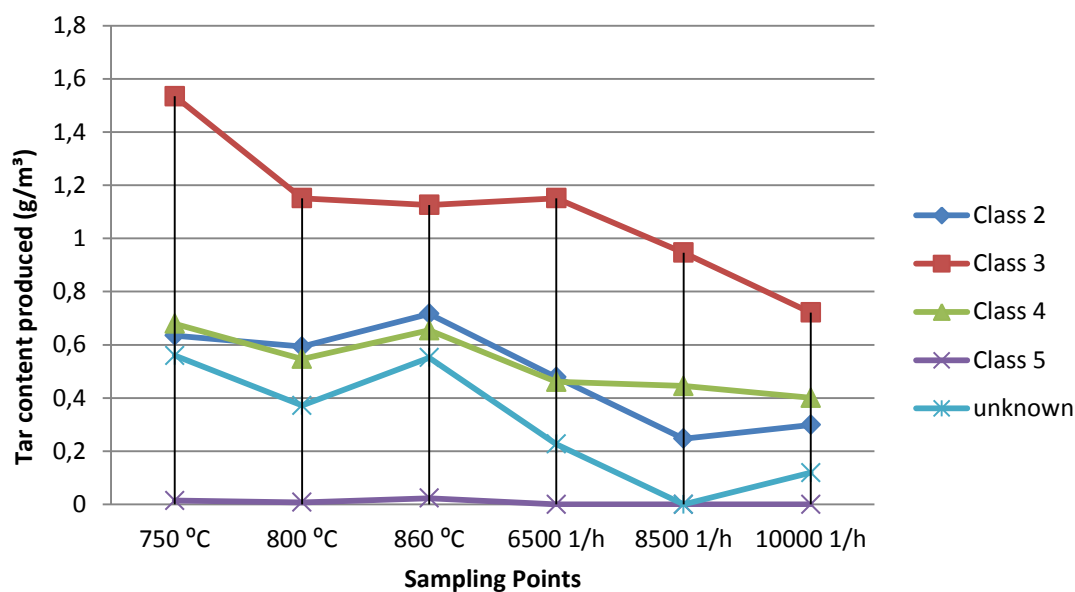
**Table 9:** Classification of tars

Class 2	Class 3	Class 4	Class 5
Phenol	toluene	naphthalene	Fluoranthen
o-Kresol	o-Xyl/Styr	Biphenyl	Pyren
m-Kresol	Inden	Fluoren	
		Anthracen	

#### *Iron based catalysts:*

It is expected that as the char is built up inside the gasifier during the experiment it acts as an in situ catalyst, so as time passed the tar produced decreased. In the following

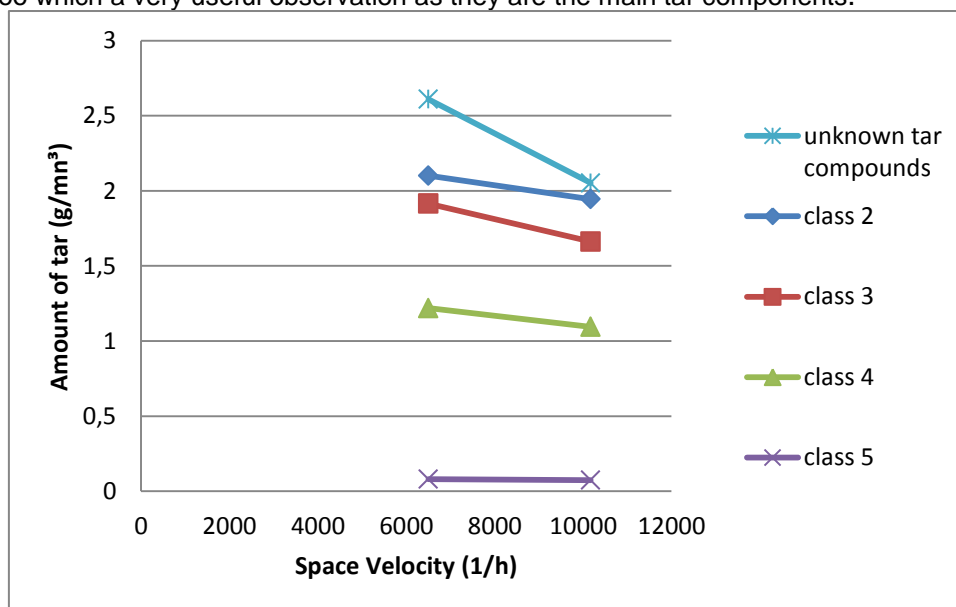
Figure 28, it is seen that as the sampling was made as the time passed there is a clear decrease in for different higher hydrocarbon molecules. The following figure is referred to each tar class compound that was detected by the GC/FID, an unknown compound that is likely benzene is not included in the graph, and the total amount of unknown compounds produced by the gasifier.



**Figure 28:** Effect of the char built up in the reactor for iron catalysts

#### Nickel based catalysts:

During the experiment with the nickel based catalysts, the 1<sup>st</sup> with the 2<sup>nd</sup> sampling points at different space velocities (~6500 1/h and ~ 10000 1/h) were taken with one hour difference. The effect of the char built up inside the reactor is evident in Figure 29. Especially for the unknown tar compounds, that can't be detected by the GC/FID. The amount of class 5 tar is very low during the whole time. Tar class 3, which includes toluene, and tar class 4, which includes naphthalene, decrease too which a very useful observation as they are the main tar components.

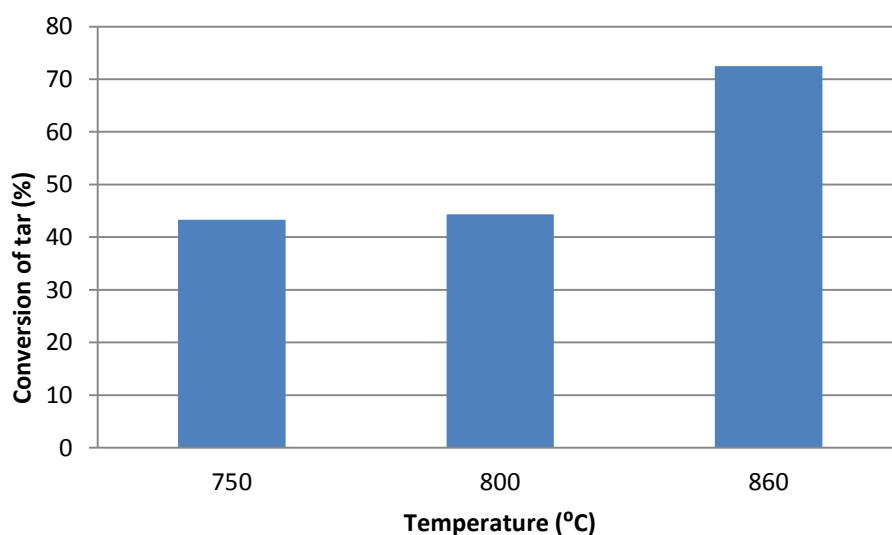


**Figure 29:** Effect of char built up in the reactor for nickel catalysts

### 7.3.1. Effect of reaction Temperature and Space Velocity for iron based catalysts

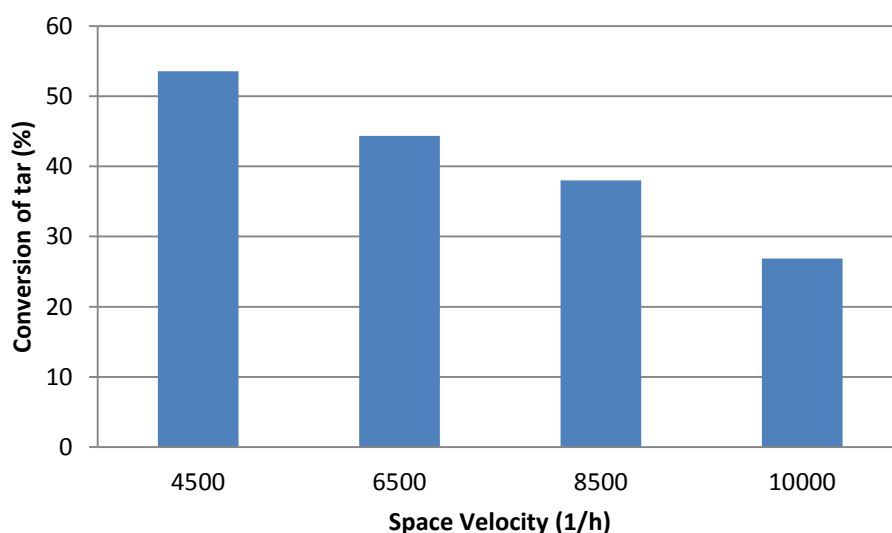
#### *Iron based catalysts:*

The three different reaction temperatures investigated were 750°C-800°C-860°C. The results obtained from the experiment verify the Le Chatelier's principle. It is clear in Figure 30 that tar decomposition is favored as temperature increases, which is in agreement with the steam reforming equations, as they are endothermic.



**Figure 30:** Conversion of known tar compounds-Effect of Temperature

Equally, the higher the residence time, the more time is available for the reactions to occur, so the conversion of the tar is higher. As seen in Figure 31, the conversion of the tar drops significantly when the space velocity increases.



**Figure 31:** Conversion tar - Effect of SV

### 7.3.2 Conversion of tar compounds

#### Iron based catalysts:

In the following Figure 32 the conversion of the tar compounds detected by the GC/FID are presented for the different temperatures that were investigated for the iron based catalysts. As seen, there are some compounds such as phenol, inden, m-kresol, pyren that are almost 100% converted in all conditions. Fluoren is also 100% converted at temperatures 800 and 860 °C. Styrol + o-xylol, o-kresol and fluoren face medium conversion, but others such as anthracen and toluene have very low conversion results. It is important to state that naphthalene increases. This can be justified by the fact that naphthalene is considered as the most difficult compound to decompose. It is the main component of the tar (50-70% of the total amount) and it has been observed that reduction effects are pronounced at higher temperatures (>850°) while its cracking doesn't depend at all on the surface potentials of the material (Nemanova,2011). This statement was reinforced by this experimental work too, as it can be seen at 860°C with a space velocity of 6500 1/h naphthalene conversion reaches 28.74 %.

There was an unknown tar compound detected by the GC/FID increased in every case except for the 860 °C sampling point, at which it reaches 56% conversion. It is likely that this compound is benzene, that is the lightest hydrocarbon which is on the verge of being considered as tar or not. As agreed, benzene is not considered in this work as tar. So the higher hydrocarbons are cracked into lighter ones, among which benzene, and its increase is observed. Biphenyl is also increased. In total, for all the compounds, at the operating conditions tested, it is evident that the conversion of the tar is not achieved. However, if we don't take into consideration the unknown compound, which is probably benzene, the total conversion is about ~27%. As a general conclusion regarding the conversion effectiveness of this type of catalyst, at temperatures lower than 850°C it doesn't react adequately with the tar compounds. But above this temperature the results are promising both for all the compounds individually and the total amount of tar, achieving almost 50% of conversion for all the tar detected by GC/FID. Of course, this great improvement of the catalyst ability is mostly due to the thermal conversion of the tar that takes place intensively as the temperature gets higher. Hence, it is essential to investigate always at which extent thermal decomposition affects the decomposition potentials of the catalysts tested.

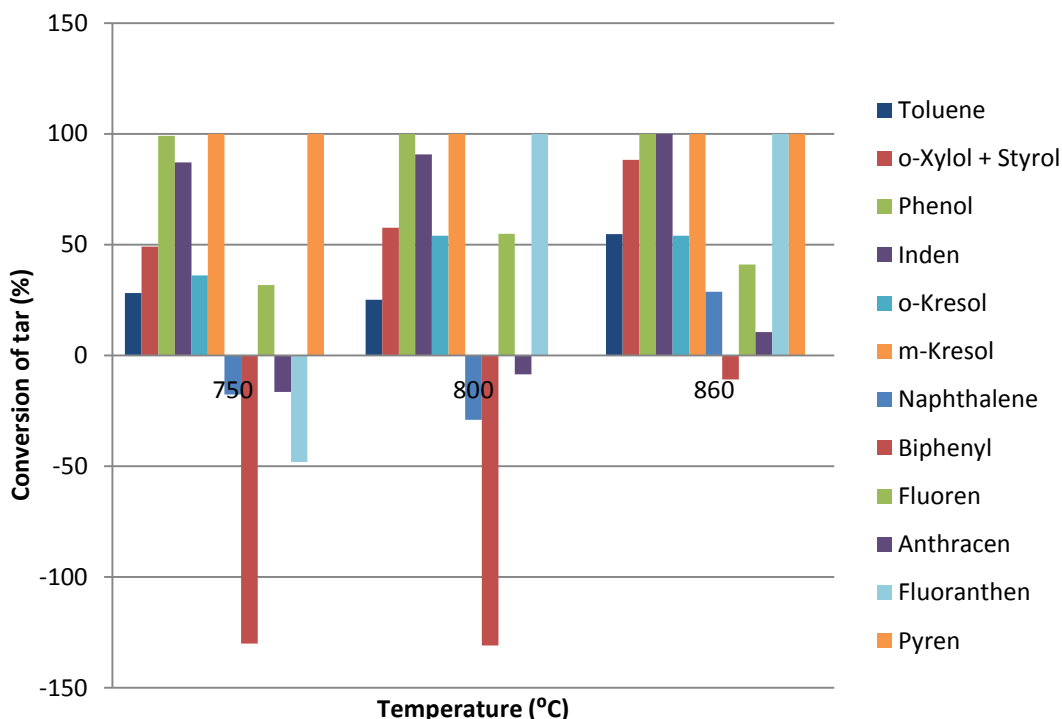
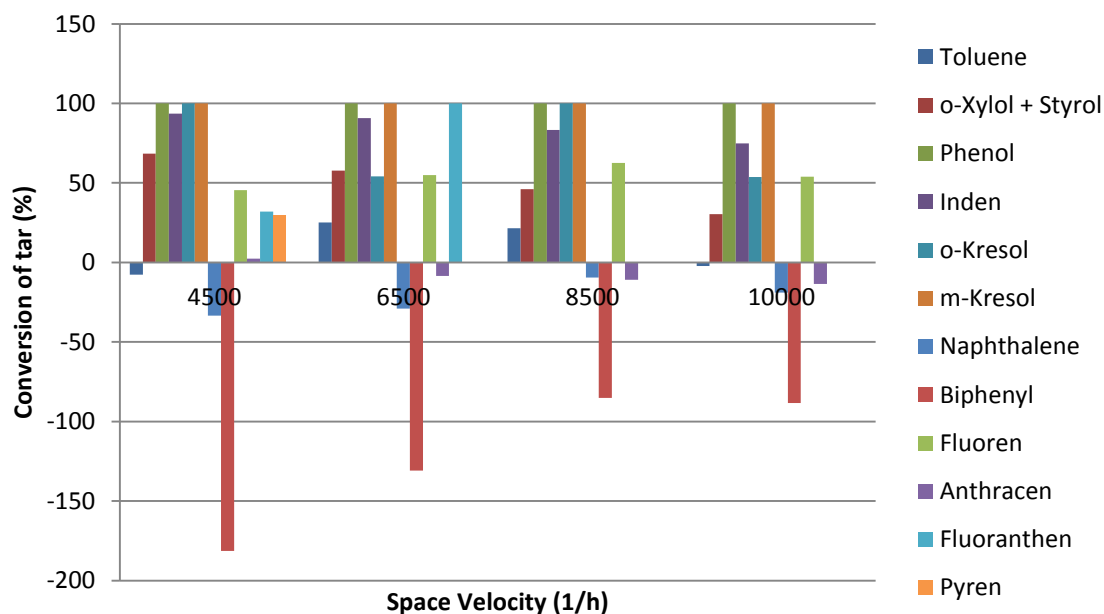


Figure 32: Conversion of tar compounds- Effect of temperature

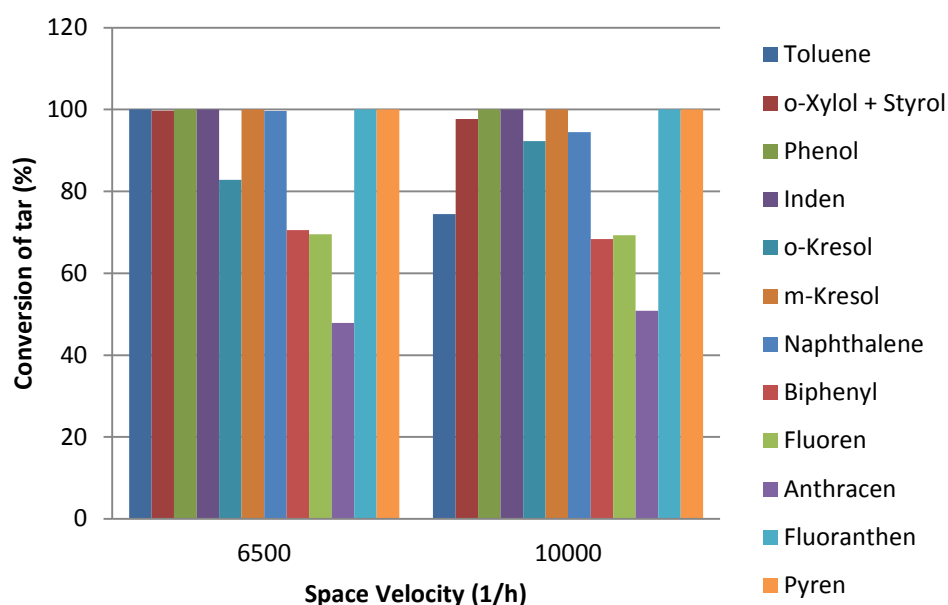
The conversion of the different compounds as residence time decreases can be seen in Figure 33. It is obvious that as the space velocity increases the conversion decreases. However there are some tar compounds such as phenol, inden, o-kresol and m-kresol that have very high conversion in the operating conditions. Toluene either increases slightly or it has a very low conversion. And again Naphthalene and biphenyl increase in the clean gas. O-xyro l+ styrol and fluoren face medium conversion and pyren and perylen are not produced at all from the gasifier.



**Figure 33:** Conversion of tar compounds –Effect of SV

#### Nickel based catalysts:

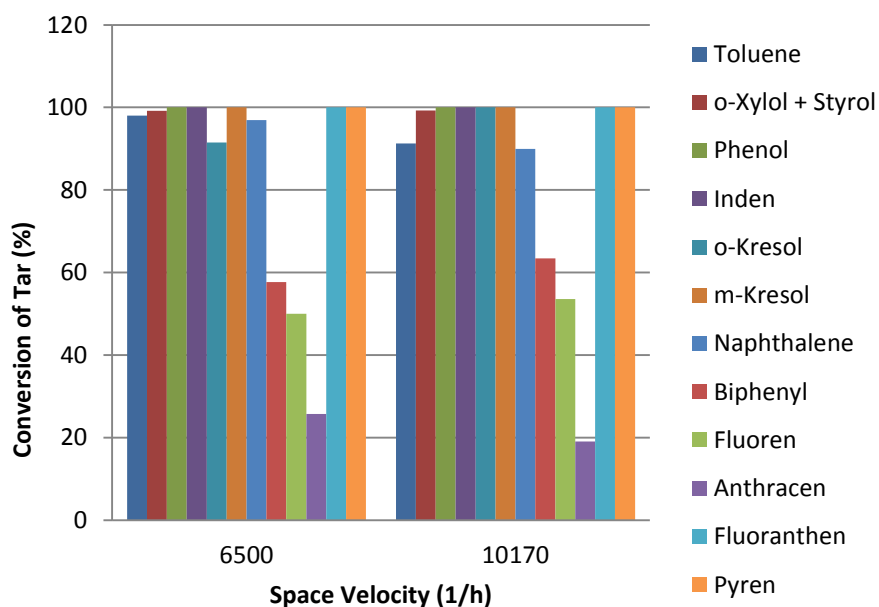
Nickel based catalysts, as known, have a very high tar conversion efficiency. As seen in Figure 34: Tar conversion for nickel based catalysts almost all the tar compounds are fully converted in both operating conditions tested. Naphthalene, which increased in the clean sample of the iron based catalysts, is converted ~99% for the lower space velocity and ~95% for the higher one. Toluene conversion for the higher space velocity is only converted around ~75% but for 6500 1/h space velocity 100% conversion is achieved. The total conversion for 6500 1/h is 98% and for 10000 1/h is 94%.



**Figure 34:** Tar conversion for nickel based catalysts

*Precious metal based catalysts:*

The precious metal catalyst proved to be very promising, Figure 35. Although toluene and naphthalene are not fully converted as with the nickel based catalysts, all the other tar compounds are equally converted with both catalysts. The total conversion for 6500 1/h is 97% and for 10000 1/h is 94%, which is totally comparable with the results obtained from the nickel based catalysts. Apparently, although  $\text{CH}_4$  is higher in the gas composition with the use of this catalyst, all the unwanted higher hydrocarbons are sufficiently converted. Hence, this type of catalyst could be used for methanation procedures.



**Figure 35:** Tar conversion for precious metal catalysts

### 7.3.3 Apparent Kinetic constant for Tar Elimination

The tar content was calculated at the inlet and the outlet of the catalyst. Therefore, Caballero et al. (Caballero,2000) came up with an apparent kinetic constant which indicates the effectiveness of tar elimination. The kinetic is related to the two main parameters that affect the tar conversion such as the temperature and the gas residence time. As the tests for the iron based catalysts were run in different residence times ( $\tau$ ) and different temperatures it is interesting to see how this constant varies with the variation of the parameters. In the studies of Caballero the calculation was made for nickel based catalysts, so a comparison between the results obtained from this work for iron based catalysts, precious metal and nickel based catalysts is worth. The kinetic can be easily calculated by the following equation (46):

$$k_{app,tar} = [-\ln(1 - X_{tar})]/\tau \quad (46)$$

The parameter is calculated for all the different operating conditions that were tested in this work. For the total amount of tar conversion with iron catalysts, the parameter ranges from ~17 to ~56  $mTb_{wet^3}/kg \times h$ . In Table 10 these results are presented. As expected the parameter's value increases with the increase of temperature and it decreases as the space velocity increases. The value of the parameter is a lot lower respectively to the values for the nickel based catalysts, which according to Caballero's work the range from 50 to 130  $mTb_{wet^3}/kg \times h$ . This is expected of course as nickel catalysts are much more active regarding tar decomposition according to literature. The range of the parameter for nickel catalysts is also affected whether it is crushed or not. As for the iron based catalysts tested in this work they are fine particles because the long term aim is to use them in situ with the fluidized in-bed material.

For the nickel based catalysts the results are much closer to the results found in literature. The parameter is ~ 137 to ~ 152  $mTb_{wet^3}/kg \times h$ .

**Table 10:**  $k_{app,tar}$  parameter for iron based catalysts

Temperature (°C)	SV (1/h)	$k_{app,tar}$ ( $mTb_{wet^3}/kg \times h$ )
750	6500	20.63
860	6500	22.95
800	6500	55.82
800	4500	18.93
800	8500	23.70
800	10000	18.43

In the following Table 11, the parameter is presented for the other too catalysts tested at the different operating conditions. As expected, the precious metal catalysts have lower parameter values as their conversion is also a little lower. Still, they are much higher respectively to the iron based catalysts.

**Table 11:**  $k_{app,tar}$  parameter for nickel based and precious metal catalysts

Catalyst Type	SV (1/h)	$k_{app,tar}$ (mTb,wet <sup>3</sup> /kg*h)
Nickel based	6500	136.80
Nickel based	10000	151.73
Precious metal	6500	112.04
Precious metal	10000	145.72

The comparison of this constant for all the types of catalysts is presented in detail in Table 12. The operating conditions that were chosen for comparison for the iron based catalyst are for 860 °C and SV=6500 1/h where the highest value of the parameter was obtained. Still the  $k_{app,tar}$  for iron catalysts is significantly low. The additional information for the nickel based catalyst is given by Caballero et al. 2000. However, it is evident that the nickel catalysts tested in this work have a comparable  $k_{app,tar}$  parameter value with the results from other researchers. As for the precious metal catalysts the parameter is high enough, but still lower than the one for nickel based catalysts. This is expected as the conversion of tars is a little lower too.

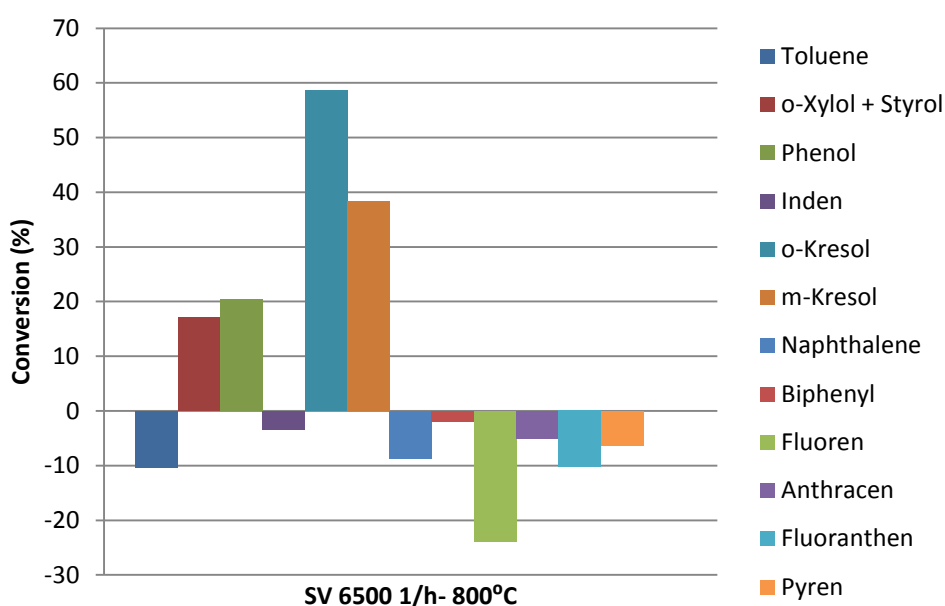
**Table 12:**  $k_{app,tar}$  of different catalyst types

	This work			Navraez et al. 1997	Corella et al. 1999	Cabellero et al. 2000	Cabellero et al. 2000
Catalyst	Iron based	Nickel based	Precious metal	BASF G1-25 S	ICI 46-1	ICI 46-1	BASF G1-50
Space time $\tau$ (kgh/mTb,wet <sup>3</sup> )	0.020	0.018	0.019	0.025	0.014	0.014	0.043
Temperature (°C)	800	800	800	800	845	840	830
$k_{app,tar}$ (mTb,wet <sup>3</sup> /kg*h)	23	152	146	194	294	130	97



## 7.4 Blank experiment

During the experiments with the iron based catalysts it was obvious that at the temperature of 860°C the conversion of the tars was significantly higher compared to the other set points. Hence, a blank experiment was conducted in order to define the role of the thermal destruction in the tar decomposition. The thermal reduction is expected to be 10-20% (Nemanova,2011). The total tar thermocatalytic reduction in Figure 30 shows that the catalytic effect increases from 5% to 25% with the increasing of temperature. To determine the exact percentage of the thermal reduction, the blank experiment was realized in an empty catalytic reactor for temperature 800°C and space velocity 6500 1/h, which is the reference point for this work. The total thermal conversion of tars was 12%. In Figure 36, the conversion of each compound is respectively presented. The tar compounds that faced reasonable conversion were o-xylol+styrol, phenol, o-kresol and m-kresol, which are also significantly converted with the present of the any catalyst.



**Figure 36:** Conversion of tar in an empty catalytic reactor

## 8 Summary/Outlook

The global energy demand is growing, so the substitution of the fossil fuel is essential. The establishment of the biomass fuel gas for heat and electricity production seems to be more and more the key option nowadays due to environmental issues. However, to achieve global use of this alternative energy source it is crucial to purify the gas beforehand its use. Tar seems one of the greater problems as it can cause fouling and blocking erosion of the engine in which the product gas is used. Therefore, the development of catalysts that are able to fully decompose tar is an important research field.

Commercial Nickel based catalysts have been widely tested and seem to have very high effectiveness. Due to their severe disadvantages though, it is necessary to turn towards the research of the effectiveness of other metallic oxides too.

The use of iron based catalysts seems to be a promising solution. Although they are not as effective as nickel catalysts, because they are not easily deactivated they can be used in situ. Precious metal catalysts are not profoundly tested, due to high costs.

The goal of this work was mainly to test these three catalyst types and compare their results. The most promising catalyst is the iron based, as it has a low cost and doesn't deactivate by carbon deposition or sulfur poisoning. All the catalysts were similarly pretreated; they were reduced under a mixture of  $H_2/N_2$  (10%/90%). The operating conditions tested were various, but the reference set point was chosen 800 °C and space velocity 6500 1/h. This was chosen, because the iron based catalysts are meant to be used in situ at some point due their advantages that have been mentioned earlier, and these conditions are typical inside the reactor.

The results indicated that iron based catalysts achieved ~40%, the nickel based ~98% and the precious metal catalysts ~97% tar conversion. These results are in total agreement with previous works. Long terms runs were not conducted to investigate how many hours on stream the nickel based catalysts could last on stream without being deactivated.

As it is obvious from the results, the iron based catalysts didn't reach very high conversion, even at 860 °C, where the thermal decomposition is very high the conversion was ~70%; a lot lower compared to the other two types.

Future work on the optimization of the quality of iron based catalysts is essential. Potentially, they could achieve a reasonable decomposition, so they can be used as an appropriate material for in situ tar conversion. However, regarding the catalysts particularly tested here, there was another drawback too; the particles of the catalyst were very fine. A reasonable amount was blown away from the catalytic bed during time on stream, despite the protective grid that was used to prevent it. Hence, the manufactures of these types of catalysts should also focus on the preparation of catalysts that have larger particles, at least the size of sand, so the material will not blow away during its use.

As for the nickel based catalysts their great potentials have been known for the past 20 years. Their numerous disadvantages must still be resolved though. Regarding carbon deposition on their surface, it is inevitable. Hence, the only possible solution to this would be to regenerate the catalyst after some cycles of usage. It has been reported that this can be achieved if they are put under an oxygen stream to burn away the carbon, but the recovery is not full. Fortunately, the use of an appropriate sorbent for sulfur before the entrance of the product gas, has resolved the sulfur poisoning effect. In addition, the fact that they can't be used in situ renders another drawback, as the use of a second catalytic bed increases a lot the cost of a facility.

The precious metal catalysts have very good potentials too as they concentrate the advantages of the two previous mentioned ones; they achieve high conversion without being deactivated. The precious metal catalysts used here didn't have fine particles enough, to consider them appropriate material for in situ use. Therefore, the manufacture of finer particle precious metal catalysts could be the solution to the need of a second catalytic bed. Plus, due to the fact that they have not been investigated thoroughly, it is not known how much they can actually last on stream. So, long term tests are important to be conducted. One last interesting point to mention for this type, is that although they have the same effectiveness in tar conversion with the nickel based catalysts, the amount of  $CH_4$  in the product gas is quite high, ~5% of the wet gas composition. Thus, they could be a useful material for methanation.

The aim is to produce synthesis gas with very low impurities content for high efficiency power production in engine, turbine or fuel cell application. The catalytic tar decomposition is a crucial and challenging task that has to be investigated. The exact appropriate material to achieve the desirable results is still to be found. However, when the point of having tar free gas is reached, then biomass gasification will be considered as the most appropriate solution to overcome the problem fossil fuel depletion.

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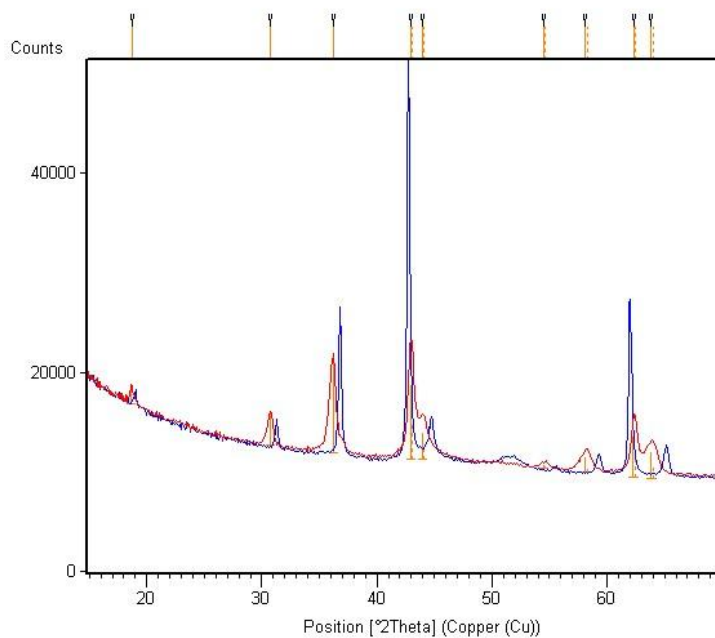
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## Appendix

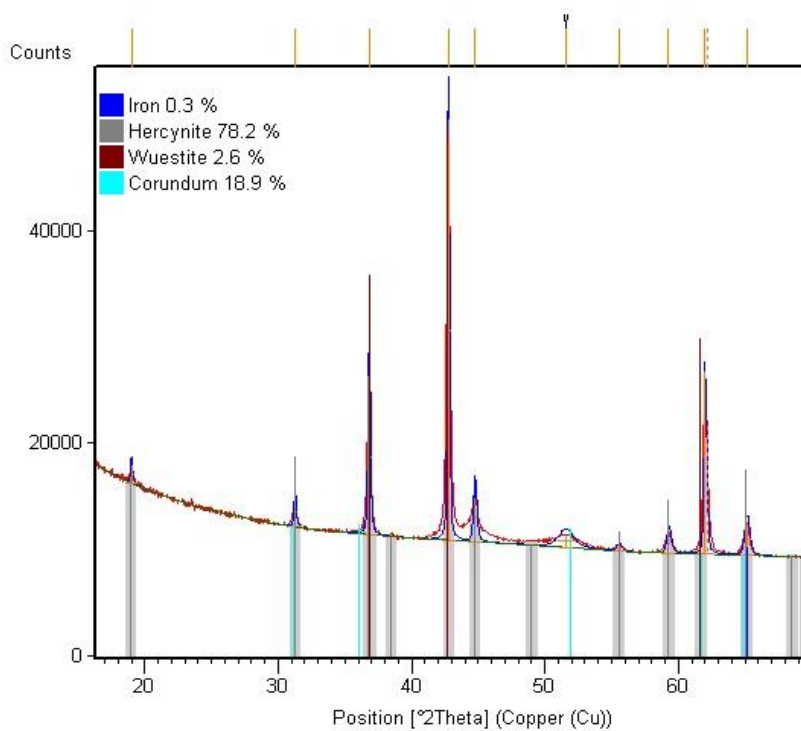
## A: Iron based catalysts in literature

Preparation-Composition	Gas Used	Operating Conditions	Conversion	Comments	Reference
	Steam gasification of wood (cedar sawdust)	600 & 850°C, 4500 /h		Carbon Deposition	(Uddin,2008)
a)Prepared in-house by co-precipitation (Fe/Al <sub>2</sub> O <sub>3</sub> )			Good	Addition of Al <sub>2</sub> O <sub>3</sub> improved the surface area and the activity	
b)Prepared in-house by precipitation with a precipitating agent (Iron Oxide Cat)			Good	The activity seemed stable with cyclic use	
Prepared in-house by impregnation (10 wt% Fe/Olivine)	toluene as tar model compound	7500 /h	91%	High H <sub>2</sub> production,Carbon Deposition (0,0 (Virginie ,2012)	(Virginie ,2012)
Prepared in-house with co-precipitation method (Fe/Al <sub>2</sub> O <sub>3</sub> /Cu)	naphthalene as tar model compound	850°C		Activity increased with the increase of Fe	(Noichi, 2010)
Fe/Zirconia					
Höganäs AB (Iron based Granules)	Gasification of bark-free birch	800°C	60%	70% naphthalene reduction at 850°C	(Nemanova,2011)
Fe-bearing silicate minerals, Fe/Mg <sub>3</sub> (Si <sub>2</sub> O <sub>5</sub> )(OH) <sub>4</sub>	benzene as tar model	700-800°C	77%	with different gas composition even 100% conversion was achieved, Carbon was removed	(Sarvarami,2012)
a)Prepared in-house by incipient wet impregnation method using Fe(NO <sub>3</sub> ) <sub>3</sub> (Calcinated Scallop Shell (2.5 wt% Fe))	Steam Gasification of pruned apple branch	650°C	Good	Reduced catalysts showed better activity	(Guan,2012)
b)Prepared in-house by impregnation of iron on olivine followed by calcination at 1600 °C (10 wt% Fe/Olivine)	Steam Gasification of pine wood	-	Good	Gas analysed for tar reduction only after steady state was reached.Low carbon content and easily oxidized in the combustion zone	(Virginie, 2010)
Höganäs AB (Iron based catalyst in metallic state)	Gasification of biomass	750-850°C	50-75%	Increase of benzene in product gas can occur.No deactivation due to high Oxygen Potentials	(Nordgreen,2012)
Ferron Dolomite Support:Carbonated rocks Sintered Iron Ore Pelletized Iron Ore	Steam Gasification of peat			Iron materials also decomposed NH <sub>3</sub> and HCN	(Simell,1992)
			high	Activity can be increased with the increase of Ca/Mg of the original rock	
			low	The only material that did not increase H <sub>2</sub> yield, high iron content	
			low	Reduction of PAH and monocyclic compounds, high iron content	
Prepared in-house by sol-gel and incipient wetness impregnation method (5 wt% Fe/CeO/Mg)	synthetic gas	700 °C	high conversion	Gas flow rate 100 Nml/ min, Most active catalyst with higher Fe+2/Fe+3 ratio,increase in Fe increased carbon accumulation	(Polychronopoulou,2006)
Small grains of hematite (Reduced metallic iron state)	Steam Gasification of birch	900°C	100%	increase of $\lambda$ improves tar cracking activity (best results for $\lambda$ =0,18	(Nordgreen,2006)
natural iron containing mineral (23 wt% Fe/ilmenite)	Steam Gasification of mallee biomass	850°C	76%	Gas flow rate 0,72-1,5 L/min, high attrition resistibility, as the amount of ilmenite increases the total surface area increases so there are more active sites,coke formation (0,4 wt %)	(Min, 2011)
prepared in-house by olivine impregnation with an iron nitrate aqueous solution (20% Fe/olivine)	toluene as tar model compound	850°C, 7500/h	95%	tar diminution 30g/Nm to 1.5 g/Nm.No high	( Virginie,2010)

## B: XRD Measurement results



**XRD pattern was fresh iron catalyst**



**XRD pattern for used iron catalyst**