Iron-based materials as tar cracking catalyst in waste gasification

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To my family
Abstract

The treatment of municipal solid waste (MSW) in Sweden has changed during the past decades due to national legislation and European Union directives. The former landfills have more or less been abandoned in favour of material recycling and waste incineration. On a yearly basis approximately 2.2 million tonnes waste are incinerated in Sweden with heat recovery and to some extent also with electricity generation, though at a low efficiency. It is desirable to alter this utilisation and instead employ MSW as fuel in a fluid bed gasification process. Then electrical energy may be produced at a much higher efficiency. However, MSW contain about 1% chlorine in the form of ordinary table salt (NaCl) from food scraps. This implies that the tar cracking catalyst, dolomite, which is normally employed in gasification, will suffer from poisoning if applied under such conditions. Then the tar cracking capacity will be reduced or vanish completely with time. Consequently, an alternative catalyst, more resistant to chlorine, is needed.

Preliminary research at KTH has indicated that iron in its metallic state may possess tar cracking ability. With this information at hand and participating in the project “Energy from Waste” an experimental campaign was launched. Numerous experiments were conducted using iron as tar cracking catalyst. First iron sinter pellets from LKAB were employed. They were reduced in situ with a stream of hydrogen before they were applied. Later iron-based granules from Höganäs AB were tested. These materials were delivered in the metallic state. In all tests the KTH atmospheric fluidised bed gasifier with a secondary catalytic reactor housing the catalytic material was deployed. Mostly, the applied fuel was birch. The results show that metallic iron possesses an intrinsic ability, almost in the range of dolomite, to crack tars. Calculations indicate that iron may be more resistant to chlorine than dolomite. The exploration of metallic iron’s excellent tar cracking capacity led to the innovative manufacture of an iron catalytic tar cracking filter as well as a general knowledge of its tar cracking capacity. This filter with dual functionality would be a general improvement of the gasification process since it among other things would make the process denser.
Sammanfattning

Avfalls- och avfallspolitiken i Sverige har under senare decennier genomgått en avsevärd förändring på grund av nationell lagstiftning och direktiv från Europeiska Unionen. De tidigare deponierna har i mycket stor utsträckning övergått till förmån för materialåtervinning och avfallsförbränning. På årsbasis nyttjas i genomsnitt 2,2 miljoner ton avfall i svenska förbränningsanläggningar med värmeutvinning och även i viss mån elproduktion, visserligen till en relativt låg verkningsgrad. Det är önskvärt att förändra nuvarande behandlingsform och i stället övergå till förgasning av avfallet. Då skulle det vara möjligt att utvinna elenergi med en mycket större verkningsgrad eller alternativt producera syntesgas. En sådan övergång är emellertid inte helt oproblematiskt eftersom avfallet i genomsnitt innehåller 1 % klor i form av vanligt bordssalt (NaCl) från matrester. Detta medför att den vanliga tillämpade tjärnedbrytningskatalysatorn i förgasningsprocesser, dolomit, med stor sannolikhet riskerar att bli förgiftad. Klor som bundit sig på ytan av katalysatorn innebär en försämrad och med tiden utebliven förmåga att bryta ned tjäror. Följaktligen finns det ett behov av att utveckla en alternativ katalysator som är mer resistent mot klorförgiftning.

List of papers

This doctoral thesis is based on the following publications, denoted by Roman numerals. The papers are appended at the end of the thesis.

I. Metallic iron as a tar breakdown catalyst related to atmospheric, fluidised bed gasification of biomass

II. Elemental iron as a tar breakdown catalyst in conjunction with atmospheric fluidised bed gasification of biomass: A thermodynamic study

III. Biomass gasification in an atmospheric fluidised bed: Tar reduction with experimental iron-based granules from Höganäs AB, Sweden
Nemanova V., Nordgreen T., Engvall K., Sjöström K.
Catalysis Today (2011)

IV. Iron-based materials as tar depletion catalysts in biomass gasification: Dependency on oxygen potential
Nordgreen T., Nemanova V., Engvall K., Sjöström K., Submitted to Fuel
Other publications and conference contributions

Papers

1. Effects of Chinese dolomites on tar cracking in gasification of birch
   1922-1926.

2. Biomass gasification with dolomite as catalyst in a small fluidised bed
   experimental and modelling analysis
   Baratieri M., Pieratti E., Nordgreen T., Grigiante M., Waste Biomass

Conference contributions

3. Partial oxidation of methane in a biomass gasification gas
   Nordgreen T., Sjöström K., 15th European Biomass Conference, Berlin
   2007.

4. Biomass gasification in atmospheric fluidised bed: Probability to
   employ metallic iron as a tar reduction catalyst
   Nemanova V., Brundu M., Nordgreen T., Liliedahl T., Sjöström K.,
Contributions to the papers

I. I am the principal author and performer of all experiments

II. I am the principal author and performer of all experiments

III. I performed part of the experimental work and I wrote part of the paper

IV. I am the principal author and performed part of the experimental work
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Preface

The concept of gas

The thermo-chemical treatment of solid materials transforming them into permanent gases is commonly known as gasification.

About 400 years ago the Flemish scientist Jan Baptist van Helmont first discovered that a “wild spirit” escaped from heated wood and coal. In 1609 he wrote in his *Origins of Medicine* about the discovery and he named the phenomenon *gas*. However, he failed to find a solution for confining the gases he obtained. In the years to come several other researchers conducted experiments in gas production from wood and coal but they were unsuccessful in turning the gas into practical use. In 1727 Dr. Stephen Hales published in his *Vegetable Staticks* pioneering results concerning airs (gases) that were released during chemical reactions. He had constructed a device allowing released airs to be captured and measured. This apparatus would later become a cornerstone in the work of Joseph Priestley and Antoine-Laurent Lavoisier, the former responsible for the phlogiston theory, suggesting that combustible substances released phlogiston when they were burnt. Priestley’s experiment led to Lavoisier’s development of the experimental theory of the chemical reactivity of oxygen.

In 1733 it seems that the first evidence of coal gas being flammable was recognised and documented by Sir James Lowther in the Philosophical Transactions of the Royal Society. During mining work in a coal pit, the workers observed airs coming out from the ground when they passed a water surface down in the pit. When they held a lit candle towards the “airs” they immediately started burning.

In 1777 the Scottish engineer William Murdoch was employed at the engineering firm of Matthew Boulton and James Watt, erecting stem engines. In the evenings he made experiments on heating coal and observed the flammability of the gases resulting from the coal distillation. In 1792 his experimentation led to his house in Redruth, Cornwall, being illuminated by gas lighting, the gas was conducted through copper tubes. He had developed a method to heat coal in a retort in absence of air which partly converted the coal into gas and left a solid residue, coke. Today, this process would be called coal pyrolysis.

The world’s first gas works, Westminster Gas Light and Coke Company, was founded in London by Frederick Albert Winsor and incorporated by Royal Charter on 30 April 1812, under the seal of King George III. The gas production was based on Murdoch’s technique and was further developed by Samuel Clegg, his former apprentice at Boulton and Watt. He patented a horizontal rotary retort and an
apparatus for cleaning coal gas with a cream of lime. Later on he also patented a gas meter. The gas lighting era had begun.

Many gasworks were built all over the world in the years to come after Murdoch’s first introduction of coal gasification, but quite a long time would elapse before the gas became available to the public. The gas industry flourished as streets, residential housing and industrial buildings were supplied with gas lighting. The invention of the Bunsen burner in the middle of the 19th century and the cyclic steam-air gasification process in 1873 made it possible for the public to use the gas for heating and cooking.

From the early 19th century until the 1940s most of the fuel gas production was based on coal or coke gasification. Concurrently with the development of the gasification process new inventions made it possible to utilise the gas in diverse applications, for example as fuel for steam engines, feedstock in chemical manufacturing and for motor fuels during World War II. Nowadays the gasification technique, at least regarding gasification of coal, is well established and far developed.
Chapter 1

Introduction

Life on earth is dependent on the sun’s radiation. It heats up the earth’s surface and makes the atmosphere warm enough for life to exist. It also provides the energy needed for the photosynthesis to proceed. The climate on earth is also dependent on this radiation since it dictates the evaporation of water from the oceans and the melting of the polar ices. However, not all of the radiated energy from the sun is absorbed by the surface of the earth, some of it is reflected back to the atmosphere as heat (infrared radiation). This infrared radiation is absorbed by the greenhouse gases in the atmosphere and reflected in all directions and some of it is radiated back to the earth’s surface. This process is necessary and normal for keeping the temperature on the earth’s surface at acceptable levels for life to exist. The major part of the greenhouse gases consists of water vapour, carbon dioxide, methane and ozone [1]. Clearly, there is a delicate balance between the concentration of greenhouse gases in the atmosphere and the temperature on the surface of the earth. In recent years many scientists have reported on the need for bringing down the emissions of carbon dioxide into the atmosphere in order to prevent reinforcement of the already existing concentration of greenhouse gases [1]. The message is that the average temperature on earth is increasing, leading to severe changes of the climate. All over the world, people realise that mankind needs to gradually reduce the energy dependence on fossil fuels and find sustainable alternatives. Gasification is one way to address the problem.

Waste may be discarded as material of no value to the owner and therefore likely to be discharged in one way or another. It is generated in all parts of society and contains a wide spectrum of different materials. In the mining industry it is represented mostly by sand and gravel, in the manufacturing industry it is dependent on the kind of product being manufactured. For instance, waste from this area may consist of polymers from plastic industry, iron and sheet-iron from mechanical industry, chips and shavings from forest industry and leavings from the food industry. In addition, all these industries also produce household waste such as paper, corrugated cardboard, glass, plastics, metals, batteries as well as electrical and food refuse. Domestic waste is represented by household waste but also contains furniture, textiles, tyres and garden residues. Household waste is also frequently characterised as municipal solid waste (MSW). Whatever the type of waste they all have in common national legislation and, in Europe, EU directives dictating handling and treatment.

Waste generation is strongly linked to the economic situation in a country and the amount is a direct consequence of the standard of living. The quantity that has to
be treated and taken care of varies from year to year but over time the trend is increasing quantities.

Incineration is the prime thermal treating process for MSW in Sweden. In 2009, about 2.2 million tonnes of MSW were incinerated, producing 12.3 and 1.6 TWh of heat and electricity, respectively [2]. This implies that approximately 48% of the total MSW was incinerated with heat recovery and electricity generation. However, the electricity is generated at a relatively poor efficiency. The generated heat is distributed as ballast in the district heating grid and represents about 15% of the total demand.

An alternative treatment process for MSW is gasification. Morris [3] reports that this process may offer simultaneous production of heat and electricity at a higher output and efficiency compared with incineration. Thus, the electricity output permits an increase of 50% compared to incineration, especially when comparing the existing fluidised bed incinerators that are fed with refuse-derived fuel (RDF, i.e. MSW which has been processed). Murphy and McKeogh [4] have examined gasification of MSW on Ireland; their conclusion is also higher efficiency for gasification compared to incineration.

Nevertheless, gasification does not bring about complete conversion of the fuel into permanent gases and ash. It implies simultaneous formation of hydrocarbons commonly designated as tars. This tar production is one of the main drawbacks of gasification but it can be mitigated by designing a process allowing the application of a tar cracking catalyst. Normally the catalyst is employed inside the gasification reactor, blended with the bed material or in a secondary reactor downstream, containing a catalytic bed.

Nickel and calcined dolomite (CaO, MgO) are the most documented to be effective catalysts for tar cracking. However, MSW contains about 1% chlorine and these catalysts do not operate satisfactorily in such an environment. Under these circumstances they form halogenated compounds and in the case of dolomite with low melting point and high volatility. This implies that the catalysts may start to malfunction through blocking of active sites or simply by leaving the system as contaminants in the product gas. Consequently, the tar cracking catalyst employed in MSW gasification has to be more resistant to high chlorine concentration than existing alternatives.

The work presented in this thesis mainly concerns how to upgrade the gasification gas. The focus is on the tar cracking capacity of iron-based materials in conjunction with atmospheric fluidised bed gasification of birch. Equilibrium calculations indicate that iron possesses a higher tolerance against chlorine than dolomite and therefore optimisation of the conditions for applying iron has been a primary goal.
During the studies a general innovation was hit upon, implying the manufacture of a high temperature catalytic filter consisting of iron materials. This feature is beneficial because it combines two operations into one. The configuration makes the process more effective and reduces the space needed for the entire process. This part of the work was performed in collaboration with Höganäs AB who supplied the iron materials and performed the iron characterisation.

Chapters 2 and 3 give an outline of the Swedish waste policy during the last decades and the circumstances involved in using waste as a fuel. Chapter 4 concerns the thermo-chemical conversion of waste whereas Chapter 5 discusses the gasification technique. Chapter 6 is devoted to the formation and maturation of tars and chapter 7 to cleaning of the resulting raw gas from waste gasification. In Chapter 8 the experimental equipment and procedure are described and Chapter 9 presents a summary of the papers constituting the basis of this thesis. Finally, Chapter 10 contains a discussion of the results from the papers and chapter 11 contains some concluding remarks and suggestions for future work.

The work was conducted at the Department of Chemical Engineering and Technology at KTH – Royal Institute of Technology in Stockholm, Sweden.
Chapter 2

Waste policies

Waste-related issues have been part of the Swedish environmental policy since the beginning of the 1970s. Questions concerning resource economisation, preventing waste from arising, material recycling, producer responsibility and environmental restrictions on waste handling were dealt with in a proposition in 1975 (prop. 1975:32). The emphasis of this proposition is on the producer responsibility, which implies strict plans for handling waste from any manufacturing process and treatment of the waste emerging when the product is used. Another approach also mentioned in the bill was to regard waste as a resource that can be used again.

Already at the end of the 1960s, the capacity for waste incineration started to grow in Sweden. The expansion continued until the middle of the 1980s and, at that time, about 20 plants were in operation. Due to the dioxin debate a moratorium was put on further expansion in the spring of 1985 and it prevailed for about a year until the spring of 1986. By that time, among other things, the emissions of mercury, cadmium and dioxins had been thoroughly mapped and stricter regulations on the emissions emanating from waste incinerators were introduced.

In 1990 a new bill was put forward (prop. 1989/90:100) which was more in the line of preventing waste from arising; actions were to be taken to minimise danger to health and environment. A tax measure was posed upon waste to encourage both decreasing levels and amounts of hazardous components in the waste.

In 1992 the bill (prop. 1992/93:180) that introduced the recycling principle was presented and the producer responsibility was enacted.

Between the spring of 1997 and 1999, additional bills were presented regarding waste handling (prop. 1996/97:172, prop. 1997/98:55 and prop. 1998/99:84). The most important outcome from these bills was the prohibition against deposition of combustible waste in 2002 and organic waste in 2005. In addition, a tax on all deposited waste was introduced on the 1st of January 2000. Those last measures are more or less a result of the European Union directive 99/31/EG, which handles the rules for deposition of waste and 2000/76/EG, which handles the restrictions for incineration of waste.
In 2008 a new framework directive concerning waste was launched in the European Union (2006/98/EG), and it was implemented in Swedish law in December 2010. It was a replacement and elucidation of the former directive 2006/12/EG. The main decision from this directive is the ratification of the waste hierarchy which entails in preferential order:

- Waste prevention
- Preparation for recycling
- Material recycling
- Alternative recycling e.g. energy recovery
- Deposition

In recent years the incineration capacity in Sweden has increased, new and rebuilt facilities have been established. A consequence of this expansion is in some cases a fuel shortage. To find remedy for this situation the incinerator owners have started to import MSW from other parts of Europe, specifically Norway. In 2009 about 36,500 tonnes of MSW were imported. This import is claimed to be justified by the superior technological standard of the Swedish incinerators compared to the treatment processes in many other countries in Europe who still use landfills as the main option for MSW disposal. Bringing the waste to Sweden for treatment would then decrease the emission of methane into the atmosphere and consequently abate emissions of greenhouse gases [5].
Chapter 3

Waste as fuel

Waste produced by the domestic, industrial and commercial sectors of the community is very similar to biomass in composition. This is the reason why birch wood has served as model fuel in most of the gasification experiments referred to in this thesis.

Waste can mainly be divided into two streams: solid wastes and liquid wastes. The solid fraction broadly includes:

- Forest, garden and wood-processing residues,
- Agricultural residues, and
- Municipal solid waste (MSW), which is domestic refuse, commercial waste and industrial waste.
- RDF (refuse derived fuel) is processed MSW i.e. sorted, shredded, dehydrated and converted into pellets.

The wet fraction typically consists of industrial effluents and sewage sludge. In Sweden MSW, also termed household refuse, consists of container and sack refuse, bulky refuse including garden refuse, noxious refuse and comparable refuse from shops, offices, industries and restaurants. The fraction of the refuse covered by producer responsibility is material-recycled or is recycled in other ways: for example newspapers, packaging, electrical and electronic refuse. These fractions are embraced by the concept MSW but are not a municipal responsibility.

The physico-chemical characterisation of the waste is reported by Kušar [6] and presented in Table 1. The composition of waste from other parts of the world is presented in Tables 2 and 3 [7]. A broad variation in composition can be seen in these tables. Perhaps this deviation is a result of differences in legislation and efforts at recycling or consumption patterns and standard of living.
Table 1. Fuel analysis of combustible waste containing 10 % RDF and 40 % RDF, respectively [6]

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Ultimate (mass % dry basis)</th>
<th>Proximate (mass % dry basis)</th>
<th>LHV$^{a}$ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>O</td>
</tr>
<tr>
<td>10% RDF</td>
<td>43</td>
<td>6</td>
<td>41</td>
</tr>
<tr>
<td>40% RDF</td>
<td>43.6</td>
<td>5.5</td>
<td>35</td>
</tr>
</tbody>
</table>

$^{a}$ LHV is lower heating value, $^{b}$ is HHV$_{dry basis}$ (higher heating value) calculated from: LHV=HHV-2.44 MJ/kg *18/2*H/100, H from table 1.

It can be seen that the composition of the Swedish waste does not differ that much from MSW2 in Table 2. In practice, the largest discrepancy is 10 % in the carbon content, even though the total composition changes to some extent. In addition to the RDF content given in Table 1 the waste material also consisted of 50-60 % paper waste, 30-40 % plastics, mainly polyethylene, and 2-3 % forest residues [6].

Table 2. Characteristics of the waste feedstocks (dry basis) [7]

<table>
<thead>
<tr>
<th>Waste type</th>
<th>C (mass %)</th>
<th>H (mass %)</th>
<th>O (mass %)</th>
<th>Ash (mass %)</th>
<th>Higher heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSW1$^{a}$</td>
<td>36.7 (49.2)$^{maf}$</td>
<td>7.2 (9.7)$^{maf}$</td>
<td>31.1 (41.7)$^{maf}$</td>
<td>25.4</td>
<td>8.4 (11.3)$^{maf}$</td>
</tr>
<tr>
<td>RDF$^{b}$</td>
<td>44.0 (53.7)$^{maf}$</td>
<td>8.0 (9.8)$^{maf}$</td>
<td>30.0 (36.6)$^{maf}$</td>
<td>18.0</td>
<td>16.0 (19.5)$^{maf}$</td>
</tr>
<tr>
<td>MSW2$^{c}$</td>
<td>47.6 (54.1)$^{maf}$</td>
<td>6.0 (6.82)$^{maf}$</td>
<td>32.9 (37.4)$^{maf}$</td>
<td>12.0</td>
<td>19.9 (22.6)$^{maf}$</td>
</tr>
<tr>
<td>Waste oil</td>
<td>83.0</td>
<td>17.0</td>
<td>0.0</td>
<td>0.0</td>
<td>34.0</td>
</tr>
<tr>
<td>Landfill gas</td>
<td>47.0</td>
<td>11.0</td>
<td>42.0</td>
<td>0.0</td>
<td>28.2</td>
</tr>
<tr>
<td>Methane</td>
<td>75.0</td>
<td>25.0</td>
<td>0.0</td>
<td>0.0</td>
<td>55.7</td>
</tr>
</tbody>
</table>

$^{a}$ Municipal solid waste typical of a low-income Asian country.
$^{b}$ Refuse-derived fuel made from MSW1.
$^{c}$ Municipal solid waste of a high-income country.
$^{maf}$ Moisture and ash free.
Table 3. Typical composition of municipal solid wastes from high (Miller, 2002; Hoornweg et al., 1999) and low-income countries (Hoornweg et al., 1999; Ramakrishna and Babu, 1982) [7]

<table>
<thead>
<tr>
<th>Category</th>
<th>MSW1 (low-income countries) %</th>
<th>MSW2 (high-income countries) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>3 – 10</td>
<td>30 – 46</td>
</tr>
<tr>
<td>Plastics</td>
<td>2 – 7</td>
<td>7 – 13</td>
</tr>
<tr>
<td>Compostable</td>
<td>36 – 80</td>
<td>23 – 38</td>
</tr>
<tr>
<td>Glass and ceramics</td>
<td>1 – 8</td>
<td>4 – 10</td>
</tr>
<tr>
<td>Metals</td>
<td>1 – 4</td>
<td>4 – 9</td>
</tr>
<tr>
<td>Others</td>
<td>14 – 54</td>
<td>8 – 22</td>
</tr>
</tbody>
</table>

The reported composition in Tables 2-3 is as collected. The moisture content depends on the season and it is in the range 25-56 % for low-income countries and 20-33% for high-income countries.

In Table 4 some examples of the composition of ordinary biomass is presented. It is interesting to notice that the deviations in composition are small between the MSW2 in Table 2 and birch wood in Table 4.

Table 4. Ultimate analysis of two kinds of biomass (weight % maf\(^b\))

<table>
<thead>
<tr>
<th>Raw material</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>HHV(^a) (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(calc. by diff.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Straw pellets</td>
<td>45.4</td>
<td>6.1</td>
<td>38.5</td>
<td>1.7</td>
<td>0.24</td>
<td>19.1</td>
</tr>
<tr>
<td>Birch wood</td>
<td>49</td>
<td>6.1</td>
<td>44.4</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
<td>19.3</td>
</tr>
</tbody>
</table>

\(^a\) HHV is higher heating value  
\(^b\) maf is moisture and ash free.

To sum up, the composition of MSW deviates to some degree from ordinary biomass, but after being processed to RDF, it may be regarded as having the same potential as biomass.
Biomass is a carbonaceous material and referred to as a biological material from living, or recently living, organisms. Consequently, the phrase biomass covers a huge range of different materials.

Wooden biomass for example, has for ages been used to supply energy and heat to mankind. Nowadays the lion’s share of the wood, in industrialised nations, is used in applications such as paper manufacturing and construction materials; only a small part is used for domestic heating. On the other hand, in developing countries wood is the prime source for supplying energy for cooking purposes.

Nevertheless, a growing interest in applying biomass and waste for chemical manufacturing and electricity generation has emerged during the past decades. This interest started to grow during the oil embargo back in 1974 and has recently gained renewed interest following the debate concerning climate change.

The aim for this thesis was to explore gasification of municipal solid waste. For practical reasons though, the fuel used in the main part of all experiments was birch wood which is quite similar in composition to MSW and therefore may serve as a model fuel.

Almost all kinds of organic fuel used in thermal conversion processes contain varying amounts of chlorine. In coal it ranges from 50 to 2000 mg/kg, in peat 200-500 mg/kg and in biomass it may vary between <100 and 7000 mg/kg [8]. The concentration depends on factors such as closeness to the sea, extent of fertilizers, minerals in the soil, human activity and leaching of the soil by rain. When it comes to coal, the main source of chlorine is the groundwater that has been incorporated into the pores after the coal’s formation. The chlorine content in MSW originates primarily from ordinary table salt and PVC. The chlorine concentration may reach levels up to about 1 %. The main amount of chlorine emitted from a coal combustion process is in the form of HCl in the gas phase whereas during gasification of biomass KCl is also emitted [8]. Zevenhoven and Saeed [9] reported that PVC decomposes into HCl and a coke-like residue in the temperature range 200-400 °C. The residue may then be combusted as any chlorine-free solid waste-derived fuel.

However, hydrochloric acid is not the only chlorine species related to incineration of waste. Borianni et al [10] also refer to the formation of gaseous chlorine and dioxins in connection with thermal treatment of waste which makes it mandatory to clean the gas. This observation may be a consequence of the Deacon reaction [11] which predicts that at temperatures in the range of 600 to 700 °C, hydrochloric acid reacts with oxygen to form chlorine and water. The chlorine may then react further with carbon ring structures.
Wang et al [12] made RDF pellets out of polyethylene, print paper and PVC or NaCl. The pellets were decomposed in a reactor consisting of a pyrolyser and a subsequent combustion zone. When the pellets with PVC were pyrolysed at different temperatures i.e. 660 – 800 °C about 65 % of the total fed chlorine formed HCl in the flue gas, whereas when NaCl constituted the chlorine source 30-40 % formed HCl in the pyrolyser with a marked increase at higher temperatures.

In Figure 1 it can be seen that the equilibrium constant for HCl formation is much larger than for the other reactions occurring during gasification.

![Figure 1. Equilibrium conditions for some gasification reactions compared to hydrochloric acid formation](image)
Chapter 4

Thermo-chemical treatment of waste

In general, three different processes are accounted for as being thermo-chemical in relation to waste or biomass transformation:

- Combustion or incineration - total oxidation of the fuel, i.e. oxygen surplus.
- Pyrolysis - conversion of the fuel in absence of oxygen
- Gasification - partial oxidation of the fuel, i.e. less access of oxygen than stoichiometrically required for total oxidation

The process of total oxidation with air as oxidising medium is also called combustion, referred to as incineration in the case of waste combustion. If pure hydrocarbons are used as fuel in a complete combustion process the end products are carbon dioxide and water. The final achievable temperature is dependent on the fuel and the oxidising medium. Typically, wood and organic matter burn in air at approximately 1900-2000 °C whereas carbon monoxide and hydrogen burn in air at 2200-2500 °C. The temperature achieved or controlled is simply a measure of oxygen supply and water content in the fuel. It is not unusual for waste to contain up to 50 % water or more [13]. In waste incineration, the combustion temperature applied is about 1200 °C and the flue gas temperature is around 160 °C.

Incineration is more or less exclusively used as the thermal treatment process for MSW in Sweden [14]. The heat in the flue gas from the incineration is mainly employed in district heating.

During the last decades there has been a great expansion in waste incineration worldwide. In parallel with this growth, voices have been raised against this development due to emissions of environmentally hazardous compounds such as NO\textsubscript{x}, SO\textsubscript{x}, CO, HCl, dioxins and other unburned hydrocarbons. Nowadays, due to regulations and legislation, most of these emissions are brought down to environmentally acceptable levels, especially the highly toxic dioxins. This achievement has been realised due to extensive research in the field of flue gas cleaning and through new improved technology for control of the incineration process. In incinerators, waste is fed to the combustion chamber through a feeding line comprised of several steps in order to roughly grade the fuel. The steps can be various kinds of grids, rocker grates, rolling grates, reciprocating grates or screening drums. During the transport along the grate line and inside the furnace the fuel is exposed to oxygen at elevated temperature. The carbonaceous/hydrogenous waste
is dried and oxidised giving ash and flue gas as products. The hot gas is passed through heat exchangers connected to a boiler for production of process steam, and then it is quenched prior to cleaning and exit to the atmosphere. The steam may be used for district heating or in a turbine for power production to an electricity grid, even though at poor efficiency. The residues or ashes, which remain after the incineration, are usually deposited into landfills. A tax has been imposed on deposition which has resulted in research programmes being initiated in an attempt to make use of the ashes. Examples of such programmes are the examination of the possibilities to use ash as filling material in road construction or as a filling material in cement manufacturing.

Pyrolysis is the thermo-chemical process that proceeds in the absence of oxygen [15-16]. However, an absolutely oxygen-free environment is very difficult to obtain and small amounts of oxygen will usually leak into the reaction chamber. The applied temperature is in the range of 350-550 °C. The products are primarily hydrogen, methane, tars, char (porous carbonaceous material), oxidation products and pyrolysis oil, also referred to as bio-oil when biomass is the raw material. The oil composition and viscosity vary over a broad spectrum and depend on the process conditions. A specific kind of pyrolysis is flash pyrolysis. In this operation, the time factor is very important since it is based on rapid heating of the biomass. The product spectrum is somewhat different from that of ordinary pyrolysis and results in more oil production [17-18].

Gasification is a thermo-chemical process that may transfer a carbonaceous material into gases and a solid residue [19]. The gas produced contains chemical energy and is normally referred to as low (3-7 MJ/m³(n)) or medium (10-18 MJ/m³(n)) calorific gas. The heating value in the gas is dependent on the type of oxygen source used for the oxidation. Air as oxidiser produces the lowest calorific gas due to large nitrogen dilution whereas pure oxygen produces the highest. The primary gas composition resulting from gasification is carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water (H₂Oₐq) and methane (CH₄). However, the distribution of the gas components is strongly connected to the selection of oxidising medium. The solid residue, char and ash, mainly consists of carbon and inorganic species.

The reason why gasification is an attractive thermo-chemical process may be illustrated in the comparison of the result between carbon combustion and carbon gasification:

\[
\text{gasification} \quad C + \frac{1}{2} O_2 = CO \quad \Delta H_{298}^0 = -111 \text{ kJ/mol} \\
\text{combustion} \quad C + O_2 = CO_2 \quad \Delta H_{298}^0 = -394 \text{ kJ/mol}
\]
It is obvious that in the case of carbon combustion there is no chemical energy left in the product gas, the whole amount of the carbon heating value is transformed into heat whereas in gasification about 72% of the heating value of carbon is preserved in the gas phase.

Schematically the gasification process may be represented by:

\[
\text{Carbonaceous fuel + heat } \rightarrow \text{ solid + gas } \quad \Delta H > 0
\]

entailing that the process is endothermic. The initial conversion of the fuel and the very first step in gasification is pyrolysis, also referred to as the primary process. This process is a thermal conversion of the fuel to char and gas. Next, the char is oxidised with an oxygen source supplied in the gasification medium, this oxidation of char is referred to as the secondary process. The most frequently used gasification media are oxygen, air, carbon dioxide, steam or a mixture of these components. Thus, gasification at steady state implies a continuous production of char which is subsequently oxidised to the end products. The composition of the end products is dictated by the process conditions, i.e. temperature, fuel, pressure etc.

In order to describe in more detail the course of events in a gasification process when an organic fuel is applied, normally a few equilibrium reactions are needed. As mentioned previously the main gasification reactions involve the char conversion, formed during the initial pyrolysis step, and may be interpreted by the reverse Boudouard reaction and the water gas reaction:

\[
\begin{align*}
C_{(s)} + CO_2_{(g)} &\rightleftharpoons 2 CO_{(g)} \quad \Delta H_{298}^0 = + 172 \text{ kJ/mol} \\
C_{(s)} + H_2O_{(g)} &\rightleftharpoons CO_{(g)} + H_2_{(g)} \quad \Delta H_{298}^0 = + 131 \text{ kJ/mol}
\end{align*}
\]

These reactions show that gasification consumes energy. This energy is normally supplied by oxygen from air or steam reacting with part of the char:

\[
\begin{align*}
C_{(s)} + \frac{1}{2}O_2_{(g)} &\rightleftharpoons CO_{(g)} \quad \Delta H_{298}^0 = - 111 \text{ kJ/mol} \\
C_{(s)} + O_2_{(g)} &\rightleftharpoons CO_2_{(g)} \quad \Delta H_{298}^0 = - 394 \text{ kJ/mol}
\end{align*}
\]

Other important reactions in gasification are the water gas-shift reaction (WGSR):

\[
CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_2_{(g)} + H_2_{(g)} \quad \Delta H_{298}^0 = - 41 \text{ kJ/mol}
\]
and the steam-reforming reaction:

\[
\text{CH}_4 + \text{H}_2\text{O} (g) \rightleftharpoons \text{CO} (g) + 3 \text{H}_2 (g) \quad \Delta H^0_{298} = + 206 \text{ kJ/mol}
\]  \( (6) \)

The WGSR reaction provides energy when it proceeds to the right. This reaction is believed to be in equilibrium at temperatures > 700 °C, thus having impact on the \( \text{CO}_2 \) and CO concentrations.

Although the reactions presented above are equilibrium reactions this does not imply that equilibrium exists at any time. This is a very important remark to have in mind concerning the mentioned reactions. The reason is that in a gasification system it is possible to reach steady-state operation. However, the total system is dynamic, since the concentrations of the constituents fluctuate due to temperature gradients, oscillations in feeding rate and fluidisation gas flow.

A broad variety of carbonaceous materials may be applied as fuel in gasification processes. In addition to biomass and municipal solid waste (MSW) it is also possible to gasify other carbonaceous materials such as black liquor, and sludge. The final gas composition and the tar concentration in the product gas are highly dependent on the fuel employed.

However, the gasification process is not an absolute transformation of fuels into gases since the gas phase at temperatures beyond 350 °C also contains tars formed during the conversion. This tar formation is a major drawback that needs to be abated. Since the boiling temperature of tars in general are high they will condense at temperatures below 350 °C. This condensation may result in blocking of pipes, filters and cause corrosion or failure in engines, turbines and fuel cells. Tars may also act as catalyst poison in downstream catalytic processes. These processes normally operate at temperatures below the tar condensation temperature in contrast to the gasification temperature that normally prevails at 800-950 °C. Since tar formation is of great importance in connection with gasification processes, Chapter 6 is devoted to this phenomenon.
Chapter 5

Gasification technology

Previous chapter presented an outline of the thermal treatment processes available for MSW. Gasification was explained in more detail since it is the suggested alternative to the presently used conversion process.

However, the selection of a particular gasification technology has major impact on the characteristics of the product gas. This includes its energy content, tar concentrations, particulate levels and actual gas composition regarding its gaseous constituents. Therefore it is essential to carefully select the gasifier design to match the characteristics of the end-use applications. These deployments may be energy utilisation or chemical commodity manufacturing. For some of these applications the requirements on the gas quality are not very severe whereas for others stringent fuel qualities are specified. Below is an overview and description of the most frequently used gasification technologies presented and in Chapter 7 the gasification gas clean-up methods are discussed. The fluid bed gasifiers are more closely examined since it is the most satisfactory alternative for MSW gasification.

Generally, there are three kinds of gasification reactors:

- Moving-bed gasifiers
- Fluid-bed gasifiers and
- Entrained-flow gasifiers

The first category comprises downdraft and updraft reactors the second includes fluidised and circulating beds while the latter solely embraces entrained flow.

In downdraft gasification the fuel is fed from the top of the reactor and the gas (gasification medium) is added in the throats at the middle [20]. The fuel and the gas move in the same direction, downward. The reduction zone is in the lower part of the reactor. The resulting high-temperature gas contains almost no tars and it possesses a medium calorific value. The construction has high carbon conversion rate, is simple, reliable, and proven for certain fuels. But it has limitations in fuel particle size distribution and moisture content as well as poor scale-up ability. The
particulate concentration is relatively low due to the non-turbulent conditions in the gasifier. Figure 2 shows a schematic sketch of a downdraft gasifier.

![Downdraft Gasifier Diagram](image)

Figure 2. Schematic view of a downdraft gasifier

In an updraft gasifier the blast is introduced at the bottom and the fuel at the top of the reactor [21]. The blast and the fuel move counter-current to each other. The resulting low temperature and low calorific gas contains large amounts of tar which are the main drawbacks of this kind of gasifier. Further, the construction is simple and robust with high carbon conversion and good scale-up ability. In this gasifier the particulate concentration is low due to the absence of turbulence. Figure 3 shows a chart of an updraft reactor.
In a fluidised bed gasifier the drying, pyrolysis and reduction take place in a fluid bed. The excellent mixing characteristics and heat conduction in the bed imply high reaction rates due to the very good gas-solid contacting. Since this reactor also is tolerant to variations in fuel quality and size it is specially suited for MSW gasification. However, the high-temperature medium calorific product gas contains rather large concentrations of particulates due to the turbulent conditions in the bed and the tar level is in between those for updraft and downdraft gasifiers. Moreover, this kind of gasifier is the only one with isothermal bed operation which makes it easier to control and also to regulate emissions. Finally, it has good scale-up ability and has capacity to handle large gas volumes. Since this kind of gasifier is appropriate for MSW gasification a closer description of the technique is presented in the following.

Generally, a packed bed supported on a permeable device, placed inside a reactor vessel, exposed to a small upward flow of fluid, gas or liquid, where the fluid percolates through the voids of the bed is commonly designated a fixed or stationary bed. However, if the flow is increased the drag force exerted on the bed particles by the fluid will start to separate the particles and consequently the bed will expand. When the increasing flow reaches a certain rate all the particles in the
bed are freely suspended or fluidised. This flow when all particles are initially fluidised is designated the minimum fluidisation velocity. The behaviour and physical characteristics of the suspension are in many aspects quite similar to those of a fluid. If the flow rate is further increased, up to some given level, it results in different categories of bubbling fluidised bed. Beyond this level at further increased flow rate, the velocity will be so high that the bed is swept out of the reactor vessel. Normally, in gasification applications the state of bubbling fluidised bed is applied since heat and mass transfer are greatly enhanced in this mode as well as particle mixing. This means that an incoming fuel particle entering the hot bubbling bed is instantaneously transformed to the end products typical for the process conditions.

The fuel may be fed directly into the hot bed by means of a screw feeder or by a drop tube placed at the top of the reactor. The fluidising medium and also the gasification agent are introduced at the bottom of the reactor and conducted upward through a gas distribution arrangement. Several solutions for even distribution of the gas flow are available, i.e. porous plate type, nozzle type, bubble cap type. Dead-burned alumina is commonly used as bed material to prevent the sand from taking part in the reactions. A cone connects the lower and upper parts of the reactor, enlarging the upper cross-section. This arrangement decreases the gas linear velocity at the top of the reactor and particles entrained in the gas flow may have time to fall back into the bed. This enlargement, technically described as the freeboard, also provides additional time for the tar particles in the gasification gas to thermally decompose. The final product gas is discharged in the top of the reactor after the freeboard. Figure 4 shows a schematic sketch of a fluidised bed reactor.
A closely-related reactor model to the one previously described is the circulating fluid bed reactor, Figure 5. This reactor possesses all the qualities previously explained for a fluidised bed but a higher fluidisation velocity entrains large parts of the bed and un-reacted char and fuel particles into the gas flow. The particles are transported in the gas to the recycling cyclone where they are separated from the gas flow and recycled back to the reactor. This implies a higher carbon conversion rate than in a bubbling fluidised bed since un-reacted fuel and char particles will be given opportunity to react in a second loop. This circulating arrangement is the reason why this kind of gasifier is extra suited for diversity in fuel size distribution. Further, the reactor configuration has capacity to handle even larger gas volumes than an ordinary fluidised bed.
Finally, entrained-flow gasifiers (not shown) operate at very high temperatures, 1200-1500 °C, the final temperature depends on whether air or oxygen is used as oxidising medium. The product gas has high temperature and calorific value and is more or less free from tars. The carbon conversion is close to 100 % but the fuel is restricted to very small fines (<100 µm). Limitations in selection of construction material (due to high temperature), fuel particle size and ash melting are the major drawbacks. This kind of reactor is mainly applied in coal dust gasification and there is little experience with biomass in such systems.

In light of the facts outlined above the most appropriate thermo-chemical treatment process for MSW is gasification in a fluidised bed, because this process is capable of handling fuels with a broad distribution in particle size as well as energy content. It has excellent qualities in process regulation and the high temperature and medium calorific product gas can be employed for generation of electrical energy as well as heat. The generated electricity is produced at a higher efficiency compared to that resulting from incineration. Finally, the product gas may alternatively be upgraded to synthesis gas and deployed in a range of chemical processes.
Chapter 6

The formation and maturation of tar

The composition of wooden biomass is mainly a mixture of organic polymers. Cellulose, hemicellulose and lignin are the predominant constituents and as a rule of thumb, each of them represents 1/3 of the total composition [22]. Figures 6-8 show schematic sketches of the molecular structure of these polymers. It should be noticed that lignin is the only compound comprising aromatic rings. When these polymers are exposed to heat and oxidative/reductive conditions bonds are broken resulting in genesis of smaller units such as CO₂, CO, CH₄, H₂, H₂O, tar and char. The tar is assumed to be largely aromatic [23].

Fagbemi et al [24] examined pyrolysis products from different biomasses. They found that the quantity of tar reaches a maximum at about 500 °C. This result was in accordance with results achieved by Scott et al [25] who used a fluidised bed reactor for production of pyrolytic oils from peat.

The IEA Gasification Task meeting in Brussels, 1998 [26] agreed to define tar as all organic contaminants with a molecular weight larger than that of benzene.

![Figure 6. Structure of cellulose [27]](image)

![Figure 7. Structure of the hemicelluloses fragment xylan [28]](image)
In a review study, Elliot [23] examined the composition of tar from various processes as a function of temperature. He concluded that at low temperature, 400 °C, the tar consisted of primary products and with increasing temperature it was transformed to phenolic compounds to aromatic hydrocarbons. This transformation process is illustrated in Figure 9. Moreover, he also reported that pressure is an important process parameter controlling tar levels and conditions. At elevated pressure the tar tends to be in a condensed phase consisting of phenols and aromatics.

Elliot also used a GC/MS instrument for analysis of the composition of the tars in different temperature regimes. This analysis is given for some compounds in Table 5.
Table 5. Characteristic tar composition in different temperature intervals [23]

<table>
<thead>
<tr>
<th>Conventional Flash Pyrolysis (450-500 °C)</th>
<th>High-Temperature Flash Pyrolysis (600-650 °C)</th>
<th>Conventional Steam Gasification (700-800 °C)</th>
<th>High-Temperature Steam Gasification (900-1000 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>Benzenes</td>
<td>Naphthalenes</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Phenones</td>
<td>Fluorenes</td>
<td>Acenaphthalene</td>
</tr>
<tr>
<td>Ketones</td>
<td>Phenols</td>
<td>Phenanthrenes</td>
<td>Phenanthrene</td>
</tr>
<tr>
<td>Furans</td>
<td>Naphthalenes</td>
<td>Benzaldehydes</td>
<td>Pyrene</td>
</tr>
<tr>
<td>Alcohols</td>
<td>Biphenyls</td>
<td>Phenols</td>
<td>etc</td>
</tr>
<tr>
<td>Phenols etc</td>
<td>etc</td>
<td>etc</td>
<td>etc</td>
</tr>
</tbody>
</table>

Milne and Evans [23] used a molecular beam mass spectrometer (MBMS) for analysing the tar composition from various processes and suggested a systematic approach for classification of pyrolysis products. They divided them in four major product classes as a result of gas-phase thermal cracking reactions:

- **Primary products:** characterised by cellulose-derived products such as levoglucosan, hydroxy-acetaldehyde and furfurals; analogous hemicellulose-derived products; and lignin-derived methoxyphenols

- **Secondary products:** characterised by phenolics and olefins;

- **Alkyl tertiary products:** including methyl derivatives of aromatics, such as methyl acenaphthalene, methylnaphthalene, toluene and indene;

- **Condensed tertiary products:** show the PAH series without substituents; benzene, naphthalene, acenaphthalene, anthracene/phenanthrene, pyrene;

Moreover, Milne and Evans also stressed the importance of gas-phase reactions that may lead to tar synthesis. Free-radical processes occur in the same thermal regimes where olefins react to give aromatics. Both these processes are ongoing at the same time as the dehydration and decarbonylation reactions causing the transformations mentioned above.

Devi et al [30] examined decomposition of naphthalene as biomass tar model over pre-treated olivine. The prime product when naphthalene is decomposed is permanent gases. They also found a strong influence of reactive gases such as H₂O, CO₂ and H₂ on naphthalene decomposition reactions. The former two showed an enhancing effect whereas the latter had an inhibiting effect. The suggested reaction scheme converts naphthalene among other things to indene that reacts further to toluene and benzene. Moreover, the formation of higher hydrocarbons was also suggested, for example pyrene, acenaphthalene, phenanthrene and anthracene. This formation of PAHs with higher masses occurs via reactions such as condensation,
dimerisation, isomerisation etc. Overall, their conclusion was that the first step for any decomposition mechanism of cyclic non-substituted aromatic compounds is the cleavage of C-H and C-C bonds; this cleavage results in ring opening and consecutive formation of lower aliphatic and aromatic compounds and finally permanent gases.

Brage et al [31] examined the temperature dependence of wooden tar evolved in a continuous bench-scale fixed bed reactor and searched for a correlation between cracking temperature and yields of condensable and gaseous products. With rising temperature, the difference in molecular thermal stability brings about a progressive accumulation of aromatics at the expense of phenols. Furthermore, in relation to total tar, they found an almost linear correlation of the ratio of phenols to aromatics in the temperature range 700-900 °C. They also assert that phenols are decarboxylated inter alia into radicals of the cyclopentadiene type, which are presumed to be intermediates in the formation of indene and naphthalene. This entails that indene and naphthalene yields are increasing at different rates with rising temperature. Thus, indene is favoured at 700-790 °C whereas naphthalene slightly predominate above this region. Also, a linear correlation in relation to total tar was found between the ratios of naphthalene to indene.

In another study Yu et al [32] examined the temperature dependence of tar composition from wooden biomass evolved in a free fall reactor. In the temperature range normally applied in gasification i.e. 700 °C and above, they found that the tar did not contain acids, alcohols or aliphatic compounds but exclusively contained phenols and aromatic hydrocarbons together with small amounts of basic compounds. This phenomenon may be explained in terms of differences in molecular dissociation energies. Increasing temperatures favour the formation of carbon monoxide and slightly decrease the formation of carbon dioxide. The formation of carbon monoxide is attributed to decarboxylation reactions involving hydroxyl and ether groups. Increasing amounts of 3-4 ring aromatics at the expense of substituted 1-2 ring aromatics is also observed when increasing the temperature. Moreover, at a temperature of 900 °C the C₂-hydrocarbons decrease while hydrogen increases and at all temperatures applied benzene is the predominating compound.
Chapter 7

Raw gas cleaning

It has been mentioned in Chapter 5 that every intended utilisation of the gasification gas involves fulfilment of a unique specification of requirements. These requirements mostly concern levels of tars, particulates, fuel-bound nitrogen, alkali metals, sulphur and chlorine. This implies that the resulting raw gas from most of the gasification processes needs to be further cleaned or/and conditioned before it can be deployed in the projected application. However, several alternative techniques may exist for cleaning the gas from a particular contaminant; the first option is normally a selection between high or low-temperature methods. This choice is ultimately dependent on whether the intention is to deploy the gas in an energy conversion process or for the manufacturing of synthesis gas. In the case of energy utilisation it is utterly important to preserve as much energy as possible in the gas prior to the end-use for efficiency reasons whereas in the case of synthesis gas this aspect is not important. Moreover, the synthesis gas alternative has strict requirements for all sorts of contaminants mentioned above and also limitations in molecular ratios whereas the energy utilisation option on some occasions can tolerate small levels of tars in the gas. Besides, no further requests on gas composition prevail for this alternative.

A different classification feasible for the high and low-temperature cleaning methods is to divide them into wet and dry methods. The dry method is more technically complicated and demanding since it requires high-temperature filtration and catalytic cracking of tars. The wet method involves scrubbers, low-temperature filters and adsorption systems. Still, the wet method entails the gas to be quenched, to lower temperature, before it can enter the cleaning process and consequently involves a severe thermal energy penalty. The projected system for MSW gasification in this thesis is the high-temperature model with preserved high temperature down through the entire process. Since catalytic tar destruction is a central issue throughout the thesis it is examined more closely in the following section.

Catalytic cracking of tars is a dry and effective method for reducing the tar content in the product gas. The catalytic material can be applied directly inside the gasifier or in a separate secondary reactor housing a catalytic material following the gasification reactor. Numerous scientists around the world have spent much research effort in finding methods for bringing down the tar concentration in biomass gasification gas. Depending on the end-use of the gas, different standards of tolerance have been suggested [23]. These standards primarily give information on tar limits for utilisation of the gas in engines and turbines. The trend is that
engines have a larger tolerance than turbines. However, the gasification gas may also be further upgraded to synthesis gas and applied in production of chemicals. This utilisation requires very low or no tar content in the gas.

Employment of a tar cracking catalyst in situ in the gasification reactor or as a catalytic bed in a secondary reactor has attracted considerable interest as a method for controlling the tar content in biomass gasification gas. Several materials have been tested and reported as to their tar cracking ability but some general requirements may be propounded. The material has to:

- be generally efficient in tar cracking;
- be inexpensive;
- be abundant;
- be considered disposable, i.e. non-toxic;
- have resistance to attrition;

Nickel is the most effective catalyst for tar cracking. Baker et al [33] used a bench-scale fluidised bed reactor for examination of the tar cracking capacity of two commercial Ni-based steam reforming catalysts and one especially made for their project. When these catalysts were tested inside the gasification reactor, a rapid deactivation occurred due to carbon build-up on the catalyst surface. However, if the catalysts were applied in a secondary fixed or fluidised bed reactor the deactivation was dramatically reduced and initially no traces of tars could be detected. Nevertheless, over time deactivation was recognised and a sort of steady state condition seemed to govern where the rates of carbon-forming and carbon-removing reactions were equalised. The proposed situation was described via the reactions:

\[
\text{tar} \rightarrow C^* + C_nH_m + \text{gas} \quad \text{tar cracking}
\]

\[
C^* + H_2O \rightarrow CO + H_2 \quad \text{carbon-steam reaction}
\]

were \(C^*\) designates carbon on the catalyst surface. They [33] also mentioned the following reactions to be important in this context:

\[
\text{CH}_4 + H_2O \leftrightarrow CO + 3 H_2 \quad \text{methane reforming}
\]

\[
C_nH_m + H_2O \rightarrow CO + H_2 \quad \text{light hydrocarbon reforming}
\]
CO + H_2O ⇌ CO_2 + H_2 \quad \text{water gas-shift reaction}

C_nH_{2n} + H_2 ⇌ C_nH_{2n+2} \quad \text{hydrogenation}

tar + H_2O → CO + H_2 \quad \text{tar reforming}

Aldén et al [34] applied a commercial Ni steam-reforming catalyst in a secondary fixed bed for breaking down tars from pyrolysis of aspen chips. They experienced a 78 % reduction of total tar in the gas stream when no steam was added and an additional 14% when steam was introduced into the reactor.

In a long-run experiment, 22h, Bangala et al [35] tested a commercial steam-reforming catalyst in a fixed bed reactor and applied naphthalene as tar model. With as high a steam/naphthalene ratio as 16 at 800 °C and a residence time of 0.55 s the resulting drop of activity from 88 % to 38 % was believed to be caused by fouling of the catalyst.

Another approach when employing Ni as a tar cracking catalyst is to reduce the tar concentration in the gasification gas, prior to the Ni-containing reactor, this by passing the gas through a catalytic guard bed containing calcined dolomite. This concept was demonstrated by Corella et al [36-38] who reported no signs of deactivation when using a Ni-based catalyst downstream a dolomite guard bed. They observed a tar conversion of almost 100 % during the long-term test (50 h). But the in-coming gas had to contain a maximum of 2 g of tar / m$^3$ (n). However, several parameters such as residence time, steam to carbon ratio, catalyst particle size and type of commercial steam-reforming catalyst play a crucial role in maintaining a high conversion.

On some occasions the biomass fuel contains sulphur which is a powerful poison for Ni catalysts. Zhang et al [39] examined the tar-cracking capacity of several commercial steam-reforming Ni-based catalysts promoted with alkali additives. They gasified discarded seed corn in an air-blown fluidised bed reactor and used a dolomite guard bed for capturing fine particulates, steam reforming of the heavy tars, and also for adsorption of hydrogen sulphide. They achieved a 99 % destruction of the tars present in the gasification gas after the guard bed, on a 12-18 h time scale, but had a severe breakthrough of sulphur to the metallic catalyst. However, intensive steam injection, at a ratio of 4-6 steam/total organic carbon, mitigated the poisoning effect but analysis revealed a decreasing pore size distribution and surface area due to temperature effects and a diminishing catalytic performance was to be expected in the long run.
Even if nickel possesses the best tar conversion ability it may not be the proper alternative for applications in atmospheric biomass gasification due to high costs and severe risk for deactivation via sulphur chemisorption and carbon deposition. Previously mentioned is the use of dolomite as tar cracking catalyst (used as a guard bed). Dolomite is a magnesium ore with the general formula $\text{MgCO}_3 \cdot \text{CaCO}_3$. It is used in the Pidgeon process for manufacturing of magnesium by thermal reduction. The exact composition varies from source to source but it generally contains 30 wt. % CaO, 21 wt.% MgO and 45 wt.% CO$_2$. Moreover, it also contains the trace minerals SiO$_2$, Fe$_2$O$_3$ and Al$_2$O$_3$. The surface area, pore volume and size distribution differ to some extent among the various types. In order to activate the rock for tar decomposition it has to be calcined. During the calcination process carbon dioxide is released leaving calcium and magnesium oxide as the main active phases [40-41].

During the past decades many researchers have made extensive investigations on the requirements for using dolomite as tar cracking catalyst in biomass gasification. Already back in the late 80’s and beginning of the 90’s, among others, Sjöström et al, Aldén et al, Donnot et al, Sutton et al, Taralas et al, Ekström et al, Simell et al and Corella et al [40-50] report on the feasibility of using dolomite as tar cracking catalyst. In these studies, which may be regarded as pioneer work in developing the biomass gasification process, it became quite clear that many parameters affect the outcome and success of the operation. More recent studies have been put forward by Myrén et al, Yongbin et al, Devi et al, Wang et al, Abu El-Rub et al and Yu et al [51-56]. Taking into account all these papers that have been written some general remarks that summarise and characterise the qualities of dolomite as a tar cracking catalyst may be presented.

Generally, the tar cracking capacity of calcined dolomite is in the region of 77-95 % of the total tar concentration in the gasification gas, resulting in an enhanced permanent gas evolution. The Ca/Mg ratio, pore size distribution, surface area and the presence of iron in the rock has a clear impact on the performance. The same is valid for applied temperature, pressure, equivalence ratio, gasification medium and residence time. The location of the catalyst, in-bed (fluidised bed) or in a separate bed has to some extent a role in the cracking ability. If dolomite is used in-bed it has to be continuously re-fed (as part of the fuel) since the attrition resistance is poor and it may be elutriated from the bed and blown away with the exit gas. However, dolomite catalysts are efficient in tar cracking; they also have some disadvantages such as sensitivity to elevated pressure, i.e. risk for re-carbonisation and thermal instability leading to loss of surface area due to sintering.

Historically, iron is known to be a capable catalyst in different applications, for example the Haber-Bosch process (ammonia), water gas-shift reaction (hydrogen) and the Fisher-Tropsch synthesis (hydrocarbon generation). In the literature,
several authors have reported on the catalytic activity of iron during gasification conditions.

Tamhankar et al [57] examined the conversion of benzene in the presence of an iron oxide/silica catalyst in a thermal twin reactor at temperatures between 400 and 700 °C. They found that about 40 % of the benzene was converted without hydrogen in the reactant gas but almost 100 % conversion was obtained when 10 vol. % hydrogen was fed along with the benzene. Mössbauer spectroscopy analysis of the catalyst revealed that without hydrogen in the reactant gas the original hematite (Fe$_2$O$_3$) phase was reduced to magnetite (Fe$_3$O$_4$), while in the presence of hydrogen the magnetite phase was further reduced to metallic iron. This implies that the most active phase for decomposing the benzene ring was the pure iron metal. However, they further reported that pre-reduced iron oxide also accomplished an almost 100 % conversion of the benzene ring in the absence of hydrogen.

Baker and Mudge [58] examined the tar cracking ability of hematite in a fixed-bed catalytic reactor. When coal was gasified they found it effective for converting aromatics in a sulphur-free environment at temperatures ranging from 450 to 690 °C while problems such as deactivation were encountered when H$_2$S was present in the gasification gas. Simell et al [59] tested several iron-containing materials (dolomite, limestone, ankerite) as well as iron pellets and sinter. In an updraft gasifier, the ammonia and tar-decomposing activity was high. Uddin et al [60] used a two step flow-type reactor for gasification of cedar wood. The bottom of the reactor contained a catalytic bed consisting of hematite. During the experiment the hematite was reduced to magnetite which possessed a tar-decomposing ability and the yields of H$_2$ and CO$_2$ increased.

In steam gasification experiments of Miscanthus pellets in a quartz tubular reactor Khelfa et al [61] incorporated hematite in various amounts into the fuel pellet. They experienced an almost 100 % conversion at 850 °C when 3 wt % hematite was mixed with the fuel. The liquid yield was 5.2 wt %, half the amount obtained in experiments without catalyst. Asami and Ohtsuka [62] used an aqueous solution of FeCl$_3$, which was available as waste acid from iron and steel pickling plants, to precipitate iron, with the aid of Ca(OH)$_2$, on brown coal particles. When the particles were subjected to steam gasification they observed an extraordinarily high activity at low temperatures.

Natural olivine, with the general formula (Mg$_{x}$• Fe$_{1-x}$) SiO$_4$, or MgO • SiO$_2$ • Fe$_2$O$_3$ (48-50, 39-42, 8-10 %), is one of the most abundant basic minerals throughout the world. Sweden’s neighbouring country Norway has, among others, ore deposits of this stone at their disposal. Olivine possesses ability to decompose tars formed in biomass gasification. It has excellent mechanical strength resulting in a high
attrition resistance, surpassing by far the characteristics of dolomite, and is therefore applied as bed material inside the gasifier.

Rapagna et al [63] compared the tar cracking capacity of sand, olivine and dolomite in a continuously fed, bubbling fluidised-bed gasifier. At 770 °C olivine showed a dramatic reduction of tars in the product gas. They report on an almost 20-fold tar reduction and at the same time an increase of 50 % in gas evolution. The char was reduced by more than 30 %. The catalyst may also be mixed with sand and located in a separate fixed bed.

Devi et al [64] compared the tar cracking ability of dolomite and olivine. A slip stream from a bubbling fluidised bed gasifier fed with beech at a rate of 1 kg/h was passed through a catalytic bed with 17 % load of catalyst material. In this test dolomite was capable of reducing the tar amount by 63 % whereas olivine only managed a 46 % reduction at 900 °C. The dolomite was activated by calcination for 1 h at 900 °C in an inert atmosphere while the olivine was not pre-treated. The low activity observed for olivine compared to dolomite may be explained by the non-porous structure of olivine in addition to the lack of pre-treatment. In another study Devi et al [65] examined the tar cracking capacity of calcined olivine. They made tests with olivine calcined in air at 900 °C for 1-20 h and reported a clear improvement of the capacity after calcination. They observed more than 80 % conversion of naphthalene after 10 h of calcination in air at 900 °C. The contribution of crystalline hematite on the olivine surface increases due to calcination and the oxidation state of iron changes. These circumstances may be an explanation for the increased activity in tar cracking for calcined olivine.

Generally, in most industrial catalyst applications deactivation reaches a point where the conversion does not fulfil the original design specifications. At this point the catalyst must either be replaced or regenerated. There are several reasons for the catalyst losing its activity with time and they may be divided in two categories:

- Physical changes
- Chemical interactions

In the first category the most common change of the catalyst is loss of surface area due to sintering. Small crystallites of the active component migrate on the surface of the catalyst and coalesce into larger particles. Sintering may also change the pore size distribution, implying loss of volume for reacting molecules to diffuse in. Other physical changes may be fouling, phase changes and component volatilisation. Catalyst poisoning is the prevalent reason for deactivation in the category of chemical interactions. This means that active sites on the catalyst
surface are blocked by elements adsorbing to these sites. This adsorption can be divided into two categories, physi-sorption and chemi-sorption. In the former molecules are attached to the catalyst by Van der Waal forces, which are comparatively weak intermolecular attractions caused by dipole-dipole forces. The adsorbed molecules can form multiple layers at the catalyst surface but are relatively easy desorbed if the electrical double layer is interrupted. On the other hand, an adsorbed molecule via chemi-sorption is a much stronger form of adsorption since it implies a chemical bond to the catalyst surface and consequently desorption is more difficult. Usually the poisoning elements are brought into the system by the fuel or introduced in one of the reacting components.

In biomass and waste gasification the risk for catalyst deactivation prevails when the biomass fuel contains sulphur or chlorine. These elements are adsorbed to the catalyst surface according to the second mechanism mentioned above i.e. chemi-sorption. Another risk for deactivation, which may be classified as fouling, is carbon deposition or coking and is generally a serious source of deactivation since carbon deposits on the catalyst surface cover the active sites. This kind of deactivation proceeds when the process conditions are such that carbon formation is favoured via the Boudouard reaction. This implies that the gas composition and the temperature are the chief parameters controlling this kind of deactivation.

If the fuel contains chlorine it will mainly be present as hydrochloric acid in the gasification gas [66-71]. This acid may react with calcium oxide in the dolomite forming an outer layer of calcium chloride.

According to Weinell et al [72] and Gullet et al [73] lime, Ca(OH)$_2$, and limestone, CaCO$_3$, lose one molecule of water and one molecule of carbon dioxide, respectively, at temperatures > 400 °C and > 650 °C. The resulting compound is calcium oxide, CaO, which is more porous and of higher surface area than the original material. However, prolonged heating may result in sintering and loss of the favourable characteristics. Moreover, CaO reacts readily with hydrochloric acid to form calcium chloride over the full range of temperatures normally applied in thermal treatment of biomass or waste. The largest binding capacity has been observed in the temperature range 500-600 °C and below 150 °C. This compound is easily abraded and may also cause blockage of the pore structure.

Figure 10 shows plots of the equilibrium at various temperatures for the reactions of chlorine and hydrochloric acid with calcium, iron and nickel. The predominant reactions are those of calcium which consume chlorine in the first case and hydrochloric acid in the second case. Metallic iron also shows affinity for hydrochloric acid but not as pronounced as for calcium. Nickel reacts faster than iron with hydrochloric acid but more slowly with chlorine. For nickel, unlike calcium and iron, the equilibrium constant increases with temperature and the affinity for chlorine is reversed.
Figure 10. Equilibrium conditions for calcium, iron and nickel chloride

Most of the biomass fuels contain sulphur, the amount is dependent on the type of fuel, on the area and kind of soil where it was grown. For example birch contains about 100-500 ppm sulphur whereas straw contains about 1 wt%. Generally, sulphur is a severe catalyst poison that chemisorbs to the active sites of the catalyst and blocks or reduces the catalytic performance. The presence of sulphur in reductive environments above 527 °C is predominantly as hydrogen sulphide (H\textsubscript{2}S) or carbon disulphide (CS\textsubscript{2}) [74]. This implies that in gasification applications these species would probably represent the sulphur content in the product gas. Figure 11 presents equilibrium calculations for several compounds formed when sulphur reacts with components occurring in a gasification gas. Figure 11 also shows that if the oxygen potential is large in the gas, sulphur has a high affinity for formation of sulphur oxides. The reactions between the formed sulphur compounds and active catalyst components are shown in Figure 12. It can be seen that dolomite reacts very readily with sulphur constituents whereas iron, in comparison with dolomite, possess a lower affinity for sulphur. It is interesting to notice in Figure 12 that carbon disulphide possesses the largest equilibrium constants in reactions with catalyst species at all temperatures.
Nevertheless, the charts in Figures 10-12 are constructed from tabulated thermodynamic data [75] and describe the equilibrium reactions. Such charts give a general idea about how possible a specific reaction is. They may also be used as a tool for judging and comparing the likeliness of some reactions under a given set of conditions. However, as has been mentioned before, it is not certain that equilibrium conditions prevail and especially in the case of catalyst poisoning there may be other preferences involved causing catalyst deactivation.

Figure 11. Equilibrium conditions for sulphur in a biomass gasification gas
Figure 12. Equilibrium conditions for dolomite, nickel and iron when sulphur is present in the biomass fuel
Chapter 8

Experimental set-up

The atmospheric fluidised bed gasification system includes a biomass feeder, a pre-heater, a fluidised bed reactor, a ceramic filter and a catalytic bed reactor. Figure 13 presents a schematic view of the gasification system. The reactor part containing the fluidised bed has an inner diameter of 5 cm and a height of 25.4 cm. A cone connects the lower part of the reactor with the freeboard. The freeboard diameter is 10 cm and the length is 50.8 cm. The total volume of the reactor is 5.1 dm³(n). The enlargement of the diameter at the top of the reactor makes it possible for bed material captured in the gas flow to fall back into the bed; it also increases the residence time. The fluidisation medium is nitrogen while the oxidising agent is pure oxygen. Both the filter and the catalytic fixed bed reactor have a length of 70 cm and an inner diameter of 5 cm. All parts of the gasification system are heated with separate external heaters and the maximum temperature is 950 °C. This heating configuration makes it possible to simulate isothermal conditions.

The fuel is fed directly into the fluidised bed near the distribution plate with the aid of a screw feeder. The fuel hopper is provided with a nitrogen purge, and a water cooling system. This is to prevent hot gases from entering the hopper and making the fuel sticky.

![Figure 13. Schematic view of the KTH atmospheric fluidised bed reactor system](image-url)
The amount of biomass (bark-free Swedish birch) with the composition presented in Table 6, loaded in the fuel hopper was 400 g. The fuel particle size was in the range of 1-1.5 mm. The total nitrogen flow was 9.5 dm$^3$(n)/min and the oxygen supply 0.65 dm$^3$(n)/min. Before the fluidisation medium enters the reactor it is pre-heated to 650 °C. The hot gasification gas is cleaned from soot and bed particles in a ceramic filter. After the filter the hot gas is passed through the catalytic bed for tar cracking. The bed material in the fluidised bed was 350 g dead-burned alumina with a particle size of 63-125 µm.

Table 6. Bark-free birch feedstock analysis, moisture and ash free (maf)

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>49.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.3</td>
</tr>
<tr>
<td>Oxygen (by difference)</td>
<td>44.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.005</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Iron-based granules, 150 g, were introduced in the catalyst container. The particles were in the range of 1-3 mm. The whole system was heated up to the defined temperatures in the reactor and the catalytic bed. The biomass screw feeder was started and the gasification commenced. Tar levels in the product gas were measured with the aid of the Solid Phase Adsorption (SPA) technique [76]. Tar sampling was conducted both before and after the catalytic bed on every occasion. This procedure implies that the filter effect was automatically subtracted in each measurement.

The gas composition was determined using a Shimadzu gas chromatograph equipped with a thermal conductivity (TCD) and flame ionisation (FID) detector. The product gas was extensively cleaned from tars and dried before it was passed on to the gas chromatograph. After each experiment, the remaining weights of biomass and bed material, respectively, were measured in order to calculate the char content and feeding rate. The gasification temperatures applied were 800 and 850 °C and the catalytic bed temperatures 750, 800 and 850 °C; the biomass feeding rate was 3-4.5 g/min and the lambda value 0.17-0.23.
Chapter 9

Summary of papers I-IV

Papers 1 and 2 address the development of a basic gasification model and a first experimental evaluation of iron sinter pellets as tar cracking catalyst. Moreover, Ellingham lines are a clear and informative method for graphical representation of equilibria within a system. In paper 2 such a representation is developed and explained for systems containing a gaseous phase (product gas) and a condensed phase (iron materials). Further, the variation of the oxygen potential due to different moisture contents in the fuel and different pre-heating temperatures of the inlet gas are presented. It also accounts for results regarding product gas composition and tar levels prevailing in the outlet gas after the catalytic bed. Paper 2 present results from supplementary examinations of employing iron sinter as tar cracking catalyst. Among other things it presents further details about the difference in tar cracking capacity between dolomite and metallic iron under pyrolysis conditions. Papers 3 and 4 present the results from numerous tests when different iron-based granules were evaluated for their tar cracking capacity. The catalyst materials were provided by Höganäs AB and delivered in their metallic state. Paper 3 presents the results from a study conducted under reducing atmosphere in the gasification system i.e. low values for the oxygen potential. Finally, Paper 4 accounts for the results in tar cracking capacity when the catalyst is employed under oxidative atmosphere in the gasifier.

Paper I

A first series of gasification tests were conducted using different kinds of catalyst materials, e.g. magnetite, hematite and metallic iron. The screening study indicated distinct differences in catalytic activity between the applied candidates. Moreover, a comparative series of experiments between calcined dolomite and metallic iron was also conducted.

The results from many experiments revealed that none of the iron oxides, FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$ was catalytically active in tar cracking. But they all initially achieved oxidation of the tars, resulting in an enhanced production of permanent gases and a reduction of the tar content in the product gas. However, this tendency declined as steady state conditions were established. When the supply of oxygen decreased the catalytic effect eventually vanished.

On the other hand, iron in its metallic state initially turned out to possess good catalytic tar cracking ability. In fact, the intrinsic catalytic ability of iron turned out
to be comparable with that of calcined dolomite. In Figure 14 the total chromatographically determined tar content in the product gas is plotted for the catalyst options presented above. The feeding rate and the ER (equivalence ratio), value were approximately equal in all experiments i.e. 5 g/min and 0.2.

![Figure 14. Chromatographically determined tar content in the product gas when different iron catalysts were employed in the catalytic bed, Fe₂O₃ (■), Fe₃O₄-FeO (▲), Fe (♦) and without catalyst (□).](image)

It is apparent that neither the oxide catalysts nor the metallic iron display any obvious effect in tar destruction at lower temperatures. At higher temperatures a distinct tar reduction can be seen for metallic iron while the oxides accomplish poorer results. Moreover, at higher temperatures also a noticeable thermal decomposition effect is included in the results which can be observed in Figure 14.
Figure 15. Tar content in pyrolysis gas at different temperatures in the catalytic bed, (■) is the results when iron is used and (●) is the result when calcined dolomite is used as a catalyst, gasification temperature = 800 °C and λ = 0.

Figure 15 presents a comparison in tar cracking capacity between calcined dolomite and metallic iron under pyrolysis conditions at an upstream temperature of 800 °C. It is interesting to notice that the tar cracking capacity of both catalysts seems to be in the same range at all temperatures.

On the basis of the results presented above metallic iron seemed to be the best candidate for catalytic tar cracking. Consequently decisions were made to concentrate further work on iron in its metallic state. It is very promising to reveal the existence of an alternative tar cracking catalyst to dolomite with almost the same ability. Especially since it fulfils all the requirements on such a catalyst mentioned in Chapter 7. However, there is still one more request it has to endure, namely being more resistant to chlorine poisoning than dolomite. This request was theoretically examined and the result is presented in Figure 16.
Figure 16. Evolution of Gibbs energy per mole HCl for dolomite and metallic iron

From Figure 16 it is apparent that dolomite reacts with HCl to a much larger extent than metallic iron at all temperatures normally applied in a gasification system. Ergo, metallic iron seems to exhibit all the qualifications needed to be an effective alternative to dolomite for cracking tars during waste gasification.

**Paper II**

Iron compounds and metallic iron, in particular, have given indications of being catalytically active for reducing hydrocarbons in a gasification gas under experimental conditions which were demonstrated in paper I. However, this result is achieved when external heaters are supplying the energy and the oxygen input is carefully adjusted, resulting in almost isothermal conditions in the gasifier. Nevertheless, in a full-scale industrial operation, different situations may prevail, which may increase the risk for catalyst deactivation either by carbon fouling or by oxidation of the metallic iron. In this study the capability of metallic iron to crack tars was examined both theoretically and experimentally. Suggestions are made on proper thermodynamic conditions that have to prevail in the gasifier in order to prevent the catalyst from being oxidised or deactivated by carbon fouling. To make such proposals a gasification model was derived and calculations were made to predict the gas composition in the output stream from the gasifier due to the main gas constituents and the lambda value (i.e. the ratio between the prevailing oxygen
input and that stoichiometrically required for complete combustion). The results from the calculation are implemented in graphs with the intention to obtain an overview of the conditions a metallic iron catalyst system must endure under industrial conditions. The basis of the calculations from the gasification model is enclosed and will not be reproduced at this moment. However, the main results are presented in the following.

Graphic representation of Ellingham lines is a very useful and informative method of clearly visualising the thermodynamic conditions that control the equilibrium between a gaseous and a condensed phase [77]. Such a plot may be the point of departure in the exploration of the conditions that have to be fulfilled in a system using metallic iron as tar cracking catalyst. In Figure 17 the line A-B represents the oxidation of metallic iron whereas D-E visualises the conditions prevailing for fouling of the catalyst. It can be seen in Figure 17 that there exists a window between those lines where the conditions are such that the catalyst will neither suffer from oxidation nor fouling.

![Graphic representation of Ellingham lines when metallic iron is oxidised or fouled by carbon deposition](image)

This implies that the oxygen potential represented by the logarithmic ratio between the partial pressures of carbon dioxide and carbon monoxide has to attain specific values in order preserve the catalyst from being deactivated.

A basic gasification model was constructed. The reason was to acquire a tool for prediction of the gas composition, specifically the oxygen potential and the lambda
value at different applied gasification temperatures. This at given conditions for moisture content, fuel composition and pre-heating temperature. Figure 18 presents some examples of the oxygen potentials and lambda values from the gasification model when the pre-heating temperature is varied between ambient temperature and 600 °C and the moisture content in the fuel is 8 %. It may be seen from Figure 18 that a pre-heating temperature of 400 °C, a lambda value of about 0.23, and a gasification temperature of 850 °C would give oxygen potentials within the area of metallic iron.

![Figure 18](image.png)

Figure 18. Some lambda values and oxygen potentials calculated from the gasification model at 8 % moisture content in the fuel and pre-heating between ambient temperature and 600 °C

The thermodynamic conditions for the elemental iron catalyst to maintain its catalytic activity without being deactivated by carbonaceous deposits or oxidation have been taken into consideration and were explained previously. Figure 19 shows the results from tests conducted at a feeding rate of 3-4.2 g/min and a lambda value between 0.17-0.20. The oxygen potential that prevails in the product gas after the catalytic bed is represented with the dash-dotted line whereas the solid line is without catalyst. However, neither of the gas compositions, except the gas composition after gasification at 750 °C, contains sufficient oxidising power to oxidise the catalyst. Moreover, at higher temperatures, the risk of the iron catalyst being deactivated by oxidising gases decreases significantly. The computed solution according to the gasification model is also shown in Figure 19.
Figure 19. Oxygen potential in the product gas with (■) and without (▲) iron catalyst; the computed solution (○); the upper coarse line represents the wustite formation and the lower coarse line carbon formation.

Figure 20 displays the difference in tar content between product gas after the catalytic reactor containing metallic iron and the tar content in the product gas upstream this reactor. It is apparent that there is a significant reduction of tar in the product gas when metallic iron is deployed as tar cracking catalyst.
Figure 20. Chromatographically determined tar contents in the gasification gas at different temperatures in the catalytic bed at a lambda value between 0.17 and 0.20, the upper line is without catalyst.

**Paper III**

In previous papers, I-II, it has been established that metallic iron generated from sinter pellets may function as a potent tar cracking catalyst. Moreover, limiting conditions for satisfactory operation have been established both theoretically and experimentally and also that iron possesses relatively good resistance to chlorine compared to dolomite. In light of these facts a general innovation was put forward, namely the manufacturing of a catalytic particulate filter. Therefore, among other things extensive experimental work was initiated and performed using pre-reduced iron-based granules as tar cracking catalyst. The work was a joint venture between KTH and the Swedish company Höganäs AB. The iron materials were provided and characterised by Höganäs AB while the gasification tests were conducted in the KTH fluidised bed gasifier.

Table 7 shows some of the characteristics of the iron materials used in this examination.
It is apparent that the characteristics of the iron materials differ in primarily two ways. Firstly, there is a quite large difference in surface area between material S with the smallest area and material H which possesses the largest area. Secondly, materials D and H contain a rather large amount of oxygen in their original state whereas the other materials seem to have more purely metallic properties. This would seem to show that their aptitude for becoming good catalyst materials differ considerably. In the test series the gasification temperature was 850 °C and the lambda value about 0.21-0.23. The catalyst bed temperature was altered between 750 and 850 °C.

The average gas composition after the catalytic bed and the raw gas composition after the gasifier at 850°C are presented in Table 8.

The oxygen potentials are also included in the table. The low values of the oxygen potential imply that the oxidation power in the raw gas is weak and consequently the metallic iron state in the catalytic bed is preserved. Figures 21-22 illustrate the tar reduction capacity of the catalysts in the experimental series.
It is shown in Figure 21 that material S decreases the tar content by a little more than 60 % while material H has capacity for about 50 %. Even if material H possesses the largest surface area (Table 8) it appears not to have a major impact on the tar cracking ability. Normally, the size of the surface area strongly influences the catalytic ability. The reason the for lower catalytic activity may be the larger initial oxygen content for material H which in turn could indicate a larger portion of iron oxide content in the material. Bleeker et al [78] point out an interrelation between the size of an iron particle grain and the oxidation state, implying a swelling of the particle when oxygen is incorporated into the iron lattice and shrinkage of the particle when oxygen is removed. This transformation implies a change in surface structure however, going from a denser state with small pores in the oxidised mode to a situation of larger porosity in the metallic state. These differences in pore structure may have a general impact on the particle inter-diffusion resistance and consequently on the total diffusion rate from the bulk to the interior of the particle. Nevertheless, these circumstances probably have influence on the tar cracking capacity and may be the reason for the iron catalysts’ behaviour described previously i.e. why the catalyst with the largest surface area does not possess the best tar cracking capacity. Figure 22 shows the tar content in the gasification gas after the catalytic bed at different applied temperatures.
Figure 22. The remaining tar content in the gasification gas after the catalytic bed at a gasification temperature of 850 °C

**Paper IV**

An all-pervading theme, expressed on several occasions, is the significance of preserving proper conditions in the gasification system regarding the oxygen potential. Otherwise the risk for deactivation of the catalyst by fouling or oxidation is imminent. It has been demonstrated in papers I-III that iron-based materials in their metallic state are effective in tar cracking.

In a series of tests the gasification temperature was lowered to 800 °C but the lambda value was kept in the region of 0.21-0.23 resulting in an enhanced oxygen potential in the product gas. The catalyst bed temperature was altered between 750 and 850 °C. Examinations of the catalysts after being applied in the catalytic bed for tar cracking during those conditions revealed a decreased metallic content in the catalysts and regions which were partly oxidised to wustite and magnetite. Thus the results from this examination revealed a decreased catalytic capacity. The average gas composition after the catalytic bed and the raw gas composition after the gasifier at 800 °C are presented in Table 9.
Table 9. Average gas composition in the product gas after the catalytic bed at 800 °C

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>CO₂</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO</th>
<th>Oxygen potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sox</td>
<td>31.0</td>
<td>24.3</td>
<td>9.1</td>
<td>33.4</td>
<td>-0.03</td>
</tr>
<tr>
<td>Fox</td>
<td>29.2</td>
<td>24.9</td>
<td>8.9</td>
<td>35.0</td>
<td>-0.08</td>
</tr>
<tr>
<td>Dox</td>
<td>28.9</td>
<td>24.4</td>
<td>9.0</td>
<td>35.8</td>
<td>-0.09</td>
</tr>
<tr>
<td>Hox</td>
<td>30.0</td>
<td>24.2</td>
<td>9.3</td>
<td>34.3</td>
<td>-0.06</td>
</tr>
<tr>
<td>Raw gas</td>
<td>32.2</td>
<td>22.9</td>
<td>9.3</td>
<td>33.4</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

Figure 23 shows the resulting tar reduction capacity when the catalysts were partly oxidised.

Figure 23. Tar reduction at the gasification temperature 800 °C

The best tar cracking capacity during oxidative conditions was demonstrated by catalyst D (Figure 23) with an almost preserved ability compared to the purely metallic situation. This implies that the tar cracking ability of material D is almost insensitive to change in oxygen potential in the product gas. This result corresponds to the line for Dox in Figure 23. The same seems to be valid for materials S and F at lower temperatures in the catalytic bed (see Figure 22). But for higher temperatures the cracking capacity is more or less reduced to half of the capacity of the metallic state. These results can be seen in Figure 23 as the lines for Sox and Fox. Finally, material H, represented by Hox in Figure 23, demonstrates a marked reduction in tar cracking capability especially at higher temperatures.
Overall it is apparent in Figure 23 that the tar cracking capacity is reduced when oxidative conditions prevail in the product gas. Figure 24 shows the tar content in the product gas during oxidative conditions.

Figure 24. The remaining tar content in the gasification gas after the catalytic bed at a gasification temperature at 800 °C
Chapter 10

Catalyst for chlorine rich environment

For the sake of completeness and since the general goal was to explore MSW gasification and the accompanying problems with high chlorine content in the fuel, it appears necessary to shortly narrate results acquired in an examination under these circumstances.

In a set of experiments PVC was blended into biomass (Miscanthus) in various proportions, i.e. 1 – 4 wt % resulting in 0.5 - 2 wt % chlorine content in the fuel. This strategy was intended to simulate the chlorine content in MSW. If the chlorine in the PVC reacts as reported by Zevenhoven and Saeed [9] it would give about 2 % HCl from the highest PVC concentration. The expectations that the catalyst would react with the HCl and form CaCl₂ which in turn would result in a decreased HCl concentration in the gas were not confirmed.

The catalyst container was filled with calcined dolomite. During the calcination the temperature was 850 °C. The outlet gas was monitored on the gas chromatograph and when the CO₂ concentration approached zero the calcination was considered finished. The gasification and dolomite catalyst temperatures were 800 °C. Figure 25 shows the gas evolution at different PVC contents in the biomass. It can be seen that increased PVC content results in a marked increase in gas yield. This finding may be a result of the increased hydrocarbon content in the fuel due to the PVC.
Figure 25. The gas yield at different PVC contents in the biomass at pyrolysis and catalyst temperatures of 800 °C, lambda value=0.

However, no chlorine was detected in the wash bottles or in the catalyst. There were also some difficulties such as collapse of the fluidised bed caused by PVC residue clogging the pores in the distribution plate and several plugs in the biomass feeder. On the contrary, Corella et al [79] conducted an examination in gasifying simulated RDF feedstock containing 3 % chlorine. They used a secondary reactor housing dolomite for tar steam reforming and chlorine capture. They experienced the dolomite in the catalytic reactor to be transferred to a compact, agglomerated or gluing cake.

The catalyst was examined in an X-ray diffraction analyser; Figure 26 shows the X-ray diffraction pattern for the dolomite after it was exposed to 4 % PVC in the biomass, the peaks represent CaO and MgO (the detection limit for the equipment is approximately 1 %).
Figure 26. An X-ray diffraction pattern for dolomite after 4% PVC exposure

With the experience taken into account of above study the strategy in following examinations was changed, as far as chlorine is concerned, in favour of conducting experiments based on theoretical calculations and literature reviews.

The results presented in this thesis, papers I-IV, illustrate a new method for cleaning chlorine-containing product gas emanating from a gasification process. Extensive literature researches within the area expose very sparse information regarding catalysts that operate under chlorine environments. The considerations, instead, appear to concentrate on removal of chlorine from the product gas by adsorption in active material or by dissolution in a wet scrubber [19]. If such a cleaning technique is applied for elimination of chlorine it may require quenching the gas to lower temperature. This will result in loss of efficiency if the gasification gas is aimed for electricity production in a gas turbine. However, if hot gas cleaning is applied, as in the case of catalytic cracking, the efficiency losses will be reduced.
Although much of the experimental results comprising this thesis have already been presented in previous chapters a closer examination of the iron system may serve to give a deeper explanation of the intrinsic qualities.

Iron in reaction with oxygen forms three different kinds of oxides, hematite, \((\text{Fe}_2\text{O}_3)\) magnetite \((\text{Fe}_3\text{O}_4)\), and wustite \((\text{FeO})\) [77]. In Figure 27, an extended plot with Elingham lines is presented for iron and its corresponding oxides. It illustrates the equilibrium conditions between metallic iron and its corresponding oxides and how they are influenced thermodynamically by the oxygen potential and temperature. Also in Figure 27 some oxygen isobars between \(P_{\text{O}_2} = 10^{-10} - 10^{-22}\) are shown. It has to bee noticed that behind any metal oxidation system represented schematically by equation (7) there exists an underlying oxygen pressure illustrated by reaction (8). This implies that the oxygen potential actually reflects the available oxygen in the system.

\[
\text{MO} (s) + \text{CO} (g) \rightleftharpoons \text{M} (s) + \text{CO}_2 (g) \quad (7)
\]

\[
2 \text{CO} (g) + \text{O}_2 (g) \rightleftharpoons 2 \text{CO}_2 (g) \quad (8)
\]

Another repercussion of the reaction system (7)-(8) is that it also represents equilibrium data between metal, oxygen and elemental carbon since reaction (8) is a combination of the following reactions:

\[
\text{C} (s) + \text{O}_2 (g) \rightleftharpoons \text{CO}_2 (g) \quad (2)
\]

\[
2 \text{C} (s) + \text{O}_2 (g) \rightleftharpoons 2 \text{CO} (g) \quad (9)
\]

these in turn may be written as the disproportionation reaction of carbon monoxide, also known as the Boudouard reaction:

\[
\text{C} (s) + \text{CO}_2 (g) \rightleftharpoons 2 \text{CO} (g) \quad (3)
\]
In Figure 27 the line A-B illustrates that the oxygen pressure in equilibrium with magnetite/wustite at about 775 °C is $P_{O_2}=10^{-18}$ implying a CO$_2$ partial pressure about three times the CO partial pressure whereas the oxides hematite/magnetite require an oxygen pressure eight orders of magnitude higher for establishing an equilibrium between the phases at the same temperature. This implies a CO$_2$ partial pressure almost 32,000 times larger than the CO partial pressure which may be regarded as thermodynamically impossible during gasification conditions. Consequently, it is possible to disregard the formation of hematite when metallic iron is considered as a starting material in gasification applications.

Figure 28 is an informative and useful tool for assessing the behaviour of an applied metallic iron tar cracking catalyst during biomass gasification; with the aid of Ellingham lines it presents the prerequisites for magnetite, wustite, metallic iron and solid carbon in the gasification system.

Figure 27. Ellingham lines for the iron oxide phases versus the oxygen potential and temperature and a few oxygen isobars
Figure 28. Ellingham lines for magnetite, wustite, metallic iron and solid carbon

For instance, this figure clearly indicates, as was reported in paper II, that the conditions in the product gas have to be such that the oxidising power is sufficient to bring solid carbon to carbon monoxide but insufficient to oxidise metallic iron to wustite.
Chapter 11

Concluding remarks and further work

Many research activities are ongoing across the world, trying to find successful abatement for tar production during gasification of biomass. However, the aim for gasification has changed over time, in the beginning of the 1970’s, during the oil crisis, the focus for biomass gasification was on production of electricity. The IGCC (Integrated Gasification Combined Cycle) process was developed which is a process for simultaneous production of heat and electricity. Nowadays the focus is on production of synthesis gas. This utilisation would probably turn out to be a very attractive possibility since it entails production of motor fuels from renewable energy sources. However, realising such desires requires effective and reliable gas cleaning methods.

The interests in employing iron material for tar cracking started to grow at KTH during the 1990s. Preliminary tests and literature research had indicated that iron materials may possess an intrinsic capacity for tar decomposition, at the same time being less sensitive than dolomite for chlorine constraints.

An extensive experimental campaign was initiated and numerous experimental examinations were performed using iron-based materials as tar cracking catalyst. The main results from this examination are:

- Iron based materials possess ability to crack tars in a biomass product gas;
- The tar cracking capacity is comparable with that of dolomite when the iron-based materials are employed in their metallic state;
- Theoretical calculations indicate that metallic iron is less sensitive to chlorine than dolomite and consequently has decreased risk for deactivation;
- Theoretical calculations and experimental activity have exposed that metallic iron deployed as tar cracking catalyst run the risk of being deactivated if the oxygen potential in the raw gas is too high;

Even though several authors report on tar cracking capacity for iron oxides [80-81] more research may remain before final conclusions can be made on this subject. Often in experimental examinations the possibilities for long-term inquiries are missing due to equipment limitations or for practical reasons. However, such a study may be necessary in order to completely understand all aspects of applying iron oxides as tar cracking catalyst. Moreover, it would also be interesting to survey the impact of chlorine on iron’s tar cracking ability during gasification conditions in
practical experiments. However this entails further development of laboratory methods.

A general innovation for manufacturing a catalytic filter was put foreword as a new application for the iron granules. This measure would contribute to make the gasification process more effective since it would be denser, i.e. particle filtration and catalytic tar cracking would be combined into one process. However, many complicated problems need to be examined in realising such a development. Alvin [82-84] reports among other things that the ceramic filters today normally applied in hot gas cleaning have to endure the presence of condensed alkali, and chlorine and sulphur species in the ash cake deposit. Further, that ash and char particles can potentially have a deleterious impact on the life of a porous ceramic filter and that they have experienced thermal fatigue, high-temperature creep, and loss of material strength when operated in extended periods of time. The pulse-cleaning system also requires the filter element to withstand vibration and thermal stress. He emphasises that the success of development and production of high durable and reliable filter elements is not solely dependent on the properties of the construction material but also on the relative stability of the material under corrosive high-temperature, high-pressure environments that contain gas-phase sulphur, alkali and chloride phases. However, developments in high-temperature gas cleaning equipment are ongoing.

Sharma et al [85-87] point out that dry hot syngas cleaning processes appear to be potentially more efficient and cleaner than the proven wet systems and that development in collectors for prevention of filter corrosion and a novel pulse-less filtration concept have been evaluated experimentally. Rapagna et al [88-89] have tested a catalytic filter inside the gasification reactor and experienced a 69 % overall increasing gas yield and a 79 % total tar reduction. Zhao et al [90] precipitated 1 wt% nickel on a ceramic filter candle and observed an almost complete conversion of naphthalene at 800-900 °C. In other examinations Nacken et al [91-92] also used catalytically prepared ceramic filter candles for tar cracking. They achieved about 97 % conversion of naphthalene at 800 °C. Hoekstra et al [93] used a wire mesh filter with pore size 5 µm, inside a fluidised bed gasifier when producing pyrolysis oil. They experienced no significant difference in the elemental composition between the oil from this filtration or that when an ordinary cyclone was used.

However, for a successful development of a catalytic iron filter, much investigation remains before finding suitable materials or combinations thereof to meet all the requirements, not only as mentioned above but also for tar cracking ability. Perhaps a substantial piece in this context is contributed by this thesis.
Chapter 12

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