Catalytic removal of biomass tars : olivine as prospective in-bed catalyst for fluidized-bed biomass gasifiers

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Chapter 1

Introduction

A general overview of biomass as an energy source is provided in this chapter. Different biomass conversion routes are presented with an emphasis on gasification. Gasification is one of the most promising conversion routes for producing syn-gas from biomass. One of the major problems with gasification is dealing with the tar produced during the process. Issues related to tars and their formations during gasification are addressed below.

1.1 Biomass as an energy source

With respect to global issues of sustainable energy, biomass is getting increased attention as a potential source of renewable energy. Major issues include reducing CO_2 emissions, increasing energy demands, too high a dependency on oil producing countries, regional development - especially for developing countries, and dwindling fossil fuel resources. The term biomass is used to refer to all forms of organic material originating from plants. Biomass is CO_2 neutral. While generating energy from biomass via gasification or combustion CO_2 is produced. This CO_2 is taken up by plants as a vital constituent for their growth, and thus the CO_2 remains in a closed cycle with net zero CO_2 emissions. Biomass is the only carbon source among all the other renewable energy sources, and as such biomass has a strong potential to be the starting material for liquid fuels and carbon-based chemicals.

Worldwide energy demand is growing strongly, thus there is an increasing need for renewable energy sources. A recent report published by the Energy Information Administration (EIA) projected that total world energy consumption is

expected to expand by 54% by the year 2025[1]. To date fossil fuel contributes the major part of world's total energy consumption. According to the World Energy Assessment report, 80% of the world's primary energy consumption is contributed by fossil fuel, 14% by renewable energy out of which biomass contributes 9.5%, and 6% by nuclear energy sources (Rogner et al., 2000). In the year 2001, the European Union (EU) and United States were responsible for 16% and 25% of the world's total energy consumption respectively[2]. Consumption of renewable energy in the United States is still limited. Renewable energy contributed about 6% to the total energy consumption in the United States in the year 2001[3].Of this 6%, biomass contributed a major part, around 47%, of the total amount of renewable energy used in the United States[3] in 2001 (see Fig. 1.1).
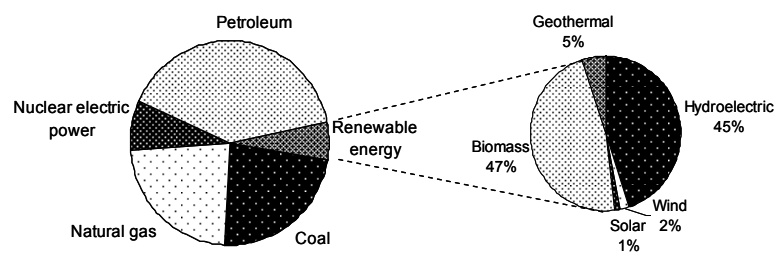
Fig. 1.1: Contribution of renewable energy consumption in the United States (2001) [3]

The EU consumed the largest amount of world's renewable energy (41% including hydro power)[2] in 2002. In the EU, Finland is the largest consumer of bioenergy, which covered 20% of the total primary energy supply in the year 2000 (Kopetz, 2003). In the Netherlands, a total of 27.8 PJ of bioenergy was consumed in 2000 (Jungineger et al., 2004), which was approximately 50% less than the predicted goal for the year 2000. The government of the Netherlands has formulated a policy goal aimed at 10 % use of renewable energy of the total energy supply for The Netherlands by the year 2020, out of which 40% should be realized using bioenergy (Kwant, 2003). In another report by the Ministry of Economic Affairs of the Netherlands, the long term vision is to have a 30% bioenergy supply in the Netherlands by the year 2040 (Schoof et al., 2004). In the same report, it is also

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[1] www.eia.doe.gov/oiaf/ieo/download.html ; September 2004
[2] www.eia.doe.gov/emeu/cabs/euro.html ; September 2004
[3] www.eia.doe.gov/cneaf/solar.renewables/page/trends/trendsov.pdf ; September 2004

predicted that biomass will contribute 20-45% as a feed-stock in the chemical industry by year 2040 (Schoof et al., 2004).

Developing countries are one of the main consumers of bioenergy, with an average between a third and a fifth of the total bioenergy consumption in the world (Turkenburg, 2000). Biomass, consisting of wood fuels, crop residue and animal dung, contributed one third of the total primary energy consumption in India for the year 2000 (Ghosh et al., 2002). The potential for biomass based power generation for India is estimated to be 19.5 GW (Ghosh et al., 2002). However, by the year 2001, only 308 MW capacity biomass based power generation systems had been installed (Banerjee, 2004).

A sustainable energy future requires a combination of factors such as renewable resources and advanced energy conversion technologies. Biomass is widely regarded as a potential source of renewable energy and considerable efforts have been made during last decades to improve the existing technologies to meet increasing energy demands and increasing demands for renewable sources of energy.

1.2 Biomass conversion processes

Biomass has been traditionally used as an energy source especially for cooking and heating, particularly in developing countries. The first commercial application of wood as a fuel was recorded in 1830 (Stassen et al., 2002). It was not untill World War II that biomass gasifiers became widely used in Europe to provide energy for transportation due to scarcity of petroleum fuels (Stassen et al., 2002).

Biomass can be converted into energy via three major conversion routes: thermochemical, biochemical conversions and extraction of oil from oil-bearing seeds. These conversion routes are summarized in Fig. 1.2 and the main conversion products are indicated. In a recent article, Bridgwater (2003) has reviewed the different possibilities for production of fuels and chemicals from biomass.

The biorefinery concept suggested by the National Renewable Energy Laboratory (NREL)[4], includes both biochemical and thermochemical conversion routes (Fig. 1.3). Industrial biorefineries may be the most promising route to a new biobased industry The basic concept of a biorefinery is to produce liquid transportation fuel; to generate electricity and process heat and to produce one or several, high value chemical products.

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[4] www.nrel.gov/biomass/biorefinery.html ; September 2004
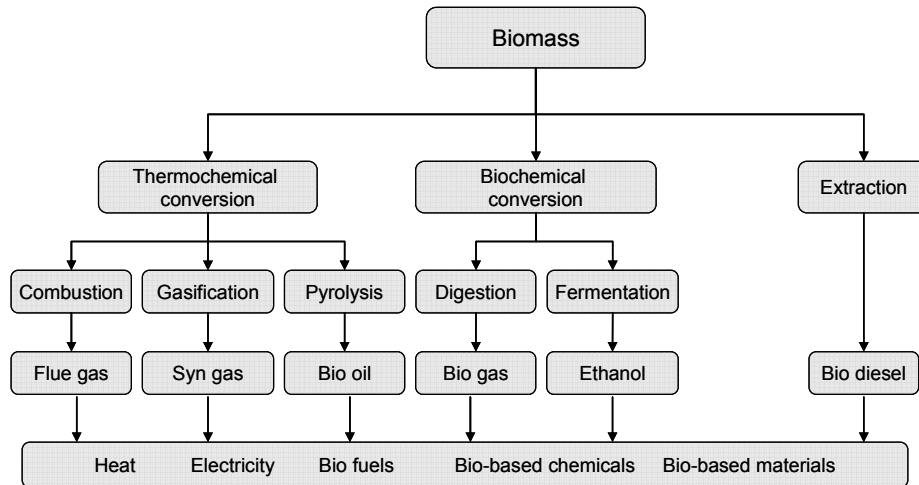
Fig. 1.2: Biomass conversion routes

Among all the possible thermochemical biomass conversion processes, gasification is one of the most promising. Gasification is the only process which converts biomass into a syn-gas mixture and this has numerous opportunities for end user applications such as for gas turbines, engines, fuel cells, producing methanol and hydrocarbons, hydrogen production and the production of synthetic natural gas. Gasification is defined as partial oxidation of carbonaceous feedstocks at elevated temperature to produce an energy carrier (Bridgwater, 1995). Biomass gasification produces a gas containing CO, CO_2, H_2, CH_4, trace amounts of higher hydrocarbons such as ethane and ethene, H_2O and N_2 (for air gasification). The major problems associated with biomass gasification is the production of fine particulates, ashes, alkali metal compounds, nitrogeneous compounds such as ammonia from the fuel bound nitrogen and higher hydrocarbons. Close coupling of gasification and the power system increases the overall conversion efficiency by utilizing the thermal and the chemical energy of hot product gases (Anonymous, 1997). Biomass integrated gasification/combined cycle (BIG/CC) systems are of prime importance as modern technologies (McKendry, 2002). The syn-gas produced via biomass gasification can be further used to produce Fischer-Tropsch liquids (Lapidus et al., 1994). The production of Fischer-Tropsch liquids via biomass gasification (BIG-FT) has become a major topic of interest for research (Tijmensen et al., 2002; Daey Owens et al., 2002).
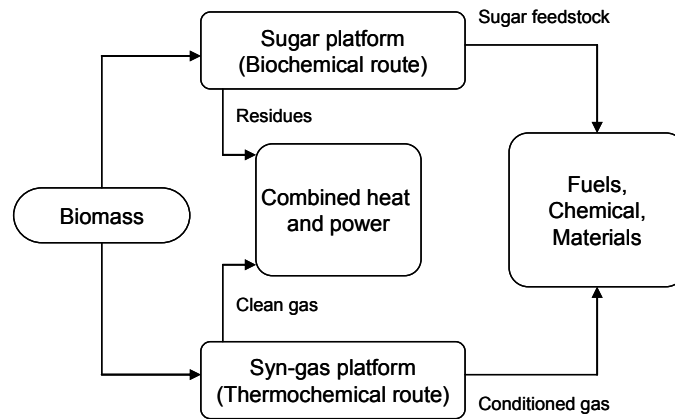
Fig. 1.3: Biorefinery concept [4]

There are three main types of gasifier design available, namely the updraft gasifier, the downdraft gasifier and the fluidized-bed gasifier. Several novel designs are also reported in the literature, these are explained in detail in the next chapter. The updraft and downdraft gasifier technologies are limited by problems associated with scaling up. Fluidized-bed gasification offers excellent mixing characteristics and thus high reaction rates. The other advantage of fluidized-bed gasification is the possibility of scaling up (Bridgwater, 1995). Fluidized-bed gasifiers have a wide range of output ranging from 1 MW to 1000 MW (Rensfelt, 1997). Examples of fluidized-bed gasification include the commercial demonstration gasification plant at Lahti, Finland which was started in 1998 with a capacity of 40-70 MW$_{th}$ and is based on circulating fluidized-bed (CFB) gasification technology (Morris et al., 2003). The gasifier at Gussing, Austria is a dual bed gasifier using steam as the gasifying medium and had been successfully operated for 9700 hours by the end of March, 2004 (Rauch et al., 2004). The Biomass Integrated Gasification Combined Cycle (BIGCC) project in Varnamo, Sweden is based on pressurized CFB technology and had successfully operated for 3600 hours by the year 2002 (Pitcher et al., 2002). The ARBRE gasifier in the UK is based on atmospheric CFB gasification technology. The power plant in Cuijk, The Netherlands, is the biggest biomass based power plant in Europe and it produces a gross electric power of 30 MW (Rasmussen and Fischer, 2002). The SilvaGas gasifier in Vermont, USA, is the first commercial demonstration plant in USA and is based on dual fluidized-bed gasification technology (Paisley and Overend, 2002). The biomass is gasified using steam in the first fluidized-bed and the mixture of char and sand is then treated with air in the second fluidized-bed. An overview of the current status and development

of different demonstration projects on biomass gasification can be found in the review of Morris et al. (2003).

1.3 Tars in biomass gasifiers

One of the major issues in biomass gasification is to deal with the tar formed during the process; the presence of tars means that gas cleaning is a major concern in the downstream processing. According to Kiel (2002), the tar problem is the "Achilles Heel" of biomass gasification processes. Tar is a term generally used to describe a complex mixture of condensable hydrocarbons, which includes single-ring to multiple-ring aromatic compounds along with other oxygen containing hydrocarbons. Various research groups define tar differently. The Biomass Technology Group (BTG, The Netherlands) defines tars as the mixture of chemical compounds which condense on metal surfaces at room temperature (Anonymous, 1995). At the EU/IEA/US-DOE meeting on the tar measurement protocol, held in Brussels in 1998, a number of experts agreed to define tar as all organic contaminants with a molecular mass larger than benzene (Neeft et al., 1999). This definition is followed throughout this thesis.

Tars are formed during gasification in a series of complex reactions. The formation of tar is highly dependent on the reaction conditions. Due to increased reaction temperature, secondary reactions occur in the gas phase which convert oxygenated tar compounds to light hydrocarbons, aromatics, oxygenates and olefins subsequently forming higher hydrocarbons and larger PAH in tertiary processes (Milne and Evans, 1997). The tar formation scheme proposed by Elliott is presented in Fig. 1.4 (Elliott, 1988):

Mixed oxygenates		Phenolic ethers		Alkyl phenolics		Heterocyclic ethers		PAH		Higher PAH
400°C		500°C		600°C		700°C		800°C		900°C
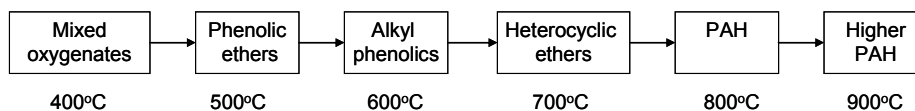
Fig. 1.4: Tar formation scheme (Elliott, 1988)

The amount and the composition of tar depends on the biomass feed properties, the gasification conditions and the type of gasifier. Updraft gasifiers produce the maximum amount of tar, whereas downdraft gasifiers produce the least. In general the estimation of tar production by an updraft gasifier is around 100 g m^{-3}

(STP)[5], by a fluidized-bed gasifier it is around 10 g m^{-3} and by a downdraft gasifier it is around 1 g m^{-3} (Milne and Evans, 1997).

Tar is undesirable due to the problems associated with condensation, which causes blockage in the process equipment and in the engines and turbines used for the application of the producer gas. Condensation also leads to formation of tar aerosols, which are very difficult to remove from the gas. Polymerization of condensed tars forms more complex structures, thus increasing the tendency for coking. The interaction of condensed tars with particulates is often problematic for particle removal devices such as cyclones, fabric filters, ceramic filters and heat exchangers. Water soluble tars create waste water disposal problems when scrubbing is used to clean the gas. However, the minimum allowable limit for tar is highly dependent on the kind of process being used and the end user application. Milne and Evans (1998) have tabulated the tar tolerance limit for various end use devices and suggested by different researchers. Table 1.1 gives an overview of the allowable tar tolerance for gas engines and turbines.

Table 1.1: Tar tolerances for gas engine and turbine

Application	Allowable tar concentration	Reference
IC Engine	< 10 mg m^{-3}	Bui et al. (1994)
	Upto 30 mg m^{-3}	Bridgwater (1995)
	< 100 mg m^{-3}	Anonymous (1995)
	< 100 mg m^{-3}	Hasler et al. (1999)
Gas Turbine	0.05-0.5 ppm	Brown (1996)
	0.5 mg m^{-3}	Aigner (1996)

Considerable efforts have been directed towards the removal of tar from fuel gas. Tar removal technologies can broadly be divided into two approaches; treatments inside the gasifier (primary methods) and hot gas cleaning after the gasifier (secondary methods). Treatments inside the gasifier are gaining considerable attention today as these may eliminate the need for downstream cleanup. The different aspects of primary methods are described in details in the next chapter. In both the primary and secondary methods, tar removal is done either by chemical treatment or physical separation. Chemical treatment includes thermal cracking, catalytic cracking or use of high voltage plasma reactors. Physical removal of tar is mainly done with cyclone separators, baffle filters, fabric filters, ceramic filters, electrostatic precipitators, scrubbers etc.

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[5] Tar concentration is expressed as the weight of tar per cubic meter of the gas produced at standard temperature and pressure (STP) and is followed throughout this thesis.

1.4 Objective and outline of the thesis

This research was carried out within the framework of the project "Primary measures to reduce tar formation in fluidized-bed biomass gasifiers", financed by the Dutch Agency for Research in Sustainable Energy (SDE) and was done in cooperation with the Energy Research Centre of The Netherlands (ECN), Toegepast Natuurwetenschappelijk Onderzoek (TNO), University of Twente (UT) and KEMA. All the project partners looked into different aspects of primary methods of tar removal.
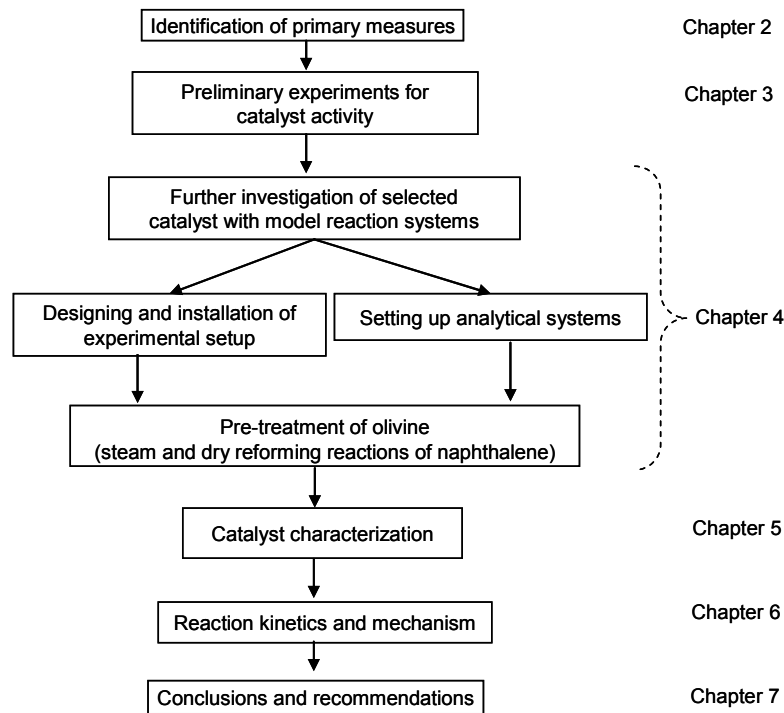
Fig. 1.5: Thesis overview

The objective of this thesis is to identify an appropriate catalyst that can be used as an active in-bed material for fluidized-bed biomass gasifiers.

Overview of this thesis is given by Fig. 1.5 where individual chapters indicate specific research items. The different primary measures for tar removal are identified and presented in Chapter 2. Different approaches for primary tar removal include selection of operating conditions, use of active in-bed material and modification of the gasifier design. The use of in-bed catalysts for fluidized-bed

biomass gasifiers is critically reviewed in Chapter 2. Preliminary experiments performed at the facility of ECN to find out the catalytic activity of dolomite and olivine are described in Chapter 3. The results of preliminary experiments on catalyst activity are elaborated in Chapter 3. A total tar of about 4 g m^{-3} was reduced to 1.5 g m^{-3} and 2.2 g m^{-3} at 900°C over calcined dolomite and untreated olivine, respectively. A tar conversion of 46% was observed with untreated olivine; this lead to an investigation of the pre-treatment of olivine which may improve the performance of the catalyst. Investigations using olivine using a model reaction system are described in Chapter 4. It is observed that pre-treatment of olivine with air at 900°C improves the catalytic activity of olivine. With 10 h of pre-treatment, a naphthalene conversion of higher than 80% is observed, which is a significant improvement with respect to untreated olivine. In the Chapter 5, several catalyst characterization techniques such as BET analysis, XPS, Mössbauer Spectroscopy, TPR, SEM/EDX, attrition resistance are preformed to understand the basic phenomenon of pre-treatment. The reaction gas medium has a significant effect on naphthalene conversion and the product distribution. It was observed that steam and dry reforming reactions show similar naphthalene conversion of around 80%. In presence of a syn-gas mixture (H_2O, CO_2, CO and H_2) naphthalene conversion decreases to 75%. The effects of all the gas components are systematically investigated in Chapter 6. H_2O and CO_2 have an enhancing and H_2 has an inhibiting effect on naphthalene decomposition. CO has an almost negligible effect on naphthalene conversion. Kinetic parameters are also determined in Chapter 6 using a simple power law kinetic model. An attempt is made to postulate the reaction network for the naphthalene decomposition in the presence of a reactive gas mixture. Finally, in the Chapter 7, the overall conclusions of this thesis are discussed along with some recommendation for future research.

Primary measures for tar elimination in biomass gasification processes

Tar removal technologies can broadly be divided into two approaches; treatments inside the gasifier, primary methods, and hot gas cleaning after the gasifier, secondary methods. The former are gaining considerable attention as these may eliminate the need for the downstream cleanup. A brief review of the different approaches primary methods is provided in this chapter, along with a discussion of strategies for tar removal.

2.1 Introduction

A major part of the ongoing research into tar removal deals with the development of efficient methods for removing it. In a recent approach, Nair (2004) investigated the possibility of using a pulsed corona reactor in combination with a biomass gasifier, for simultaneous tar and dust removal. A catalytic reverse flow reactor has been designed at the Biomass Technology Group (Anonymous, 1995), The Netherlands, on a laboratory scale, for cleaning the hot producer gas from a biomass gasifier. A total tar conversion of 96% was observed over a Ni-based catalyst in that reactor. The catalytic reverse flow reactor involves periodic reversal of the gas flow through a packed bed of the catalyst. In another approach, Narváez et al. (1996, 1997)

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reported the use of a guard bed of dolomite before the hot gas enters the catalytic reactor containing the Ni-based catalysts. This kind of three-stage gasification process could reduce 99% of the total tar originally present in the hot gas. The methods available for tar removal can be categorized into two types, removal of tar in the gasifier itself, known as a primary method, or downstream the gasifier, known as secondary method. The following sections describe both methods with an emphasis on the primary method.

2.2 Secondary methods

Secondary methods are conventionally used as treatments for the hot product gas from the gasifier. The concept of secondary methods is given in Fig. 2.1. These methods may be chemical or physical treatment such as:

   • tar cracking downstream the gasifier, either thermally or catalytically.
   • mechanical methods such as the use of a cyclone, a baffle filter, a ceramic filter, a fabric filter, a rotating particle separator, an electrostatic filter or a scrubber.
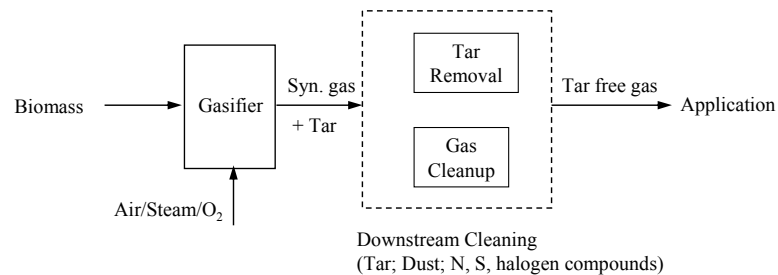
Fig. 2.1: Tar reduction by secondary methods

Secondary tar cracking methods are energy intensive and require secondary equipments. Thermal cracking needs high temperature of around 1000-1100°C, which causes considerable losses of efficiency of the gasification process (Neeft et al., 1999). Complete conversion of naphthalene like molecules require temperature as high as 1400°C (Jess, 1996b). Another problem with thermal cracking of tars is the tendency to form soot (Neeft et al., 1999). Catalytic cracking may be an attractive option for tar removal. However, it has been observed that the production of a clean gas with considerably low tar content requires a complex catalytic process. Narváez et al. (1997) reported a three step process that could produce a very clean gas, with less than 10 mg m^{-3} of tar. Several researchers have reported secondary catalytic methods to be effective in terms of ammonia reduction

(Mojtahedi et al., 1995b; Simell et al., 1996). The use of Ni- monolithic catalyst can decrease ammonia by 80% (Simell et al., 1996). Mojtahedi et al. (1995b) reported a 75% reduction in ammonia using a Ni-Alumina secondary catalyst. Mechanical separation creates disposal problems, waste water treatment problems, etc. As stated in the previous chapter, the focus of this work is on primary methods and hence secondary measures for tar elimination are out of the scope of this thesis. Interested readers are advised to look into the excellent reports of Milne and Evans (1998) and Neeft et al. (1999).

2.3 Primary methods

Primary methods can be defined as the measures taken in the gasification step to prevent the tar formation or to convert the tar formed into lighter compounds. An ideal primary method will eliminate the need for secondary treatments as shown in Fig. 2.2.
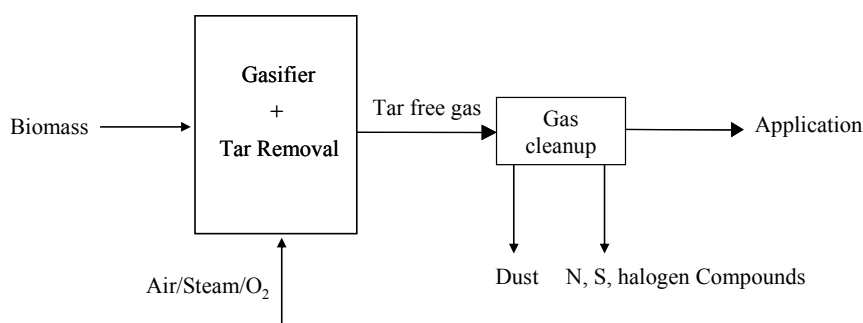
Fig. 2.2: Tar reduction by primary methods

To obtain the best quality exit gas, the gasifier performance has to be optimised. The main factors for an optimised performance of the gasifier are the design and the operation of the gasifier. Corella et al. (1999) reported that in-bed use of dolomite results in a similar tar content (~ 2 g m^{-3}) for air gasification of biomass, as using it in a downstream catalytic reactor. If the gasifier bed is well designed and operated, the measures taken during the gasification step can produce a clean gas with respect to the end user application, eliminating the use of downstream secondary steps.

The main primary measures are i) the proper selection of the operating conditions, ii) the use of a proper bed additives or a catalyst during gasification, and iii) a proper gasifier design. In the following sections, some of the main aspects of

primary methods and the research and development in this area are reviewed. A direct comparison of the data available for tar in the literature is difficult for the following reasons; the use of different operating conditions, a different type of gasifier is used, different tar capturing techniques are used, the sampling and analysing method differ, and most importantly, a lack of consistency regarding a definition of tar, thus different definitions are used by different researchers. Detailed discussions regarding a definitive definition of tar, methods of tar sampling and analysing methods are out of the scope of this chapter.

2.3.1 Gasification conditions

Operating conditions play an important role during biomass gasification. The operating conditions influence the carbon conversion, the product gas composition, tar formation and reduction. The most important influencing parameters include temperature, pressure, gasifying medium, catalyst and additives (explained in the next section), equivalence ratio and residence time. The selection of these parameters also depends on the type of gasifier used. A homogeneous bed temperature profile and a well functioning bed fluidization are critical to avoid operational disturbances.

To achieve a high carbon conversion of the biomass and low tar content in the resultant product gas, a high operating temperature (above 800°C) in the gasifier is preferred. Several temperature ranges are reported in the literature to produce a relatively clean gas by increased temperature. Only a few of these works are cited in this chapter. Temperature affects the amount of tar formed and the composition of tar by influencing the chemical reactions involved in the whole gasification reaction network. Kinoshita et al. (1994) observed, during sawdust gasification in a fixed-bed gasifier, that the total number of detectable tar species decreased with increasing the temperature. Oxygen containing compounds such as phenol, cresol and benzofuran exist in significant quantities only at temperatures below 800°C. They also confirmed that temperatures higher than 800°C favor the formation of fewer aromatic tar species without substituent groups such as benzene, naphthalene, phenanthrene etc. Destruction of these aromatic hydrocarbons occurs only at temperatures above 850°C. Yu et al. (1997) performed pyrolysis experiments of birch wood in a free fall reactor to observe the temperature effect on the process and found that an increasing temperature promotes the formation of gaseous products at the expense of the total tar. More than a 40% reduction in tar yield was reported when the temperature was raised from 700 to 900°C. With an increase in temperature, the total amount of oxygen containing components is drastically reduced, the amount of substituted 1-ring and 2-ring aromatics also decrease, but formation of 3-ring and 4-ring aromatics increases rapidly. An almost 40% increase

in naphthalene content was reported at $900^{o}C$. Similar results were reported by Brage et al. (2000) for gasification of birch wood. When the temperature was raised from 700 to $900^{o}C$, Brage et al. (2000) observed almost a complete reduction of phenol content, a 50% decrease in toluene content, but a considerable increase in benzene (14 mg l^{-1} to 24 mg l^{-1}) and in naphthalene content (2 mg l^{-1} to 8 mg l^{-1}). By changing the bed temperature of the bubbling fluidized-bed from $700^{o}C$ to $850^{o}C$, Narváez et al. (1996) observed an increase in H_2 content from 5 to 10 vol%, CO content from 12 to 18 vol%, a slight decrease in CO_2 content from 16 to 13 vol% and almost no change in the amount of CH_4 and C_2H_2. They also observed a drastic decrease in tar content by about 74%; the tar amounts being 19 g m^{-3} at $700^{o}C$ and 5 g m^{-3} at $800^{o}C$. It is also possible to decrease the amount of tar to a considerably lower value by increasing the freeboard temperature in case of fluidized-bed gasifiers (Narváez et al., 1996; Gil et al., 1999a). Besides tar, temperature also influences the formation of NH_3 and N_2. The level of these two species in the product gas largely depends on the thermochemical reactions occurring in the gasifier and these reactions are directly related to temperature. Zhou et al. (2000) reported an almost 58% decrease in NH_3 content when the temperature was raised from 700 to $900^{o}C$ for sawdust gasification. Over the same temperature range, NO and HCN were also detected, but at a much lower level than NH_3. For leucaena gasification, an 80% decrease in NH_3 content has been reported when the gasifier temperature was increased from 750 to $900^{o}C$. Increases in molecular nitrogen were observed in the product gas which is basically due to the thermochemical conversion of NH_3 (Zhou et al., 2000).

There are several other factors that influence the selection of the operating temperature. Hallagren (2002) mentioned a typical temperature range for different feed materials with respect to various critical factors that largely influences the entire gasification system. Besides the tar content, these factors, shown in Fig. 2.3, are the gas heating value, char conversion and the risk of sintering.

Several researchers have also investigated pressurised biomass gasification. Knight (2000) investigated the effect of system pressure for biomass gasification. When the pressure was increased to 21.4 atm, almost complete elimination of phenols was observed for Wisconsin whole tree chips. Although the amount of total tar decreased, the fraction of PAH increased with increasing pressure. Molilanen et al. (1997) studied the dependence of pressure on the wood char gasification. The pressure was raised from 1 to 15 atm of CO_2 and H_2O at temperatures of $750^{o}C$ and $850^{o}C$. Increase in CO_2 pressure slightly reduced the char gasification, whereas the char gasification increased with increasing H_2O pressure. Pressurised gasification (5-20 atm) is also being investigated in Lund University in Sweden (Wang et al.,

2000b; Padban, 2000). Wang et al. (2000b) observed a decrease in the amount of light hydrocarbons, LHC, lower than naphthalene, and that of tar in the fuel gas with an increasing equivalence ratio (ER) for pressurised gasification with 100% carbon conversion.

Higher	←	Gas heating value	→	Lower
Higher	←	Tar content	→	Lower
Lower	←	Char conversion	→	Higher
Decreasing risk	←	Sintering	→	Increasing risk
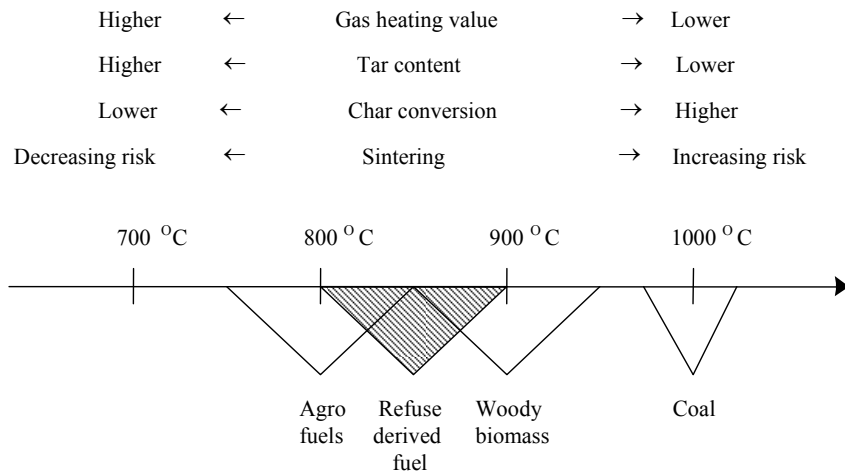
Fig. 2.3: Typical gasification temperature for various feedstock and influence of
temperature change on some critical factors as reported by Hallgren (2002)

Different gasifying agents such as air, steam, steam-oxygen and carbon dioxide have been reported in the literature. Selectivity of the gasification reactions varies with different gasifying media, thus affecting the product gas composition as well as the heating value. The heating value of the product gas with air as a gasifying medium is lower because of dilution of the gas by nitrogen. Narváez et al. (1996) reported a gas composition of 10% H_2, 14% CO, 15% CO_2 (vol %) from a gasifier with gasification temperature of 800^oC with an ER of 0.26. However, the tar content decreased sharply as the ER was increased upto 0.45, being as low as 2 g m^{-3}. The ER strongly influences the type of gasification products. According to Kinoshita et al. (1994) tar yield and tar concentration decreases as the ER increases because of more availability of oxygen to react with volatiles in the flaming pyrolysis zone. This effect of ER is more significant at a higher temperature. The ER is crucial because its higher value results in lower concentration of H_2, CO and higher CO_2 content in the product gas, thus decreasing the heating value of the gas. Although the total tar concentration decreased by almost 30% when the ER was increased from 0.22 to 0.32 for a temperature of 700^oC, the fraction of PAH increased in the total tar. The decrease in total tar concentration could be much

higher at a higher temperature. Almost all phenols were converted at an ER of 0.27. Increased contents of benzene, naphthalene, 3-ring and 4-ring compounds were reported (Kinoshita et al., 1994). Narváez et al. (1996) reported a similar trend with increasing ER for gasification of pine sawdust at 800°C. A tar content of about 2-7 g m^{-3} was reported when the ER was increased up to 0.45. They also gave a comparison of various experiments with varying ER by other researchers. According to Zhou et al. (2000), ER does not significantly influence the concentration of nitrogenous products during the biomass gasification. A slight increase in NH$_3$ (from 310 ppm to 350 ppm) was observed when the ER was increased from 0.25 to 0.37 at 800°C for the sawdust gasification.

In view of the lower heating value and the poor gas composition, several researchers used pure steam and they observed a completely different product gas distribution. The steam gasification product gas is free from N$_2$ and has more than 50% H$_2$. Herguido et al. (1992) reported steam gasification and the effect of steam/biomass ratio (SB) on the gasification products. They observed an increase in H$_2$ (as high as 60%) and CO$_2$ (10% to 30%) contents, a sharp decrease in the CO, (35% to 10%) content, a slight decrease in CH$_4$ content and relatively no change of C$_2$-fractions (C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$) when the SB ratio was increased from 0.5 to 2.5. In spite of sharp reduction in tar, 8% yield at 0.5 SB decreased to almost nil at 2.5, there was a sharp decrease in the lower heating value that was attributed to the decrease in CO. García et al. (1999, 2001) used steam as a gasifying agent for pine sawdust over a Ni/Al co precipitated catalyst. The catalyst improves the reaction rate of steam with char and also can participate in secondary reactions, thus leading to a decrease in tar content of the gas. The high H$_2$ production during steam gasification can be attributed to the following chemical reactions

$$C_nH_x + nH_2O \longrightarrow (n + x/2)\ H_2 + n\ CO \tag{2.1}$$

$$CH_4 + H_2O \rightleftharpoons 3\ H_2 + CO \qquad \Delta H^O_{298} = +\ 205.81\ kJ\ mol^{-1} \tag{2.2}$$

$$C_2H_4 + 2H_2O \rightleftharpoons 4\ H_2 + 2\ CO \qquad \Delta H^O_{298} = +\ 210.07\ kJ\ mol^{-1} \tag{2.3}$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad \Delta H^O_{298} = -\ 41.16\ kJ\ mol^{-1} \tag{2.4}$$

$$C + H_2O \rightleftharpoons H_2 + CO \qquad \Delta H^O_{298} = +\ 131.29\ kJ\ mol^{-1} \tag{2.5}$$
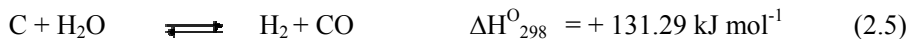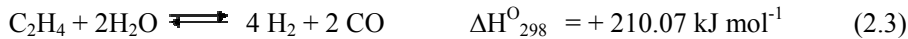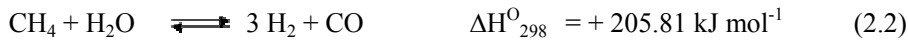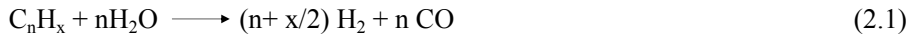
Reaction (2.1) represents a tar reforming reaction which contributes to an increment in the content of H$_2$ and CO gases.

Steam gasification is endothermic and hence sometimes requires a complex design for heat supply in the process. The use of some amount of oxygen in the gasifying medium can provide the necessary heat for gasification and then the gasifier works as an autothermal reactor. In view of this, many researchers used a

steam-oxygen mixtures for biomass gasification. Aznar et al. (1997) reported more than 85% reduction in total tar when they increased the (steam+O_2)/biomass ratio termed as Gasifying Ratio (GR) from 0.7 to 1.2. The researchers also reported that for low GR values, the gasifier produces light tars, which can be easily destroyed using catalyst (Aznar et al., 1998). Gil et al. (1997) recommended H_2O/O_2 ratio of around 3.0 (mol/mol) for steam-O_2 mixture for the gasification. When the GR was increased from 0.6 to 1.7, they observed the following changes in gas composition, decrease in H_2 content from 29 to 13%, decrease in CO content from 50 to 30%, increase in CO_2 content from 14 to 37%, slight decrease in CH_4 content from 7 to 5% and a change in C_2 hydrocarbons from 3.5 to 2.3%, note all percentages are expressed in volume on dry basis. Tar content of the raw gas sharply decreases with GR, less than 5 g m^{-3} at a GR of 1.2. The same researchers also observed that the effect of gasifier bed temperature on tar content is significant at lower GR values (<1.0). Gil et al. (1997) recommended a gasifier bed temperature between 800-860°C with GR of 0.8-1.2 and a gas residence time of 2 s, and they also compared their work with that of Narváez et al. (1996) and Herguido et al. (1992), which involved gasification with air and steam, respectively. A relationship between ER, SB and GR values is mentioned for the purpose of comparison (Gil et al., 1999b) by the authors of the paper. Under selected conditions, more tar is formed with pure steam, than that with a steam-O_2 mixture and less with air as the gasifying agent. It should be mentioned at this point that the operating parameters of the works compared were not exactly the same and also the gasifiers used were different in design. Hofbauer et al. (1997) and Fercher et al. (1998) report using a combination of steam and air in a fast internally fluidized-bed biomass gasifier see the following section of this chapter. Air combustion provided the heat required for the steam gasification.

The use of CO_2 as gasifying medium is promising because of its presence in the gasification atmosphere. Tar reduction is also enhanced by dry reforming reactions of CO_2, which is a gasification product. According to Minkova et al. (2000), a mixture of steam-CO_2 gives the highest degree of carbonization for pyrolysis and gasification of biomass in a horizontal rotating reactor. García et al. (2000) investigated CO_2 gasification in the presence of Ni/Al coprecipitated catalyst and compared the results with those of steam gasification (García et al., 1999, 2001). CO_2 gasification in the presence of a catalyst transformed tars and also causes a decrease of the amounts of CH_4 and the C_2 fraction (C_2H_2, C_2H_4, C_2H_6) and an increase in H_2 and CO yields. A significant decrease in the CO_2 content was also observed with a CO_2/biomass ratio of 1.16 indicating that CO_2 converts to other products. Deposition of carbon in the catalyst particles can be avoided to a certain

extent by feeding CO_2 in excess. The main chemical reactions with CO_2 as a gasifying medium are listed below

$$C_nH_x + nCO_2 \longrightarrow (x/2) H_2 + 2n\ CO \qquad\qquad\qquad\qquad\qquad (2.6)$$
$$CH_4 + CO_2 \rightleftharpoons 2\ H_2 + 2\ CO \qquad \Delta H^O_{298} = + 246.98\ kJ\ mol^{-1} \quad (2.7)$$
$$C_2H_4 + 2CO_2 \rightleftharpoons 2\ H_2 + 4\ CO \qquad \Delta H^O_{298} = + 292.41\ kJ\ mol^{-1} \quad (2.8)$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^O_{298} = + 41.16\ kJ\ mol^{-1} \quad (2.9)$$
$$CO_2 + C \rightleftharpoons 2\ CO \qquad \Delta H^O_{298} = +172.46\ kJ\ mol^{-1} \quad (2.10)$$

The reaction (2.6) represents the dry reforming reaction of tar.

According to Kinoshita et al. (1994) residence time has little influence on the tar yield, but it significantly influences the tar composition. The residence time they reported was based on the superficial velocity of the wet product gases in the gasifier. Amounts of O_2 containing compounds tended to decrease with increasing residence time. Yields of 1-ring and 2-ring compounds, except benzene and naphthalene, decreased whereas that of 3-ring and 4-ring compounds increased in the total tar fraction. Corella et al. (1999) observed a decrease in the total tar content when the space time was increased for biomass gasification with in-bed use of a dolomite catalyst. The space time was expressed as (kg calcined dolomite/kg biomass $_{daf}$ h^{-1}). The tar amounted to 2 g m^{-3} at space time 1.0 this was 6 g m^{-3} at a space time of 0.1. Houben et al. (2002) reported a sharp decrease in amount of tar with an increase in residence time. However, with increasing residence time a significant increase in soot formation was also observed (Houben et al., 2002).

In addition to the optimised operational conditions, the presence of some active materials in the gasifier can largely improve the product gas distribution. The following section covers some of the reported literature on use of bed additives.

2.3.2 Bed additives

Catalytic tar reduction has been extensively reported in the literature (Sutton et al., 2001). These catalysts include Ni-based catalysts, calcined dolomites and magnesites, zeolites, olivine and iron catalysts. Among all these only few have been tried as active bed additive inside the gasifier during gasification. There is a great potential for in-bed additives in terms of tar reduction and thus avoiding complex downstream tar removal methods. These bed additives act as *in-situ* catalysts promoting several chemical reactions in the same gasifier. The presence of additives influences the gas composition, and the heating value of the product gas. The use of catalytically active materials during biomass gasification promotes char gasification, changes the product gas composition and reduces the tar yield. Besides

these, the addition of active bed materials also prevents solid agglomeration tendencies and subsequent choking of the bed.

Limestone was one of the first additives used in a gasifier to improve gasification. Walawender et al. (1981, 1985) performed a series of experiments using limestone as a bed additive in a fluidized-bed gasifier. They used a mixture of 25 wt% limestone and 75 wt% silica sand as a bed material for steam gasification of alpha cellulose with the intention of predicting the behavior of the gasifier with increasing temperature (Walawender et al., 1985). The researchers also applied the same mixture of bed material for steam gasification of manure (Walawender et al., 1981). Although no attempt was made to observe the tar formation, the authors reported that the gas composition, heating value and yield were all influenced by the presence of 25 wt% limestone in the bed. The most important outcome of their experiments was that the addition of limestone to a bed of silica sand could prevent the agglomeration of the bed.

Among all the active materials used as in-bed additives, dolomite is the most popular and mostly studie. A lot of research has been done using this catalyst with regard to tar cracking in-bed as well as in a secondary reactor. Karlsson et al. (1994) reported the successful demonstration of biomass IGCC process (VEGA Gasification with combined cycle) which involved dolomite as a bed material. The tar content observed was about 1-2 g m^{-3} of light tars, excluding benzene, and 100-300 mg m^{-3} of heavy tars. Rapagnà et al. (1998a) also mentioned the use of calcined dolomite directly in the gasifier and observed improvements in the gas yield. Corella et al. (1988) reported that the use of calcined dolomite inside the gasifier could decrease the tar amount from 6.5 wt%, without dolomite, to 1.3 wt% with dolomite. A research group in Spain (University of Complutense and University of Saragossa) has done several experiments with in-bed use of dolomite. Narváez et al. (1996) suggested that the addition of calcined dolomite, 1-5 wt% of the biomass feed, improves the quality of the product gas. Their experiments resulted in a tar reduction of about 40% with the addition of 3% calcined dolomite to the biomass feed. A 10 wt% of calcined dolomite is reported (Olivares et al., 1997) to be sufficient for significant improvement of the gas quality and a reduction in tar production. The elimination of tar over calcined dolomite is mostly due to steam and dry reforming reactions.

Corella et al. (1999) observed almost no difference in the lower heating value of the gas produced by using in-bed dolomite and that of downstream use of dolomite. The increase in H$_2$ production compensated the CO decrease; there was also hardly any variation in the CH$_4$ and C$_2$H$_n$ amounts in the product gas. The tar content in the product gas with the use of in-bed dolomite was significantly reduced

and this reduction is comparable to using downstream dolomite. Besides the use of an active additive in the bed, the researchers also observed that the gasifying medium plays an important role in the tar reduction, this has been discussed in the previous section of this chapter. An amount of 20-30 wt% dolomite, rest being silica sand, in the gasifier was reported to reduce the tar content to as low as 1 g m^{-3} at an equivalence ratio of 0.3 (Gil et al., 1999a). The authors also studied the influence of several operating parameters in combination with use of in-bed dolomite and found that a proper selection of parameters in addition to dolomite can significantly enhance the production of a clean gas. Although dolomite has been proven to be a very effective bed additive in terms of tar reduction, it has some critical limitations. Dolomite is softer and thus gets eroded by the silica sand particles, also some dolomite particles break during calcination and give rise to a large proportion of fines. Thus, there is a great problem of carry over of solids from the bed.

Naturally occurring particles of olivine, which is a mineral containing magnesium, iron and silica is an attractive in bed material. Olivine is advantageous in terms of its attrition resistance over that of dolomite. Rapagnà et al. (1998b) investigated the catalytic activity of olivine and observed that it has a good performance in terms of tar reduction and the activity is comparable to calcined dolomite. They reported more than 90% reduction in average tar content, the tar amounted 2.4 g m^{-3} compared to 43 g m^{-3} with only sand. The authors also performed experiments with olivine as the bed material and a La-Ni-Fe perovskite catalyst in a secondary reactor. The combined action of the materials was very promising; a gas with around 0.3 g m^{-3} of tar was produced (Rapagnà et al., 2000). Rosén et al. (1997) reported the use of olivine as a bed material for pressurized gasification (4-10 atm) of birch. Abu El-Rub et al. (2002) used olivine to decompose naphthalene as a model tar compound and observed a conversion of around 55%. Whereas Courson et al. (2000) reported that olivine alone dose not show any activity for methane reforming. They prepared Ni-olivine catalyst by impregnation of natural olivine with an excess of nickel salt solution (Courson et al., 2002). The catalyst was then calcined under air for 4 h at different calcination temperatures of 900-1400°C. They reported that this Ni-olivine catalyst is active for dry reforming of methane. In a recent publication, Pfeifer et al. (2004) reported 75% reduction in tar due to in-bed use of Ni-olivine catalyst (43 wt%) during steam gasification of wood at 850°C. In a recent investigation, Rauch et al. (2004) reported the need of 100 hours of activation time for olivine to be active in terms of tar removal.

Mudge et al. (1981) studied the catalytic steam gasification of biomass using alkali carbonate and Ni-based catalyst at the Pacific Northwest Laboratory (PNL). Supported Ni catalysts were found to be very effective in producing high yields of synthesis gas (Mudge et al., 1981; Mitchell et al., 1980). Baker et al. (1984) studied a number of catalysts (Ni/Al_2O_3, K_2CO_3, $NiCuMo/SiO_2-Al_2O_3$) for pressurized steam gasification of bagasse and wood to produce synthesis gas for methanol and ammonia production in a laboratory scale gasifier. The catalytic gasification resulted in an increase in the gas yield at the expense of tar and char. They also carried out gasification tests in a 1ton d^{-1} fluidized-bed process development unit (PDU) using the same catalyst. They observed severe deactivation of the Ni-based catalyst due to carbon deposition.

A number of other metal oxide catalysts such as V_2O_5, Cr_2O_3, Mn_2O_3, Fe_2O_3, CoO, NiO, CuO, MoO_3 on Al_2O_3 were tested by Yoshinari et al. (1984) for wood gasification to produce methanol from the synthesis gas. All these metal oxides produced high yields of gas, but the gas composition strongly varied depending on the type of metal oxide used. MoO_3, CoO and V_2O_5 produced higher amount of CO_2, whereas NiO, Cr_2O_3 and Fe_2O_3 produced relatively low amounts of CO_2. The most suggested favorable gasification catalyst was NiO/Al_2O_3, which could produce a gas with a H_2/CO ratio close to 2.0. They also observed that NiO/Al_2O_3 produce only traces of total olefins. Although the authors did not quantitatively measure the tar amount, their results showed that the additives greatly improve the overall product distribution and the gas heating value. Several other researchers have reported in-bed use of Ni-based catalysts. Bilbao et al. (1998) observed that addition of 50 wt% of the Ni-Al catalyst to bed material (sand) increases hydrogen production up to 62% with a considerable decrease in the methane content. The same Ni/Al coprecipitaed catalyst was also observed to be very effective for CO_2 gasification of biomass (García et al., 2001). The ratio of catalyst weight and biomass flow rate significantly influences the product gas distribution. Asadullah et al. (2002) developed a $Rh/CeO_2/SiO_2$ catalyst for low temperature gasification and observed a complete carbon and tar conversion for cellulose gasification at temperature between 500-600°C.

The major problem with Ni-based catalysts is fast deactivation of the catalyst due to carbon deposition and poisoning due to the presence of H_2S. These problems can be partially avoided by increasing the temperature (Simell et al., 1996; Wang et al., 1999). In view with the experiences of PNL, in-bed use of a Ni catalyst is not an attractive option. Baker et al. (1987) and Mudge et al. (1987) reported that the lifetime of a Ni catalyst could be extended by placing it in a secondary bed instead of using it in the gasifier. Placing the NiCuMo on Si-Al_2O_3 and Ni on α-alumina

catalysts in a secondary fluidized-bed reactor downstream from the gasifier, they observed no deactivation for 30-40 hr tests. Researchers from National Renewable Energy Laboratory (NREL) are actively involved in developing new fluidizable catalyst for hydrogen production from biomass derived products. Czernik et al. (2002) investigated Ni-based commercial reforming catalyst (C11-NK) for gasification of biomass derived liquids in a fluidized-bed gasifier and reported good activity for H_2 and CO production. This catalyst was deactivated due to coke formation, but could be easily regenerated by steam or CO_2. French et al. (2002) and Magrini-Bair et al. (2004) prepared several Ni-based catalysts supported on alumina and tested for hydrogen production by steam reforming of biomass derived pyrolysis products. They observed that these catalysts have a high activity, and high attrition resistance, thus making them suitable for fluidized-bed reactors.

Ni based catalysts are also effective for NH_3 reduction. Wang et al. (1999) reported that NH_3 can be decomposed effectively with a Ni based catalyst above 800°C. Wang and his coworkers reported 95% conversion of NH_3 along with 89% conversion of light hydrocarbons (C_2H_6, C_6H_6, C_7H_8 and C_9H_8) with Ni based catalyst in a secondary reactor at a temperature of 874°C, a pressure of 12 atm and a space time of 3 s (Wang et al., 2000b). Their observation was that the amounts of light hydrocarbons have a negative effect on NH_3 decomposition. Mojtahedi et al. (1995a) investigated Ni/Alumina and Ru/Alumina catalysts for NH_3 decomposition in a synthesis gas mixture. The same catalysts were studied for ammonia and tar decomposition in an actual biomass gasification system (Mojtahedi et al., 1995b). These catalysts are less effective in terms of NH_3 reduction in the presence of tars. Simell et al. (1996) also observed that Ni/Alumina catalyst is effective for NH_3 and for tar reduction. The authors observed that NH_3 decomposition could be enhanced with iron containing materials over a temperature of 900°C. It should be noted that all above mentioned studies on catalytic NH_3 decomposition were carried out in external reactors as secondary treatments for the hot gas from the gasifier.

Douglas and baker (1986) used 8 wt% potassium carbonate impregnated on wood as a bed additive for steam gasification in a fluidized-bed gasifier at an operating temperature of 750°C. They observed a reduction of phenolic tar compounds by a factor of 5 and PAH by a factor of about 10. It was observed that alkali metals, especially potassium, act as a promoter in unzipping the cellulose chains during the thermal decomposition of woody biomass, thus effecting the product gas distribution.

Corella et al. (1988) reported the use of in-equilibrium FCC catalyst as a bed additive for steam gasification of pine sawdust. This catalyst contains zeolite in a silica-alumina matrix, and was once used in oil refineries. The experiment was done

by feeding the catalyst with biomass feed (biomass/catalyst=10) and a 20% reduction in tar content was reported. However, this catalyst was reported to deactivate rapidly due to coke deposition and the catalyst particles were entrained out of the bed in just a few seconds. The same researchers performed some more experiments with in-bed use of the same catalyst at a higher temperature range (800-820°C) and observed an almost 60% decrease in tar content with the in-bed use of a 5% in-equilibrium FCC catalyst. Besides cracking, hydrocracking might be a possible reason of tar decomposition (Gil et al., 1999a).

Another inexpensive material can be char and its use is also widely reported in the literature (Abu El-Rub et al., 2004; Ekstrőm et al., 1985; Seshadri, 1998; Chembukulam et al., 1981). Char is not only a cheap and available material, it is indigenously produced inside the gasifier. Char has been reported to be used in secondary tar cracking reactors by several researchers (Ekstrőm et al., 1985; Seshadri, 1998). Chembukulam et al. (1981) reported that cracking over a char bed at a temperature of 950°C resulted in an almost complete decomposition of tar and pyroligneceous liquor into gases of low calorific value. It should be noted that char gets converted during the gasification process into gaseous products mainly to CO and CO_2, and hence there may be need for an external continuous supply of char into the gasifier. Several researchers reported use of char in a two-stage gasifier this is explained in the next section of this chapter.

Based on the reported literature the following general observations can be made about the addition of active bed material during gasification, they produce:

- a change in product gas distribution
- a decrease in tar amount
- an increase in hydrogen production
- a slight decrease in the amount of CO and an increase in the amount CO_2
- slight variation in the amount of CH_4
- problems regarding catalyst deactivation and the carry over of fines an be severe
- catalytic tar reduction depends on gasification conditions and gasifier design

A summary of some of the research work done using bed additives is given in the Table 2.1 below.

2.3.3 Gasifier design modification

Reactor design is crucial for gasification in terms of efficiency, heating value of the product gas and also for tar formation. Modification of the gasifier design can be very effective in producing clean gas. Several attempts have been reported in this

Table 2.1: In-bed additives used by researchers under different operating conditions

Feed	Feed Properties		Operating conditions			Additive	Results	Reference
	Moist (%)	Size (mm)	Gasif. agent	Temp(°C)	Time (s)			
Cellulose		1.0 -- 2.0	Steam	600--800	1.26--1.54	Limestone	Improved gas distribution	Walawender et al. (1985)
Wood	-	-	Steam	750	-	K_2CO_3	5-10 fold decrease in tar	Douglas and Baker (1986)
Pine sawdust	8.5	1.0	Steam	750	-	Dolomite	80% decrease in tar	Corella et al. (1988)
						FCC	21% decrease in tar	
Pine Chips	10--12	-5.0 -- 1.0	Steam/O_2	795--835	-	Dolomite	80% decrease in tar	Olivares et al. (1997)
Pine sawdust	10	-	CO_2	700	-	Ni-Al	Improved gas distribution	García et al. (2001)
Pine chips	-	-	Air, Steam/O_2	800--850	-	Dolomite	10 fold decrease in tar	Corella et al. (1999)
Pine chips	10--15	-	Air	800--845	-	Dolomite	90% decrease in tar	Gil et al. (1999 a)
						FCC	56% decrease in tar	
Almond Shell	7.9	1.1	Steam	770--820	-	Olivine	94% decrease in tar	Rapagnà et al. (2000)
						Dolomite	98% decrease in tar	
Birch	6—8	1.0 -- 3.0	$O_2 - N_2$	700--900	-	Silver sand	5.3 g tar/kg dry fuel	Rosén et al. (1997)
						Olivine	4 g tar/kg dry fuel	
Pine/ Bagasse	-	-	Steam	750	30	Ni-based	High carbon conversion	Baker et al. (1984)

regard and have been found to be successful in tar reduction. Secondary air injection to the gasifier results in significant tar reduction. A higher temperature could be attained due to the secondary air injection the gasifier. Pan et al. (1999) injected secondary air just above the biomass feeding point in the fluidized-bed. They reported that an optimal secondary to primary air ratio of about 20% is sufficient to reduce 88.7 wt% of the total tar for a gasification temperature range of 840-880°C. Narváez et al. (1996) performed a few experiments with secondary air injection in the freeboard of a fluidized-bed gasifier. They observed a temperature rise of about 70°C and a tar reduction from 28 g m^{-3} to 16 g m^{-3}. They expected that with longer gasifiers the temperature rise in the freeboard due to air injection might be higher, thus there would be a higher possibility of lower tar content in the gas.

Two-stage gasifier design has been reported to be effective in producing clean gas. The basic concept of this design is to separate the pyrolysis zone from the reduction zone. A two-stage gasifier is equivalent to two single-stage gasifiers. Tars formed during the pyrolysis (first stage) are decomposed in the reduction zone (second stage). A two-stage gasifier has been studied in the Asian Institute of Technology (AIT) in Thailand, it gave a gas with a tar content of about 50 mg m^{-3}, about 40 times less than a single-stage reactor under similar operating conditions (Bui et al., 1994). This concept involves two levels of air intake. Primary air injection is done in the pyrolytic zone. While the secondary air helps to achieve high temperature in the second zone, thus reducing the tar level to a considerably lower value. The two-stage gasification concept applied in the AIT is shown in Fig. 2.4. It was observed that most of the tars were formed during the warm-up period due to lower temperatures. This could be avoided by filling the gasifier with a bed of char just above the primary air inlet. The gasifier was loaded with char before ignition. It was reported that with filling char almost totally eliminates tar formation during start-up in the reactor. Further modification was done by Bhattacharya et al. (1999) in such a way that char was produced inside the gasifier, thus avoiding input of external charcoal for subsequent experiments. An extra primary air inlet above the original air supply was added for this purpose. The researchers coupled the char gasifier with the original two-stage gasifier and reported that this design could produce considerably low tar content (19 mg m^{-3}) producer gas.

Successful operation of this type of gasifier depends largely on the stability of the pyrolysis zone (Bui et al., 1994). The stabilization of this zone is however dependent on the balance between downward solid movement and upward flame propagation. If the wood particles move faster than the flame propagation, the pyrolysis zone reaches the secondary air intake thus making the whole system act as an single-stage gasifier. If flame propagation upward exceeded wood consumption,

both stages remained in stable operation. The flame propagation control was done by adjusting the airflow by changing the width of the secondary air inlet.
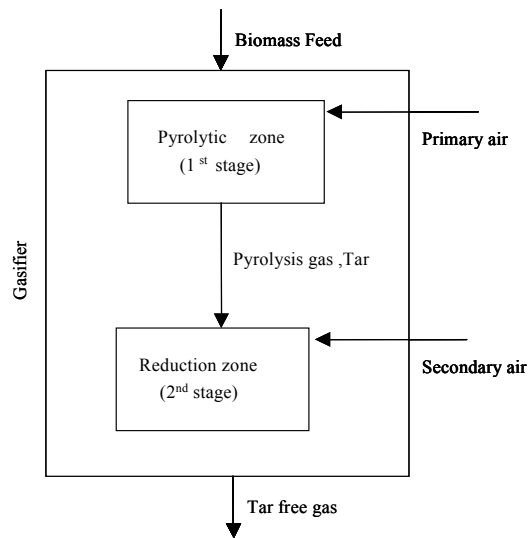
Fig. 2.4: Two-stage gasification concept of Asian Institute of Technology (Bui et al., 1994; Bhattacharya et al., 1999)
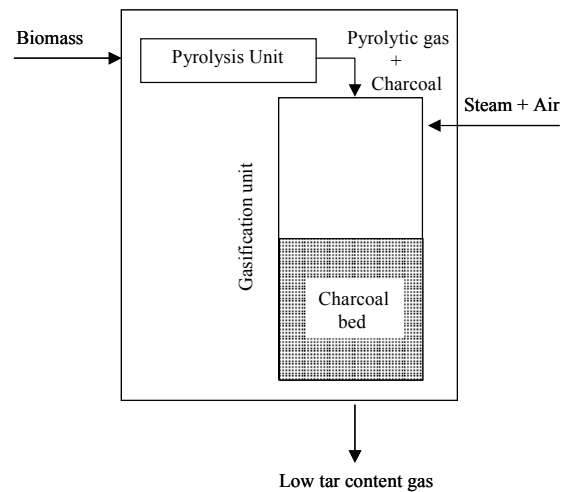
Fig. 2.5: Two-stage gasifier of Technical University of Denmark (Henriksen et al., 1994; Brandt et al., 2000)

Another two-stage gasifier designed at the Technical University of Denmark combines the pyrolysis of the biomass feed with the subsequent partial oxidation of the volatile products in the presence of a charcoal bed as shown in Fig. 2.5 (Henriksen et al., 1994; Brandt et al., 2000). Henriksen et al. (1994) reported a successful demonstration of this type of gasifier (50 kW) for straw gasification. Brandt et al. (2000) also use the same reactor design (100 kW) for gasification of wood chips. The char and the volatile pyrolysis products from the pyrolysis unit entered the top of the gasification unit where the gases were mixed with the preheated steam and air triggering partial combustion. The char formed is thus transported to the char gasification unit. Allowing the gases to pass through the bed of char, causes a significant tar reduction in the total tar content (15 mg m^{-3}). The lower amounts of tar are attributed to the partial combustion of the pyrolytic gases and the catalytic effect of the charcoal bed. High char conversion was reported ranging from 70% upto 90%.
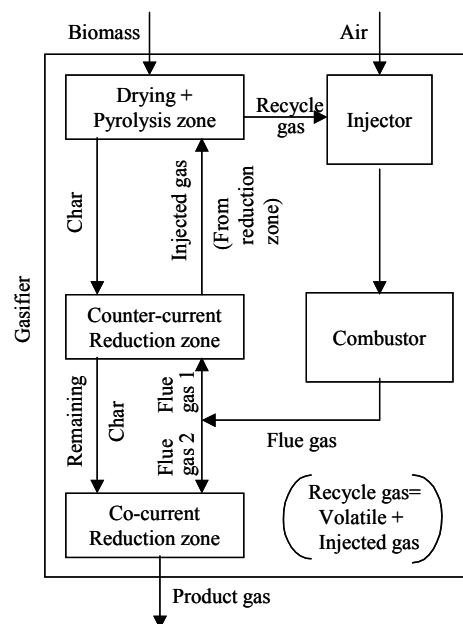
Fig. 2.6: Moving bed gasifier with internal recycle (Susanto et al. and Beenackers 1996)

Susanto and Beenackers (1996) have developed a cocurrent moving-bed gasifier with internal recycle and separate combustion zone of pyrolysis gas. Their aim was to produce a design suitable for scaling up a downdraft gasifier maintaining a low tar content in the product gas. This system was able to produce a clean gas with tar content as low as 0.1 g m^{-3}. This gasifier concept is presented in Fig. 2.6. In

this design, biomass is first pyrolysed and the produced char enters the reduction zone. The volatile pyrolysis gases are sent to the injector where it is burnt with the gasifying air. The flue gas from this chamber then acts as the gasifying medium for the gasifier. The flue gas is divided into two parts, one part being fed to the first reduction zone. This recycled gas flows countercurrently with the solid feed and char, thus enabling a more complete pyrolysis of the solids upon entering the reduction zone. The second part is sent to with the remaining char to the second reduction zone, thus providing more complete gasification. The main reasons reported by the researchers for tar reduction in such design is due to the fact that the tar flow is premixed with air prior to combustion and all tars pass through hot flame. They also mentioned that any tar that might escape from the hot combustion chamber is subsequently converted over the char in the combustion zone. A recycle ratio of 0.6-0.9 is suggested as optimal with regard to clean gas production and good gasification efficiency.
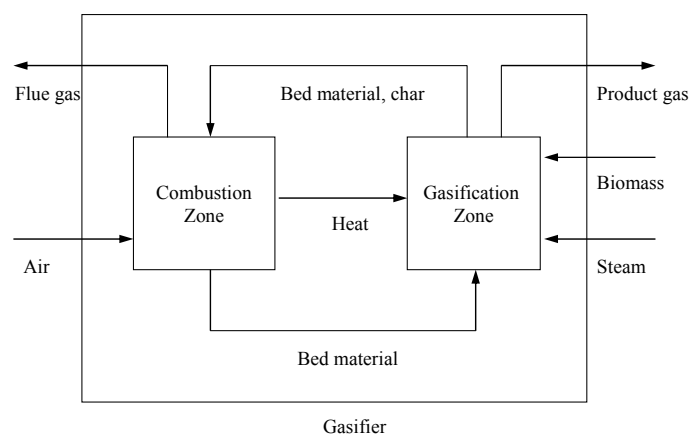
Fig. 2.7: Fast internally circulating fluidized-bed gasification (Hofbauer et al., 1997)

Several attempts have been made to develop new fluidized gasification techniques in view of better efficiency and quality of fuel gas. A two-stage fluidized gasifier which is a fast internally circulating fluidized-bed gasifier (FICFB), has been reported and observed to produce a gas with a higher calorific value that was nearly free of N_2 (Hofbauer et al., 1997; Fercher et al., 1998; Zschetzche et al., 1994). This gasifier concept is shown in Fig. 2.7. The fluidized-bed gasifier was divided into two zones, a gasification zone with steam as the fluidizing and gasifying medium and a combustion zone using air. Between these two zones, a circulation of bed material is created and this bed material acts as a heat carrier from

the combustion to the gasification zone. The biomass is fed into the gasification zone and the bed material, together with char produced, circulates to the combustion zone. In the combustion zone the charcoal is burnt. The exothermic reaction in the combustion zone provides the energy for the endothermic gasification reactions with steam. Hafbauer et al. observed that total tar amounted about 1 g m^{-3} that can be reduced to a lower value with the addition of some catalyst as bed additives. Fercher and his coauthors have performed several experiments to determine the effect of olivine particles in the same gasifier (Fercher et al., 1998). The addition of olivine decreases the tar content of the product gas, but this depends on the gasification temperature. A total tar amount of about 0.5 g m^{-3} was observed for wood gasification with olivine at a temperature of 800°C. The biomass demonstration plant at Guessing is based on this FICFB concept and had been successfully operated for 9700 hours at the end of March, 2004 (Rauch et al., 2004).

2.4 Concluding remarks

An optimised gasification process can produce an almost clean gas thus eliminating the need for downstream hot gas cleaning. This approach is termed as an ideal "primary method", which is shown in Fig. 2.2. According to this concept all tars can be prevented or eliminated in the gasifier and hence no additional after treatments for tar removal will be required. The following factors are most important for the success of primary measures.

- Selection of operating parameters, especially temperature, gasifying medium, ER and residence time, can reduce the amount of tars produced during gasification. Operating parameters mainly depend on the type of a gasifier. High temperature gasification, higher than 850°C, favours high carbon conversion and less tar formation. A higher value of ER is better for less tar in the exit gas, but increasing the ER is observed to increase the amount of CO_2 in the exit gas; an optimum value is reported to be 0.25-0.3. Tar distribution was reported to be different with different gasifying medium. Higher amounts of phenolic compounds were formed for steam gasification and higher amounts of aromatic hydrocarbons were formed with air gasification of biomass (Gill et al., 1999b).

- The addition of some active bed materials has been proven to be effective. However there are a number of factors that have to be taken into account when selecting bed materials. These bed additives should be economically available, attrition resistant and most importantly active and selective in terms of tar reduction. Among all additives used so far dolomite, olivine and char have been found to be attractive. However, there is a need for further research to develop other cheap additives.

- The modifications made to the gasifier design must be easily implementable. For most of the attempts made to modify the gasifier design researchers claim to produce a clean gas. However, a few factors should be kept in mind while designing the entire gasification chain: it should be simple, environmental friendly and should be able to produce a gas with a high heating value and low tar content.

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Chapter 3[*]

Catalytic decomposition of biomass tars: use of dolomite and untreated olivine

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The purpose of this chapter is to describe the activity of olivine and dolomite for tar decomposition. The experiments presented here were performed at the ECN facility using a slip stream from a lab-scale atmospheric bubbling-fluidised-bed gasifier. A new approach to tar classification is described and followed throughout this chapter. The results are represented in terms of the following tar classes; GC-undetectable tars (class 1), heterocyclic compounds (class 2), aromatic compounds (class 3), light polyaromatic compounds (class 4) and heavy polyaromatic compounds (class 5).

3.1 Introduction

The use of catalytically active bed materials during biomass gasification was critically reviewed in the previous chapter. Although dolomite and Ni-based steam reforming catalysts have been proven to be active in terms of tar reduction, dolomite is relatively soft and very easily eroded, whereas Ni-based catalysts are easily deactivated. Therefore, a lot of research still needs to be directed at finding a catalytically active fluidizable bed material for biomass gasifiers. As described in Chapter 2, olivine may be a potential candidate as an in-bed additive. Olivine has advantages over dolomite in terms of its attrition resistance. In parallel with this research, some research groups have been investigating olivine as a tar removal catalyst (Rapagnà et al., 2000; Courson et al., 2000, 2002; Abu El-Rub et al., 2002; Corella et al., 2004). The amount of reported literature on the use of olivine is

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[*] This chapter is published in Renewable Energy 30, 565-587, 2005

limited. There is still ambiguity over the prospective use of olivine as a tar decomposing catalyst. It is not yet well known how tars behave in the presence of olivine. Therefore, olivine was selected as the catalyst for investigation during this research.

The focus of this chapter is to determine the performance of olivine as a tar decomposing catalyst. In order to compare the activity of olivine with dolomite, experiments were also performed with calcined dolomite. Furthermore, a new approach to tar classification is described in this chapter, which will be followed throughout this thesis. In addition, tar dewpoints are calculated after catalytic treatment as the dewpoint of tar in the syn-gas determines its condensation behaviour.

3.2 Tar classification

Tar is a complex mixture of condensable hydrocarbons, which includes single ring to multiple ring aromatic compounds along with other oxygen containing hydrocarbons. Tar is normally considered to be a single lump of hydrocarbons. Considerable efforts have been directed towards identifying all the constituent
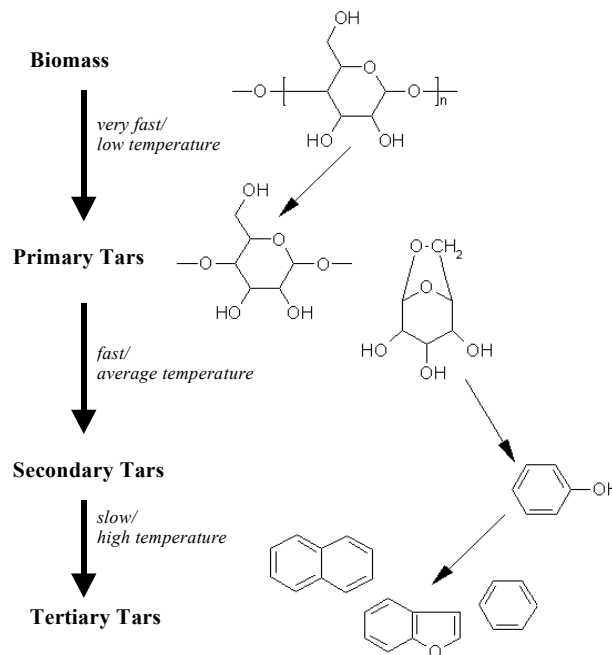

Fig. 3.1: Tar classes as reported by Milne and Evans (1998)

components of tar and the interconnection between them. Several researchers have tried to put tars into different classes and to study the behaviour among these classes. Different approaches of tar classification are reported in the literature. Milne and Evans (1998) classified tars in three groups depending on the reaction regimes as shown in Fig. 3.1. These three groups are: "primary products" which are characterised by cellulose-derived, hemicellulose-derived and lignin-derived products; "secondary products" which are characterised by phenolics and olefins; "alkyl tertiary products" which are mainly methyl derivatives of aromatic compounds; "condensed tertiary products" which are PAH without substituent groups. Primary products are destroyed before the tertiary products appear (Milne and Evans 1998). Corella et al. (2000) lumped all the tar species into 6 groups, namely benzene, 1-ring compound, naphthalene, 2-ring compounds, 3- and 4-ring compounds and phenolic compounds. The authors also proposed a reaction network suggesting the inter-dependency of each group. In another approach Pérez et al. (1997) and Corella et al. (2002) divide tars into two groups, namely "easy to destroy" which are characterised by more reactive tar species and "hard to destroy" which are mainly less reactive tar species.

In this work, tar is considered to be all the organic contaminants with a molecular weight larger than benzene. For an overview of the tar classes see Table 3.1 below. This tar classification system was developed in cooperation with the Energy research Centre of The Netherlands (ECN), Toegepast Natuurwetenschappelijk Onderzoek (TNO) and University of Twente (UT) within the framework of the project "Primary measures for the inhibition /reduction of tars in biomass fuelled fluidized-bed gasifiers", funded by the Dutch Agency for Research in Sustainable Energy (SDE). This classification is mainly based on solubility and condensability of different tar compounds, rather than reactivity of the compounds. At this point, it should be clearly stated that the objective of this present chapter is to determine the decomposition of different tar classes. Inter relation between the tar classes s not taken into account and this is out of the scope of the present chapter.

3.3 Experimental

3.3.1 Setup
The experiments were conducted at the facility of ECN, (Petten, The Netherlands). A slip stream of the biomass gasification gas from the lab-scale atmospheric bubbling fluidized bed gasifier was passed through a secondary fixed

Table 3.1: List of tar compounds that are considered for different tar classes

Tar Class	Class name	Property	Representative compounds	Compounds considered in this study
1	GC-undetectable	Very heavy tars, cannot be detected by GC	None	None
2	Heterocyclic	Tars containing hetero atoms; highly water soluble compounds	Pyridine, Phenol, Cresols, Benzonitril, Quinoline, Isoquinoline, Dibenzophenol	Benzonitril, Phenol, Quinoline
3	Light aromatic	Uusually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene, Ethylbenzene, Xylenes, Styrene	Styrene
4	Light polyaromatic	Two and three ring compounds; condense at low temperature even at very low concentration	Indene, Naphthalene, Methylnaphthalene, Biphenyl, Acenaphtylene, Fluorene, Phenanthrene, Anthracene	Indene, Naphthalene, 1-Methyl naphthalene, 2-Me-naphthalene, Bi-phenyl, Acenaphtylene, Fluorene, Phenanthrene, Anthracene
5	Heavy polyaromatic	Larger than three-rings, these components condense at high temperatures at low concentrations.	Fluoranthene, Pyrene, Chrysene, Perylene, Coronene, Triphenylene, Benzo(a)anthracene, Benzo(c)phenanthrene, Benzo(e)pyrene, Benzo(j)fluoranthene, Benzo(k)fluoranthene	Fluoranthene, Pyrene, Triphenylene, Benzo(a)anthracene Benzo(c)phenanthr-ene, Benzo(e)pyrene, Benzo(j)fluoranthene, Benzo(k)fluoranthene

bed reactor where the catalysts were placed. The gasifier operates with a capacity of 1 kg h^{-1}. A schematic representation of the experimental setup is given in Fig. 3.2. The stainless steel secondary reactor has a 3 cm internal diameter and is 50 cm long. To preheat the gasifier gas, a standard tube with a 6 mm outside and 4 mm inside diameter is wounded around the reactor. Temperature sensors are installed at the gas entrance and exit points and in the middle of the catalyst bed to ensure that the reactions occurred at the desired temperatures. The experiments were performed in a temperature range of 800-900°C and temperature across the catalyst was taken to be constant during each experiment. The position of the bed was chosen from the temperature profile over the reactor, which was determined by the oven temperature set to 1010°C and a gas flow of 1 l min^{-1}. The catalysts were mixed with sand and the mixture was placed on top of a bed of coarse sand. Temperature readings were taken from the bottom of the sand bed to the top. Fig. 3.3 shows the profile of the 10 cm above the sand bed. Prior to experiments dolomite was heated at 900°C for 1 h under a nitrogen flow. No pre-treatment was carried out for the olivine except for sieving to obtain the right size fraction. Typical experimental conditions are given in Table 3.2.
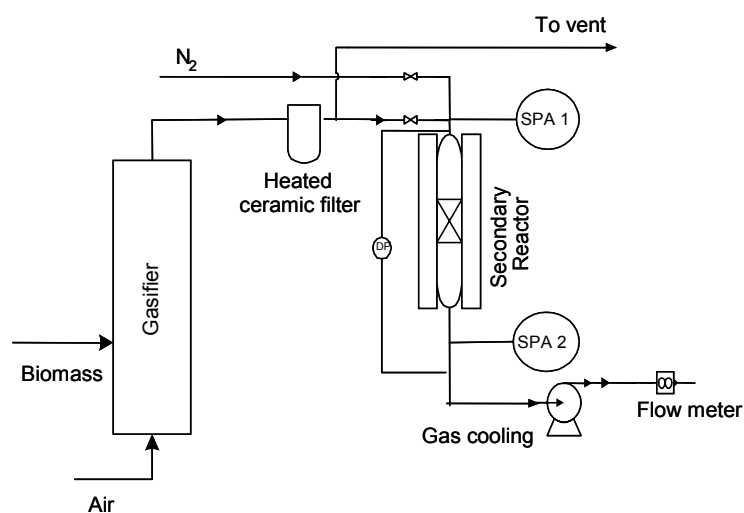
Fig. 3.2: Schematic representation of the experimental setup for tar decomposition
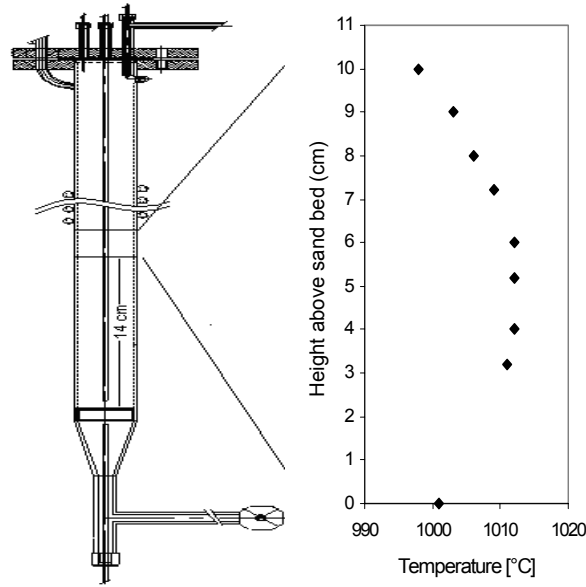
Fig. 3.3: Temperature profile over the bed

Table 3.2: Experimental conditions

Condition	Parameter	
Gasification conditions		
Biomass Feed	Beech	
Gasification temperature (^{o}C)	850	
Bed material	Sand	
Feed rate (kg h^{-1})	1	
Gas composition of the syn-gas (vol %)		
H$_2$	10.9	
CO	15.7	
CO$_2$	16.5	
CH$_4$	4.7	
Conditions of the secondary reactor		
Temperature (^{o}C)	800-900	
Catalyst particle size (μm)	250-355	
Mass fraction of catalysts mixed with sand	0.17	
Bed material (catalysts)	Dolomite/Sand	Olivine/Sand
Amount of catalysts (g)	4.88	4.75
Average gas flow through the reactor (l min^{-1})	1.1	1.2
Residence time (s)	0.30	0.26
Space time (kg h m^{-3})	7.4x10^{-2}	6.6x10^{-2}
Pre-treatment	Calcination	None

3.3.2 Sampling and analysis

The inlet and outlet tar compositions were sampled using the SPA (solid phase adsorption) method developed by KTH, Sweden (Brage et al., 1997). The SPA samples were taken at a temperature of 300°C. The samples taken during the experiments at Petten were transferred to Eindhoven in a cool box for analysis. The SPA samples were analysed using a Shimadzu QP5000 GCMS with a WCOT fused silica column. Several samples were taken at the same operating condition and the average value is presented here. Concentrations of individual tar compounds were calculated in mg m^{-3} and then added to get the concentration of a particular tar class. The tar compounds that were considered for a particular class are tabulated in Table 3.1. Concentrations of compounds with a higher boiling point than pyrene were determined using the calibration data for pyrene. The heaviest compound identified was benzofluoranthene. Benzene is not considered to be tar. Light tar, e.g. toluene, was identified, but could not be measured accurately, especially at lower temperatures. If the samples are not analyzed immediately, there is a possibility that some of the one ring tars volatilizes, thus preventing accurate measurement of toluene. Thus toluene was not taken into account during total tar calculation, but presented separately. Very high molecular weight (Class 1) tars and final gas composition could not be measured due to experimental limitations.

3.3.3 Catalyst characterization

Two types of additives, olivine and dolomite were tested during the experiments. Calcined dolomite is a porous catalyst; its internal surface area and the presence of oxides in its matrix (CaO, MgO) make it an active catalyst with respect to tar reduction. Olivine is a naturally occurring silicate mineral in which magnesium and iron are embedded in the silicate tetrahedral (Rapagnà et al., 2000). The properties of both additives are tabulated in Table 3.3. The BET surface area for both catalysts were measured using chemisorption and Micromeritics ASAP 2000 equipment. Olivine was found to be a nonporous material with an extremely low surface area (0.42 m^{2}g^{-1}), whereas dolomite has 9.1 m^{2}g^{-1} of surface area. The results of mercury porosimetry for calcined dolomite are included in Table 3.3; mercury porosimetry could not be done for olivine because of the negligible pore volume. The Scanning Electron Microscopy (SEM) scans for calcined dolomite and olivine are shown in Fig 3.4. X-ray diffraction (XRD) reveals that olivine has an orthorhombic structure whereas calcined dolomite has a simple cubic structure. Figs. 3.5 and 3.6 show the typical X-ray diffractogram for calcined dolomite and olivine respectively.

Table 3.3: Catalyst properties

Properties	Dolomite	Olivine
Chemical Composition (wt%) [a]		
CaO	31.5	--
MgO	20.3	49
SiO_2	0.3	41
Fe_2O_3	0.4	7
Al_2O_3	0.1	0.5
Cr_2O_3	--	0.3
NiO	--	0.3
Physical Properties		
Colour	Greyish	Greenish [b]
Density [a]	-	3.3 g cm^{-3} [b]
Hardness [a]	Soft	6.5-7.0 Moh's scale [b]
Melting point [a]	na	Approx. 1760°C [b]
Thermal expansion [a]	na	Linear; approx. 1.1% upto 1200°C [b]
Mercury porosimetry (with Micromeritics instrument, Auto pore IV 9500)		
Total pore area (m^2 g^{-1})	5.05	nd
Total pore volume (ml g^{-1})	0.08	nd
Average pore diameter (4 V/A) (nm)	62.4	nd
Bulk density	2.54	nd
Apparent (skeletal) density	5.35	nd
Nitrogen adsorption (with Micromeritics ASAP 2000 instrument)		
BET surface area (m^2 g^{-1})	9.12	0.42
X-ray diffraction (determined with Rigaku Geigerflex D/MAX-B XRD equipment)		
Structure	Cubic	Orthorhombic
State of material	Calcium oxide (CaO) Magnesium oxide (MgO)	Ferroan-forsterite $(Mg,Fe)_2SiO_4$ Syn-forsterite (Mg_2SiO_4)

a: as indicated by the supplier; b: from www.olivin.com; last visited July, 2003; na: not available
nd: could not be determined due to extremely low porosity
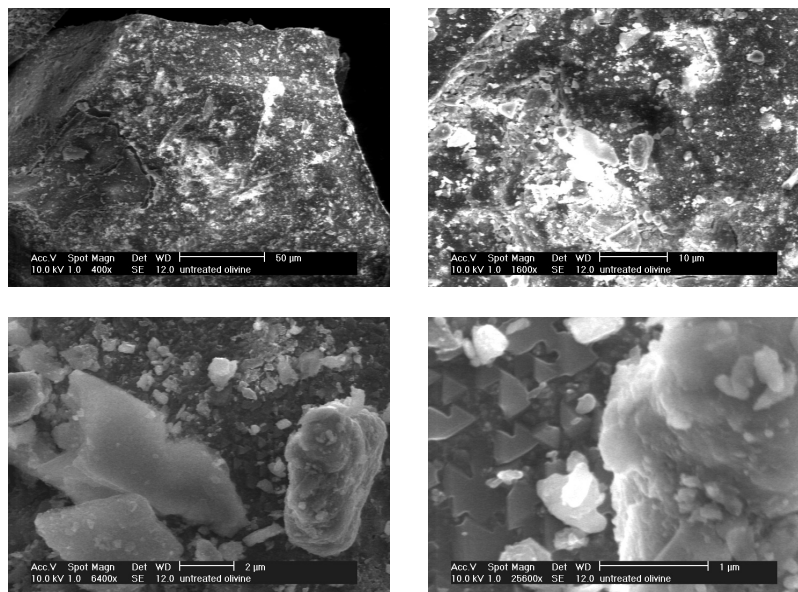
a. SEM scans for olivine
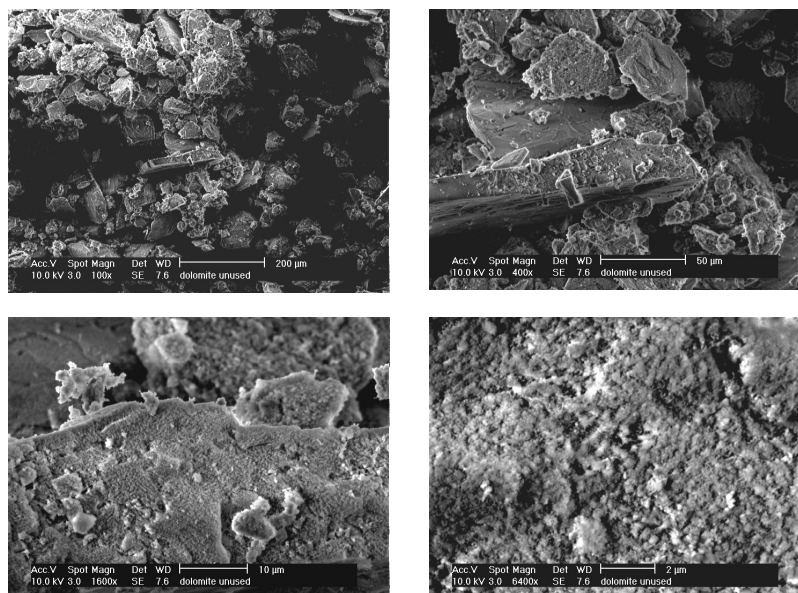
b. SEM scans for calcined dolomite

Fig. 3.4: Scanning Electron Microscope scans for olivine and calcined dolomite

Fig. 3.5: X-ray diffraction pattern for olivine, along with references

Fig. 3.6: X-ray diffraction pattern for calcined dolomite, along with references
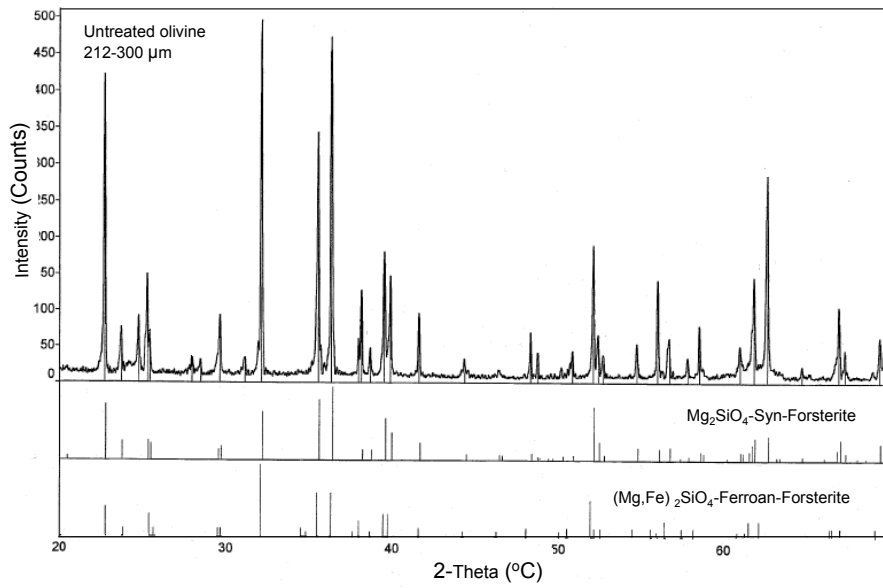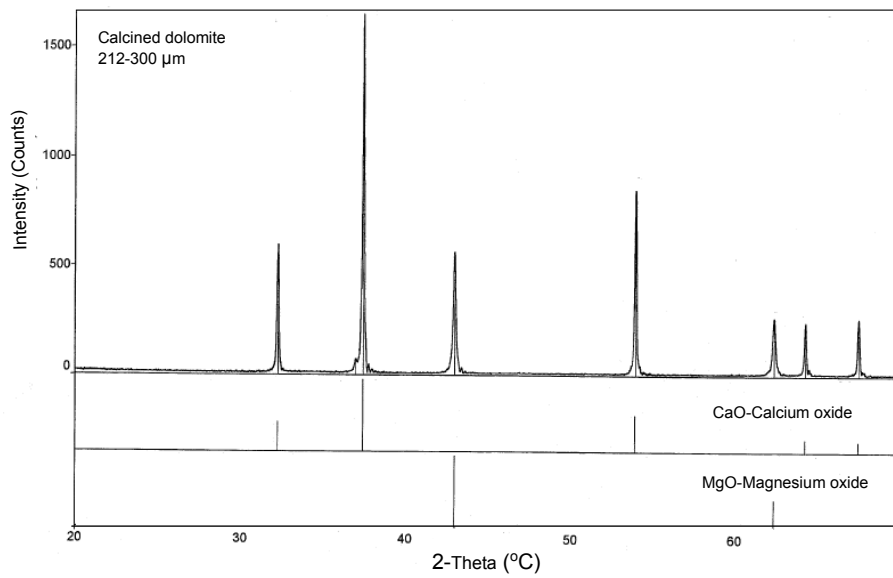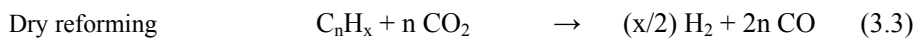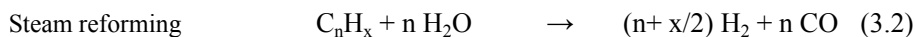
3.4 Results and discussion

Tar decomposition occurs due to a series of complex, multiple and simultaneous reactions. The main reactions during are shown below.

Thermal Cracking	$p\ C_nH_x$	$\rightarrow$	$q\ C_mH_y + r\ H_2$	(3.1)
Steam reforming	$C_nH_x + n\ H_2O$	$\rightarrow$	$(n+ x/2)\ H_2 + n\ CO$	(3.2)
Dry reforming	$C_nH_x + n\ CO_2$	$\rightarrow$	$(x/2)\ H_2 + 2n\ CO$	(3.3)
Carbon formation	C_nH_x	$\rightarrow$	$n\ C + x/2\ H_2$	(3.4)
Water gas shift	$CO_2 + H_2$	$\rightleftharpoons$	$CO + H_2O$	(3.5)
Boudouard reaction	$C + CO_2$	$\rightleftharpoons$	$2\ CO$	(3.6)

C_nH_x represents tar, which can be a mixture of several individual tar compounds. Besides these reactions, different tars can also react with other tars in several ways such as by polycondensation, dimerization etc. Due to these complexities, it is difficult to understand the exact behaviour of the catalyst towards tar removal. The simplest way to measure activity is in terms of conversion of tar in a particular condition. The results are expressed in terms of conversion of individual tar classes defined as

$$X\ (\%) \ = \frac{\left(C_{t,in} - C_{t,out}\right)}{C_{t,in}} x 100\ \% \tag{3.7}$$

Once the concentration of each class is known upstream and downstream the catalytic reactor, conversion for each class is calculated using Eq 3.7. The conversions of different tar classes, using calcined dolomite and olivine as catalysts, as a function of temperature are shown in Figs. 3.7 and 3.8, respectively. The results include the thermal effect and the catalytic effect on tar decomposition. Temperature plays a crucial role in decomposing tars. Conversion of each tar class increases when the temperature is raised from 800°C to 900°C. At a temperature of 800°C, production of class 3 tars, i.e. single ring compounds, is observed leading to a negative conversion over dolomite. Probably, this is mainly due to the fact that higher hydrocarbons are broken down to form class 3 tars. At 850°C and 900°C, decomposition of class 3 tars is also observed. Olivine shows a moderate activity in terms of tar reduction and only becomes active at a higher temperature. At 850°C, conversion of class 3 and class 5 tars remains same as it is at 800°C. Conversion of class 4 tars decreases at 850°C indicating the formation of 2- and 3- ring compounds, probably from the breakdown of heavy polyaromatic compounds with 4- or more aromatic rings. At 900°C olivine shows considerable activity towards the

decomposition of all the four tar classes. Heterocyclic (class 2) tars are very easily converted by both dolomite and olivine. Temperatures higher than 900°C are required for thermal conversion of tar (Houben et al., 2002).
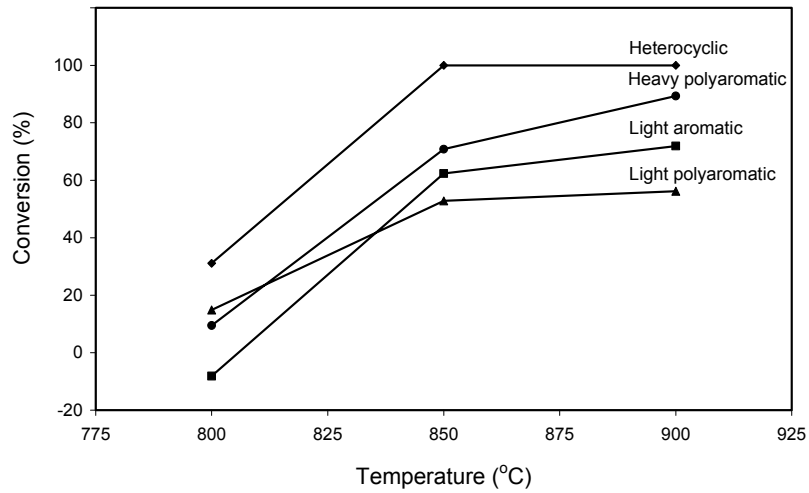
Fig. 3.7: Conversion of different tar classes with dolomite as catalyst. T_R: 800-900°C; Gas flow: 1.1 l min^{-1}; τ': 0.3 s; τ: 7.4x10^{-2}kg h m^{-3}
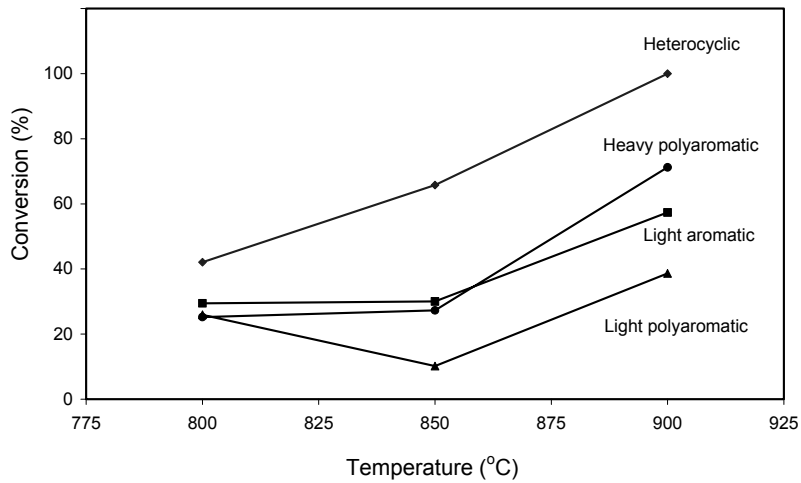
Fig. 3.8: Conversion of different tar classes with olivine as catalyst T_R: 800-900°C; Gas flow: 1.2 l min^{-1}; τ': 0.25 s; τ: 6.6x10^{-2} kg h m^{-3}

A comparison of dolomite and olivine is shown in Fig. 3.9, which shows the conversion of different tar classes at 900°C. To provide a comparison, an experiment with sand only was conducted under the same operating conditions. It can be seen that at a temperature of 900°C, all the water-soluble heterocyclic compounds are completely converted for all the three cases. A 48% decrease of heavy PAHs (class 5) is observed for sand. The addition of olivine leads to a decrease of 71% for the total heavy PAHs, which is an improvement of about 50%. The addition of calcined dolomite causes a decrease of almost 90% at the same operating conditions. The light PAHs (class 4) also show a considerable increase in decomposition when olivine is added. The decrease in tar when only sand is used amounts to 25% whereas the decrease is 54% when olivine is added. Again adding calcined dolomite increases the conversion the most; the decrease in light PAHs amounts to 56%. In case of light aromatic compounds (class 3), olivine shows a slight increase in conversion when compared to sand. The conversion when dolomite is used is 71%, whereas the sand-only case yields 48%; olivine shows a conversion of 57%. Apparently, calcined dolomite is more reactive than olivine with respect to tar decomposition. As can be seen from Fig. 3.9, class 4 tars are the least reactive and need severe treatment.
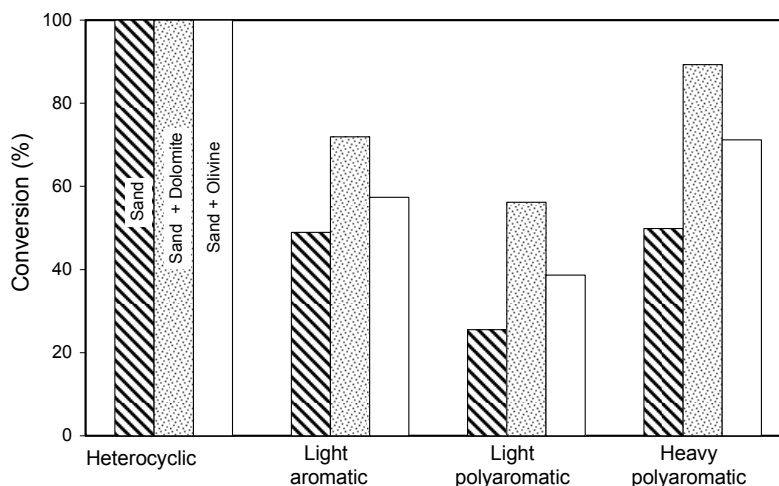
Fig. 3.9: Conversion of tars with different additives $T_R = 900°C$;
Gas flow: 1.2 l min^{-1}; τ': 0.26 s; τ: 6.6x10^{-2} kg h m^{-3}

Adding the concentration of the different classes gives the amount of total tar considered and with it the total for tar conversion. Fig. 3.10 shows the conversion for the bulk tar, and Fig. 3.11 shows the exiting concentrations of the combined considered tars. It is clear that calcined dolomite is more active additive. At 850°C

the conversion for calcined dolomite amounts to 56%, whereas the olivine shows a conversion of about 16%. When the temperature is raised to 900°C, a slight increase of total tar conversion is observed for dolomite; but for olivine, this temperature effect is prominent. At 850°C, the total tar conversion decreases probably due to formation of class 4 tars. When the temperature is increased further to 900°C, a total tar conversion of 46% is observed for olivine. The entering tar concentrations for the dolomite and olivine experiment were approximately 4.0 g m^{-3} at 900°C. After catalytic treatment with dolomite, the total tar concentration dropped to 1.5 g m^{-3}, and with olivine the concentration dropped to 2.2 g m^{-3}. It should be noted that this is only a part of the tar present in the system. The unidentified heavy and very light tars are not included, because they cannot be captured by the SPA analyses method. Rapagnà et at. (2000) observed tar concentration of approx. 2.4 g m^{-3} at the exit of the gasifier, even at a temperature of 770°C using olivine as bed material. It must be made clear that Rapagnà and his co-workers used olivine inside the gasifier and used steam as a gasifier medium which favours more steam reforming reactions in the gasifier, thus less tar in the exiting gas.
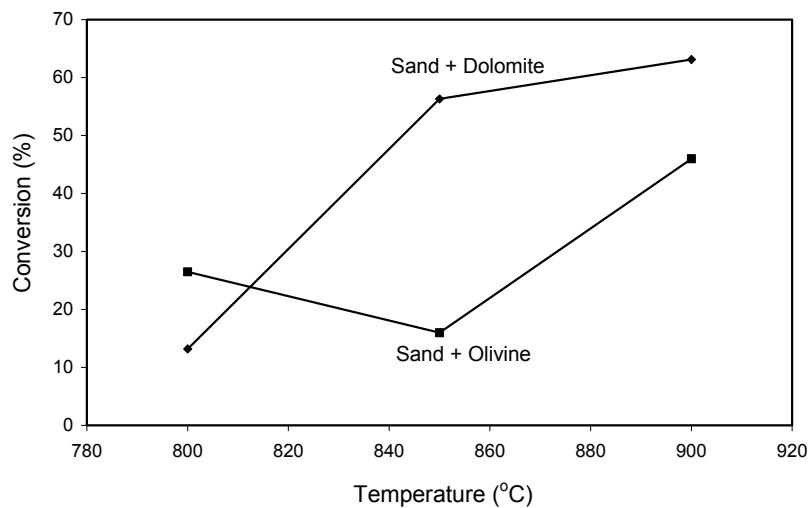
Fig. 3.10: Conversion of total considered tars with additives T_R: 800-900°C; Gas flow: 1.1-1.2 l min^{-1}; τ': 0.25 -0.3 s; τ: 6.6x10^{-2}-7.4x10^{-2}kg h m^{-3}; Catalysts: Calcined dolomite, olivine, initial tar concentration: ~4.0 g m^{-3}

Fig. 3.11 gives the concentration of total considered tars remaining after catalytic treatment along with the individual contribution of each class of tar. At lower temperature, the total amount of considered tar is lower for olivine than that for dolomite. This is mainly due to a higher naphthalene concentration. It is clear

from Fig. 3.11 that class 4 contributes the major part of the total tar for both catalysts. As the temperature of the catalytic reactor increases, its percentage in the remaining tar increases, although the amount of class 4 tar decreases. At the lower temperature range investigated, class 4 tar contributes around 80% of the total tar, whereas with increasing temperature the contribution of class 4 tar becomes around 90%. Simell and his co-workers also reported the effect of temperature on tar removal using dolomite as a catalyst (Simell et al., 1992). They reported similar values of tar content as those given in this present chapter for the investigated temperature range except for 900°C, where they found less than 100 mg m^{-3} of tars. It should be noted, however, that the properties of the dolomite investigated in the present study are quite different from those of the dolomite used by Simell et al. (1992).
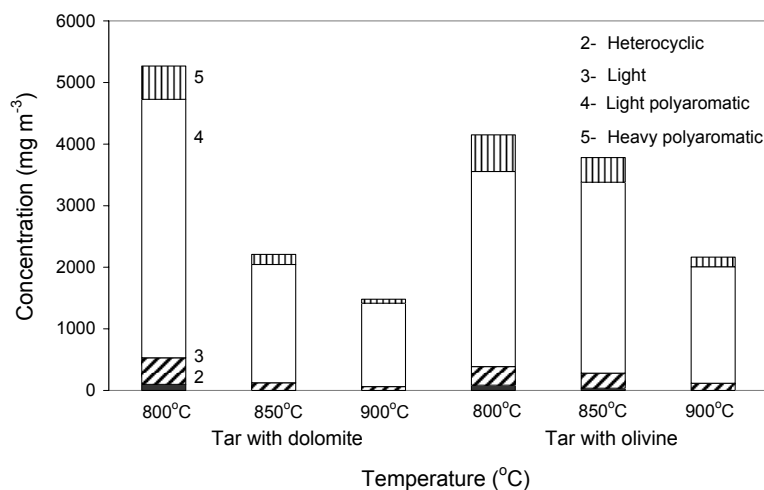
Fig. 3.11: Contribution of individual tar classes on the amount of total tar T_R: 800-900°C; Gas flow: 1.1-1.2 l min^{-1}; τ': 0.25 -0.3 s; τ: 6.6x10^{-2}-7.4x10^{-2}kg h m^{-3}; Catalysts: Calcined dolomite, olivine

Among all the compounds identified in class 4 tars, naphthalene contributes to more than 50% at the lower temperature range as shown in Fig 3.12. At 900°C, the contribution of naphthalene is more than 70%, thus more than 60% is contribution in total tar for both dolomite and olivine. The conversion of naphthalene is also observed to be lower as shown in Fig. 3.13. This low conversion might be due to the fact that either naphthalene is a very stable compound, or decomposition of higher tars, i.e. higher than naphthalene, leads to the formation of naphthalene. At 850°C, formation of naphthalene and thus class 4 tar is observed

over olivine. Due to this formation, the total tar conversion decreases as the reaction temperature was raised from 800 to 850°C as shown in Fig. 3.10 over olivine.
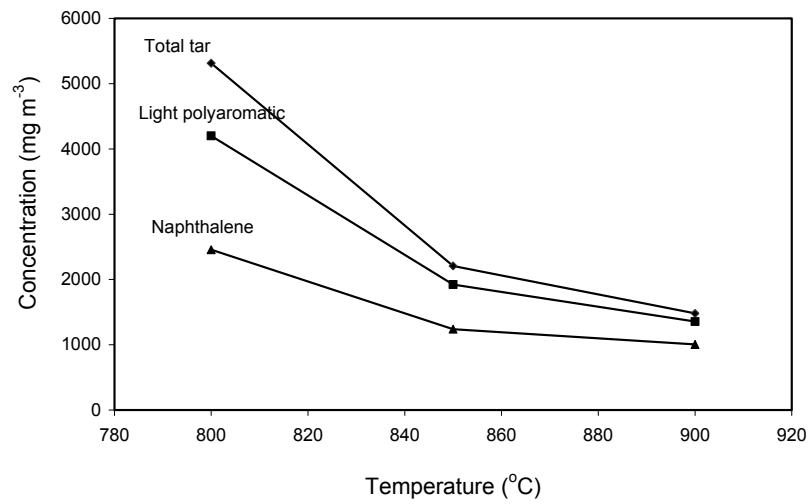
(a) over calcined dolomite
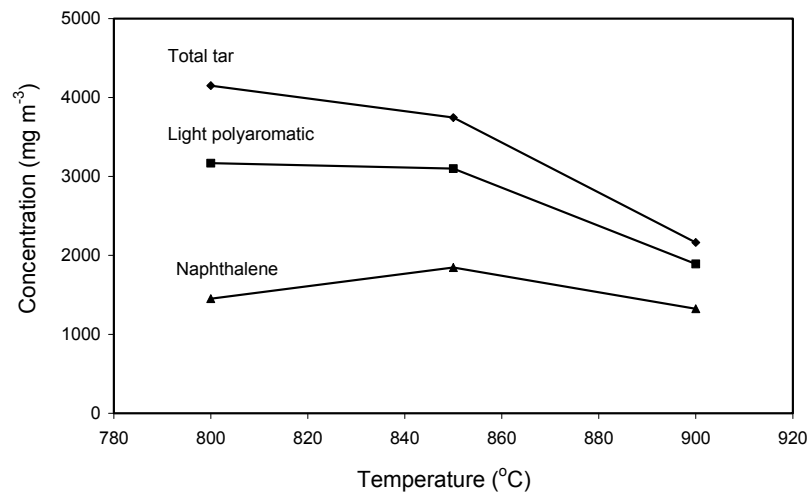
(b) over olivine

Fig. 3.12: Amount of naphthalene after catalytic treatment compared to class 4 and total tar. T_R: 800-900°C; Gas flow: 1.1-1.2 l min^{-1}; τ': 0.25 -0.3 s; τ: 6.6x10^{-2}-7.4x10^{-2} kg h m^{-3}; Catalysts: Calcined dolomite, olivine
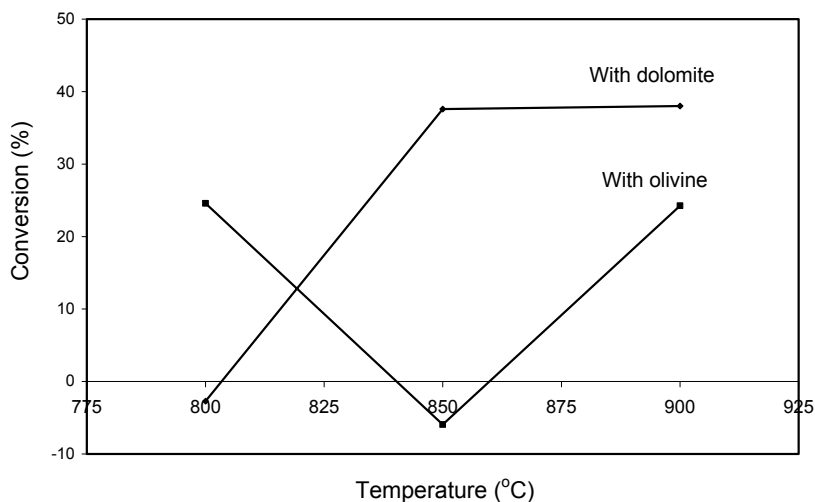
Fig. 3.13: Conversion of naphthalene. T_R: 800-900°C; Gas flow: 1.1-1.2 l min^{-1};τ: 0.25 – 0.3 s; τ: 6.6x10^{-2}-7.4x10^{-2}kg h m^{-3}; Catalysts: Calcined dolomite, olivine

Although benzene is not considered to be a tar, it is formed during the decomposition reactions. Benzene normally do not pose problem of condensation. The amount of benzene was observed to increase up to a maximum value by Simell et al. (1992) with increasing temperature. At 800°C benzene contributes almost 80% of the total tar. As mentioned earlier, in this study benzene and toluene were not taken into account while calculating the total tar. The approximate concentration of these two compounds before entering the reactor and after catalytic treatment at 850°C and 900°C is given in Fig. 3.14. The formation of benzene is observed to be very high, especially when olivine is used as a catalyst. Formation of toluene is also found for dolomite and olivine at 850°C.

Dolomite and olivine show different catalytic behaviour for each tar class. Their activity is very much dependent on temperature. At a temperature of 900°C, a total tar concentration at the inlet of around 4.0 g m^{-3} could be decreased to 1.5 g m^{-3} and 2.2 g m^{-3} at the outlet with dolomite and olivine respectively. It is anticipated, that the difference in activity will be mainly due to structural differences and differences in the composition of the catalysts, as shown in Figs. 3.5-3.8. The moderate activity of calcined dolomite, compared to literature data, can probably be attributed to its moderate surface area. These results also reveal that olivine is active towards tar decomposition at higher temperatures, but its activity is still much lower than that for dolomite.
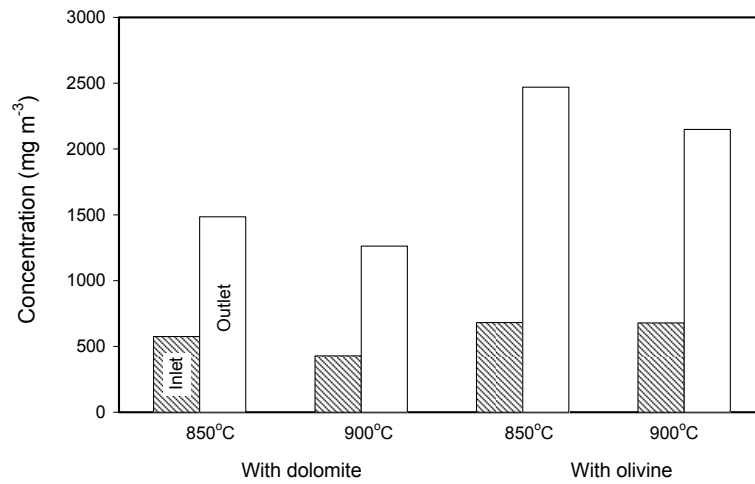
a. Amount of benzene
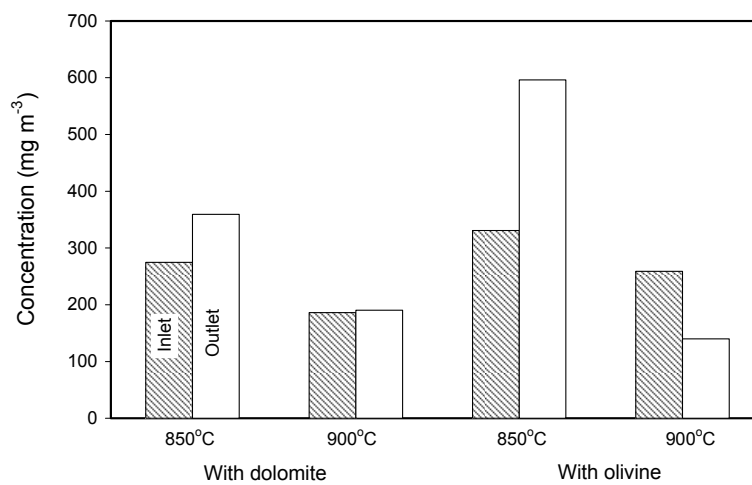
b. Amount of toluene

Fig. 3.14: Concentration of benzene and toluene, at the inlet and outlet of the catalytic reactor. T_R: 850-900°C; Gas flow: 1.1-1.2 l min^{-1}; Catalysts: Calcined dolomite, olivine; τ': 0.25 -0.3 s; τ: 6.6x10^{-2}-7.4x10^{-2}kg h m^{-3}; (These are not the exact values, but only indication. The SPA method does not give accurate measurements for light tars especially when the samples are not analysed immediately)

3.5 Apparent activation energy

The apparent rate constant and the apparent activation energy for total tar decomposition are calculated assuming a first order reaction with respect to tar as a

single lump to have an idea about the approximate activation energy required for calcined dolomite and olivine. A major advantage of assuming a first order reaction is that it is easy to evaluate and compare with other references. The overall rate can be described using the following equation, assuming a first order reaction in tar:

$$- r_{tar} = k_{app} \cdot C_{tar} \qquad (3.8)$$

Under plug-flow conditions, the apparent rate constant can be calculated as:

$$k_{app} = \frac{[-\ln(1-X)]}{\tau} \qquad (3.9)$$

$$\tau = \frac{W}{v_0} \qquad (3.10)$$

The temperature dependency according to Arrhenius' Law can be represented as

$$k_{app} = k_{0,app} \cdot e^{\frac{-E_{app}}{RT_R}} \qquad (3.11)$$
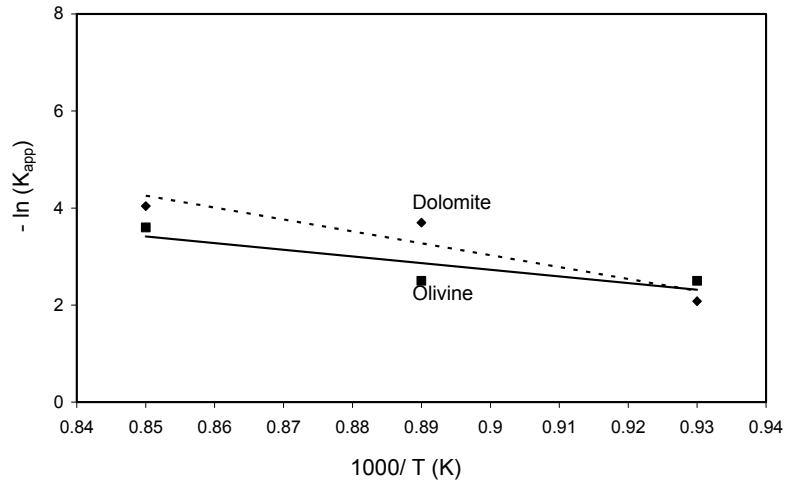
Fig. 3.15: Arrhenius plot for calculation of apparent activation energy T_R: 800-900°C; Gas flow: 1.1-1.2 l min^{-1}; τ': 0.25 -0.3 s; τ: 6.6x10^{-2}-7.4x10^{-2}kg h m^{-3}; Catalysts: Calcined dolomite, olivine

The Arrhenius plot shown Fig 3.15 gives an approximate E_{app} of 196 and 114 kJ mol^{-1} for calcined dolomite and olivine respectively, for a temperature range of 800-900°C. Apparent activation energies reported by several other research groups are listed in Table 3.4. A comparison of the values of E_{app} and k_{app} reported in the literature may be sometimes misleading. The gas composition and the type of catalyst affect the value of k_{app}. The space-time (τ) can be represented in several

ways as indicated by Corella et al. (1996) this significantly affects the k_{app} value, thus the apparent activation energy. Activation energies for individual tar compounds such as benzene, naphthalene etc are much higher than those reported for total tar. When a set of multiple first order reactions are approximated with a single first order expression, the apparent activation energy and the pre exponential factor tend to converge on the lower value of the set (Corella et al., 2002)

Table 3.4: Apparent activation energy for tar decomposition

Gasification Conditions		Cracking catalyst	Kinetic parameters		Remark	Reference
Temp (^{o}C)	Agent		E_{app} (kJ mol^{-1})	$K_{o,\,app}$		
800-860	H_2O+ O_2	BASF G1-25S	58±30	1.56×105 m^3 kg^{-1}h^{-1}	Under some internal diffusion	Aznar et al. (1998)
800	Air	BASF G1-25S	72±12	1.43×10^5 m^3 kg^{-1}h^{-1}	Under some diffusion control; use of dolomite guard bed	Narvaez et al. (1997)
-	-	SiC SFCC FWC CPRD	96.81 85.69 81.09 76.24	3.83×10^4 1.59×10^4 1.30×10^4 9.26×10^4 s^{-1}	Cracking of coal derived liquid	Shamsi (1996)
800	Air	Dolomite (Norte)	100±20	1.51 ± 0.80 $\times 10^{-6}$ m^3 kg^{-1}h^{-1}	Catalytic bed is fluidized	Orio et al. (1997)
780	Steam	Dolomite Magnesite Calcite	42 42 42	1.96×10^3 1.46×10^3 1.28×10^3 m^3 kg^{-1}h^{-1}	Under internal diffusion control	Delgado et al. (1997)
850	Air	Dolomite Olivine	196 114	7.2×10^{10} 3.6×10^6 m^{3}kg^{-1} h^{-1}	Catalysts are mixed with sand	This chapter

3.6 Condensability/tar dewpoint

The tar dewpoint is the temperature at which the real total partial pressure of tar equals the saturation pressure of tar. Once the actual process temperature passes the thermodynamic tar dewpoint, tar can condense out. The tar dewpoints of the inlet and exit gas at 800-900°C were determined using the calculation tool developed by ECN. The model is based on ideal gas law. The calculation is done using Raoult's

law and the vapour pressure data of individual tar compounds. Further explanations of the model can be found on the internet (www.thersites.nl). The results of these calculations are presented in Table 3.5 and represent the dewpoints of the measured tar composition.

Heavy tar compounds dominate the tar dewpoint. According to van Paasen et al. (2002) class 3 tar compounds only condense at a very high concentration (10000 mg m^{-3}), whereas class 5 tars condense at low concentration (0.1 mg m^{-3}) when the gas is at atmospheric pressure and at ambient temperature. In the classification system, the heaviest tars are grouped in class 1. These tars cannot be measured using the SPA-GC tar measurement method, which was applied in the present study. Therefore, the tar dewpoint in Table 3.5 may be an underestimate.

Present calculation results give a relative measurement of dewpoints, as class 1 tars are not considered at the inlet and at the outlet. At a temperature of 800 and 850°C, there is no significant decrease in the dewpoint for both dolomite and olivine. At 900°C, a considerable decrease in the dewpoint of around 42% is observed for calcined dolomite corresponding to a tar conversion of 63%; whereas only a very slight decrease in dewpoint is observed for olivine with a corresponding tar conversion of 46%.

Table 3.5: Dewpoints of tar at the inlet and outlet of the catalytic reactor

Dewpoints calculated before and after catalytic reactor (°C)				Reactor Temperature (°C)
Treatment with dolomite		Treatment with olivine		
At the inlet	At the outlet	At the inlet	At the outlet	
172	170	177	172	800
170	152	171	161	850
170	97	173	150	900

3.7 Concluding remarks

The experimental results reveal that the class 4 tars remain in a substantial amount even after severe catalytic treatment at a temperature of 900°C. These tars are either very stable compounds or formed due to the breakdown of other higher tars such as class 1 and class 5 tars. Formation of class 3 tar was observed especially at the lower temperature investigated, at 800°C. Class 3 tars do not pose any problem as they condense only at very high concentration. It was observed that thermal treatment (sand bed only) is sufficient to remove all of the class 2 tars, thus solving the solubility problem.

The addition of olivine and calcined dolimite to the sand bed improved the conversion of each class of tar. The observed total tar conversions of 63% over calcined dolomite and 46% over olivine are lower than reported in the literature for traditional tar removal catalysts. This may be attributed to the fact that the sand bed contained only 17 wt% of the additives. Increasing the catalyst loading may improve the conversion of tars. It is expected that the lower activity of olivine compared to calcined dolomite is due to the fact that no pre-treatment was done for the olivine; whereas the dolomite was calcined to activate it. Some pre-treatment might improve the activity of olivine, also olivine is not porous; thus no internal surface area is available for tar conversion. It is furthermore believed that the moderate activity of olivine is related to its iron content. Although both catalysts lead to a substantial reduction in total tar concentration, this reduction appears to had a limited impact on the tar dewpoint.

Pre-treated olivine as a tar removal catalyst for biomass gasifiers: naphthalene as a model biomass tar

Steam reforming of naphthalene over olivine catalyst is considered to be a model reaction to compare the different pre-treatment methods for olivine. In the present chapter the pre-treatment of olivine, in relation to an improvement in activity towards tar removal is investigated. The effect of pre-treatment time is also investigated and the results are compared with an inert material SiC which only causes thermal cracking. Steam and dry reforming reactions of tar are investigated. The results of the effect of syn-gas composition on tar decomposition are also presented in this chapter.

4.1 Introduction

As described earlier, tar is a complex mixture of condensable hydrocarbons, which includes single to multiple ring aromatic compounds along with other oxygen containing hydrocarbons. It is difficult to understand the catalytic decomposition behaviour of real biomass tar, because of the wide range of different compounds present in tar. To ease understanding, a decomposition mechanism is usually studied using model tar compounds. The tar classification system described in the previous chapter is useful for choosing the right model tar compound, i.e. one that is representative of a range of other chemical compounds. Among all biomass tars, naphthalene, which is a class 4 tar, is one of the most stable and it is a difficult tar to

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decompose (Coll et al., 2001; Jess, 1996a). Kinoshita et al. (1994) confirm that the formation of aromatic tar species without substituent groups, e.g. benzene, naphthalene, phenanthrene etc is favoured in the temperature range from 750 to 900°C. Hydrocarbons without such a substituent group attached to the benzenoid ring structure are relatively stable. Decomposition of these hydrocarbons occurs at temperatures above 850°C and naphthalene is observed to be the most stable. As indicated in Chapter 3 (Fig. 3.12), naphthalene contributes a major part of the total tar even after severe catalytic treatment with calicnated dolomite and olivine at very high temperature of 900°C. Naphthalene contributes to more than 50% of all the compounds identified in class 4 tars, at the lower temperature range. At 900°C, the contribution of naphthalene is more than 70%, thus a more than 60% contribution in total tar for calcined dolomite and olivine. The conversion of naphthalene over olivine and calcined dolomite, is observed to be lower than 40%. This low conversion may be due to the fact that either naphthalene is a very stable compound, or that the decomposition of higher tars, higher than naphthalene, leads to the formation of naphthalene. Given the above, naphthalene was considered to be a model tar compound to use for the present study.

4.2 Decomposition of model biomass tar compound

(literature review)

Tar decomposition mainly occurs due to cracking, steam and dry reforming reactions as shown by reactions 3.1-3.3. Several researchers have studied these decomposition reactions using model biomass tar compounds. Simell et al. (1999) used benzene as the tar model compound. During steam reforming cracking tests at 900°C, only 2% of benzene converts without any additive, this can be attributed to the thermal effect. While investigating the steam reforming reaction of benzene using stoichiometric amount of water, Simell et al. (1999) observed that the water gas shift reaction was much faster than the primary steam reforming reactions. They also observed that when only CO_2 is used, benzene decomposes into CO and H_2 (Simell et al., 1997a; 1997b). Simell et al. (1995) also investigated toluene as model tar compound. Using dolomite at a temperature of 950°C, conversion of toluene into gaseous compounds (H_2, CO_2 and CH_4) and benzene is 40% and this rises to 80% at 1000°C. In their study the partial pressure of CO_2 was increased; when it reached the equilibrium decomposition pressure of $CaCO_3$, calcined dolomite lost its tar decomposing activity. Simell et al. (1997b) investigated the catalytic activity of different catalysts such as calcined dolomite, a Ni-Al catalyst, SiC and alumina. It was observed that dry-reforming reactions take place six times faster at 900°C over

Ni-Al and the dolomite bed than steam-reforming reactions do. Simell et al. (1997b) also reported that hydrocracking is the dominating reaction in a mixed gas medium. Toluene decomposition rate was lower for the mixed gas medium, thus showing the inhibiting effect of CO and H_2.

Coll et al. (2001) studied the steam reforming reaction over two types of nickel-alumina catalysts with the following model compounds: benzene, toluene, naphthalene, anthracene and pyrene. The experiments show that the reactivity of the different model tar compounds over an ICI 46-1 catalyst, decreases as follows: benzene > toluene >> anthracene >> pyrene > naphthalene. It should be made clear that for these experiments, the steam to carbon ratio and the catalyst loading used were different for each tar compound depending on the reactivity of the organic compound. In contrast, Jess (1996b) reported that benzene is a more stable compound; his order of increasing reactivity was established as toluene >> naphthalene > benzene without use of any catalyst in the presence of H_2O and H_2. Jess found that primary reactions take place without the participation of steam showing that steam has only a small influence on the reaction rate. Hydrogen was found to inhibit the conversion of benzene and naphthalene, whereas it increased the reaction rate for toluene.

Taralas (1996) investigated the steam reforming reaction of n-heptane as a model tar compound in the presence of different catalysts. He observed that the selectivity to H_2 and CO_2 increases and the selectivity of C_2-C_7 hydrocarbons decrease, by increasing the partial pressure of the water (upto 34.2 kPa). The yield of CO_2 was decreased with addition of H_2 over calcined dolomite. When CO_2 is added, the conversion decreased, and a reduction in the yield of H_2 and CH_4 was observed. Taralas (1996) suggested that this inhibiting effect of CO_2 might be due to the recarbonation of the calcined dolomite. Using a Ni-Mo-catalyst favoured the formation of coke, whereas the use of calcined dolomite reduced the formation of these carbonaceous residues.

Aldén et al. (1994) investigated the influence of gas components on naphthalene decomposition over calcined dolomite. They reported that CO_2 and H_2O enhance the cracking efficiencies, whereas H_2 is a strong inhibitor. They also proposed that the fragmentation of naphthalene, which involves breaking the aromaticity of the molecule, is the rate determining step. The outlet gas contains some light compounds, such as toluene and benzene, and compounds like chrysene ($C_{18}H_{12}$) and binaphthyl. The presence of binaphthyl and chrysene implies that polymerization reactions take place. Jess (1996b) reported that thermal decomposition of naphthalene starts at 1100-1200°C. the complete decomposition of naphthalene occurs at much higher temperature of around 1400°C. In the

presence of a Ni-MgO catalyst, the naphthalene completely converts at a much lower temperature of 750°C (Jess, 1996a). The Ni catalyst reduces the temperature requirement for naphthalene conversion, and changes the product distribution. At a temperature of 800°C, naphthalene is completely converted to CO, CO_2 and H_2 reaching the thermodynamic equilibrium. Jess also reported that H_2O and H_2 only have a slight influence on conversion rates. The activity of this Ni-based catalyst towards benzene conversion is much higher than that for naphthalene. No soot formation was observed in the presence of the catalyst, whereas severe soot formation was observed during thermal treatment of naphthalene (Jess, 1996a; 1996b). The experiments of Garcia and Hüttinger (1989), dealing with non-catalytic steam reforming decomposition of naphthalene, show that addition of H_2 leads to a decrease in the formation of CO and has an inhibiting effect on the steam reforming reaction. Depner and Jess (1999) reported that catalytic conversion of naphthalene and benzene over a Ni-MgO catalyst is not affected by changes in H_2 and steam concentration. Naphthalene decomposition over a nickel activated candle filter was tested by Zhao (2000) with a sulphur-free synthetic biomass gasification gas. At temperatures of above 800°C full conversion of the naphthalene was observed. Zhao also reported high yields of CO and H_2 from naphthalene.

A brief overview of all the investigations using model biomass tar compounds reported in the literature are listed in Table 4.1.

4.3 Experimental

4.3.1 Setup

The experimental setup consisted mainly of a quartz fixed-bed reactor, which was externally heated by a three-zone split-type electrical oven, and a naphthalene saturator. A schematic representation of the experimental setup is given in Fig. 4.1. The inner diameter of the reactor is 33 mm and the length is 600 mm. The reaction zone consists of the catalyst bed, supported by a quartz grid. The catalyst is placed on top of this porous quartz grid. An N-type thermocouple was kept inside a 3 mm quartz thermal-well which was installed in the middle of the catalyst bed to ensure that the reactions occurred at the desired temperatures. The position of the bed was chosen according to the temperature profile over the reactor, which was determined with the oven temperature set to 700-900°C and a gas flow of 625 ml min⁻¹. Temperature readings were taken from 10 cm above the grid to the top of the reactor as shown in Fig. 4.2. The temperature profile in the reactor was uniform and the zone had a length of about 40 cm, thus the experiments could be considered to

Table 4.1: Overview of literature on decomposition of model biomass tar

Model tar	Catalyst	Operating Conditions	Flow rate ml min^{-1}	Tar concentration	Inlet gas composition	Observations
Benzene (Simell et al., 1999)	Dolomite	T_R=750-900°C, P=1 atm, M=0.1-10 g, τ=560-1200 ·kg h m^{-3}	520-2660	40-3400 ppmv	H_2, CO, CO_2, H_2O	H_2 adsorption inhibited reaction rate
Benzene (Simell et al., 1997a)	Dolomite	T_R=550-900°C, M=0.15 g	1000-3000	50-500 ppmv	CO_2, N_2	Conversion < 10%. No carbon formation. Dry reforming is faster than steam reforming.
Toluene (Simell et al., 1997b)	Al_2O_3, Dolomite Ni-Al_2O_3, SiC	T_R=900°C, P=20-50 atm, V=5 cm^3, τ'=0.007-0.13 s	4700	720 ppmv	CH_4, CO, CO_2, H_2, H_2O, N_2, NH_3	For steam reforming, $X_{dolomite,900°C}$ = 75%; $X_{Ni-cat,900°C}$ = 93%
n-Heptane (Taralas, 1996)	Limestone, Dolomite, NiMo/γAl_2O_3	T_R=700-900°C, P=1 atm τ=0.11-0.13 ·kg h m^{-3}	-	2.4-7 kPa	H_2O, CO_2, H_2, N_2	$X_{dolomite,900°C}$ = 87%; $X_{limestone,900°C}$ = 88.4%; $X_{NiMo-Alumina,900°C}$ = 74.7%; Coke formation with Ni based catalyst.
Naphthalene (Abu El-Rub et al., 2002)	Dolomite, Olivine, Ni-based	T_R=900°C, P=1 atm τ'=0.3 s	1167	40 g m^{-3}	CO_2, H_2O, N_2	$X_{dolomite,900°C}$ = 61%; $X_{olivine,900°C}$ = 55%; $X_{Ni-based,900°C}$ = 100%;
Naphthalene (Aldén et al., 1994)	Dolomite	T_R=800-900°C, M=70 g, τ'=0.6 s	n.a.	7.5-8 g	CO_2, H_2, H_2O, N_2	$X_{CO_2,800°C}$ = 96% $X_{H_2O,800°C}$ = 79% $X_{H_2,800°C}$ = 46%

Compound (Reference)	Catalyst	Conditions		Concentration	Product gases	Results
Naphthalene (Zhao et al., 2000)	Ni-activated candle filter	T_R=750-900°C, SV =0.58-1.39 s^{-1}	247-590	5 g m^{-3}	CH$_4$, CO, CO$_2$, H$_2$, N$_2$, H$_2$O	100% conversion at 800°C
Naphthalene Benzene (Depner and Jess, 1999)	Ni-MgO	T_R=450-1150°C, P=15 atm, τ'=0.1 s	2500	0.05-1 vol% 0.1-1.4 vol%	CH$_4$, H$_2$, H$_2$O, H$_2$S, N$_2$, NH$_3$	H$_2$S addition reduces the rate of decomposition
Naphthalene 1-Naphtol Indene (Garcia and Huttinger, 1989)	None	T_R=800-950°C, τ'= 6-60 s	-	1.0 - 2.8 mol%	Ar, H$_2$O	Soot formation is inhibited by H$_2$ addition
Anthracene Benzene Naphthalene Pyrene Toluene (Coll et al., 2001)	UCI G90-C, ICI 46-1 (Ni-based)	T_R=700-875°C, M= 0.5-1 g, τ = 0.0004-0.0247 ·kg h m^{-3}	-	0.075 g min^{-1} 0.67 g min^{-1} 0.076-0.123 g min^{-1} 0.033 g min^{-1} 0.68 g min^{-1}	H$_2$O	$X_{toluene,800°C}$ = 80% $X_{benzene,800°C}$ = 85% $X_{naphthalene,825°C}$ = 40% $X_{anthracene,825°C}$ = 70% $X_{pyrene,825°C}$ = 45%; Larger the aromatic ring, stronger the coke formation
Naphthalene Toluene Benzene (Jess, 1996b)	None	T_R= 700-1400°C, P= 1.6 atm, τ'= 0.3- 2 s	1333	0.25-1 vol% 0.6 vol% 0.3-1.2vol%	H$_2$O, H$_2$, N$_2$	For 95% conversion at 1200°C, τ needed are τ$_{Toluene}$ ~ 0.1 s; τ$_{Benzene}$ ~ 5 s; τ$_{Naphthelene}$ ~ 1 s Severe soot formation
Naphthalene Benzene (Jess, 1996a)	Ni-MgO	T_R=450-950°C, P=1.6 atm, M=32.1 g, τ'= 0.26 s at 700°C	2500	0.2-0.8vol% 0.2-0.23vol%	CH$_4$, H$_2$, H$_2$O, H$_2$S, N$_2$	100% conversion at 750°C. No soot formation observed

T_R = Temperature, P = Pressure, τ' = Residence time, τ = Space time, M= Mass of catalyst, SV=Space velocity, V=volume, X=conversion

be isothermal. Naphthalene feeding was done via a saturator in which the naphthalene was kept. The naphthalene saturator was uniformly heated using an oil bath. Naphthalene vapour was carried to the reactor by an argon flow that was continuously passed through the liquid naphthalene. At the exit of the saturator, the saturated gas was mixed with another argon dilution line via a static mixer and fed to the reactor. To prevent blockage by condensation of naphthalene inside the piping, all lines were traced at a temperature of $250^{\circ}C$. The concentration of naphthalene could be changed by varying the temperature inside the saturator. All the other gases such as CO, CO_2 and H_2 were passed through moisture and oxygen filters and directly fed via the second inlet to the reactor.

All the gas flows were controlled with individual mass flow controllers. H_2O was added using a HPLC-pump and entered the reactor through a heated capillary. The exit gas from the reactor went through the analytical section where online GC and MS were installed. After analysis, the exit gas was passed through a tar-trap to condense out any hydrocarbons present in the gas before purging it to the ventilation. Several experiments were performed to investigate the catalytic activity of olivine. Different pre-treatment methods for olivine were compared via a steam reforming reaction of naphthalene. Dry reforming reactions and the effects of the presence of the gas mixture of H_2O, CO_2, H_2 and CO (referred to as syn-gas medium throughout this thesis) on naphthalene conversion were also investigated. All experiments were performed at atmospheric pressure. Detailed experimental conditions for all the performed experiments are given in Table 4.2.

4.3.2 Sampling and analysis

During the study, online GC and offline SPA (solid phase adsorption) measurement methods were used for sampling and the analysis of tar. The inlet and outlet tar compositions were sampled using the SPA method developed by KTH, Sweden (Brage et al., 1997). The tar samples were analyzed offline using a Varian CP 3800 GC. A Shimadzu GCMS-QP5000 with WCOT fused silica column was used to identify some of the higher hydrocarbons that could not be identified with the GC. Online measurement of the hot exit gas was possible using the Varian CP-3800 GC, this gives the gas composition as well as that of the tars. The three different detectors (2 TCD and 1 FID) in the GC allowed us to analyse all the permanent gasses, 2-4 carbon compounds and higher compounds ranging up to benzo(α)-pyrene. The three different columns were able to separate all the reaction products; Molsieve 13X separated out all the permanent gases; the CP-pora PLOT Q-HT separated out all the light hydrocarbon gases; Fused silica was used to separate out all the heavy hydrocarbons (tars). The results presented in this paper are mean value

of 3 or 4 sample points. The experiments were repeated and found to be reproducible. An error of about 5% was observed for the different sets of experiments.
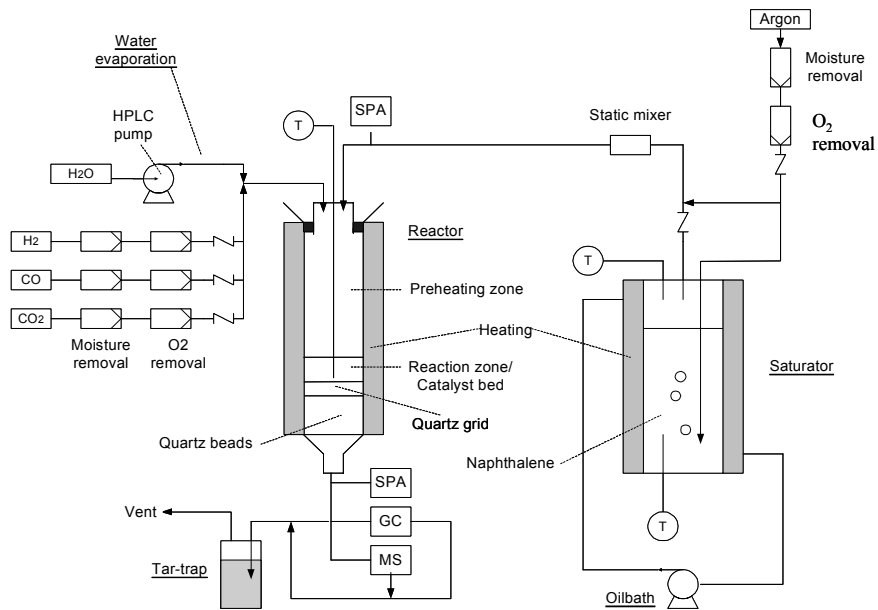

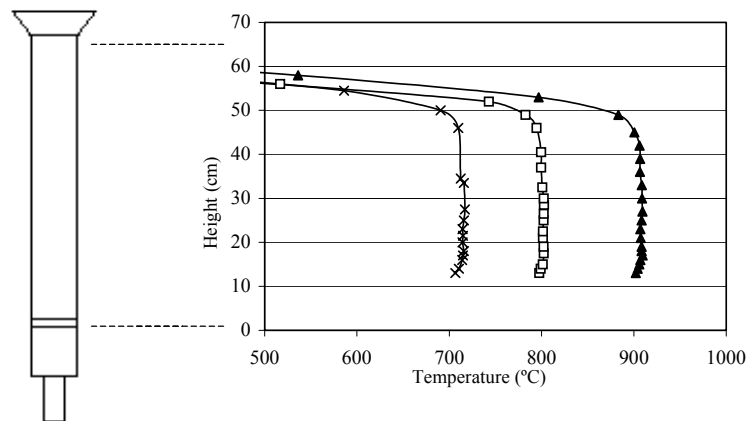Fig. 4.1: Experimental setup for decomposition of model biomass tar

Fig. 4.2: Temperature profile over the reactor

Table 4.2: Experimental conditions

Naphthalene concentration	~ 5 g m^{-3}		
Temperature	750- 900 $^{\circ}$C		
Pressure	Atmospheric		
Bed additives	SiC, Untreated Olivine, Pre-treated Olivine		
Particle size catalysts	212-300 μm		
Residence time	0.3 s		
Space time (at 900°C)	0.147 kg·h m^{-3}		
Pre-treatment method	900 $^{\circ}$C, Air, 1/5/10/20 h treatment time		
Total gas flow rate	625 ml min^{-1} (at STP)		
Gas composition (vol%)	Steam reforming	Dry reforming	Syn-gas
H$_2$O	10	-	10
H$_2$	-	-	10
CO	-	-	12
CO$_2$	-	12	12
Ar	90	88	56

4.3.3 Catalyst investigation

The olivine used for the study came from Norway, the chemical composition is given in Table 3.3. Olivine is a nonporous material which has an extremely low surface area. Olivine has an orthorhombic structure, the detailed physical properties of olivine can be found in the previous chapter. The hardness of olivine makes it attractive as an in-bed additive for fluidized-bed biomass gasifiers. Some researchers (Rapagnà et al., 2000; Orio et al., 1997) state that Fe (III) is responsible for the tar cracking reactions. Since some olivines have quite high percentages of iron, they should be able to remove tar if used as a catalyst. However, preliminary experiments with olivine showed less than 50% conversion of total tar with olivine see in Fig. 3.10. This low conversion rate may be due to the fact that we used only 17 wt% of olivine, the rest of the bed being sand. Pure olivine was used for the experiments described here. Pre-treatment may improve the performance of a catalyst. The pre-treatment method for olivine was chosen based on preliminary experiments and outlined in Table 4.3. First, calcination of olivine was carried out at 900°C for 1 h in an inert medium (Ar). No improvement in naphthalene conversion was observed using olivine pre-treated with Ar with respect to untreated olivine. It is probably feasible to change the oxidation state to Fe$_2$O$_3$ using air.

Significant improvement in naphthalene conversion was observed when olivine was pre-treated with air. Therefore the olivine was pre-treated with air. The temperature for pre-treatment was chosen arbitrarily in the beginning. More experiments were performed with lower pre-treatment temperatures of 700 and 800°C. Naphthalene conversion was observed to increase with increasing pre-treatment temperature. Probably further increases in pre-treatment temperature would improve the performance of air pre-treated olivine, but due to experimental limitation, a maximum of 900°C was all that could be reached during this present experiment. Further investigations with pre-treatment of olivine with air at 900°C were done for different treatment times.

Table 4.3: Selection of pre-treatment method

Catalyst	Pre-treatment	Pre-treatment procedure			Naphthalene
		Temp. (^{o}C)	Medium	Time (h)	Conversion (%)
SiC	No	--	--	--	33
Olivine	No	--	--	--	47
	Yes	900	Ar	1	45
	Yes	700	Air	1	46
	Yes	800	Air	1	51
	Yes	900	Air	1	62

4.4 Results and discussion

4.4.1 Effect of catalyst pre-treatment

The effect of pre-treatment of olivine was investigated using the steam reforming reaction of naphthalene as a model biomass tar. The catalytic activity of olivine is expressed in terms of conversion of naphthalene as given by Eq. 3.7. The effect of pre-treatment is evident from Fig. 4.3, which shows conversion of naphthalene as a function of temperature in a range of 750-900°C. SiC is considered to be an inert material and the corresponding conversion represent the thermal effect. Increased conversion is observed with increasing temperature for all the cases investigated. A lot of soot/carbon formation was observed during the experiments for all cases, especially at 850 and 900°C. Increased pressure inside the reactor was observed due to the formation and deposition of carbonaceous materials on the catalyst bed. The catalytic activity of olivine is directly related to the operating temperature. At 850°C both untreated and pre-treated olivine show a similar conversion of about 45%. When the temperature is raised to 900°C, similar naphthalene conversion is

still observed for untreated olivine, but for air pre-treated olivine, this increase in temperature shows a bigger effect; a conversion of 62% is observed.
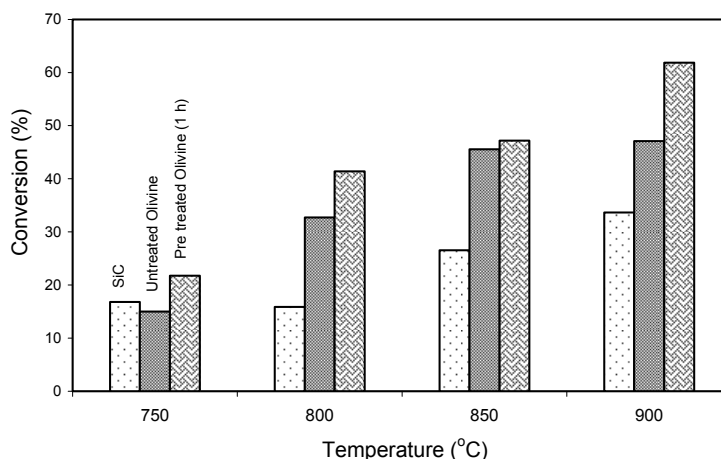

Fig. 4.3: Effect of pre-treatment of olivine on naphthalene conversion. T_R: 750-900°C; τ' :0.3s; v_o: 6.25x10^{-5} m^3 min^{-1}; Gas mixture: H_2O, Ar; T_t: 900°C (in air); t: 1h

Besides the main reactions, naphthalene cracking and steam reforming, see Eqs. 3.1 and 3.2, formation of polymerized products was observed for all the above mentioned cases. The major by-products detected were higher hydrocarbons, higher than naphthalene. Some lower hydrocarbons such as toluene and indene were also detected, but they were in too low concentration to be quantified. Furthermore, 1,2-binaphthalene was the most abundant product formed. Other reaction products were 1,1-binaphthalene, 2,2-binaphthalene, perylene and benzo-j-fluoranthene.

Distribution of these tars with respect to reaction temperature is given in Figs. 4.4-4.6. As the reaction temperature is increased to 850°C, formation of binaphthalenes reaches a maximum; further increase in temperature leads to the formation of perylene and benzo-j-fluoranthene. The amount of these heavy tars is the lowest over pre-treated olivine. It may be that naphthalene most likely dehydrogenates and forms naphthalene radicals. Naphthalene radicals react with naphthalene forming a polymer. This polymerization is also evident from the presence of 1,1-, 1,2- and 2,2-binaphthalene in the exit gas. At temperatures of 850°C and higher, the binaphthalenes start to dehydrogenate. The reaction pathway is terminated by the formation of H_2 from two hydrogen radicals. Kabe et al. (1997) also confirm the formation of perylene from binaphthalene at a temperature of 850°C, further condensation of these products leads to coke formation.

At 900°C, 1 h pre-treated olivine gives a better conversion of naphthalene than other temperatures. Hence the temperature was kept fixed at 900°C for further investigations into pre-treatment of olivine.
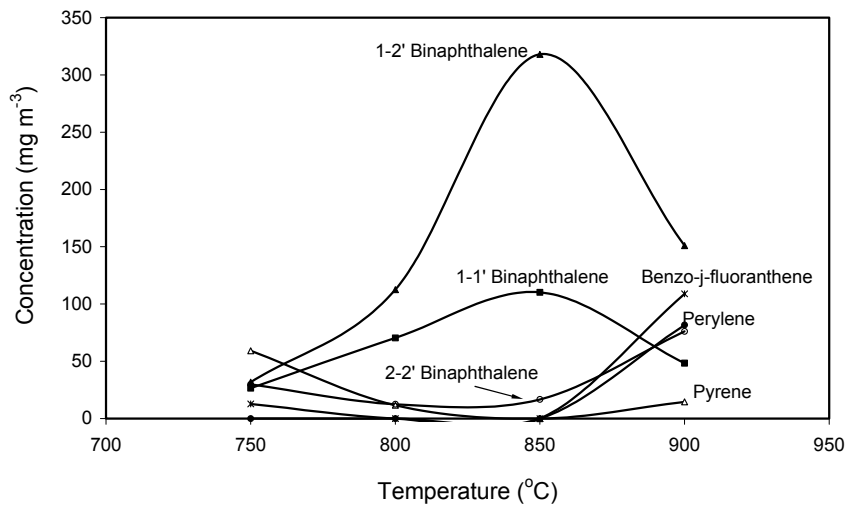

Fig. 4.4: Temperature effect on tar distribution over SiC. T_R: 750-900°C; τ': 0.3 s; v_o: 6.25×10^{-5} m^3 min^{-1}; Gas mixture: H_2O, Ar.
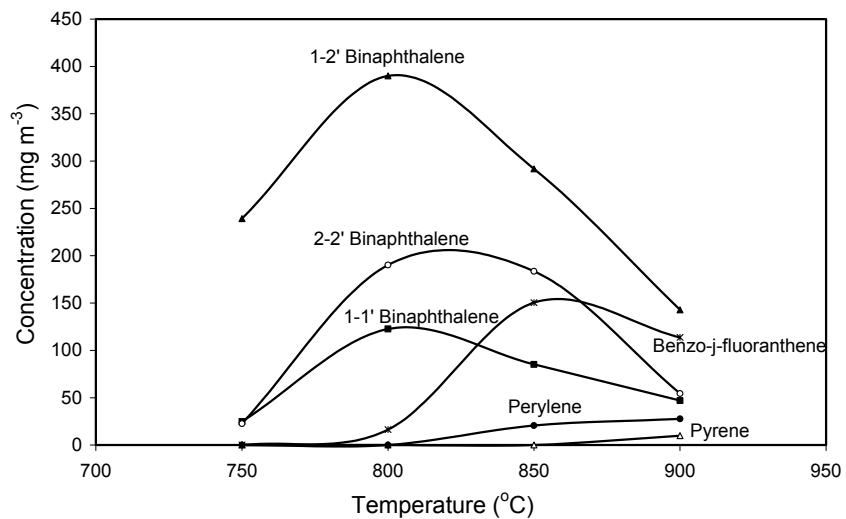

Fig. 4.5: Temperature effect on tar distribution over untreated olivine. T_R: 750-900°C; τ': 0.3 s; v_o: 6.25×10^{-5} m^3 min^{-1}; Gas mixture: H_2O, Ar

The effect of pre-treatment time of olivine was investigated via steam reforming experiments over an olivine catalyst with different pre-treatment times at a fixed temperature of $900^{\circ}C$. It can be clearly seen from the Fig. 4.7 that higher pre-treatment time gives a higher conversion. With a pre-treatment time of 5 h, a naphthalene conversion of around 69% was observed. Increasing the pre-treatment time further upto 10 h showed significant improvement in the catalytic activity of olivine (more than 81%). Further increases in the pre-treatment time upto 20 h did not increase naphthalene conversion (conversion was around 78%). Pre-treatment of 10 h was the optimum for naphthalene conversion in the tested region of calcination times.
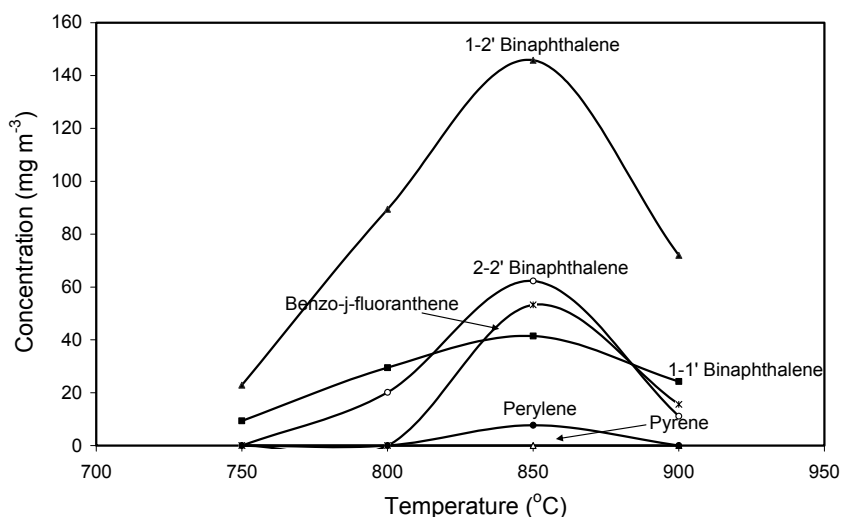
Fig. 4.6: Temperature effect on tar distribution for 1 h pre-treated olivine. T_R: 750-900$^{\circ}C$; τ': 0.3s; v_o: 6.25x10^{-5} m^3 min^{-1}; Gas mixture: H_2O, Ar; T_t: 900$^{\circ}C$ (in air); t: 1h

Activation of olivine occurs due to pre-treatment with air at a high temperature, and its use as a catalyst improves with increasing the treatment times. For 1 h pre-treated olivine, only a few higher tar compounds with significant concentration could be detected, almost no lighter hydrocarbons were formed as shown in Fig 4.6. There were some tars that are detected in GC but could not be identified for all cases, these tars were not taken into consideration. A total of 123 mg m^{-3} of identified tars was formed over 1 h pre-treated naphthalene at 900$^{\circ}C$; whereas a total of 69.0 mg m^{-3} was formed over 10 h pre-treated olivine (Table 4.4).

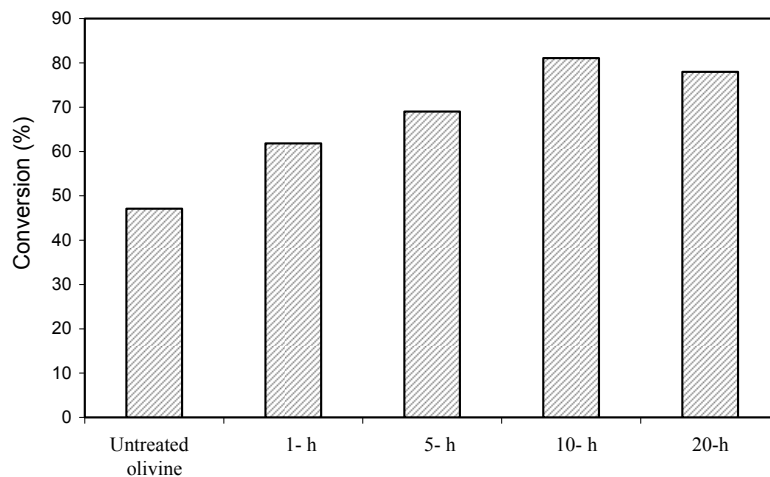Fig. 4.7: Effect of pre-treatment time on naphthalene conversion. T_R: 900°C; τ': 0.3 s; v_o: 6.25x10^{-5} m^3 min^{-1}; τ: 0.147 kg h m^{-3}, Gas mixture: H_2O, Ar; T_t: 900°C (in air); t: 1, 5, 10 and 20 h

4.4.2 Tar decomposition with different gas mixture

Gas composition has a significant effect on naphthalene conversion and on product distribution. Besides steam reforming reactions, dry reforming reactions were also performed in this study to get information on the hydrogen balance. Experiments were also performed in a syn-gas medium to simulate the biomass gasification environment. All these experiments to find the effect of reaction medium were performed over 10 h pre-treated olivine at 900°C. The detailed results of the steam reforming, dry reforming and under syn-gas medium over 10 h pre-treated olivine at 900°C are given in Table 4.4.

During steam reforming, naphthalene is converted mostly into gases, some tar and soot or solid carbon. The distribution of carbon in the exit gas was evaluated to get an idea of the products distribution. All the carbon atoms in the products that were detected by GC were added together; subtracting this from the total carbon input in form of naphthalene gave the unaccounted carbon atoms which were assumed to form higher carbonaceous residue or soot. The distribution of the total carbon in the exit gas is shown in Fig 4.8. It was found that a total of 53.7% of all the naphthalene entered formed gaseous products. Water-gas shift and Boudouard reactions (Eqs. 3.5 and 3.6) also occur. The amount of hydrogen produced was 1.8 vol%, which is much more than the amount of H_2 that enters via naphthalene, and therefore H_2 is produced from H_2O. The formation of methane proved the presence of methanation reactions (Eqs. 4.1 and 4.2) as a minor side reaction.
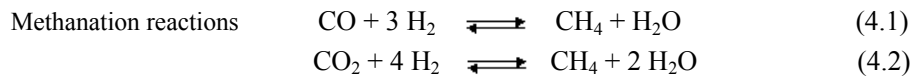
Methanation reactions

$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O \qquad (4.1)$$

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O \qquad (4.2)$$

Table 4.4: Experimental results (effect of reaction medium)

Experimental Conditions	Steam reforming		Dry reforming		Gas mixture	
Inlet Naphthalene (g m^{-3})	6.3		5.0		6.6	
Reactor Temperature	900°C					
Catalyst	10 h pre-treated olivine					
Results						
Conversion (%)	81.1		80.9		75.4	
Product distribution						
Tar (mg m^{-3})						
Class 3	1.03		0		0.44	
Class 4	17.29		50.46		7.74	
Class 5	50.74		32.16		2.23	
Unidentified	44.23		24.87		8.40	
Total Tar (mg m^{-3})	113.30		107.49		18.81	
Benzene (mg m^{-3})	12.40		14.60		19.00	
Gas composition after reaction (vol%)						
CO	0.23		1.20		-	
CO$_2$	0.33		11.69		-	
H$_2$	1.84		0.03		-	
H$_2$O	8.60		0.11		-	
CH$_4$	0.03		0.02		-	
C-balance	Gases	53.70	-		-	
(% total carbon inlet in	Benzene	0.19	-		-	
the form of naphthalene)	Tar	1.63	-		-	
	Soot	25.58	-		-	
			Gases	51.40	-	
H-balance	-		Benzene	0.38	-	
(% total hydrogen inlet)	-		Tar	2.15	-	
	-		Soot	26.97	-	
	-					

Other hydrocarbons were produced in low concentrations giving a total of 1.8% of the total carbon entered. Next to gases, carbonaceous residue/soot was the other main product during steam gasification. Coll et al. (2001) also report coke formation during steam reforming of aromatic compounds. They observed that for naphthalene, at a reaction temperature of 795°C, the rate of reaction for coke formation was higher than that of carbon gasification, thus leading to an accumulation of a layer of carbon on the catalyst bed. The tendency towards coke

formation increases as the molecular weight of the hydrocarbon increase; the larger the number of aromatic rings in a hydrocarbon molecule, the stronger is the tendency to coke formation (Coll et al., 2001).
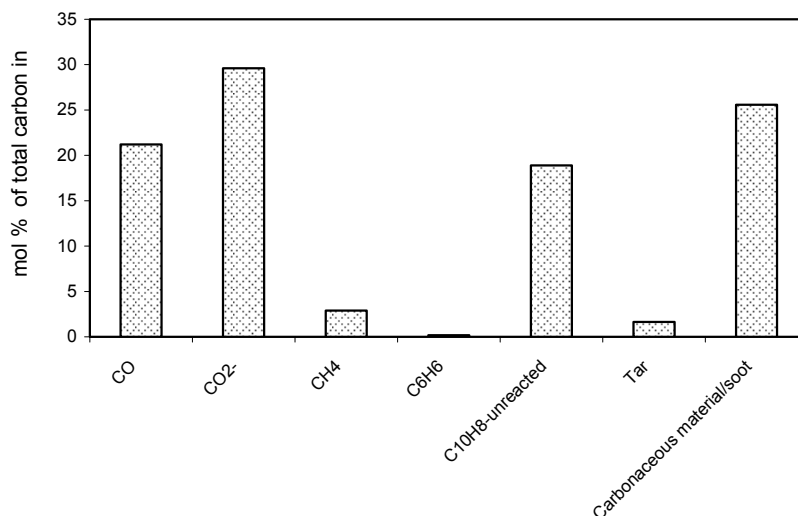

Fig. 4.8: Product distribution for steam reforming reaction: T_R=900°C; τ': 0.3 s;
v_o: 6.25x10^{-5} m^3 min^{-1}; τ: 0.147 kg h m^{-3}, Gas mixture: H_2O, Ar;
T_t: 900°C (in air); t: 10 h

During a dry reforming reaction with CO_2, a naphthalene conversion of about 80% is observed. Decomposition of naphthalene by CO_2 should produce only CO and H_2 according to reaction 3.3. Besides these gases, H_2O and small amount of CH_4 were also detected. A typical gas composition after the dry reforming reaction is given in Table 4.4. A hydrogen balance is set-up as all the hydrogen entered during the dry-reforming process originates from the naphthalene. All the hydrogen atoms in the products that are detected by GC were added, the unaccounted hydrogen atoms were assumed to be present in higher carbonaceous material or soot. The detailed hydrogen balance with respect to the total hydrogen is shown in Fig. 4.9. Out of all the hydrogen atoms present in naphthalene that entered the reactor, 51% present in gases, 2% in other tars, 27% in carbonaceous material or soot, and rest remain in untreated naphthalene. A water-gas shift reaction also occurred. The amount of CO produced as indicated in Table 4.4, was too high to be only the result of the dry reforming of naphthalene. The presence of water as a reaction product also proves the occurrence of a water gas shift reaction. Methanation occurred to a low extent comparable with steam-reforming conditions.

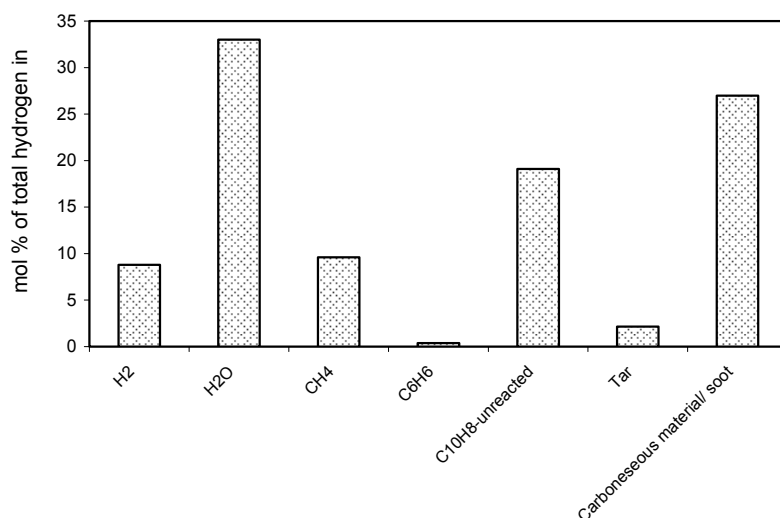Severe carbonaceous residue/soot formation was observed in the case of steam and dry reforming reactions.

Fig. 4.9: Product distribution for dry reforming reaction. T_R 900°C; τ : 0.3 s; v_o : 6.25x10^{-5} m^3 min^{-1}; τ: 0.147 kg h m^{-3}, Gas mixture: CO_2, Ar; T_t: 900°C (in air); t: 10 h.

Under a syn-gas environment with a gas composition as indicated in Table 4.2, naphthalene conversion was observed to be 75.4%, which was lower than that of the steam/dry-reforming conditions. This may be due to the presence of H_2 and CO, which are proven inhibitors during the reforming of tars (Jess, 1996a; Simell et al., 1997b; Zhao et al., 2000). The volume percentages of the different gas components were sufficiently in excess with respect to added naphthalene, the change in the outlet gas composition was insignificant and hence can not be detected by the GC. The total volume of the gas remained almost the same. A total of 18.8 mg m^{-3} of tars was produced from naphthalene which is considerably lower compared to the cases of steam and dry reforming reactions. The formation of carbonaceous residue/soot could not be quantified as the evaluation of mass balance was difficult due to there being little change in the outlet gas composition. However, after the experiments with mixed gases, a much lower amount of carbonaceous material/soot could be seen on the reactor wall and on the catalyst bed indicating lower carbon formation. The reason for low carbon formation may be due to the presence of H_2 in the gas mixture. Jess (1996b) reported that increasing the amount of H_2, decreased the yield of soot significantly during non-catalytic treatment of naphthalene with steam. Another reason for low carbon formation

might be the presence of H_2O and CO_2, the rate of the Boudouard reaction (Eq. 3.6) is much faster in the forward direction.

The tar distribution is slightly different for the above mentioned three different gaseous environments. Figs. 4.10, 4.11 and 4.12 show the detailed tar distribution of naphthalene decomposition with steam, CO_2 and syn-gas mixture respectively. The steam reforming reaction produced the highest amount of higher tars. The formation of benzene is highest for gas mixture as shown in Table 4.4. The amount of 1,2-binaphthalene is higher for steam and dry reforming reactions. The dry reforming reaction produces the highest amount of phenanthene. The produced tar can be put together in different tar classes as indicated in Table 4.4. Some of the detected hydrocarbons could not be identified and they have been put together in one class as unidentified tar. No class 2 (phenolic) tars were identified. During steam/dry reforming high amounts of the class 5 tars were identified, especially 1,1 binaphthalene and 1,2 binaphthalene. During dry-reforming conditions there seemed to be a high amount of class 4 tars, especially acenaphthalene, phenanthrene and anthracene. Tar decomposition occurs due to destabilization of the hydrocarbon, which leads to fragmentation of the molecule by breakage of C-C or/and C-H bonds. These fragments undergo different reactions forming gaseous products, other tars and soot.
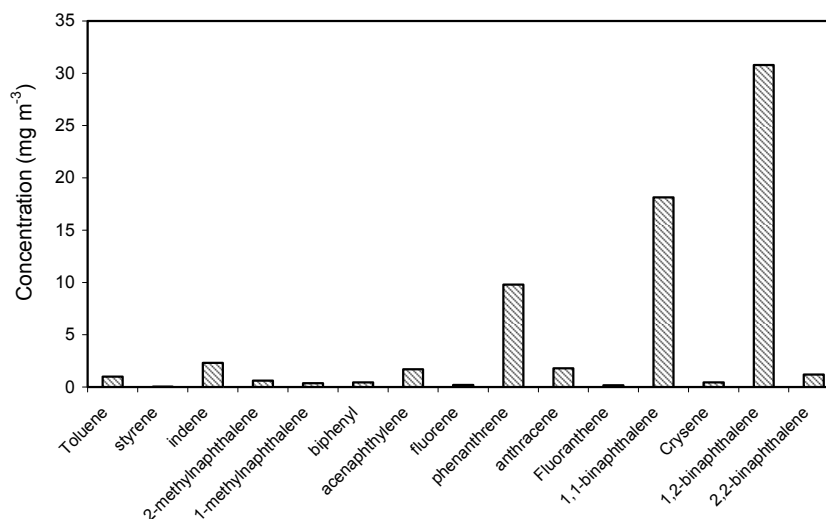

Fig. 4.10: Tar distribution for steam reforming reaction over 10 h pre-treated olivine. T_R:900°C; τ: 0.3 s; τ: 0.147 kg h m^{-3}; v_o: 6.25x10^{-5} m^3 min^{-1}; Gas mixture: H_2O, Ar; T_t: 900°C (in air); t: 10 h.
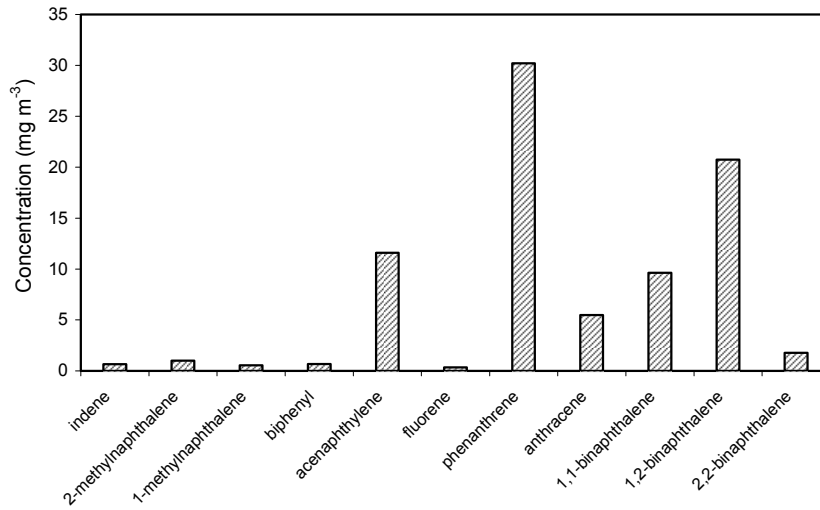
Fig. 4.11: Tar distribution for dry reforming reaction over 10 h pre-treated olivine.
T_R: 900°C; τ': 0.3 s; τ: 0.147 kg·h m^{-3}; v_o: 6.25x10^{-5} m^3 min^{-1};
Gas mixture: CO_2, Ar; T_t: 900°C (in air); t: 10 h.
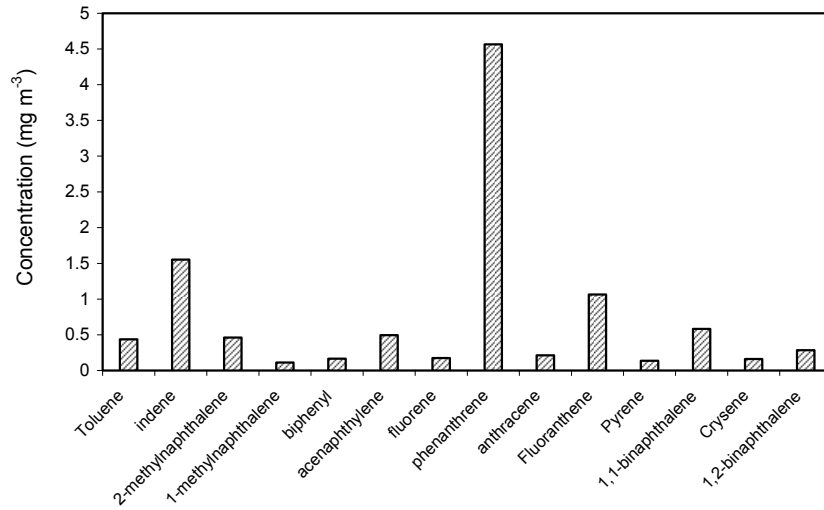
Fig. 4.12: Tar distribution for gasification gas mixture over 10 h pre-treated olivine.
T_R: 900°C; τ': 0.3 s; v_o: 6.25x10^{-5} m^3 min^{-1}; τ: 0.147 kg·h m^{-3}; Gas mixture:
H_2O, CO_2, CO, H_2, Ar; T_t: 900°C (in air); t: 10 h.
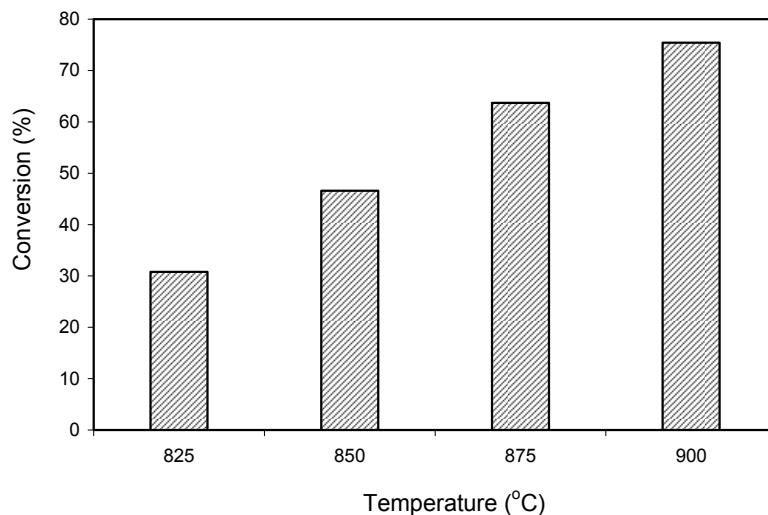
Fig. 4.13: Temperature effect on naphthalene conversion with 10 h pre-treated olivine.
T_R: 825-900°C; τ: 0.3 s; v_o : 6.25x10^{-5} m^3 min^{-1}; Gas mixture: H_2O, CO_2, CO, H_2, Ar; T_t: 900°C (in air); t: 10 h.
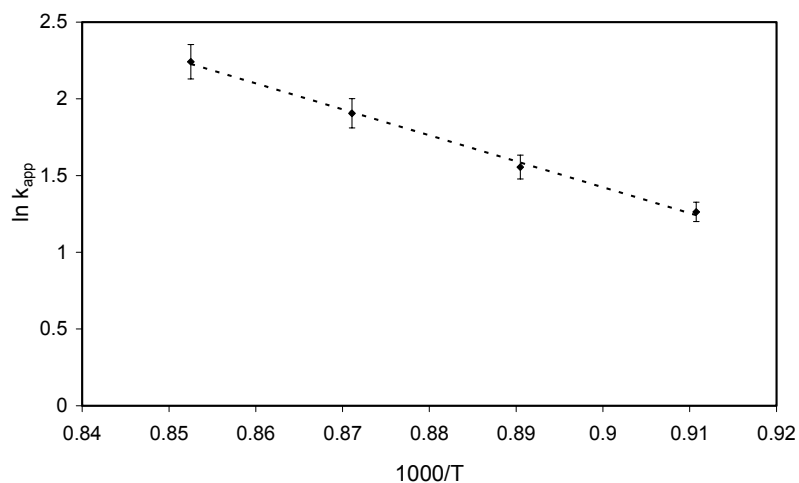
Fig. 4.14: Arrhenius plot for calculation of apparent activation energy. T_R: 825-900°C;
τ' : 0.3 s; v_o : 6.25x10^{-5} m^3 min^{-1}; Gas mixture: H_2O, CO_2, CO, H_2, Ar
Catalyst: Olivine; T_t: 900°C (in air); t: 10 h.

4.4.3 Apparent activation energy

The apparent rate constant and the apparent activation energy for naphthalene
decomposition over 10 h pre-treated olivine under syn-gas mixture was calculated

assuming a first order reaction with respect to naphthalene. To find the activation energy, experiments were performed in a temperature range of 825-900°C with gas composition as shown in Table 4.2. The inlet concentration of naphthalene was kept at around 6.5 g m^{-3}. The temperature effect on naphthalene conversion is shown in Fig. 4.13. Naphthalene conversion was observed to increase with increasing temperature. The apparent activation energy for naphthalene conversion over 10 h air pre-treated olivine calculated from Fig. 4.14 is 141 kJ mol^{-1} with frequency factor of 1.7 x 10^7 m^3 kg^{-1} h^{-1}. Activation energy for thermal conversion of naphthalene with H_2O and H_2 is reported to be much higher, around 350 kJ mol^{-1} (Jess, 1996b).

4.5 Concluding remarks

Pre-treatment of olivine with air at 900°C improves the catalytic activity of olivine. Naphthalene conversion increases with increasing pre-treatment time. Naphthalene conversion of higher than 80% is observed with 10 h of pre-treatment, which is a significant improvement with respect to untreated olivine. Steam and dry reforming reactions of naphthalene mainly produce gaseous products such as H_2 and CO. Besides the gaseous products, cracking reactions lead to the formation of other hydrocarbons with a lower carbon number than naphthalene. Hydrocarbons with a higher carbon number than naphthalene are formed via polymerization reactions. Further condensation of these higher hydrocarbons leads to soot formation. Equilibrium gas phase reactions, such as water gas shifts, Boudouard and methanation reactions also take place. Naphthalene conversion under a syn-gas mixture is lower than that of steam and dry reforming. This decrease in conversion is due to the fact that H_2 and CO are reported to be inhibitors for dry and steam reforming reactions of tar. An apparent activation energy of 141 kJ mol^{-1} was calculated for 10 h pre-treated olivine under a gasification-gas medium.

In conclusion, air pre-treated olivine shows catalytic activity for tar reduction and thus may be a prospective candidate as a in-bed catalyst in the gasification of biomass. The influence on the material properties of the catalyst during pre-treatment should be investigated further. Different catalyst characterization techniques should reveal the main cause of improvement in the catalytic activity of olivine due to pre-treatment.

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Chapter 5 [*]

Olivine as a tar removal catalyst for biomass gasifiers: catalyst characterization

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Catalyst characterization tests carried out to determine the characteristics of olivine pre-treated with air for different pre-treatment times are described in this chapter. Techniques such as BET surface area analysis, XPS, Mössbauer spectroscopy, TPR, SEM/EDX analysis were used to analyse the basic phenomena of the pre-treatment of olivine. BET surface area analysis showed olivine to be a non-porous material. SEM/EDX and XPS analysis showed severe non- uniform segregation of iron at the catalyst surface after pre-treatment. Mössbauer spectroscopy revealed the appearance of iron III phase in the olivine after pre-treatment. Pre-treated olivine, in conjunction with its catalytic activity to promote tar removal, was also observed to highly attrition resistant thus making it an attractive option as in-bed additive for biomass gasifiers.

5.1 Introduction

The effect of pre-treatment of olivine on tar removal was described in the previous chapter. It was observed that the pre-treatment of olivine improves the activity of the catalyst considerably. Pre-treatment of olivine was done with air at 900°C for different treatment times. An improvement in tar conversion of around 30% was observed with 1 h pre-treated olivine, compared to untreated olivine. Increasing the pre-treatment time for olivine causes tar conversion to increase; more than 80% naphthalene conversion was observed over 10 h pre-treated olivine.

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[*] This chapter has been submitted for publication to Applied Catalysis. A: General, 2004

Further investigations for the causes of the improved activity of the olivine catalyst after pre-treatment are described in this chapter. It has been reported in the literature (Courson et al., 2002; Orio et al., 1997) that Fe (III) is responsible for the tar cracking reactions. Since olivine has a high percentage of Fe in its matrix, its activity might be due to the presence of Fe. In olivine, the Fe is embedded in Si and Mg and pre-treatment with air at higher temperature may change the oxidation state of the Fe. Experiments are performed with both untreated and pre-treated olivine to study the effect of pre-treatment on olivine. The study included Brunauer-Emmett-Teller (BET) analysis, X-ray photoelectron spectroscopy (XPS), mössbauer spectroscopy, temperature programmed reduction (TPR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. Besides being catalytically active for tar reduction, a catalyst also needs to be attrition resistant to be used as an in-bed additive for biomass gasifiers. Therefore, the attrition resistance of olivine was measured using a repeated impact tester (RIT) and a standard fluidized-bed attrition tester.

5.2 Experimental: catalyst characterization techniques

The BET-surface of untreated olivine and 1 h pre-treated olivine was determined using N_2 chemisorption on Micromeretics ASAP-2000 equipment.

XPS measurements were done in a VG-Escalab 200 spectrometer using an aluminium anode (Al-Kα = 1486.3 eV) operating at 510 W with a background pressure of 2 X 10^{-9} mbar. XPS is based on the photoelectric effect; the kinetic energy of the emitted photoelectron is used to calculate the binding energy of the photoelectron, which is characteristic of an element (Niemantsverdriet, 2000). The surface of the sample was excited by Al-Kα X-rays and the photoelectrons coming from the first 3-10 nm of the sample were detected.

SEM combined with EDX analysis was performed on an FEI XL 30 ESEM-FEG. SEM is a technique that is used to give information about the composition and internal structure of the particles.

The Mössbauer spectra for all the olivine samples were recorded on a constant acceleration spectrometer using a triangular velocity profile. The isomer shifts were reported relative to the NBS standard sodium nitro prusside (SNP), hyperfine fields were calibrated using the 330 kOe field of α-Fe at 300 K. A 57 Co in Rh source was used for the experiments. The spectra were folded to remove the parabolic background. The spectra were then fitted using sub-spectra consisting of Lorentzian shaped lines using a non-linear minimization routine.

TPR was performed for untreated, 5 h pre-treated, 10 h pre-treated and 20 h pre-treated olivine samples weighing 500 mg. The temperature was increased at a rate of 20°C min^{-1} from 25°C to 800°C, where it was kept isothermal. Further increase in temperature was not possible due to experimental limitations.

Two techniques were employed to evaluate the attrition resistance of olivine; repeated impact testing to determine the strength of the catalyst and fluidized-bed testing which incorporates inter particle interactions as well. The impact testing for olivine was carried out in a newly developed equipment Repeated Impact Tester (RIT) at the Delft University of Technology (Pitchumani, 2003). The main feature of this equipment is the possibility of generating controlled and well-defined collisions of particles with a target, thus allowing the study of the mechanical behaviour of particles after many controlled impacts. Untreated olivine and 10 h pre-treated olivine samples of size fraction 500-700 μm, weighing between 70 mg and 80 mg were kept in the particle chamber. The initial weight of the sample was measured accurately with a laboratory scale balance. The samples were subjected to impacts for residence time varied on a logarithmic time scale to ensure that conditions were well defined at relatively low and extremely large numbers of particle-wall collisions. After each time period, the sample was taken out and the small particles produced due to damage were separated by sieving through a mesh size of 270 μm. If w_o is the initial mass of the sample of particles and after each time period i, the mass of the residue is w_i, then the fraction undamaged is defined as w_i/w_o.
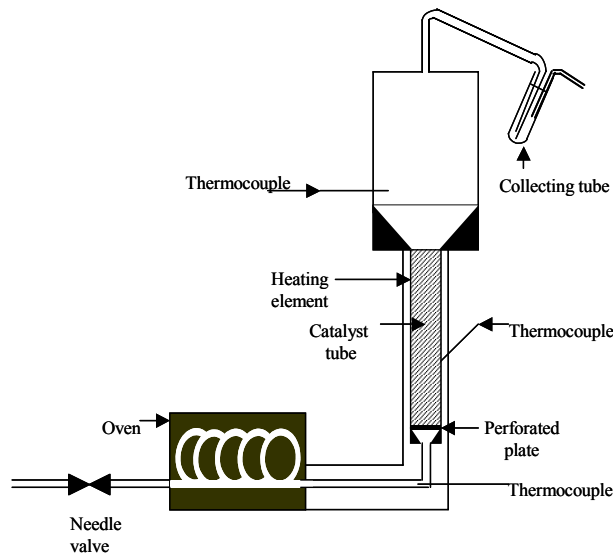

Fig.5.1: Fluidized-bed attrition tester

Relative attrition resistance of olivine was measured with respect to that of sand and dolomite. A standard ASTM D5757-00 fluidized-bed attrition tester based on the design of Gwyn (1969), shown in Fig. 5.1, was used for this purpose.

This method involves passing a high flow rate of air through the perforated plate just below the bed. Through these holes air is passed at high rates, producing attrition of the particles in the fluidized-bed above the plate. Smaller particles that are produced from the parent particles, either they are taken to the freeboard and falls back to the fluidized-bed, or are carried over and collected in the collecting bottle. The test was carried out using 50 g of the additive at room temperature. Air with a flow rate of 26 l min^{-1} was passed through the perforated plate at the bottom of the tester.

5.3 Results

The pre-treatment of olivine as described earlier improves its catalytic activity and changes the olivine. Visually the typical pale green colour of olivine disappears after pre-treatment and it becomes brown-reddish as shown in Fig. 5.2, which shows microscopic photographs of untreated and pre-treated olivine taken using a Axio vision optical microscope. With increasing pre-treatment time, the colour darkens further.

5.3.1 BET surface area

The BET-surface area for untreated olivine was determined to be 0.43 m^2 g^{-1}, which is extremely low, with pore diameters in the range of 3-4 nm. This analysis is repeated for 1 h-pre-treated olivine to see if there has been some enhancement in the surface area of olivine due to pre-treatment. A BET-surface area of 0.18 m^2 g^{-1} for 1 h pre-treated olivine was observed. The extremely low pore size and BET-surface area indicate that olivine is a non-porous material.

5.3.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was done for all pre-treated olivine samples to gather information about the surface of the different pre-treated olivine catalysts. The spectrum shows the intensity of the photoelectrons versus the binding energy of the electron. The intensity of the peaks is a measure of the surface concentration, whereas the binding energy depends on the chemical state. The wide scans of olivine are shown in Fig. 5.3 (a) and two binding energy regions are highlighted in Fig. 5.3 (b). Peaks of the other trace elements such as Al, Ni, Cr were not detected, which means that these components are not present at the surface. It is evident from Fig. 5.3 (b) that Fe-2p and Fe-3p peaks appeared for all pre-treated olivine samples, whereas these two iron peaks are not noticeable for untreated
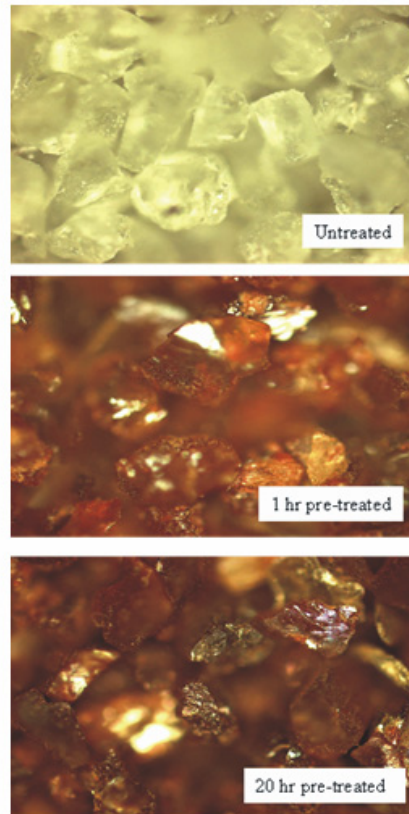
Fig.5.2: Microscopic photographs of untreated and pre-treated olivine

olivine. This indicates that after pre-treatment, segregation of iron occurs at the surface of olivine. The peaks at the binding energies of Fe-2p (710 eV) and Fe-3p (56 eV) were very intense for all the pre-treated olivine samples. No shifts were observed. For a good comparison of the data, the intensities of the peaks were normalized to the total oxygen peak area for all samples. Fig. 5.4 shows the quantitative analysis of the atomic concentration of the major elements at the surface with respect to different pre-treatment times. It immediately reveals a significant difference between pre-treated and untreated olivine. The concentration of the major elements at the surface changes with different treatment times. During the first hour of pre-treatment, segregation of Fe occurs at the surface; further increasing the pre-treatment time upto 10 h does not significantly increase the amount of Fe at the surface.

Further increasing the pre-treatment time to 20 hours showed a slight decrease in the iron content at the surface. The concentration of the Mg-2p peak significantly decreased for the 1 and 5 h pre-treatment; with a further increase in treatment times to 10 and 20 h, the Mg-2p peak started to increase slightly. For all pre-treated samples, the concentration of Mg was lower than that found in untreated olivine. With the Si-2p peak, at first an increment and then a decrement was observed as the pre-treatment time was increased.
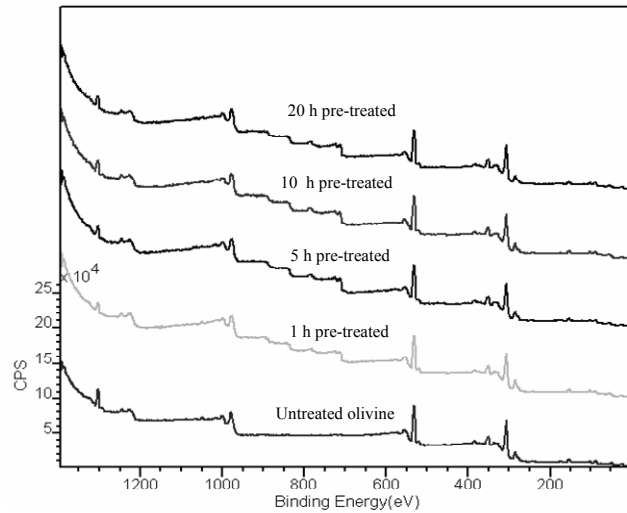

Fig. 5.3(a): Wide scan XPS spectra for untreated and pre-treated olivine with different pre-treatment times
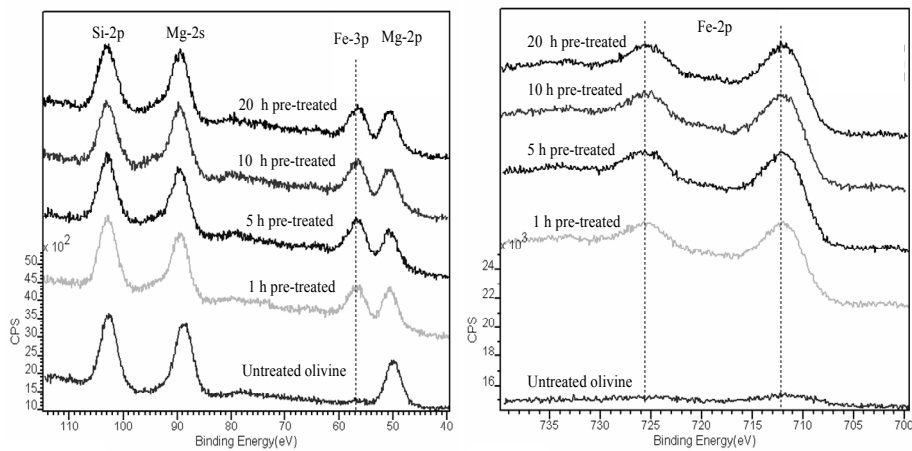

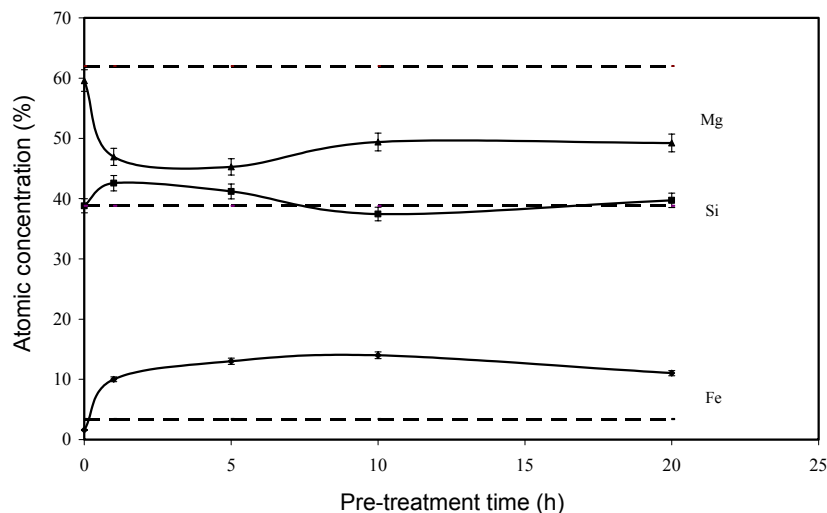Fig. 5.3(b): XPS spectra for two binding energy regions

Fig. 5.4: Quantitative analysis of surface concentration by XPS (Dashed lines represent the atomic concentration for untreated olivine)

5.3.3 Scanning electron microscopy/ Energy dispersive X-ray analysis

Figs. 5.5 (a)–(c) show the SEM scans for all the different olivine samples with different treatment times. All the SEM-scans show bright and dark spots. The contrast is caused by the orientation, parts of the surface facing the detector appear to be brighter than the parts of the surface with their surface normal to the detector. It was observed that the surfaces of all the olivine samples were highly non-uniform. Elemental analysis of these phases was performed to determine the composition at the different spots. The elemental compositions of few randomly selected spots are shown in Figs. 5.5 (a)-(c). It can be seen that the composition is different for each of the spots and the elements present in olivine are not uniformly distributed throughout the samples. It is evident that with increasing treatment times, segregation of iron is taking place, but non-uniformly. Due to the heterogeneous nature of the samples, it is not possible to indicate exactly the percentage of the elements present at the surface. At some spots charging of the sample occurred, whereas for few spots no severe charging was observed. The sample surface was also not smooth, so the scans were not very accurate. Nevertheless, the analysis still gives an indication of the presence and amount of each element, and gives a better comparison for treated and untreated olivine.

EDX (wt %)
Fe   5.25
Mg 30.27
Si   26.04
O   38.43

EDX (wt %)
Fe   8.49
Mg 34.88
Si   24.52
O   32.12

EDX (wt %)
Fe 10.40
Mg 31.90
Si   20.45
O   37.24

Acc.V Spot Magn Det WD Exp   20 µm
10.0 kV 3.0 1400x SE 10.1 1   Untreated Olivine
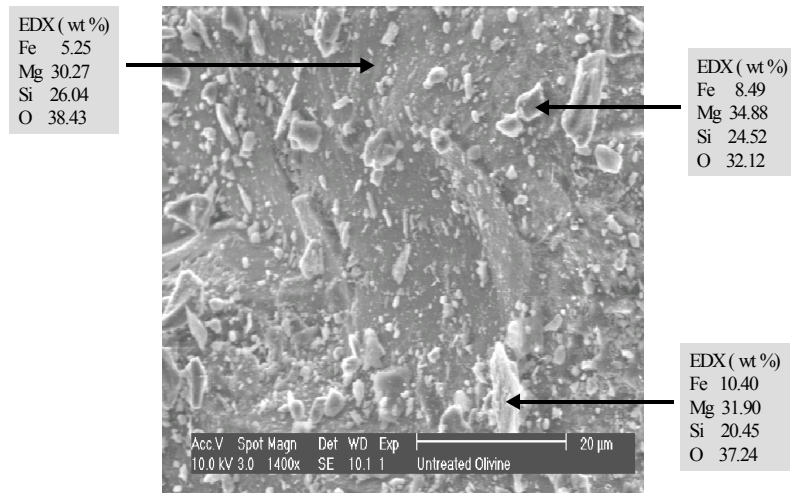
Fig. 5.5(a): SEM/EDX analysis for untreated olivine

EDX (wt %)
Fe   7.19
Mg 31.78
Si   26.47
O   34.56

EDX (wt %)
Fe   12.68
Mg 32.07
Si   19.30
O   36.00

EDX (wt %)
Fe   13.11
Mg 31.00
Si   19.19
O   36.70

EDX (wt %)
Fe   8.65
Mg 30.11
Si   23.06
O   38.19

Acc.V Spot Magn Det WD Exp   20 µm
15.0 kV 3.0 1400x SE 10.0 1   1 hr treated olivine
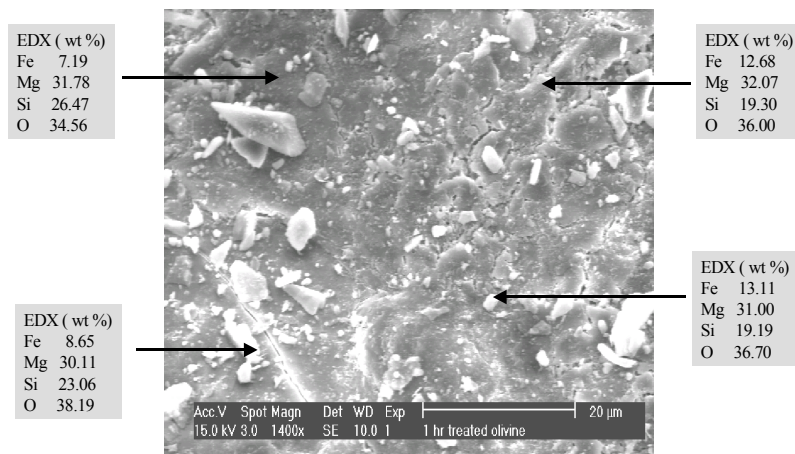
Fig. 5.5(b): SEM/EDX analysis for 1 h pre-treated olivine

EDX (wt %)
Fe   8.44
Mg 29.43
Si   20.53
O   35.82
Al   5.78

EDX (wt %)
Fe   30.30
Mg 27.62
Si   12.90
O   29.17

EDX (wt %)
Fe   34.01
Mg 29.14
Si   8.94
O   27.90

EDX (wt %)
Fe   24.58
Mg 30.83
Si   15.36
O   29.23

Acc.V Spot Magn   Det WD Exp ├──────┤ 20 µm
6.00 kV 3.0 700x   SE   10.0 1   10 hr treated olivine

Fig. 5.5(c): SEM/EDX analysis for 10 h pre-treated olivine

5.3.4 Mössbauer spectroscopy

Mössbauer spectroscopy was performed on the olivine samples to determine the oxidation state of Fe present. The Mössbauer spectra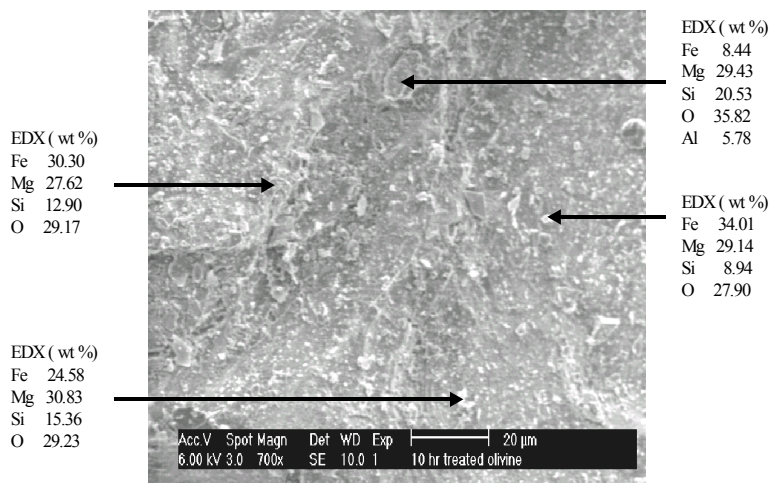 were recorded on a constant acceleration spectrometer using a triangular velocity profile and are shown in Fig. 5.6. The detailed results of the Mössbauer spectroscopy for all the 5 olivine samples are presented in Table 5.1. The accuracy for the isomer shift (IS) is +/- 0.03 mm s^{-1}, for the electric quadruple splitting +/- 0.05 mm s^{-1}, for the magnetic hyperfine field +/- 5 kOe and for the spectral contribution +/- 5%. The fresh olivine sample only contained olivine, characterized by a doublet with IS = 1.40 mm s^{-1} and QS = 3.00 mm s^{-1}. The spectrum after 1 h pre-treated showed a small contribution of a sextuplet. The IS indicates that it is a Fe^{3+} species and the small H_{eff} and large linewidth show that this phase is poorly crystalline. Furthermore, a contribution of a doublet with IS = 0.69 mm s^{-1} was seen. This doublet should also be assigned to an oxidic species, but one that is very highly dispersed (super paramagnetic). After the pre-treatment for 5 h, the sextuplet contribution was more pronounced. It could be fitted with two sub spectra. One sub spectrum with an H_{eff} of 506 kOe, which is only a little smaller than the value of 515 kOe for bulk α-Fe_2O_3. Small particles of crystalline hematite were formed. Furthermore, a sextuplet with the smaller Heff and large line width as well as a doublet of super paramagnetic iron (III) oxide was observed. The trend observed above proceeded during treatment for 10h. Sextuplet one can most probably be assigned to hematite (α-Fe_2O_3). For bulk hematite, the

hyperfine field should be 515 kOe (= 51.5 T) at 300 K. However, a slightly smaller value was found in the present study. The decrease of the hyperfine field might be caused either by the particle size i.e., for small particles in the nanometre range a decrease of the hyperfine field was observed or by non-magnetic impurities in the hematite lattice. The latter explanation might be valid in this case. High amounts of Mg are present in the olivine and it is highly probable that this Mg is incorporated in the hematite lattice. For Fe atoms with a Mg atom in their first coordination shell, a sextuplet with the small hyperfine field (sextuplet 2, H_{eff} = 460 kOe) was found. For the other Fe atoms (sextuplet 1) the slight decrease of the net magnetic field may be caused by the Mg atoms in their second and/or third coordination shells.
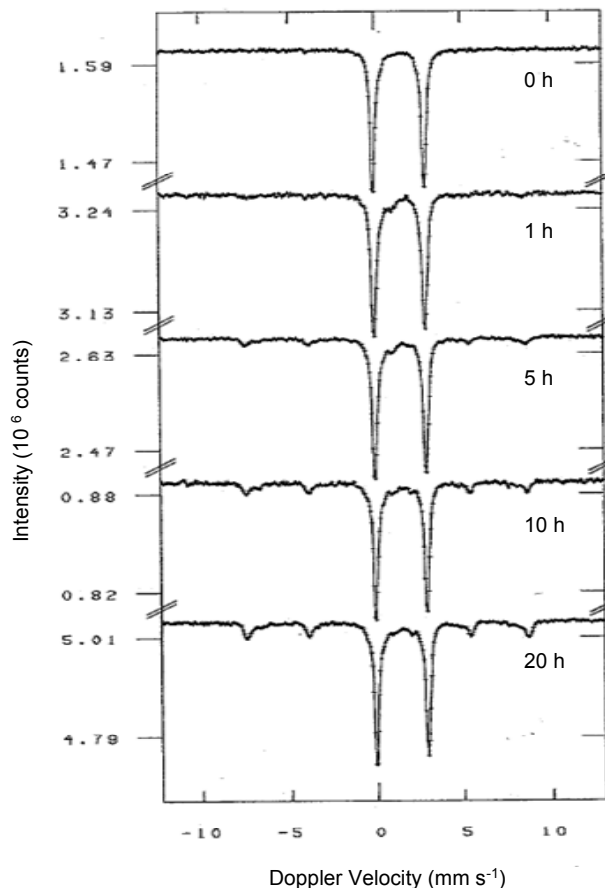

Fig. 5.6: Mössbauer spectroscopy for olivine with different pre-treatment time

5.3.5 Temperature programmed reduction

The olivines investigated here are intended for use as a catalytic bed material in fluidized-bed biomass gasifiers and hence it is important to understand their

behaviour in a reducing environment. The reduction profiles for all these olivine samples are shown in Fig. 5.7. Untreated olivine was not at all reducible due to the absence of reducible Fe present at the surface. In all the pre-treated olivine samples, a reduction peak was observed between 606°C and 621°C with a small shoulder at 800°C where the samples were kept isothermal. The broad peak can be associated with the reduction of iron oxide (α-Fe$_2$O$_3$) present at the olivine surface.

The intensity of this reduction peak increased with the increase in pre-treatment time, with a highest intensity for 20 h pre-treated olivine. A small shift in reduction temperature was observed for different pre-treated olivine samples; 606°C for 5 h pre-treated, 615°C for 10 h pre-treated and 621°C for 20 h pre-treated olivine. This shift may be due to the change in Fe phase and the presence of a different Fe phase at the outer surface. The small shoulder observed at 800°C can be attributed to the reduction of various iron oxides present inside the olivine structure. A similar TPR trend was also observed by Courson et al. (2002) for different olivine samples calcined at different temperatures.
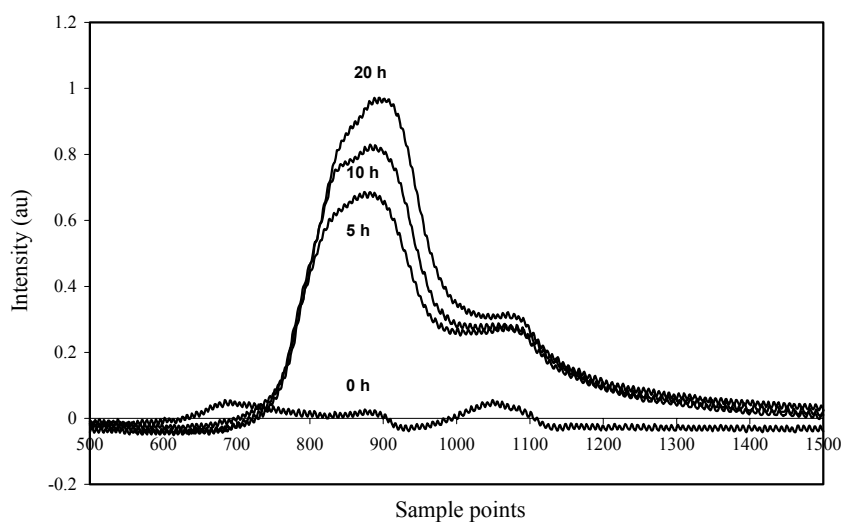

Fig. 5.7: TPR profile for olivine of different pre-treatment times

Table 5.1: Mössbauer spectroscopy results

Olivine (treatment time, h)	Sextuplet 1					Sextuplet 2					Doublet 1				Doublet 2			
	IS	QS	Γ	H_{eff}	SC	IS	QS	Γ	H_{eff}	SC	IS	QS	Γ	SC	IS	QS	Γ	SC
0											1.41	2.99	0.33	100				
1	0.55	0.00	0.79	492.3	7.0						1.40	2.97	0.36	85.0	0.69	0.61	0.48	8.0
5	0.63	0.10	0.45	505.7	8.8	0.60	0.00	1.03	465.3	8.1	1.40	2.98	0.33	76.1	0.69	0.63	0.47	6.9
10	0.62	0.09	0.37	507.5	14.1	0.51	0.00	0.82	463.0	11.1	1.40	2.97	0.30	69.2	0.69	0.63	0.49	5.6
20	0.64	0.08	0.39	506.8	19.7	0.59	0.00	0.91	459.5	11.5	1.41	3.00	0.30	61.1	0.69	0.64	0.54	6.7

IS: Isomer shift, mm s^{-1}; QS: Quadruple splitting, mm s^{-1}; H_{eff}: Hyperfine field, kOe; Γ : mm s^{-1}; SC: Spectral Contribution,

5.3.6 Attrition resistance

Attrition can be described as the extent to which particles are eroded by the influence of collisions between the catalyst particles and with the reactor wall. The produced particle pieces then are carried by the gas flow, this is called elutriation. Due to attrition catalysts are lost during usage in a fluidized-bed reactor, which makes it necessary continuously to add new catalyst material. Problems can also arise due to carry over of small catalyst particles with the cleaned synthesis gas, which makes it more difficult to clean the gas for downstream applications. The major problem with dolomite, the most well known catalyst for tar removal, is its softness and hence this catalyst is not attractive as an in-bed additive for biomass gasifiers. Attrition is defined as the unwanted breakdown of particles within a process. This includes both abrasion and fragmentation, provided these are unwanted (British Standards, 1958).

The Repeated Impact Tester (RIT) is a simple technique for characterizing the impact strength of a particle. The device consists of a particle chamber in which the granules are subjected to many impacts by the unidirectional movement at a predetermined frequency and amplitude. As seen from Fig. 5.8, pre-treatment doses not change the mechanical strength of olivine. Majority of the particles remain undamaged even after severe impact of 10,000 collisions/sec; only around 15% of the particles were lost from the parent particles after 48,000 collisions s^{-1}.
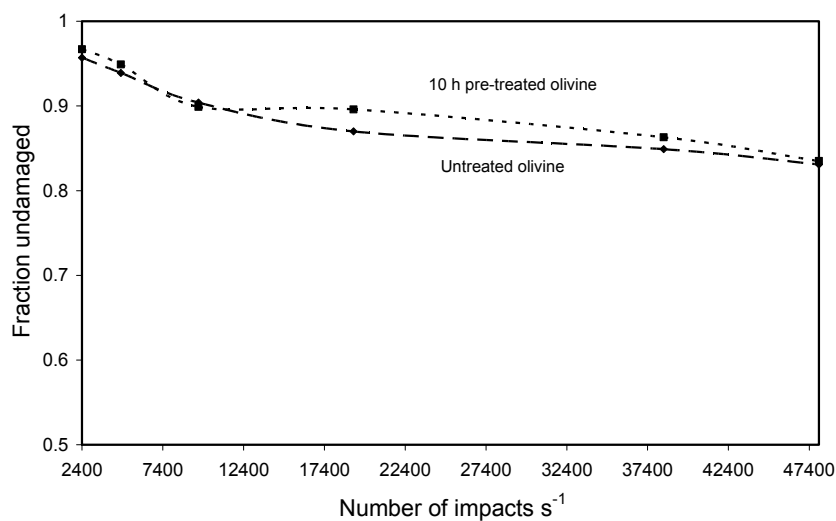

Fig. 5.8: Repeated Impact Analysis for untreated and 10 h pre-treated olivine

The relative attrition resistance of olivine was measured with respect to that of sand and dolomite. In this method, one way to express the attrition resistance of the catalyst, is to determine the elutriation graph of the catalyst. In this graph the amount of elutriated particles is given as a function of the attrition time. The size fraction of the catalyst is very important in attrition tests, the minimal fluidization velocity is directly dependent on the size of the particles, and higher sized particles have a higher minimal fluidization velocity.
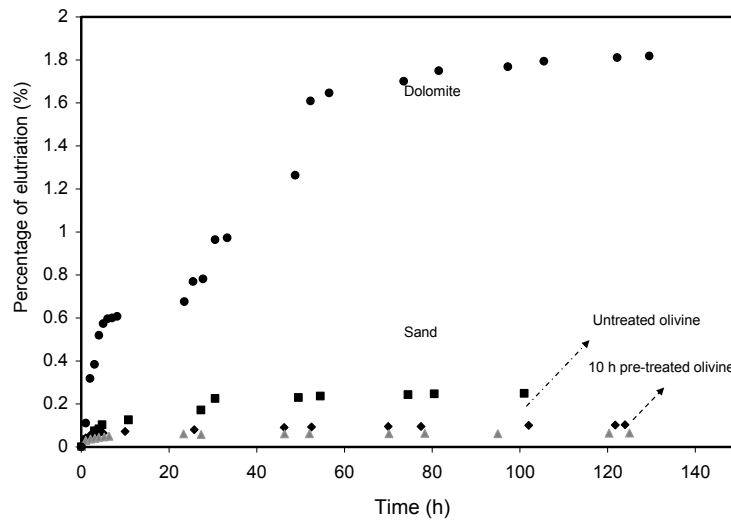

Fig. 5.9: Relative attrition resistance measurement for different additives

It is a relative measurement; the numeric numbers associated do not mean the absolute attrition resistance. The attrition resistance of olivine was compared with sand, bed material for gasifiers, and dolomite, a active catalyst for tar removal. As can be seen in Fig. 5.9, olivine is highly attrition resistant thus making it more attractive as an in-bed additive for biomass gasifiers; only 0.1% of olivine was elutriated after an operation of 120 h, which is much lower than that of dolomite.

5.4 Discussion

Use of untreated olivine as catalyst did not show higher naphthalene conversion. Pre-treatment of olivine with air at 900°C improved its catalytic activity towards naphthalene conversion. The pore volume for pre-treated and untreated olivine remained very small; thus pre-treatment has no influence on pore size, pore distribution and the BET surface area of olivine.
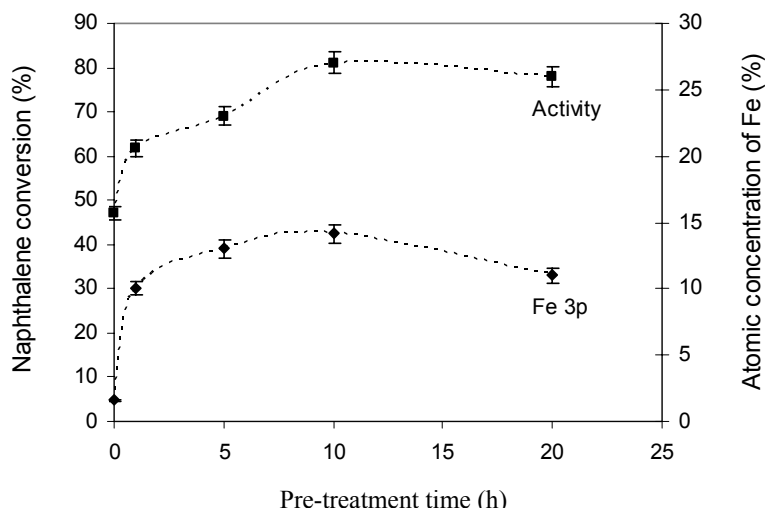
Fig. 5.10: Activity (naphthalene conversion) of olivine and atomic concentration of
        Fe-3p at the surface of olivine (determined by XPS) as a function of pre-
        treatment time

All the characterization techniques performed during this work led to two major observations regarding the changes due to pre-treatment of olivine. Firstly, segregation of Fe at the olivine surface was observed which was indicated by XPS and by TPR. This segregation increased with increasing pre-treatment time, upto 10 hours. During pre-treatment both the concentration of Fe at the surface and the activity of olivine increase with increasing time of pre-treatment and decrease after 10 hours, see Fig. 5.10. The behaviour of the elements of Fe, Mg and Si are shown in Fig. 5.4. Major Fe segregation occurs after the first hour of pre-treatment, percentage of Si also increases at the surface, at the expense of Mg. After 5 hours the concentration of Fe at the surface remains almost the same for 10 hours and then slightly decreases for 20 hours of pre-treatment time. The concentration of Mg decreases drastically after the 1st hour of pre-treatment (upto 25% decrease) and then increases at the cost of the atomic concentration of Si. It is concluded that the surface is enriched with Fe at the cost of Mg. Thus, it can be suggested though without experimental evidence, that Fe, Si, Mg and O are the ingredients for the active site and that Fe plays a major role.

SEM/EDX analysis revealed that the segregation of Fe at the surface is not uniform. The surface contains Fe-rich and Fe-poor phases. In some positions Fe concentrations as high as 34 wt% were detected for olivine samples pre-treated for 10 and 20 h.

The other important phenomenon was the change of oxidation state of Fe present in olivine. The Mössbauer spectroscopy clearly indicate the oxidation of the Fe (Fe^{2+} to Fe^{3+}) during the pre-treatment process which is responsible for the colour change of the olivine samples. The valency of the Fe in the fresh sample is clearly high-spin 2+. The valency of the iron in the sextuplets and in doublet 2 is 3+. Mössbauer spectroscopy reveals appearance of mainly three Fe III phases; crystalline hematite, a poorly crystalline Fe III phase and a super paramagnetic Fe III phase (Table 5.1). The contribution of the crystalline hematite increased during the oxidation treatment with increasing pre-treatment time. Also the contribution of the poorly crystalline Fe III oxide phase increased. However, the contribution of the super paramagnetic Fe III oxide is more or less constant. After 20 h pre-treatment, only the contribution of the crystalline phase further increased. The contributions of the poorly crystalline phase and of the super paramagnetic phase seem to be rather constant.

The Mössbauer data give no evidence for the hypothesis that the Fe atoms move back into the olivine lattice during pre-treatment for more than 10 h. Instead, the contribution of hematite increases, and the colour of the sample became darker brown. As the XPS results showed that the contribution of Fe decreased relative to that of Mg, most probably the Fe species sinter on the surface of the olivine crystals. The spectral contribution of sextuplet 2 increases up to the 10 h pre-treatment time, but remains the same after 20 h of pre-treatment. This seems to correlate with the activity of the samples, which was maximal after 10 h treatment and slightly less after 20 h. After 20 h, part of this phase might be covered with the large hematite particles. As discussed earlier, this sextuplet might be assigned to magnetite with Mg incorporated in the lattice. Pre-treatment changes the original structure of olivine. This change is around 30% for 10 h of pre-treatment, which increases to around 40% when pre-treated for 20 hours.

TPR showed the highest reduction in the case of 20 h pre-treated olivine. The extent of reduction was directly proportional to the contribution of Fe oxide present in the olivine. The presence of more Fe increases the possibility of a higher reduction of olivine in gasification condition. The decrease in naphthalene conversion over 20 h pre-treated olivine may be due to the reduction of the Fe oxide as hydrogen is present as a product gas.

5.5 Concluding remarks

Pre-treatment of olivine with air at 900°C for different treatment times of 1/5/10/20 h, can improve its activity significantly towards tar removal. Pre-treatment time of 10 h was observed to be the optimal for tar conversion among the tested pre-

treatment times. A further increase of pre-treatment time to 20 h did not improve the conversion, rather a slightly lower conversion was observed. Visually a colour change of olivine from typical pale green to brown-red was observed after pre-treatment. The BET-surface of treated and untreated olivine, determined using ASAP-2000 was less than 0.5 m^2 g^{-1}, hence olivine can be regarded as non-porous. Segregation of Fe to the surface of olivine was observed due to pre-treatment. This segregation of Fe was found to be non-uniform. Also the oxidation state of Fe changed due to pre-treatment. The contribution of crystalline hematite increased with an increase in the pre-treatment time of olivine. The concentration of Fe at the surface increases for higher treatment times, thus increasing the possibility of higher reduction due to presence of H$_2$ as a product gas. Although the exact correlation between catalytic activity of olivine and pre-treatment is not completely understood, it has been found in this work that the activity is related to the presence of Fe at the olivine surface and appearance of Fe III phases after pre-treatment. Besides catalytic activity for tar reduction, olivine has been observed to be highly attrition resistant and thus it makes an attractive candidate as an in-bed catalyst for fluidized-bed biomass gasifiers.

Chapter 6[*]

Decomposition of naphthalene as a biomass tar over olivine: effect of gas composition, kinetic approach and reaction scheme

The effect of different gas components on naphthalene conversion is described in this chapter. Kinetic parameters were determined using a simple power law kinetic model. An attempt is made to postulate the reaction network for naphthalene decomposition in the presence of a reactive gas mixture.

6.1 Introduction

Tar decomposition in the presence of a gaseous mixture mainly occurs due to cracking, steam and dry reforming reactions. Biomass gasification gas mainly consists of the following major components: H_2O, CO_2, H_2, CO and low quantities of CH_4. Each of these gas components has influence on the tar decomposition. The combined effect of the major gas components on tar decomposition must be well understood in order to solve tar problems in biomass gasification,.

Several researchers have investigated the effect of individual gas components or gas mixtures on tar decomposition (Jess 1996a; Jess 1996b; Simell et al. 1997b; Garcia and Hüttinger, 1989; Abu El-Rub et al., 2004). Different researchers have used different model tar compounds. Simell et al. (1997b) report that the hydrocracking is the dominating reaction for toluene decomposition in a mixed gas medium. The toluene decomposition rate is lower for a mixed gas medium than that in the presence of individual gas components. Thus showing the inhibiting effect of

CO and H_2. Coll et al. (2001) report a lower reaction rate for the steam reforming reaction of naphthalene and they had to increase the catalyst loading to achieve measurable naphthalene conversion. Aldén et al. (1994) investigated the influence of gas components on naphthalene decomposition over calcined dolomite. They report that CO_2 and H_2O enhance the cracking efficiencies, whereas H_2 is a strong inhibitor. In contrast, Jess (1996a) reported that H_2 has almost no influence on conversion rates for naphthalene decomposition. Experiments of Garcia and Hüttinger (1989), concerning the non-catalytic steam reforming decomposition of naphthalene, showed that addition of H_2 leads to a decrease in the formation of CO and thus has an inhibiting effect on the steam reforming reaction.

Literature on the combined effect of all the gas components mainly, H_2O, CO_2, CO and H_2 on tar conversion is limited. Abu El-Rub et al. (2002, 2004) investigated naphthalene decomposition with different gas medium such as only steam, only CO_2, a mixture of steam and CO_2 and finally a mixture of steam, CO_2, H_2, CO and CH_4, over char as catalyst. The researchers report a naphthalene conversion of higher than 90% for all the cases mentioned above. It was observed that the steam reforming reaction gave lower conversion than that of the dry reforming reaction and reaction in the presence of all gas components. During the present investigation, as indicated in Chapter 4, similar naphthalene conversion was observed for steam and dry reforming reaction. Naphthalene conversion decreased in the mixed gas environment. This decrease was due to the inhibiting effect of one or more gas components. In this chapter, results are given related to experiments performed in syn-gas medium to simulate the biomass gasification environment with different gas composition. The effect of each of the gas components is investigated to determine its influence on naphthalene conversion.

One of the most challenging tasks is to determine the kinetic parameters for tar decomposition reactions, due to the complex nature of the reaction network. This reaction network consists of multiple simultaneous reactions in series, and in parallel, including steam reforming, dry reforming, thermal cracking, hydrocracking, catalytic cracking, carbon formation, recombination of hydrocarbons etc. In response to this complexity, the majority of the published kinetic models assume decomposition to be a first order reaction with respect to tar (Corella et al., 1996; Lammers et al., 1997; Abu El-Rub, 2004). Lammers et al. (1997) assume that the naphthalene decomposition occurs via two sets of reactions, namely thermal homogeneous decomposition reactions and heterogeneous decomposition reactions on a catalyst surface. Lammers et al. calculated overall activation energy assuming a first order overall reaction mechanism and report activation energy for calcined dolomite catalysed decomposition reaction to be 227

kJ mol^{-1}. Jess (1996b) determined reaction orders with respect to all the reactants using a power law model equation. He investigated the naphthalene reforming reaction in the presence of H_2O and H_2 and further determined the reaction orders by systematically varying the gas composition. Until now, the reaction order with respect to all the other gases present in biomass gasification gas has not been determined. Experiments to determine the reaction order with respect to individual gasification gas component are described in this chapter. A reaction scheme for naphthalene decomposition is also postulated.

6.2 Reaction kinetics

Individual elementary reactions of naphthalene with the each of the gas components must be considered to describe the kinetics of naphthalene decomposition. However, an exact pathway of naphthalene decomposition in the presence of all these gas components, is not yet known. The product distributions obtained from naphthalene in the presence of different gaseous components, indicate the existence of a complex reaction network involving reactions between naphthalene, reactant gases, produced tars, benzene and solid carbon. The simplest way to express the naphthalene decomposition reaction in the presence of gases is to write a single reaction as given in Eq. 6.1, rather than independent reactions.

$$C_{10}H_8 + H_2O + CO_2 + CO + H_2 \longrightarrow \qquad \text{Products} \tag{6.1}$$
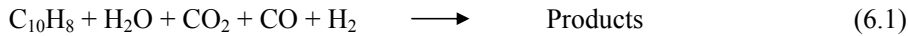
For this kind of reaction, the rate of disappearance of naphthalene can be approximated by power law expression as follows:

$$-r_n = k_n C_n^a C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e \tag{6.2}$$

Eq. 6.2 is valid when $C_n, C_{H_2O}, C_{CO_2}, C_{CO}, C_{H_2} \neq 0$. The reaction orders a, b, c, d and e can be determined using the method of excess (Levenspiel, 1995).

Jess (1996a, 1996b) used Eq. 6.2 to evaluate the kinetic rate constants for tar decomposition reactions in the presence of different gas mixture. The rate can be expressed in terms of naphthalene conversion under plug flow condition, given in Eq. 6.3.

$$r_n = \frac{dX_n}{d\tau} C_{n,in} \tag{6.3}$$

$$C_n = C_{n,in}(1 - X_n) \tag{6.4}$$

Combining Eqs. 6.2, 6.3 and 6.4 gives Eq. 6.5.

$$-\frac{dX_n}{d\tau}C_{n,in} = k_n\left[C_{n,in}(1-X_n)\right]^a C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e \tag{6.5}$$

$$-\frac{dX_n}{(1-X_n)^a} = k_n C_{n,in}^{(a-1)} C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e \, d\tau \tag{6.6}$$

Integration of Eq. 6.6 gives a relation for conversion of naphthalene while keeping the concentration of the gas components constant.

$$-\int_0^{X_n}\frac{dX_n}{(1-X_n)^a} = \int_0^{\tau} k_n C_{n,in}^{(a-1)} C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e \, d\tau \tag{6.7}$$

$$-\frac{(1-X_n)^{1-a}-1}{1-a} = (k_n C_{n,in}^{(a-1)} C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e)\tau \tag{6.8}$$

$$(1-X_n)^{1-a} = 1+(a-1)\,\tau\,k_n C_{n,in}^{(a-1)} C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e \tag{6.9}$$

$$X_n = 1-\left\{1+(a-1)\,\tau\,k_n C_{n,in}^{(a-1)} C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e\right\}^{\frac{1}{1-a}} \tag{6.10}$$

Eq. 6.10 gives an expression relating the conversion of naphthalene with the reactions orders, concentration of the gas components, space time and the rate constant and valid only for $a \neq 1$. For first order reaction with respect to naphthalene, Eq. 6.7 becomes as follows:

$$X_n = 1-e^{-k_n\,\tau\,C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e} \tag{6.11}$$

Systematic variation of concentration of each reactant gives data points for conversion versus concentration and can be used to determine the reaction orders. To determine the reaction order of naphthalene, the concentration of all the other reactants were kept constant and only the concentration of naphthalene was varied. Under this condition, Eq. 6.10 can be rewritten as follows:

$$X_n = 1-\left\{1+(a-1)\,k_1 C_{n,in}^{(a-1)}\right\}^{\frac{1}{1-a}} \tag{6.12}$$

where $k_1 = k_n\tau C_{H_2O}^b C_{CO_2}^c C_{CO}^d C_{H_2}^e$ is a constant. Eq. 6.12 is solved for unknowns k_1 and a by fitting the data for conversion versus concentration using STATGRAPHICS. Similarly the reactions orders with respect to the gas components are determined by changing concentration of only one gas component, while keeping all other conditions fixed. For such conditions, Eq. 6.10 can be rewritten as:

$$X_n = 1-\left\{1+k_x C_{comp}^y\right\}^{\frac{1}{1-a}} \tag{6.13}$$

where

$$C_{comp}^y = C_{H_2O}^b \text{ or } C_{CO_2}^c \text{ or } C_{CO}^d \text{ or } C_{H_2}^e \tag{6.14}$$

$$k_x = (a-1)k_n \tau C_{n,in}^{a-1} C_{CO_2}^c C_{CO}^d C_{H_2}^e \text{; for } H_2O \tag{6.15}$$

$$k_x = (a-1)k_n \tau C_{n,in}^{a-1} C_{H_2O}^b C_{CO}^d C_{H_2}^e \text{; for } CO_2 \tag{6.16}$$

$$k_x = (a-1)k_n \tau C_{n,in}^{a-1} C_{H_2O}^b C_{CO_2}^c C_{H_2}^e \text{; for } CO \tag{6.17}$$

$$k_x = (a-1)k_n \tau C_{n,in}^{a-1} C_{H_2O}^b C_{CO_2}^c C_{CO}^d \text{; for } H_2 \tag{6.18}$$

The temperature dependency of rate constant can be represented by Arrhenius' Law

$$k_n = k_{o,n} e^{(-E_a/RT_R)} \tag{6.19}$$

The rate constants can then be calculated using Eq. 6.9, once the reaction orders with respect to the reactants are known which further allows the calculation of activation energy using Eq. 6.19.

6.3 Experimental

Naphthalene decomposition experiments under different gas composition were carried out in an externally heated quartz fixed-bed reactor as described in Chapter 4. A schematic representation of the experimental setup is given in Fig. 4.1. Experiments with a syn-gas mixture were done with a fixed composition of different gas components such as H_2O, CO_2, CO and H_2. The effect of these gas components on naphthalene conversion was investigated by varying the individual gas components while keeping all other process parameters constant. Total inlet gas flow was kept constant using Ar as an inert medium. Tar sampling was done using the SPA method and analysed in a Varian CP-3800 GC. The detailed experimental conditions are given in Table 6.1.

Table 6.1: Experimental conditions

Temperature (^{o}C)	900
Pressure	Atmospheric
Catalyst	10 h pre-treated olivine
Space time (kg h m^{-3})	0.586 (at STP)
Particle size of catalysts (µm)	212-300
Inlet naphthalene concentration (g m^{-3})	3.2-9.3
Total gas flow (ml min^{-1})	625
Gas composition (vol%)	
H_2O	0-15
CO_2	0-20
CO	0-20
H_2	0-20

6.4 Results and discussion

6.4.1 Effect of different gas components on tar conversion

The reaction gas medium has a significant effect on naphthalene conversion and the product distribution. The experiments to investigate the effect of different gas components on naphthalene conversion were performed over 10 h pre-treated olivine at 900°C. The concentration of one of the gas component was varied, keeping the percentages of all other gas components constant; the naphthalene concentration was kept constant at 6.5 g m^{-3}. The experimental results for naphthalene conversion under different reaction media are summarised in Table 6.2.

Table 6.2: Effect of gas composition on naphthalene conversion

Experimental set	Gas composition (vol %)					Naphthalene conversion (%)
	H_2O	CO_2	CO	H_2	Ar	
Steam reforming	10	0	0	0	90	81.1
Dry reforming	0	12	0	0	88	80.1
Syn-gas mixture	10	12	12	10	56	75.4
Effect of steam	0	12	12	10	66	52
	6	12	12	10	60	55.1
	8	12	12	10	58	66.7
	12	12	12	10	54	81.5
	15	12	12	10	51	85.1
Effect of CO_2	10	0	12	10	68	54
	10	4.4	12	10	63.6	57.8
	10	7.8	12	10	60.2	67.6
	10	16	12	10	52	82.4
	10	20	12	10	48	84
Effect of CO	10	12	0	10	68	69.7
	10	12	4	10	64	72
	10	12	6	10	62	73.1
	10	12	14	10	46	76.8
	10	12	20	10	48	77.2
Effect of H_2	10	12	12	0	66	81.5
	10	12	12	5	61	78.9
	10	12	12	12	54	69
	10	12	12	15	52	64.2
	10	12	12	20	46	59.5

Under a syn-gas environment with a typical gas composition as in the exit gas of a gasifier ie H_2O:10 vol %, CO_2: 12 vol%, CO:12 vol%, H_2: 10 vol%, naphthalene conversion was observed to be 75.4%, which is lower than that for steam or dry-reforming conditions. Significant improvement in the naphthalene conversion was observed by increasing the amount of steam in the gas mixture. Similarly, with an increasing concentration of CO_2 in the gas mixture, naphthalene conversion increases. Thus both steam and CO_2 enhance the naphthalene decomposition reactions. Aldén et al. (1994) have reported similar observations with respect to steam and CO_2. CO has only small influence on naphthalene conversion. Increasing CO percentage upto 20 vol% in the total gas mixture, only a slight increase in conversion was observed. Increase the amount of H_2 in the gas mixture, caused naphthalene conversion to decrease, thus showing the negative effect of presence of H_2 in the reaction environment. When the H_2 concentration in the gas mixture is increased upto 20 vol%, conversion decreases considerably.
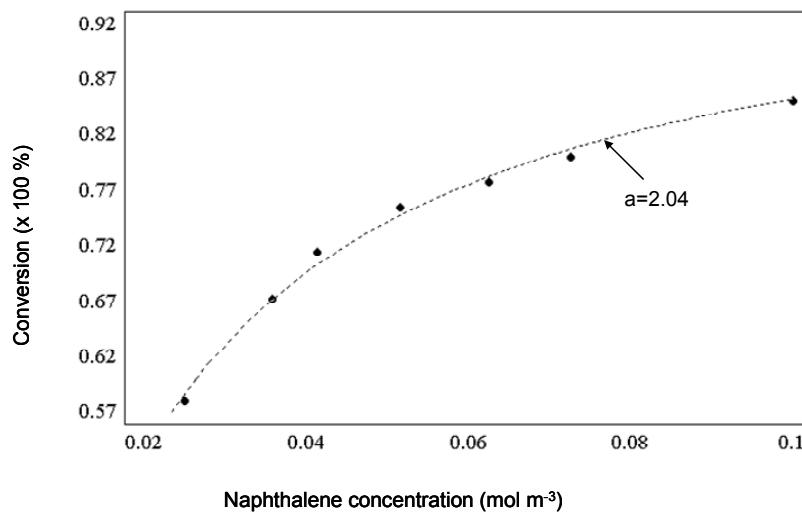

Fig. 6.1: Reaction order with respect to inlet concentration of naphthalene

6.4.2 Reaction kinetics

Reaction order with respect to naphthalene is determined by solving Eq. 6.12 using STATGRAPHICS. This equation gives conversion as a function of initial concentration of naphthalene and can be solved using experimental data points. Fig 6.1 shows the dependency of naphthalene conversion with respect to its initial concentration. The dotted line gives the best fit and gives a reaction order of +2.04 with respect to naphthalene. It was observed that change in the initial concentration of naphthalene significantly influences its conversion. In contrast, Garcia and

Hüttinger (1989) report that the initial concentration of naphthalene had no influence on the steam reforming reaction. It should be mentioned here that the investigations by Garcia and Hüttinger (1989) were carried out using a different initial naphthalene concentration range (0.5-3 mol%) and with different operating conditions (850°C, steam, τ': 20 s). The present investigation was done for an initial naphthalene concentration range of 0.1-0.48 mol%. Jess (1996b) reports a reaction order of +1.6 for naphthalene for non-catalytic decomposition with a mixture of steam and hydrogen gas. This indicats strong dependency of initial concentration of naphthalene on the decomposition behaviour.
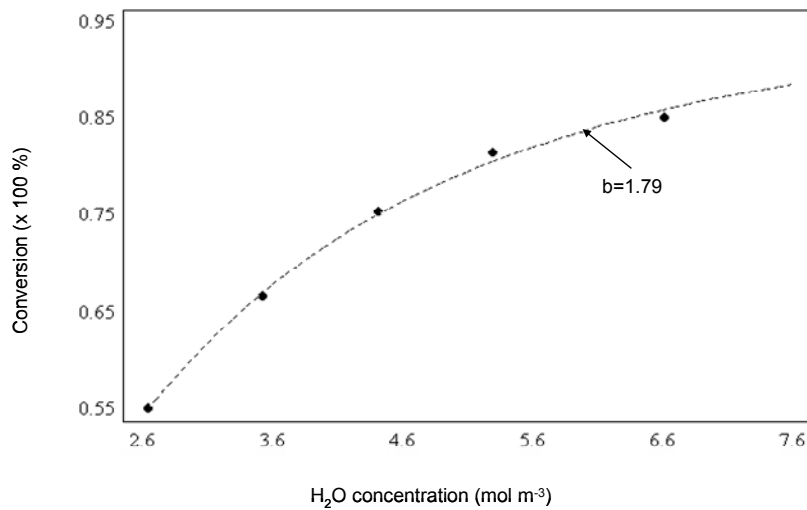

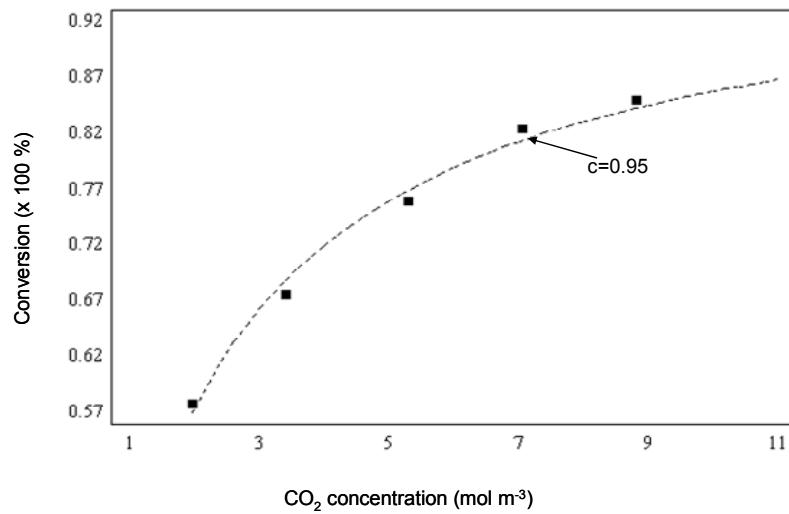Fig. 6.2: Reaction order with respect to inlet concentration of H_2O

Fig. 6.3: Reaction order with respect to inlet concentration of CO_2

Reaction orders with respect to H_2O, CO_2, CO and H_2 were determined using equation 6.13 which takes naphthalene conversion as a function of initial concentration of the gas components. Systematic variation of the inlet concentration of a particular gas component, keeping all others constant, allowed determination of reaction order with respect to the gas under consideration. Figs 6.2- 6.5 give the possible reaction orders of individual gas components in gas mixture which are +1.79, +0.94, +0.20 and -0.74 for H_2O, CO_2, CO and H_2 respectively. These values show the strong dependency of the inlet concentration of the reactants on naphthalene conversion. The negative order with respect to H_2 indicates that it has inhibiting effect on naphthalene conversion. Tar conversion with the syn-gas mixture is lower than that with only steam or CO_2 due to the presence of H_2.
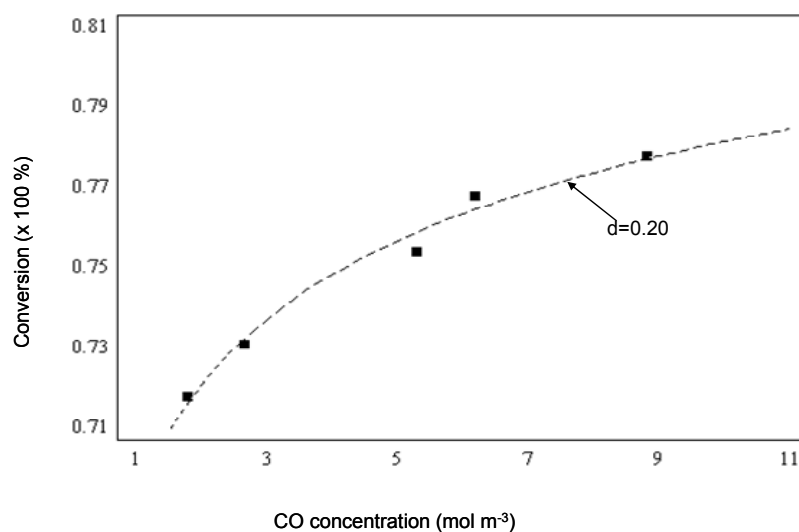

Fig. 6.4: Reaction order with respect to inlet concentration of CO

Experiments were performed in a temperature range of 825-900°C with fixed gas composition to determine the activation energy. The inlet concentration of naphthalene was kept at around 6.5 g m^{-3}. The temperature effect on naphthalene conversion is shown in Fig. 4.13. The activation energy for naphthalene conversion over 10 h pre-treated olivine was calculated from Fig. 6.6 and is 213 kJ mol^{-1} with a pre-exponential factor of 4.36 x10^{10} $m^{12.72}$ h^{-1} $kg^{-1}mol^{-3.24}$.

Kinetic data for naphthalene decomposition is very limited in the literature. Very few researchers have experimentally determined these parameters which are highly dependent on the reaction medium and the reaction conditions. The kinetic data reported in the literature are summarized in Table 6.2 along with the

determined kinetic parameters given in this chapter. This table gives estimated activation energies for different operating conditions studied by different researchers. Abu El-Rub et al. (2002, 2004) reported lower apparent activation energies for naphthalene decomposition assuming a first order reaction with respect to naphthalene. A first order reaction kinetic model underestimates the overall activation energy. This is also evident if one compares the apparent activation energies determined in Chapter 4 and in this chapter. In Chapter 4 where first order kinetics is assumed, the activation energy is estimated to be lower than the energy determined in this chapter under the same experimental conditions.
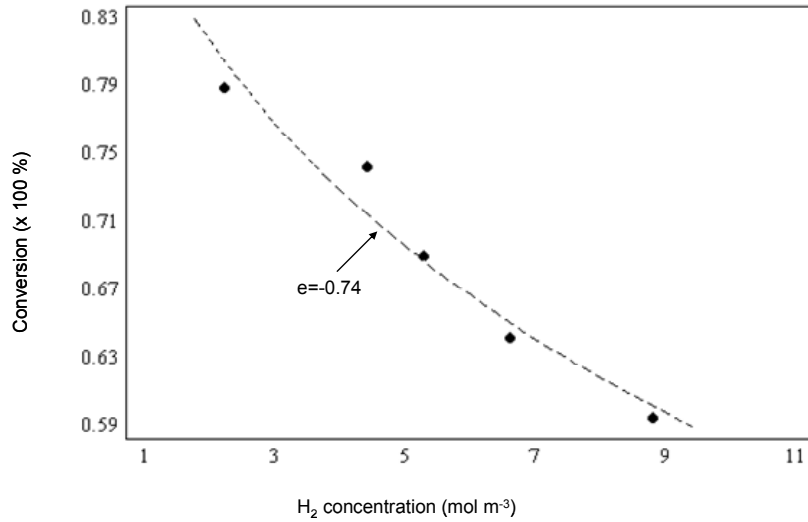

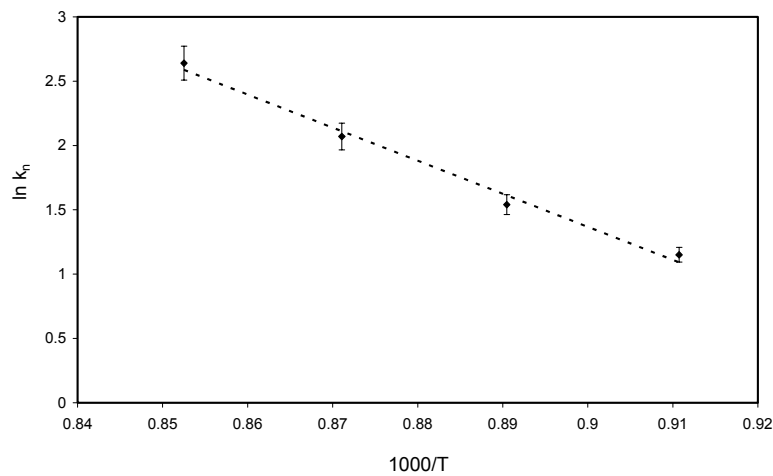Fig. 6.5: Reaction order with respect to inlet concentration of H_2

Fig.6.6: Arrhenius plot for calculation of activation energy

These kinetic parameters for naphthalene decomposition are valid in the presence of the all four gas components. The kinetic parameters in the presence of a single gas component (for example steam reforming or dry reforming reactions) or in the absence of one of the components can also be determined using the same procedure. Due to limited data, it was not possible to make kinetic calculation for individual gas reactions during the investigations presented in this thesis.

6.4.3 Reaction scheme

As observed under the different gasification conditions, decomposition of naphthalene mostly leads to the production of permanent gasses. The first step for any decomposition mechanism of non substituted aromatic compound is the C-H or C-C bond cleavage. This cleavage leads to ring opening/breakage of the aromatic compound forming lower aliphatic or aromatic hydrocarbons. Consecutive reactions of these lower hydrocarbons produce permanent gases. Based on the product distribution, a reaction scheme is proposed, and presented in Fig. 6.7. This reaction network is based on analogy with available literature (Badger et al., 1964; Marinov et al., 1998; Gräbet et al., 1982; Ritcher et al., 2000; Garcia et al., 1989). It should be clearly mentioned that there is no fixed experimental validation as it was not possible to measure the intermediate products.

Indene is the most likely first stable decomposition product as one carbon is subtracted from the naphthalene radical. Two pathways are reported in the literature for the formation of indene from naphthalene (Gräber et al., 1982; Marinov et al., 1998). Gräber et al. (1982) propose indene formation via hydrogenation of naphthalene. The reaction path described by Marinov et al. (1998) goes via the production of a naphthoxy radical. Nair (2004) also proposes naphthalene decomposition proceeds via the formation of a naphthoxy radical. Indene has been found under all gasification conditions and is an intermediate compound for the production of other stable (aromatic) compounds. Benzene is also an aromatic compound; it is likely that this compound is produced directly from indene by the exclusion of a 3-carbon compound. However, 3-carbon compound has not been detected by GC. Because toluene is present in low amounts during the gasification conditions, the production of benzene could well be going via toluene producing a 2-carbon compound (C_2H_2, acetylene) and a one carbon compound (CH_4). Acetylene has been detected by GC, however, it is likely to react with naphthalene, producing acenaphthalene and is very active in producing soot (Tenser et al., 1995). Methane may react with the naphthyl radical producing 1- or 2-methylnaphthalene. It is therefore not surprising that the concentration of methylnaphthalenes during steam reforming conditions is higher than that during mixed gas conditions. The production of crysene, by dimerization of indene is therefore a thermodynamically favourable reaction.

Table 6.2 Kinetic data for decomposition of naphthalene

Reaction conditions					Reaction order						E_a (kJmol⁻¹)	Pre-Exponential Factor	Ref.
Temp (°C)	Initial $C_{10}H_8$	Reaction medium	Catalyst	Res. Time (s)	$C_{10}H_8$	H_2O	CO_2	CO	H_2	CH_4			
700-900	90 g m⁻³	$H_2O+ CO_2$	FCC	0.3	1[a]	nd	nd	-	-	-	50	650 s⁻¹	Abu El-Rub et al. (2002)
700-900	20 g m⁻³	$H_2O+ CO_2$ $+CO+H_2$ $+CH_4$	Char	0.3	1[a]	nd	nd	nd	nd	nd	60	18700 s⁻¹	Abu El-Rub et al. (2004)
950-1400	0.25-1 vol%	$H_2O +H_2$	--	0.3-2	1.6	0	-	-	-0.5	-	350	1.7×10^{14} m$^{0.3}$mol$^{-0.1}$s^{-1}	Jess (1996b)
660-800	0.2-0.8 vol%	$H_2O +H_2$	Ni-MgO	0.26	0.2	0	-	-	0.3	-	332	4.3×10^{13} m$^{0.5}$mol$^{1.5}$ s^{-1}kg^{-1}	Jess (1996a)
825-900	6.5 g m$_o$⁻³	H_2O+CO_2 $+CO+H_2$	Olivine	0.3	1[a]	nd	nd	nd	nd	-	141	1.7×10^7 m³kg⁻¹hr⁻¹	Chapter 4
825-900	3.3-12 g m$_o$⁻³	H_2O+CO_2 $+CO+H_2$	Olivine	0.3	2.04	1.79	0.95	0.20	-0.74	-	213	4.36×10^{10} m$^{12.72}$h⁻¹ kg⁻¹mol$^{-3.24}$	This chapter

a :assumption;   nd: not determined

Crysene was detected for steam reforming reaction and reaction under mixed gas condition, but not during dry reforming reaction. Biphenyl was produced in small quantities for all gas mediums, probably by the dimerization of benzene
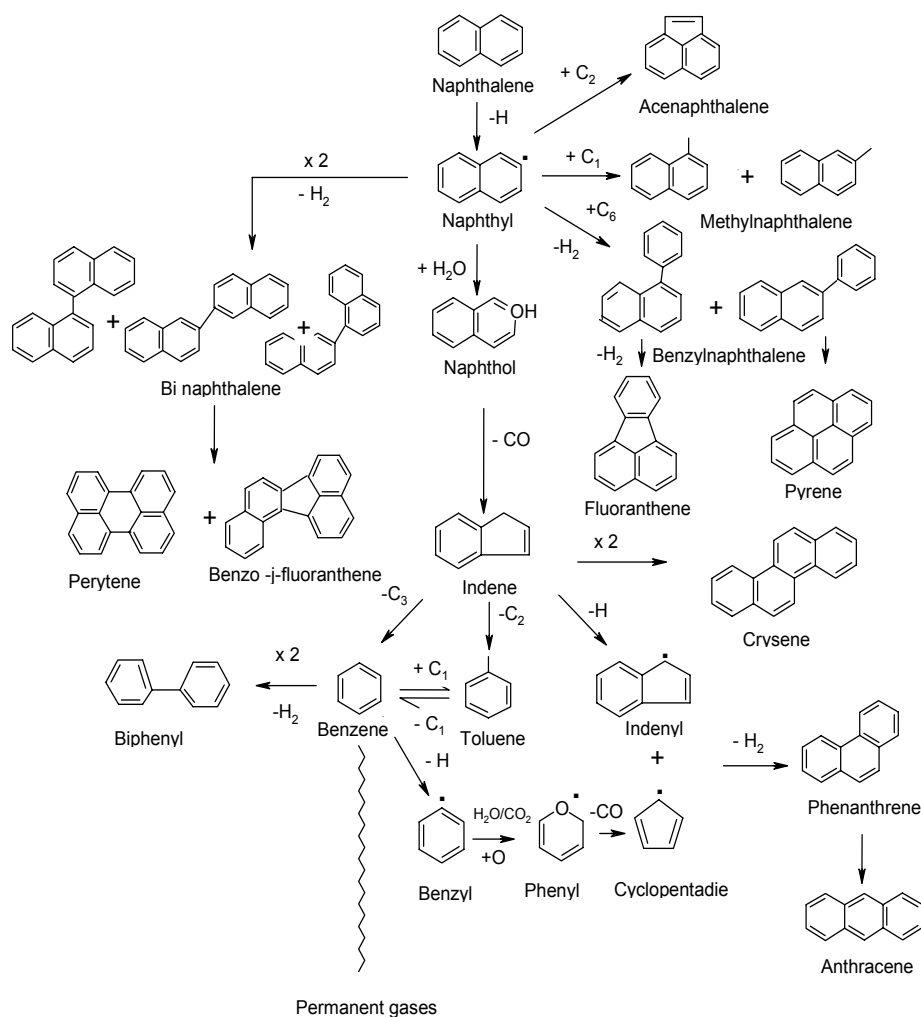

Fig.6.7: Reaction scheme for naphthalene decomposition

The formation of phenanthrene and anthracene were observed for all cases. The phenanthrene formation pathway is most likely based on the combination of cyclopentadienyl with indenyl followed by rearrangement as suggested by Richter et al. (2000). Cyclopentadienyl is formed via oxidation of benzene and indenyl is formed via hydrogen abstraction from indene. Anthracene formation occurs by

isomerization from phenanthrene (Marinov et al. 1998). During CO_2 reforming reaction, the amount of phenanthrene and anthracene detected was very high and no crysene was detected. Indene was observed in very low quantity. This indicates that most of the indene produced reacts further to produce phenanthrene /anthracene and dimerization did not happen.   Growth of fluoranthene and pyrene goes via benzylnaphthalene route (Ritcher et al., 2000; Gräber et al., 1982). Benzylnaphthalene is an intermediate product which readily rearranges itself into fluoranthene and pyrene. This route is prominent for mixed gas condition as both the compounds were detected. None of these compounds are present for dry reforming condition, which proves that phenyl radicals form cyclopentadienyl instead of combining with naphthyl radicals. The formation of binaphthalene from naphthalene has been described Badger et al. (1964). During steam and dry reforming conditions binaphthalenes in a significant quantity were observed. The combination of naphthalene with naphthyl radical is the pathway for the formation of mainly 1,1-, 1,2- and 2,2-binaphthalene. When using mixed gas conditions, binaphthalenes formed in low quantities. Further, the fission of C-H bonds produce binaphthyls, which eventually can produce condensed hydrocarbons such as perylene and benzofluoranthene (Badger, 1964). During the present investigation, perylene and benzofluoranthene were detected for steam reforming reactions over SiC, untreated olivine and 1 h pre-treated olivine. These two hydrocarbons were not formed over 10 h pre-treated olivine. Binaphthalenes were the biggest detectable tar compounds formed over 10 h pre-treated olivine.

The tendency towards coke/soot formation increases as the molecular mass of the hydrocarbon increase; the larger the number of aromatic rings in a hydrocarbon molecule, the stronger the tendency to coke/soot formation. The deposition of coke/soot is a frequently occurring problem during catalytic decomposition of tars. The formation of coke/soot is described by Bartholomew (2001) as chain reactions of polynuclear aromatics like benzene that after protonation can polymerise to higher hydrocarbons and finally terminate at the catalyst surface. He also reported that at longer residence times soot deposition is faster. Houben et al. (2002) also reported an increase in soot formation with increasing residence time. According to Bartholomew (2001), a typical soot composition ranges from $C_{30}H_{40}$ to $C_{40}H_{44}$. Tenser et al. (1995) investigated the tendency for soot formation for different hydrocarbons ie methane, acetylene, benzene, toluene and p-xylene. Soot formation in all cases seems to increase linearly with the hydrocarbon concentration, and when comparing the activation energies for soot particle formation the following arrangement was made acetylene> benzene>toluene>p-xylene>methane (Tenser et al., 1995). Investigating the

tendency for soot formation of higher PAHs like naphthalene, anthracene and pyrene, Tenser et al. (1997) found that naphthalene seems to have the highest tendency to form soot exceeding methane by 112 times and acetylene by 15 times. Jess (1996a) studied the catalytic decomposition of naphthalene, benzene and methane using a nickel catalyst in the presence of H_2O and H_2. Under these conditions and at temperatures between 500 and 800°C soot formation did not occur. Jess also reported that coke/soot formation decreases with increasing the H_2 concentration in the gaseous medium.

6.5 Concluding remarks

H_2O, CO_2 and H_2 have strong influence on naphthalene decomposition reactions. H_2O and CO_2 have an enhancing and H_2 has an inhibiting effect. Naphthalene conversion in a syn-gas mixture was observed to be lower than that of only in steam and only in CO_2, which is due to the presence of H_2 in the reaction mixture. With an increase in the amount of H_2 in the gas mixture, naphthalene conversion decreases, whereas a slight increase was observed with increasing CO concentration. Kinetic parameters were determined in the presence of the main gas components from a gasifier and activation energy of 213 kJ mol^{-1} was found over 10 h pre-treated olivine as catalyst.

Steam and dry reforming reactions of naphthalene are mainly responsible for the formation of gaseous products such as H_2 and CO. Besides these gaseous products, cracking reactions give rise to the formation of other hydrocarbons with lower carbon numbers than naphthalene. Hydrocarbons with higher carbon numbers than naphthalene are also formed via polymerization reactions. Formation of naphthyl radicals by C-H bond fission is probably the first step in naphthalene decomposition. Higher PAH formation occurs via the combination of naphthyl radicals with other hydrocarbons. Further condensation of these higher hydrocarbons leads to soot formation.

Chapter 7

Conclusions and recommendations

The conclusions drawn in this thesis are highlighted in this chapter. Some of the problems and issues that occurred during the research are outlined here along with possible ways to overcome these problems. Further, some recommendations for future work are given here.

7.1 Introduction

Tar formation is identified as one of the major problems during biomass gasification to form a syn-gas mixture. Tar removal technologies can broadly be divided into two approaches; treatments inside the gasifier (primary methods), and hot gas cleaning downstream the gasifier (secondary methods). Primary methods are presntly begin to gain considerable attention as these methods may eliminate the need for downstream cleanup equipment for tar removal. According to this concept the tar formed during gasification might be reduced at source, by supressing tar producing reactions, or it might be broken down into smaller non condensible molecules. A critical literature review of primary methods provided in Chapter 2, indicated that the use of an active bed material during gasification is an attractive option to reduce the tar. These bed additives act as *in-situ* catalysts promoting several chemical reactions in the same gasifier. The presence of additives influences the gas composition and the heating value of the product gas.

7.2 Olivine as a tar removal catalyst

Olivine has been identified as a promising bed material because of its attrition resistance. Olivine, if catalytically active can be mixed with sand or substitute sand completely in a fluidized-bed gasifier. A detailed investigation of the catalytic

behaviour of olivine is presented in this thesis. The preliminary experiments performed at ECN (Chapter 3) revealed that untreated olivine could convert only 46% of the total tar present in the hot gasification gas at 900°C, which can not be considered as a significant reduction of tar. This led to an investigation of ways to improve the catalytic activity of olivine. A simple method of pre-treatment was developed in this work that can significantly improve the catalytic activity of olivine (Chapter 4). With pre-treated olivine, the conversion of naphthalene, considered as a model biomass tar compound, was as high as 80%. The pre-treatment was done by heating the olivine catalyst at 900°C in presence of air for different pre-treatment times. Treatment at lower temperatures (700-800°C) did not activate the catalyst. Pre-treatment of olivine for 10 h was observed to be an optimum period needed for a high naphthalene conversion among the investigated region of treatment times. Further increase in the pre-treatment time up to 20 h did not increase naphthalene conversion. It is probable that a further increase in pre-treatment temperature (higher than 900°C) will improve the performance of olivine and may decrease the time needed to activate it. However, during this research, only a maximum temperature of 900°C could be reached due to experimental limitations. The effect of higher pre-treatment temperature on the activity of olivine should be investigated in future. It was also observed that the gas composition significantly effects the tar conversion. H_2O and CO_2 have an enhancing and H_2 has an inhibiting effect, whereas CO has only slight influence on the conversion. Kinetic parameters were determined in the presence of the main syn-gas components from biomass gasifier and an activation energy of 213 kJ mol^{-1} (825-900°C) was found over 10 h pre-treated olivine as catalyst. The chemical composition of olivine can differ depending on which geographical location it originates from. Catalytic behaviour of olivine from different origin should be investigated in future.

Although olivine is observed as a potential candidate as a catalyst for in-bed biomass gasification, there are still many issues that require answers and that need further investigation. One of the main issues is catalyst deactivation and aging. The long-term activity of olivine needs to be investigated. During the present work, maximum experimental time of 2 hours could be reached after which the initial concentration of naphthalene started to decrease. With increasing time, the naphthalene saturator got empty, thus lowering the inlet concentration. The behaviour of olivine also needs to be investigated in a real fluidized-bed gasification system. This thesis gives valuable information regarding the behaviour of olivine with respect to biomass tars, but issues like biomass-olivine interaction, interaction of olivine with ashes, agglomeration of the bed etc. still need to be investigated. Another area that needs more research is coke/solid carbon formation in the

presence of the catalyst. During the present investigation, severe coke/carbon formation was observed for steam and dry reforming reactions, which also lead to deposition on the catalyst surface. Simply burning the coke/carbon in air could regenerate the catalyst. Coking behaviour of olivine should be investigated in a real gasification system. A fast internally circulating fluidized-bed gasifier design (FICFB) as at the Guessing demonstration plant in Austria, is good for coking catalysts. In this 2-stage gasification concept (Fig. 2.7), the hot bed material circulates to the combustion zone where non-gasified carbon is burnt with air along with the coke deposited on the surface of the bed material.

7.3 Tar classification system

A new tar classification system has been developed within the framework of the SDE project, (Chapter 3). The tar classification system provides a basis for a systematic approach to understand the tar problem. Heterocyclic (class 2) tars cause severe waste water problems due to their high aqueous solubility. Condensation problems are mainly caused by the heaviest tar fractions, which are GC-undetactable (class 1) and heavy polyaromatic (class 5) tars. These tars condense out even at a very low concentration at relatively high temperatures (van Paasen and Kiel, 2004). Light hydrocarbons (class 3) do not pose any problem as they condense only at very high concentrations. Light polyaromatic hydrocarbons (class 4, 2- and 3- ring compounds) condense at relatively high concentrations. Heterocyclic compounds are most easy to destroy. Full conversion of these compounds was observed even without the use of a catalyst. Two and three ring compounds (class 4) were observed to be the most difficult tars to deal with. The heaviest tar fractions (class 5) start breaking down at a higher temperature to naphthalene-like hydrocarbons. Due to the catalytic treatment, a matrix of complex reactions among different tars and gases occurs. At this moment, the inter-relation among different tar classes is not known. To exactly predict the mechanism of the breakdown and the recombination reactions of tar, class 1 tars should be measured as well. It was not possible to measure any class 1 tars during this research. The SPA sampling method fails to capture very heavy tars. More attention should be directed to identify and quantify the class 1 tars. A proper understanding of the inter-relations among different tar classes will provide insight regarding how to solve tar cracking problems. Identifying the heaviest fraction of tar is a challenge as these compounds tend to stick to the GC column, thus current analytical equipment like GC fails to measure the very heavy tars. Gravimetric measurement can be used to give information about the total quantity of the heavy tar. In a recent approach,

researchers at ECN used HPLC technique to analyse the gravimetric tar and could detect tars heavier than coronene (van Paasen and Kiel 2004). With proper calibration, this analysis method could be used to give valuable information regarding the quantitative composition of the heaviest tar fraction. This approach needs more attention from the research community.

7.4 Characterization of olivine

Different characterization techniques used during this work reveal some vital information about olivine as a catalyst (Chapter 5). Olivine was observed to be a non-porous material. The relative attrition resistance of olivine with respect to sand and dolomite was experimentally determined. It was found that pre-treatment causes segregation of Fe to occur at the surface of olivine. XPS measurements gave approximate atomic concentrations for the different elements present at the surface of olivine. During the course of this thesis, an attempt was made to find the exact elemental analysis of the surface of olivine using SEM/EDX. But the X-ray goes to few μm level below the surface, thus giving only local compositions instead of the surface composition. In such cases, low energy ion scattering (LEIS) technique might be helpful to determine the elemental distribution of the surface as LEIS is exclusively sensitive for outer surface layers. This technique is expensive and it could not be done during this work due to budget limitations.

The Mössbauer spectroscopy clearly indicated changes of the oxidation state of iron (Fe II to Fe III) during the pre-treatment process, this is also responsible for the colour change of the olivine samples. New Fe III phases appear which were not present in the fresh olivine samples. This indicates that pre-treatment changes the original structure of olivine. This change is around 30% for 10 h of pre-treatment, and it increases to around 40% when olivine is pre-treated for 20 hours. The characterization methods applied during this research do not allow to say much about the interaction of Mg present in the olivine with other elements such as Fe. Mg might be active for tar removal and hence, research should be directed towards the effect of the presence of Mg in the future.

Although the exact mechanism behind the catalytic activity of olivine is not clearly understood yet, the results presented in this thesis show that the activity is related to the presence of Fe at the surface of the catalyst. All the characterization techniques were performed on pre-treated olivine sample. The olivine catalyst is under severe reaction conditions during catalytic decomposition experiments. Hence *in-situ* characterization of the olivine catalyst might help to provide a better understanding of the possible active sites.

7.5 Mechanisms of naphthalene decomposition

The prediction of naphthalene decomposition pathway is extremely difficult. This is the result of the presence of reactive gases and a number of reactions occurring simultaneously in series and in parallel between them. A reaction mechanism was proposed for naphthalene decomposition based on the product distribution and on an analogy drawn from the available literature. Formation of naphthyl radicalS by C-H bond cleavage is probably the first step of naphthalene decomposition. This cleavage leads to ring opening/breakage of the aromatic compound forming lower aliphatic or aromatic hydrocarbons. Consecutive reactions of these lower hydrocarbons produce permanent gases. Formation of PAH with higher masses occurs by combiningf different aromatic compounds via reactions like condensation, dimerization, isomerization etc. Further condensation of these higher hydrocarbons leads to soot formation. An exact decomposition mechanism can be predicted provided the intermediate products are known. During this work, the intermediate products could not be identified because tar sampling was done at the entrance and at the exit of the reactor, which only gave initial and final tar compositions. Intermediate products can be determined if online tar measurement can be done along the reactor length. The addition of some intermediate products at the inlet of the reactor may also give information about the reaction network.

The introduction of labelled reactants together with online mass spectrometry (MS) measurement may be a strong tool for deriving the naphthalene decomposition pathway. If one of the carbons present in naphthalene is replaced by ^{13}C and subsequently lead to reaction with reactive gases, the product distribution may reveal vital information about bond breakage etc. As the ^{13}C-label is stable during the decomposition the label can only be transferred to other compounds by a chemical reaction of the reactant. These labelled compounds can be detected in MS as they differ in mass with non-labelled compounds. So just by measuring the amount of ^{13}C-labels per product formed it should be possible to determine if a certain product, directly or indirectly, comes from a reaction with the ^{13}C-labeled reactant. ^{13}C-labeled naphthalene is very expensive, 50 mg costs approximately 1100 euro. Due to budget limitation, an investigation with labelled compound was out of the scope of this research, but might be of interest for future research. During the present research, we tried to investigate the mechanisms of the dry reforming reaction using labelled $^{13}CO_2$, however during the experimentations several problems arose due to blockages of the injection valve and the capillary of the MS. With the present MS, the injector valve could be kept at maximum temperature of 200^oC, thus tars started to condense.

7.6 Combined tar removal approach

Untill now investigations indicated that using only primary methods will not produce a complete clean gas, but primary methods can reduce the tar level considerably. If olivine can be used as an in-bed material in the gasifier instead of sand, the hot gas may still contain some tar. The removal of the remaining tar might need a secondary clean up step. However, the type of treatments that have to be used in the gasification system depends highly on the end-use applications. The first step for process selection for biomass gasification must be to evaluate the future application. Depending on the application for the gas produced, it must be decided whether a primary or secondary tar removal method or a combination of both should be applied. This combined approach is shown in Fig. 7.1.
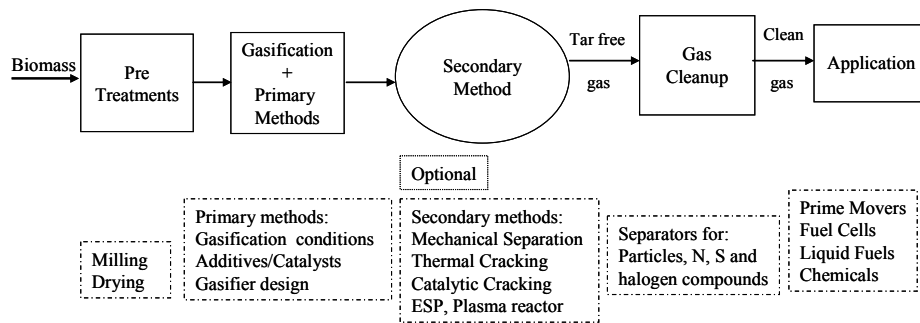
Fig 7.1: Tar removal approach in biomass gasification

For applications such as that of the Amer power plant wood gasification process, where the gasification gas is kept at a temperature of 500°C and then combusted or co-combusted directly in a coal fired boiler (Meijer, 2003), there is no need for a rigorous tar cleaning step. In the case of production of liquid fuels and chemicals via Fischer Tropsch synthesis, the cleaning requirements are very stringent. Tijmensen et al. (2002) report a need of 99.999% tar removal from the gasification gas for production of Fischer Tropsch liquids. Hasler et al. (1999) report that the tar tolerance for IC engines is less than 100 mg m^{-3} and Milne and Evans (1998) report a tar tolerance of 0.5 mg m^{-3} for gas turbines. A fluidized-bed biomass gasifier typically produces tar at around 10 g m^{-3}. For such applications, rigorous tar cleaning techniques are required. Although primary methods are of potential importance for the biomass gasification process as a whole, complete tar removal can not be achieved with the measures that are presently used. A combination of proper primary measures with downstream methods may be effective in all respects. The use of olivine as the bed material inside a gasifier

instead of sand, will reduce the amount of tar in the exit gas. Further tar removal can be achieved using a polishing step downstream of the gasifier. More research is required to develop an efficient primary technique, ie a combination of optimal operational parameters, bed additives and reactor design, which will serve to produce a clean gas and eliminate the need for downstream tar removal techniques.

Nomenclature

Abbreviations

AIT	Asian institute of technology
BET	Brunauer-Emmett-Teller
BFB	Bubbling fluidized-bed
BIGCC	Biomass integrated gasification combined cycle
CFB	Circulating fluidized-bed
daf	Dry, ash free
ECN	Energy research centre of The Netherlands
EDX	Energy dispersive X-ray analysis
EIA	Energy information administration
ER	Equivalence ratio: O_2 content of air supply/O_2 required for complete combustion
EU	European Union
FCC	Fluid catalytic cracking
FICFB	Fast internally circulating fluidized-bed
FID	Flame ionization detector
GC	Gas chromatography
GR	Gasifying ratio: (H_2O+O_2)/Biomass $(kg\ h^{-1})\ (kg_{daf}\ h^{-1})^{-1}$
HPLC	High performance liquid chromatography
IEA	International energy agency
KTH	Royal institute of technology, Stockholm
LHC	Light hydrocarbons
LIES	Low energy ion scattering
MS	Mass spectroscopy
NREL	National renewable energy laboratory
PAH	Polycyclic aromatic hydrocarbon
PNL	Pacific northwest laboratory
RDF	Refuse derived fuel
RIT	Repeated impact testing

SB	Steam to biomass ratio; H_2O / Biomass $(kg\ h^{-1})\ (kg_{daf}\ h^{-1})^{-1}$
SDE	Agency for research in sustainable energy
SEM	Scanning electron microscopy
SPA	Solid phase adsorption
TCD	Thermal conductivity detector
TNO	Toegepast natuurwetenschappelijk onderzoek
TPR	Temperature programmed reduction
USA	United States of America
USDOE	United States department of energy
UT	University of Twente
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Symbols

a	Reaction order with respect to naphthalene
b	Reaction order with respect to H_2O
c	Reaction order with respect to CO_2
C_{CO}	Concentration of CO $(mol\ m^{-3})$
C_{CO_2}	Concentration of CO_2 $(mol\ m^{-3})$
C_{H_2}	Concentration of H_2 $(mol\ m^{-3})$
C_{H_2O}	Concentration of steam $(mol\ m^{-3})$
C_{comp}	Concentration of individual gas component $(mol\ m^{-3})$
C_n	Concentration of naphthalene $(mol\ m^{-3})$
$C_{n,in}$	Inlet concentration of naphthalene $(mol\ m^{-3})$
$C_{t,in}$	Inlet concentration of the considered tar or tar class $(mg\ m^{-3})$
$C_{t,out}$	Outlet concentration of the considered tar or tar class $(mg\ m^{-3})$
C_{tar}	Concentration of tar $(mol\ m^{-3})$
d	Reaction order with respect to CO
E	Activation energy $(kJ\ mol^{-1})$
e	Reaction order with respect to H_2
E_{app}	Apparent activation energy $(kJ\ mol^{-1})$
k_{app}	Apparent rate constant $(m^3\ kg^{-1}\ h^{-1})$
k_n	Rate constant $(m^{3\ (a+b+c+d+e-1)}\ mol^{-(a+b+c+d+e-1)}\ kg^{-1}\ h^{-1})$
$k_{o,app}$	Apparent pre-exponential factor $(m^3\ kg^{-1}\ h^{-1})$
$k_{o,n}$	Pre-exponential factor $(m^{3\ (a+b+c+d+e-1)}\ mol^{-(a+b+c+d+e-1)}\ kg^{-1}\ h^{-1})$
r_n	Rate of naphthalene decomposition
r_{tar}	Rate of tar decomposition

R	Universal gas constant (J mol^{-1} K^{-1})
t	Catalyst pre-treatment time (h)
T_R	Reaction temperature (^{o}C)
T_t	Catalyst pre-treatment temperature (^{o}C)
W	Catalyst weight (kg)
X	Conversion (%)
X_n	Naphthalene conversion

Greek letters

τ	Space time: amount of catalyst/ gas flow rate (kg m^{-3} h)
τ'	Residence time (s)
ν_o	Gas Flow rate (m^3 h^{-1})

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Summary

With respect to global issues of sustainable energy and reduction of CO_2, biomass is getting increased attention as a potential source of renewable energy. Among all the biomass conversion processes, gasification is one of the most promising. One of the major issues in biomass gasification is how to deal with the tar formed during the process. The average tar concentration in the exit gas from a fluidized bed gasifier is about 10 g m^{-3} (STP). The minimum allowable limit for tar, however, is highly dependent on the end user application. The preferable tar and dust loads in gases for engines must be lower than 10 mg m^{-3} (STP). Considerable efforts have been directed on tar removal from the fuel gas. Tar removal technologies can broadly be divided into two approaches; hot gas cleaning after the gasifier (secondary methods), and treatments inside the gasifier (primary methods). Primary methods are gaining much attention as these may eliminate the need for downstream cleanup.

The objective of the present research is to find an appropriate catalyst that can be used as an active in-bed material for biomass gasification processes. Olivine is considered as prospective in-bed additive and catalytic activity of olivine is investigated in this thesis. The present research mainly includes fundamental aspects of catalytic tar decomposition, the kinetics and tar decomposition behavior over olivine. The performance of olivine under different gasification medium is also evaluated. Several characterization techniques have been utilized to understand the properties of olivine. Olivine used in this study, is a naturally occurring silicate mineral from Norway, containing oxides of magnesium, iron and silicon. Preliminary experiments are performed at ECN to compare the catalytic activity of olivine with dolomite. Total tar conversion of only 46% is observed at 900°C over olivine, which is lower than that of dolomite.

Naphthalene is identified as one of the major tar compounds that contributes to more than 60% of total tar hence it is considered as a model biomass tar compound during this research.

A fixed-bed reactor has been used to investigate catalytic decomposition of naphthalene over olivine. It is observed that pre-treatment of olivine with air at

900°C, could improve its activity towards tar removal significantly. Segregation of iron at the surface of olivine is observed due to pre-treatment. This results in a higher activity of olivine. Also the oxidation state of iron changes from 2 to 3. Crystalline hematite is formed, which increases with the increase in the pre-treatment time.

A naphthalene conversion of more than 81% is obtained over 10 h pre-treated olivine, which is observed to be the optimum among the selected range of pre-treatment times. The effect of the presence of various reactive gases is investigated as well. Naphthalene conversion in gas mixture containing H_2 and CO is found to be lower than that of only in presence of steam and CO_2. The presence of H_2 has a negative effect in terms of tar conversion. Steam and dry reforming reactions of naphthalene are mainly responsible for formation of valuable gaseous products such as H_2 and CO. Cracking reactions lead to formation of other lower tars. Polymerization reactions form higher tars which further condense leading to soot formation.

Olivine shows an attrition resistance, which is higher than that of sand and dolomite. The properties of olivine mentioned above make it a prospective candidate as an in-bed tar removal catalyst for fluidized-bed biomass gasifiers.

Samenvatting

Biomassa komt steeds sterker in de belangstelling te staan als het gaat om duurzame energie opwekking en het terugdringen van CO_2 emissies afkomstig van fossiele brandstoffen.

Vergassing is een veelbelovende technologie om biomassa om te zetten in energie, waterstof en biobrandstoffen. Een belangrijk nadeel is de teervorming tijdens de vergassing van biomassa. Gemiddeld wordt er ongeveer 10 g m^{-3} (STP) teer tijdens wervelbed gevormd. De toelaatbare hoeveelheid teer in het gas wordt echter bepaald door het gebruiker van het gas. De toegestane hoeveelheid teer in het gas dat verbrand wordt in gasmotoren dient veel lager te zijn dan 10 mg m^{-3} (STP). Uit de literatuur blijkt dat er reeds veel studie is verricht op het gebied van teerverwijdering. Technologieën voor teerverwijdering kunnen worden onderverdeeld in twee categorieën; namelijk primaire en secundaire technologie. In geval van secundaire technologie wordt teer verwijderd met een nageschakelde gasreiniging. Bij primaire methoden wordt teer in de vergasser zelf omgezet.

Dit proefschrift handelt over het onderzoek naar katalysatoren die geschikt kunnen zijn om teren in de vergasser om te zetten. Gekozen is voor olivine omdat dit een geschikte katalysator blijkt te zijn om teren in de vergasser om te zetten. De stabiliteit, selectiviteit en activiteit van deze katalysator in verschillende gassamenstellingen zijn onderzocht. Onderzoek is verricht naar de fundamentele aspecten van de ontleding en de kinetiek van de ontleding van teren. Hierbij is gebruik gemaakt van een breed spectrum aan karakteriseringtechnieken.

De katalysator olivine die in deze studie is toegepast is een natuurlijk voorkomend mineraal dat gewonnen wordt in Noorwegen. Het mineraal bevat silicaten en de oxiden van ijzer en magnesium. De katalytische activiteit van dolomiet en olivine zijn met elkaar vergeleken tijdens experimenten met vergassings gas van de ECN vergasser. Het bleek dat de activiteit bij 900^{0}C van olivine lager was dan die van dolomiet. Om het onderzoek te vergemakkelijken is naftaleen als representant gekozen voor teer. Dit omdat 60% van gevormde teerhoeveelheid uit naftaleen bestaat.

Een vast-bed reactor is toegepast om de katalytische ontleding van naftaleen over olivine bij 900^0C in synthetisch vergassingsgas te onderzoeken. Gebleken is dat de activiteit van olivine sterk toeneemt als de katalysator gedurende tien uren gecalcineerd wordt bij eveneens 900^0C. Een optimale conversie van 81% van naftaleen over olivine werd bepaald. De activiteitstoename is waarschijnlijk toe te schrijven aan de segregatie van ijzer aan het oppervlak van olivine. Gedurende de voorbehandeling werd een toename van de hoeveelheid van kristallijn hematiet in de tijd gevonden.

De samenstelling van het gas dat over de katalysator geleid werd, werd gevarieerd. De aanwezigheid van waterstof heeft een negatief effect op de conversie. De omzetting van naftaleen in een mengsel van H_2 en CO_2 bleek lager te zijn dan die in een mengsel van stoom en CO_2. Stoom en CO_2 reforming van naftaleen zijn verantwoordelijk voor de vorming van H_2 en CO. Er treden tijdens de omzetting van teer ook kraak- en polymerisatiereacties op. Polymerisatie leidt tot de vorming van roet en kool.

Als laatste kan gemeld worden dat olivine vergeleken met zand en met dolomiet een hoge attritie weerstand heeft. Dit maakt samen met de hoge activiteit dat olivine een veelbelovende kandidaat is voor de toepassing in wervel-bed vergassers.

List of publications

Journal papers

Devi, L., Ptasinski, K.J., Janssen, F.J.J.G., 2003. A review of the primary measures for tar elimination in biomass gasification processes. Biomass and Bioenergy 24, 125-140.

Devi, L., Ptasinski, K.J., Janssen, F.J.J.G., van Paasen, S.V.B., Bergman, P.C.A., Kiel, J.H.A., 2005. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. Renewable Energy 30, 565-587.

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Devi, L., Ptasinski, K.J., Janssen, F.J.J.G., 2005. Olivine as prospective tar removal catalyst for biomass gasifiers: kinetic approach. Industrial & Engineering Chemistry Research, in review.

Related publications

Devi, L., Smits, B. A., Ptasinski, K.J., Janssen, F.J.J.G., Bergman, P.C.A., Kiel, J.H.A., 2003. Catalytic decomposition of tars from biomass gasifiers. Proceedings of International Nordic Bioenergy Conference, Jyväskylä, Finland. pp. 418-420.

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Acknowledgements

Curriculum Vitae

Lopamudra Devi was born on March 1st, 1975 in Guwahati, India. In 1992 she completed higher secondary education from Cotton College, Guwahati. She received a Bachelor of Engineering degree with honours in chemical engineering from Assam Engineering College, Gauhati University (India). She joined the University Institute of Chemical Technology (formerly known as UDCT), Mumbai University in 1997 for post graduation in Chemical Engineering. Her Masters thesis was "Utilization of industrial waste: de-alkylation of di-tert-butyl hydroquinone". Immediately after obtaining Master's degree (M.Chem.Eng.) she started working as a lecturer in D.J. Sanghvi College of Engineering, affiliated to Mumbai University. In December 2000, she joined the group of Environmental Technology in the laboratory of Chemical Reactor Engineering at Eindhoven University of Technology. Her research was within the framework of the project "Primary measures for inhibition of tar formation in biomass fueled fluidized bed gasifiers" funded by the Dutch Foundation for Research in Sustainable Energy (SDE), The Netherlands. The research results have been published in various international journals and presented at different national and international conferences.