Tar reforming in biomass gasification gas cleaning

Noora Kaisalo
Tar reforming in biomass gasification
gas cleaning

Noora Kaisalo

A doctoral dissertation completed for the degree of Doctor of
Science (Technology) to be defended, with the permission of the
Aalto University School of Chemical engineering, at a public
examination held at the lecture hall Ke2 of the school on 18th August
2017 at 12:00.

Aalto University
School of Chemical Engineering
Department of Chemical and Metallurgical Engineering
Industrial Chemistry
Supervising professor
Professor Riikka Puurunen, Aalto University, Finland

Thesis advisors
Dr. Pekka Simell, VTT Technical Research Centre of Finland Ltd, Finland
Research Professor Juha Lehtonen, VTT Technical Research Centre of Finland Ltd, Finland

Preliminary examiners
Professor Lars J. Pettersson, KTH Royal Institute of Technology, Sweden
Professor Hermann Hofbauer, TU Wien, Austria

Opponent
Dr. Tilman J. Schildhauer, Paul Scherrer Institute, Switzerland

Aalto University publication series
DOCTORAL DISSERTATIONS 132/2017

© 2017 Noora Kaisalo

ISSN-L 1799-4934 ISSN-L 2242-119X
ISSN 1799-4934 (printed) ISSN 2242-119X (printed)
ISSN 1799-4942 (pdf) ISSN 2242-1203 (pdf)

Unigrafia Oy
Helsinki 2017

Finland
Abstract

Thermochemical conversion of biomass can be used to produce synthesis gas via gasification. This synthesis gas can be further upgraded to renewable fuels and chemicals provided that the gas is ultra clean. To achieve this, impurities, such as light hydrocarbons and tar compounds present in the gasification gas can be converted to syngas by reforming.

The amount of tar in gasification gas can be reduced already in the gasifier by using catalytically active bed materials. Typical bed materials in fluidized bed gasification are sand, olivine, dolomite and MgO. The tar conversion activity of dolomite and MgO were found to be high at atmospheric pressure. However, the activity was lost when the pressure was increased to 10 bar. Gasification gas contains, in addition to tar, ethene, which may contribute to further tar formation in high temperature zones of the process, especially at elevated pressures. Ethene forms tar compounds by radical chain reactions. The tar formed by thermal reactions of ethene resembles the tar from high temperature fluidized bed gasification, which contains mainly secondary and tertiary tar compounds.

Carbon formation on the reformer catalysts presents a challenge in biomass gasification gas cleaning. The presence of sulfur in the gas, mainly in the form of H2S, also complicates reforming. Typical catalysts used in the reformer after the gasifier are precious metal and nickel catalysts. The heat for reforming can be brought either indirectly in the case of steam reforming or by adding oxygen to the feed for autothermal reforming. Nickel and precious metal catalyst activities were analysed in experiments of around 500 hours with several different gas compositions. Catalyst deactivation was higher with steam than autothermal reforming. The use of catalytically active bed materials to reduce tar concentration already in the gasifier is especially favourable for steam reforming as the catalyst deactivation rate was decreased by the lower hydrocarbon content of the gas.

Benzene, a highly stable compound, is a typical residual compound in the gas after the reformer. Thus, the reformer could be designed based on the reforming kinetics of benzene, for example in the production of synthetic natural gas. For this purpose, qualitative analysis of the effect of the main gasification gas compounds (H2, CO, CO2, H2O) on reforming kinetics were studied with a nickel catalyst. Benzene reforming can be described by first order kinetics if the parameters are estimated for the specific gas composition.
Tiivistelmä
Biomassan termokemiallisella konversiolla voidaan tuottaa synteesikaasua kaasutusreitin kautta. Synteesikaasu voidaan jatkojalostaa uusiutuviksi poltttoaineiksi sekä kemikaaleiksi.
Synteeseisouluksia varten kaasun tulee olla ultrapuhdasta. Tämän saavutamiseksi epäpuhautetud, kuten keveät hiilivedet ja tervahdysteet voidaan konvertoida synteesikaasuksi reformoimalta.
Tervan määrää kaasutuskaasussa voidaan vähentää jo kaasuttimessa käyttämällä katalyytisesti aktiivisia petimateriaaleja. Leijukerrokskaasutuksessa tyypillisesti käytettyjä petimateriaaleja ovat hiekka, oliviini, dolomiitti ja MgO. Dolomiittiin ja MgO:n aktivisuus tervakonversion suhteen oli korkea ilmanpaineessa. Jos painetta nostettiin 10 bar:iin, katalyytinin aktivisuus käyttännössä katosi.
Kaasutuskaasu sisältää tervan lisäksi eteeniä, joka voi lisätä tervan muodostusta erityisesti paineistetuissa olosuhteissa prosessin kohdissa, joissa on korkea lämpötila. Eteeni muodostaa tervahdysteitä radikaaliketjureaktioilla. Terva, joka muodostuu eteenin termisiä reaktioista, muistuttaa korkean lämpötilan leijukerrokskaasuttimen tervaa, joka koostuu pääasiassa sekundäärisistä ja tertiäärisistä tervahyisteistä.

Avainsanat: biomassa, kaasutus, reformointi, terva, synteesikaasu, nikkeliatalyyt, jalometallikatalyyti

ISSN-L 1799-4934 ISSN (painettu) 1799-4934 ISSN (pdf) 1799-4942
Julkaisupaikka Helsinki Painopaikka Helsinki Vuosi 2017
Preface

The work presented in this thesis has been carried out at VTT Technical Research Centre of Finland Ltd during years 2012-2017. I would like to acknowledge financial support from VTT Technical Research Centre of Finland Ltd and Tekes -- the Finnish Funding Agency for Innovation through Vetaani and 2G2020 projects.

I would like to express my gratitude to my instructor Dr. Sc. Pekka Simell for sustained support and advice. I thank my original thesis supervisor Professor Juha Lehtonen for his interest and guidance in my work, and Professor Riikka Puurunen who agreed to be the official supervisor in 2017.

My sincere thanks to my co-authors Johanna Kihlman and Sanna Tuomi for fruitful and inspiring discussions. I am indebted to Mari-Leena Koskinen-Soivi, Katja Heiskanen and Päivi Jokimies for the experimental work and expertise in laboratory. Warm thanks to my co-authors Ilkka Hannula, Esa Kurkela, Ilkka Hiltunen and Matti Nieminen. I thank my colleagues at Biologinkuja 5 for providing a pleasant working atmosphere.

For my parents, Leena and Yki: thank you for your encouragement during my studies. My friends, I appreciate your support and taking my mind of work. Aapo, thank you for support to make this thesis ready.

Espoo, April 2017
Noora Kaisalo
List of publications

This thesis is based on the following original publications which are referred to in the text as I–V. The publications are reproduced with kind permission from the publishers.


Author’s contributions

Publication I: “Effect of process conditions on tar formation from thermal reactions of ethylene”
Author contributions: N. Kaisalo designed the experiments and calculated the results and was the main contributor in interpreting the results and writing of the manuscript. M-L Koskinen-Soivi carried out the experiments and gas chromatography analysis. P. Simell instructed the work, took part in planning of the experiments and commented the manuscript. J. Lehtonen reviewed and commented the manuscript.

Publication II: Effect of pressure on tar decomposition activity of different bed materials in biomass gasification conditions
Author contributions: S. Tuomi designed the biomass gasification experiments and calculated and analysed the results. N. Kaisalo designed the laboratory experiments and calculated and analysed the results of those. S. Tuomi and N. Kaisalo co-authored the article. P. Simell and E. Kurkela took part in the experimental design and commented on the manuscript.

Publication III: Reforming solutions for biomass-derived gasification gas – Experimental results and concept assessment
N. Kaisalo and J. Kihlman planned the experiments, calculated and analysed the results and wrote the experimental part of the article. N. Kaisalo carried out two of the experiments. I. Hannula carried out and wrote the concept assessment section of the article. P. Simell commented on the experimental design and the manuscript.

Publication IV: Benzene steam reforming kinetics in biomass gasification gas cleaning
N. Kaisalo designed the experiments, analysed the results, carried out the modelling work and wrote the manuscript. P. Simell participated in experimental design and result analysis. J. Lehtonen guided and assisted in the modelling work and commented on the manuscript.

Publication V: Clean syngas from biomass—process development and concept assessment
Author contributions: P. Simell was the main writer of the manuscript and the main developer of the catalytic reforming work reported in article. I. Hannula carried out and wrote the techno-economical assessment. S. Tuomi and M. Nieminen were responsible for the filtration part of the article. E. Kurkela and I. Hiltunen were responsible for the pilot-scale experimental planning and results. N. Kaisalo planned the laboratory catalyst testing experiments and calculated and wrote the results. J. Kihlman took part in experimental planning of reforming experiments and commented on the article.
# Contents

Preface .................................................................................................................................................. 1

List of publications ............................................................................................................................ 3

Author's contributions ....................................................................................................................... 4

List of abbreviations and symbols .................................................................................................. 7

1. Introduction .................................................................................................................................... 9

   1.1 Background and motivation ......................................................................................... 9

   1.2 Scope of the thesis ....................................................................................................... 9

2. Biomass gasification gas cleaning from tar and light hydrocarbons .......................... 11

   2.1 Process description .................................................................................................. 11

   2.2 Tar compounds and light hydrocarbons in the gasification gas ....................... 15

   2.3 Catalytically active gasifier bed materials ......................................................... 16

   2.4 Tar reformer ........................................................................................................... 18

       2.4.1 Catalysts and reactions ............................................................................. 18

       2.4.2 Demonstration plants with a reformer ..................................................... 19

       2.4.3 Carbon formation on the catalyst ............................................................ 20

       2.4.4 Kinetics of tar reforming ......................................................................... 21

3. Experimental ............................................................................................................................... 23

   3.1 Test apparatus ........................................................................................................... 23

   3.2 Composition of the feed gases ............................................................................. 24

   3.3 Catalyst materials ..................................................................................................... 25

4. Results and discussion .................................................................................................................. 28

   4.1 Tar formation from ethene .................................................................................. 28

   4.2 Catalytic activity of gasification bed materials in tar reduction ......................... 32

   4.3 Steam reforming versus autothermal reforming in biomass gasification gas cleaning .................................................. 35

   4.4 Reactor modelling ..................................................................................................... 41

   4.5 Kinetics of benzene reforming ............................................................................ 42

5. Conclusions .................................................................................................................................. 46

References ......................................................................................................................................... 49

Publications I–V
# List of abbreviations and symbols

**Abbreviations**

- **Air gaga** air gasification gas
- **BFB** bubbling fluidized bed
- **Bz** benzene
- **CFB** circulating fluidized bed
- **CHP** combined heat and power
- **DFB** dual fluidized bed
- **FID** flame ionization detector
- **FT** Fischer-Tropsch
- **FTIR** Fourier transformation infrared spectroscopy
- **GC** gas chromatograph
- **HACA** hydrogen abstraction and acetylene addition
- **HAVA** hydrogen abstraction and vinyl radical addition
- **HC** hydrocarbon
- **LH** low hydrocarbon content gas
- **MAC** methyl addition and cyclization
- **MH** medium hydrocarbon content gas
- **PAC** phenyl addition and cyclization
- **PDU** process development unit
- **SNG** synthetic natural gas
- **TCD** thermal conductivity detector
- **WGS** water gas shift
Symbols

$\text{c}_i$  concentration of a compound i (mol/m$^3$)

$E_a$  activation energy (kJ/mol)

$\Delta H_i$  adsorption enthalpy of a compound i (kJ/mol)

$K_i$  equilibrium constant for adsorption of a compound i

$K_{\text{ref}}$  equilibrium constant at reference temperature, 850 °C

$k'$  apparent reaction rate constant (m$^3$/s/kg$_{\text{cat}}$)

$k_{\text{ref}}$  apparent reaction rate constant at reference temperature, 850 °C (m$^3$/s/kg$_{\text{cat}}$)

$m_{\text{cat}}$  mass of the catalyst (kg)

$n_i$  molar flow of a compound i (mol/h)

$p_i$  partial pressure of a compound i (Pa)

$R$  gas constant (kJ/(K*mol))

$r_i$  rate of reaction of a compound i (mol/kg$_{\text{cat}}$*h)

$T$  temperature, K

$z$  dimensionless weight of the catalyst bed

$\alpha$, $\beta$  reaction orders

$\Theta_s$  surface coverage by sulfur
1. Introduction

1.1 Background and motivation

Levels of anthropogenic greenhouse gas emissions in the atmosphere have been rising since the beginning of the industrial era (1750), yet around half of all emissions occurred since 1970 [1]. Increasing carbon dioxide emissions have been identified as a primary cause of global warming [1]. The Paris Agreement on climate change, which entered into force in 2016, sets goals for greenhouse gas emission reductions [2]. For example, the EU has committed under the Paris Agreement to reducing greenhouse gas emissions by at least 40% by 2030 compared to 1990 levels [3]. To mitigate CO₂ emissions and achieve climate objectives, the use of renewable energy sources is essential. In addition to environmental drivers, also political drivers exist for the exploitation of locally produced energy sources instead of dependency on geographically limited oil reserves.

Biomass is an important part of the renewable energy mix alongside with solar, wind and hydropower. Use of cellulosic biomass, especially wastes and residues, avoids competition with the food chain. Searle and Malins [4] have evaluated the total amount of sustainably available cellulosic waste and residue to be around 220 million tonnes per year in the EU. The amount of forest residue was evaluated at 40 million tonnes per year. The amount of all sustainably available cellulosic waste and residue corresponds to 1 million barrels of oil equivalent per day, which would mean 13% of road fuel consumption in the EU in 2020. However, they evaluated that only 8% of forest residue in the EU was used in 2013. In Finland, forest industry residues are a major potential biomass feedstock. By using biomass for fuel or chemical production, dependency on imported oil can be reduced.

Thermochemical conversion of biomass is an option for the production of renewable fuels or chemicals. By gasification, solid biomass can be converted to synthesis gas (syngas), which is a platform for various end products from combined heat and power (CHP) production to fuels and chemicals. An essential aspect of biomass conversion to syngas is the cleaning of the gas from various impurities. A typical feature of biomass gasification is tar formation. Tar consists of a range of aromatic hydrocarbons; by converting them by reforming to H₂ and CO, the syngas yield increases. However, the reforming conditions are challenging and require understanding of how the process conditions affect the operation of the reformer.

1.2 Scope of the thesis

The thesis comprises five publications related to catalytic gas cleaning of hydrocarbons either in a gasifier or in a reformer after the gasifier. The relations of the publications to each other and to the gasification process are presented in Figure 1. The scope of the thesis was mainly to investigate the reformer. The hydrocarbon
load and gas composition from the gasifier affect the reformer operation, for example, by affecting the carbon formation. Thus, the reformer studies were supported by studies of thermal reactions of ethene and the catalytic activity of the bed materials of the fluidized bed gasifier.

Figure 1. Relation of thesis publications to each other and to the gasification process.

The formation of tar compounds from ethene was studied in Publication I. Light hydrocarbons in the biomass gasification gas may form tar compounds in high temperatures and thus affect the operation of the reformer by adding the hydrocarbon load on the catalyst. Such high temperature zones may exist, for example, in the inlet area of the reformer or in the gasifier free board.

The hydrocarbon and tar content of biomass gasification gas can be reduced already in the gasifier by catalytically active bed materials. Publication II addresses the questions: Can catalytically active bed materials help to achieve conditions where reforming can be done easily and how does pressure affect their efficiency in reducing tar levels?

Pressurizing the gasification and gas cleaning processes is beneficial for process economics and efficiency, but it may present operational challenges for reforming. Thus, the thermal reactions of ethene (Publication I) and the activity of the bed materials (Publication II) were studied under pressurized conditions.

Steam and autothermal reforming of tar and light hydrocarbons with nickel and precious metal catalysts were studied in Publications III and V. The catalyst lifetime in both reforming modes and the effect of hydrocarbon load in the gas was investigated in Publication III by long-term catalyst testing. Publication V focused on the effect of the catalyst choice on methane conversion. The desired level of methane conversion in reforming depends on the process concept.

Benzene steam reforming kinetics was studied in Publication IV. The study addresses the effect of gas composition on the kinetics of benzene steam reforming.
2. Biomass gasification gas cleaning from tar and light hydrocarbons

2.1 Process description

Gasification of biomass in fluidized bed gasifiers has been identified to be feasible for forest residue gasification at scale of around 100-300 MW fuel input [5]. The gasification reactions are endothermic and thus require heat. The heat for the reactions can be brought directly by partly oxidizing the feedstock with air or oxygen. Alternatively, steam can be used as a gasification medium, in which case the heat for the reactions needs to be brought indirectly by circulating the hot bed material. The fluidized bed gasifiers can be operated as circulating or bubbling fluidized beds. In dual fluidized bed gasifiers, the gasification of biomass takes place in one fluidized bed and the combustion of residual char in the other. The heat is transferred between the fluidized beds by the bed material. The circulating fluidized bed (CFB) and dual fluidized bed (DFB) gasifiers at VTT are presented in Figure 2 and Figure 3, respectively.

Figure 2. CFB gasifier at VTT
The gas composition obtained by gasification depends on the gasifying agent, process conditions and feedstock. Typical gasification temperatures in fluidized bed gasifiers are 750 – 950 °C. With air gasification, a downside is that the product gas is diluted by N₂. For synthesis purposes, the nitrogen is an inert gas and dilution by it would lead to high costs of gas compression [6]. The air gasification gas also has low energy contents: 3-7 MJ/Nm³ compared to 7-15 MJ/Nm³ for oxygen gasification gas [7].

The gas exiting the gasifier contains impurities that need to be removed for the advanced use of biomass gasification gas. For example, the synthesis processes require ultra clean syngas. An example process concept for the production of synthetic fuels by Fischer-Tropsch (FT) synthesis is presented in Figure 4 (Publication V). The particulates in the gas exiting the gasifier can be removed by a hot gas filter, whereas the tar compounds and light hydrocarbons can be converted by reforming to syngas. For tar removal, another possibility is scrubbing by an organic solvent [8,9]. However, the gasification gas also contains minor impurities, such as H₂S, COS, NH₃ and alkali metals. Especially sulfur compounds further complicate the reforming of hydrocarbons by poisoning the catalyst. In addition to hydrocarbons, ammonia is partly converted to N₂ in the reformer [10]. The alkali metals, in turn, will condense in hot gas filtration taking place at around 500 °C [11]. The final conditioning of gas for synthesis purposes can be realized by conventional commercial technologies for acid gas removal, such as the Rectisol process, and the H₂/CO ratio can be adjusted by a water gas shift reactor [12].
Figure 5 presents the concepts for FT, synthetic natural gas (SNG) or \( \text{H}_2 \) production by gasification developed at VTT. The \( \text{O}_2 \)-steam blown gasification concept with FT synthesis has been demonstrated in Varkaus [13] and the gasification and gas cleaning has been tested extensively at VTT’s process development unit (PDU) [14,15]. Prior to the demonstration, the gasification and gas cleaning by filtration and reforming were developed at VTT and tested on VTT’s 0.5 MW fuel input PDU test rig. The gas cleaning was realized by hot gas filtration and reforming of hydrocarbons followed by final gas ultra-cleaning and conditioning at Varkaus. Kurkela et al. [14] have reported the results of a 215 h-run of gasification and gas cleaning on the PDU. The concepts based on steam gasification in DFB combined with filtration at the gasifier outlet temperature followed by steam or oxidative reforming are under development.

For the pressurized oxygen blown gasification concept, Hannula and Kurkela [12] have calculated the cost estimates for the production of FT liquids in a stand-alone plant. Forest residues were used as feedstock for plants with 300 MW biomass input. The cost estimates were developed for a so-called \( \text{N}^{\text{th}} \) plant, i.e. after the technology has been commercialized. The thermal efficiency of producing FT liquids was calculated to be 52% (LHV). The levelized production cost was estimated at 75 €/MWh. The total capital investment cost for the plant was estimated at 370 M€. The gasifier accounted for 51 M€ and hot gas cleaning including the filtration and reformer for 38 M€. The share of the reformer in the cost of the hot gas cleaning train was about 75%.

Pressurised oxygen blown gasification is targeted at a relatively large scale, around 300 MW fuel input, to be economic, whereas steam gasification would be suitable for 100-200 MW scales where the production of oxygen would render the process uneconomic [16]. For example, in the oxygen blown gasification concept, the investment cost of the air separation unit was evaluated at 47 M€ [12]. In addition, steam gasification is suitable for uses where high \( \text{H}_2/\text{CO} \) ratios are desirable, such as SNG production, since the large steam input drives the water-gas shift reaction on the side of \( \text{H}_2 \) (Publication III).
Figure 5. Gasification and gas cleaning concepts for FT production by steam-oxygen blown gasification, and steam gasification concepts for SNG and H₂ production with autothermal or steam reforming.

Pressurizing the process is of interest for concepts where the final steps are at high pressure, such as FT or methanol synthesis. Pressurization reduces the production cost by reducing the compression costs [17]. For example, in methanol production by oxygen-blown gasification of biomass, the production costs decrease around 3-4% by increasing the gasification pressure from 1 to 5 bar [6]. However, high pressure may lead to operational problems, such as ash sintering and melting [15].

Steam-blown DFB gasifiers are more suitable for relatively low pressure due to more difficult operation of the dual fluidized bed, whereas oxygen blown gasifiers could be pressurized to higher pressures close to synthesis pressures [17]. The low operation pressure makes the DFB gasifier suitable for relatively low pressure synthesis, such as methanation, or for H₂ production. The economic feasibility of both gasification concepts is strongly dependent on the integration of the process with forest industry or other heat-consuming industry [6], Publication III.

Biomass gasifiers are industrially used for CHP production, for example, air-blown CFB gasifiers in Finland and indirectly heated DFB steam gasifiers in Austria and Germany [14]. The Güssing gasifier in Austria is a steam-blown DFB reactor operating at 8 MW of fuel [18]. There are several other gasifiers based on the same technology in Senden 15 MWth, Villach 15 MWth, Oberwart 8.5 MWth [19]. These
DFB gasifiers have been equipped with gas cleaning by scrubbing with organic solvent [19]. In addition to CHP production, a biomass gasification plant in Gothenburg produces 20 MW of SNG [20]. There the gasification process is based on a similar steam-blown DFB concept as the Güssing plant. Gas cleaning for the synthesis is carried out by scrubbing the tars and converting the remaining light hydrocarbons in a reformer before the synthesis.

2.2 Tar compounds and light hydrocarbons in the gasification gas

Tar compounds are formed during gasification when biomass decomposes in pyrolysis and gasification reactions. Primary tar compounds are mostly oxygenated compounds that are decomposition products of biomass [8,21]. These compounds react further and form secondary and tertiary tar compounds [8], which consists of compounds that do not exist in the source biomass [22]. The secondary tar is described as alkylated one- and two-ring aromatic compounds including heterocyclic compounds [21], whereas tertiary tar consists of aromatic hydrocarbons such as benzene, naphthalene and various polycyclic aromatic hydrocarbons (PAH) [22]. In addition to describing tar compounds by their formation process [23], tar is typically classified based on the number of rings in the tar compound [8,24] or by boiling point distribution or physical properties [25]. In tar protocol [26], tar is defined as aromatic compounds that are heavier than benzene. Furthermore, an operational definition for tar depending on the end-use application has been used [22].

During the gasification process, radicals and small hydrocarbon molecules are formed from biomass pyrolysis vapours [27]. At high temperatures these light compounds react to form tar compounds in pyrolysis reactions, the majority of which takes place in the gas phase by free radical mechanisms [28]. A schematic figure of tar formation is presented in Figure 6. Shukla and Koshi [29,30] have explained aromatic growth by various radical reaction mechanisms such as hydrogen abstraction and acetylene addition (HACA), hydrogen abstraction and vinyl radical addition (HAVA), phenyl addition and cyclization (PAC) and methyl addition and cyclization (MAC). Via the radical chain reactions, the tertiary and secondary tar compounds can be formed at high temperature from light hydrocarbons, such as ethene, in the gasification gas.

The composition and amount of tar depends on the gasifier type and gasification temperature. Tar from the fluidized bed gasifier can be characterized as secondary and tertiary tar [8]. Increasing gasification temperature typically reduces the amount of tar but increases the share of heavier compounds. The effect of pressure on tar composition has been less studied and not in a systematic manner [21,31–34]. Based on these studies, no general trend of tar amount evolution with pressure increase can be deduced. However, it can be seen that with pressure increase the composition of tar shifts more towards heavier compounds.
In addition to tar and main gasification product gases (CO, CO₂, H₂), the main light hydrocarbon compounds are typically methane and ethene [15,35]. In steam gasification, the ethene content is typically higher, up to 4 vol-% in dry gas [35], than in air or steam-oxygen blown gasification, where it reaches 0.2-1.2 vol-% in dry gas [11,15]. Often the light hydrocarbons are not reported in detail in biomass gasification studies since they are not considered as problematic as tar compounds. However, they may contribute to further tar formation in the process.

2.3 Catalytically active gasifier bed materials

In fluidized bed gasifiers, catalytically active bed materials can be used to ease the cleaning of biomass gasification gas by reducing tar load. In addition to their catalytic tar decomposing effect, the bed materials affect the sintering properties of the bed. By selecting a proper bed material, higher temperatures or pressures may be used in the gasifier without problems.

The typical bed materials used in biomass gasification are low-cost natural minerals. Catalytically active materials, such as dolomite, olivine, magnesite and limestone, may be used alone or mixed with sand. Catalytically active bed materials are reviewed by, e.g., Abu El-Rub et al. [36], Sutton et al. [37], Dayton [38] and Shen & Yoshikawa [39].

Dolomites are the most widely studied non-metallic catalyst for biomass gasification gas cleaning [38]. The use of dolomites has been studied as bed materials as well as catalysts for a separate reformer after the gasifier. Dolomite is used at the
commercial scale in the Skive plant in Denmark, for example [40]. Dolomites are calcium magnesium ores (CaCO$_3$·MgCO$_3$), the exact composition of which depends on their geological origin [41,42]. Dolomites are effective in reducing heavier tar compounds, but less effective for benzene, naphthalene and methane decomposition [38]. Tuomi et al. [43] report the activity of dolomite compared to sand: with dolomite as a bed material the tar level was 5.7 g/Nm$^3$, whereas sand as a bed material lead to a tar concentration of 20 g/Nm$^3$ in steam gasification of wood at 800 °C. Dolomite has been reported to be especially effective for tar compounds formed in steam gasification compared to more refractory tar of air gasification gas [42].

For dolomite to be active it has to be calcined, as the carbonate form is not nearly as active as the oxide form [41]. The calcination temperature depends on the partial pressure of CO$_2$. If the partial pressure of CO$_2$ increases over the calcination/carbonation limit of dolomite, the calcium in dolomite forms carbonate. This limits the usage of dolomites to low pressures. A downside of dolomite is that in calcined form it is brittle and suffers from attrition in the fluidized bed [38]. In addition, at pressures higher than 4 bar, bed sintering and formation of agglomerates has been observed with dolomite[15].

Olivine has been studied as an alternative to dolomite. The key advantage of olivine over dolomite is its attrition resistance comparable to sand [44]. However, its activity is generally somewhat lower than that of dolomite [25,44–48]. Olivine is a silicate mineral that contains magnesium and iron (Mg,Fe)$_2$SiO$_4$. Olivine is used, for example, in steam gasification plants using woody biomass as feedstock at Güssing [49] and at Gothenburg [20].

Olivine is activated during the gasification of biomass by formation of a calcium-rich layer on top of the particles from biomass ash and possible bed additives, such as dolomite [50,51]. At the Gothenburg biomass gasification plant, olivine is activated by addition of K$_2$CO$_3$ to the gasifier [20]. The addition of K$_2$CO$_3$ reduced tar amounts from 43.1 g/Nm$^3$ to 13.1 g/Nm$^3$. Marinkovic et al. [52] have investigated how olivine activates during gasification. They followed tar concentrations over three days without replacing the bed material and tar levels were reduced 30% from the levels of the first day. They did not observe migration of iron to the surface of the particles. They explained the activity of olivine as being due to the potassium in the biomass remaining in its active form and catalysing the gasification reactions, whereas sand binds potassium leading to low tar decomposition activity. In addition, Devi et al. [53,54] have reported that calcination may improve the catalytic activity of olivine.

Magnesium oxide has also been tested as a bed material. Kurkela et al. [15] reported in pressurized steam-oxygen gasification of woody biomass that tar levels were almost similar with magnesium oxide as with dolomite. They also observed that magnesium oxide could be used as bed material even at 6 bar pressure without the bed sintering problems encountered with dolomite.
2.4 Tar reformer

2.4.1 Catalysts and reactions

For synthesis purposes, secondary cleaning measures are required to convert tar compounds and light hydrocarbons to synthesis gas. In the gasifier itself, tar levels lower than 2-4 g/Nm³ are difficult to achieve due to insufficient contact between the gas and bed material [55]. Reforming is widely studied and shown to be an efficient technology for gas cleaning. In addition to reforming, tar compounds can be decomposed to syngas by thermal cracking. However, thermal cracking suffers from soot formation and efficiency penalty since the temperature needs to be >1100 °C [39, 58], which is higher than typical gasifier outlet temperatures. This high temperature can be achieved by partial oxidation of the gas. Reforming of tar, instead, takes place approximately at the gasifier outlet temperatures.

Steam reforming of hydrocarbons is a well-established industrial process for natural gas and naphtha feeds. Reforming of biomass gasification gas, however, has some special features compared to natural gas or naphtha reforming. The hydrocarbons that need to be reformed from biomass gasification gas are aromatic tar compounds and light olefins, such as ethene, which are more prone to carbon formation than typical steam reformer feedstocks. Another special feature is that the gas contains sulfur compounds. Sulfur is mostly in the form of H₂S (around 100 ppm) and a few ppm of COS. Kaufman-Rechulski et al. [57] have reported small amounts of organic sulfur compounds, such as thiophene, methyl-thiophenes and benzo[b]thiophene, in air gasification of wood at 730-740 °C with a total concentration of organic sulfur compounds of 3.2-8.5 mg S/Nm³. Sulfur compounds complicate reforming by poisoning the catalyst. However, study by Hepola [58] shows that catalyst activity can be retained by using reforming temperatures above 900 °C.

Steam reforming reactions for benzene are presented in reactions (1) and (2). Since the gasification gas contains CO₂, the dry reforming reaction (3) may take place as well. In addition to reforming reactions, the water-gas shift (WGS) reaction (4) takes place simultaneously with reforming reactions, affecting the product distribution [59]. Also, due to high temperatures, hydrocarbons may crack thermally (5). Since steam reforming reactions are strongly endothermic, heat is required to process the gas. The reformer may be an indirectly heated steam reformer or an autothermal reformer where the heat for reforming is obtained by partial oxidation (6) by adding air or oxygen to the gasification gas.

\[
\begin{align*}
C_6H_6 + 6H_2O &\rightarrow 6CO + 9H_2 \\
C_6H_6 + 12H_2O &\rightarrow 6CO_2 + 15H_2 \\
C_6H_6 + 6CO_2 &\rightarrow 12CO + 3H_2 \\
CO + H_2O &\leftrightarrow CO_2 + H_2 \\
C_6H_6 &\rightarrow wC_H + (3 - wy/2)H_2 \\
C_6H_6 + 3O_2 &\rightarrow 6CO + 3H_2
\end{align*}
\]
Several types of catalysts have been studied for reforming hydrocarbons in biomass gasification gas and these are reviewed in [38,39,56,60,61]. Typical catalysts are nickel and precious metal catalysts. Nickel catalysts have been traditionally used in industrial steam reforming of natural gas. Steam reforming nickel catalysts are active in tar and methane conversion and, in addition, have WGS activity and are effective in ammonia conversion [38]. Their disadvantage is that they are prone to coke formation. Precious metals are less prone to this, but their price is high. Kurkela et al. [17] reported in biomass gasification gas reforming that at pressurized conditions carbon formation was more of a problem with a nickel catalyst than with precious metals. In addition to better carbon gasification with precious metals compared to nickel, they are reported to be more resistant to sulfur poisoning. Rönkönen et al. [62] reported that the Rh/ZrO$_2$ catalyst was more resistant to sulfur poisoning than the Ni/ZrO$_2$ catalyst in tar reforming. In addition, Rhyner et al. [63] observed that precious metal catalysts are highly active in converting organic sulfur compounds.

2.4.2 Demonstration plants with a reformer

Catalytic gas cleaning developed by VTT has been demonstrated at the Skive, Kokemäki and Varkaus plants. In Skive and Kokemäki, the gas was unfiltered and monoliths were used, whereas in Varkaus the gas was filtered before reforming. Filtering the gas before reforming allows the use of fixed bed of catalyst particles instead of monoliths, which makes the catalyst packing more simple [14]. Most of the demonstration results and details of reformers are confidential information and are not published.

At Kokemäki, a tar reformer was connected to a fixed bed updraft type Novel gasifier with a plant capacity range of 1-4 MW [64]. The reformer at Kokemäki was operated in catalytic partial oxidation mode, whereas the reformer at Skive operates in steam reforming mode [65]. Kurkela et al. [64] reported that the reformer of Kokemäki gasifier consisted of zirconia and nickel monoliths operated at a temperature range of 700-900 °C. Several catalysts were tested in slip stream and the optimized version was tested for 750 h showing stable activity. Heavy tar conversion of 75% and naphthalene conversion of 50% were achieved allowing use of the gas in a gas engine.

VTT has patented [55,66–68] a staged reformer which consists of three stages. The reactor concept is presented in Figure 7. In the first stage, heavy tar compounds are partially oxidized by a zirconia catalyst. The zirconia pre-reformer part is followed by a precious metal catalyst, which is used to further reduce the amount of tar and light intermediates, such as ethene and butadiene, in the gas. The last nickel stage is for final conversion of tar and methane. Zirconia and precious metal catalysts are needed to protect the nickel catalyst from carbon formation. The reformer is operated autothermally by feeding O$_2$ to different stages. The use of ZrO$_2$ catalyst allows lower operational temperatures, and the temperature of the reformer is gradually increased from around 600 °C in the ZrO$_2$ stage to 950 °C at the outlet.
Figure 7. Staged reformer concept developed by VTT.

The staged reformer concept with zirconia catalyst as a pre-reformer stage has been demonstrated to be technically feasible in connection with oxygen blown gasifier. Kurkela et al. [14] reported a 215 h gasification experiment at 2 bar pressure where the staged reformer was used connected to an oxygen blown gasifier and a hot gas filter. In the experiment, the pre-reformer consisted of a ZrO₂ and a precious metal catalyst in monolith form, whereas the nickel catalyst in the final stage of the reformer was in particulate form. The oxygen was fed in the pre-reformer and O₂/steam mixture to the nickel bed to achieve the target operation temperatures. In the pre-reformer, the temperature was increased from the filtration temperature of 550 °C to 800-850 °C. No signs of coke formation during the experiment were observed. In the reformer, complete C₂ conversion was obtained. Tar conversion was 98-99% and benzene conversion 93-99%, whereas methane conversion was 55-80%. The highest conversions were obtained with crushed wood pellets due to lower sulfur content of the feedstock compared to bark or forest residues.

2.4.3 Carbon formation on the catalyst

Catalyst deactivation by carbon formation on the catalysts is one of the main problems in tar reforming. To be economically feasible, the catalyst lifetime in the reformer should be at least 1-2 years (Publication V), which means that coke formation should be completely avoided.

Carbon may form on the catalyst by many routes. Rostrup-Nielsen [69] has classified the formation of carbon on the catalyst based on operation conditions. At low
temperatures, encapsulating gum may be formed by polymerization reactions of adsorbed hydrocarbons. At intermediate temperatures on nickel catalysts, carbon may form whiskers which mechanically destroy the catalyst. With precious metals, whisker carbon formation is avoided since they do not dissolve carbon [70]. Pyrolytic carbon and soot are formed at high temperatures and are therefore the most relevant for biomass gasification gas cleaning conditions due to high temperatures in the reformer.

Pyrolytic carbon is formed from hydrocarbons by thermal cracking reactions [71]. Firstly, the unsaturated molecules and hydrocarbon radicals are formed at high temperature. Secondly, they polymerize and dehydrogenate forming larger, tar-like compounds that deposit on the reactor walls and catalyst surfaces covering and encapsulating the particles and filling the voids. Thirdly, the deposited compounds dehydrogenate further to form solid coke leading to blockage of the reactor. The low activity of the catalyst may lead to takeover of thermal cracking reactions leading to soot formation [70].

Process parameters, such as temperature, pressure, steam-to-carbon or oxygen-to-carbon ratio and the nature of hydrocarbons affect the carbon formation on the catalyst. The O/C and H₂O/C ratios of the inlet gas are typically used to describe the conditions in which the steam reformer can be operated in coke-free conditions. The minimum H₂O/C ratio is based on experimental knowledge, not on any fundamental or theoretical calculations although a principle of equilibrated gas can be applied for methane steam reforming [69]. A safe H₂O/C ratio depends on the catalyst type: nickel or precious metal, as well as on the nature of the hydrocarbons in the feed. Unsaturated hydrocarbons form carbon more easily than saturated ones [72]. For example, compared to n-paraffins, benzene and ethene showed much higher coking rates [73]. Consequently, the hydrocarbons in biomass gasification gas form carbon more easily than natural gas.

2.4.4 Kinetics of tar reforming

Kinetic studies of steam reforming of biomass gasification gas are carried out either by using a side-stream of real gasifiers or with model gas mixtures in the laboratory. In studies using real biomass gasification gas, the tar compounds have been typically combined in one or several lumps. The data obtainable for modelling from side stream studies with real gasifiers is more limited in the sense that the gas composition cannot be varied as freely as with model gases. On the other hand, many studies conducted with model gases and tar model compounds do not include, for example, H₂S in the gas feed, even though it is present in biomass gasification gas at levels of 40-120 ppm (Publication V) and is a known catalyst poison. The models used in kinetic studies of tar reforming are often first order kinetic models towards tar or tar model compounds. The kinetics of steam reforming of tar compounds has been reviewed by Font Palma [74].

Steam reforming is a fast, strongly endothermic surface reaction, which is easily limited by mass and heat transfer. Thus, for kinetic studies, the conditions have to
be chosen carefully. In typical industrial natural gas (or naphtha) steam reformers, the effectiveness factor for the catalyst particles is very low [71]. Gas film diffusion limits the reaction rate severely with industrial-scale catalyst particles [75].

Jess [76] has studied benzene and naphthalene steam reforming with a nickel catalyst in gas atmospheres consisting of \( \text{H}_2 \), \( \text{H}_2\text{O} \) and \( \text{N}_2 \). For benzene, the first-order kinetics was assumed, but with naphthalene the reaction order was modelled to be 0.2 and for \( \text{H}_2 \) and \( \text{H}_2\text{O} \) the orders were 0.3 and 0, respectively. The activation energy for naphthalene reforming was 332 kJ/mol, whereas for benzene it was 196 kJ/mol. Swierczynski et al. [77] studied toluene reforming on a Ni/olivine catalyst in \( \text{H}_2\text{O} \) and argon atmosphere. They used first-order kinetics for modelling. Corella et al. [78] used a lump model for the kinetics of tar reforming for tar from the air gasifier. Their model consists of six tar compound lumps for which they have established a reaction network in which each of the reactions is represented by the first-order kinetics.

A power law model for naphthalene reforming without \( \text{H}_2\text{S} \) in the feed was used by Devi et al. [79]. The reaction order for naphthalene in their study was 2.04, which is quite far from the reaction order obtained by Jess [76], which was 0.2. The gas composition used by Devi et al. included \( \text{H}_2 \), \( \text{H}_2\text{O} \), \( \text{CO} \) and \( \text{CO}_2 \), whereas the gas composition used by Jess consisted only of \( \text{H}_2 \) and \( \text{H}_2\text{O} \).

Simell et al.[80,81] have used a Langmuir-Hinshelwood type model for steam and dry reforming of benzene on a dolomite catalyst. They found that hydrogen inhibits the reforming reaction rate. In contrast, Depner and Jess [75] studied kinetics of methane, benzene and naphthalene reforming on Ni/MgO catalyst and, in their model, steam or hydrogen had no influence on the reforming rate. Their gas contained \( \text{H}_2 \), \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) but no \( \text{CO} \) or \( \text{CO}_2 \) in the feed.

Rhyner et al. [82] have studied kinetics on precious metal catalyst in the presence of sulfur compounds. For methane steam reforming and for WGS reaction, they used a Langmuir-Hinshelwood type kinetic model with a sulfur adsorption term in denominator. For tar, ethene and sulfur containing hydrocarbons they used first-order power law kinetics.
3. Experimental

3.1 Test apparatus

The experimental work in this study was based on a laboratory-scale fixed bed reactor. The general layout of the system is presented in Figure 8. The gases were fed from the gas cylinders by mass flow controllers. The ion exchanged water and tar model compounds were fed by the HPLC pumps. Water was fed through a vaporizer to the heated line with the gases, whereas tar was fed straight to the heated gas line. The experiments were conducted in a quartz reactor placed in a three-zone furnace; in the pressurized experiments the quartz reactor was placed in a pressure vessel made of steel. The products were analysed by an online gas chromatograph (GC/FID and/or GC/TCD), FTIR and gas analyser.

Figure 8. General layout of the experimental set-up

For studies of thermal reactions of ethene (Publication I), an empty quartz reactor tube was used with an inner diameter of 10 or 15 mm depending on the conditions. The reactor was equipped with a thermocouple pocket of 4 mm. The temperature profile of the reactor was measured under N₂ flow. During the experiments, the thermocouple was placed at the maximum point of this profile. The measured temperature was used in the calculation of the residence time. The flow was adjusted to maintain a constant residence time when changing the temperatures and pressures. Typically, each experimental condition was kept for 2-3 h. For the analysis of H₂ a gas analyser was used, whereas hydrocarbons were analysed by online GC/FID. In
addition to the online analysis, gas bags and liquid tar samples were taken at certain experimental conditions.

In the bed material tests (Publication II), the gas flow was adjusted to keep the residence time at 0.1 s when the pressure was varied. To keep the residence time constant, two different quartz reactors were used with inner diameters of 16 mm and 27 mm. The temperature was measured from the centre of the catalyst bed. Each experimental condition was maintained for around 2 h. The dolomite was calcined at 900 °C in experiments where conditions were such that the dolomite was in oxide form. The experiments with dolomite in carbonate form were done separately from the experiments in which dolomite was in oxide form.

In catalyst testing experiments (Publication V) and in long-term experiments (Publication III), a gas flow of 2 dm³/min was used. The quartz reactor had an inner diameter of 27 mm and was equipped with a 4 mm thermocouple pocket. Temperature was measured below the catalyst bed. The catalyst was reduced in-situ by exposure to model gasification gas. In the catalyst testing experiments (Publication V), the duration of each experimental condition was around 1.5-2 h.

In the steam reforming kinetics study (Publication IV), a reactor with an inner diameter of 10 mm with a 4 mm thermocouple pocket was used. The gas flow used in the experiments was 1 dm³/min. The catalyst was reduced in-situ with a H₂:N₂ 1:1 mixture for 1 h. The first experimental condition was run for at least 4 h to stabilize the catalyst activity. Further conditions were run for 1-2 h. Every fifth experimental condition was a reference condition where the catalyst activity was checked.

### 3.2 Composition of the feed gases

In the studies of thermal reactions of ethene (Publication I), the gas consisted of 5 vol-% of ethene in nitrogen. The gas compositions used in the catalyst activity testing (Publication V) and in long-term experiments (Publication III) are presented in Table 1. The gas compositions corresponded to different kinds of biomass gasification gases. The low hydrocarbon content gas (LH) corresponded to steam gasification gas with dolomite as the bed material. The medium hydrocarbon content gas represented steam gasification gas with sand as the bed material, which was also close to the composition of steam-oxygen blown gasification gas. The tar model compound mixture contained 10 wt-% benzene, 80 wt-% toluene and 10 wt-% naphthalene. The gas composition (Air gas, Table 1) used for testing the activity of the bed materials was based on the atmospheric air gasification of crushed bark pellets in BFB with sand as bed material.

The gas mixtures used for benzene steam reforming kinetic studies contained, depending on the conditions, CO, CO₂, H₂, N₂, H₂S and H₂O in addition to benzene. In the kinetic experiments, pure benzene was used instead of a tar model compound mixture. An H₂S level of 100 ppm was chosen based on the typical concentration of H₂S in biomass gasification gas.
Table 1. Dry gas compositions used in long-term reforming experiments (LH is low hydrocarbon content gas and MH is medium hydrocarbon content gas) (Publication III), the composition of air gasification gas (Air gasa) used in activity testing of bed materials (Publication II), and the gasification gases (Gasification gas 1 and 2) used in kinetic experiments (Publication IV).

<table>
<thead>
<tr>
<th></th>
<th>LH</th>
<th>MH</th>
<th>MH+O₂</th>
<th>Air gasa</th>
<th>Gasification gas 1</th>
<th>Gasification gas 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, vol-%</td>
<td>19.2</td>
<td>25.0</td>
<td>25.0</td>
<td>15.0</td>
<td>12.5</td>
<td>25.0</td>
</tr>
<tr>
<td>CO₂, vol-%</td>
<td>22.7</td>
<td>20.0</td>
<td>20.0</td>
<td>15.0</td>
<td>15.0</td>
<td>20.0</td>
</tr>
<tr>
<td>H₂, vol-%</td>
<td>50.6</td>
<td>35.0</td>
<td>35.0</td>
<td>20.0</td>
<td>11.0</td>
<td>35.0</td>
</tr>
<tr>
<td>CH₄, vol-%</td>
<td>6.3</td>
<td>10.0</td>
<td>10.0</td>
<td>3.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O₂, vol-%</td>
<td>0.0</td>
<td>0.0</td>
<td>3.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N₂, vol-%</td>
<td>0.0</td>
<td>7.8</td>
<td>4.4</td>
<td>45.4</td>
<td>61.5</td>
<td>20.0</td>
</tr>
<tr>
<td>C₂H₄, vol-%</td>
<td>1.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NH₃, vol-%</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂S, ppm</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Tar, g/Nm³</td>
<td>10</td>
<td>20</td>
<td>20</td>
<td>10</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>H₂O, vol-%</td>
<td>30.0</td>
<td>40.0</td>
<td>40.0</td>
<td>12.0</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

3.3 Catalyst materials

The catalytic activity of gasification bed materials (Publication II) was investigated with dolomite (Myanit D, Sweden), MgO (M85, Slovakia), olivine and silica sand (Maxit hiekkatuote). The silica sand was considered an inert reference material. The properties of the bed materials are shown in Table 2. The particle size of the bed materials was 0.25-0.56 mm in the laboratory experiments, whereas a smaller fraction of 0.10-0.25 mm was used in the gasification experiments.
Table 2. Properties of the tested bed materials.

<table>
<thead>
<tr>
<th>Bed material</th>
<th>Sand</th>
<th>Dolomite (Myanit D)</th>
<th>MgO (M85)</th>
<th>Olivine A</th>
<th>Olivine B/kaolinite mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area*, m^2/g</td>
<td>3.1</td>
<td>5.2^b</td>
<td>16.2</td>
<td>3.5</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Element, wt-% (XRF)

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Rb</th>
<th>Sr</th>
<th>Zr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.1</td>
<td>0.56</td>
<td>6.7</td>
<td>35</td>
<td>0.07</td>
<td>-</td>
<td>0.01</td>
<td>2.8</td>
<td>2.2</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>1.8</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>12</td>
<td>0.44</td>
<td>2.3</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>0.08</td>
<td>21</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>50</td>
<td>0.14</td>
<td>0.42</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>4.1</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>6.0</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>29</td>
<td>0.52</td>
<td>19</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.19</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>24</td>
<td>2</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>2.1</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>29</td>
<td>6.2</td>
<td>18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.19</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>6.4</td>
<td>-</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* Determined from unused bed material samples

b Determined from the carbonate form (CaCO\(_3\)-MgCO\(_3\))

**"." = below detection limit (< 0.01 wt-%)**

The precious metal and nickel catalysts used for reforming in the catalyst activity testing (Publication V) and in long-term experiments (Publication III) were commercial catalysts. The catalysts used in the experiments are listed in Table 3. Catalyst particles of around 2-3 mm were applied in the long-term experiments and catalyst
activity testing. In the kinetic experiments (Publication IV), nickel catalyst powder of 0.2-0.3 mm particle size was used to avoid mass transfer limitations. The nickel catalyst in the kinetic studies contained 14.7 wt-% of NiO on α-Al₂O₃ support. In the kinetic experiments, the nickel catalyst was diluted with SiC to 1:1 volume ratio to obtain more isothermal behaviour in the catalyst bed.

Table 3. Catalysts used in experiments

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shape</th>
<th>Particle size, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>cylinder</td>
<td>3x3</td>
</tr>
<tr>
<td>Nickel in kinetic studies</td>
<td>irregular particles</td>
<td>0.20-0.30</td>
</tr>
<tr>
<td>PM1</td>
<td>sphere</td>
<td>2.5</td>
</tr>
<tr>
<td>PM2</td>
<td>cylinder</td>
<td>3x3</td>
</tr>
<tr>
<td>PM3</td>
<td>cylinder</td>
<td>3x3</td>
</tr>
<tr>
<td>PM5</td>
<td>sphere</td>
<td>2.6</td>
</tr>
<tr>
<td>PM6</td>
<td>sphere</td>
<td>1.9</td>
</tr>
</tbody>
</table>
4. Results and discussion

4.1 Tar formation from ethene

High temperatures in the gasification process may induce thermal reactions of hydrocarbons leading to heavier tar compounds and pyrolytic carbon formation. Biomass gasification gas typically contains C₂ hydrocarbons especially ethene and acetylene, which can react at high temperatures to form tar and soot. Typical ethene concentration at the gasifier outlet is 0.2-4% depending on the gasification conditions [15,35,43]. The tar compounds formed from ethene may cause problems in reforming of gasification gas. High temperature spots causing tar formation may form in autothermal reforming near to where oxygen is fed. Thus, ethene may form tar and soot and plug the front face of the catalyst or cause coke formation in the catalyst bed. Operation pressure has a strong effect on tar formation from light hydrocarbons, which is an essential question when considering pressurizing the gasification and gas cleaning process.

The effect of process conditions on tar formation from ethene was studied with an empty quartz reactor (Publication I). In the experiments, 5 vol-% of ethene was used in nitrogen atmosphere. First, the temperature region of 787-978 °C was screened at atmospheric pressure with a 0.3 s residence time. As can be seen from Figure 9, the formation of tar and benzene increased steeply with temperature, likewise the ethene conversion. A reaction temperature of around 950 °C was chosen for further experiments in which pressure and residence time effects were investigated.

![Figure 9](image_url)

Figure 9. Conversion of ethene and amount of tar formed from ethene as a function of temperature.
The main compounds formed in thermal reactions of ethene were hydrogen, methane, acetylene and 1,3-butadiene. The most abundant aromatic compound formed was benzene. The pressure increase from 1 to 3.5 bar increased the ethene conversion and the selectivity to tar, Figure 10. With increasing pressure, the composition of products shifted more towards heavier compounds. The same change in composition with increasing pressure has been observed in biomass gasification [21,31,32]. When the pressure was further increased to 6 bar with a longer residence time of 2 s, the amount of tar was not increased considerably, likely due to soot formation. Although the amount of soot was not measured, the large error in the carbon balance indicates that soot formation was likely.

Figure 10. a) Conversion of ethene, b) amount of benzene formed and c) tar amount at 954 °C.

The observed effect of pressure on tar formation and the change in composition towards heavy tar compounds with increasing pressure indicates that when designing pressurized gasification gas cleaning, the thermal reactions of light hydrocarbons should be taken into account. However, their effect in biomass gasification
gas, which contains hydrogen and steam, is not likely to be as pronounced as they affect the radical chain reactions by terminating them.

Since the thermal reactions of ethene produce similar compounds to those formed during biomass gasification, ethene could be used to produce a mixture of tar for gas cleaning studies at the laboratory or bench scale. In Table 4, typical tar compositions of fluidized bed gasification processes are compared with the tar composition from thermal reactions of ethene. The tar composition from the thermal reactions of ethene resembles the tar formed in high temperature gasification, which mainly contains more stable aromatic compounds instead of oxygenated compounds. Tuomi et al. [83] have used ethene pyrolysis combined with natural gas partial oxidation to produce model tar and biomass gasification gas for bench-scale filtration studies.
Table 4. Tar product distribution in different types of gasification experiments and selected results of thermal reaction of ethene for comparison.

<table>
<thead>
<tr>
<th></th>
<th>CFB air</th>
<th>CFB O₂/H₂O</th>
<th>BFB H₂O</th>
<th>BFB H₂O</th>
<th>BFB air</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
<th>C₂H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>[84]</td>
<td>[14]</td>
<td>[43]</td>
<td>[43]</td>
<td>Publication II</td>
<td>Publication II</td>
<td>Publication I</td>
<td>Publication I</td>
</tr>
<tr>
<td>Raw material</td>
<td>sawdust</td>
<td>forest wood residue</td>
<td>wood</td>
<td>wood</td>
<td>bark</td>
<td>bark</td>
<td>C₂H₄</td>
<td>C₂H₆</td>
</tr>
<tr>
<td>Bed material</td>
<td>sand</td>
<td>sand/dolomite</td>
<td>sand</td>
<td>dolomite</td>
<td>sand</td>
<td>dolomite</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P, bar</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>T, °C</td>
<td>940</td>
<td>930</td>
<td>800</td>
<td>800</td>
<td>850</td>
<td>850</td>
<td>954</td>
<td>956</td>
</tr>
<tr>
<td>Residence time, s</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>7</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Benzene, g/Nm³</td>
<td>7.1</td>
<td>13.6</td>
<td>11.8</td>
<td>7.4</td>
<td>7.1</td>
<td>3.4</td>
<td>2.8</td>
<td>6.2</td>
</tr>
<tr>
<td>Total tar, g/Nm³</td>
<td>4.3</td>
<td>5.7</td>
<td>20.5b</td>
<td>4.7b</td>
<td>3.7</td>
<td>0.5</td>
<td>2.1</td>
<td>3.9</td>
</tr>
<tr>
<td>1-ringa, %</td>
<td>6</td>
<td>6</td>
<td>20</td>
<td>32</td>
<td>20</td>
<td>34</td>
<td>42</td>
<td>39</td>
</tr>
<tr>
<td>2-ring, %</td>
<td>49</td>
<td>64</td>
<td>29</td>
<td>38</td>
<td>57</td>
<td>61</td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td>3-ring, %</td>
<td>29</td>
<td>22</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>0</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>4-ring, %</td>
<td>14</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Heterocyclic, %</td>
<td>2</td>
<td>2</td>
<td>11</td>
<td>7</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tot, %</td>
<td>100</td>
<td>100</td>
<td>76</td>
<td>91</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

a Benzene is not included in 1-ring compounds

b Unidentified tar compounds included in total amount of tar
4.2 Catalytic activity of gasification bed materials in tar reduction

Tar concentration can be reduced already in the gasifier by catalytically active bed materials, which makes the operation of the reformer easier. The catalytic activity of the different bed materials was studied in Publication II. The activity of the bed materials was first compared in atmospheric air gasification of bark in a BFB gasifier. Figure 11 shows the amount and composition of tar from biomass gasification experiments. Dolomite and MgO were clearly the most active, with olivine/kaolin mixture being less active but still giving tar amounts of around half of that produced with silica sand as the bed material. In addition to reducing the amount of tar, the catalytically active bed materials changed the tar composition to lighter compounds compared to silica sand. With dolomite as the bed material, the tar contained no three- or four-ring compounds and with MgO three-ring compounds were present only in trace amounts.

![Figure 11. Tar concentration (in dry gas) in fluidized-bed experiments. Error bars represent the standard deviations of total tar concentrations.](image)

The catalytic activity of the bed materials in pressurized conditions was tested in a fixed bed reactor with a model gasification gas composition (air gaga, Table 1). The aim in the laboratory experiments was to compare the tar reforming activity of the bed materials. The easily controllable laboratory conditions were more suitable for this purpose than experiments in a fluidized-bed gasifier. The model gas composition resembled the gas composition in the air gasification of bark pellets with silica sand as the bed material. The dolomite, MgO and silica sand were the same materials as used in the biomass gasification experiments, whereas pure olivine A instead of olivine B/kaolin mixture was used in the laboratory experiments.
The total hydrocarbon conversion was calculated to clarify the effect of the bed material. As can be seen from Figure 12, MgO was the most active of the tested bed materials, followed closely by dolomite. Conversely, olivine A behaved almost like inert silica sand. However, when the pressure was increased from atmospheric to 10 bar, all bed materials were equally inactive and the total hydrocarbon conversion was only around 5% at 850 °C as well as at 900 °C.

Figure 12. Total conversion of hydrocarbon based on carbon moles at 850 °C (left) and 900 °C (right).

According to the literature [50,51], olivine is activated by formation of a calcium-rich layer during biomass gasification due to contact with ash. In our experiments, fresh olivine was used, which might explain the observed low activity of the olivine. Our atmospheric gasification experiments were only 6-7 hours long, whereas, Marinkovic et al. [52] have observed the activation of olivine during gasifier operation to take place over three days. By conducting longer experiments or by using already activated olivine, the catalytic activity, at least in atmospheric pressure, might be higher than observed in these experiments. Other parameters possibly affecting the inactivity of olivine may be the origin of the olivine, possible thermal treatment, and also the lack of kaolin in the laboratory experiments.

When the pressure was increased, calcium in the dolomite changed from oxide to carbonate form. Figure 13 presents the oxidation/carbonation curve for CaO/CaCO₃. Magnesium in the dolomite was present as MgO [41] in all experimental conditions. In the laboratory studies, however, the decrease in catalytic activity in tar decomposition with increasing pressure was not only due to carbonation of dolomite. At 900 °C, the dolomite was in carbonate form only at 10 bar pressure; however, the conversion of hydrocarbons dropped most when the pressure was increased from 1 to 5 bar, as can be seen from Figure 12. The same behaviour was observed with MgO.
Figure 13. Equilibrium decomposition curve of CaCO$_3$ in relation to the partial pressures of CO$_2$ in dolomite test conditions. Filled symbols represent CO$_2$ partial pressures measured at the catalyst bed inlet and open symbols those measured at the catalyst bed outlet.

The effect of the calcination state of dolomite was also studied at 5 bar pressure at 850 °C by changing the CO$_2$ partial pressure so that calcium was at oxide form at 5 bar pressure (Table 5). Interestingly, the tar conversion was similar for both cases. Thus, in the conditions of the study, the decrease in the catalytic activity of dolomite with pressure was not due to the change of oxide to carbonate, which is in contrast with earlier results by Simell et al. [41]. A possible explanation for the contradicting results is a more realistic gas composition in this study, including ethene, which may contribute to tar formation. It should also be noted that the pressure level of this study was 1-10 bar, whereas Simell et al. studied tar conversion at a constant pressure of 20 bar by varying the CO$_2$ partial pressure.

Table 5. Benzene and tar conversions in tests with dolomite (5 bar and 850 °C) where the CO$_2$ content in the feed gas was varied.

<table>
<thead>
<tr>
<th>Form of calcium</th>
<th>oxide</th>
<th>carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ partial pressure, kPa</td>
<td>25.7</td>
<td>75.0</td>
</tr>
<tr>
<td>Toluene, %</td>
<td>92</td>
<td>99</td>
</tr>
<tr>
<td>Naphthalene, %</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Total tars (excl. benzene), %</td>
<td>81</td>
<td>88</td>
</tr>
<tr>
<td>Total C conversion, %</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>
As in the study of thermal reactions of ethene (Publication I), the conversion of ethene increased with pressure in the bed material experiments with model gasification gas (Figure 14). Ethene might be converted by steam reforming reaction to syngas or it might have reacted to form tar compounds. The formation of tar compounds other than in the feed (benzene, toluene, naphthalene) increased with pressure. The formation of these compounds might be due to thermal reactions of ethene or polymerization of tar compounds.

Figure 14. Conversion of ethene with different bed materials as a function of pressure.

4.3 Steam reforming versus autothermal reforming in biomass gasification gas cleaning

Steam and autothermal reforming can be applied in biomass gasification gas cleaning to convert tar and light hydrocarbons to syngas. In autothermal reforming, oxygen is used to partially oxidize the hydrocarbons and to produce heat for the reforming reactions. In contrast, the steam reformer needs to be heated indirectly, for example, by burning the flue gases of the process. Autothermal reforming also brings more oxygen to the gas, reducing the coke formation potential of the gas. On the other hand, if steam reforming of biomass gasification gas is technically feasible, the investment costs of the reformer could be reduced by omitting the air separation unit.

The activity of the nickel and three different precious metal catalysts was tested in steam and autothermal reforming modes (Publication V). Moreover, long-term stability was tested for both reforming modes (Publication III). The process concepts in which the reforming modes relate are presented in Figure 5. For steam-oxygen blown gasification, where the target product is FT-liquids, the high methane conversion is an asset. Based on techno-economical evaluation (Publication V), if methane
conversion is increased, for example, from 55% to 95%, the production costs of FT-liquids can be reduced by 5%. In the steam-blown gasification concept, the reforming mode was found to have only a limited impact on the amount of the main product, which was considered to be H₂ or SNG. However, because investment in the oxygen plant increases the production costs, the steam reforming concept could be an attractive choice for the steam gasification case. In the steam gasification concept, the reforming temperature can be lower than in the oxygen-blown gasifier case since low methane conversion is desired.

The activity comparison of the catalysts was based on the same geometrical catalyst surface area in the catalyst bed. For all the catalysts and for both steam and autothermal reforming experiments, the geometrical surface area was 125 cm². The gas compositions (MH and MH+O₂) used in the catalyst activity testing are presented in Table 1. Tar conversion was higher with the precious metal than the nickel catalyst, which is especially clear when comparing naphthalene conversions, Figure 15. Furthermore, ethene conversion was higher with the precious metal catalyst than with the nickel catalyst. The precious metal catalysts differed with regard to methane conversion; one of the precious metal catalysts (PM5) was clearly more active than the other precious metal catalysts, showing similar activity to a nickel catalyst. The precious metal catalyst that was highly active in methane conversion would be beneficial for the FT synthesis concept, whereas the other catalysts would be more suitable for SNG or H₂ production by steam gasification.

In addition to the catalyst choice, methane conversion can be affected by operating conditions; higher reforming temperatures favour higher methane conversion. High tar conversions, especially with precious metal catalysts, could be obtained already at around 850 °C, whereas for high methane conversions temperatures above 900 °C were required to achieve higher than 90% conversion. Lower methane conversion compared to tar or ethene conversion can be explained by the high stability of methane. It is also possible that the H₂S in the gasification gas deactivates the active sites for methane reforming more than the tar reforming site.

The addition of oxygen to the feed did not improve the methane reforming activity with the precious metal catalysts. However, tar conversion was slightly higher with oxygen addition, which could be seen especially in naphthalene conversion (Figure 15d). These activity experiments were only 1-3 h long per experimental condition, which was too short to observe possible deactivation of the catalyst. However, in an actual gasification process oxygen can be used to increase the reforming temperature and in that way increase the methane conversion.

The addition of oxygen to the feed did not improve the methane reforming activity with the precious metal catalysts. However, tar conversion was slightly higher with oxygen addition, which could be seen especially in naphthalene conversion (Figure 15d). These activity experiments were only 1-3 h long per experimental condition, which was too short to observe possible deactivation of the catalyst. However, in an actual gasification process oxygen can be used to increase the reforming temperature and in that way increase the methane conversion.

To discover the long-term stability of the catalyst in different reforming conditions (Publication III), several precious metal and nickel catalysts were tested in extended experiments reaching around 500 h time on-stream. Steam and autothermal reforming modes were tested with medium hydrocarbon content gas (Table 1, MH and MH+O₂) representing oxygen-blown gasification gas. In steam reforming conditions, lower hydrocarbon content gas was also tested (Table 1, LH).
Figure 15. a) Methane, b) ethene, c) tar and benzene, and d) naphthalene conversion. Filled symbols with oxygen, empty symbols without oxygen.

The conversions of the hydrocarbons are presented in Figure 16. The levels of the conversions varied between the experiments, which was mostly due to different space velocities and geometrical surface areas. In addition, it should be noted that the oven temperature in the experiments with oxygen was 950 °C and without oxygen 900 °C. With the nickel catalyst, the initial tar conversion including benzene was high for all gas compositions. However, with precious metal catalysts the tar conversions were clearly higher for PM1 and PM2 catalysts with MH+O2 gas than for PM3 catalyst with MH and LH gases. The higher activity of PM1 and PM2 is likely due to better catalyst formulation in addition to higher temperature. With oxygen addition, the temperature was higher and thus the conversions were also higher than with other gas compositions.
Figure 16. Methane conversion on a) nickel and b) precious metal catalyst, tar and benzene conversion on c) nickel and d) precious metal catalyst, and total carbon mol based hydrocarbon conversion on e) nickel and f) precious metal catalyst.
The rate of deactivation was calculated for total hydrocarbon conversion based on the number of carbon moles in hydrocarbons, Table 6. The deactivation rate was calculated after about 100 h onwards from start-up. As can be seen from Figure 16, the decrease in conversion was nearly constant over the time of the experiment. Figure 17 illustrates the starting phase of the experiment with the nickel catalyst. Deactivation was faster in the initial phase of the experiment, but then levelled-off to a nearly constant value, which is typical behaviour in catalyst deactivation [85]. Rostrup-Nielsen et al. [85] explain the exponential decrease in reaction rate at the beginning of the operation to be due to sintering. Sulfur poisoning of the catalyst reaches steady state in less than one hour [58].

Table 6. Activity decrease in total hydrocarbon conversion based on carbon moles in percentage units per 100 h after the initial activity decrease.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gas</th>
<th>m&lt;sub&gt;cat&lt;/sub&gt; g</th>
<th>GHSV h&lt; sup&gt;-1&lt; /sup&gt;</th>
<th>Geometric surface area mm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Run time h</th>
<th>T at catalyst outlet °C</th>
<th>T oven °C</th>
<th>T&lt;sub&gt;decrease&lt;/sub&gt; in total hydrocarbon conversion, % units/100 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>MH+O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15.5</td>
<td>8800</td>
<td>11330</td>
<td>450</td>
<td>916</td>
<td>950</td>
<td>-0.8</td>
</tr>
<tr>
<td>Ni</td>
<td>MH</td>
<td>22.8</td>
<td>5400</td>
<td>16670</td>
<td>500</td>
<td>851</td>
<td>900</td>
<td>-2.5</td>
</tr>
<tr>
<td>Ni</td>
<td>LH</td>
<td>22.8</td>
<td>5400</td>
<td>16670</td>
<td>478</td>
<td>850</td>
<td>900</td>
<td>-0.8</td>
</tr>
<tr>
<td>PM1</td>
<td>MH+O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.2</td>
<td>12000</td>
<td>12150</td>
<td>570</td>
<td>888</td>
<td>950</td>
<td>-2.0</td>
</tr>
<tr>
<td>PM2</td>
<td>MH+O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9.6</td>
<td>12000</td>
<td>8150</td>
<td>564</td>
<td>916</td>
<td>950</td>
<td>-0.1</td>
</tr>
<tr>
<td>PM3</td>
<td>MH</td>
<td>12.4</td>
<td>10200</td>
<td>15950</td>
<td>503</td>
<td>860</td>
<td>900</td>
<td>-1.0</td>
</tr>
<tr>
<td>PM3</td>
<td>LH</td>
<td>13.4</td>
<td>8600</td>
<td>11380</td>
<td>501</td>
<td>862</td>
<td>900</td>
<td>-1.2</td>
</tr>
<tr>
<td>PM3+Ni</td>
<td>LH</td>
<td>7.6+ 15.0</td>
<td>5400</td>
<td>6480+ 10940</td>
<td>477</td>
<td>868</td>
<td>900</td>
<td>-0.5</td>
</tr>
</tbody>
</table>
With the nickel catalyst, the deactivation rate was highest for the MH gas without oxygen, whereas reducing the hydrocarbon content or adding oxygen to the feed resulted in the same deactivation rate in total hydrocarbon conversion (Table 6). With the PM1 catalyst, the percentage reduction in total hydrocarbon conversion with the MH+O₂ was high due to decrease in methane conversion, whereas tar conversion remained almost 100% throughout the experiment. The decrease in methane conversion was constant during the experiment without levelling off. Despite the relatively high deactivation rate, methane conversion was clearly higher than in other experiments. For the PM2 catalyst with MH+O₂ gas, conversion levels were lower but almost stable with only a 0.1 %-unit reduction per 100 h for total hydrocarbon conversion. With the PM3 catalyst, the total hydrocarbon conversion decrease was around the same for the MH and the LH, but slightly higher than for the nickel catalyst with LH gas. A combination of a precious metal and the nickel catalysts was also tested, and a low deactivation rate was obtained.

With the gasification gas experiments, the H₂O/C and O/C ratios were more descriptive and corresponded with the observed tendency to carbon formation if the carbon atoms only in the hydrocarbons were accounted for in the ratios. The MH gas contained two times the amount of ethene and tar model compound mixture compared to LH gas. The higher hydrocarbon content can be seen in the H₂O/CH₄ and in O/CH₄ ratios presented in Table 7. If CO and CO₂ were included, there was almost no difference at all in O/C ratio between the gas compositions, whereas a difference was observed in the experiments in carbon formation and catalyst deactivation.

With the MH+O₂ gas, the precious metal and nickel catalyst exhibited different carbon formation behaviour. After the experiment, the surface of the precious metal catalyst was clean of carbon (Figure 18a), which was not the case with the nickel catalyst (Figure 18b). The carbon formed on the nickel catalyst was characteristically pyrolytic carbon; the carbon had filled the voids of the top of the catalyst bed and encapsulated the catalyst particles. However, carbon did not form to an extent
that would have blocked the reactor or increased the pressure drop during the 450 h run time. Even though the precious metal catalyst seemed to be clean of carbon, the activity slightly decayed. To determine the cause of deactivation of the precious metal catalyst, detailed surface analysis of the catalyst would be needed to reveal possible sintering or other changes in catalyst structure.

Table 7. H₂O/C and O/C ratios for the tested gases, HC refers that only the hydrocarbons were calculated in the ratio.

<table>
<thead>
<tr>
<th>Test gases</th>
<th>H₂O/CH₃</th>
<th>O/CH₃</th>
<th>H₂O/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH</td>
<td>3.8</td>
<td>7.6</td>
<td>1.07</td>
<td>2.1</td>
</tr>
<tr>
<td>MH+O₂</td>
<td>3.8</td>
<td>8.0</td>
<td>1.07</td>
<td>2.2</td>
</tr>
<tr>
<td>LH</td>
<td>4.3</td>
<td>10.7</td>
<td>0.83</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Figure 18. Top of the catalyst bed after experiment with MH+O₂ gas with a) PM2 catalyst, 564 h, and b) nickel catalyst, 450 h.

In industrial operation, the superficial gas velocities are typically higher than in the laboratory scale. In the industrial steam reformers the gas velocities in the tubes are in the range of 1.5 m/s [71], whereas in laboratory experiments the velocity was only 0.2 m/s. This might affect the radical formation in the reactor tube before the catalyst bed. The longer the residence time in the hot zone, the more time there is for radical formation [71], for example, from ethene, as was studied in Publication I. In addition, sulfur poisoning of the catalyst increases the risk of pyrolytic carbon formation from unconverted hydrocarbons [86].

4.4 Reactor modelling

The reactor model used for benzene steam reforming kinetics (Publication IV) was a pseudo-homogeneous plug flow model. Isothermal behaviour of the catalyst bed
was assumed based on the measured axial temperature gradient. The radial temperature gradient was assumed to be negligible due to the narrow reactor tube. Steam reforming is a fast surface reaction and the experiments easily suffer from mass transfer limitations. The mass transfer limitations were evaluated by calculating the criteria for inter- and intra-particle resistances. The Weisz-Prater criterion was used for intra-particle limitations and Mears’ criterion for inter-particle limitations. Based on the calculated criteria, it was concluded that the mass transfer did not limit the reaction rate (Publication IV).

The parameter estimation was performed with MATLAB using the Nelder-Mead simplex and Levenberg-Marquardt algorithms to minimize the residual sum of squares of molar flow of benzene. The model equation (7) was an ordinary differential equation that was solved by the ODE15s.

\[
\frac{dn_i}{dz} = -n_i \cdot m_{cat}
\]  

(7)

Arrhenius (8) and Van’t Hoff (9) equations were used in the temperature centralized forms to minimize the correlation between the parameters and to enhance the convergence of the model. The initial values for parameters for estimation routines were obtained by linearization of the Arrhenius equation.

\[
k' = k_{ref} \cdot \exp \left( -\frac{E_a}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)
\]  

(8)

\[
K_i = K_{ref} \cdot \exp \left( -\frac{\Delta H_i}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)
\]  

(9)

4.5 Kinetics of benzene reforming

The required degree of reforming varies depending on the end-use of the biomass gasification gas. For energy production, all condensable tar compounds should be removed. For synthesis purposes, however, the goal is to reform all hydrocarbons to syngas, except for methane synthesis where the conservation of methane in the gas is desirable. For cases where only tar compounds are to be reformed, benzene reforming kinetics could be used as the design basis. When tar compounds are measured after reformer, most of them are benzene [14]. The thermal stability of benzene is also higher than that of toluene or naphthalene [87]. The qualitative effect of the main gasification gas compounds on steam reforming of benzene was studied with a nickel catalyst in the presence of H2S in Publication IV.

The stoichiometry of the steam reforming of benzene was investigated for modelling purposes. All products were measured at 900 °C for two different gas compositions, one with a gas mixture containing benzene and steam and the other containing H2 in addition to the afore-mentioned compounds. The elemental balances were calculated for the stoichiometric ratios presented in Table 8. The ratios indicate that the main reaction was steam reforming with CO and H2 as products (1). Without H2 in the gas mixture, a small amount of CO2 was also formed by reforming reaction (2) or by WGS (4). With a nickel catalyst, the product distribution obtained in this
study is typical [79, 78] whereas with a dolomite catalyst a quite different product distribution was obtained [80].

Table 8. Measured stoichiometry in steam reforming without and with hydrogen at 900 °C (mol formed/mol of benzene reacted) compared to the stoichiometry of the steam reforming reaction (1). Bz refers to benzene.

<table>
<thead>
<tr>
<th></th>
<th>Bz+H₂O</th>
<th>Bz+H₂O+ +H₂</th>
<th>Steam reforming reaction (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene conversion, %</td>
<td>65</td>
<td>62</td>
<td>6</td>
</tr>
<tr>
<td>CO₂/Bz</td>
<td>4.8</td>
<td>5.7</td>
<td>6</td>
</tr>
<tr>
<td>CO₂/Bz</td>
<td>0.7</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>H₂/Bz</td>
<td>9.7</td>
<td>10.8</td>
<td>9</td>
</tr>
<tr>
<td>H₂O/Bz</td>
<td>6.1</td>
<td>5.7</td>
<td>6</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>2.0</td>
<td>1.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The reforming of benzene at high temperatures may lead to thermal reactions as well. The thermal reactions were investigated by experiments with SiC instead of a nickel catalyst. However, the conversion of benzene on SiC was 3.7% at 900 °C and was considered negligible. With SiC, around 15 ppm of tar compounds calculated as benzene were formed, whereas with the nickel catalyst no hydrocarbon products were detected, indicating the activity of nickel in reforming possible intermediates formed by thermal cracking.

The reaction order was defined by fitting the results to a power law model (10). In addition to benzene and H₂O, the feed gas in all experiments contained 100 ppm of H₂S and N₂ for balance. The reaction order for benzene was close to one, which is the value typically used in literature [76–78]. For H₂O, the reaction order was close to zero, which is also typical for steam reforming at high temperature [73, 82, 90].

\[-r_{\text{Bz}} = k' c_{\text{Bz}}^{\alpha} c_{\text{H₂O}}^{\beta}\] (10)

The effect of the main gasification gas compounds, i.e. H₂, CO and CO₂, on the steam reforming rate of benzene was studied qualitatively by investigating the effect of each compound on the benzene steam reforming rate. The rate expression was a first-order equation with respect to benzene and was fitted separately to the data sets of different gas mixtures. The clearest effect was caused by H₂ and CO₂, as can be seen from the estimates of reaction rate constant at the reference temperature and activation energy presented in Table 9. Hydrogen decreased the reaction rate, whereas CO₂ increased it. The first-order kinetics for the dry reforming reaction indicate that it is clearly slower than the steam reforming reaction. Thus, the increased reaction rate observed with the Bz+H₂O+CO₂ gas mixture could be due to a dual effect of H₂O and CO₂. Co-adsorption of CO₂ and H₂O on the catalyst surface may have some beneficial effect by bringing more oxygen to the surface, since in both reaction mechanisms the surface species O* and HO* react with adsorbed hydrocarbons [89,90]. The increased rate with CO₂ could not be explained by parallel steam and dry reforming reactions.
Table 9. Parameter estimates for first-order kinetics calculated by linearization for different gas compositions

<table>
<thead>
<tr>
<th></th>
<th>$k_{\text{ref}}$</th>
<th>95% confidence limit</th>
<th>$E_\alpha$</th>
<th>95% confidence limit</th>
<th>Correlation</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bz+H$_2$O</td>
<td>133</td>
<td>±7</td>
<td>230</td>
<td>±13</td>
<td>-0.65</td>
<td>2.28*10^{-6}</td>
</tr>
<tr>
<td>Bz+CO$_2$</td>
<td>34</td>
<td>±19</td>
<td>295</td>
<td>±36</td>
<td>-0.89</td>
<td>1.79*10^{-7}</td>
</tr>
<tr>
<td>Bz+H$_2$O +H$_2$</td>
<td>59</td>
<td>±24</td>
<td>378</td>
<td>±100</td>
<td>-0.939</td>
<td>3.18*10^{-6}</td>
</tr>
<tr>
<td>Bz+H$_2$O +CO</td>
<td>173</td>
<td>±58</td>
<td>206</td>
<td>±98</td>
<td>-0.58</td>
<td>1.94*10^{-6}</td>
</tr>
<tr>
<td>Bz+H$_2$O +CO$_2$</td>
<td>247</td>
<td>±12</td>
<td>169</td>
<td>±15</td>
<td>-0.204</td>
<td>2.96*10^{-8}</td>
</tr>
<tr>
<td>Gasification gas 1</td>
<td>103</td>
<td>±32</td>
<td>307</td>
<td>±73</td>
<td>-0.907</td>
<td>4.83*10^{-6}</td>
</tr>
<tr>
<td>Gasification gas 2</td>
<td>212</td>
<td>±46</td>
<td>272</td>
<td>±79</td>
<td>-0.348</td>
<td>4.07*10^{-7}</td>
</tr>
</tbody>
</table>

In addition to the effect of single compounds, two types of model gasification gases (Table 1) were also tested. Interestingly, the steam/O$_2$ gasification gas (Gasification gas 2) resulted in a higher reforming rate than the Bz+H$_2$O mixture and higher than the air gasification type of gas (Gasification gas 1). The benzene reforming rate with the air gasification type of gas was between Bz+H$_2$O and Bz+H$_2$O +H$_2$.

Compared to a study by Świerczynski et al. [77] without H$_2$S in the feed, the reaction rates were lower in this study. Interestingly, it was noticed in this study that the benzene steam reforming rate with different gas compositions were around the same at 900 °C. Only the dry reforming rate was still clearly lower than the steam reforming rate. Thus, the differences in benzene steam reforming rates with different gas composition could only be observed at lower temperatures. This is likely due to H$_2$S poisoning of the catalyst. According to Hepola [58], at temperatures above 900 °C, catalyst poisoning by H$_2$S can be avoided. However, if the surface coverage for sulfur is calculated according to equation (11) from Rostrup-Nielsen and Christiansen [71], at 900 °C with gas containing 10% of H$_2$ the surface coverage is 1 and at lower temperatures >1. The catalyst with the surface fully covered by sulfur should be completely deactivated, which was not the case in our experiments. This might be due to inaccuracy of the equation (11) close to full coverage, or due to sulfur being preferentially adsorbed on edges and corners leaving some facet sites free for reforming reaction to take place. Additionally, it is possible that sulfur was adsorbed in multi-layer or sub-surface form [91]. Although the gasification gas also contains compounds other than hydrogen, according to Rostrup-Nielsen and Christiansen [71], steam and carbon does not compete with sulfur adsorption.

$$\theta_S = 1.45 - 9.53 * 10^{-5} * T * \ln \left( \frac{P_{H_2}S}{P_{H_2}} \right)$$

(11)

Based on the first-order kinetics with different gas compositions, three Langmuir-Hinshelwood models were fitted with Bz+H$_2$O and Bz+H$_2$O +H$_2$ gas compositions. The models and the parameter estimates are presented in Table 10. The models
differed in the adsorption term. Model A was taken from the study of Simell et al. In model B, benzene adsorption was assumed to take place on a single site and hydrogen adsorption to be dissociative. Compared to model B, model C assumed dual site benzene adsorption. The models were tested for gasification gases; all of the tested models represented the air gasification gas reasonably well, whereas the O$_2$/H$_2$O gasification gas was not well described solely by retarding effect of H$_2$ in the denominator, likely due to higher product concentrations in the gas and the rate enhancing effect of CO$_2$. The estimated adsorption enthalpy was clearly higher than reported in the literature [59,92], which may be due to high correlation of the parameter or to H$_2$S poisoning of the catalyst.

Table 10. Parameter estimates with 95% confidence intervals, the RSS for models fitted with data sets Bz+H$_2$O and Bz+H$_2$O+H$_2$ and the RSS for simulation with gasification gases.

<table>
<thead>
<tr>
<th>Model</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model equation</td>
<td>( \frac{k' \cdot c_{Bz}}{1 + K_{H_2} \cdot c_{H_2}} )</td>
<td>( \frac{k' \cdot c_{Bz}}{1 + \sqrt{K_{H_2} \cdot c_{H_2}}} )</td>
<td>( \frac{k' \cdot c_{Bz}}{(1 + \sqrt{K_{H_2} \cdot c_{H_2}})^2} )</td>
</tr>
<tr>
<td>( k_{\text{ref}} )</td>
<td>142.5±15.95</td>
<td>172.5±43.18</td>
<td>165.9±31.06</td>
</tr>
<tr>
<td>( E_a )</td>
<td>226±29.72</td>
<td>212.2±63.49</td>
<td>217±49.01</td>
</tr>
<tr>
<td>( K_{\text{ref}}(H_2) )</td>
<td>0.896±0.5023</td>
<td>1.343±1.832</td>
<td>0.2023±0.1996</td>
</tr>
<tr>
<td>( \Delta H_{H_2} )</td>
<td>-336.6±178.5</td>
<td>-455.2±370.8</td>
<td>-415.5±287.8</td>
</tr>
<tr>
<td>RSS</td>
<td>6.1437*10$^{-6}$</td>
<td>6.6255*10$^{-6}$</td>
<td>6.5151*10$^{-6}$</td>
</tr>
<tr>
<td>RSS for gasification gas 1</td>
<td>1.6000*10$^{-5}$</td>
<td>1.6187*10$^{-5}$</td>
<td>1.6366*10$^{-5}$</td>
</tr>
<tr>
<td>RSS for gasification gas 2</td>
<td>4.8322*10$^{-5}$</td>
<td>3.7844*10$^{-5}$</td>
<td>4.0395*10$^{-5}$</td>
</tr>
</tbody>
</table>
5. Conclusions

The main objective of this thesis was to study and develop the reforming technology for biomass gasification gas for synthesis use. A key parameter with respect to reformer operation is the tar load at the outlet of the gasifier. Catalytically active gasifier bed materials can be used to lower the tar content in the gas to protect the catalysts in the reformer from excessive tar load. Typical bed materials used in fluidized bed gasification are silica sand, dolomite, olivine and MgO. Dolomite and MgO were found to be highly active bed materials in tar decomposition at atmospheric pressure. Olivine/kaolin mixture was less active resulting about half of the amount of tar compared to silica sand in atmospheric gasification experiments. In contrast, pure olivine was inherently as inactive as silica sand. Compared to silica sand, the catalytically active bed materials also shifted the composition of tar towards lighter tar compounds.

Interestingly, the catalytic activity of dolomite and MgO dropped when the pressure was increased. At only 5 bar pressure, activity was almost completely lost dropping almost to the level of activity of silica sand and olivine, and at 10 bar, the total hydrocarbon conversion was the same for all bed materials. Dolomite has been reported to be highly active only in oxide form. When the CO$_2$ partial pressure increases, the calcium in dolomite changes to carbonate. However, the decrease in activity of dolomite could not be explained by the carbonation.

The gasification gas contains light hydrocarbons such as ethene, in addition to tar compounds. Ethene reacts at high temperatures forming more tar compounds. High temperature zones in the gasifier or reformer, for example in the oxygen inlet areas, may lead to tar formation by radical chain reactions from ethene. The conversion of ethene as well as the selectivity towards tar compounds increased with increasing pressure from 1 to 3 bar. With increasing pressure, the tar composition shifted towards heavier tar compounds. The tar formed by thermal reactions of ethene resembles high temperature gasification tar. Therefore, ethene can be used in gas cleaning studies to produce a tar mixture resembling real tar.

Combined together, the decreasing activity of bed materials and increasing amount of tar formed from ethene with increasing pressure make steam reforming in pressurized conditions challenging. An acceptably low inlet tar content for a steam reforming reactor seems difficult to achieve. Both studies were performed with model gas compositions. Further experiments in a real biomass gasifier are required to confirm the trends observed in this study.

The level of methane conversion can be affected in addition to temperature by catalyst choice. The desired level of methane conversion depends on the process concept and the end product. For FT synthesis, high methane conversion leads to lower production costs, thus a highly active catalyst for methane reforming combined with high reforming temperatures achieved by autothermal reforming would be a suitable combination. Conversely, for SNG or H$_2$ production by steam gasifi-
cation, low methane conversion is desired. Thus, an indirectly heated steam reformer and a catalyst with high activity towards tar but lower methane reforming activity would be a suitable combination.

Methane conversion activity of several precious metal catalysts and a nickel catalyst was compared. Significant differences between the catalysts were observed. One of the precious metal catalysts proved highly active in methane conversion, whereas the activity of the other tested precious metal catalysts was at the same level as the nickel catalyst. With precious metal catalysts, the steam and autothermal reforming modes were tested. The reforming mode did not affect methane conversion but did affect naphthalene conversion: oxygen addition slightly increased the conversion compared to results without oxygen, especially at temperatures around 800 °C. In a real gasification process, however, oxygen can be used to increase the reformer temperature leading to higher methane conversion.

A pressurized oxygen-blown gasification process with hot gas filtration and an autothermally operated staged reformer has been demonstrated to work for FT-liquids production. However, steam gasification followed by hot gas filtration and reformer has been less studied. The steam gasification concept is more suitable for a smaller scale of around 100 MW and low-pressure synthesis products, such as SNG, or H₂. For this concept, steam reforming instead of autothermal reforming would be beneficial due to lower investment costs as the oxygen plant would not be required.

The technical feasibility of steam reforming of biomass gasification tar compared to autothermal reforming was studied in extended experiments of around 500 h. The deactivation rate was found to be lower in autothermal mode than in steam reforming mode. With a nickel catalyst, lowering the hydrocarbon content of the gasification gas before the reformer allows operation in steam reforming mode with the same deactivation rate as with the higher hydrocarbon content gas in autothermal mode. With a precious metal catalyst, the decrease in total hydrocarbon conversion was approximately the same irrespective of the hydrocarbon content in the gas in steam reforming mode.

Based on the long-term reforming catalyst stability studies, the concentration of hydrocarbons in the gas needs to be low enough to avoid carbon formation and subsequent catalyst deactivation and plugging of the reactor. An H₂O/CH₄ ratio above 4 and O/CH₄ ratio above 8 are recommended for gasification gas reforming. Low enough tar content could also enable steam reforming of gasification gas without oxygen addition.

For SNG or H₂ production by steam gasification where preserving methane in the gas is desired, the kinetics of benzene reforming could be used as the basis of design of the reformer. The gas composition affects the kinetics of benzene steam reforming; high CO₂ concentration had a beneficial effect, whereas H₂ had a rate decreasing effect. Interestingly, it was also found that the steam reforming rate of benzene was roughly the same at 900 °C and the effect of gas compounds could be seen only at lower temperatures, where H₂S poisoning of the nickel catalyst is more severe. Further research is required to present the qualitative observations as a kinetic model encompassing the gasification gas compositions from air to steam.
gasification gases and describing, in particular, the effect of CO$_2$. However, benzene reforming can be modelled with a simple first-order power law kinetic model if the parameters are fitted for a certain gasification gas composition.
References


[12] Hannula I, Kurkela E. Liquid transportation fuels via large-scale fluidised-bed gasification of lignocellulosic biomass. VTT Technology 91. Espoo:
VTT; 2013.


Kirnbauer F, Hofbauer H. Investigations on Bed Material Changes in a Dual


[61] Xu C (Charles), Donald J, Byambajav E, Ohtsuka Y. Recent advances in catalysts for hot-gas removal of tar and NH3 from biomass gasification. Fuel 2010;89:1784–95.


[92] Hou K, Hughes R. The kinetics of methane steam reforming over a Ni/α-