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INTERNAL TAR/CH_4 REFORMING IN BIOMASS DUAL FLUIDISED BED GASIFIERS TOWARDS FUEL SYNTHESIS

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ABSTRACT

Production of high-quality syngas from biomass gasification in a dual fluidised bed gasifier (DFBG) has made a significant progress in R&D and Technology demonstration. An S&M scale bio-automotive fuel plant close to the feedstock resources is preferable as biomass feedstock is widely sparse and has relatively low density, low heating value and high moisture content. This requires simple, reliable and cost-effective production of clean and good syngas. Indirect DFBGs, with steam as the gasification agent, produce a syngas of high content H_2 and CO with 12-20 MJ/m_n^3 heating value. The Mid Sweden University (MIUN) gasifier, built for research on synthetic fuel production, is a dual fluidised bed gasifier. Reforming of tars and CH_4 (except for methanation application) in the syngas is a major challenge for commercialization of biomass fluidised-bed gasification technology towards automotive fuel production. A good syngas from DFBGs can be obtained by optimised design and operation of the gasifier, by the use of active catalytic bed material and internal reforming. This thesis presents a series of experimental tests with different operation parameters, reforming of tar and CH_4 with catalytic bed material and reforming of tar and CH_4 with catalytic internal reformer.

The first test was carried out to evaluate the optimal operation and performance of the MIUN gasifier. The test provides basic information for temperature control in the combustor and the gasifier by the bed material circulation rate.

After proven operation and performance of the MIUN gasifier, an experimental study on in-bed material catalytic reforming of tar/CH_4 is performed to evaluate the catalytic effects of the olivine and Fe-impregnated olivine (10%wtFe/olivine Catalyst) bed materials, with reference to non-catalytic silica sand operated in the mode of dual fluidised beds (DFB). A comparative experimental test is then carried out with the same operation condition and bed-materials but when the gasifier was operated in the mode of single bubbling fluidised bed (BFB). The behaviour of catalytic and non-catalytic bed materials differs when they are used in the DFB and the BFB. Fe/olivine and olivine in the BFB mode give lower tar and CH_4 content together with higher H_2+CO concentration, and higher H_2/CO ratio, compared to DFB mode. It is hard to show a clear advantage of Fe/olivine over olivine regarding tar/CH_4 catalytic reforming.

In order to significantly reduce the tar/CH_4 contents, an internal reformer, referred to as the *FreeRef* reformer, is developed for in-situ catalytic reforming of tar and CH_4 using Ni-catalyst in an environment of good gas-solids contact at high temperature. A study on the internal reformer filled with and without Ni-catalytic pellets was carried out by evaluation of the syngas composition and tar/CH_4 content. It can be concluded that the reformer with Ni-catalytic pellets clearly gives a higher H_2 content together with lower CH_4 and tar contents in the syngas than the reformer without Ni-catalytic pellets. The gravimetric tar content decreases from 25 g/m^3 down to 5 g/m^3 and the CH_4 content from 11% down below 6% in the syngas.

The MIUN gasifier has a unique design suitable for in-bed tar/CH_4 catalytic reforming and continuously internal regeneration of the reactive bed material. The novel design in the MIUN gasifier increases the gasification efficiency, suppresses the tar generation and upgrades the syngas composition.

Keywords: Allothermal gasification, Bio-automotive fuels, Biomass gasification, Catalytic bed-material, Dual fluidised bed, Ni-catalyst, Syngas cleaning, Tar removal, Tar/CH_4 reforming

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LIST OF PAPERS

This thesis is mainly based on the following five papers, herein referred to by their Roman numerals:

Paper I **Review of Syngas Production via Biomass DFBGs**
Göransson K., Söderlind U., He J. and Zhang W.
Renewable and Sustainable Energy Reviews 15 (2011) 482-492.

Paper II **Experimental Test on a Novel Dual Fluidised Bed Biomass Gasifier for Synthetic Fuel Production.**
Göransson K., Söderlind U. and Zhang W.
Fuel 90 (2011) 1340-1349.

Paper III **Simulation of Biomass Gasification in a Dual Fluidized Bed Gasifier**
He J., Göransson K., Söderlind U. and Zhang W.
Biomass Conversion and Biorefinery 2 (2012) 1-10.

Paper IV **An Experimental Study on Catalytic Bed Materials in a Biomass Dual Fluidised Bed Gasifier**
Göransson K., Söderlind U., Engstrand P. and Zhang W.
Manuscript in progress (2014), submitted to Renewable Energy.

Paper V **Internal Tar/CH_4 Reforming in a Biomass Dual Fluidised Bed Gasifier**
Göransson K., Söderlind U., Henschel T., Engstrand P. and Zhang W.
Manuscript in progress (2014), submitted to Energy & Fuels.

AUTHOR'S CONTRIBUTIONS

The author's contributions to the papers in the thesis are as follows:

Paper I — The author was responsible for the literature study and a major part of the work with the article structure.

Paper II — The author participated in the practical/laboratory work and took some responsibility for the hypothesis of the experimental design, the experimental plan and data evaluation.

Paper III — The author provided parts of the introduction chapter and the experimental data as the input to the mathematic model

Paper IV — The author was responsible for the main part of the experimental plan, measurement and data evaluation. The author contributed to the experimental data behind all figures and tables.

Paper V — The author was responsible for some development of the measurement method, the main part of the experimental plan, measurement, and data evaluation. The author contributed to the experimental data behind all figures and tables.

RELATED PATENTS AND PAPERS

A Fluidized Bed Gasifier System
Söderlind U., Zhang W., Göransson K. and Engstrand P.
Patent application: EP14163446.9, (2014, Europe)

BTL Laboratory at Mid Sweden University
Göransson K., Söderlind U. and Zhang W.
Proceedings of the 16th European Biomass Conference and Exhibition (BC&E) Valencia, Spain 2008

Tar/CH_4 Reforming by Catalytically Active Materials in a Biomass Dual Fluidised Bed Gasifier
Göransson K., Söderlind U., and Zhang W.
Proceedings of the 2nd International Symposium on Gasification and its Applications (iSGA-2) Fukuoka, Japan 2010

Tar/CH_4 Reforming by Catalytic Bed Materials in a Biomass Fluidised Bed Gasifier
Göransson K., Söderlind U., Engstrand P. and Zhang W.
Proceedings of the 20th European Biomass Conference and Exhibition (BC&E) Milano, Italy 2012

Internal Tar/CH_4 Reforming using a Novel Design in a Biomass Dual Fluidised Bed Gasifier
Göransson K., Söderlind U., Henschel T., Engstrand P. and Zhang W.
Proceedings of the 21st European Biomass Conference and Exhibition (BC&E) Copenhagen, Denmark 2013

ABBREVIATIONS

τ	gasification residence time
BFB	bubbling fluidised bed
BTL	biomass to liquid
CFB	circulating fluidised bed
CLC	chemical loop combustion
CTL	coal to liquid
DFB	dual fluidised bed
DFBG	dual fluidised bed gasifier
d_p	biomass/char particle size
FID	flame ionization detector
FORE	forest as a resource
FSCN	Fibre Science and Communication Network
GC	gas chromatography
GCMS	gas chromatography-mass spectrometry
GHG	greenhouse gas
G_s	bed-material circulation rate [kg/m^{2}s]
GTL	gas to liquid
IGCC	integrated gasification combined cycle
M	biomass moisture content
MIUN	Mid Sweden University
Nm^3	normal cubic meter
PIMC	Pressure-induced Measurement of Circulation
S/B	steam-to-biomass ratio [kg/kg]
S/C	steam-to-carbon ratio [kg/kg]
SEM	scanning electron microscope
SFC	Swedish Gasification Centre
T	temperature [°C]
TCD	thermal conductivity detector
U_c	gas velocity in the combustor (riser)
U_g	gas velocity in the gasifier
WGS	water-gas-shift

1. INTRODUCTION

According to the European Commission, more than half of the EU's total energy consumption in 2010 was imported from outside the EU. Most of oil and natural gas used in EU are imported from Mid Eastern Region, Russia etc. with political instability. The energy supply security is a big challenge for EU as well as the rest of the world. Furthermore, the world oil reserve is being depleted, and global warming is perceived as a threat to our environment, which requires a decreased use of fossil fuels. Swedish government strongly promotes a sustainable society with a target of fossil fuel free transportation fleet in Sweden by 2030. A new bio-automotive fuel industry is expected to be built up within a fairly short time and great number of new companies associated with bio-transport fuels has to be created.

The 1st generation of bio-transport fuels produced from sugar, starch and oil crops are no longer encouraged as it is usually difficult to meet criteria of greenhouse gas (GHG) saving when replacing fossil fuels. On the other hand, the 2nd generation of biofuels from lignocellulosic biomass can be produced from biomass through either hydrolysis (biochemical pathway) or gasification (thermo-chemical pathway), which is attractive for development and commercialization. A number of biomass gasification demonstration plants towards fuel synthesis can be found in Sweden, e.g. in Gothenburg, Värnamo and Piteå/Örnsköldsvik.

The *Fibre Science and Communication Network* (FSCN) is a multi-disciplinary research centre at Mid Sweden University (MIUN). FSCN aiming for improved profitability of mechanical paper and pulp industry and to find new ways to use the forest as a resource. An EU research project, *Forest as a Resource* (FORE), runs from 2011-01 to 2013-12 in FSCN, which deals with production of fibre-based products in synergy with extraction of materials, chemicals and bioenergy. The principle structure of the FORE concept is shown in Figure 1.

Fig. 1: The concept of *Forest as a Resource* (FORE) with the role of biomass gasification.

The work in this thesis is included in the FORE-subproject *Gasification-based Biorefinery for Mechanical Pulp Mills,* where the bio-energy research group focuses on synthesis gas production for bio-automotive fuels. The group consist of Wennan Zhang, asso. Prof., Ulf Söderlind, Ph.D student and research engineer, Jie He, Ph.D student, Till Henschel, Master's student and Kristina Göransson. The project has two tasks, 1) development of biomass to liquid (BTL) pilot plant and experimental test, 2) mathematic simulation of the BTL system and its application to the pulp industry. The author, Kristina Göransson, undertakes the 1st task together with Ulf Söderlind.

The bio-energy research group is included in Swedish Gasification Centre (SFC), a research centre with academic and industry cooperation supported by Swedish Energy Agency from 2011 to 2020. The research in SFC supports the Swedish industry for commercialization of bio-transport fuel production.

1.1. Objectives

The definition of syngas emphasizes two chemical components, CO and H_2. In addition to these, the syngas from a typical biomass fluidised bed (FB) gasifier contains CO_2, CH_4, H_2O, trace amounts of higher hydrocarbons (tars), possible inert gases from biomass, gasification agent and various contaminants. Synthetic chemical and fuel production from coal and natural gas has been well

commercialized by Sasol, Shell, Mobil etc.. But for biomass, the technology has not been established. The main reason is difficulty in syngas production including biomass collection, pre-treatment, gasification and syngas cleaning. An expensive cleaning process is generally required for syngas production towards automotive fuels synthesis. This thesis addresses the critical area in commercialization of fluidised-bed gasification for automobile fuel production – the reforming of tars and CH_4 (see Fig. 2).

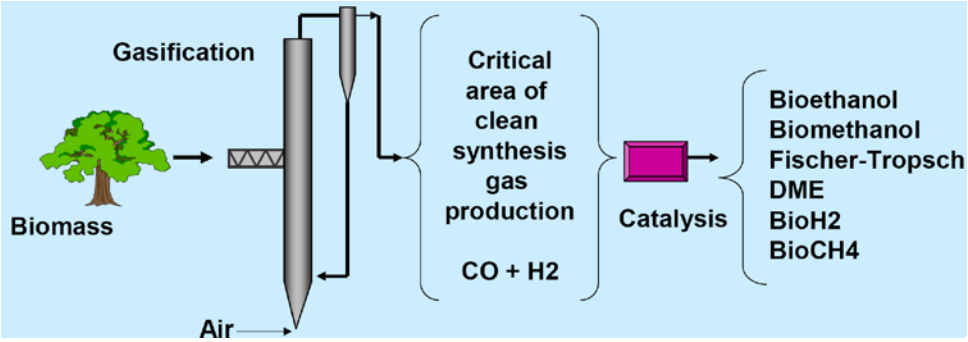

Fig. 2: The critical area in commercialization of fluidised-bed gasification for automobile fuel production

The specific objective in this thesis is to develop a method to produce high quality syngas with low tar and CH_4 content from dual fluidised bed (DFB) gasification of biomass. The work investigates catalytic bed material and an internal reformer in the MIUN gasifier to achieve a highly active zone with catalytic monoliths or catalytic particles to increase the gasification efficiency, suppress the tar generation and to upgrade the syngas inside the gasification vessel. The work includes:

a. Optimization of gasifier design and operation with three key parameters, solid circulation rate, gasification temperature and biomass-to-steam ratio.
b. Use of circulating catalytic bed materials, olivine and Fe-doped olivine.
c. Installation of a novel FreeRef reformer for internal reforming of tar and CH_4 with Ni-catalytic pellets

1.2. Content description

Chapter 2 presents the background of biomass gasification, DFB gasifiers, a short definition of tars, the internal reforming of tars and CH_4, and a brief presentation of different biomass feed stocks and end products (paper I).

Chapter 3 provides an understanding of how the experimental tests have been carried out (paper II-V), includes a description of the gasifier (paper II) and the sampling and analysis of syngas composition and tars (paper II, IV, V).

Chapter 4 presents and discusses the results from the designed experimental tests: bed material circulation (Paper II), influence of operation parameters, catalytic activity of the bed material (paper Paper III-IV), and the performance of the *FreeRef* reformer (paper V)

Chapter 5 presents the main conclusions from this thesis, chapter 6 suggests some recommendations for future work in internal reforming of tars and methane, chapter 7 present the acknowledgments and chapter 8 lists the cited references.

2. BACKGROUND

This chapter presents background information for understanding of the results presented in this thesis. First is an overview of biomass gasification and gasifier technologies, followed by a short description of DFB gasifiers and bed materials in DFB gasifiers. Finally, biomass tars are described with a brief review of internal tar- and CH_4 reforming.

2.1. Biomass feedstock and end-products

The second generation bio-automotive fuels, such as methane, DME, FT-fuels, alcohol fuels, and chemicals can be produced via gasification and synthesis based on various forest and agricultural biomass residues [1]. The production may commercially be realised energy-efficiently and environmentally by integration with existing agricultural and forest industries, energy industry or chemical industry in a concept of biorefinery.

The modern concept of "biorefinery" is characterized by the conversion of biomass into various biobased products, including thermochemical processes such as gasification and fast pyrolysis. In mechanical pulp mills, the available feedstock to the gasification-based biorefinery is significant, and can be classified in 5 categories:

1) residues from thinning and logging such as tree tops and branches when timber is harvested from forest (this is about 30% of the harvested trees);
2) bark taking up 10-13% of the pulp wood flow;
3) fibre material rejects of 10-20% pulp fibre production that deteriorate paper properties,
4) wastewater treatment sludge from sedimentation or primary clarification operations and secondary/biological treatment operations as microbial biomass (biosludge).
5) other available fuels such as peat, recycled wood and paper products.

These biomass residues are a promising feedstock in co-production of bio-automotive fuels, chemicals, biopower, electricity and steam, via gasification in the context of paper & pulp industry.

2.2. Biomass gasification

The application of combustible gas from coal, petroleum coke or biomass was commercial as early as 1812 [2]. The first attempt to use the gas for the internal combustion engine was carried out in 1881 [3]. Gasifers were widespread and used for industrial applications to power and heat. In Europe there were compact gasifier systems for automobile application developed between 1920 and 1940 due to the imminent Second World War and hence the unreliable petroleum supply [2].

Biomass gasification is a thermo-chemical conversion technology with a change of the chemical structure of the biomass at 500-900°C in the presence of a gasifying agent (for instance air, oxygen, steam, CO_2, or mixtures of these components). In general, the biomass gasification process occurs through three steps: (a) pyrolysis, which produces volatile matter and char residue; (b) secondary reactions, involving the volatile products; (c) gasification reactions of the remaining carbonaceous residue with steam and carbon dioxide. The pyrolysis of biomass is the first step of biomass gasification. The volatile and char subsequently participate in a series of complex and competing reactions, as given below [4-6].

Oxidation:				
$C+O_2 \rightarrow CO_2$	ΔH	-394	kJ/mol	(1)
$C+\frac{1}{2}O_2 \rightarrow CO$	ΔH	-111	kJ/mol	(2)
Boudouard:				
$C+CO_2 \rightarrow 2CO$	ΔH	+172	kJ/mol	(3)
Water gas (steam oxidation):				
(1^{st}) $C+H_2O \rightarrow CO+H_2$	ΔH	+131	kJ/mol	(4)
(2^{nd}) $C+2H_2O \rightarrow CO_2+2H_2$	ΔH	+97	kJ/mol	(5)
Methanation:				
$C+2H_2 \rightarrow CH_4$	ΔH	-75	kJ/mol	(6)
Water-gas shift (WGS):				
$CO+H_2O \rightarrow CO_2+H_2$	ΔH	-41	kJ/mol	(7)
Steam reformation:				
$CH_4+H_2O \rightarrow CO+3H_2$	ΔH	+206	kJ/mol	(8)

Gasifiers can be classified on the basis of gasification agent (air-blown, oxygen-blown or steam-blown), pressure (atmospheric or pressurised), temperature (slagging or non-slagging), fluid dynamics (updraft, downdraft, fluidised-bed or entrained flow), heat supply (indirectly or directly heated) and application towards fuel synthesis (directly, indirectly and entrained flow) [1]. The research in SFC for biomass gasification, presented in the introduction chapter, is mainly divided in three nodes where three different gasification technologies are studied: 1) direct gasification, 2) indirect gasification and 3) entrained flow gasification.

Direct gasification (or autothermal gasification) occurs when the oxidant gasification agent partially oxidises the feedstock and provides the heat for the endothermic gasification reactions. Low temperature direct gasification (below 900°C) can be carried out in a fixed bed, a fluidised bed (FB) or a circulating fluidised bed (CFB) [7].

Indirect gasification (or allothermal gasification) does not use an oxidising agent such as air or oxygen, it employ an external energy source for the necessary gasification heat, and produces a nitrogen-free gas. Steam is commonly used as gasification agent, which is easily produced and increases the hydrogen content of the syngas. Dual fluidised-bed gasifiers with steam as the gasification agent, turns out to be a promising biomass gasification technology.

In **entrained flow gasification**, fuel is fed as a suspension of particles in liquid or as a powder in the gasifier at a high temperature (over 1200°C), and in most cases the gasifiers are operated at high pressure (typically 20-50 bar) with pure oxygen and with capacities in the order of several hundreds of MWth. The syngas contain little or no methane and other hydrocarbons [1]. Entrained flow gasification technology has been well commercialised in large-scale integrated gasification combined cycle (IGCC) coal power plants. The technology is presently demonstrated for black liquor gasification for production of DME and methanol.

Direct gasification with air produces a fuel gas of heating value 4-7 MJ/m_n^3 – not suitable for synthesis of bio-automotive fuels. Pure oxygen gasification generates a fuel heating value of 10-12 MJ/m_n^3, but an oxygen plant is needed, which can be economic only for large-scale bio-automotive fuel production plants. Indirect gasification produces a syngas of 12-20 MJ/m_n^3 heating value, and can be suitable for small & middle scale bio-automotive fuel production plants.

2.3. Dual Fluidised Bed Gasifiers

Syngas application for production of transportation fuels in the form of synthetic liquid fuels has been well developed in terms of CTL (coal to liquids) based on coal, and GTL (natural gas to liquids) focusing, to a large extent, on remotely located natural gas reserves. For biomass however, an small or medium scale bio-automotive fuel plant close to the feedstock resources is preferable as this kind of feedstock is widely sparse and has relatively low density, low heating value and high moisture content [8]. This requires a simple, reliable and cost-effective

production of clean and good syngas. An oxygen production system costs about the same as the gasification system, and is too expensive for a small biomass-based plant. For a DFB gasifier, no oxygen and pressurization are required, which makes the gasifier robust and cost-efficient for small-scale.

The main advantages of dual fluidised bed gasifiers are easily treatment of various solid fuels, including high moisture biomass, and fairly simple pre-treatment of biomass, similar to conventional fluidised beds. Indirect gasification technology can use inhomogeneous and moist biomass as a source for gasification. This means that this technology is a good candidate to be integrated into a mechanical pulping mill where the gasifier can utilize low value fibre material and wood residuals from the pulp and paper production process. Comparing to auto-thermal pressurised gasifiers, the advantages of a DFBGs are [1]:

- no oxygen demand to obtain almost nitrogen-free syngas
- lower investment costs
- no or simple pre-treatment of biomass
- easy feeding of biomass due to no pressurisation
- suitable for biomass-based S & M scale bio-automotive fuel plant
- low temperature operation
- technology has been developed and demonstrated for heat and electricity production

DFBGs have been used for three purposes: 1) to indirectly supply heat for endothermic gasification, 2) to transfer oxygen from oxidation reactor to reducing reactor (Chemical Loop Combustion (CLC) process), and 3) to increase hydrogen concentration by capturing CO_2 (Absorption Enhanced Reforming (AER) process). The CLC process employs a metal oxide as a bed material, and renders a redox cycle possible. The AER process uses limestone (CaO) as sorbent for in-situ CO_2 capture during gasification [9]. The concepts are sketched in Fig. 3.

For the first concept, used most commonly, one bed is fluidised with steam to gasify biomass and to produce syngas at 700 – 900 °C; the bed material together with char from gasification is circulated to the other bed, the combustion bed. The combustion bed is fluidised with air to burn char to produce heat. The bed material is circulated between these two beds to transfer heat from the combustion bed to the gasification bed, while the flue gas in the combustor is separated from the syngas in the steam gasifier. DFBG produce two gases: syngas with little or no nitrogen and flue gas.

The heat produced in the combustor must be sufficient to manage the heat loss from the gasifier and the thermal energy requirements of the gasification reactions. Usually, additional fuel is required in the combustor. The temperatures of the gasifier and the combustor are maintained by the char combustion and the bed material recirculation. The bed material circulation is controlled with the gas velocity in the combustor, the total solids inventory and aeration in the tube connecting the bottoms of the gasifier and the combustor. The gas flow through the gasifier can also enhance the aeration in the abovementioned tube, so that the bed material circulation increases with gas velocity in the gasifier.

A lower gasifier temperature leads to higher char yield, and subsequently results in higher combustor temperature, with increased temperature of the circulating bed material. This results in higher gasifier temperature, with less char produced in the gasifier. Thus a balance of temperatures between the gasifier and the combustor can be reached – the system is auto-stabilising.

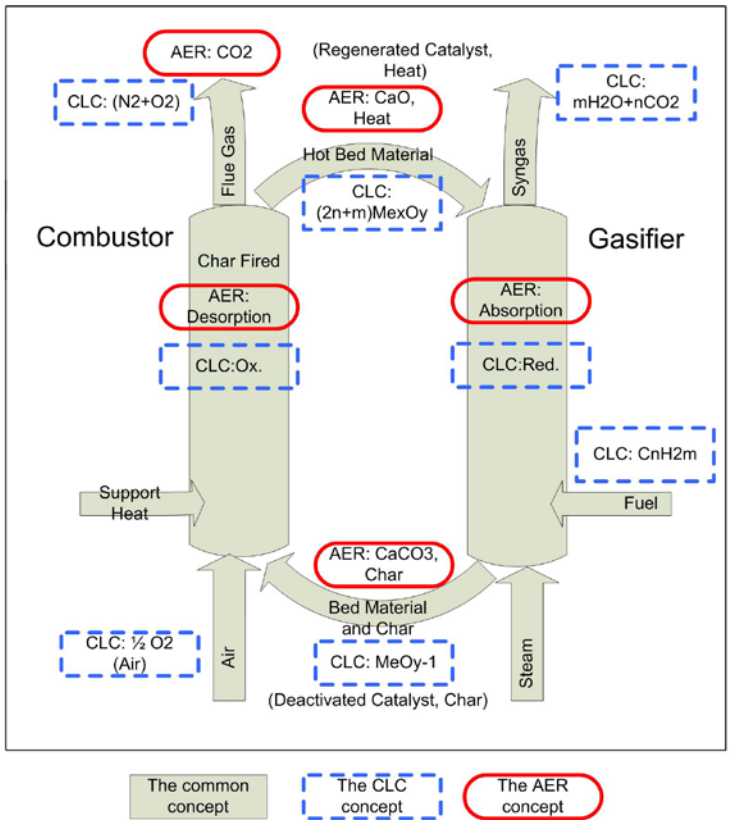

Figure 3: Three concepts of DFBG gasification

2.4. Bed materials in DFB gasifiers

The main function of bed material in a DFBG is to supply the gasification zone with energy for conversion of biomass. The bed material makes in-situ gas conditioning possible in the same time. Reactive bed materials can be applied to improve agglomeration behaviour, to enhance tar cracking and to increase H_2 content. Moreover, the bed material can be used to perform catalytic activity, CO_2 capture, oxygen transportation, etc.. Catalytic reforming can be performed either with catalytic bed material during gasification or after gasification using a separate, downstream catalytic reactor. Catalytic bed material promotes char gasification, water-gas-shift and steam reforming reactions, which can enhance tar/CH_4 reforming and increase the H_2 content in the syngas. There is a great interest using in in-bed additives since complex downstream cleaning methods can be simplified [10].

For bed materials used in DFB gasifiers, examples of natural minerals are dolomite, limestone, olivine and iron ores, and examples of synthetic minerals are Ni-supported olivine, Fe-supported olivine, alkali metal-based material, and char [11]. Sulphur (H_2S and COS) can be retained in the bed (up to 90%) by sorbents such as limestone [12].

An inexpensive material for tar cracking can be char. But, as char itself gets converted during the process, an external continuous supply of char into the gasifier is required [10].

Olivine ($(Mg, Fe)_2 SiO_4$) is a natural mineral containing magnesium, iron oxide and silica. The produced gas in the gasifier can be partially oxidized by olivine since olivine acts as an oxygen carrier in DFB operation. The oxygen transport capacity of olivine can be 0.5wt% [13]. Reduction of bed material in the steam gasifier with the following oxidation in the air combustor achieves a catalyst recovery cycle, similar to the chemical looping combustion (CLC) [14].

A number of articles have reported catalytic activity of olivine in cracking and reforming of tars and enhanced steam and dry reforming of hydrocarbons [14-19]. The catalytic activity of iron species is considered to be related to their oxidation state. Some researchers suggest that the efficiency of olivine in tar cracking relies on free iron (III) oxides present at the surface, while other researchers have different opinions. Nordgreen et al. [20] studied the decomposition of tars on metallic iron and iron oxides in the temperature range of 700-900°C. In this study, only iron in the metallic state showed considerable activity for tar decomposition.

At 900°C the tar decomposition activity was similar to calcined dolomite [20]. Metallic iron is known to be an active species for aromatic hydrocarbon decomposition and iron oxides are known to be an good catalyst for the WGS reaction [21].

Compounds of iron and oxygen occurring in nature, include $Fe_{1-x}O$ (wustite), α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite), and Fe_3O_4 (magnetite). The ideal and stoichiometric FeO consists of Fe^{2+}-ions, the α-Fe_2O_3 and γ-Fe_2O_3 of Fe^{3+} -ions, and the Fe_3O_4 of Fe^{2+} - and Fe^{3+} -ions [22]. In the air combustor, the olivine decomposes to binary iron oxide, silica oxide and magnesium silicate, reaction (9):

$$(Fe_{0.1}, Mg_{0.9})_2\,SiO_4 + 0.05O_2 \rightarrow 0.1Fe_2O_3 + 0.1SiO_2 + 0.9Mg_2SiO_4 \quad (9)$$

The binary iron oxide diffuses to the surface of the bed material. Fe_2O_3 enters the steam gasifier, where it reacts with hydrocarbons and is reduced to FeO, reaction (10):

$$5Fe_2O_3 + 2C_xH_y \rightarrow 10FeO + 2xCO_2 + yH_2O \quad (10)$$

Reduced iron oxide (FeO) is transported back to the air combustor where it reacts with air and is oxidized to Fe_2O_3 [14], reaction (11):

$$FeO + 0.5O_2 \rightarrow Fe_2O_3 \quad (11)$$

Olivine bed material can be pre-treated by calcination [16] to increase the free iron (III) concentration on the surface for better catalytic activity. Besides, olivine is a very flexible structure that can be a host for transition metal [23]. A better conversion can be achieved by the use of modified olivine, such as Ni-supported olivine or Fe-supported olivine. Ni-supported olivine is highly effective in reduction of tars and CH_4 [24], but an important drawback is the toxicity of nickel and the volatiles particles that occurs in FB gasifiers. Fe/olivine, however, is a relatively harmless and cheap catalyst [25]. Many investigations, e.g. the research project UNIQUE [26], have shown that Fe/olivine is efficient in tar reforming and also active in CH_4 steam reforming [21, 23, 27-29].

Although many in-bed catalysts performed good results concerning syngas quality, some of them are very expensive and some leave contaminated residues behind [30]. Additionally, there have been attrition problems and loss of catalytic activity. Ni-based catalysts can be quickly deactivated due to carbon deposition and sulphur or chloride poisoning, oxidation, and sintering [10]. However, the lifetime of the catalyst can be prolonged by the oxygen balance in a DFBG [24, 42].

2.5. Biomass tars

Biomass gasification results in higher tar content in the product gas compared to coal gasification. Tar concentration in biomass syngas is in the order of 10 g/m^3_n for fluidised-bed gasifiers [31]. In condensation-related issues the tar dew point is one of the important parameters. The fouling problems are not significant as long as all the tar is present in the gas phase. The water solubility of the tar is another important parameter. The pollution of wastewater is related to the type of tar components being present in the syngas, i.e. the water solubility of the tars [32].

Various research groups are defining tar differently. Evans and Milne described tar as "The organics, produced under thermal or partial-oxidation regimes (gasification) of any organic material, are called "tars" and are generally assumed to be largely aromatic."[33]. According to the ECN definition tar comprises all organic components having a higher molecular weight than benzene which is not considered to be a tar [32]. It is worth noticing that benzene is one of the major and more stable aromatic compounds and may cause technical or environmental problems, and hence some researchers consider benzene a tar.

Besides the different definitions of tar, the tars can either be classified in system focusing on their physical properties (water solubility or condensation) [32] [34], or in system focusing on the process conditions in which the compounds are formed [33] [31]. In addition, tars can be divided into heavy tars and light tars. Heavy tars comprise high molecular weight hydrocarbon compounds that have a high dew point. Light tars comprise the range in molecular weight from ~78 to ~300, which are volatile and semi-volatile aromatics and phenolics.

A common **tar classification system** suggests five different tar classes based on the physical properties of water solubility and condensation [34]:

- **Class 1:** The heaviest tars, condense at high temperature even at very low concentration.
- **Class 2:** Heterocyclic components which exhibit high water solubility due to their polarity.
- **Class 3:** Aromatic compounds, light hydrocarbons, which are not important in condensation and water solubility issues.
- **Class 4:** Light polyaromatic hydrocarbons (2-3 ring PAH compounds) that condense at relatively high concentrations and intermediate temperatures.
- **Class 5:** Heavy polyaromatic hydrocarbons (4-7 PAH compounds) that condense at relatively high temperatures at low concentrations.

Evans and Milne proposed a tar classification system to characterise tar from different types of biomass gasifiers, with four major classes [33]:

- **Primary tars:** products from the main components of the biomass.
- **Secondary tars:** characterised by phenolics and olefins, products from the conversion of primary tars.
- **Alkyl tertiary tars:** characterised by methyl derivates of aromatics.
- **Condensed tertiary tars:** polyaromatic hydrocarbons (PAH) without substituent.

2.6. Internal Tar- and CH_4 Reforming

A challenge for fluidised-bed gasification is the reforming of tars and CH_4. Tars in the syngas make gas cleaning difficult and CH_4 may have a volume content above 10% leading to 1/3 energy lost in the once-through synthesis. Once tars are absent, other impurities, such as NH_3, H_2S, COS, HCl, volatile metals, dust and soot, can be removed by standard wet gas cleaning technologies.

Reduction of tars and CH_4 to an acceptable low level is usually achieved by high temperature thermal cracking, low temperature catalytic cracking, or physical tar treatment like water scrubbing + sedimentation and oil scrubbing + combustion [31, 33, 35-38]. Catalytic cracking efficiency can be 90-95 % at reaction temperatures about 800 ~ 900°C [39], whereas thermal cracking requires temperatures above 1200°C to reach the same efficiency at expense of energy losses and big investments on high temperature materials.

Syngas can be conditioned to different degree depending on a balance of economic cost against technical specification for downstream synthesis. The downstream syngas cleaning usually accounts for up to 38% of the transport fuel production cost [40]. The major challenge in the production of high quality syngas through biomass fluidised-bed gasification is the reforming of tars and methane (except for methanation application) to a minimum allowable limit.

Catalysts can be used in downstream catalytic reactors *(secondary methods)*, [41, 42], such as catalytic beds, monoliths and filters, or directly inside the gasifier (*primary methods*), e.g. added directly in the fluidised bed gasifier as the bed material. There are various of primary methods to reduce tar content in the syngas: optimal gasifier design and operation, high gasification temperature, long gas residence time in a hot zone, catalytic bed material addition (dolomite, olivine, char, nickel-based material, iron etc.) and so on. Primary methods are more cost-effective attributed to lower thermal losses, less downstream reactors and lower investment cost than secondary methods.

Tar/CH_4 reforming performance by catalytic bed materials is still limited [43]. The performance might be improved by more intensive contact between volatile gas and catalytic bed material at a higher temperature zone in the gasifier, above the dense bed where the hot bed material returning from the combustor.

An innovative concept of internal reforming, by integrating a catalytic hot gas filter in the freeboard of a fluidised-bed steam gasifier, has been tested by S. Rapagná et.al.. They used Ni catalyst filled into a hollow-cylindrical silicon carbide based filter [44]. The average variation of the content in the produced gas showed an increase of the hydrogen yield by 130% and a decrease of the methane- and the tar content by 20% and 79% respectively.

Another approaches have been suggested by a few researchers. One example is the two-stage DFBG, proposed by Xu and his colleagues in 2008 [45]. This design uses the principle of two fluidised beds without external upper pressure lock. Another example is the G-Volution design concept proposed by Schmid et al.[46] with integrated flow obstacles to create a counter current flow pattern to increase gas-solids contact.

3. EXPERIMENTAL

This chapter describes the pilot gasifier, the conditions of the FreeRef reformer, the biomass feedstock, biomass feeding system and bed material. Thereafter, it explains the method used for sampling and analysis of the syngas composition and tar content in the syngas. Finally, there is a short description of the model study. Experimental details and specific operation conditions for each test can be found in the appended papers.

3.1. MIUN Gasifier

The MIUN gasifier is a DFBG (see Fig. 4) and consists of a bubbling fluidised bed (BFB) steam gasifier and a circulating fluidised bed (CFB) riser combustor, and has the biomass treatment capacity of 150 kWth, i.e. approx. 25 kg biomass feed per hour. The heat carrier between the reactors is silica sand bed-material or catalytically active bed-material. The biomass is fed into the dense bed in the gasifier. The fluidisation agent in the gasifier is steam and the syngas exits from the top of the gasifier. The residual biomass char is then transferred by bed-material into the combustor through the lower pressure lock (see Fig. 5). In the combustor, the fluidisation agent is air, which results in an oxidation of the char that produces heat at the temperature of 950-1050°C. The hot bed-material separates from the flue gas in the particle separator to be recycled into the gasifier through the upper pressure lock, which prevents gas leakage between the separate environments in the gasifier and the combustor. Due to operation convenience the upper pressure lock is fluidised with air instead of steam. Likewise, air is used for aeration of the lower pressure lock if necessary. The gasifier is supported by electrical heaters and is heavily insulated. The gasifier and the combustor have the height of 2.5 and 3.1 m, and the inner diameters (Di) of 300 and 90 mm, respectively. Temperatures and pressures, at a number of points from the distributor to the top of the gasifier and the combustor, at the upper pressure lock and at the particle separator, as well as gas flows, are registered through the computer data collection system.

The electrical heaters allow separate operation of the steam gasifier as a BFB gasifier. At BFB operation, the interconnections between the gasifier and the riser are blocked, and hence are the vessels divided.

Fig. 4. The 150 kW_{th} MIUN biomass DFB gasifier.

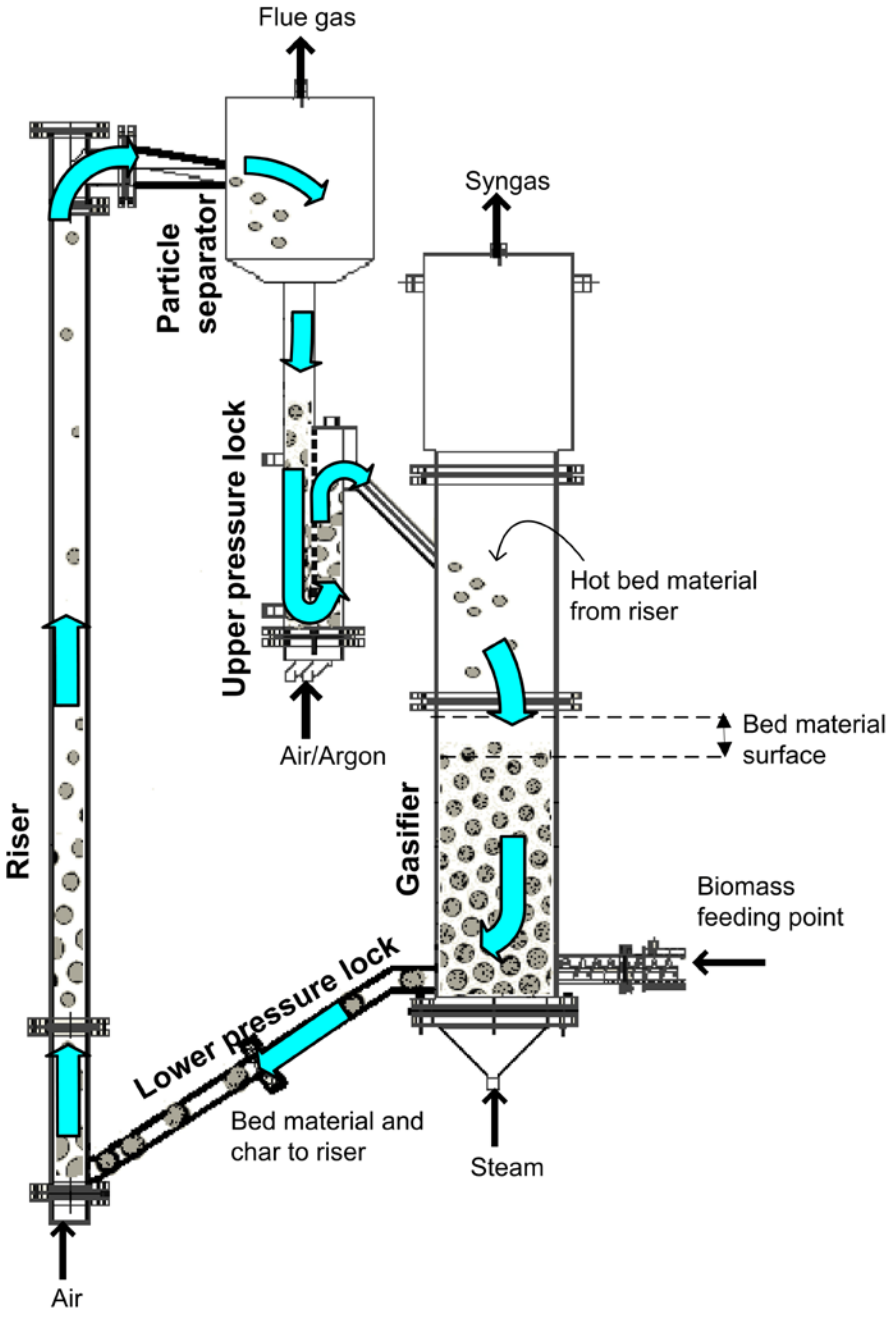

Figure 5. The 150 kW_{th} MIUN biomass DFB gasifier

3.2 In-situ *FreeRef* reformer

In general, the biomass gasification process occurs through three steps: 1) pyrolysis which devolatilises biomass into char and volatile matter including tars; 2) secondary reactions such as cracking and reforming of tars; 3) gasification reactions of remaining carbonaceous residue with steam and carbon dioxide. Steps 1 and 3 take place in the dense bed of the fluidised bed gasifier, while step 2 takes place in the freeboard of the fluidised bed. Thus, the reforming of tars and CH_4 in the freeboard is important for high quality syngas production, which is favoured by a good contact of volatile with catalytic bed material at a sufficiently high temperature. This might not be the case for the freeboard region of MIUN gasifier, where the hot bed material returns next to the wall while the volatile passes through the centre. This insufficient gas-solids contact may be one reason for the relatively high tar content in the syngas of MIUN gasifier[43], although Fe/olivine were used as circulating catalytic bed material.

A good gas-solids contact can be realized by an in-situ reformer installed above the dense bed of the fluidised bed gasifier but under the hot bed material return position. Such an in-situ reformer, the *FreeRef* reformer, similar to an upper fluidised bed, is developed in this work for MIUN gasifier as shown in Fig.6. The hot bed material circulated from the combustor passes through the reformer and creates a fluidisation region with the highest temperature in the gasifier, on the way down to the bottom bed of the gasifier to provide heat for biomass pyrolysis. The volatile from biomass pyrolysis, on the other hand, flows through the in-situ reformer and experiences cracking and reforming of tars and CH_4 in the reformer at high temperature.

The in-situ reformer can be combined with a catalytic monolith or a catalytic bed with better effect of tar reforming, i.e. Ni-based catalytic pellets (see Table 1 and Fig. 7). Nickel oxide is the active component with alumina as support material.

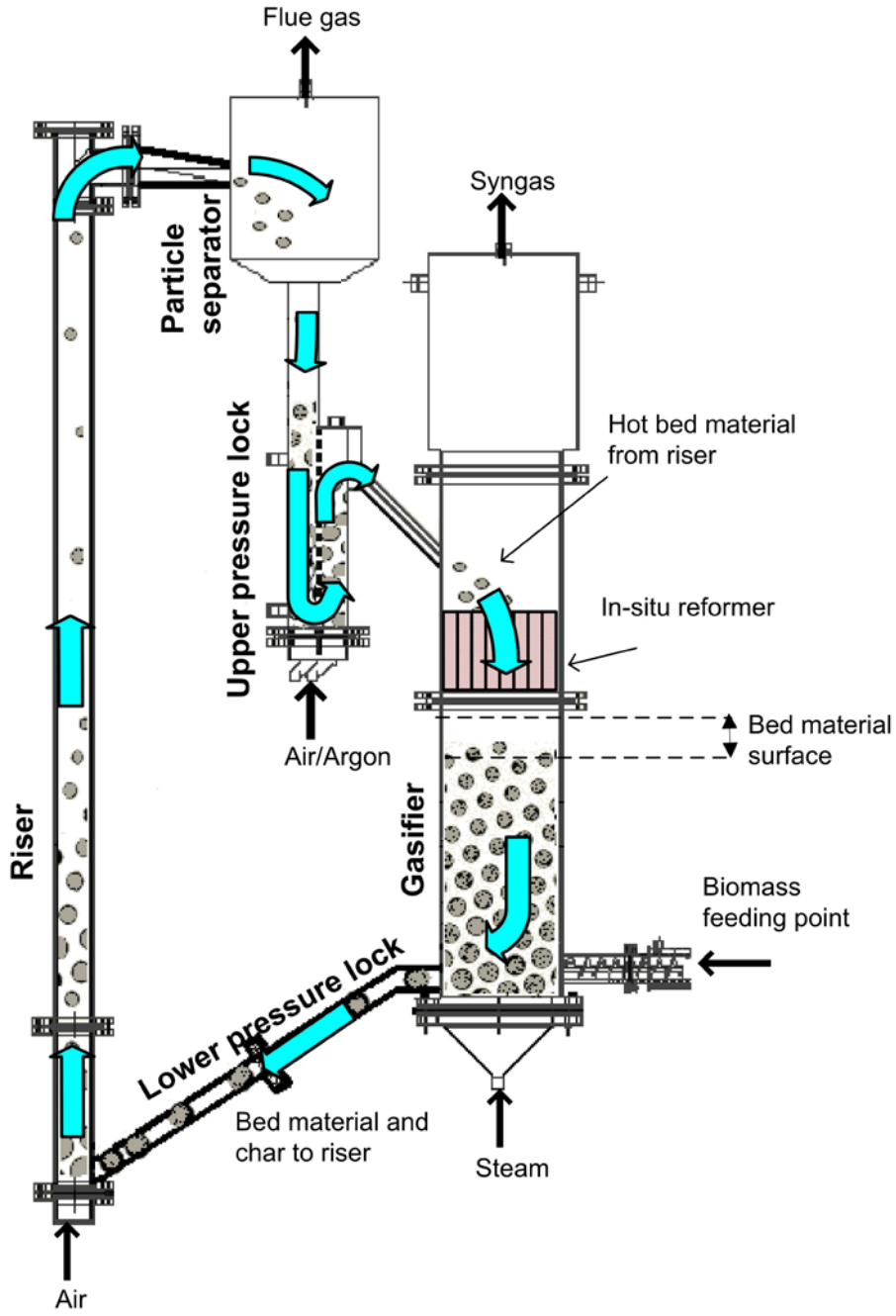

Fig. 6. MIUN DFB gasifier with in-situ *FreeRef* reformer.

Table 1. Physical and chemical properties of the steam reforming catalytic pellets

Appearance	5 holes drums
Particle size (mm)	19-20
Pore diameter (mm)	3-5
Bulk density (kg/l)	0.90-0.95
Crushing strength (N/particle)	>300
NiO (%)	>14
Free silica (%)	0.2

Fig. 7: Ni-based catalytic pellets for steam reforming of tars and CH_4

3.3. Biomass feedstock and feeding system

The biomass feedstock is wood pellets (see Table 2). The PLC-operated (Process Logic Controller) feeding system is designed for constant biomass feeding. The biomass is fed into a pneumatic oscillatory vane feeder to achieve high precision. A coaxial left- and right- handed thread screw feeder thereafter makes a steady stream of biomass into the final screw feeder without plugging the pipe. The final screw feeder is rapidly feeding biomass into the gasifier to avoid reaction in the screw feeder and particle congestion. The feeding rate can be controlled by frequency-controlled motors of screw feeder. Nearest to the gasifier, the final screw feeder is cooled by water flow through a cylindrical jacket.

Table 2. Fuel analysis of wood pellets (6 mm) produced by SCA BioNorr AB, Sweden.

Elementary analysis	% db	
Ash cont.	0.4	
Sulphur S	<0.01	
Chlorine Cl	<0.01	
Carbon C	50.9	
Hydrogen H	5.9	
Nitrogen N	<0.1	
Oxygen O (calc.)	42.7	
Moisture	6.5	%
Durability of pellets	98.1	%
Bulk density	667	kg/m^3
Net calorific value as rec.	18.849	MJ/kg
Net calorific value db	20.159	MJ/kg

3.4. Olivine and Fe/Olivine bed material

Two catalytic bed materials are used in this test, olivine and 10% wt Fe/olivine. The reference bed material is non-catalytic silica sand bed material (see Table 3). In these tests the olivine is calcined inside the DFB reactor at 900°C in 10 hours, with air at slightly elevated pressure.

The 10 wt%Fe-olivine catalyst is synthesized by impregnation of an aqueous iron nitrate solution. The iron nitrate is received as an aqueous solution (9.3-9.7 wt% Fe; 40.3-42.0 wt% $Fe(NO_3)_3 9H_2O$). The natural olivine ($(Mg,Fe)_2SiO_4$) is added and stirred vigorously in the aqueous solution of iron nitrate, followed by solvent evaporation and drying in a vertically revolving kiln with a propane flare, as heat source. Finally the Fe/olivine is calcined as the natural olivine.

The bed-material circulation rate (Gs) is measured by the solid circulation measurement system Pressure-induced Measurement of Circulation (PIMC) (detailed information in Paper II).

Table 3. Bed material (Fe/olivine is here considered to have equal properties as olivine)

Material	**Silica sand**	**Olivine**
Mean particle size (μm)	200	223
Density (kg/m^3)	2650	3300
Minimum fluidisation velocity U_{mf} (m/s)	0.02	0.03
Terminal velocity Ut (m/s)	2.2	2.8
Gasifier Superficial Velocity (U/U_{mf})	11-16	7-10

[a] steam at bed temperature 750-900°C

3.5. Measurements and analysis of syngas composition

The main syngas stream from the gasifier is led to an incinerator for complete combustion. A slip stream of the syngas passes through the gas sampling and analysis system. Electrical heaters are used to keep the syngas temperature at about 400°C to avoid tars condensation in the pipes. For the measurements of gas composition, the syngas is subtracted by a vacuum pump and sampled manually in Tedlar gas sampling bags to be analyzed off-line in a parallel FID and TCD GC-detection system. The gas was sampled approx. four times in each experimental test under the same gasifier operation condition. Gas contents H_2, CO, CH_4, CO_2 and O_2 are also analyzed on-line with *X-STREAM Enhanced XEGP – General Purpose Gas Analyzer.*

3.6. Measurements and analysis of tars

Most heavy tars are GC-undetectable and are here gravimetrically analyzed. The results include GC-undetectable heavy tar compounds together with some GC-detectable tars (from 2-3 rings) [34] in addition to all compounds larger than 3 rings [47]. The gas passes a high temperature filter (Munktel ET/MK 360 Quartz thimble 34*150 mm, penetration <0,002% DOP (0.3 μm)) held at 400 °C during sampling, and cooled down to 25°C while passing through two tar capture glass fibre filters in series (Whatman GF/D, particle retention 2.7 micron, thickness 675 micron at filtering speed about16.5 ml/s) (see Fig. 8). It took about 45 sec. to collect 4 litres product gas from the gasifier. After each sampling, the glass fibre-filter adapters in the tar collector are washed with isopropanol. Finally, the tars and isopropanol are collected in a round flask containing isopropanol. The detailed sampling procedure can be found elsewhere[48].

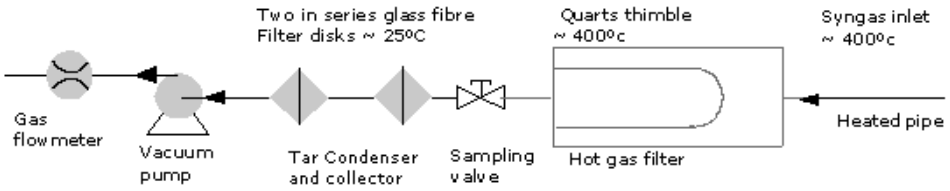

Fig. 8. Gravimetric tar sampling system (the syngas passes through two tar capture glass fibre filters in series at ambient temperature whereas the tars condense).

The solution containing the tar sample together with some possible filter fibres is filtered through a glass fibre funnel (pore size 10-16 μm) and collected to a new round flask that has been weighted ahead.

Finally, the round flask is inserted into an evaporation condenser. When the tar sticks on the inside of the round flask the evaporation is finished. The weight difference, i.e. the tar content, can finally be calculated. The remaining tars are referred to as "gravimetric tar". The analytical balance applied is a *Precisa XR 205SM-DR*, readability 0.01 mg/ 0.1 mg, with a built-in self calibration system.

3.7. DFBG modelling

In this work, biomass gasification with steam in a DFBG is simulated with *ASPEN Plus.* To deal with the simulations on biomass pyrolysis and the evolutions of tar and char, some subroutines are designed based on relevant empirical equations from literature. The sub-models are setup based on the thermodynamics and reaction kinetics. The flow-sheet is depicted in Fig. 9. The yield and composition of the syngas, and the contents of tar and char can be calculated from the model. The concerned variables are: structure of the gasifier, gasification temperature (T), steam to biomass mass ratio (S/B), biomass moisture content (M), gasification residence time (τ), and biomass/char particle size (dp). The model is evaluated with the experimental results measured from MIUN gasifier.

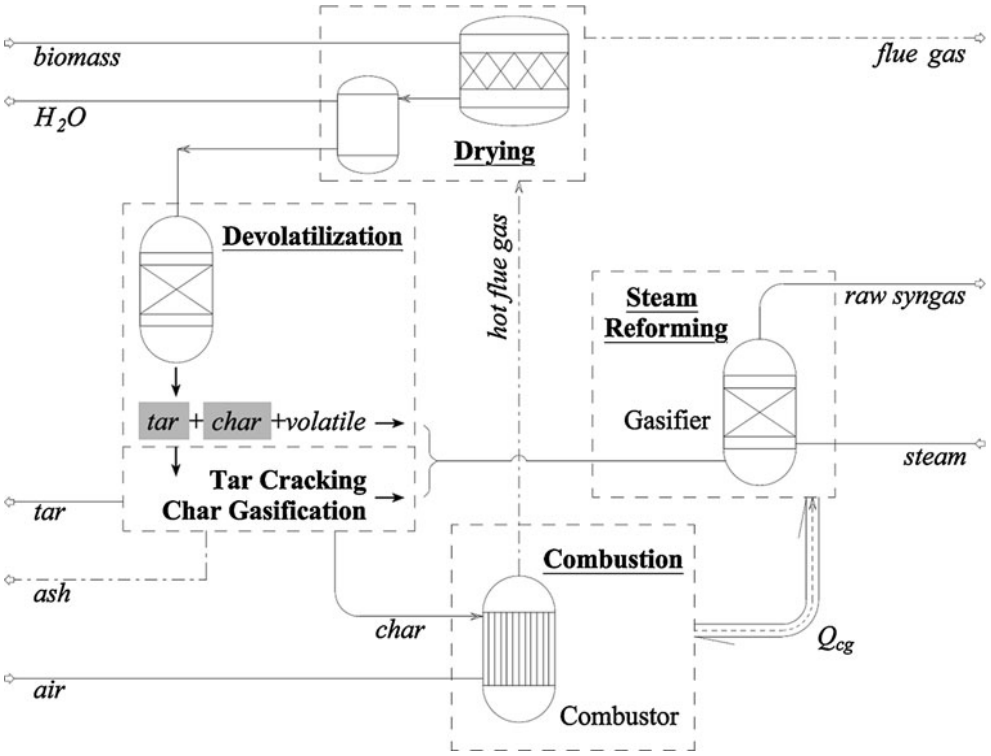

Fig. 9: Flow-sheet of the DFBG biomass gasification model

4. RESULTS AND DISCUSSION

This chapter presents a review of the main results presented in paper I-V. Section 4.1. presents the general performance of the MIUN gasifier. Section 4.2 to 4.4. presents the influence of gasification temperatures, steam-to-carbon ratios and bed materials on the syngas composition and tar content in the syngas. Section 4.5. presents the performance of the FreeRef in-situ reformer at various operation conditions on the syngas composition. Finally, section 4.6.summarize and evaluate how the gasification modes included in this test series influence the produced syngas.

4.1 General performance of MIUN gasifier

4.1.1. Bed material circulation rate

To maintain a sufficient heat transfer between the gasifier and the combustor, the solid circulation rate, Gs, must be held at a certain high level. Gs is mainly determined by the gas velocity in the combustor, Uc, and the bed material inventory. Gs is also affected by the gas velocity in the gasifier, Ug, since is the gas in the gasifier partly serving as an aeration of the lower pressure lock that connecting the gasifier and the combustor. A novel method to measure solid circulation rate was developed, which also works well at high temperature condition.

Fig. 10 shows the effect of Ug on Gs, while Uc was kept constant at 3.5 m/s. Gs increased gradually with Ug. The results in Fig. 11 show the dependency of solids circulation rate on the superficial gas velocity in the combustor and the bed material inventory. The bed inventory strongly influences Gs due to the change of solids concentration in the upper part of the combustor.

A circulation rate of at least 20 kg bed material per 1 kg biomass is required in normal gasifier operation condition. At the full load of the 150 kW gasifier, i.e. approx. 25 kg wood pellets feed per hour, a solid circulation rate of 600 kg bed material per hour is needed, which corresponds to a bed material circulation rate of 26 kg/m^2s.

The temperature difference between the gasifier and the combustor is strongly dependent on Gs as seen in Fig. 12. A high Gs gives a small temperature difference and vice versa. Gs values that exceeded 10 kg/m^2s is required for a sufficiently low temperature difference.

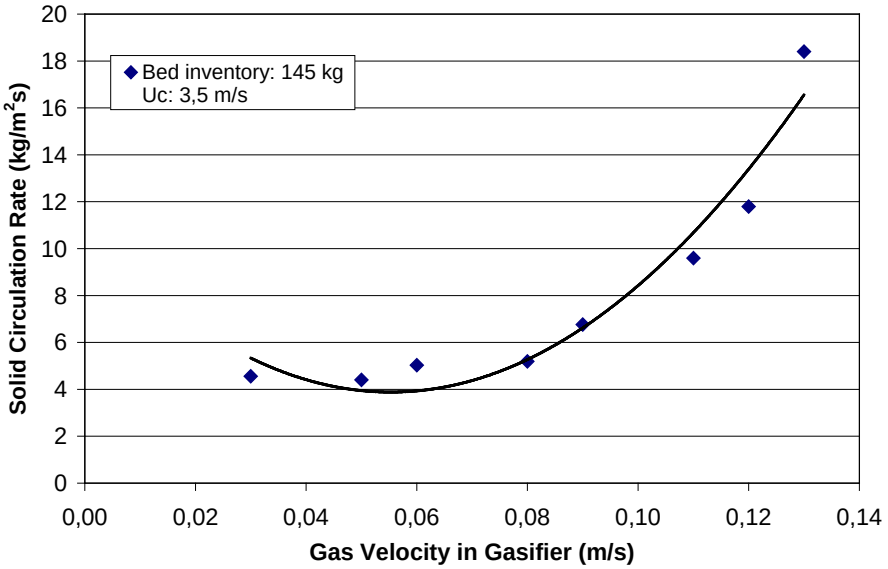

Fig. 10. Solid circulation rate as a function of gas velocity in the FB gasifier

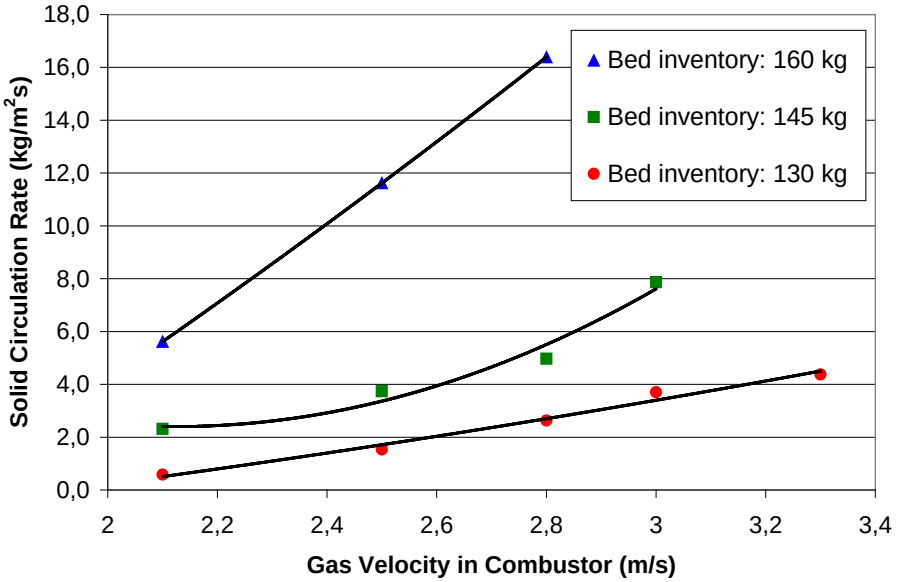

Fig. 11. Solid circulation rate as a function of bed inventory and the gas velocity in the combustor

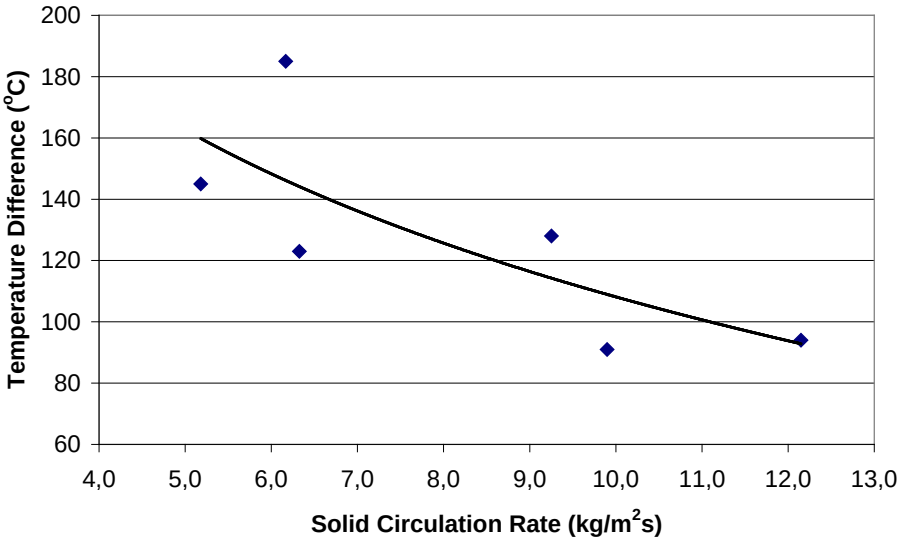

Fig. **12.** Temperature difference between the gasifier and the combustor as a function of the solids circulation rate

4.1.2. Temperature profile for MIUN gasifier

The temperature profiles for MIUN gasifier over the reactor height in BFB and DFB mode for same operation conditions of temperature 850°C and S/C 1.2.are shown in Fig. 13. In BFB mode (without bed material circulation), the temperature holds constant over the dense bed but drops down in the freeboard due to the wall cooling effect, steam reforming and cracking reactions as well as pyrolysis and gasification of entrained biomass and char particles in the freeboard.

In DFB mode, the recycling of hot bed material gives rise to a hot spot in contrast to the BFB mode. Unfortunately, insufficient mixing of the returning hot bed material particles with the volatile gas in the freeboard results in limited heat transfer between the gas and solid phases.

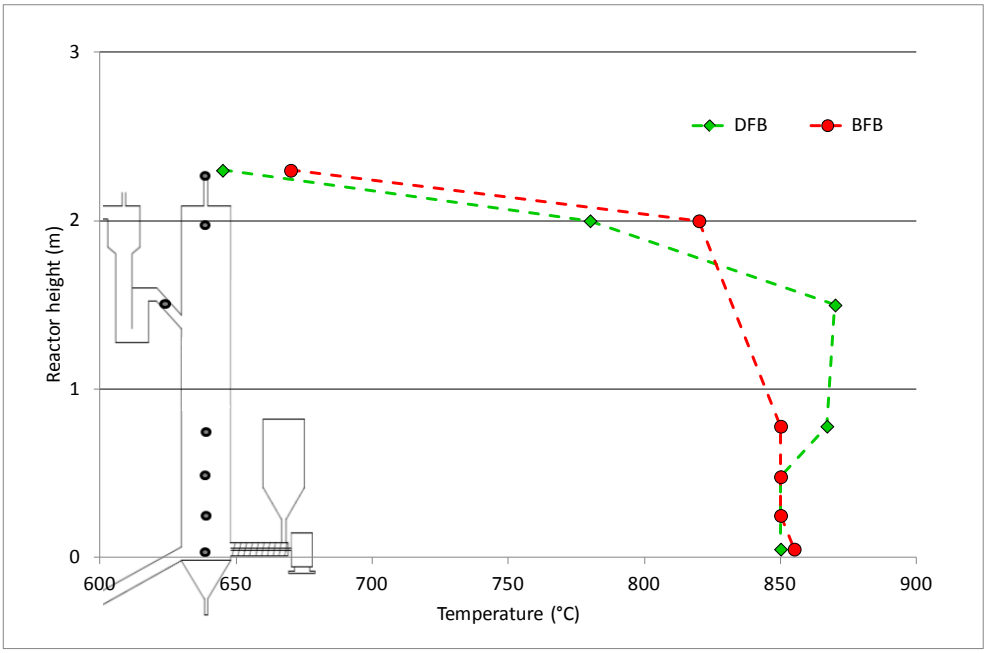

Fig. 13. Temperature profiles for MIUN gasifier over reactor height in BFB and DFB modes.

4.2. Influence of gasification temperature

A higher gasification temperature will be in favour of the H_2 and CO yields since the endothermic gasification reactions are enhanced (see reactions 3,4,5 and 8, in chapter 2.2.). Tar/CH_4 reforming is to a great degree strongly endothermic, and favoured by high temperature.

4.2.1. Results from the model

Figure 14 shows results from the model for the effect of the gasification temperature on the syngas composition. As seen in Fig. 14 a, the syngas yield increases with temperature as a result of the enhanced gasification and reforming at a higher temperature. Tar content decreases from 50.0 g/m^3 at 750°C down to about 13.0 g/m^3 at 900°C due to tar thermal cracking and steam reforming. The char fraction decreases from 22.5 wt.% at gasification temperature 750°C to 11.5 wt.% at 950°C. Ideally, the lower gasification temperature leads to higher char yield, and subsequently results in higher combustion temperature, hotter bed material, and higher gasification temperature, so that less char will be produced. The system is auto-stabilising.

As seen in Fig. 14 b, the concentration of CO increases with temperature, while that of H_2 reaches a maximum value at about 850°C. This is because H_2 probably takes part in the hydrogenation reactions at higher temperatures. H_2 concentration is higher than CO concentration under normal DFBG operation conditions, but they will change positions when the gasification temperature in the model is above 950°C. The CH_4 concentration is around 10.0 vol.% and not sensitive to temperature. Significant reduction of CH_4 takes place at a temperature higher than 1,250°C or by use of catalysts, e.g., nickel-based catalysts.

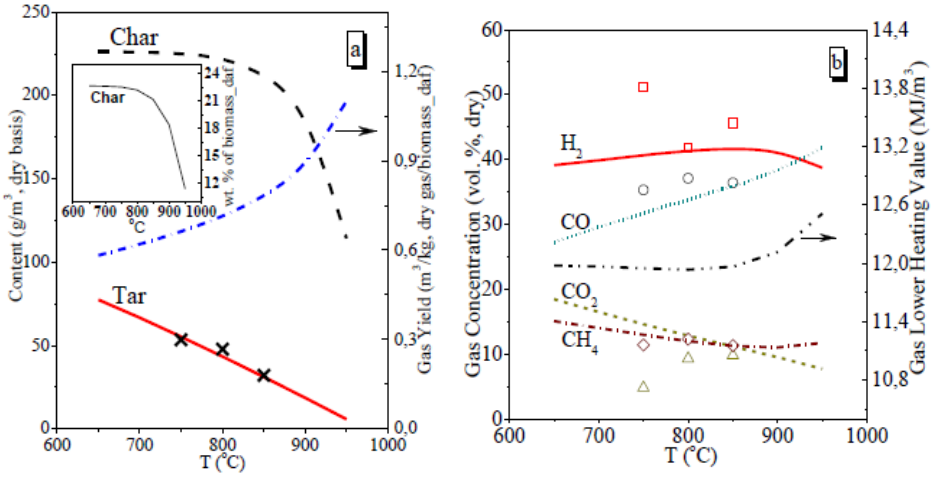

Fig. 14. Effect of temperature on the gasification (wood pellets, silica sand bed material, S/B 0.6, τ 5.0 s, and dp 5.0 mm)

4.2.2. Experimental results

The effect of gasification temperature on the syngas composition including CH_4 is shown in Fig.15 for three different bed materials when the steam-to-carbon (S/C) ratio is held at 1.2. It can be seen from the figure that higher temperature enhances the tar/CH_4 reforming reactions and results in higher content of H_2 and CO, while the CO_2 content slightly decreases since the exothermic shift reaction is favoured by low temperature.

CH_4 is the most recalcitrant hydrocarbon to reform, which very much depends on the temperature (see Fig. 16). The CH_4 content is not sensitive to the temperature change up to the temperature 800°C. From temperature 800°C to 900°C, the CH_4 content decreases clearly from about 11% to 9%, and even down to 7% when

catalytic bed materials are used. These results indicate that hydrocarbon reforming is strongly sensitive to the temperature around 900°C, especially for reforming with catalytic bed materials.

Figure 17 shows the temperature dependency of the gravimetric tar content in the syngas when the S/C ratio is held constant at 1.2. The tar content decreases with increasing of temperature as a general trend. At 850°C, Fe/olivine gives a slightly higher tar content which is a vague result compared to olivine. The tar content follows the downward tendency for Fe/olivine when the gasification temperature increases to 900°C. Similar behaviour with Fe/olivine for GCMS tars can be found in article [49], where no significant change can be recognized in the temperature range of 770-860°C.

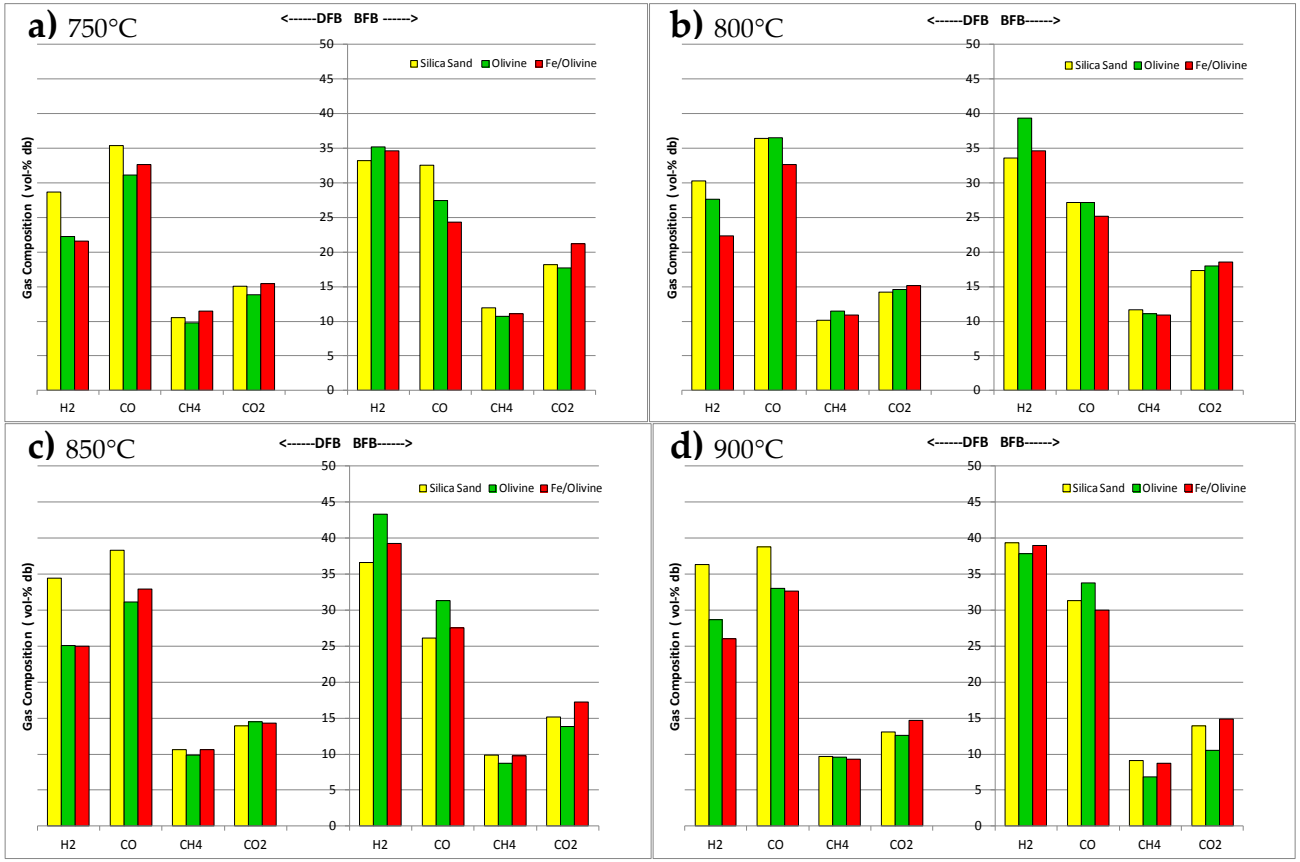

Figure 15 a-d. The effect of the gasification temperature on syngas composition for three different bed materials, at S/C 1.2

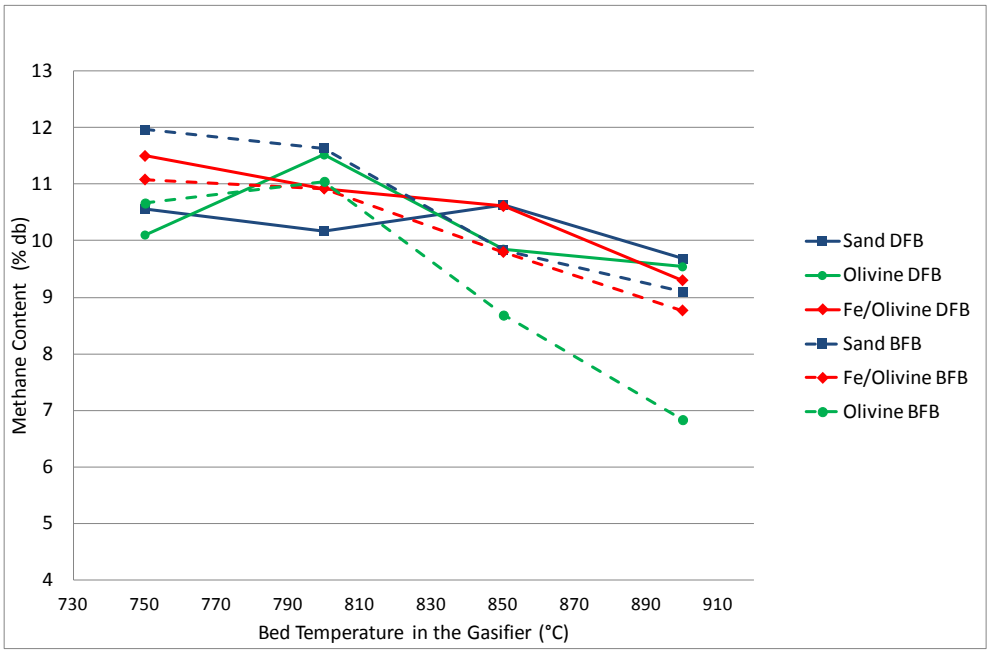

Figure 16. Methane content vs. gasifier temperature at S/C 1.2

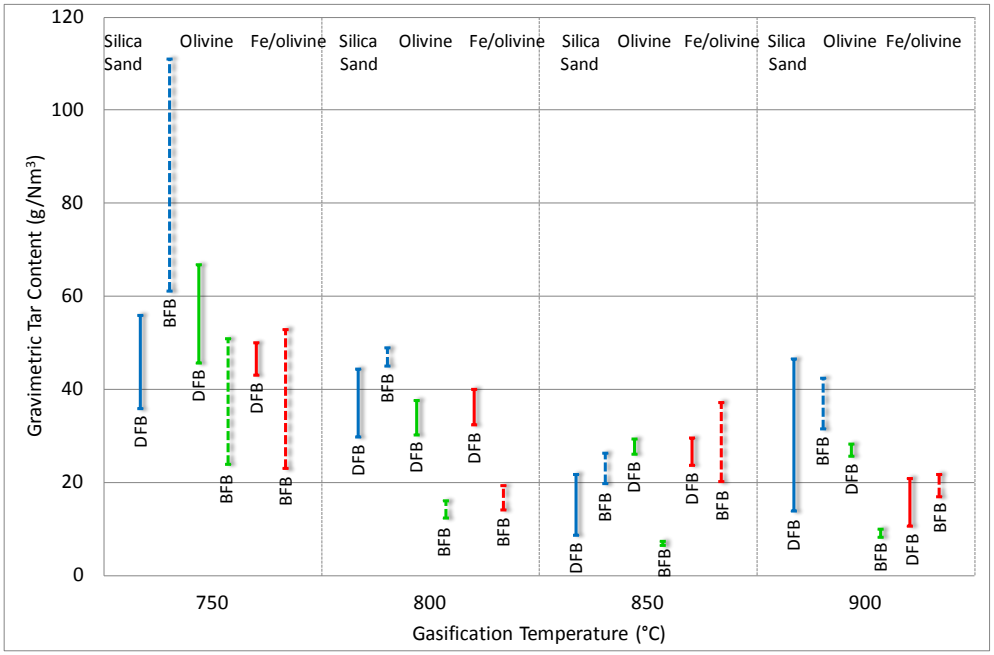

Figure 17. Temperature dependency of gravimetric tar content in syngas when S/C ratio is held constant at 1.2.

4.3. Influence of steam-to-carbon ratio

A higher steam-to-carbon (S/C) ratio means a higher steam partial pressure that pushes the water-gas shift reaction to the right hand for more H_2 production at the expense of CO. steam reformation reactions. At low S/C ratio the carbon is only partially gasified. A higher S/C ratio results in greater carbon conversion as a result of the enhanced water-gas-shift reaction and steam reformation reactions. Thus the methane and carbon monoxide contents decrease, and the hydrogen and carbon dioxide contents increase. When carbon conversion is completed, an increase of the S/C ratio results in dilution of the syngas [50].

4.3.1. Results from the model

The expression steam-to-biomass (S/B) ratio is used in the modelling. The wood pellets in these tests contains 50.9% db carbon (see Table 2) i.e. S/C 0.6 = S/B 0.3, S/C 1.2 = S/B 0.6, and S/C 1.8 = S/B 0.9. Figure 18 shows the effect of S/B on the syngas composition. The tar content decreases from 50.0 g/m³ at S/B 0.3 down to about 10.0 g/m³ at S/B 1.2 due to the enhanced steam reforming of tar. The char fraction is insensitive to S/B as shown in Fig. 18 a. The syngas yield is in the range of 0.8–1.0 Nm³/kg daf biomass, and the LHV is about 11.65 MJ/Nm³. The H_2/CO ratio is a strong function of the S/B ratio, which is primarily controlled by the water–gas shift reaction. The H_2 concentration is higher than that of CO under the normal DFBG operation conditions, but they will change positions when the S/B ratio is below ~0.15 as seen in Fig. 18 b. The CH_4 concentration is around 10.0 vol.% and not sensitive to the S/B ratio.

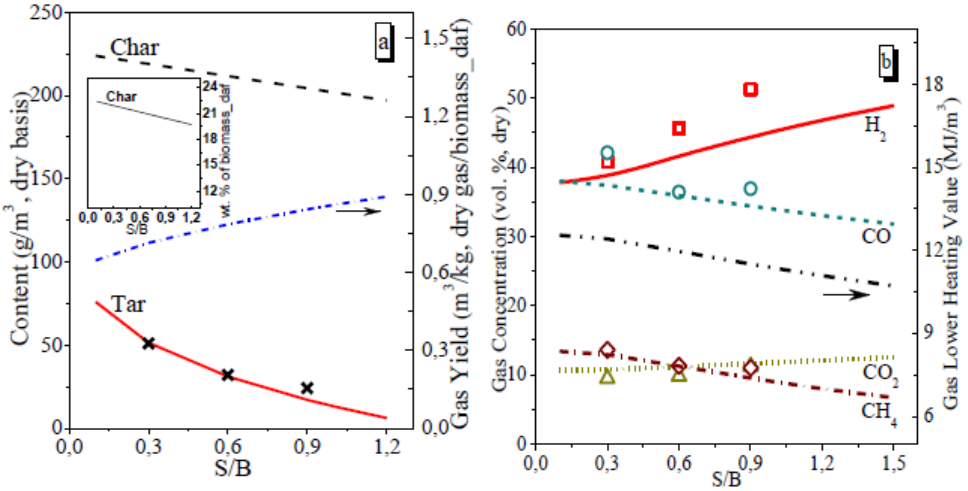

Fig. 18. Effect of S/B on the gasification (wood pellets, silica sand bed material, 850°C, τ 5.0 s, and dp 5.0 mm)

4.3.2. Experimental results

Fig. 19 shows the syngas composition at different S/C ratio of 0.6, 1.2 and 1.8 for three different bed materials when the gasification temperature is held constant at 850°C. For all cases of different bed materials, both the H_2 content and the ratio of H_2/CO increase with S/C ratio due to the enhanced WGS reaction. A higher S/C ratio means a higher steam partial pressure that pushes the WGS reaction ($CO+H_2O \leftrightarrow CO_2+H_2$) to the right hand side of the equilibrium equation, and produces more H_2 at the expense of CO, i.e. the CO yield decreases with S/C.

Increased S/C ratio from 0.6 to 1.8 results in a slightly decrease of CH_4 for all the bed materials, which can be seen more clearly in Fig. 20 where the methane content decreases from around 11% to around 9%. Figure 21 shows the gravimetric tar content at S/C ratios of 0.6 to 1.8. Both olivine and silica sand shows a decreasing tendency at higher S/C ratios, which can be explained by an enhanced steam reforming of tar. This trend is not clear for Fe/olivine from the present test.

In the present experimental test, the measurement data is scattering much when the tar content is plotted against S/C ratio as seen in Fig. 21. A decreasing trend of tar content with S/C cannot be clearly noted here. This might be explained by several reasons: 1) a much weaker effect of S/C on the gravimetric tar comparing to the catalytic bed materials and the difference between the BFB and DFB modes; 2) the S/C range applied in the test are too narrow to clearly show effective steam reforming of tar; 3) a bad mixing of steam with catalytic bed material and volatile; 4) a low tar reforming rate by steam.

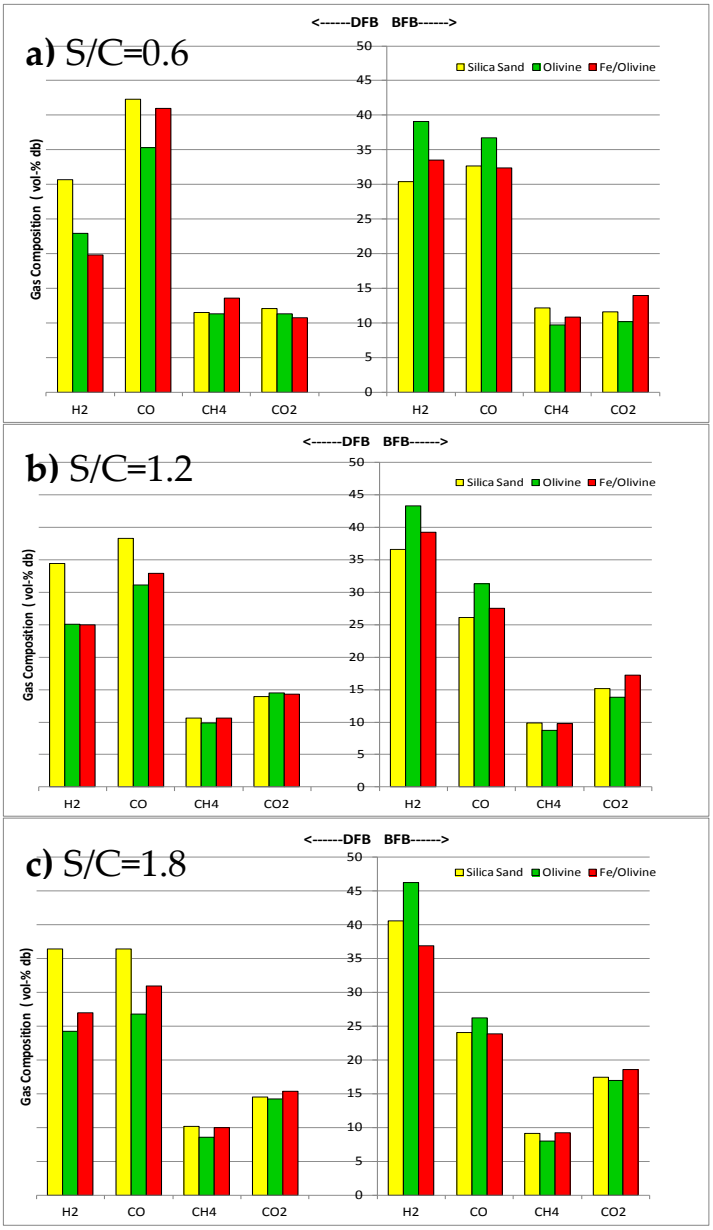

Figure 19 a-c. Syngas composition at different S/C ratio for three different bed materials when the gasification temperature is held constant at 850°C.

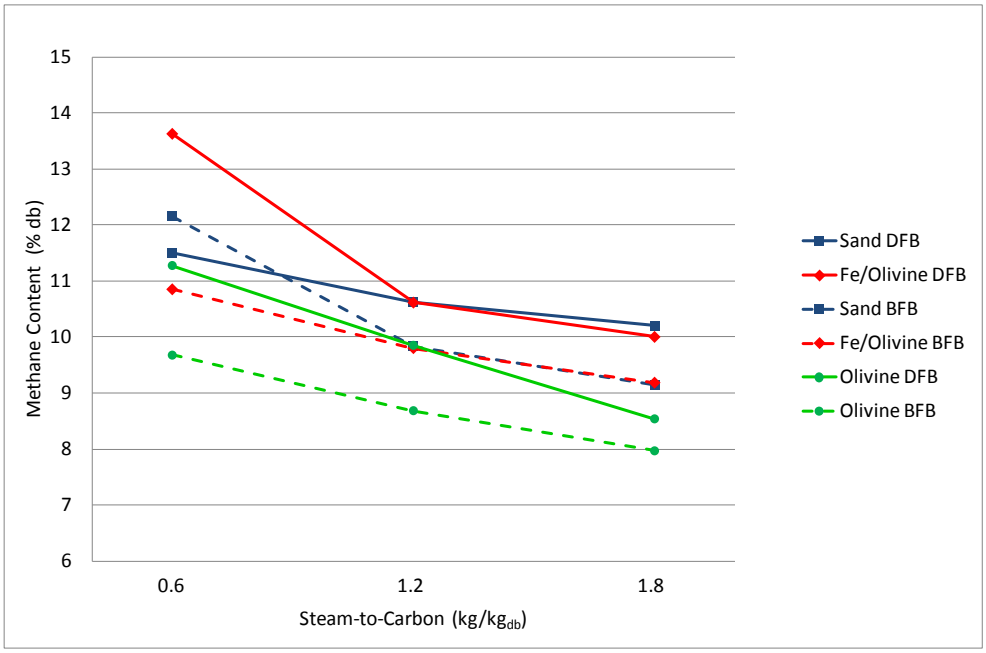

Figure 20. Methane content vs. S/C ratio at 850°C.

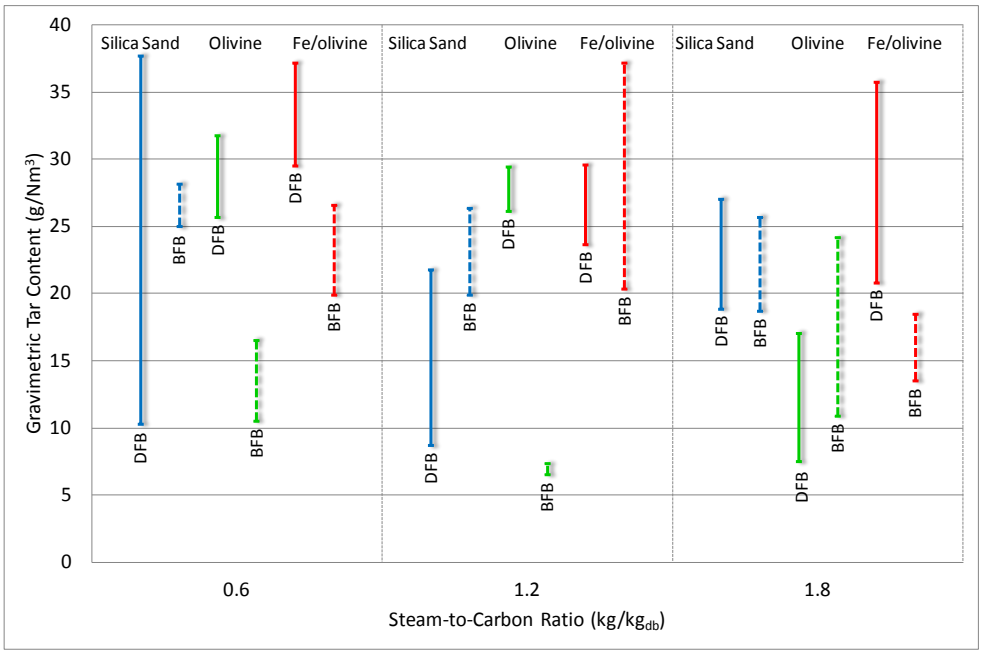

Figure 21. Gravimetric tar content at S/C 0.6-1.8, gasification temperature 850°C.

4.4. Influence of different bed materials

From overview of the measurement results shown in Figs 15 and 19, the concentration of H_2 + CO is higher for silica sand than the catalytic bed materials in the mode of DFB, while this situation is reversed in the mode of BFB. This indicates catalytic effect of hydrocarbon reforming in the BFB mode. The lower concentration of H_2 + CO in the cases of catalytic bed materials used in the DFB mode can be explained by oxygen transfer by the catalytic bed materials from the riser into the gasifier, which results in partially oxidation of H_2 and CO to H_2O and CO_2. The oxygen transport capacity of olivine can be 0.5wt% [13] due to the Fe contents in olivine. Thus Fe/olivine, with increased content of Fe, will have a higher oxygen transport capacity, which gives the lowest concentration of H_2 + CO as indicated in Fig. 15.

Considering the methane catalytic reforming in the test as seen in Figs 16 and 20, the methane content in the syngas is reduced somewhat when the catalytic bed materials are used. This catalytic effect is seen clearly at higher temperatures for the BFB mode, and is independent of S/C ratio. Olivine is more efficient than Fe/olivine, and shows much lower methane content than silica sand at the high temperature of 900°C, whereas Fe/olivine catalytic effect is not clear from the present test.

Comparing to CH_4, a similar tendency of tar reforming by the catalytic bed materials can be seen in Figs 17 and 21. The gravimetric tar content is slightly lower for the catalytic bed materials than the silica sand with an overview of the present test results except for the case at the temperature of 850°C. Higher gasification temperature leads to a lower gravimetric tar content and a better catalytic reforming of tar, which is significant for olivine used in the BFB mode.

In summary, the olivine used in the BFB mode gives the highest concentration of H_2+CO, the lowest concentration of CH_4 and the lowest content of tar in the syngas. This tendency is clearer at higher temperature but insensitive to the S/C ratio. Fe/olivine did not show an advantage over olivine regarding tar/CH_4 catalytic reforming based on the results of this test.

4.5. Performance of the FreeRef reformer

4.5.1. Temperature profile for MIUN gasifier with in-situ reformer

The hottest region up to 900°C of the in-situ reformer can be seen in Fig. 22 for the case without Ni-catalytic pellets, which can be well-explained by the heating-up from the hot circulating bed material. The in-situ reformer has a uniform temperature due to the characteristics of intensive heat and mass transfers in fluidised beds. But for the in-situ reformer with Ni-catalytic pellets, the temperature drops down at the bottom level of the reformer. This indicates a strong endothermic reaction of steam reforming of tars and CH_4 by use of Ni-catalyst. The cold spot close to the bottom of the reformer can be attributed to an interaction of two effects, the cooling by the endothermic reforming of tars and CH_4 and the heating by the hot circulating bed material.

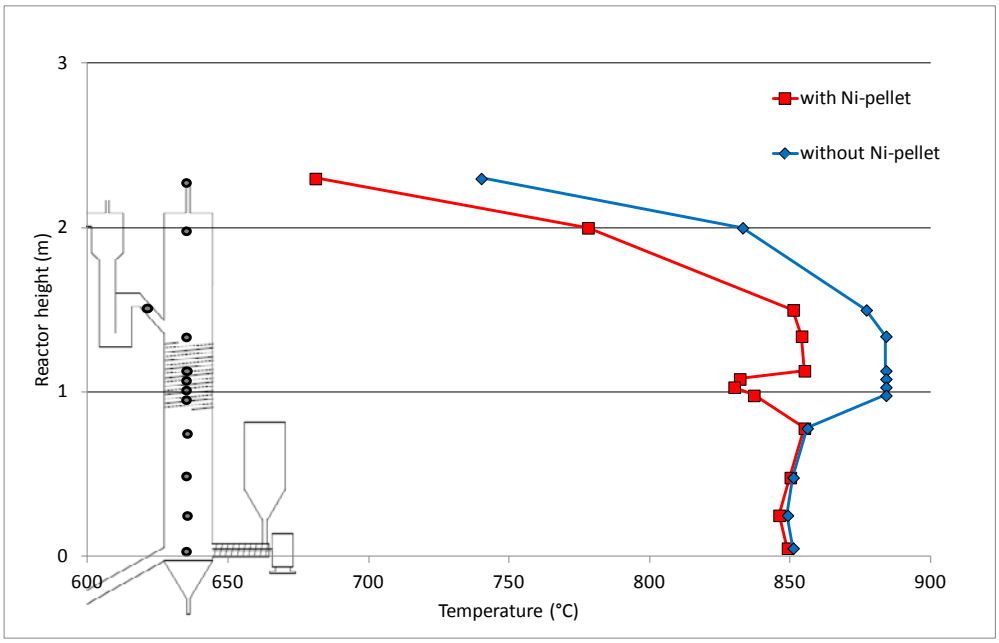

Fig. 22: Temperature profiles for MIUN gasifier with an in-situ reformer for two cases, with and without Ni-catalytic pellets.

4.5.2. Main gas components versus temperature

Figs. 23-26 show main gas components as a function of the gasification temperature for comparison of two cases, with or without Ni-catalytic pellets in the in-situ reformer. It can be seen from the figures that higher temperature enhances the tar/CH_4 steam reforming reactions and results in higher content of H_2 and CO, while the CO_2 content slightly decreases since the exothermic shift reaction is

favoured by low temperature. The contents in CO_2 and CH_4 are decreasing with temperature.

As seen in Figs 23 and 24, the $CO+H_2$ concentration clearly increases with temperature from 60% to 70% for the case without Ni-pellets, and from 55% to 74% for the case with Ni-pellets. The most significant change is the increasing H_2 concentration, from 24.8% at 750°C to 41.5% at 940°C, when Ni-pellets are added in the in-situ reformer. H_2 concentration exceeds CO concentration at 780°C. The Ni-pellets hardly change the CO concentration. These lead to a H_2/CO ratio under 1 for the reformer without Ni-pellets and above 1 for the reformer with Ni-pellets as seen in Fig. 25.

The H_2/CO ratio varies from 0.9 to 1.0 for the reformer without Ni-pellets, and from 0.9 to 1.3 for the reformer with Ni-pellets (see Fig. 25). A clear trend of H_2 concentration increasing with temperature, suggests a strong steam reforming of hydrocarbons in the in-situ reformer by the Ni-catalyst.

Steam reforming of CH_4 is a strongly endothermic reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H°298 = +206\ kJ/mol \qquad (8)$$

Under the condition of the in-situ reformer, the moderately exothermic water-gas shift (WGS) reaction is extremely fast leading to the equilibrium state:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H°298 = -41\ kJ/mol \qquad (7)$$

Steam reforming of hydrocarbons is favoured by high temperature; in contrast, the exothermic shift reaction is favoured by low temperature. Increased amount of steam will enhance the CH_4 conversion. The syngas composition is thus governed by the reactions (7) and (8) above, including reforming of other hydrocarbons. Fig. 26 shows the CH_4 concentration. CH_4 is the most recalcitrant hydrocarbon to reform, which very much depends on the temperature as also shown in Fig. 26. For the in-situ reformer without Ni-pellets, a decrease in CH_4 content from 11 to 9% is found at the higher temperatures. For the in-situ reformer with Ni-pellets, the CH_4 content is decreasing more clearly from 11% to 6%. These results indicate that the in-situ reformer with catalytic pellets is active in the steam reforming of hydrocarbons.

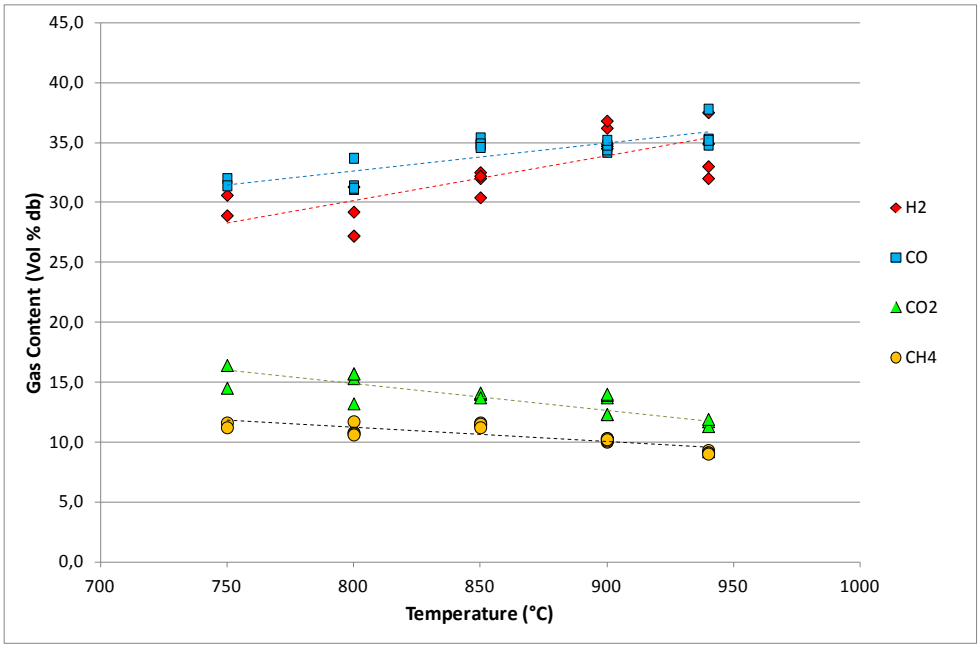

Fig. 23 Main gas components of syngas from MIUN gasifier with in-situ reformer.

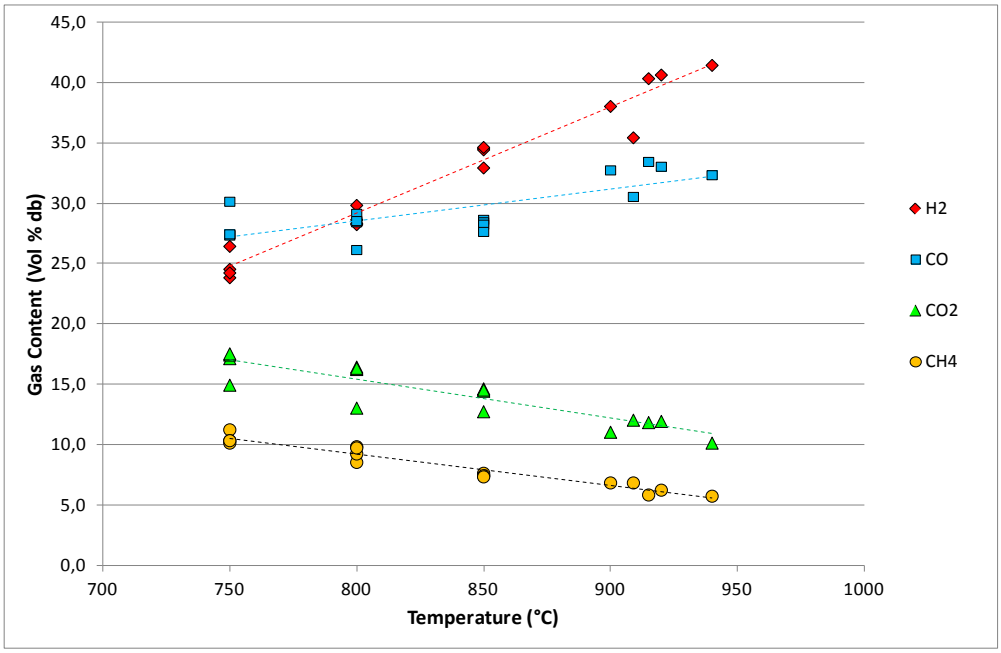

Fig.24 Main gas components of syngas from MIUN gasifier with in-situ reformer when Ni-catalytic pellets is added.

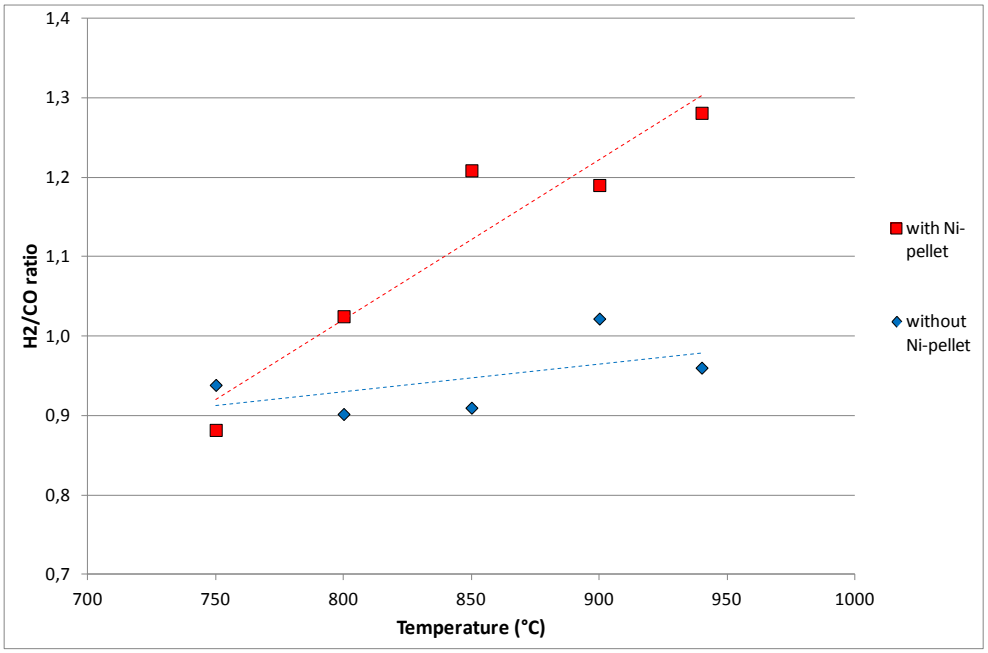

Fig. 25: The H_2/CO ratio (mean values of four samples) of syngas from MIUN gasifier with in-situ reformer.

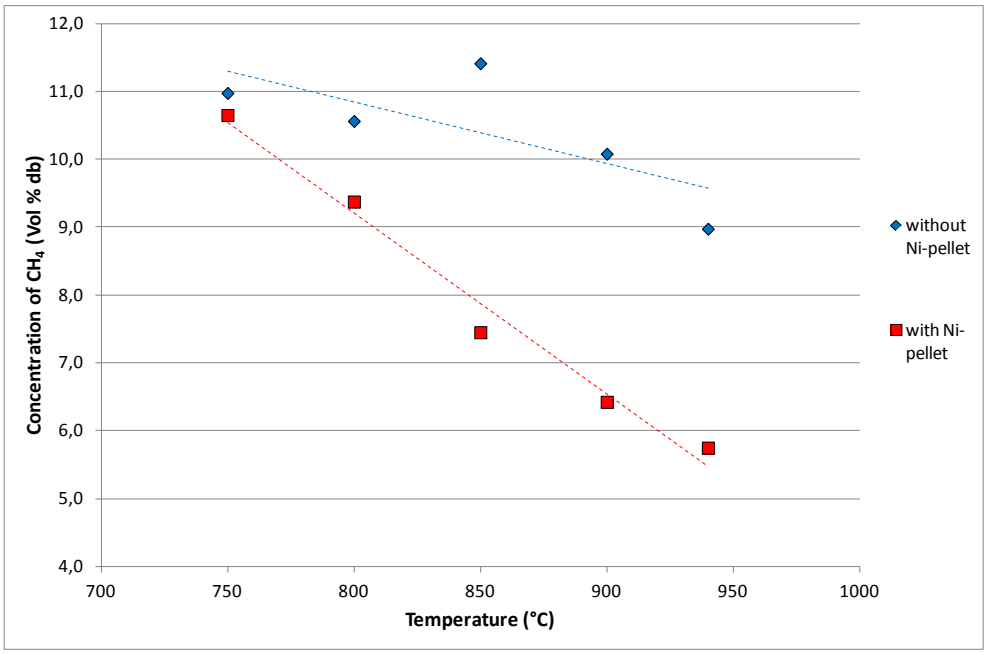

Fig. 26: Methane concentration (mean values of four samples) in the syngas from MIUN gasifier with in-situ reformer.

4.5.3. Gravimetric tar content versus temperature

Fig. 27 shows that the tar content decreases with temperature as a general trend similar to CH_4. The reformer filled with Ni-catalytic pellets shows a higher reduction of tars than the unfilled reformer. By means of the in-situ reformer with Ni-pellets, the gravimetric tars significantly decrease from about 25g/m³ at 750°C down to 5g/m³ at approx. 920°C. The relatively high tar yield of the tests with in-situ reformer filled with Ni-catalytic pellets, in comparison with other reported gasification tests with downstream Ni-catalyst reactor (tar yield <2 g/m3 [51, 52]), can be explained by a short gas residence time in the reformer and an insufficient specific surface area of the catalyst.

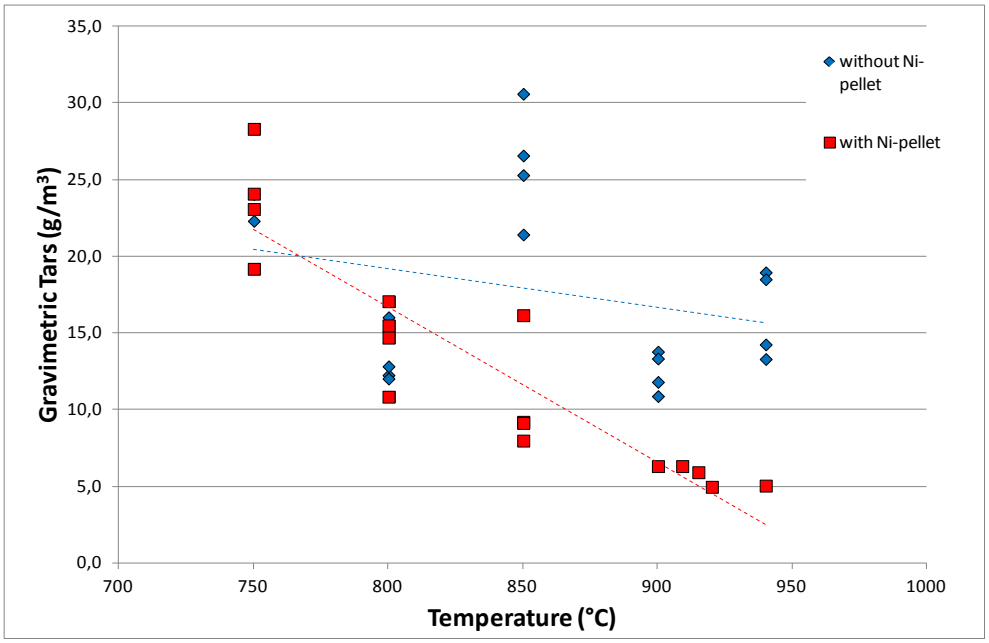

Fig. 27: Gravimetric tar content in the syngas from MIUN gasifier with in-situ reformer.

4.6. Comparison of gasification modes

With regard to the main gas components and gravimetric tars content in the syngas, a comparison of four modes of gasifiers is made: BFB, DFB without in-situ reformer, DFB with in-situ reformer and DFB with in-situ reformer filled with Ni-pellets, and shown in Fig. 28 in averaged values of all tests.

The concentrations of CO_2 and CO stay at the same level for the four modes, but the H_2 concentration varies to a great degree. When olivine particles re-circulate from the riser and returns in a counter-current mode from the upper loop- seal into the gasifier, a part of the product gas can be immediately oxidized with a rapid

oxidation reaction close to the gasifier inlet. Thus, the drop of the H_2 concentration from the BFB to the DFB mode can be well-explained by the olivine bed material as an oxygen carrier from the riser to the gasifer, and by some slipstream of air from the upper pressure lock. The H_2 concentration increases from the DFB mode without in-situ reformer to the DFB mode with in-situ reformer, and increases further in DFB mode with in-situ reformer filled with Ni-pellets. This can be attributed to the effective steam reforming of hydrocarbons in the reformer.

Corresponding to the H_2 concentration increase seen in Fig. 28, the tar content in the syngas decreases significantly for the mode with the in-situ reformer filled with Ni pellets. Ni catalyst is highly effective in reforming of hydrocarbons such as tars and CH_4, and able to dramatically decrease the tar content and increase the hydrogen content in the syngas from biomass fluidised bed gasification [51-53].

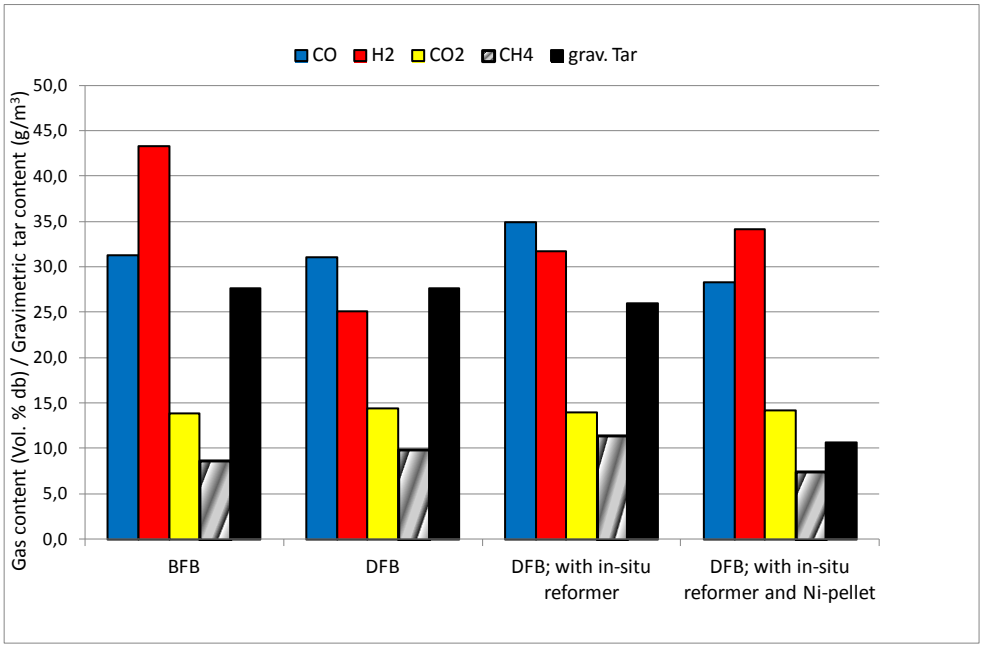

Fig. 28: Mean values of main gas components and gravimetric tars in the syngas of MIUN gasifier operated at T=850°C and S/C=1.2.

5. CONCLUSIONS

A challenge in fluidised-bed biomass gasification is the reforming of tars and CH_4. A 150 kW DFBG was built at Mid Sweden University (MIUN) in 2007 [48] which has a unique design suitable for in-bed tar/CH_4 catalytic reforming and continuously internal regeneration of the reactive bed material.

A mathematic model based on ASPEN Plus was used to predict the operation and performance of the MIUN biomass gasifier. The model reasonably shows the variations of tar and CH_4 concentrations and H_2/CO ratio with temperature and biomass-to-steam ratio. The model showed an increasing trend of H_2 and CO concentration (with a maximum value for H_2 at about 850°C) and a decreasing tar content with gasification temperature and S/B ratio. The predicted CH_4 concentration seems not sensitive to S/B ratio or temperature. CH_4 is highly stable, and much more difficult to be cracked or reformed than tar. Therefore, CH_4 concentration is far from its chemical equilibrium value which is close to zero. Significant reduction of CH_4 takes place at a temperature higher than 1,250°C or with help of catalysts, e.g., Ni-based catalysts.

The catalytic effects of calcined olivine and Fe-doped olivine (10%wt Fe/olivine Catalyst) were studied in the MIUN gasifier [43]. Although catalytic bed materials were used, the experimental results showed fairly high methane and gravimetric tar contents in the raw syngas (~10 Vol% and 7-67 g/m3 respectively). In order to further reduce the tar and CH_4 contents in the syngas, an in-situ reformer referred to as FreeRef reformer [54] was developed and installed in the freeboard of the fluidised bed gasifier.

It can be concluded that the FreeRef reformer with Ni-catalytic pellets clearly results in higher H_2 content together with lower CH_4 and tar contents in the syngas than the reformer without Ni-catalytic pellets. The gravimetric tar content decreases from 25 g/m^3 down to 5 g/m^3, and the CH_4 content from 11Vol% down below 6 Vol% in the syngas. These results suggest a strong endothermic reaction of steam reforming of hydrocarbons, such as tars and CH_4, by using Ni-catalytic pellets in an in-situ reformer placed in the highest temperature zone in the DFB gasifier.

The novel design in the MIUN gasifier increases the gasification efficiency, suppresses the tar generation and upgrades the syngas. This enables production of high quality syngas with low tar and CH_4 content from DFBGs.

6. FUTURE RESEARCH

- The design of the FreeRef in-situ reformer (i.e. the gas residence time in the reformer) should be optimized to minimise the tar content and methane concentration in the syngas
- A detail study on the performance of Ni-catalytic pellets in the in-situ reformer of a fluidised bed environment needs to be done further (i.e. the specific surface area of the catalyst)
- Deactivation of transition metal catalysts and attrition phenomena are important issues for in-bed catalysts in fluidised bed processes. These issues require further investigations and research in the field of new catalytic material for biomass gasification.
- A long time study is required, although this study did not indicate deactivation of the Ni-catalyst.

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Sist men inte minst, vill jag tacka för oumbärligt stöd och uppmuntran från:
Min sambo, Håkan Pettersson
Mina barn, Robin och Nadja Göransson
Min mamma, Margot Göransson
Övrig släkt och vänner

Till minnet av min pappa Stig Göransson:
Tack för att du gav mig inspiration till att börja studera,
jag önskar du funnits här vid min disputation.

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