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Biomass Product Gas Reforming Solutions

BioProGReSs

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**BIOMASS PRODUCT GAS REFORMING SOLUTIONS
- BIOPROGRESS**

Jörgen Held, Baltic Energy Innovation Centre

Preface

BioProGReSs has received funding from the European Union's Seventh programme for research, technological development and demonstration under grant agreement 321477. The funding came from the Swedish Energy Agency, the German Federal Ministry of Food and Agriculture through Fachagentur Nachwachsende Rohstoffe e.V. and the European Commission within the ERA-NET BESTF initiative. The multidisciplinary project was coordinated by Gothenburg Energy with Chalmers University of Technology, Technische Universität Berlin and Renewtec AB as project partners. In addition Wandschneider + Gutjahr and AMENKO were involved as subcontractors.

The project has been monitored by a steering group with representatives from Gothenburg Energy, Chalmers University of Technology, Technische Universität Berlin and Renewtec AB.

The Baltic Energy Innovation Centre has been engaged to make a public version of the final report and disseminate the results through social media.

A large number of people have contributed directly or indirectly to this report. The author would like to thank the whole project team with the steering group chairperson, Anna Svernlöv, and the project coordinator Ingemar Gunnarsson, Gothenburg Energy in the lead. A special thanks to Martin Seemann, Chalmers University of Technology and York Neubauer, Technische Universität for their contributions to the final report.

Summary

BioProGReSs is an acronym for Biomass Product Gas Reforming Solutions and within the project advanced syngas cleaning based on chemical looping reforming (CLR) was successfully demonstrated.

The work was conducted in close collaboration between the seven work packages (WP) within the project, including efficient information and personnel exchange. Together with unique experimental, pilot and demonstration facilities the high ambition related to improved competitiveness of any large-scale biofuel production plant based on gasification was reached.

The project received funding from the European Union's seventh programme for research, technological development and demonstration under grant agreement 321477. The support was made possible by the corresponding industrial co-financing in the form of access to the Chalmers gasifier and the GoBiGas plant for development and evaluation of a new innovative technology for syngas cleaning based on CLR. Furthermore, an innovative and novel analyzer for online detection of the tar content (CON-TAR), developed at Technische Universität Berlin, was implemented and demonstrated with the objective of developing new monitoring and control strategies for GoBiGas.

The aims of the project were among others to reduce the investment and operating cost of the syngas cleaning and increase the amount of biofuel from the gasified biomass.

The project showed the following for the GoBiGas I plant:

- The estimated reduction in investment cost (excl. buildings and commissioning) for a plant of size of GoBiGas I is approx. 10% by replacing the RME scrubber with CLR.
- An additional reduction in the specific investment cost is achieved when scaling, enabled by the introduction of CLR, to a five times larger unit of 150 MW_{th} fuel input. The total reduction in specific investment cost for such a unit including CLR is about 50%.
- The operating cost can be reduced by 5-7% by replacing the RME scrubber with the CLR demonstrated within the project.
- The specific product cost (methane) for a scaled-up plant can be reduced by about 37%, and by an additional 9% percentage points when the CLR is applied.
- The amount of biofuel from the input biomass can be increased by 2-10% without altering the overall efficiency when the RME scrubber is replaced by CLR, depending on the operational conditions of the plant.
- The remaining part of the produced tar can be valorized as products with a higher value than biomethane due to the achieved stabilization of the hydrocarbon mixture by the CLR.

The CON-TAR was further developed within the project by replacing the laser with newly available high-power UV-diodes. The new analyzer was implemented and demonstrated in both the Chalmers gasifier and the GoBiGas plant providing a

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new way to monitor and control the operation of the gasifier and the syngas cleaning.

The close and collaborative effort, conducted during the period of October 2014 to December 2017, resulted in numerous articles, papers and presentations which can be found on the project website www.bioprogress.se. The website will be maintained until end of 2019.

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Abbreviations and expressions used in this report

ANF	Annuity factor
BESTF	Bioenergy Sustaining the Future
BFB	Bubbling fluidised bed
bioSNG	See SNG. The prefix bio indicates that the SNG has been produced from renewable sources.
BTX	Benzene, Toluene and Xylene isomers
CLC	Chemical Looping Combustion
CLR	Chemical Looping Reforming
CON-TAR	Continuous On-line Tar-Analyzer
CTH	Chalmers Tekniska Högskola (Chalmers University of Technology)
ERA-NET	European Research Area Network
DFB	Dual fluidised bed
DME	Dimethyl Ether
FICFB	Fast internally circulating fluidized bed
FID	Flame Ionization Detector
FB	Fluidised bed
FNR	Fachagentur Nachwachsende Rohstoffe e.V. (German Agency of Renewable Resources)
F-T Diesel	Fischer-Tropsch Diesel
GoBiGas	Gothenburg Biomass Gasification
h/a	Hour/annum
l/h	Litre/hour
LED	Light Emitting Diodes
LIF	Laser-Induced Fluorescence
Nm ³	Normal cubic metre
PAH	Poly-aromatic hydrocarbons
PSI	Paul Scherrer Institute
SNG	Substitute or Sustainable Natural Gas. Sometimes the expression Synthetic Natural Gas is used but it's a contradiction to have the words Synthetic and Natural in the same expression.
Renewtec AB	Renewable Energy Technology International AB
RME	Rapeseed Methyl Ester
TU Berlin	Technische Universität Berlin (Berlin University of Technology)
UV	Ultraviolet
WP	Work Package

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1. Introduction

The industrial implementation of the DFB biomass gasification paths is at present largely dependent upon its potential to produce 'tar-free' gas with simultaneous valorisation of the energy contained within the tar forming hydrocarbon species. The possibilities regarding direct use of raw gas with remaining tar from a biomass gasifier are rather limited. However, if the gas is maintained at a temperature > 350 °C, the gas can be used directly, or after the removal of particles, to substitute fossil gas and oil in industrial burners. The demands for gas cleaning and process equipment increase as the raw gas is refined from a low-grade to a high-grade fuel. If further advanced gas cleaning is installed to also remove tar species, the gas can be used as a fuel for modified internal combustion engines and gas turbines. Additional process steps are required if the gas is to be used as a feedstock for synthetic fuel production. For synthesis into Substitute Natural Gas (SNG), the H₂/CO ratio needs to be controlled, the olefines have to be taken care of and the gas needs to be cleaned of sulfur and chlorine to protect catalyst beds from deactivation. If additional downstream processes are available, the gas can be further refined to liquid fuels, such as dimethyl ether (DME)¹, methanol², and Fischer-Tropsch diesel (F-T Diesel)³.

1.1 Background

Already when Gothenburg Energy started the GoBiGas project in 2005 it was recognized that the need for biofuels in the transport sector was much bigger than the potential production from fermentation of bio-wastes. In that situation, gasification of forest residues and production of biomethane was an obvious solution to the problem especially in Sweden where there is a big and growing potential for use of residues from forest and forest industry. The pre-studies of the project also showed that the overall efficiency of the conversion of woody biomass, by gasification and then synthesis to biomethane, could be very high compared to most other alternative ways of producing biofuels. In addition there are other benefits of biomethane than the high conversion efficiency from the feedstock to the final product⁴.

- Since bioSNG is miscible with natural gas in any proportion it can be distributed in an efficient and environmentally friendly way through the existing natural gas grid.
- The versatility and the low combustion emissions make bioSNG an attractive renewable fuel not only within the transportation sector but also for efficient heat and power production and in industrial processes where clean and efficient combustion is required.
- The greenhouse gas emissions are significantly reduced when bioSNG replace fossil fuels and for countries like Sweden with vast biomass resources the bioSNG route offers several other benefits such as increased security of supply, regional development and new job opportunities.

In 2007 the Chalmers gasifier based on dual bed atmospheric gasification was built and started. This made it possible to test the technology in pilot plant scale (2-4 MW). After a contribution of 222 MSEK in funding from the Swedish Agency, and

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acceptance of the state funding by the European Commission, the final investment decision on the GoBiGas I project was taken in 2010. The plant was designed and built as a first of its kind to demonstrate methane production from gasification of biomass feedstocks. The capacity of this first phase is 20 MW_{SNG} but the plan was to build a fully commercial plant (GoBiGas II) with 100 MW_{SNG} capacity a few years later.

Operation of the gasifier started in December 2013 and one year later the first biomethane was delivered to the gas grid. In the beginning wood pellets was used as feedstock, but later also woodchips, bark and residues have been used as fuel. Until autumn 2017 GoBiGas has been demonstrating gasification for 10,000 hours and delivered 45 GWh of biomethane to the gas grid.

After four years of operation a lot of experiences have been gathered in several research and development projects such as BioProGReSs. As soon as the commercial incentives are in place, these experiences can be used to design and build a “full scale” commercial plant.

The BioProGReSs project was started 2014 with funding from the Swedish Energy Agency, the German Federal Ministry of Food and Agriculture through Fachagentur Nachwachsende Rohstoffe e.V. and the European Commission. The aim was to demonstrate, how the CLR-technology could further reduce the tar content in the product gas which will result in higher reliability and efficiency of the process. The project was a cooperation between Gothenburg Energy, Chalmers University of Technology, Technische Universität Berlin and Renewtec AB.

The project was organized in seven closely connected WPs, see Figure 1. The main idea was to test and develop the technology in pilot scale at the Chalmers Gasifier (2 MW_{th}) first, and then demonstrate it in the GoBiGas plant (33 MW_{th}).

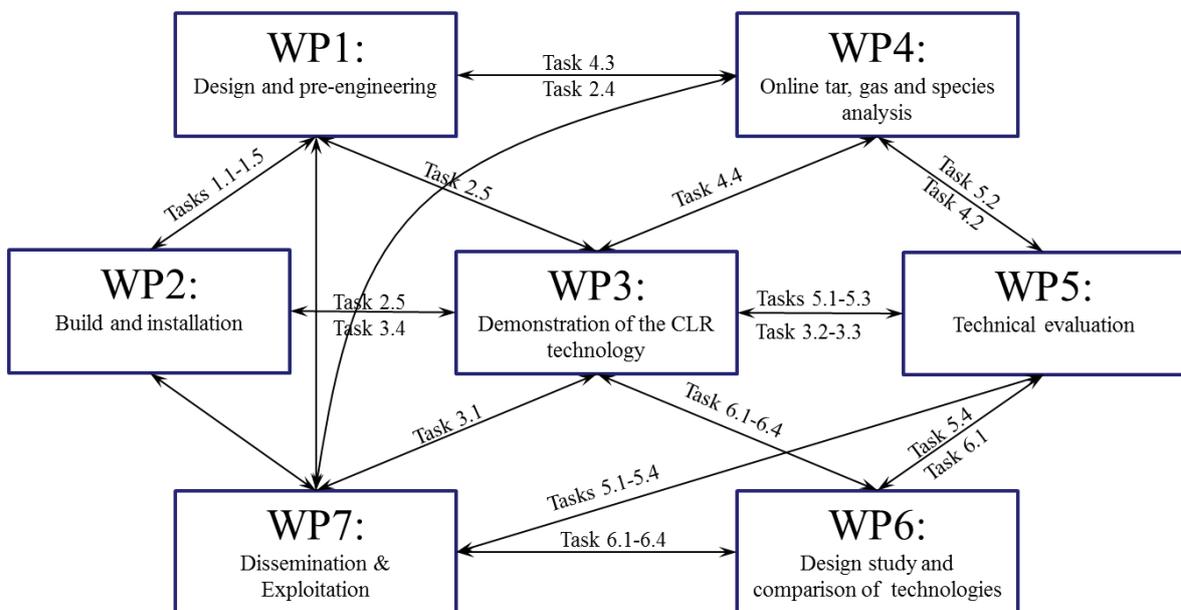


Figure 1. Structure of the project; interacting work packages through neighbouring tasks. Arrows without a task number stand for standard reporting.

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Installation, test and evaluation of the results were done in WP1, 2, 3 and 5, and the technology for online measurement of tar content developed at TU Berlin was done in WP4. In WP6 TU Berlin made a comparison of different technologies for gasification and gas cleaning competing with dual bed gasification and CLR. Dissemination and exploitation of the project and its results were done in WP7 by Renewtec AB. The presentations and publications of the results can be found on the project website, www.bioprogress.se.

1.2 Objectives

The objectives of this project were to

- review commercially or pre-commercially available technologies for upgrading of the gas leaving a fluidized bed biomass gasifier
- demonstrate the potential of CLR using the freeboard and the raw gas channel of the gasifier as reaction volume by modifying and enhancing the circulation of fine particles.
- implement and demonstrate an innovative and novel analyzer for online detection of the tar content (CON-TAR), developed at TU Berlin, with the objective of developing new monitoring and control strategies for GoBiGas.
- provide data that can be directly used in a near future for commercial projects in biomethane in general, and the GoBiGas II in particular.

The quantitative targets were among others to

- reduce the investment and operating cost of the syngas cleaning.
- increase the amount of biofuel from the gasified biomass.

1.3 Methodology

The modifications needed in order to implement the CLR was first tested, developed and demonstrated in the Chalmers gasifier and then at the GoBiGas I plant. Design of the required modification and the complementing equipment to conduct the demonstration at the Chalmers gasifier and the GoBiGas I plant were done with a focus to enable generalization of the results.

The demonstrations at the Chalmers gasifier and at the site of the GoBiGas plant were investigated thoroughly jointly by industrial and academic partners. In parallel suitable analytical tools were developed to monitor the tar concentrations online allowing for continuous optimization of the process conditions. Connected to the operation of the demonstration unit technical and economic aspects were assessed and evaluated.

2. Chemical looping and DFB gasification

The idea for the application is based on the chemical looping combustion (CLC) technology where a solid material with the capacity to transfer oxygen is circulated between two different atmospheres, as shown in Figure 2. The aim of this technology is to create a pure CO_2 stream for carbon capture and sequestration from combustion without the necessity of an air separation unit. Commonly a dual fluidized bed reaction system is applied with similar layout as an indirect dual fluidized bed gasifier. The fuel reactor and the boiler depicted in Figure 2 correspond to the gasifier and the combustor reactor in case of dual fluidized bed gasification.

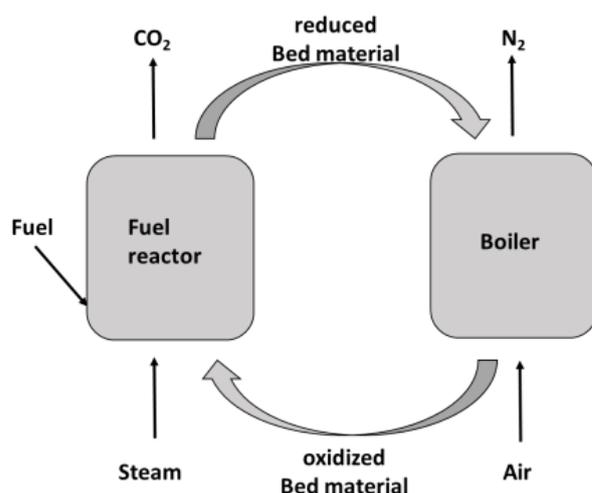


Figure 2. Chemical looping combustion system.

The concept of chemical looping reforming (CLR) was originally presented by Mattisson et al.⁵ as a spin-off technology from Chemical Looping Combustion and was thought initially as a method for the partial oxidation of methane into CO and H_2 . For gasification application this was also investigated as a possibility for secondary tar cleaning in a small bench-scale reactor system. In this previous research^{6,7} the application of inexpensive and nontoxic ores, e.g. ilmenite (iron titanium ore) was investigated with promising results. In contrast to the chemical looping combustion the reforming process does not necessarily benefit from oxygen transferred to the particles in the combustion side, but rather from the cleaning effect during the residence time in the combustion section. As a matter of fact the name is misleading as the catalytic effect is induced by the reduced metal phase while the oxygen carrying capacity is a rather unwanted side-effect.

In an optimized system, the oxygen carrying rate and consequently the circulation rate needs to be controlled to avoid excessive oxidation of the product gas. Direct application of chemical looping in a gasifier by blending the bed material with an oxygen carrier is not desirable, as the oxygen carrying capacity of those materials is too high⁸. In auto-thermal reaction systems there is no further benefit by the oxygen surplus since the materials do not show a specific selectivity towards oxidizing just tar species instead of the desired gas compounds e.g. hydrogen⁹.

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Instead the integration via an added reactor volume at the exit of the gasifier with help of a smaller particle size which always is entrained from the bubbling fluidized bed gasification reactor is seen as a more suitable possibility as shown in Figure 3. In such a set-up the circulation rate of the bed material and the state of oxidation of the oxygen carrier/catalyst can be adjusted independently of the heat demand of the gasification system.

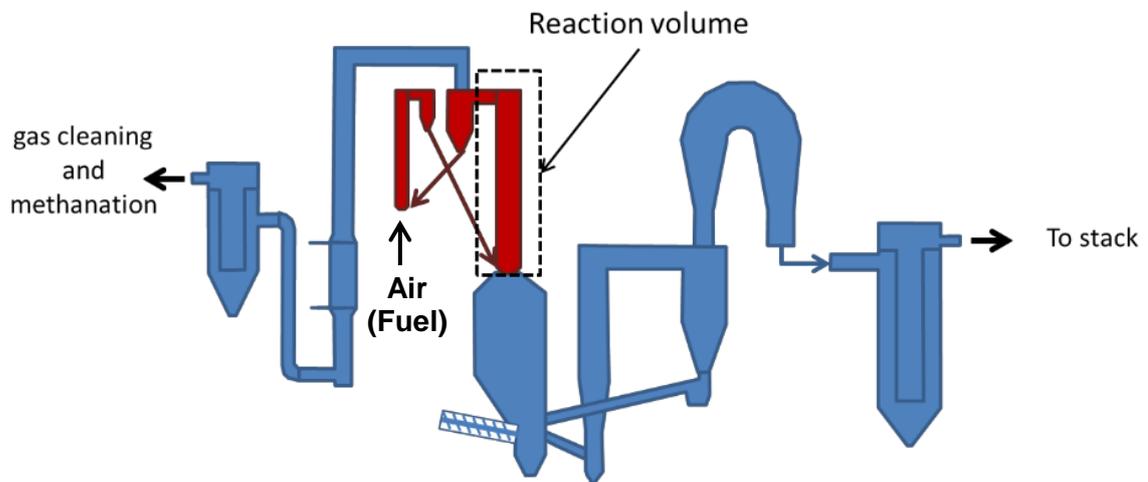


Figure 3. Principal layout of a separate reactor for chemical looping reforming.

However, as the materials interact with their surrounding atmosphere various other species are transferred in such a system. Besides the transfer of oxygen, which is an undesired effect¹⁰ specifically, the transfer of sulphur and alkali was also investigated^{11,12}. The former was investigated for the potential of intrinsic sulphur cleaning, and the latter, to understand the ash chemistry. In this project the freeboard and the raw gas channel of the gasifier were used as a reaction volume by modifying and enhancing the circulation of fine particles (see Figure 4).

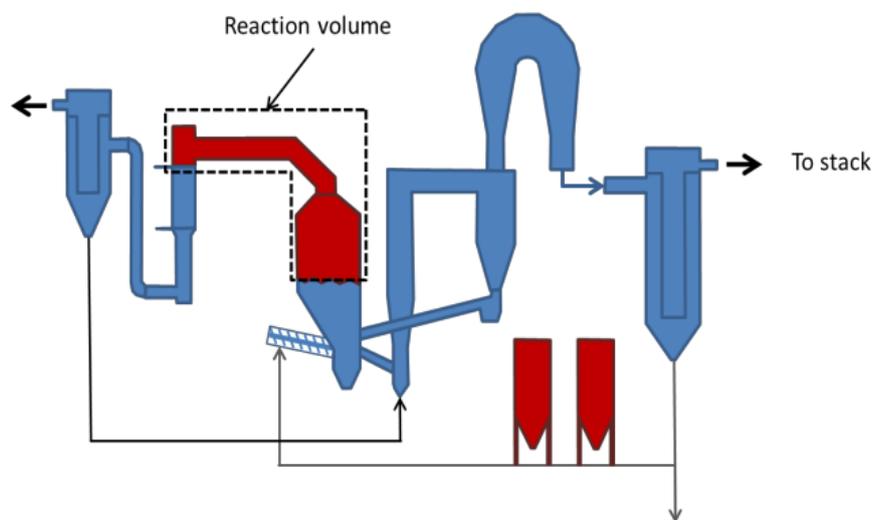


Figure 4. Schematic layout of the GoBiGas I plant. The freeboard and the raw gas channel of the gasifier were used as reaction volume for the tar reforming.

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It was found that a net transport of sulphur and alkali occurs from the combustion reactor to the gasification reactor, when applying olivine as bed material in a DFB gasification system. To affect the tar yield, its formation and decomposition must be understood.

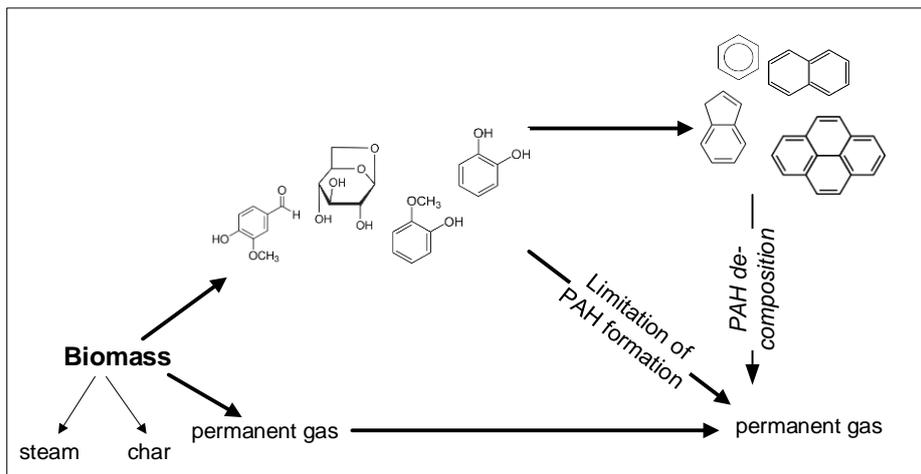


Figure 5. Simplified tar formation scheme

Tar is a generic term for a vast variety of aromatic and poly-aromatic compounds (PAH) which are formed from precursors evolving from the thermal decomposition of biomass. A mechanistic scheme of the evolution from biomass to PAH is shown in Figure 5.

Once the fuel is immersed into the fluidized bed it goes through three principal conversion steps, drying, devolatilization and gasification of char, which are governed by heat transfer. The devolatilization occurring between 300 and 500 °C results in the formation of precursors of tar which convert while heated by the surrounding gas (mostly steam) to either permanent gas (desired) or aromatic species (undesired). Principally there are two ways to a low tar yield: the limitation of the formation of PAH and the decomposition of already formed PAH.

In regard to the GoBiGas I dual fluidized bed gasifier comprising olivine as a bed material there are two key effects that are important to keep in mind for a comprehensive picture of the catalytic environment. While heterogeneous catalysts such as dolomite, ilmenite and olivine are catalysing even the decomposition of tar equally as the precursors of tar they require a gas solid contact. As the fuel will predominantly float on the surface of a fluidized bed the contact of gas and bed material is limited¹³. Besides abovementioned effect it was shown that the presence of leachable potassium that can be released as vapour limits the formation of tar and in that way attacking the issue at its source¹⁴, a finding that is in line with experiences from steam cracking of naphtha¹⁵. As those species are vapours they follow a different flow pattern compared to the solid materials which opens up supplementary possibilities. Overall, the understanding of these synergistic effects has increased dramatically during the project and has widened the perspective on tar reduction measures.

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2.1 Loops in large scale DFB gasification plants

The material flows in indirect gasifiers, built after the example of the Güssing plant, employ two material cycles as shown in Figure 6. Here they are distinguished as the primary cycle of bed material between the gasifier and the combustor (in blue), and the secondary cycle of ash fractions (in green and umber).

The primary cycle is the flow of bed material between the gasifier and the combustor (blue in Figure 6) through a seal in the bottom of the gasifier and a cyclone at the exit of the boiler with the main function of the bed material as heat carrier, catalyst and carrier of reactive species. At GoBiGas I the bed material consists of olivine with a particle size distribution between 180 and 500 micron.

The secondary cycle (green/umber in Figure 6) consists of the material caught in the product gas filter (3) and the coarse ash from the flue gas train (umber). The product gas ash (green) is rich in carbon (around 10-15 % mass) and is reintroduced into the combustor for carbon/energy recovery. Other main constituents of the raw gas ashes are entrained bed material particles ($\leq 100 \mu\text{m}$), limestone which is added as pre-coat material for the filters and biomass ash. The ashes from the two reversing chambers (6,7) (Umbre, Figure 6) are recycled to recover entrained bed material (mean particle size $>100 \mu\text{m}$) (umber). The main function is the recovery of entrained bed material and the recovery of carbon in the product gas ash (PG-ash) other effects have not been reported.

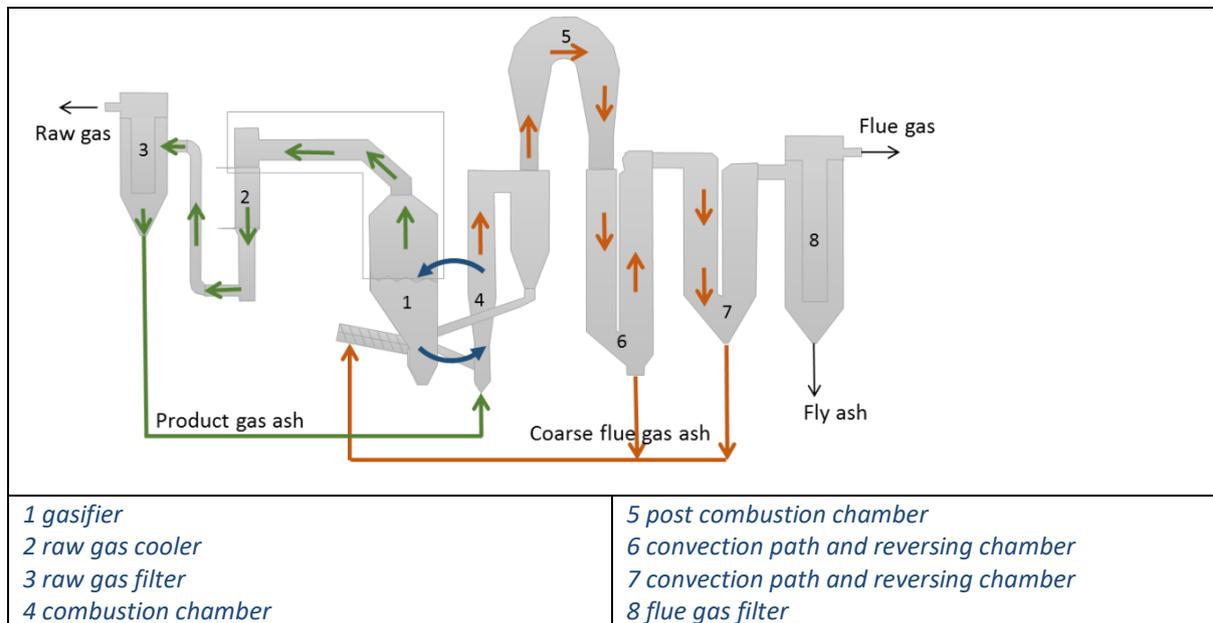


Figure 6. Scheme of the material flows in the gasification section of the GoBiGas I plant, bed material (blue), product gas ash (green), coarse flue gas ash (umber).

2.2 Enhanced material cycles in a DFB gasifier by chemical looping

The concept of the enhanced material cycles was developed based on the principle of a downstream chemical looping reformer. Capitalizing on the existing ash recirculation system by internalization of the chemical looping cycle into the recy-

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cle system, an additional reaction volume is created reaching from the surface of the bubbling fluidized bed (1) to the raw gas cooler (2). For that reason, additional equipment was installed at GoBiGas I to enhance the recirculation with selective materials to achieve an overall satisfactory gas quality. As the pneumatic sender was equipped in the reconstruction with load cells an additional benefit from this installation is that for the first time since the start of the GoBiGas I gasifier the ash flows of the recycled streams are accessible.

3. Ash and bed material chemistry

Unnoticed before this project started, was the above mentioned interrelationship of alkali species and the catalytic activity of olivine as bed material on the gas quality and as a consequence the functionality of the overall gasification system.

3.1 Catalytic bed material and the role of ash species

The reactivity of potassium in gasification is nothing new and has been developed for instance for coal gasification in the 80`ies e.g. Exxon process¹⁶, here the main mean is to accelerate the gasification rates of char. The principles of the physical and chemical interactions and the benefit of addition of chemical as well as the recirculation of ash fraction consisting of different carrier materials in dual fluidized bed gasification have been investigated at Chalmers in detail^{17,18}. A schematic description of the interaction of the alkali species with the solid material is given in Figure 7. Alkali species are released from the fuel in the gasifier and are partially reacting with the bed material inventory. This interaction with the bed material can go in both directions: loading of the available surface with alkali or unloading depending on the partial pressures of alkali and oxygen.

Alkali metals

One source of alkali, mostly potassium, is the fuel. The potassium is partially reacting with silicon in the biomass ash and the bed material. This share is bound chemically and is stable under all conditions prevailing in the system. As a matter of fact introduced sandy material that might come with badly treated fuel will counteract the activation and on top of that it poses a risk for agglomeration. It is important to keep in mind that the concentration of free silicon to react in the olivine is very limited and this reaction with the bed material is negligible after some days of operation but very relevant for the start-up. Another part of the potassium is released mostly in form of KOH to the atmosphere (g2) following with the raw gas. On the way through the cooling section the alkali condenses on available surfaces, particles etc., and is retained to a great extent in the product gas filter ash (g3).

The product gas filter ash is recycled to the combustor where the alkali is vaporized again (c4). Additionally, alkali from the char are released in the boiler as KOH and K_2CO_3 and depending on the partial pressure adsorbed on the bed material (c1) and subsequently reintroduced to the gasification chamber. In the gasification chamber the equilibrium between gaseous and adsorbed KOH is more on the side of the gas phase and potassium is released (g1) creating the desired catalytic activity. Gaseous alkali in the combustor is leaving the reactor through the cyclone (c2), condenses in the convective path and is separated in the two reversing chambers (c3) and on the textile filters (c3*). As mentioned above the material from the two reversing chambers is reintroduced into the gasifier together with the fuel. The potassium species with low evaporation temperatures (KOH) and those that decompose under reducing atmosphere (K_2SO_4) are released to the gas phase (g4).

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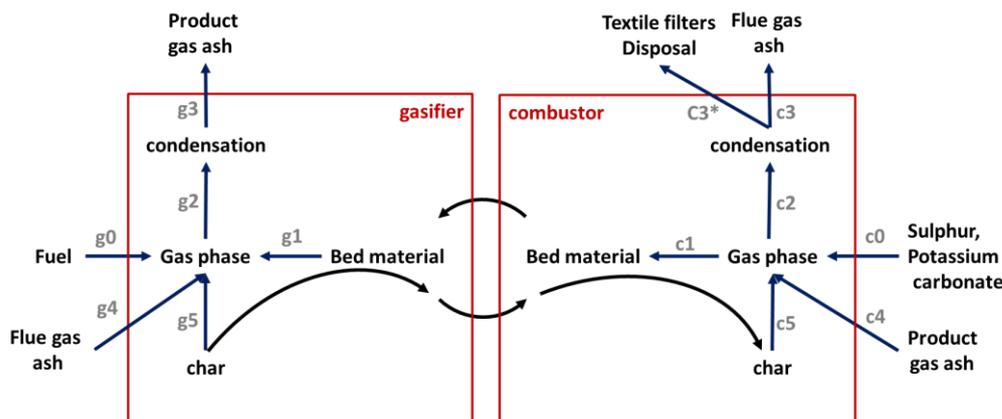


Figure 7. Scheme of the distribution of alkali species in a dual fluidized bed gasifier with recirculation of ashes.

In case of potassium deficiency there is the possibility at GoBiGas I to add potassium carbonate solution 40% to the combustor (c0), which distributes in the same way as the potassium from other sources between routes c2 and c1. During start-up 20 NI/h which corresponds roughly to the amount of potassium added with pellets as fuel and between 0-10 l/h during steady state operation¹⁹.

Similar results in regard to tar yields are achieved with ash rich fuels as demonstrated in Senden under the condition that the silicon content in the ash and bed material can be restricted. This is currently obtained by classification of the extracted bed material, large sintered and silicon containing particles are disposed, activated bed material particles are reintroduced²⁰. With the conditions created by an ash rich fuel addition of alkali or ash recirculation might overload the system and lead to clogging of the filters with salt. There is however an ongoing discussion about what the contribution of different sources to the catalytic effect in olivine beds is and both heterogeneous effects (of particles) as well as homogeneous effects of volatile species are most likely of importance.

Impact of sulfur

As the driving force of the KOH transport is the adsorption equilibrium the amount is naturally limited by the available surface and the gas phase concentration. To circumvent this limitation the uptake of alkali in the bed material can be enhanced by the addition of sulfur (0-1kg/h) to the combustor, forming potassium sulfate (K_2SO_4) which is condensing at those conditions and therefore obeys a different equilibrium. In other words the addition of sulfur intensifies the route c1 without requiring higher partial pressures of potassium. Sulfur added by the fuel or artificially is either bound as sulfates e.g. $CaSO_4$ or are released in the gasifier as predominantly H_2S , only minor amounts SO_2 were measured in the flue gases. Gaseous sulfur components are captured partially in the raw gas filter ash, minor amounts in the scrubbing liquid and all the rest in the active carbon beds. The first two streams are returned to the combustor, while regeneration gases from the active carbon beds are injected in the post combustion chamber.

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3.2 Bed material and chemical addition tests at Chalmers

To facilitate the test of materials suitable for chemical looping gas cleaning and to implement the results that gave effect, equipment was modified and installed both at GoBiGas and at the Chalmers gasifier.

In a first stage equipment was assembled to inject particles with a maximum diameter of 100 μ m and chemicals onto the entrance of the loop seal between the gasifier and the boiler. The feeding point was later modified to enable both fuel feeding and feeding of chemicals in the same spot (Figure 8).

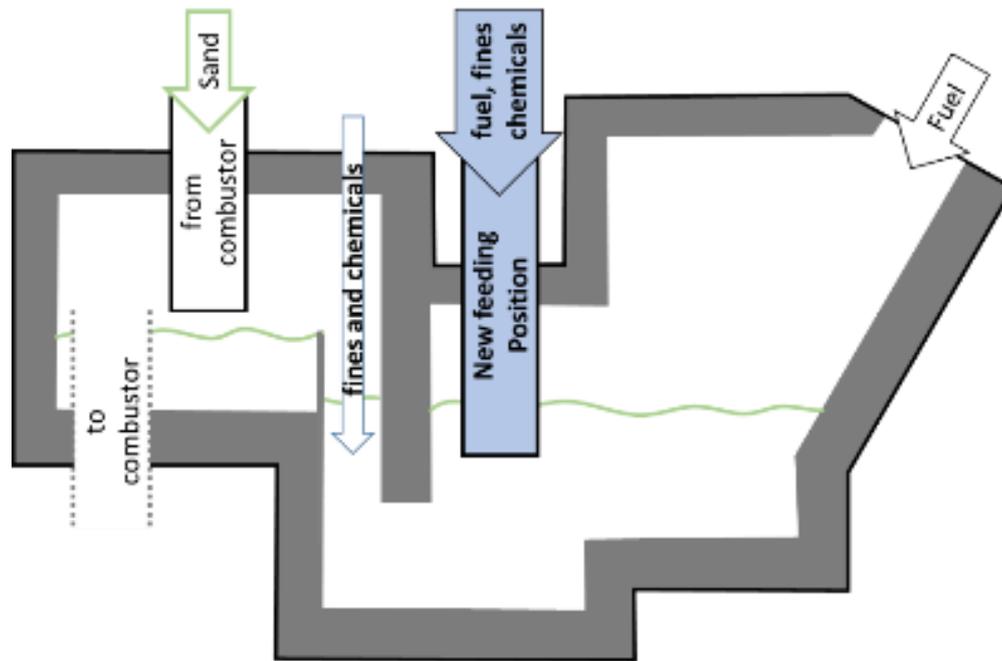


Figure 8. Modification of the loop seal one with integrated feeding possibility at Chalmers.

As there are both heterogeneous effects (of particles) as well as the homogeneous effects of volatile species to be considered two principle types of tests, utilizing the free-board and raw gas channel in the gasifier at Chalmers, were conducted. The effect of added fine particles, consisting of different materials for investigating of the heterogeneous effect, and the activation with different alkali components for the homogeneous effects were tested at Chalmers, evaluated and in case of positive results demonstrated or even implemented into the regular operation at GoBiGas I.

In contrast to the DFB gasifier at GoBiGas I there are three peculiarities to consider:

- There is no recovery of flue gas ash under regular operation
- Fuel is fed to the boiler/combustor continuously
- And the raw gas from the gasifier is combusted (flared) in the boiler, which results in a continuous internal circulation of raw gas ash.

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The ash-recirculation of fine particles and fly-ash species from the gasifier to the combustor is continuously obtained as the raw gas in this installation is flared in the boiler. The recirculation of flue gas ash was established by collecting the secondary cyclone ash and reintroducing it into the loop seal connecting the particle distributor and the gasifier.

Procedure

The fresh material was injected at a feeding rate of 200 kg/h to the inlet of the loop seal 1. Five different materials with a particle diameter below 100 micron were employed to test the heterogeneous effects. Minerals of Ilmenite, Feldspar, Olivine, Limestone and Bauxite were tested. To even cover the effect of enrichment with ash more than one recycle was performed for each material. Additionally the effect of potassium salts, calcium carbonate and sulfur were tested. The dry gas composition was analyzed continuously before, during and after the injection. Additionally tar samples were collected before and after the injection. To follow the transformation of the employed materials bed material and ash samples were taken for each cycle.

Chemicals addition

As recirculation of ash enriched olivine fines displayed a powerful effect pure chemicals dominant in fly ashes was investigated. The effect of Ca and K on the catalytic activity was tested by adding a high purity CaCO_3 and K_2CO_3 consecutively to the gasifier via loop seal 1. Sulfur was added to the return leg of the boiler. Reference gas-, tar- and bed material samples were taken before the addition of any chemical. One chemical was added at a time, and the gas and tar compositions were sampled during the addition to assess the activity of the chemical added. Gas and tar samples were taken after the addition of the chemical, when the operation was stable again. This measurement is a reference case for the next addition. Both chemicals were added in the same position as the fines in form of powder into a steam atmosphere consequently turning partially into the hydroxides.

CaCO_3 and K_2CO_3

The injection of 3.5 kg of pure CaCO_3 did neither give an immediate nor a lasting effect, this could be due to calcium remaining in particle form thus being entrained fast without interacting with the surrounding bed material. Potassium carbonate instead resulted in a direct and lasting effect. In contrast to calcium, potassium in the hydroxide form is a liquid at said conditions with a high tendency to form vapor, thus is easily interacting with the surrounding bed material.

Sulphur

In contrast to the other two chemicals sulphur was fed to the boiler, due to the fact elemental sulphur being prone to dust explosions when transported pneumatically. However, in previous works it was shown that sulphur is transported from the combustor to the gasifier in dual fluidized bed systems²¹. The tar concentration is significantly affected by the sulphur addition. The tar concentration measured 11 hours after the injection of sulphur was approximately three times lower than that measured before any addition of sulphur. This high catalytic activity of the bed can

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be attributed to the injection of sulphur which also resulted in high potassium content in the bed particle layer, as seen in Figure 9.

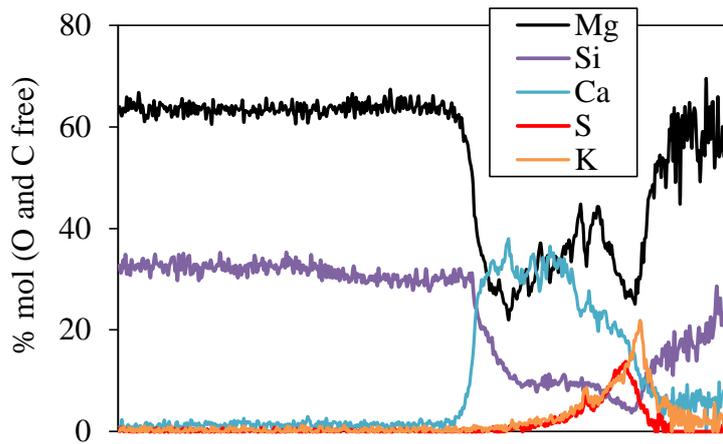


Figure 9. Line-scan of the ash layer of an olivine particle. Sample taken in the loop seal 1 (inlet to the gasifier), after addition of elemental sulfur to the boiler.

Conclusions from the assessment of materials

The effects of alkali and sulfur were dominating most of the other catalytic effects observed during the tests. Based on results of tests at Chalmers the following implementation and tests at GoBiGas I were prepared:

- To compensate for eventual lack of ash components the K_2CO_3 addition system was complemented with a sulfur feeding.
- Ash recirculation system was upgraded with weighing equipment to be able to follow and understand the effects of ash recirculation, this important stream of chemicals, at GobiGas I.
- A dosing system for fine minerals was designed and constructed.

3.3 Implementation and demonstration of the enhanced secondary circulation at GoBiGas I

The overall effects of the enhanced circulation led to a drastic improvement of the raw gas quality and ash species present from the fuel play the decisive role in the improvement. Notably balancing potassium and sulfur are the key parameters as they form together with the available calcium from the fuel and the filter pre-coat a reactive environment that does prevent the formation of tar or even contributes to the decomposition of already formed aromatic and poly-aromatic species.

With more than 10,000 operational hours of the GoBiGas I gasifier, it has been concluded that the yield of tar can be controlled by feeding potassium to the process. Further, an empirical correlation between the concentrations of tar and CH_4 in the produced gas has been found, which is used to monitor the tar yield and thereby the activation of the olivine online, see Figure 10. Through operational experience it has also become clear, that the olivine can be deactivated when the bed material particles lose alkali load, with increased tar yield as consequence.

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Based on this experience all the observed/recorded/characterized operational cases of the GoBiGas I gasifier can be divided into three different zones (as indicated in Figure 10): *Non-activated*, *Deactivated* and *Activated*.

The *Non-activated* zone corresponds to the operation of the unit before addition of potassium was tested. For these cases, the tar yield was very high and the plant could only be operated for a few hours before the cooler was clogged, therefore only two of these cases could be investigated. As previously described¹⁹, with operating time, activation of the olivine bed is decreased, resulting in an increase of the tar concentration. This corresponds to the area specified as *Deactivated* in Figure 10, which can be coupled to high tar yields that would clog the cooler within about 100h of operation. The deactivation mainly occurs during heat up of the process and most of the measurement points in this zone were made close to start-up of the process. Finally, the *Activated* zone corresponds to standard operation of the GoBiGas I gasifier where continuous operation for more than 1,800h has been achieved with only minor clogging of the cooler.

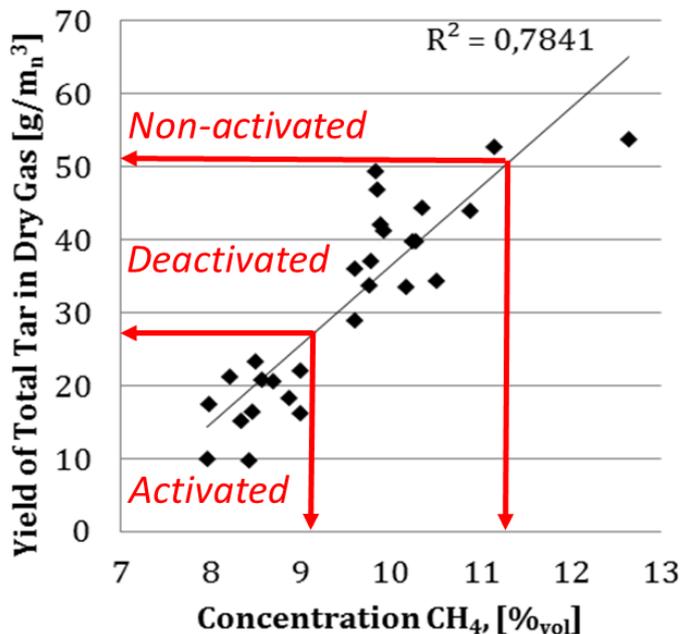


Figure 10. Yield of tar as a function of the CH₄ concentration in the dry gas produced in the GoBiGas I unit.

The activation of the olivine at the GoBiGas I plant is achieved by feeding a water based solution with 40 % of the mass of K₂CO₃ to the combustion side of the gasification unit. 0-30 l/h of the solution can be fed. For comparison, roughly 20 l/h of this solution corresponds to the amount of potassium added with the wood pellets at 100 % load. At steady state operation about 2-10 l/h is added to the process to keep the CH₄ concentration below 9 % and avoid clogging of the cooler. These operational cases are referred to as K-activated in this report.

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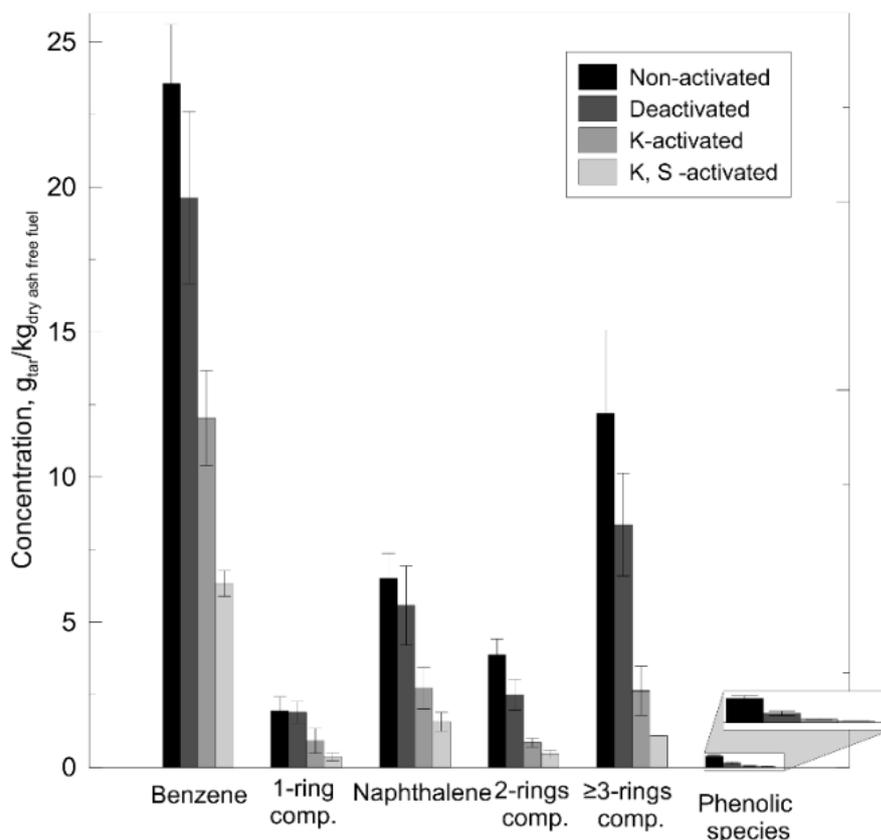


Figure 11. Typical yields of the specific tar groups presented as a mean value with standard deviation. Chalmers/GoBiGas gasifier operating with olivine in the different activation zones.

The addition of the K_2CO_3 and S simultaneously into the boiler side resulted in an immediate response of the system and additional decrease of tar concentration in the gas down to $10 \text{ g}_{\text{tar}}/\text{Nm}^3$. More importantly the issues of cooler clogging were contained as the property of the tar created was less prone to polymerize. In other words the tar spectrum was “stabilized”, the oxygenated reactive species disappear (Figure 11) and the complexity of the molecules within the groups was decreasing (not shown).

Results from injections of mineral fines

Injection of fines into the GoBiGas I gasification system was demonstrated in two campaigns. Bauxite was chosen as a first material due to its differing composition (both from bed material and biomass ash). Main focus was the assessment how bauxite particles distribute in the system which can give information on the fluid dynamic behavior of the plant and facilitate an easier ash balance. Furthermore, the ability of alumina containing material such like bauxite to associate with free silicon allows investigation of the ability to maintain high activity despite high ash, and potentially silicon contamination. The injection was performed in two periods and it was measured in parallel with CON-TAR.

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The main observations were:

- The taken SPA samples indicated a tar reduction effect, however the operation was interrupted twice during the campaign and such conclusion requires confirmation from a long term operation.
- Addition of 2% bauxite to the bed increased the storage capacity for potassium of the solid inventory of the primary loop to more than the double. This finding is in line with the observed tar reduction.
- The gas velocities in the gasifier were low during the operation with bark, limiting the entrainment of bauxite particles with the raw gas.

To demonstrate the effect of olivine fines circulation a second injection campaign was performed. Two observations from the campaign:

- Fine olivine particles displayed a positive effect on the fouling of the product gas cooler, which is recognized by a decreasing gas outlet temperature, indicating an improved heat transfer.
- Feeding of fine particles together with the fuel through the same screw wears on the screw which could be clearly seen from the momentum the engine needed to supply during feeding periods. An alternative final feeding concept is therefore recommended.

Implications for the equipment and bottlenecks in the ash circulation

The source of the catalytic enhancement was found mainly in the balance of the chemicals dominating the biomass ash, calcium, potassium and sulfur. As the full effect can be seen even with on bed feeding (Chalmers), mixing of bed material and gas is of minor importance to utilize the effect of the chemical looping enhanced gas cleaning. As a matter of fact the geometry of the bed does not require a specific shape or inclined bottom. This has important implication for the design of future indirect gasification plants. Taking the Chalmers boiler/gasifier as an example regular boiler design with insulated walls can be applied. This opens up to utilize existing fluidized bed boiler infrastructure which can be extended into indirect gasification units as proposed in the publication by Thunman et.al²². Furthermore, to cope with the increased load of fly ash in the raw gas adaption of the design of convection path for ash rich fuels is recommended.

The high tendency of oxygenated tar species to react and polymerize on surfaces is one of the reasons biomass tar is only seen as a problem which either needs to be dissolved in a scrubbing liquid or decomposed. The above-mentioned efforts, however, led to a minimized tar yield and even more important a non-reactive stabilized tar composition comprising predominantly oxygen-free aromatic and poly-aromatic rings. With gas of this quality a major milestone towards improving product gas cleaning was reached in March 2017 within the “Coated heat exchangers as self-cleaning producer gas condensers” project financed by the Swedish Energy Agency when it was shown an RME scrubber could be replaced by a regular plate heat exchanger with coated surfaces, upon which both steam and aromatic structures with two or more rings could be condensed. Testing was performed using a slipstream of product gas from the Chalmers gasifier, which was cooled in a down-scaled plate heat exchanger. Validating tests were performed in July 2017 at the GoBiGas-plant. This proof-of-concept work, as illus-

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trated in Figure 12 represents a major breakthrough for the technology, as it allows the removal of an otherwise costly and troublesome process unit. More importantly the aromatic species recovered can be valorized as products as they are not mixed into a solvent stream such like RME.

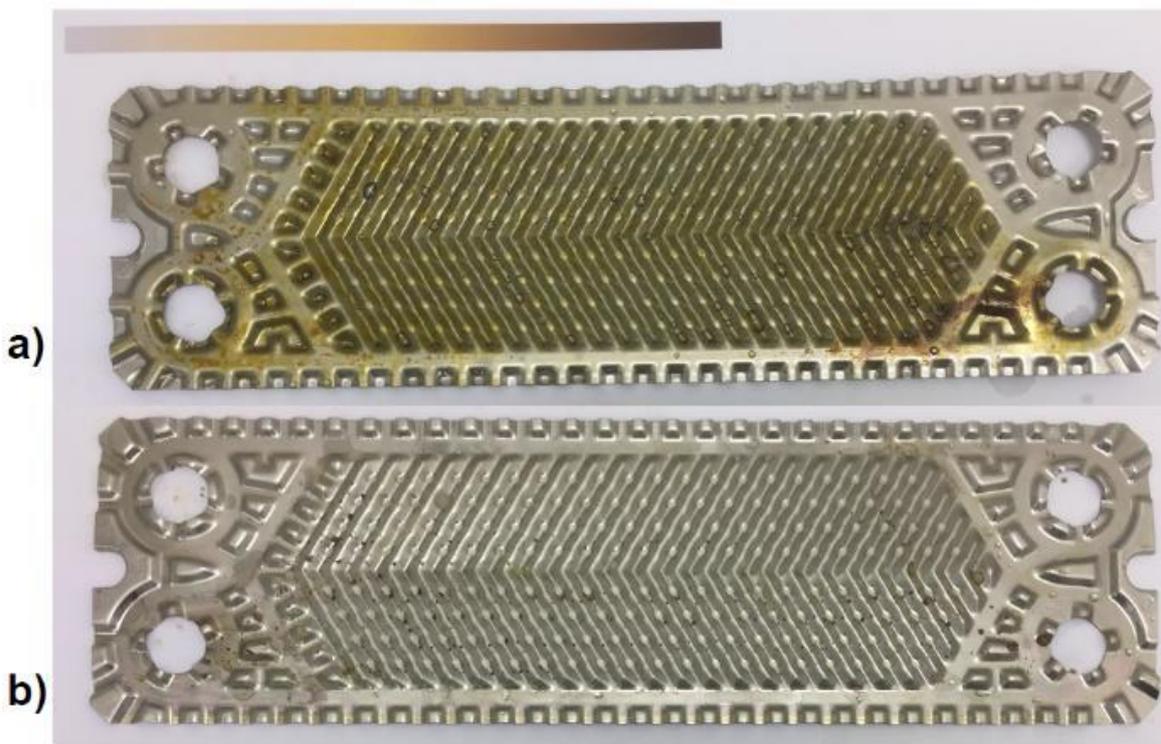


Figure 12. Comparison of a conventional (a) and a novel, coated (b) heat exchanger plate after several hours of exposure to a raw gas side-stream in the Chalmers research gasifier. The degradation of the uncoated plate by a yellow-brownish tar residue is clearly visible. In contrast, the coated plate has remained virtually unaffected. The tests were conducted within the “Coated heat exchangers as self-cleaning producer gas condensers” project, financed by the Swedish Energy Agency.

Ash recirculation was implemented at GoBiGas, and is effective when applied. In contrast to the Chalmers setup, where the fines are transported pneumatically, the fine material at GoBiGas is fed to the fuel feeding screw. High momentum on the engine rotating the feeding screw was observed and ash recirculation is therefore currently not applied. A modification of the fuel feeding port with implemented ash recirculation similar to the modification done at Chalmers is therefore recommended.

Conclusions from the implementation and demonstration at GoBiGas I

The enhanced chemical looping by chemical balancing is fully implemented at GoBiGas allowing to run with fuel of varying ash content and composition. Currently this is achieved by additions of the pure substances even though looping of ash enriched olivine fines displayed equal potential. Due to mechanical issues in the feeding looping of ash enriched fines is not a preferred option with the current set-

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up. The observed positive effects onto the raw gas cooling by added fines observed at GoBiGas I during the test period is not fully understood and requires further investigation. However, decision was taken to keep fine olivine material available to stabilize the operation at GoBiGas I on demand.

4. Tar analysis, relevance and state of the art

The availability of data on tar in product gases is a necessity. To overcome the plentiful sampling systems and to be able to have recognized and comparable results led to the initiative of the tar protocol or tar guideline. It later was brought to pre-normative form as CEN/TS 15439. This effort was supported by the EU mainly aiming at small scale CHP plants and their market introduction a little more than a decade ago. Also about twenty years ago the so called SPA-method was introduced by Brage et al.²³ from KTH Stockholm. This is easier to operate and therefore received wide attention and is today also a state of the art method. But still results differ and there are several varieties of these methods around, so numbers given on 'tar values' have to be treated with care. Obtained values with the same sampling system and the same laboratory procedures should be repeatable. Comparing tar contents obtained with different sampling systems can differ in the order of 10 to 20 %. Further efforts were undertaken also to sample benzene and toluene as part of tar since especially benzene together with naphthalene, as the smallest aromatic or polycyclic aromatic compound respectively, are of high relevance in describing the current condition of a gasifier. Both mentioned approaches do not just need quite some effort in sampling, it also takes a while for the subsequent laboratory analysis. Typically, results are available days if not weeks after sampling. Many attempts were made to have information on tar available more recent if not immediately. So online systems were set-up and tested. An overview is given by Knoef and Neubauer²⁴.

A comprehensive and recent state of the art is currently compiled at ECN in the Netherlands for the IEA biomass task 33 and will be available in mid-2018.

The method applied for the measurements at the Chalmers gasifier and at the GoBiGas I plant is an adapted version of the above mentioned SPA-method. The method was extended by utilizing sample extraction columns that contained a secondary bed of active carbon, as proposed by Osipovs²⁵, in addition to columns with only 500 mg of aminopropyl-bonded silica adsorbent. This allowed for more accurate quantification of all the tar species, ranging from benzene to coronene.

4.1 On-line tar analyzer

The aim of this project part was the development and application of an on-line tar monitoring device for the use in an industrial plant environment. The goal was to build and demonstrate a robust system for monitoring tar reduction strategies and downstream cleaning equipment in real-time. It had to be applicable to the Chalmers Gasifier and the GoBiGas I plant to help to visualize the effects of the applied looping concept on tar content and tar composition in the gas. Therefore, it represents a substantial part helping to fulfill the overall aims of the BioProGRess project.

It is based on previous work applying Laser induced fluorescence (LIF) with a Nd:YAG laser as UV light source. Recent semiconductor developments made UV-LED's with the necessary specifications, especially a high enough power, available at reasonable prices. UV-LED's were applied instead of a laser within this project, bringing down the equipment cost substantially. The underlying measurement principle is 'laser'- or in this case 'light'-induced fluorescence (LIF). Light from an

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ultraviolet (UV)-light source (traditionally a laser) is led into a gas stream of hot product gas sampled from the gasification system. There it excites selectively aromatic molecules which represent most of the tar forming species present in the gas. With the energy of the excitation light source, the analyte molecule is excited, which means that electrons in its structure are moved to higher electronic states. The molecules release this energy again in form of light. This emitted fluorescence light has wavelengths which depend on the individual molecular structures of the molecules present in the gas sample. This light is collected and sent to a spectrometer through fiber optics. As the PAH that shall be detected for this purpose have unique excitation energy (The excitation energy for PAH is much lower than for permanent gases because of the unique π -electron system) compared to the other gas contents, this is a viable technique for the quantitative measurement of the tar load of the gas.

Development work started with the LIF-setup from two earlier projects with a laser as excitation source. With the "old" system test measurements were carried out together with the project partners on site at the Chalmers gasifier. After that a new system was fundamentally new designed to meet the requirements of large scale plant environments. As light source an array with UV-LED's of different base wavelengths was used. A heated containment was built, in which all components that are in contact with tarry gas are enclosed. This assures that all parts in it have the same temperature, avoiding any condensation of tar species in the analyte-gas pathway and in the control equipment e.g. valves. This part of the device was also equipped with a robust ejector-pump for ensuring a steady sample gas flow and a combustion unit to combust the analyzed gas stream so that no labor-intensive gas cleaning was necessary. In addition, a temperature controlled volume (constant 25°C) was designed and set up. It contains the sensitive optical and electronic components and increases stability and robustness of the system. The device was equipped with an industrial control system which monitors all sub-systems of the device. It processes spectroscopic data, records the results and can submit a 'tar signal' to the control system of the gasification plant to give direct feedback to the operators. The finalized system was then tested in the laboratory with relevant tar species and mixtures of aromatic species. Results were used for establishing an analysis and evaluation software for processing the spectroscopic data.

The above mentioned initial measurement campaign took place in February 2015 with the existing setup for tar monitoring at the Chalmers gasifier. It allowed the determination of the requirements for the on-line tar monitoring device. One of the main challenges was to avoid condensation of tar in the system under all circumstances, especially optical windows are challenging regarding that issue.

The device was then built and programmed as specified and first went into operation at the Chalmers gasifier in April 2016. During that campaign, the general capabilities of the new system were demonstrated for the first time. Special focus and a substantial amount of work was put into issues such as signal strength, repeatability of measurements, unsupervised operation and safe operation in the GoBiGas I facility. The necessary improvements were made and the system could first prove its capabilities during a measurement campaign at the GoBiGas I plant in November 2016. The system was used during various Chalmers measurement campaigns in Spring 2017, focus was laid on the influence of different fuel and

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steam flow rates regarding the accordance of the measurement signal with SPA results. A good correlation between these measurements was observed. The steam content of the producer gas plays a substantial role, as SPA measurements are on a dry basis while the measurement principle of the LIF system only allows wet gas measurements (the steam cannot be removed from the gas before the measurement). Further, the system was used in a measurement campaign in the October 2016 at the Paul Scherrer Institute in Villigen, Switzerland. Comparison measurements were carried out with the flame ionization detection (FID) based on-line tar measurement device developed at the University of Stuttgart and Ratfisch Analysensysteme GmbH and the measurement equipment present at PSI together with a second off-line wet chemical sampling method.

4.2 Campaigns at Chalmers

The tar signal calculated by the system is generally linearly correlated to the SPA measurements of tar species with higher molecular weight than naphthalene. But as expected, changes in the gasification conditions cannot be anticipated (Figure 13). A changing steam content of the gas is not being monitored, and has a direct influence on the signal. The measurements from March 16th and 20th 2017 show the limitations of the system when it comes to high concentrations of tar in the gas. The system does not behave linearly for high tar levels as too much of the excited fluorescence is being absorbed by other aromatic molecules in the product gas.

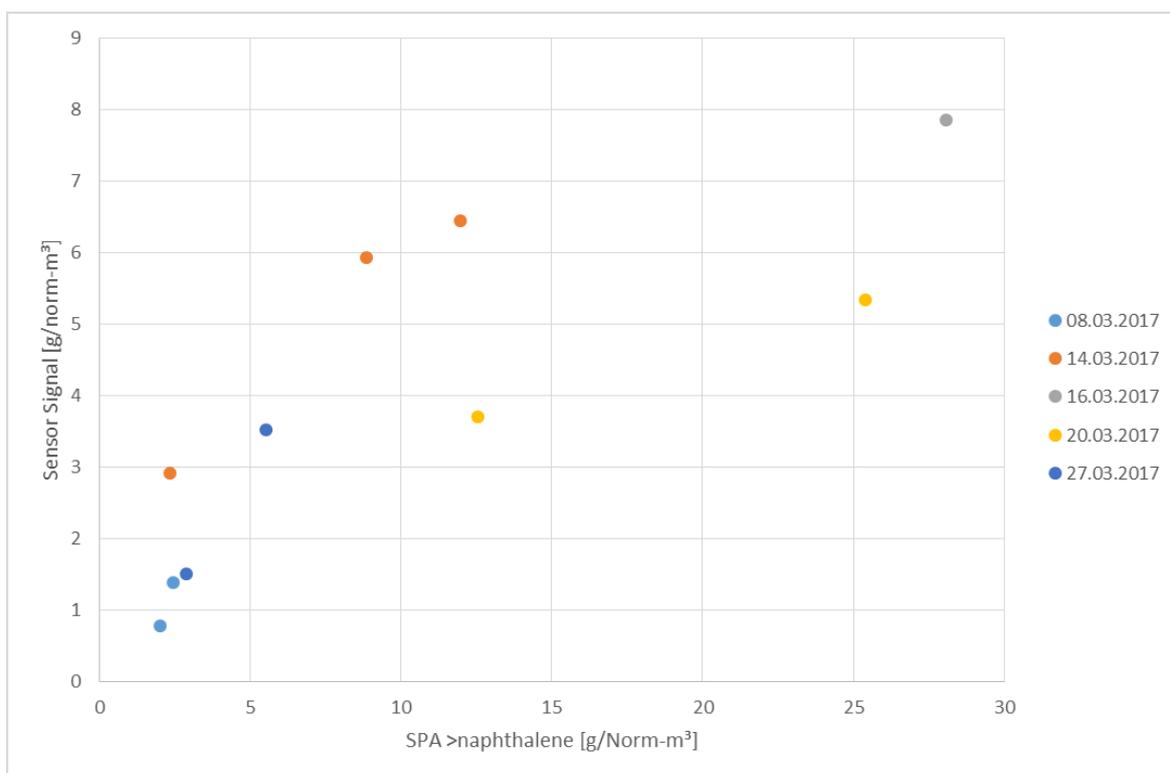


Figure 13. Comparison of the sensor signal with SPA measurements.

4.3 Campaigns at GoBiGas I

A correlation between total tar and CH₄ concentrations was found/confirmed.

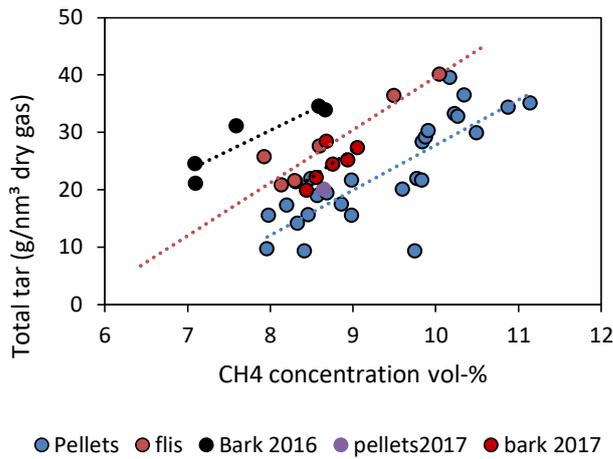


Figure 14. Tar versus methane content. Measurements at the GoBiGas I gasifier with different fuel types and at different loads. Tar sampled by SPA and analysed by GC-FID.

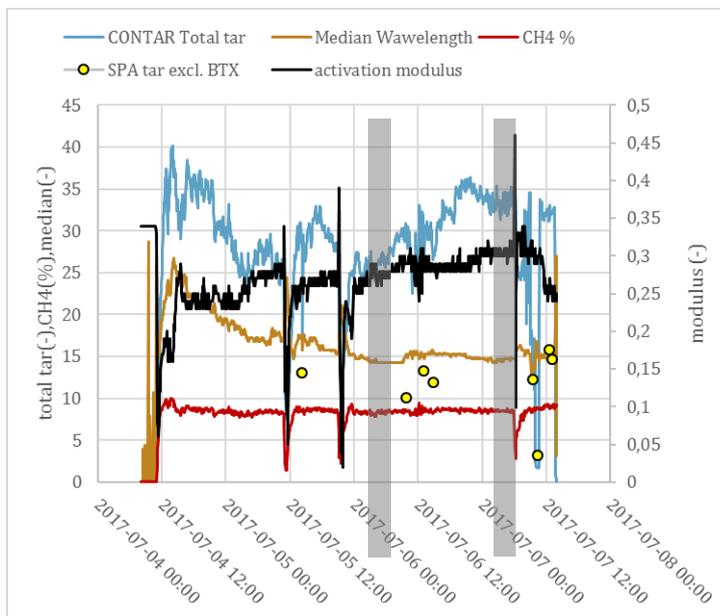


Figure 15. Comparison of the derived CON-TAR signals with the analyzed SPA samples, periods of bauxite injection is indicated by the grey areas in the diagram, two operational interruptions (not related to the injections) happened on the 5th of July around 11:00 and 20:00. The Yellow dots indicate SPA sampling and the corresponding analysis results where the first five were taken after the filter, while the last three correspond to positions after the scrubber, before the raw gas cooler and after the raw gas cooler. Measurement position for CON-TAR was adjusted correspondingly.

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The median of the emission wavelengths of all excited aromatic species in the gas gives a rough indication of the distribution of the tar components in the gas. It was the intention to create a second signal which can be used for control purposes. A higher value for the median indicates a larger fraction of heavy components. During start-up there was a significantly higher median, which slowly decreased with time and stabilized after about 2 days. This lower median is correlating well with Naphthalene as being the dominating tar component in the gas.

Comparing the CON-TAR signal with data obtained with the SPA-method there is a clear correlation in a broad span which was shown by sampling also after the filter as well as after the scrubber. The best correlation can be found with the sum of tar components, naphthalene and larger, including unknown components. However, CON-TAR can yield additional information about the composition of the tar thus indicating gas condition and condensation tendency more detailed. Even differences due to varying fuel load can be distinguished in that way.

4.4 Sensor for measurements after the scrubber

To potentially allow feedback control of the fresh RME stream flow rate, a similar sensor for a lower temperature gas was set up towards the end of the project. The design is much simpler as the cell is only heated to 70 °C and no window purge gas is used. The sensor fits in a box of approximately 40x30x20 cm and was installed in line with the gas analysis-system of the GoBiGas I plant. The system is intended to be used in the cleaner gas after the scrubber to monitor and to control scrubber performance.

4.5 Conclusions from the on-line tar monitoring

The on-line monitoring of tar within BioProGReSs turned out to be really successful. The LIF approach with the adaptations made in this project proved its long term operability and its usefulness for giving on-line feedback from different sampling points in the plant. Confidence of the operators was gained and possible uses and requirements were identified. This potentially can enable faster success in starting up plants like the GoBiGas. As gasification technology faces a challenging market environment a specialized device such as the CON-TAR is not easy to be placed commercially in this market niche. It seems easiest to keep these achievements in academia and combine it with follow up projects with scientific entourage of gasification projects.

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5. Design study of a commercial scale process and comparison with alternative technologies

GoBiGas I was built to demonstrate the thermo-chemical route from wood to methane in a pre-commercial scale with 20 MW methane output. The next step should have been the commercially operating GoBiGas II with a five times larger scale. A similar aim followed EON's Bio2G project at an even larger scale of 200 MW biomethane. Both concepts were planned with fluidized bed gasifiers but with a rather different underlying basic principle. For the moment both projects have been put on hold.

5.1 Defining commercial scale in biomass gasification for SNG production.

In the past decade numerous projects were developed with the intention to build and operate demonstration and first commercial plants. Most of them were in a first phase focused on CHP production. Well known examples of realized projects are the FICFB technology demonstrated first in the Güssing plant in Austria and its follow-up plants, the Värnamo IGCC plant in Sweden and the Carbona/U-Gas Technology demonstrated in the CHP plant in Skive, Denmark. Throughout Europe and in North America plants were put into operation at very different scales. Ambitious project ideas were brought up with the main goal to reduce carbon emissions in the electricity and fuels sector. Many were introduced and developed, but were finally not built due to unsecure market and political framework conditions allowing a sustainable operation for at least the amortization period of the plant.

Table 1. Overview of FB gasification plants intended for SNG development.

Gasification types	Plant/Project	Location	Additional information	Use	Size, MW _{th} fuel input
Testing and development					
FICFB	GAYA	Lyon, FR	DFB	SNG	0.5
DFB	MILENA/ OLGA	Petten, NL		Test, demo	0.8
DBF	Chalmers	Gothenburg, SE	Valmet	Test	2-4
Demonstration (partly commercial operation)					
FICFB	Güssing	Güssing, AT	DFB Re-potec	CHP 1 MW SNG slipstream	8
FICFB	GoBiGas I	Gothenburg, SE	DFB Repo-tec/Valmet	SNG	32
Reported planned demo and commercial scale projects (not yet realized)					
DFB	AMBIGO	Alkmaar, NL	MILENA/ OLGA	SNG demo	4
FICFB?	GoBiGas II	Gothenburg, SE	Not finally determined	SNG	~150
BFB	Bio2G	Scania, SE	Andritz-Carbona	SNG	340

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The minimum size of a plant to achieve favourable economic conditions depends on the fuel availability and its associated costs, the investment into the plant, the delivery infrastructure for the energy or chemicals produced and finally the achievable product price. Table 1 gives an overview of plant sizes with fluidized bed gasification intended for SNG. Based on reported planned commercial scale plants and literature it seems that gasification based on DFB gasification has to be at least in the order of 100 MW_{th} to be economically feasible. Approaches for smaller (multiple) plants have also been investigated - compare Held²⁶ or Rabou and Overwijk²⁷.

Within the project competing gasification techniques were analysed e.g. direct, indirect, entrained flow and fluidized bed gasification as well as pressurized versus atmospheric gasification. Different gas cleaning and gas conditioning techniques were also analysed e.g. catalytic tar reforming and single stage and multi-stage scrubbing.

At the scale of a planned GoBiGas II facility there was no clear winner but the indirect gasification showed a little bit higher conversion from fuel into product and seemed more beneficial when going to a scale around 100 MW_{th}. With increasing size, oxygen production by an air separation unit and direct gasification become more interesting as well as pressurized operation. So the plant economics change with the boundary conditions given for a specific site.

Based on these results supported by modelling and literature^{28,29,30} the more detailed economic analysis started therefore with the idea of scaling the same dual fluidized bed approach applied for GoBiGas I to a five times larger unit (150 MW_{th}) to be used for GoBiGas II.

5.2 Economic evaluation of up-scaling and implementation of CLR

5.2.1 Effects of Chemical Looping Reforming

The effects of different active materials which can be applied and transported within the loop on the product gas composition are described in detail in different publications from Chalmers University^{21,31,32,33, 34}. In this study, the effects have been quantified and applied to data obtained from the GoBiGas plant to discuss improvements for the steady state process of a large-scale plant. Summarized the effects can be stated as:

1. Total reduction of condensable organic species by more than 50%

In Table 2 the SPA (solid phase adsorption) results concerning organic species are shown. The measurements showed that a reduction of condensable organic species of more than 50% is observed when applying CLR to a dual fluidized bed gasifier with a bed with activated olivine as bed material.

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2. Shift of the composition of condensable organic species from heavy species to light species

The CLR especially enhanced the reduction of condensable organic species that were larger than phenol reducing this part of the total spectrum by more than 50%. This shift in composition reduced the “tar dew point” from 161.7 °C to below 100 °C (calculated from ECN tar dew point calculator on wet basis)³⁵.

3. Increased H₂/CO ratio

For methanation a H₂/CO ratio of 3 is needed. In the base case plant a ratio of 1.8 was achieved while with CLR it was increased to 2.7.

Table 2. Comparison of product gas leaving the gasifier (*measurement at GoBi-Gas, ** measurement at the Chalmers gasifier)

Component	H ₂	CO	CO ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆
	Vol-%							
Base case plant*	39.5	21.9	25.7	9.3	0.1	2.8	0.5	0.3
CLR**	43.8	16.0	31.3	6.5	0.0	1.8	0.3	0.2

5.2.2 Improved downstream equipment

The above listed effects have a positive influence on the overall efficiency of a gasification plant. A best-case scenario based on this is presented to identify to which extent the Chemical Looping Reforming technology can improve the economic performance of a dual fluidized bed gasification plant. The improved product gas quality results in more efficient downstream unit operations which were studied and quantified in Aspen Plus V8.8.

Removal of Condensable Organic Species and Product Gas Cooling

The change in product gas composition by applying CLR shifts the dew point of condensable organic species to below the water dew point. Due to this shift a different and more efficient approach to the removal of water and condensable organic species is facilitated. For this reason, the cost intensive scrubbing process is not needed in the case of CLR.

By shifting the “tar dew point” to temperatures below the water dew point it should become possible to cool the gas below 30 °C instead of 150 °C in the product cooler. This option is feasible also due to a hydrophobic nano-coated surface in the gas cooler^{36,37}. The coating ensures that condensable organic species that fall below their vapor pressure and therefore condense at the temperature present at the cooler outlet do not stick to the surface and are drained out with the constant water flow arising from condensing steam. The largest contributors to condensable organic species in the gas phase are naphthalene and benzene. Benzene will only start to condense in substantial amounts at temperatures below 0 °C, while naphthalene is present with concentrations below 1 g/Nm³ at 20 °C. For cooling below 0 °C a second product gas cooler in series is required.

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The optimum of the cooler outlet temperature is defined by a low concentration of condensable organic species reducing the downstream effort on the one hand and on the other keeping the heat removal equipment and operation at low cost. Two cases were compared here. In case 1 the outlet temperature of the cooling system lies at 30 °C which is identical to the outlet temperature in the base case plant after the scrubber. In case 2, the gas temperature is cooled to 10 °C reducing the amount of condensable organic matter. Condensation of water occurs at temperatures below 80 °C increasing the amount of heat that needs to be removed drastically and resulting in a large surface demand for the cooler. For temperatures below ambient temperature the installation of a refrigeration machine must be considered. For both cooling cascades three cooling stages were suggested of which the second and third stages were installed redundant for a longer uptime between cleaning intervals. In the first cooling step the gas temperature was cooled to 150 °C by employing thermal oil as cooling agent. In the second step the wall temperature of the cooler should not exceed 65 °C to ensure the film of condensed water on the cooler wall on the product gas side.

The calculations showed that the savings due to a lower load of condensable organic species (i.e. cost of operation and regeneration of the carbon beds after the product gas cooling) was higher than the cost of a refrigeration machine. Based on this calculation case 2 in combination with CLR was therefore chosen for the further economic calculation of the 150 MW_{th} plant setup.

By omitting the product gas scrubber no RME is being fed to the combustions zone. The lack of thermal input to the combustion side needs to be compensated to ensure the energy balance for the gasification and combustion zone. For the base case plant 0.03 MW_{RME}/MW_{biomass} are consumed³⁸. For a 150 MW plant the lack of thermal input results in 4.5 MW. Biomass is far less expensive, so it is beneficial to supply this energy demand with biomass instead of RME.

Shift Reactor

Due to the increased CO/H₂ ratio less CO and H₂O must be reformed to H₂ and CO₂. This is beneficial for the capacity of the shift reactor located downstream of the sulfur removal step. The ratio of CO/H₂ in the cold gas treated with CLR was maximized to 2.8 from an initial value of 1.8. The slip steam which is led to the shift converter can be reduced 80%.

Methanation

The methane content in the cold gas leaving the gasifier is lower compared to the base case plant. Additionally, the carbon monoxide and hydrogen concentration is higher. This leads to an increase of 16.8% in the demand for the methanation reactors.

Compressors

Due the increased product gas yield resulting in a 4.4% higher methane production compared to the base case plant, the compressor step needs to be increased in capacity.

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Installations for CLR

The installation cost for the CLR equipment is given in Table 6 for the 150 MW_{th} plant. The operational costs of the system consist mainly of lost and consumed looping material which can be neglected due to low amounts and costs.

Deriving Benzene from the Process for Valorization

When reducing the gas temperature to 10 °C before entering the carbon beds 420 kg/h of benzene can be derived with a purity of 93%. Due to the low purity further upgrading of this side product is necessary. This could be done in refineries or companies dealing with coal tar products. For the considerations here a price of 170-250 €/t was assumed. Prices for pure aromatics such as benzene, styrene or phenol or their conventional pre-product Naphtha vary in between 400 and 1000 USD/ton³⁹. The total potential of the valorization of tar as a side product was calculated to about 0.5 and 0.74 M€.

5.2.3 Scaling exponents and cost of resources and products

Economic efficiency improves with increasing scale, since specific investment cost for the installed equipment decrease with size. The CLR is intended to ensure stable operation of a plant and improves the efficiency further. For the economic assessment a DFB plant based on the existing GoBiGas I design was scaled up to 150 MW_{th}. This scale seems reasonable for a commercial operation in Sweden. In this study the implementation of CLR was assessed. Associated with the CLR several downstream improvements were due to improved raw gas quality.

A gasifier size of 150 MW_{th} represents nowadays a gap between existing biomass and coal gasifiers. SNG based on gasification of coal is carried out in much larger scales, typically 1-10 GW_{th}. So for the GoBiGas I the gasifier represents a scale-up whereas the adapted TREMP methanation process from Haldor Topsøe, originally developed for coal based SNG production, was scaled down. A large plant size shows positive effects on the specific equipment and operation cost. Therefore, one intends to increase the size as far as possible. But at larger scale the biomass logistics are limited due to low energy density and the water content which lead to higher transportation expenses. The largest biomass converters are pulp and paper plants. They can be seen as the largest reasonable scale of thermo-chemical biomass conversion.

To estimate the cost of an up-scaled GoBiGas plant the existing GoBiGas I was used as reference and scaling exponents were applied (see Table 3).

*Table 3. Installation cost of a gasification plant of 32 MW_{th} and 150 MW_{th} size for methane production and scaling exponents ($Cost = Cost_{ref} * (Size/Size_{ref})^{SE}$)³⁸*

Unit operation	32 MW_{th} (reference)	150 MW_{th}	Scaling exponent (SE)
Fuel feeding	8.18	21.69	0.63
Dual fluidized bed gasifier	10.91	37.61	0.80
Gas cooler/filter/scrubber	4.55	15.43	0.79
Flue gas cleaning	8.18	19.17	0.55

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Carbon beds	13.64	35.60	0.62
Hydrogen/sulfur removal	7.27	18.99	0.62
CO ₂ removal	7.27	18.99	0.62
Shift/pre-methanation	10.00	26.11	0.62
Methanation and drying	13.64	35.60	0.62
Compressor	13.64	34.52	0.60
Building	15.45	28.72	0.40
Burst wall	5.45	10.14	0.40
Auxiliaries	9.09	24.86	0.65
Commissioning	36.36	67.58	0.40
Total	163.64	395.02	

When scaling this plant configuration to 150 MW_{th} without any changes to the equipment design the investment cost will be 395.02 M€. With an interest rate i of 5% and an operation period n of 20 years the annuity is calculated by calculating the equivalent annual cost (EAC) using the annuity factor (ANF).

$$ANF = \frac{(1+i)^n * i}{(1+i)^n - 1}$$

With an ANF of 8% the EAC results in 31.7 M€ for the 150 MW_{th} plant.

The considered operation, feedstock and product prices are presented in Table 4.

Table 4. Cost of resources and products

Position	Value	Reference
Biomass	23 €/MWh	⁴⁰
RME	1.25 /l (with tax)	⁴¹
Electricity	59 €/MWh	⁴²
Heat	30 €/MWh	⁴³
Maintenance		
Equipment	3% of investment	⁴⁴
Building	1% of investment	⁴⁴

With a conversion efficiency of 65% of biomass to methane⁴⁵ and full load operation of 7,000 h/a the cost for the production of 1 MWh methane for the 150 MW_{th} plant are composed as presented in Table 5.

Table 5. Production cost per MWh biomethane for a 150 MW_{th} plant

Capital Cost	44.02 €
Maintenance	11.66 €
Feedstock	35.94 €
RME	7.56 €
Electricity	10.37 €
Revenue from heat output	-5.13 €
Total production cost	104.43 €

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The total production cost for 1 MWh of methane from wood in the scaled-up plant was calculated to 104.43 €.

5.2.4 Economics of the full-scale process

The aim of this investigation was the evaluation of the economic performance of a biomass gasification plant for SNG production at large scale based on the technology investigated during the BioProGRess project.

Table 6. Investment cost comparison for the up-scaled plant and for the same plant by incorporation of the CLR.

	Plant component	32 MW_{th}	150 MW_{th}	150 MW_{th} with CLR
Investment [1000 EUR/ MW]	Fuel feeding	255.63	144.62	144.62
	Dual fluidized bed gasifier	340.94	250.75	250.75
	Gas cooler/filter/scrubber	142.19	102.88	51.44
	Flue gas cleaning	255.63	127.81	127.81
	Carbon beds	426.25	237.35	237.35
	Hydrogen/sulfur removal	227.19	126.58	126.58
	CO ₂ removal	227.19	126.58	141.73
	Shift/pre-methanation	312.50	174.05	64.17
	Methanation and drying	426.25	237.35	261.61
	Compressor	426.25	230.12	236.15
	Building	482.81	191.48	191.48
	Burst wall	170.31	67.58	67.58
	Auxiliaries	284.06	165.74	165.74
	Commissioning	1136.25	450.55	450.55
	Installations for CLR	-	-	3.93
	Total	5113.44	2633.45	2521.50

The scale-up of the plant to a size of 150 MW_{th} was discussed in the previous section together with the discussion of downstream improvements based on the CLR effects and adaptations needed. In this section the discussed alterations were evaluated. The cost of equipment and operation for the adapted plant setup are presented in Table 6.

The achievable cost reduction was analyzed and the specific investment cost decreased from 5,113 to 2,633 EUR/MWh bioSNG representing a decline of 49 %. A larger cost reduction can be achieved by replacing the RME scrubber by a novel heat exchanger concept, which indeed serves as water condenser for the unreacted fluidization agent.

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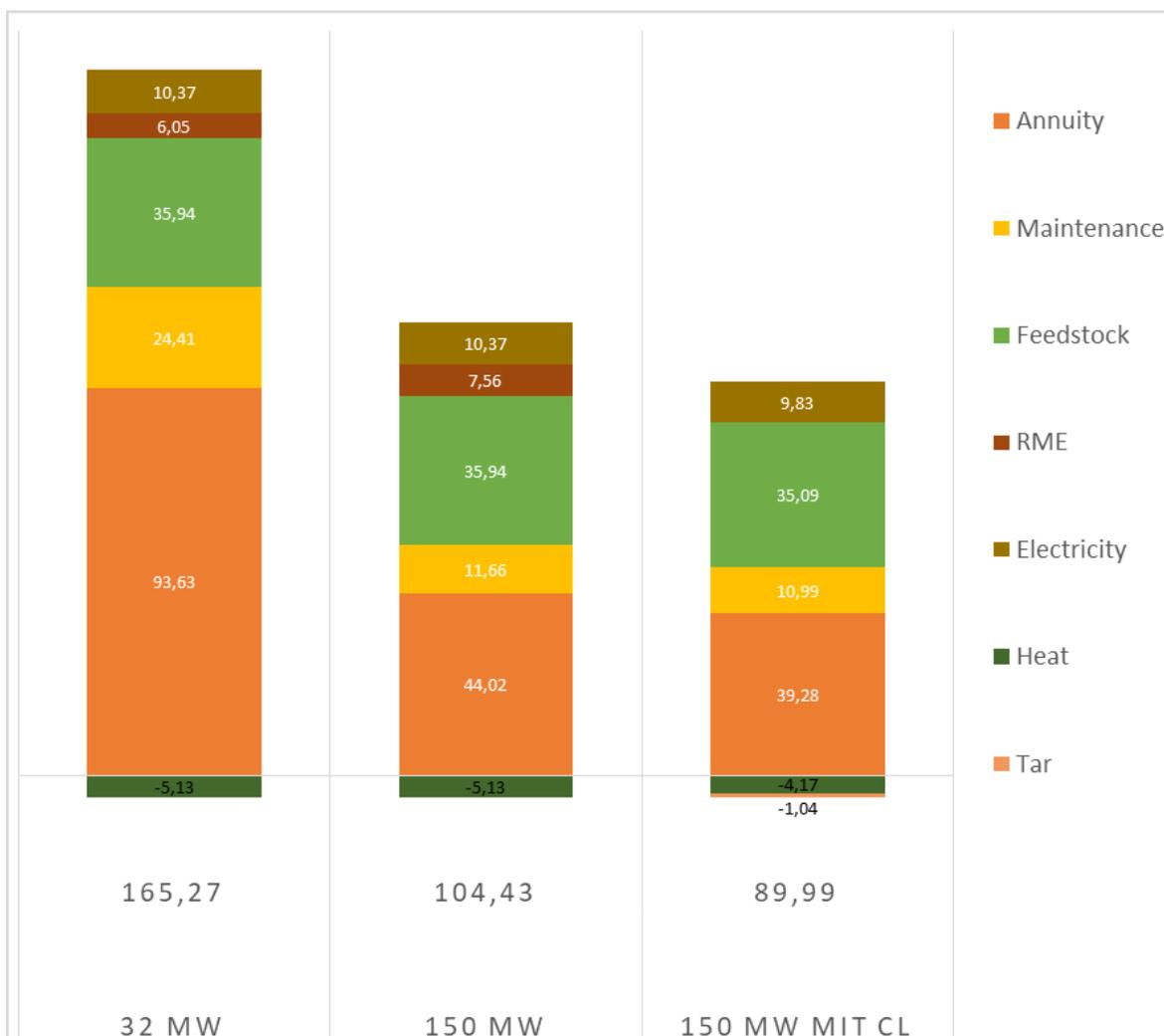


Figure 16: Share on cost in €/MWh of produced methane for GoBiGas I (left), an up-scaled facility of 150 MW_{th} (middle) and an up-scaled facility of 150 MW_{th} with CLR (right), based on 7,000 operating hours per year and a feedstock cost of 23 EUR/MWh.

To achieve more beneficial overall economics the option of using parts of the organic phase from the condensates as washing medium as well as for separate valorization as by-product was looked at.

The applicability of the Chemical Looping Reforming approach demonstrated at Chalmers and GoBiGas I was evaluated for the larger scale. Since the GoBiGas II project was put on hold further options of implementing this technological approach e.g. for retrofitting or expanding existing biomass fed boiler systems were examined. The implementation of CLR at the scale of 150 MW_{th} taking into consideration an exchange of the RME scrubber and several adaptations downstream lead to an additional specific product cost reduction of 9 %. It has to be mentioned that this was not a detailed engineering study but rather a design study that discussed options. There are numerous details and questions that have to be taken into account when going for a specific plant design.

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Based on 7,000 operating hours/year and a feedstock cost of 23 EUR/MWh a cost of approx. 90 EUR/MWh bioSNG was achieved for an up-scaled facility of 150 MW_{th} including CLR (see Figure 16). Final prices can only be given when performing a detailed design study going deeper into the engineering details of the plant with all requirements for a specific site where such a unit shall be operated.

Such a detailed study including a more comprehensive description of the process has been performed by Thunman, H. et al.⁴⁶ and published after the BioProGReSs project was finished. In this study 8,000 h/a operation (which was one of the aims with the GoBiGas I demonstration) and the feedstock cost in Sweden (Gothenburg area) of approx. 16.5 EUR/MWh for forest residues were used. The resulting production cost was approx. 70 EUR/MWh biomethane for a 100 MW_{SNG} plant. The result is consistent with the findings of BioProGress, the main difference originates from the difference in assumed number of operational hours and feedstock cost.

6. Conclusions

At the start of the project the status at GoBiGas was that no steady operability was achieved due to the elevated tar content in the syngas. The syngas cooler was repeatedly clogged resulting in corresponding shut downs of the plant. The findings of this project on how to lower the tar content have contributed to facilitate stable operation of the gasification unit. The knowledge was continuously transferred lowering the tar content from initially 25g/Nm^3 to below 5g/Nm^3 (excluding BTX).

The reduction was made possible by creating a catalytic environment that limits the formation of tar rather than decomposing already formed tar. While the decomposition is a heterogeneously catalyzed effect that depends on the surface composition of the particles, limiting the tar formation is most likely based on homogeneous gas phase reactions where alkali vapors play a crucial role. The growing understanding in the project has emphasized the importance of chemical looping of calcium, potassium and sulfur, where the looped solid material is primarily a carrier of the catalyst and in second place a catalyst on its own.

The balance between the species calcium, potassium, sulfur and silicon, can be kept and enhanced by three measures; the chemical looping of specific ash fractions, the utilization of ash rich fuels with the right composition of species such as bark and the addition of pure chemicals in the form of potassium carbonate and sulfur. As silicon is an irreversible alkali getter the content of silicon in the fuel should be controlled. The understanding of the synergistic effects of the above-mentioned species is crucial for the utilization of fuels with low or varying ash content, such as forest residues, bark, refused derived fuel (RDF), or waste.

Since the CLR concept demonstrated here is scalable and independent of reactor type it can be used for improved competitiveness not only for bioSNG plants such as GoBiGas but any large or medium scale biofuel production plant based on gasification.

To enable proactive control of the balance on-line tar measurement is a requisite which cannot be provided by the currently applied offline methods or indirect methods. The on-line tar measurement, developed by the research group in Berlin, is a superior way to monitor and control the operation of the gasifier and the gas cleaning equipment. Within the BioProGRess project the analyzer was implemented into the operation at both the Chalmers and the GoBiGas sites. Stable operation was demonstrated over extended periods under realistic conditions in a challenging industrial environment. Regarding the robustness and cost of the applied analysis technique the application of newly available high-power UV-diodes instead of a laser can be seen as a major milestone.

From the experiences during the collaborative measurements and the identified needs a simplified device was designed, which can be in operation together with the conventional gas analysis of the plant, monitoring continuously the lighter fraction of condensable e.g. naphthalene in cleaned gas after the scrubber.

When biomass gasification is discussed often the focus is directed on the amount of tar. However, the high content of oxygenated species and the tendency to react even when condensed has prevented the utilization of biomass tar as a product. The applied CLR concept favors the transformation of the tar spectrum into a stable mixture of predominantly aromatic species, which pose a considerably value

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as a product. In an adjacent project the use of a regular heat exchanger with coated hydrophobic surfaces for the condensation of steam and the two-rings and larger aromatic structures instead of costly RME-scrubbing was successfully demonstrated.

The effect of a condensation instead of scrubbing is twofold, the operational cost can be reduced by up to 7% as RME is an expensive consumable and the retrieved tar mixture can be valorized, as it is not anymore diluted by a solvent, creating additional revenue. As a matter of fact, even the layout of the gas cleaning section can be simplified and the size of the units can be adjusted to the new tar levels. Those two effects can add up to an estimated reduction of the investment costs (excl. buildings and commissioning) by approx. 10%. If one takes into account the up-scaling effect of dual fluidized bed gasification to commercial scale ($\sim 150 \text{ MW}_{\text{th}}$), enabled by the introduction of CLR, the specific investment cost can be reduced with up to 50%. The resulting specific production cost at large scale with CLR implemented were found to be 90 EUR/MWh, based on 7,000 operational h/a and a feedstock cost of 23 EUR/MWh, representing an overall reduction of 46% compared with the GoBiGas I demonstration plant. With 8,000 operational h/a, which was the aim of the GoBiGas I demonstration and the current feedstock cost for forest residues in the Gothenburg area the production cost is 70 EUR/MWh biomethane.

7. Outlook

The transition from a fossil based to a sustainable energy system requires efficient use of renewable resources such as woody biomass. While there are many options to produce electricity and heat the options to produce a biofuel suitable for the transportation sector are more limited. There is ongoing work to use woody biomass for ethanol production but the yield is relatively poor compared to gasification of the same biomass. One of the highest conversion efficiencies is reached if the final product is biomethane. In addition biomethane plants are not penalized as hard as other second generation biofuels plants based on gasification when going down in scale, due to the development of indirect gasification⁴⁷.

When GobiGas I was built, no supplier was offering a dual fluidized bed gasification system in the size range 50-150 MW due to uncertainties in the upscaling. The new syngas cleaning based on looping of catalytic material and fines showed that catalytic effects are scale independent and can be utilized independent of the design of the gasifier bed and the fuel feeding strategy. That allows the utilization of knowledge from boiler design and consequently upscaling to capacities well above 100 MW_{th}, where the current size of commercial BFB and CFB boilers (300-500 MW) is the limit.

The introduction of CLR improves the economics of biofuel production by gasification and enables upscaling to commercial scale but the high investment cost associated with large scale facilities such as GoBiGas II is discouraging under the current European policy framework. On the other hand new and stronger instruments are likely to be implemented if the high political ambitions to replace fossil fuels in the transportation sector are to be fulfilled. Meanwhile the CLR opens up another option where new insights on fuel feeding and reactor design, form the basis for a process layout that utilizes CLR in combination with existing fluidized boilers. By complementing the combustor with a gasification reactor a dual fluidized bed system is generated. As existing boilers in district heating, pulp, paper and saw mills are retrofitted the investment costs will be lowered, not only due to the utilization of existing equipment but through the availability of sites and permissions.

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