EUDP-13-I Journalnr-64013-0170 -Final report

1.1 Project details

Project title	Katalytisk fjernelse af tjære fra biomasse forgassere II
Project identification (program abbrev. and file)	EUDP-13-I Journal nr. 64013-0170
Name of the programme which has funded the project	EUDP 13-I
Project managing company/institution (name and address)	Haldor Topsøe A/S, R&D Haldor Topsøe Alle 1 2800 Lyngby
Project partners	Skive Fjernvarme 7800, Skive, Teknologisk Institut, 2630 Taastrup, ChimneyLab Europe Aps, 8370 Hadsten
CVR (central business register)	41853816
Date for submission	01/09-2016

1.2 Short description of project objective and results

1.2.1 Dansk version

Fremstilling af syngas ud fra biomasse forgasning til kraftvarme værker og til fremstilling af nye biobrændstoffer, begrænses af ineffektiv fjernelse af tjærer i forgasningsgassen. Sod dannelse, støv nedslag på katalysatoren og regenerering af tjærekatalysatoren skal studeres og en ny katalysator samt et nyt og effektiv reaktor koncept vil blive udviklet og installeret i Skive Fjernvarmes anlæg. Med kombination af de ovenfor nævnte tiltag gennemført vil Skive forgasning anlæggets totale effektivitet og drift blive væsentlig forbedret
Et forstudie til opstilling af et Haldor Topsøes biogas baseret kemisk anlæg til fremstilling syntetisk metan gas viz. SNG, biobrændstof f.eks. benzin, metanol eller dimethylether (DME) i Skive vil blive gennemført

1.2.2 English version

Production of syngas based on biomass gasification for Combined Heat and Power plants (CHP) and for production of new bio fuels are slowed due to the inefficient removal of tar in the biogas from the gasifier. Soot formation, dust settlements on the catalysts as well as the regeneration of the catalyst shall be analysed and a new and more dust and Sulphur tolerant catalyst as well as an efficient reactor concept will be developed and installed in the Skive Combined Heat and Power Plant (CHP). With the above combination of the two tasks executed the overall efficiency of the Skive gasification plant will be considerable improved
Furthermore a pre-study of the possibilities for installation of a Topsøe biogas based chemical plant for production of synthetic methane gas, wiz, SNG, biofuels e.g. gasoline, methanol or dimethyl ether in Skive shall be performed

1.3 Executive summary

Enabling biomass gasification technology to gain further attractiveness requires the development of next generation reliable and efficient tar reforming technology viz catalysts as well as reactor system lay-out

Biomass gasification is used for Combined Heat and Power (CHP) plants besides this it can be used for production of synthesis gas for production of synthetic biofuels, this will further add business potential and the benefits of storable renewable energy to biomass gasification technology. The synthetic biofuels can be e.g. methanol, methane, dimethyl ether (DME) or gasoline (TIGAS). On a biomass gasification plant in general, first biomass is gasified and subsequently the amount of tar and dust in the gas is reduced before it is used as feed gas for any chemicals production downstream. This project focuses on catalytic reduction of the amount of tar components in the gas and development of a dust resistant catalyst as well as a robust and efficient reformer reactor system.

The aim of the current project is the development and implementation of such a new generation of robust and efficient Haldor Topsøe A/S tar reforming catalyst and reactor concepts technology at the gasification plant in Skive Fjernvarme. Soot formation and deposition of dust on the tar reformer catalyst shall be solved by development of a new dust and more Sulphur tolerant monolith catalyst, development, design and implementation of a new reactor concept along with modified and improved regenerations procedures to extend the operation time between regeneration and the catalyst replacement times. The new developments and designs will increase the plant availability which is one very important parameter to the financial sustainability of biomass gasification plant.

The new reactor concept will be developed and designed in such a way that the working conditions for the people who have to work inside the reformer during the loading and unloading of the catalyst shall be improved considerably and fully in accordance with the authorities' requirement

A pre-study of the conditions for establishment of a Haldor Topsøes biomass based chemical plant for production of synthetic methane gas(SNG), biofuels like methanol, DME Gasoline etc. in Skive will be reported. In this project, a preliminary study will be performed, that can determine how Haldor Topsøe can use the gasification plant in Skive as demonstration host for the production of synthetic fuels from gasified wood and other biomass. Meetings between the Technical Authorities in Skive, Haldor Topsøe and the Skive CHP plant management have taken place in order clarify and develop the conditions for implement this kind of biomass based chemical plant.

It has been shown that with the new dust and Sulphur tolerant catalyst and the new robust reformer technology implemented at the Skive CHP plant during the summer stop 2014 the down-time in both frequency and duration has been reduced considerably due to the new reactor concept and Mega monolith design of the catalyst. After the implementation of the new concepts and designs the plant availability and heat and power production rate has increased. For the production year 2015 the increase in electric power and heat production has increased with 18%. The yearly plant efficiency (energy output/fired input) has reached 86% in 2014/2015, which is the ever highest efficiency for the plant.

Besides improving on handling tar components and solids in the gas stream during operation, an important issue is the solids removal by combustion with air during regeneration; the degree of success is particularly sensitive to the temperature and air addition conditions. A study on solids combustion optimization and implementation of reformer temperature control via gas-heated reformer recycle gas is part of the project scope. Burner systems integrated with the reactor tubes in the reactor and a burner system in the transfer to the reformer has been implemented with great success thus making temperature control much easier.

The gasification technique used in Skive is ideal for production of liquid transportation fuel. Haldor Topsøe has a strong global position in plants that converts syngas into liquid fuel, and the experiences from Skive Gasification Plant can be utilized by Haldor Topsøe in the establishment of Biomass-to-liquid or Biomass-to-gas plants as new areas of business.

The aided by improvement within the general issue of reactor clogging by carbon-rich dust, particles and soot (solids) during operation

1.4 Project objectives

Skive Fjernvarme Gasification plant-Combined Heat and Power plant (CHP) was taking on stream back in 2009. However from the very beginning there were severe operating problems with dust, bed material, slagging and with the catalyst for the tar reforming process. The catalyst delivered at the time was a square type monolith arranged in squared trays in the tar reactor. The catalyst itself had difficulties in handling the tar components in the gas from the gasifier and the geometrical arrangement of catalyst trays accumulated too much dust, slags and bed material from the gasifier thus resulting in very poor operation i.e. short operation time and long downtimes resulting in poor output from the plant

Based on the observations above and in order to improve the operation it was decided initiate a project with the overall goal to develop:

- A new robust and more sulphur tolerant catalyst for the tar reactor
- A new reactor concept for better handling of dust, slag and bed material

The project was initiated in 2013 with the main goals as above and a number of important sub goals:

- Working conditions during unloading should be improved
- Unloading time of catalyst should be reduced
- Downtime of the plant due to the long change-out time of the tar reforming catalyst should be reduced
- The clean-up of the gas, i.e.tar and decomposition of ammonia, should be improved
- Improved on stream factor

In order to achieve the above goals the project was defined work packages as follows:

WP1: Development of regeneration procedure of monolith catalyst (DTI and CLE)

The objective of this work package, WP1, was to investigate the reactions in the tar reformer that are responsible for the increase in pressure loss over the tar reformer that occur over time. The hypothesys in the WP is that soot is formed in a polymerization reaction between the aromatic tar molecules. The following tasks were considered:

Task 1.1: Pre-study and modelling of process
Task 1.2: Material selection diagram, PI-diagram, safety issues
Task 1.3: Development and construction of lab-scale tar reformer for studying soothing and regeneration
Task 1.4: Execution of lab-results
Task 1.5: Implementation of regeneration protocol at Skive Fjernvarme

WP2: Revamp or tar reformer (HTAS)

The objective of this work package, WP2, was to make Reactor analysis and modelling, establishing the PI Diagram and implementing modifications to the operation procedures and Basic and detailed engineering of Tar reformer comprising:

- Outline flow sheets before and after revamp
- Pipe and Instrument diagram (PID)
- Clean up of gas i.e. tar and ammonia shall be improved (improved catalyst)
- Dust blowing system to be improved (process design of burner system)
- Burner system to be improved (process design of burner system and basis for CFD calculation)

The following tasks were considered:

Task 2.1: Basic Engineering (HTAS) inclusive operation line out at max. gasifier capacity
Task 2.2: Detail Engineering (mechanical) of Tar reformer
Task 2.3: Development and production of mega monoliths (HTAS)

WP3: Installation phases (Skive, HTAS, CLE)
The objective of this work package, WP3, was to install the procure, produce and install the developments achieved during WP 2 at Skive Fjernvame. The following tasks were considered:

Task 3.1: Procurement of equipment (HTAS, Skive)
Task 3.2: Construction (HTAS, Skive)
Task 3.3: Installation (HTAS, Skive, CLE)

WP4: Wood-to-synthetic fuel in Skive – preliminary study (HTAS)
The objective of this work package, WP3, was to look at future perspectives and subsequent activities for extended production from Skive Fjernvarme so that the plant would not only supply heat and power, but also gasoline. The following tasks were considered:

Task 4.1: Pre-study of gas composition and utilisation and unexploited gas
Task 4.2: Basic Engineering Study for high quality synthesis gas production
Task 4.3: Commercial possibilities for the synthesis gas
Task 4.4: Regulatory requirement for the facility and product storage
Task 4.5: Reporting of the feasibility study

1.5 Project results and dissemination of results

WP1: Development of regeneration procedure of monolith catalyst (DTI)

A design of the tar reformer resembling the flow conditions in Skive was made in laboratory scale.
The reactor system constructed in the laboratory setup consisted of a gas- and liquid delivery system, a reactor tube and gas analysis, where we used a gas chromatograph with online sampling possibility, see diagram in Figure 1. Two gas inlets to the reactor was made; one main inlet with a premix of the main gasification gas components, CO, H_2, CH_4, CO_2, N_2, toluene, naphthalene, H_2S, and one inlet with air that was injected into the centre of the hot reactor. The reason for having this separate injection of air was that this resembles how air is injected into the main tar reformer in Skive during operation.
In order to determine if soot is formed, we have installed a filter holder that contains a flat round filter at the exit of the reactor. The filter we use is well suited for filtering small soot particles. The pressure drop over the filter is also measure during all experiments with a differential pressure transmitter, and in the initial experiments, we also had an electrodynamic rod installed in a housing to get an online measurement of the soot formation.

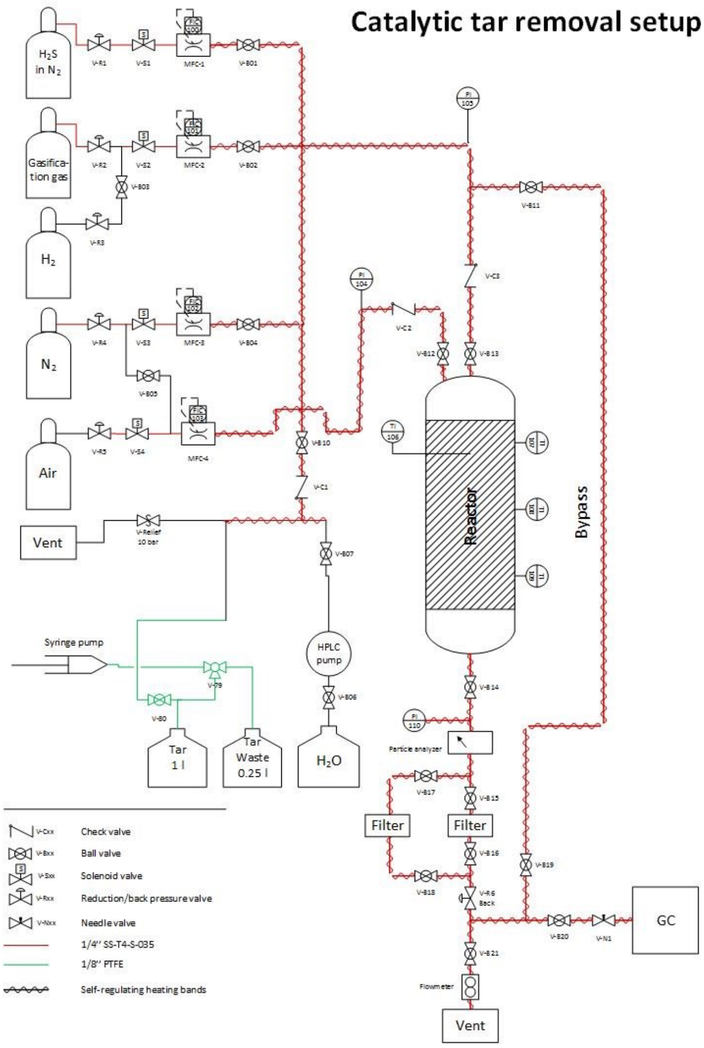


Figure 1: Piping and instrumentation diagram of the laboratory setup.

The initial experiments where conducted with a gas consisting of only N_2, toluene and naphthalene to verify if the reactor-walls, that consist of a nickel-chrome steel alloy, participate in a reaction with tar. The result was that all the tar was consumed in the reactor-tube; it was concluded that the tar was probably reacting on the reactor surface forming whisker-particles in carbon formation reactions. This was also verified since H_2 was measured in the exit-gas. Later we added water to this mixture, which reduced the carbonization reaction considerately. It was concluded that the reactor walls were catalysing different reactions with the tar, and it was decided to run future experiments with a more realistic gasification gas composition. It was expected that especially H_2S would inhibit many of the reactor wall reactions that was seen when running with only N_2 and tars.

A series of experiments were subsequently performed where air was gradually added to a gas mixture that had approximately the same gas composition as the gasification gas that is leaving the gasifier in Skive. The composition of the gas is shown in Table 1:

		Skive gas post revamp
H2	vol%	15,01
H2O	vol%	6,00
CO	vol%	20,63
CO2	vol%	13,13
N2	vol%	40,33
CH_4	vol%	5,16
C_6H_7	vol%	0,10
Naphtalene	vol %	0,02
H2S	ppmv	30

Table 1: Composition of test gas mixture

In the combustion experiments, the concentration of CO, CO_2, CH_4, N_2, H_2, O_2, toluene, benzene, naphthalene, H_2S and carbonyl sulphide (COS), is measured by passing part of the exit gas through the Gas Chromatograph (GC). The pressure drop over the particle filter is also measured and we measured the temperature inside the reactor.

The results were analysed with emphasis on understanding the effect of adding O_2 to the gasification gas and a possible formation of soot due to polymerization reactions with tar molecules. That is, we focus on the reactions that occur in a tar reformer after air is added to the gasification gas, and before the gas is in contact with the reformation catalyst. This is the region where we expect soot particles to form due to the increased temperature.

It was decided not to add a tar reforming catalyst the reactor, since this would interfere with the reactions.

WP 1: Experimental overview:

In the sections below, we will present the results of two series of experiments.

In the first series of experiments, a reference gas consisting of CO, CO_2, CH_4, H_2, N_2, H_2O, H_2S, toluene and naphthalene was passed into reactor, with the composition shown in Table 1. Then air was added to the reactor through the central tube, i.e. the gasification gas and the air was not premixed before entering the reactor. The concentration of air was increased from 0% to 37%, calculated as volume flow of air divided with the volume flow of CO, CO_2, CH_4 and H_2 and H_2O and H_2S and toluene and naphthalene. The flow of air was kept at around 120 minutes, which was sufficient time to ensure constant conditions, i.e. the exit concentrations did not fluctuate.

The first series was conducted at both 900°C and at 1000°C.

A second series of experiments was conducted where air was added to the gasification gas in a fixed concentrations for an extended period of time, (more than 24 hours). We did two sets of experiment where we added 10% air and 37% air respectively. We will present the experiments with 10% added air since addition of 10% air in gasification gas, under adiabatic conditions, gives an increase of approximately 300°C of the gasification gas, assuming that the O_2 reacts only with H_2. The difference in 300°C corresponds approximately with the endothermic temperature decrease if all the methane in the gasification gas reacted with an excess of water. This second experiment series was conducted at both 900°C and at 1000°C.

Experimental results: Effect of temperature:

Figure 2 shows the fraction of the gases consumed or generated in the reactor versus air percentage added. The temperature in the reactor ranged from 860 to 886 °C depending on the fraction of air introduced in the system. The fraction is calculated according to the equation below:

(Eq 1) $$\text{Generation/consumption} = \frac{n_{out}-n_{in}}{n_{in}} \times 100$$

The last two columns represent the oxygen and carbon balance. Positive values for the independent gases indicate generation and negative consumption. For the oxygen and carbon balances, positive values indicate that there is an excess of carbon or oxygen in the exit gas relative to the amount present in the feed. Negative values indicate that there is less carbon and oxygen measured in the outlet of the reactor than the amount expected from the composition of the feed gas.

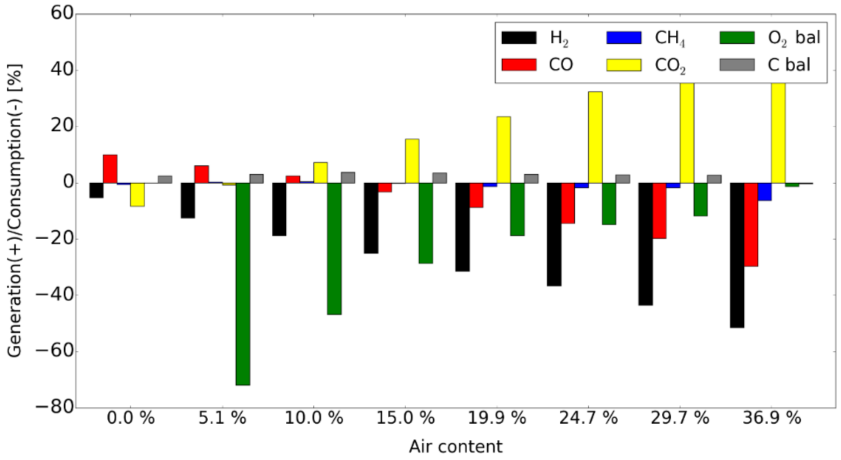


Figure 2: Fraction of the gases consumed or generated in the reactor versus air percentage added at 900°C.

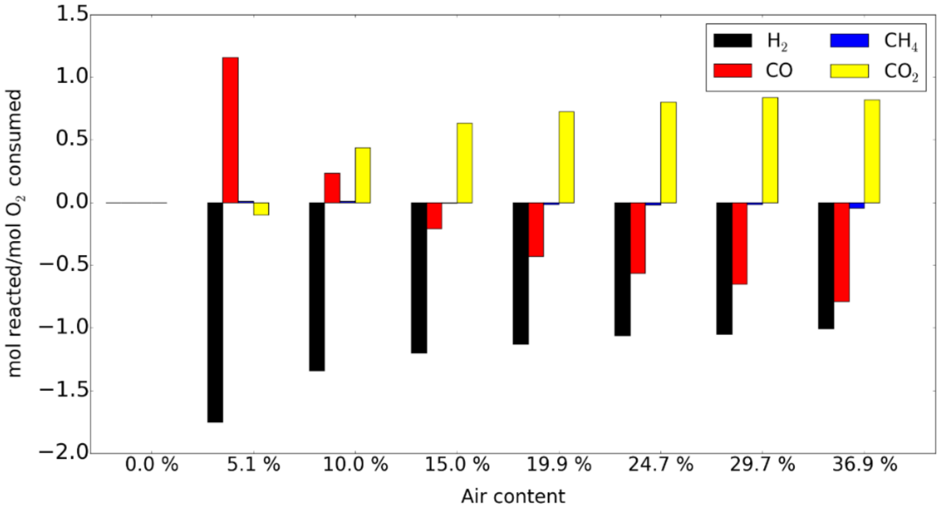


Figure 3: Reacted/generated moles of the different components present in the gas feed per mol of oxygen introduced at different air concentrations. 900°C

Figure 3 shows the reacted and generated moles of the different components present in the gas feed per mole of oxygen introduced at different air concentrations. The temperature in the reactor ranged from 860 to 886 °C depending on the fraction of air introduced in the system.

Based on the results in Figure 2 and Figure 3 we can conclude that it is manly hydrogen and CO that is removed by adding air to the gasification gas at 900°C. In addition, we can account for most of the injected carbon in a carbon balance.

Figure 4 shows the fraction of the gases consumed or generated in the reactor versus air percentage added. The temperature in the reactor ranged from 963 to 981 °C depending on the fraction of air introduced in the system. The fraction is calculated according to Equation(1). The last two columns represent the oxygen and carbon balance. Positive values for the independent gases indicate generation and negative consumption. For the oxygen and carbon balances, positive values indicate that there is an excess of carbon or oxygen in the exit gas relative to the amount present in the feed. Negative values indicate that there is less carbon and oxygen measured in the outlet of the reactor than the amount expected from the composition of the feed gas.

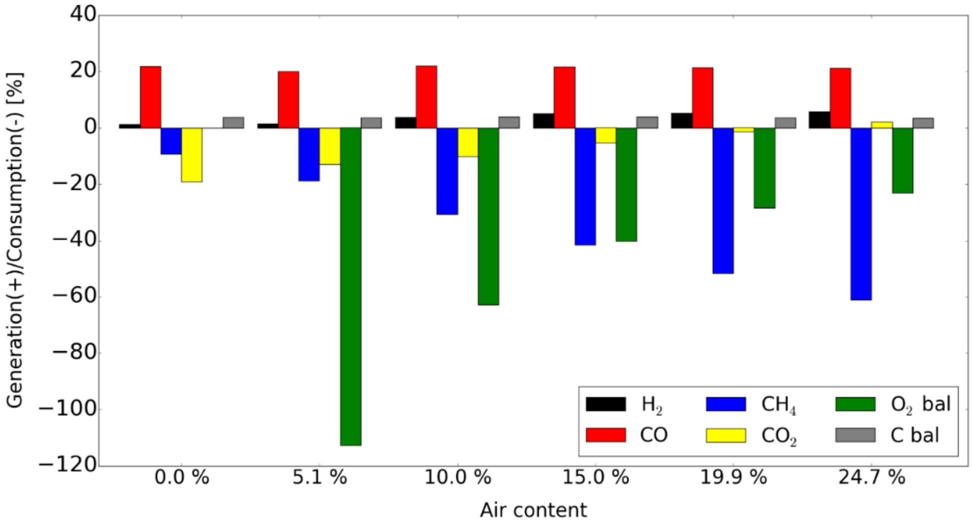


Figure 4: Fraction of the gases consumed or generated in the reactor versus air percentage added at 1000°C

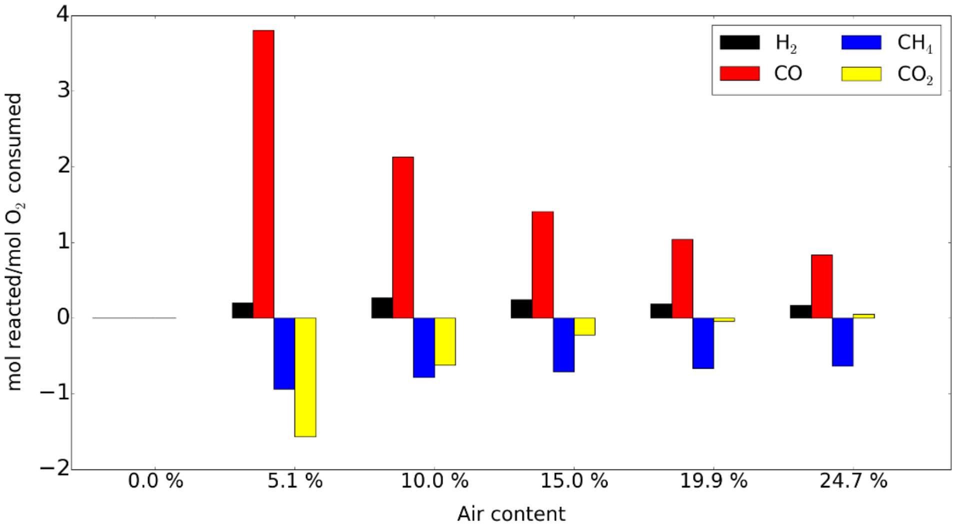


Figure 5: Reacted/generated moles of the different components present in the gas feed per mol of oxygen introduced at different air concentrations at 1000°C

Figure 5 shows the reacted and generated mole of the different components present in the gas feed per moles of oxygen introduced at different air concentrations. The temperature in the reactor ranged from 963 to 981 °C depending on the fraction of air introduced in the system.

From Figure 4 and Figure 5 we see that methane is removed as air in injected at 1000°C, which was not the case at 900°C. Figure 4 also shows that there is a shift between hydrogen, CO and CO_2 when no air is injected, which must be due to the water gas shift reaction.

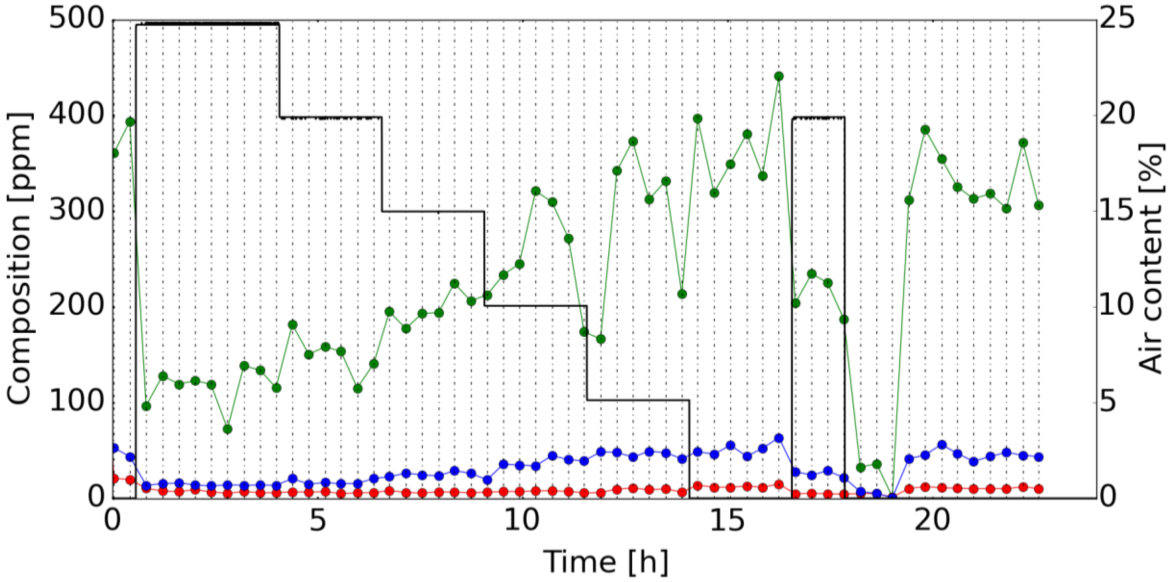


Figure 6: Evolution of toluene (red), benzene (green) and naphthalene (blue) in the exit gas at 1000°C.

Figure 6 shows the evolution of benzene, toluene and naphthalene as air is firstly injected in a high concentration and gradually decreased in concentration. It is seen that as less air is injected, the concentration of benzene, toluene and naphthalene increases. As air is added, less toluene is converted into benzene. At no point does the concentration of benzene plus toluene and naphthalene increase above the injected amount of toluene and naphthalene. The reduction of tar with increased air could be due to partial combustion or perhaps steam reforming of tar with water, since more water is formed in the reaction with hydrogen.

Experimental results: Soot formation or not

In order to do a more systematic investigation on soot formation, a number of experiments were performed where a specific amount a gasification gas was added to the reactor and 10% of air was added to this gas.

The exit gas was passed through the filter that was subsequently taken out and examined. The pressure drop was also monitored during the experiment.

The filter from the two experiments, 10% air to the gasification gas mixture at 900°C and 1000°C are shown in Figure 7. As seen, there is no significant residue of visible particles on either of the filters, neither do we see any pressure build-up over the filter.

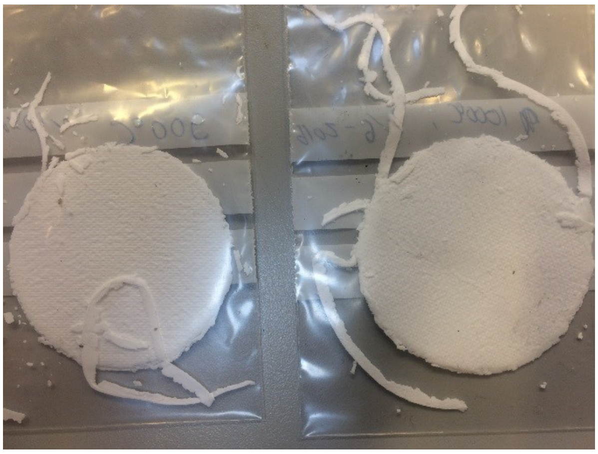


Figure 7: Filter after 24 hours at 900°C (left) and 24 hours at 1000°C (right).

Figure 8 shows the pressure drop over the filter during the long term experiment at 900°C. The actual temperature in the reactor is also plotted. As seen, the pressure drop does not increase. The pressure drop plot for the experiment done at 1000°C looks similarly and is not shown here.

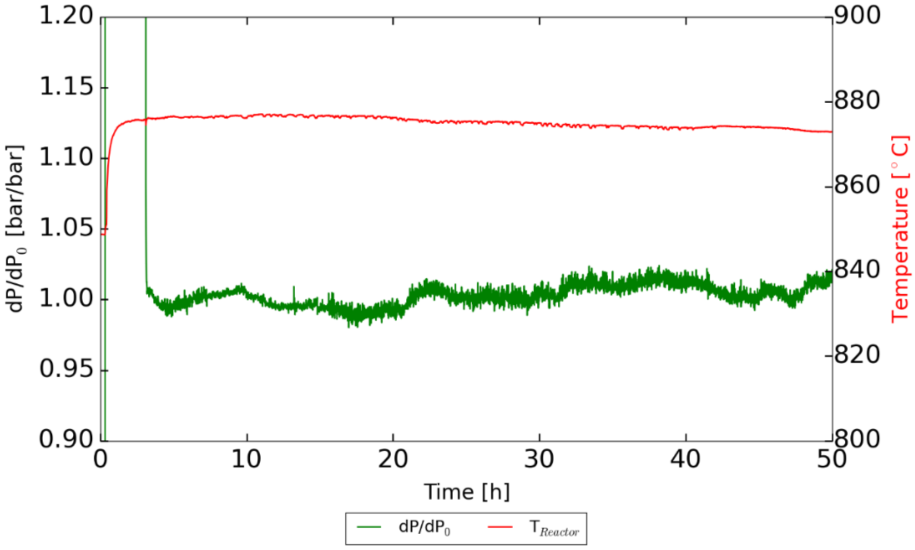
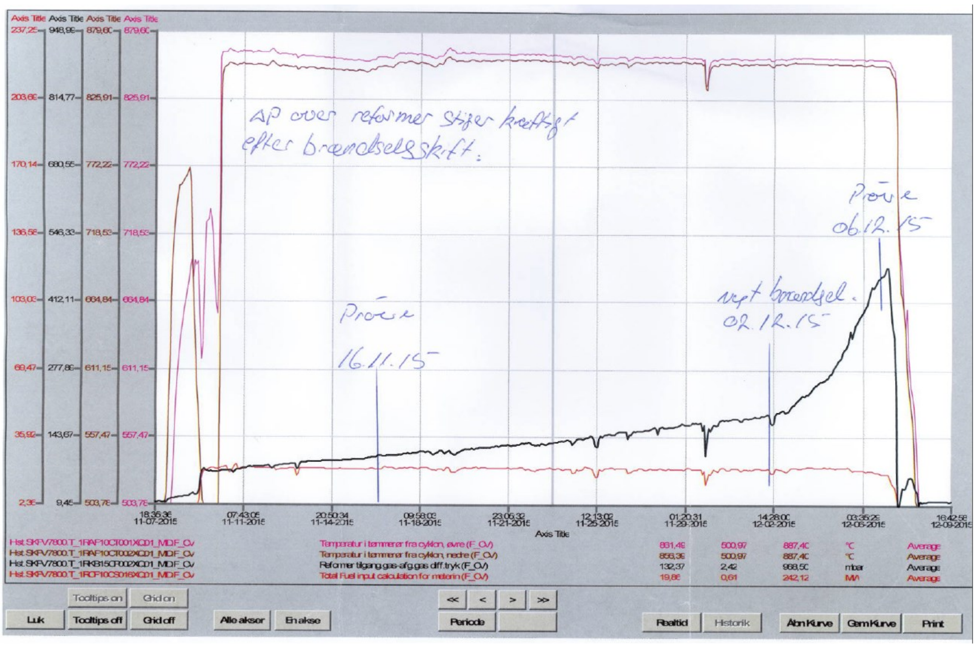


Figure 8: Evolution of the pressure drop in the glass fiber filter during a long-term experiment at 900°C

The exit gas measurements on the GC did not show any formation of additional naphthalene or formation of any higher molecular weight like phenanthrene and pyrene, that are detectable by the GC and that are early PAH compounds.

Experimental results. TGA analysis on dust from Skive Fjernvarme:
In addition to the combustion experiments described above, another approach was used to investigate one of the problems that Skive Fjernvarme with increasing pressure drop over the tar reformer. The background for the investigation is, that Skive Fjernvarme in a period from start November 2015 to December 2nd 2015 was running on a batch of biomass fuel that was giving a relatively stable pressure loss over the tar reformer. At December 2nd 2015 the fuel was changed to a new batch and this resulted in a considerately increase in pressure drop. The reformer pressure difference, ∆P, is shown in Figure 9.


ΔP over reformer stiger kraftigt efter brændselsskift:

Prøve 16.11.15

nyt brændsel. 02.12.15

Prøve 06.12.15

Hst.SKFV7800.T_1RAP10CT001XQ01_MDF_Cv	Temperatur i tømmerør fra cyklon, øvre (F_CV)	881,49	500,97	887,40	°C	Average
Hst.SKFV7800.T_1RAP10CT002XQ01_MDF_Cv	Temperatur i tømmerør fra cyklon, nedre (F_CV)	856,39	500,97	887,40	°C	Average
Hst.SKFV7800.T_1RKB15CP002XQ01_MDF_Cv	Reformer tilgang gas-afg.gas diff.tryk (F_CV)	132,37	2,42	968,50	mbar	Average
Hst.SKFV7800.T_1RCF10CS016XQ01_MDF_Cv	Total Fuel input calculation for meterin (F_CV)	19,88	0,61	242,12	MW	Average

Figure 9: Pressure drop over the reformer, black line, November and December 2015.

Samples of the dust, collected in the bag filters downstream the tar reformer, were collected November 16th and December 6th. These samples were analysed using Thermal Gravimetric Analysis, TGA, at DTI. A procedure was used, where the sample was placed in the instrument and heated to 1100°C in N_2 to drive off water and organic volatiles. The temperature was then decreased to 25°C and the atmosphere was changed to O_2, and the temperature was increased again to 1000°C. This procedure enabled us to determine the volatile content, the organic carbon content- and the inorganic content in the sample. The results are given in Table 2 on dry basis:

Sample name	Description:	Volitiles, dry basis. w/w%	Carbon content, dry basis, w/w%	Inorganics, non combustible, dry basis, w/w%
161115	Taken where Δp over the reactor was stable	17,60	55,33	27,07
061215	Taken after a significant increase in Δp over the reactor after change of fuel	16,36	35,20	48,44

Table 2: Results of TGA analysis of two dust samples

The amount of inorganic content in sample 061215, where Δp increased, is considerately higher than for sample 161115, where Δp was stable. This could indicate that the inorganic content in the dust, and also in the wood feed, could explain the increase in Δp. One explanation is that the inorganic dust is less reactive with the gas components, and therefore more likely to accumulate in the reformer.

Experimental results: Raman analysis

The dust particles described in Table 2 were examined using Raman spectroscopy. Raman spectroscopy gives a chemical "fingerprint"-spectrum of the samples and can be used to determine the type of carbon-to-carbon bonds in the sample and the spectrum can be compared to naphthalene and graphite.

Figure 10 shows the Raman spectrum of sample 061215 and the spectrum of the tip of a grafite pensil. Figure 11 shows the Raman spectrum of sample 161115 and solid naphthalene.

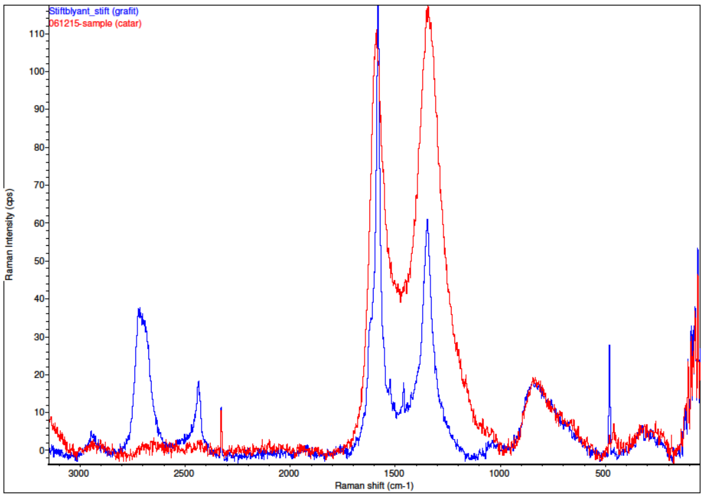


Figure 10: Raman spectrum of sample 120615 and the tip of a grafite pensil. The laser wavelength used is 532 nm.

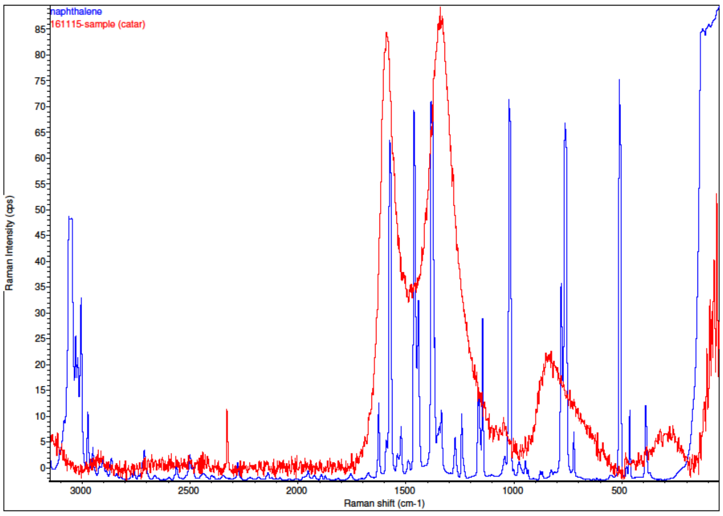


Figure 11: Raman spectrum of sample 161115 and solid naphthalene.

The spectrum for sample 061215 is almost identical to sample 161115. As seen, the spectrum for sample 061215 and 161115 resembles the graphite pensil reasonably having distinct peaks at 1620 cm^{-1} and at 1360 cm^{-1} that both are characteristic for graphite. The dust samples do not resemble naphthalene.

Conclusion on WP1:

From the experiments done in the first experimental series we see, that at both 900°C and 1000°C, the added air to the gasification gas mixture, the O_2 reacts with both H_2, CO and CH_4 and also with toluene and naphthalene. No additional formation of naphthalene is seen, neither do we see formation of other higher molecular weight poly cyclic aromatic hydrocarbons that are detectable in the GC, like phenanthrene and pyrene. A series of experiments was done at a fixed addition of air to the gasification gas, and no visibly detectable formation of soot is observed by inspecting the glass fibre filter after the experiments, nor do we observe any increase over the filter over the time of the experiment.

We observe that the added naphthalene and toluene is partly removed by adding air, indication partial combustion.

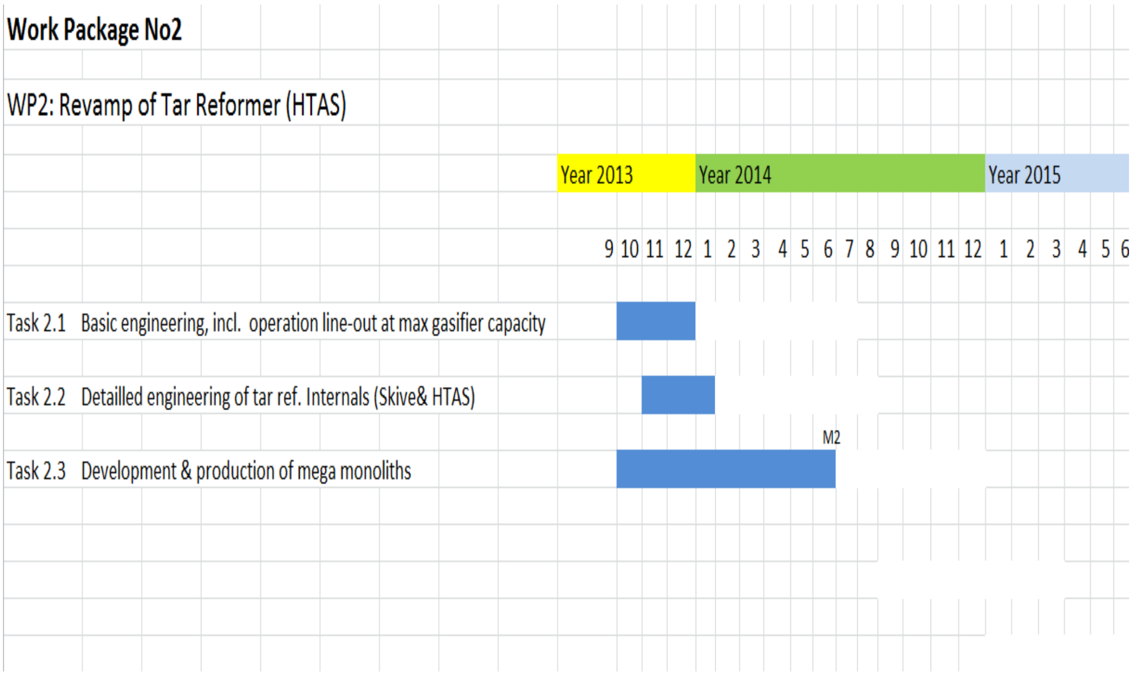
A Raman analysis of dust collected at the bag filters after the tar reformer at Skive Fjernvarme show that the dust does not resemble naphthalene; instead, the signal resembles graphite.

Thermal gravimetric analysis of the dust from Skive Fjernvarme shows, that the dust from an operation period where the pressure loss over the reformer increased considerately had a higher content of inorganic matter that the dust collected when the pressure loss was almost constant. This indicates that the pressure increase over the reformer is perhaps related to the content of inorganic or ash in the biomass feed.

WP2: Revamp or tar reformer (HTAS)

In Task 2.1 Haldor Topsøe A/S had to provide a basic engineering sufficient enough to establish a basis for the detailed engineering (Task 2.2) of the reactor system. As seen from the time schedule here below the time is very limited because the reconstruction and implementation had to be during the summer stop 2014, otherwise one year delay would be the result, see time schedule below:

WP2 time schedule:



Work Package No2

WP2: Revamp of Tar Reformer (HTAS)

Task 2.1 Basic engineering, incl. operation line-out at max gasifier capacity

Task 2.2 Detailled engineering of tar ref. Internals (Skive& HTAS)

Task 2.3 Development & production of mega monoliths

Task 2.1 Basic engineering.

Ultimo 2009/ primo 2010 Haldor Topsøe A/S entered into cooperation with Skive Fjernvarme. It was clear already from that point in time that there were major problems with the catalyst delivered from elsewhere, dust, soot formation, bed material, slagging due the burner systems and burn off of carbon lay down/soot. The catalyst system which was arranged as squared monolith in trays, 5 trays per beds. 2 beds in all, could not get rid of the dust and soot settling/clogging the catalyst / trays during operation and this gave very frequent stops and over all a very poor on stream factor, see Picture 1 below.

Picture 1Close up picture showing the first catalyst tray in first bed (upper bed) seen from above, all monoliths and tubing are covered by dust /slags thus obstructing the catalyst function

In 2010 the over-all energy output was only 10,000 MWh (el) out of plant maximum output of 36,000 MWh (el) due the above operation conditions. Due to this and the fact that regeneration in the form of burning off soot/carbon deposit very often led to melting down of the catalyst trays / the monoliths because the burning process was very difficult to control, see Picture 2

Picture 2 Damaged and partly melted trays

Furthermore the cleaning, and repair was difficult and took extraordinary long time, see picture below.

Picture 3 Change out of internals i.e. catalyst trays and internals I in very dusty environment

The only way out this situation could only be to develop a more robust and sulphur resistant type of catalyst and at the same time develop a new reactor concept and furthermore introduce a revised regeneration procedure to overcome the operation difficulties.

In order to establish the basis for the development of the above and execute the detail engineering, basic information was established partly by measurement in the plant and thereby confirming the flow calculation, see flowsheet below and partly based by information from Skive Fjernvarme in the kind of operation experiences and documentation

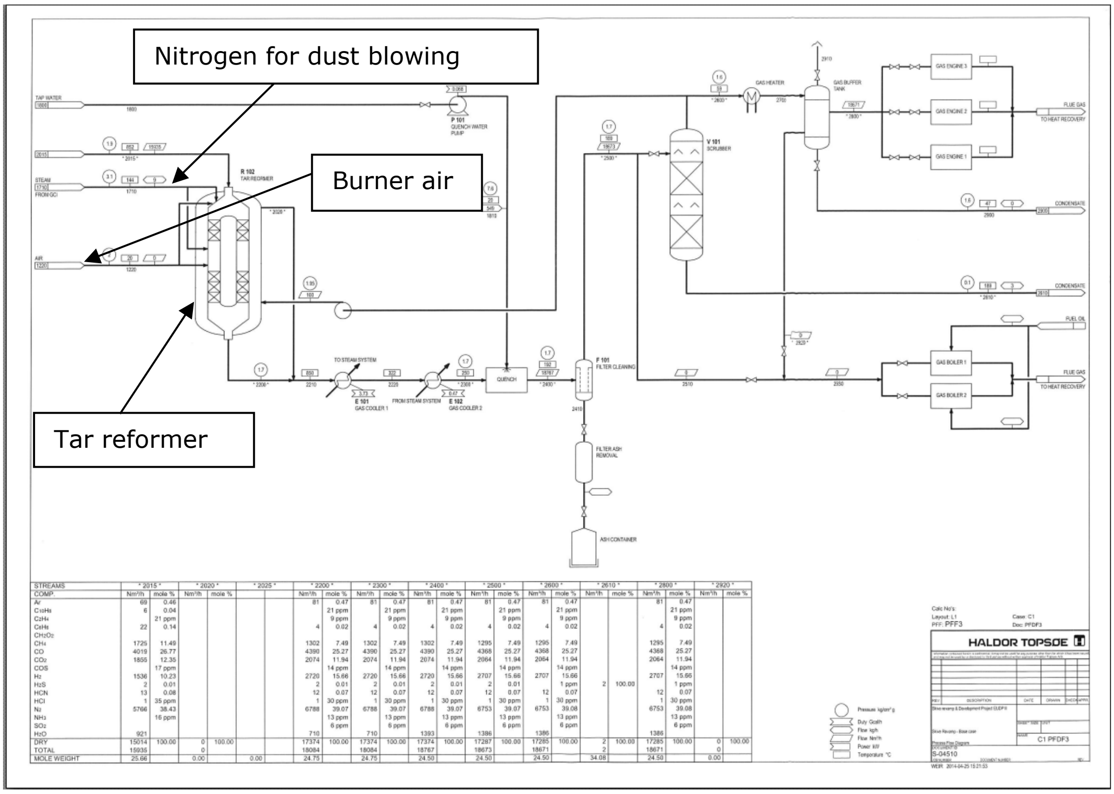


Figure 12 Basic flow diagram of the tar reformer section

From the basic flowsheet it appears that 4 different systems had to reconsidered and redesigned:

1. Reactor concept
2. Burner system
3. Dust blowing system
4. Pipe & Instrument Diagram (PID) – Control system

Re 1: Based on the evaluation of the operation and process parameters and internal process reactor calculation a possible reactor configuration was defined, see Figure 13

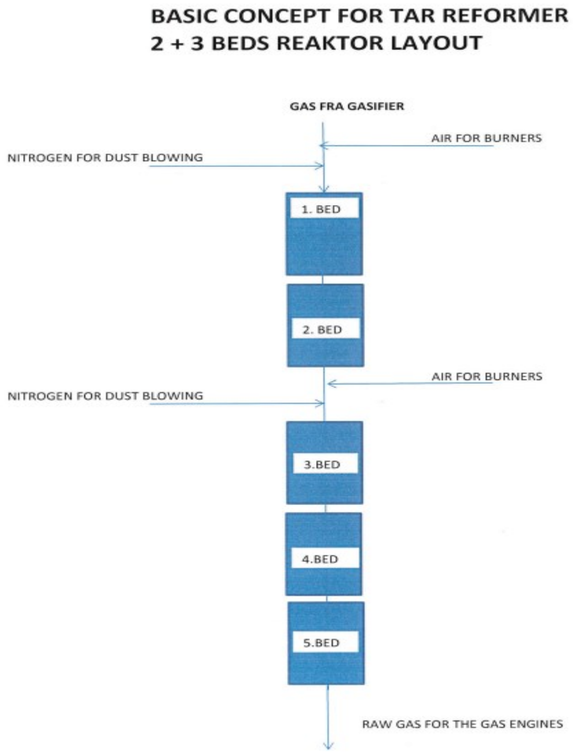
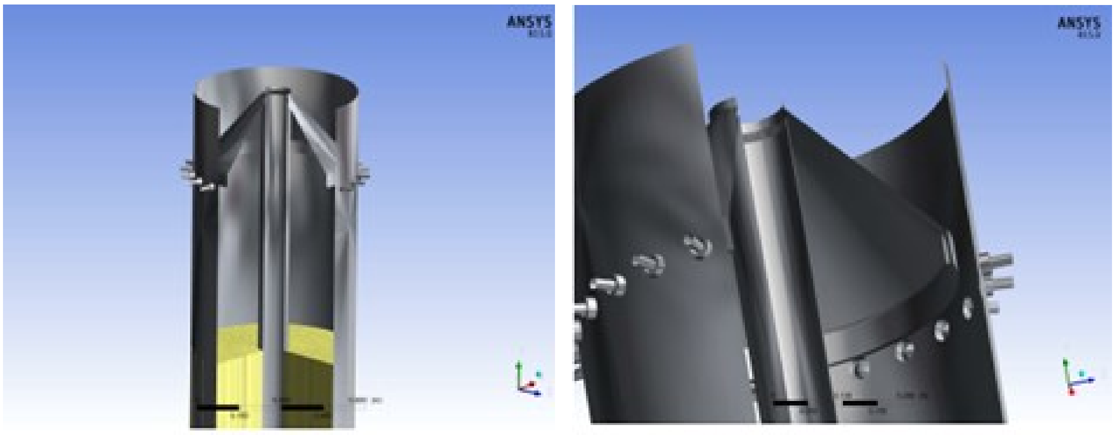


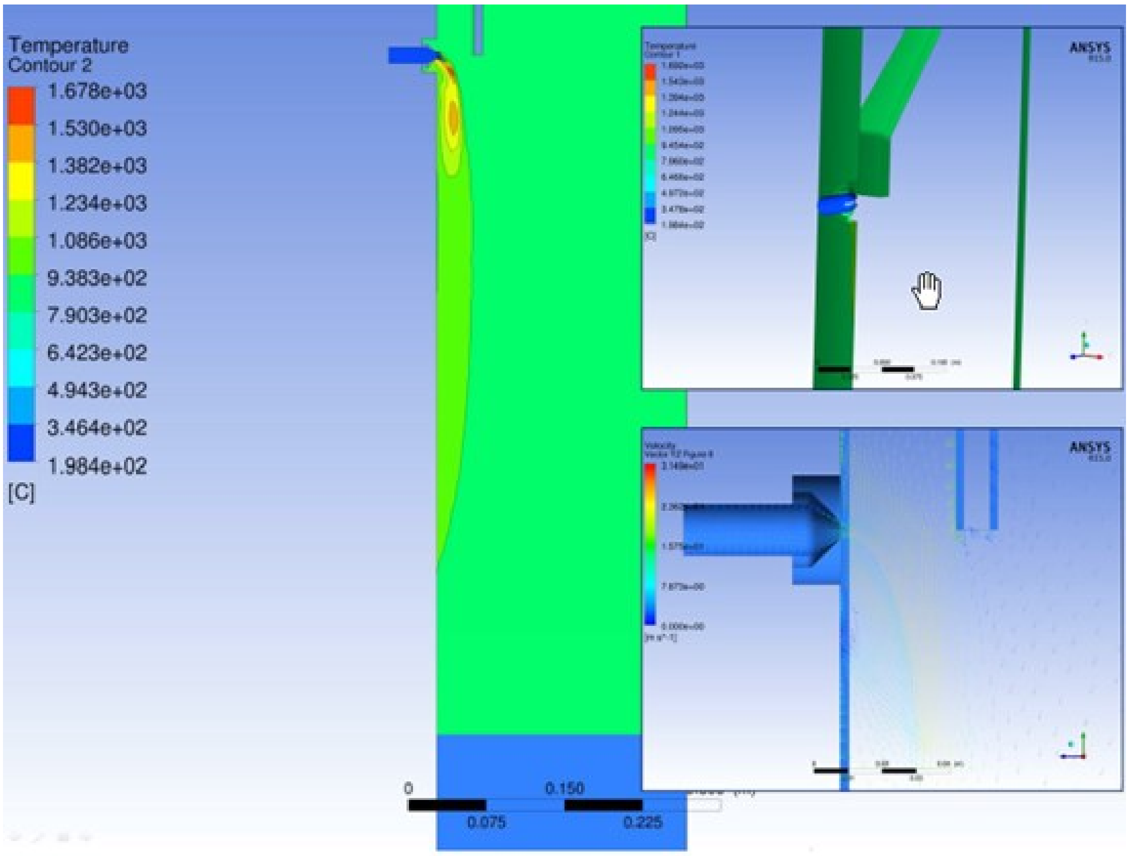
Figure 13 Basic reactor layout

The original reactor consisted of a pressure shell with two reactor beds inside. It was a desire that plant people when doing repair work should working in dust free environment. Therefore the reactor basket was developed in such a way that the reactor bed was divided into four "reactor tubes" with a dimension fitted for the mega monoliths being developed. The above sketch represent one out of the four reactor "tubes". The reactor pressure shell was then foreseen to be pressurized to a pressure higher than the operating pressure inside the reactor tubes thus making the surrounding free space dust free.

Re 2: The burner system was redesigned from a burner grid design into a nozzle system. Based on operation data and process simulation the system was redesigned by using Topsøe internal CFD- design / simulation tools, see Picture 4 and Picture 5.



Picture 4 Geometry of MEGA monolith installation used in CFD simulation of reactor internal



Picture 5 Temperature contour plot from CFD simulation of inlet to MEGA monoliths

Based on the above calculation and CFD simulation the burnersystem was developed for both the first and second bed in the tar reformer.

Re 3: the dust blowing system was developed by using Topsøe experiences and design rules for dusty environment in reactor systems.

Re 4: Pipe and Instrument diagram (PID) was developed based on partly the existing control principles and the new principles based on the new development in the plant, see the Figure 14showing the existing lay out and Figure 15 showing the new lay out

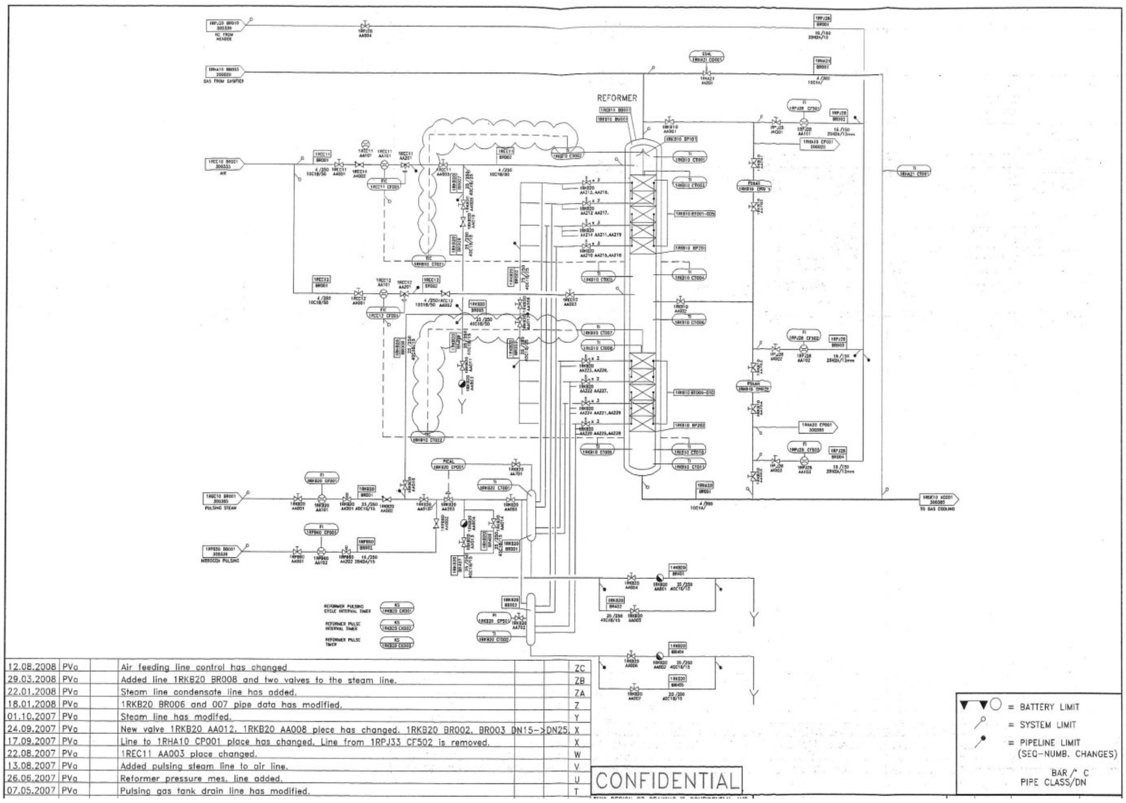


Figure 14 Pipe &Instrument Diagram of the tar reformer the existing reactor system with the reactor beds fitted to the full size diameter of the reactor

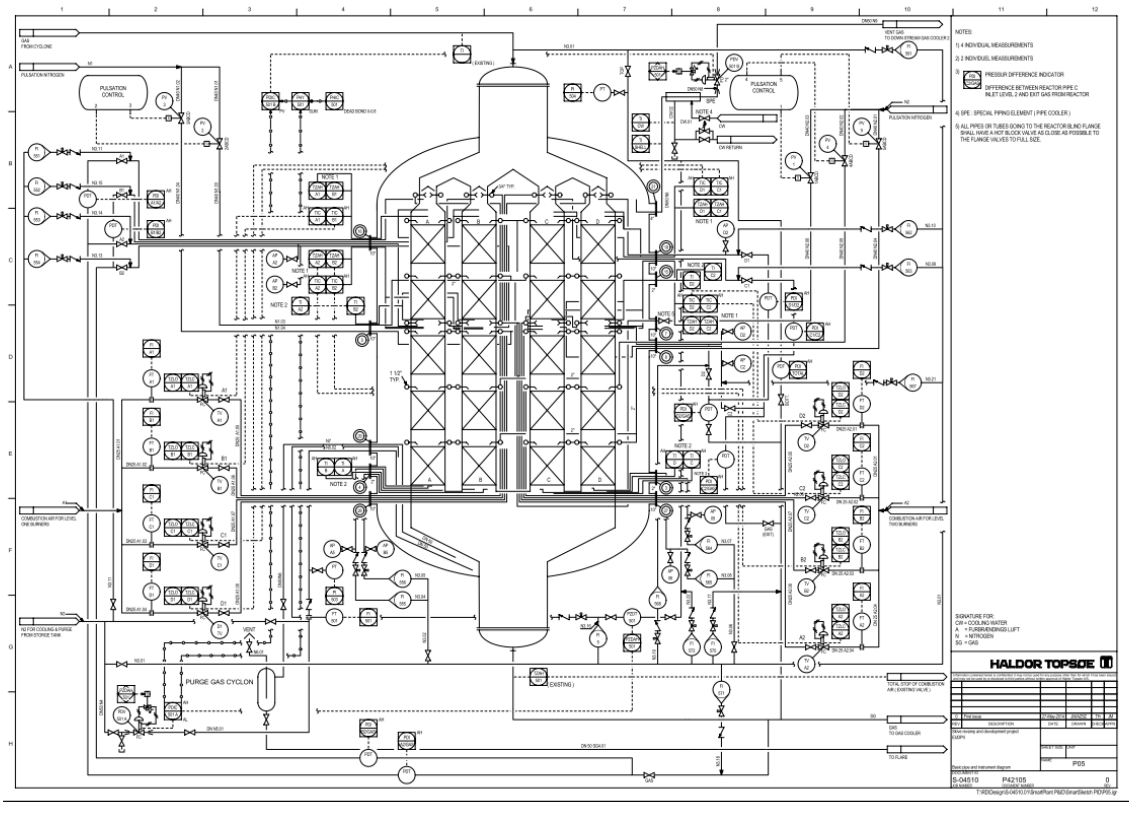


Figure 15 Pipe &Instrument Diagram of the tar reformer for the new reactor system with the four reactor tubes fully isolated/integrated inside the pressure shell

In connection with the development of the PID a safety diagram (ESD-Diagram) was developed in order to the full overview of cause /action situations

Based on the new design and proces conditions the Instrument Package was developed and made prepared for the procurement of instruments

HASOP analysis by COWI A/S
When the process diagram, the PID and ESD-Diagram was finalized the company COWI A/S, was engaged as "third party inspector" by Skive Fjernvarme and Topsøe to perform a safety analyses (HASOP) of the modified plant thus ensuring that safety level was at minimum the same level as before the design changes.

Task 2.2: Detail Engineering (mechanical) of Tar reformer:

- Working conditions during unloading shall be improved (layout of internals, see also above)
- Down time of plant due to long change- out time of tar reforming catalyst shall be reduced (layout of internals)
- Clean up of gas i.e. tar and ammonia shall be improved – mechanical structural design of mega monoliths
- Dust blowing system to be improved (see above)
- Burner system to be improved (see above)
- Reactor Internals to be re-designed to reduce dust / ash sedimentation
- Reactor Internals to be able to operate with higher delta p than today

After the basic engineering was made the detailed design was executed. The first edition of engineering documents were compiled and formed basis for the procurement package, which had to be submitted to the bidders i.e. A.K.S. Teknik A/s Denmark and Ekstrøm & Son Sweden. The scope of supply was defined in the procurement package

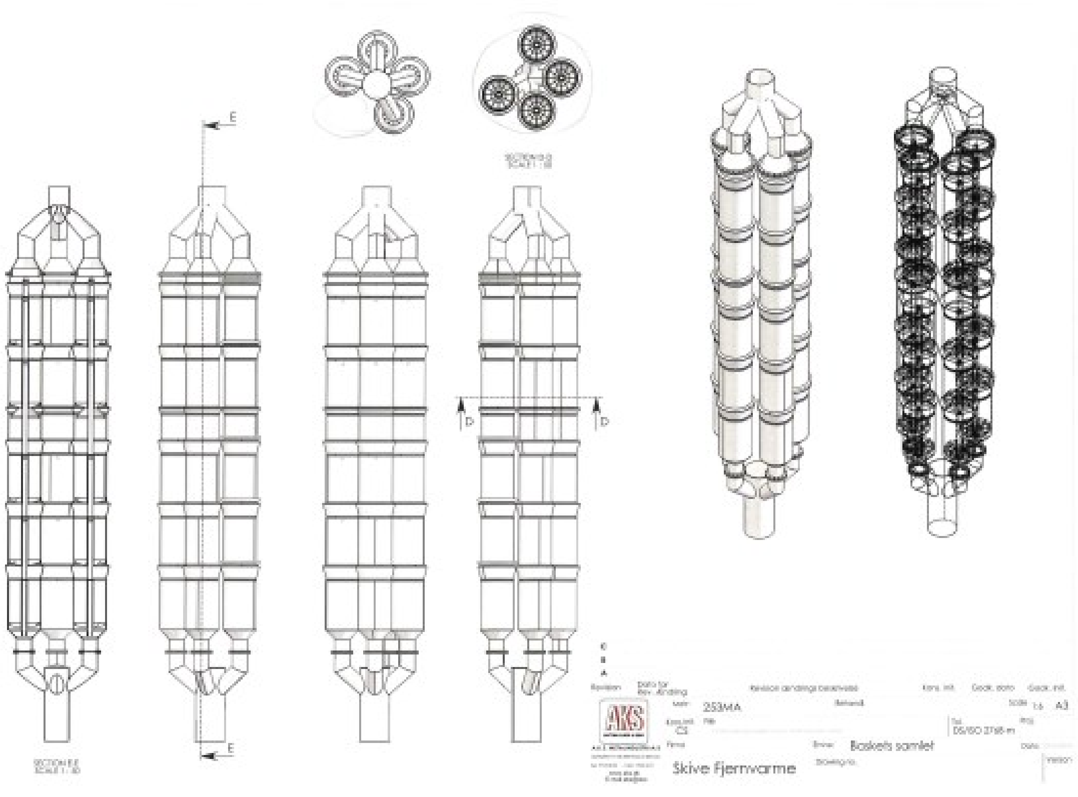


Figure 16Illustration of reactor internals

Task 2.3: Development and production of mega monoliths (HTAS)
In order to develop a new chemical receipt for a new more active and sulphur resistant catalyst the present applied (adopted in 2010, but at a size of DxH = 150x 300 mm) monoliths were impregnated with the new receipt and installed in the reactor trays and thus tested under actual coming operating conditions. Figure 17 below show at which position and at which level the individual test monoliths were installed at e.g. Basket 6 means tray no 2 in bed no 2 counted from above at the reactor inlet.

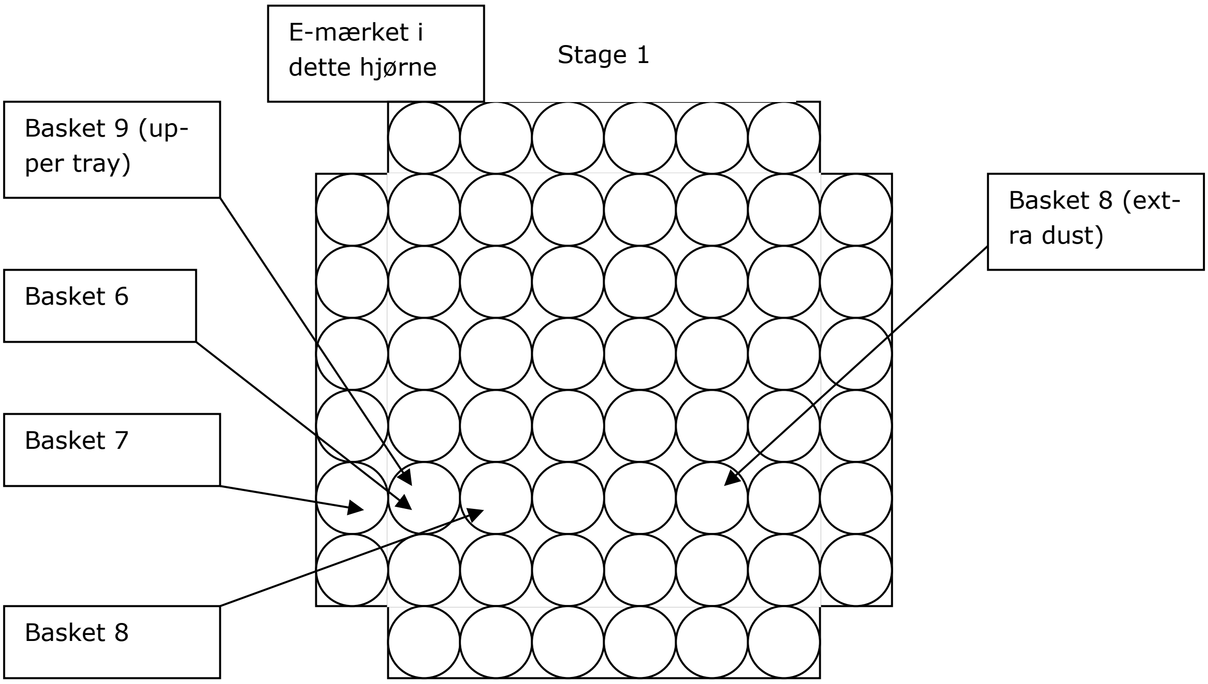


Figure 17 Illustration of old tar reformer catalyst loading in baskets

After a certain operation period the test monoliths were taken out and submitted to Haldor Topsøe A/S for detailed chemical analysis and activity measurements. By these testing under actual operation condition Topsøe succeeded in developing a considerable more robust and active and Sulphur tolerant monolitic catalyst, which is already implemented at Skive gasification plant and furthermore the new receipt has already been adopted as impregnation fluid for other catalyst type like the pellet type
The proto type MEGA monolith structure system was developed Haldor Topsøe A/S, see Figure 18 below and the development and production the final monolith took place together with a Swedish partner who made the monolith structure and the wash coating whereafter the monoliths are impregnated with the new receipt by Haldor Topsøe A/S.

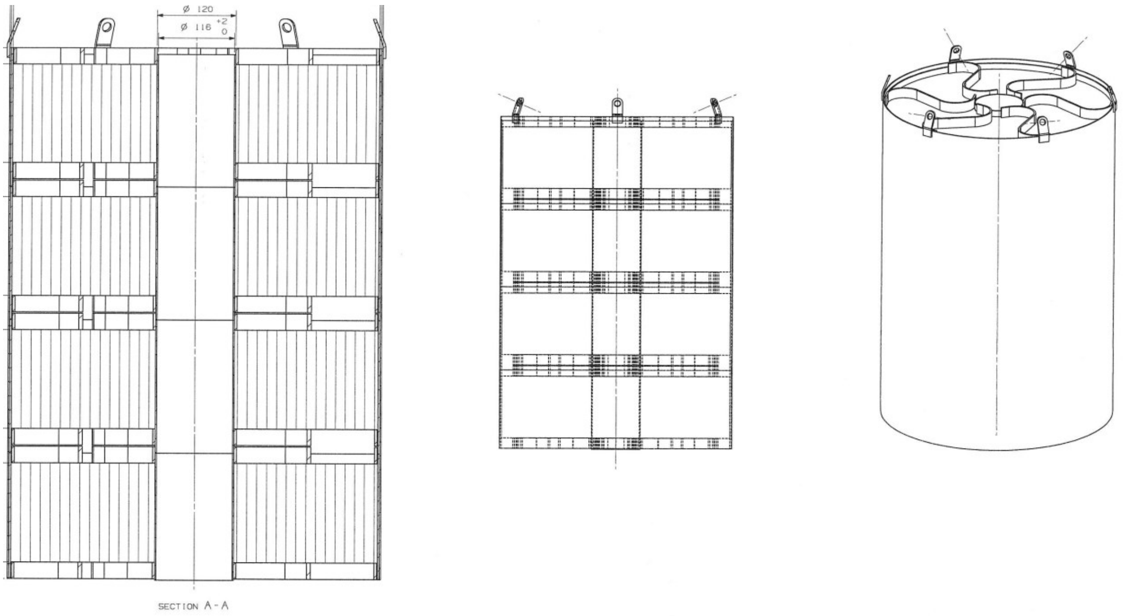


Figure 18 Sketch of the new MEGA monolith structure

WP 2 Conclusion

Process data from the operation on the first loading of the revamped tar reformer (consisting of three cycles running from 15th of September 2014 to 6th of January 2015) has been evaluated. Offline gas analyses have been compared to the process data for the first cycle. The immediate comparison revealed that the data sets were not consistent, rendering the further analysis in GIPS with the extrapolated tar reforming model useless.

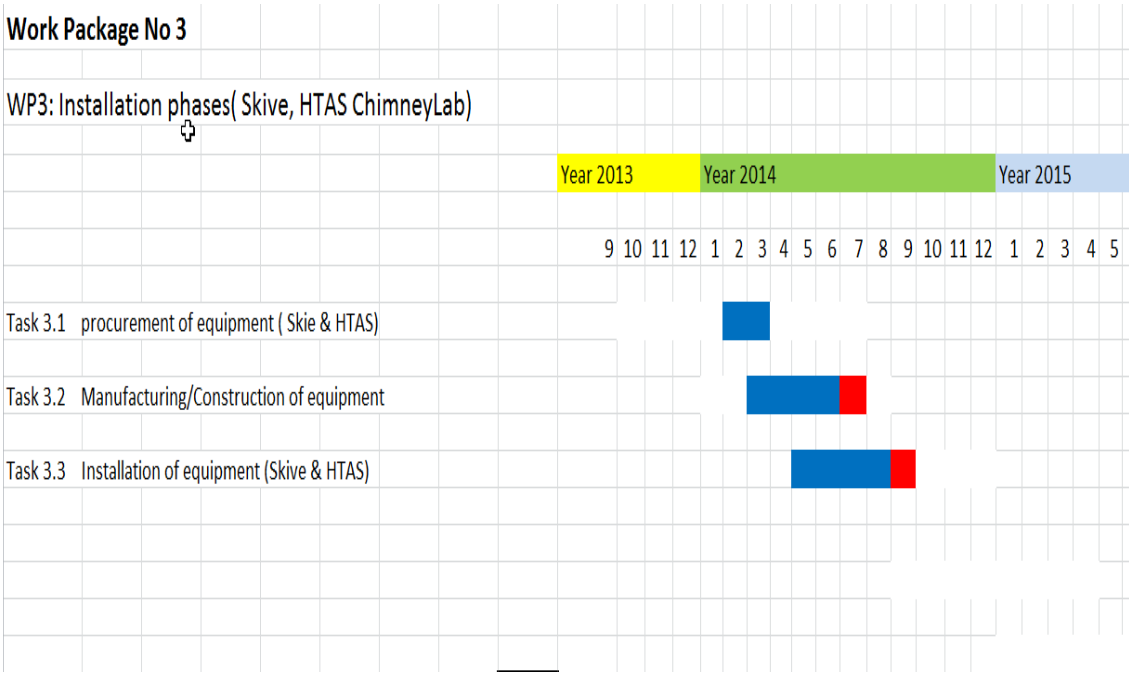
Graphic representations of process data and gas analyses indicate an expected/modest deactivation over time for the first cycle in line with the deactivation observed for pellets in the side stream pilot (note: 'Relative tar reforming activity development evaluation of R-67 based on a 1000 h stability test in Skive side stream pilot' by BOV, DMS-S-04848 August 1st, 2014).

There has been found a high robustness of the tar reforming mega monoliths in the second stage of the revamped tar reformer in spite of dust issues arising from carry-over of bed material from the cyclone. After regeneration, cleaning, and reloading of the mega monoliths, the fresh catalyst activity was largely restored.

With the new revamped design it is possible to follow the performance and condition of the tar reformer by reading the process temperatures, pressure drops and the methane concentration in the exit gas. As compared to the earlier design based on mini-monoliths the temperature control of the revamped design has been immensely improved, and the right corrective actions to maintain satisfactory tar removal has become easier. A suggestion to *further* improvements comprises a regeneration set-up which ensures proper temperature control in the regeneration phase as well.

WP3: Installation phases (Skive, HTAS, CLE)

WP3 Time schedule



Task 3.1: Procurement
The procurement followed the normal rules for "Request for Bid" procedures. However only 2 bidders was asked because the time for construction and implementation in the plant was extremely short and strictly limited as the stop was the yearly summer stop / turnover of the plant
After the basic engineering was made the detailed design was executed. The first edition of engineering documents were compiled and formed basis for the procurement package, which had to be submitted to the bidders i.e. A.K.S. Teknik A/s Denmark and Ekstrøm & Son Sweden. The procurement phase was as follows:

- Haldor Topsøe A/S received the bids from vendors
- Haldor Topsøe A/S invited the bidders for clarification meetings and at the same time invited representative from Skive fjenvarme to participate
- Haldor Topsøe A/s forwarded one copy of the bid document to Skive Fjernvarme for their own evaluation
- Haldor Topsøe A/S evaluated the incoming bids and succeeding submitted their recommendation to skive Fjernvarme
- Skive Fjernvarme evaluated the bids and placed and signed the order with the successful bidder.

After the bidding rounds and evaluation the A.K.S. Teknik A/S was selected as supplier of the reactor internals, with a supply was defined in the procurement package, partly due to price and partly because of the importance of easiness of inspection, interaction with A.K.S during the manufacturing of the internals

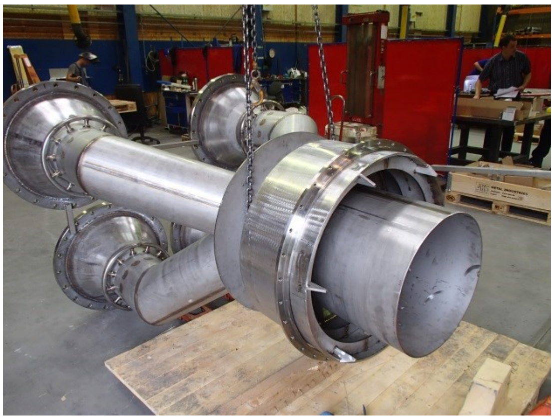
The work package 3.1 was executed according to the time schedule shown above.

The project was over all only delayed by 2 weeks during the construction and installation phase and was implemented smoothly as outlined here below

Task 3.2: Construction and Task 3.3: Installation (HTAS, Skive, CLE)
Manufacturing at A.K.S. Teknik A/S
During the manufacturing of the reactor internals the communication was very intense, positive, and constructive. Inspections were very frequent and intense. See pictures below

Reactor pipe sections
ready for shipment to Skive

Reactor top part



Inlet top-part to reactor pipes

Test assembled reactor internals

Reactor pipes almost assembled

Reactor pipes ready for shipment to Skive

The manufacturing of the reactor internals was approx. 1 week delayed which on the other hand delayed the installation phase with 1-2 weeks, see time schedule above

Task 3.3: Installation
Reactor tar sample system.
ChimneyLab Europe ApS was, together with the other participants, involved in design and layout of the tar sample system in the tar reformer reactor.

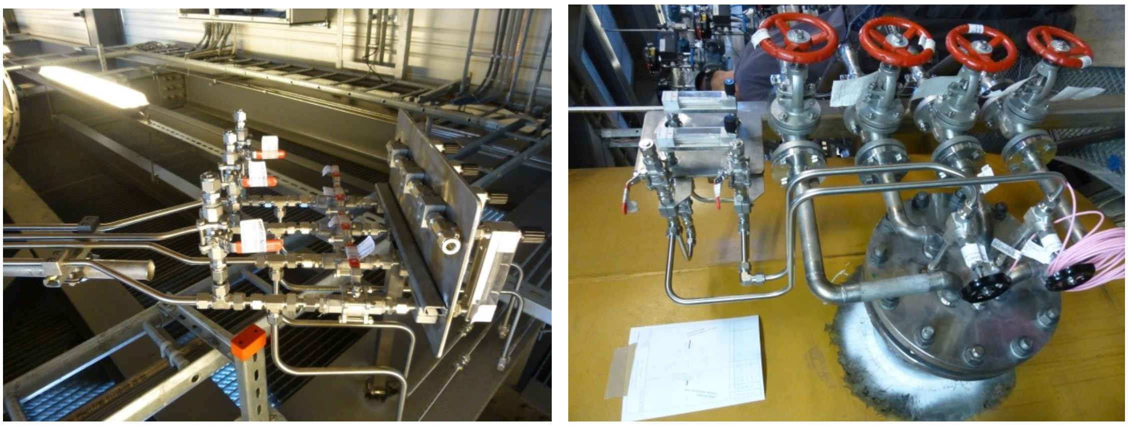
Beside the continuous analysed gas composition, O_2, CO, H_2, and CH_4, the manually sampled tar composition is, not surprising, a very important parameter to evaluate the performance of the tar reformer.

On the old reformer reactor it was only possible to sample tar at inlet and outlet, but with the new reactor design it would now be possible to sample at inlet, outlet and after stage 1 and 2. However, the reactor design with a pressurized shell, made it necessary to install the entire tar sample tubing as fixed installation (the old tubes were removable). This increased the length of the sample tubing significant, from 1 meter up to 5-10 meter.

In order to decrease catalytic tar reaction in the sample line, it was decided to use steel quality MA253.

Another issue was dust plugging of sample line when not in use. Therefore, all five sample lines were equipped with 3-way valves, which are switched over on nitrogen when not sampling. The nitrogen flows are measured and adjusted by purge meters with needle valves.

After putting the new tar reformer reactor in operation, the tar sampling program showed lower tar concentration after stage two, than after tar reformer.
One explanation could be, that the sample point at exit tar reformer is a mixture of the entire gas stream, while the sample point after stage two only measures on a small segment of the gas.
Another explanation is catalytic tar reaction in the sample tubes, but this doesn't explain why only stage two deviates from expected results.

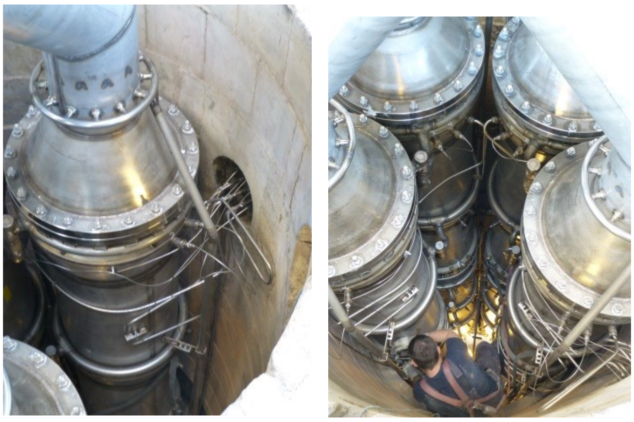


Picture 6 Sampling / analysis arrangement

Installation of new internals in the existing reformer pressure shell
In the weeks of 27-34, 2014 new internals in the tar Reformer in Skive Fjernvarme was installed. The installation was carried out by Skandinavisk Industri Montage (SIM) in collaboration with Haldor Topsoe (HTAS) and Skive Fjernvarme (SFV).

The installation was executed according to the following phases:

1. The reformer was emptied of existing internals and pressure shell was cleaned.
2. The refractory were checked for cracks and damages.
3. The reactor system was marked up for the new reactor pipes and new penetrations in the pressure shell were made, see pictures below



Picture 7 Installation of reactor tubes

Subsequently, new 10 "nozzles and new manhole were welded into the pressure shell and there was established a bottom flange for the new reactor pipes. The bottom flange was lined up and fixed to the existing refractory lining. There was established a bottom flange for the reactor tubes. The bottom flange was lined up and fixed in the existing refractory. The bottom manifold system was mounted on the bottom flange. New stuffing boxes were welded into the top and bottom of the reactor system. There were mounted air and nitrogen tubes to the reactor pipes and the pipes were hoisted down into the reactor pressure shell and installed. There was continuously checked for cracks and leaks. Instrumentation was installed and thermocouples and pressure taps were installed and led out through the flanges of the pressure shell. Monoliths were smoothly loaded into the reactor pipes

Picture 8 Installation of monolith

Finally:

1. The top manifold system was installed
2. Final leak test was performed
3. Stuffing boxes were tighten
4. The T-piece in the bottom was installed

The entire process was supported and supervised by HTAS, who had also made the detailed design of the reactor internals.

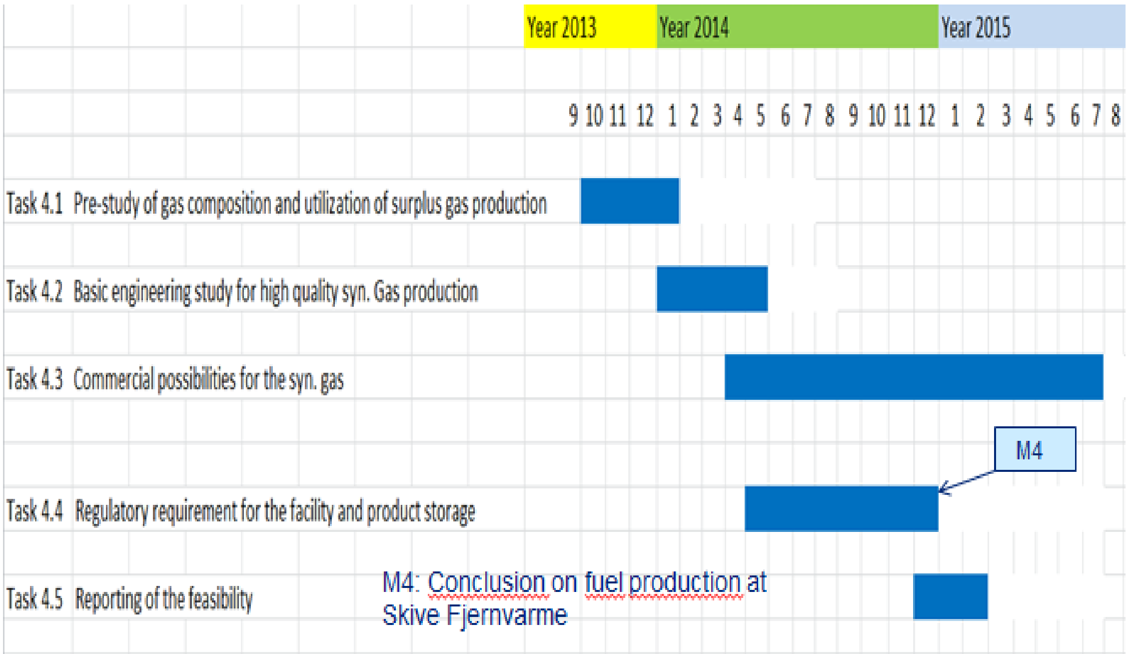
WP 3 Conclusions
Stuffing boxes:
After the first stoppage of the gasifier, it was found that the stuffing boxes between the reactor pipes and the pressure shell was no longer tight. It appeared as a constant nitrogen flow to the space between the pressure shell and the reactor pipes to maintain a slight positive pressure in the pressure shell compared to the pressure in the reactor pipes
It turned out that the used graphite packing cord used in the stuffing box, could not withstand the temperature and gas composition. The cord was changed into a glass tape, howev-

er it turned out that the glass cord crept at the given temperature resulting in leakage. Finally a ceramic cord was chosen and it has proved to withstand conditions with a limited leakage.
It has been determined that in place of the stuffing box at the bottom a bellows shall be installed to eliminate the small leakage. The installation of the bellows at the bottom was possible because the longitudinal extension of the outlet pipe is minimal.
Top stuffing box at the top will be changed out with spring-load stuffing box of the spectacles type. This is done to maintain a constant pressure to the wrap cord after thermal expansion, thereby eliminating the small leakage.

Air Nozzles:
It has subsequently been found that the air nozzles at the 2nd reactor bed was pressed into the reactor pipe walls which complicates the replacement of the monoliths. The assumption is that the relatively cold air pipe feeding the air nozzles, via a closed ring is relatively stiff compared to the reactor pipe. The air ring cannot expand as much as the reactor pipes and therefore the air nozzles are pressed into the reactor pipe wall when thermal expansion is taken place. A re-design is being worked out for the repair work

WP4: Wood-to-synthetic fuel in Skive – preliminary study (HTAS)

WP4 Time schedule



Task 4.1
Several gas composition measurements were taken from the tar reformer at Skive Fjernvarme. The pilot tar reformer setup from previous EUDP project (Catalytic decomposition of tar from biomass gasifiers) was utilized in order to obtain gas composition upstream and downstream of the tar reformer at Skive Fjernvarme. The gas composition showed possibilities for high quality synthesis gas production with a ratio of H_2 to CO of 1:1 out of the tar reformer.

Task 4.2
The composition study revealed that the synthesis gas of a 1:1 ratio of H_2 and CO could be used for production of methanol, DME, or TIGAS on a commercial level.

Task 4.3
A basic engineering package was developed with the aim of producing TIGAS at Skive Fjernvarme. The package emphasized the need for modifications at Skive Fjernvarme in order to

deliver high quality synthesis gas for the TIGAS production unit. The modifications included addition of a PSA unit and more than one compressor.

Task 4.4

The basic engineering package was sent to Tekniske Forvaltning in Skive Kommune for evaluation of regulatory requirements for a possible future unit. The evaluation revealed that the unit cannot be placed on the site owned by Skive Fjernvarme due to different restrictions and regulations. However several sites in the surrounding area of Skive were possible locations for the TIGAS unit. An external company would be needed for unit operation, and an over-the-fence agreement would be required. No preliminary approval could be obtained at the point of the study. The governing authority was Miljøstyrelsen required a concrete project in order to evaluate the requirements for approval.

It can be recommended to conduct another EUDP project with the focus of evaluation of the project in details, with the purpose of obtaining an approval for construction of a gasoline plant.

Task 4.5

An internal report was composed with details of the findings in this study. The main results are presented in the current report.

1.6 Utilization of project results

The project has been very successful in meeting the project objectives in relation to the design construction a, installation and operation with MEGA monolith and reactor internals and the barrier for commercialization of this new technology has been reduced significantly. Moreover, the continues cooperation between the project partners through the project activities has contributed significantly to improving the operation at Skive Fjernvarmeværk, which is illustrated via the sessional production increase from the plan in Figure 19 below.

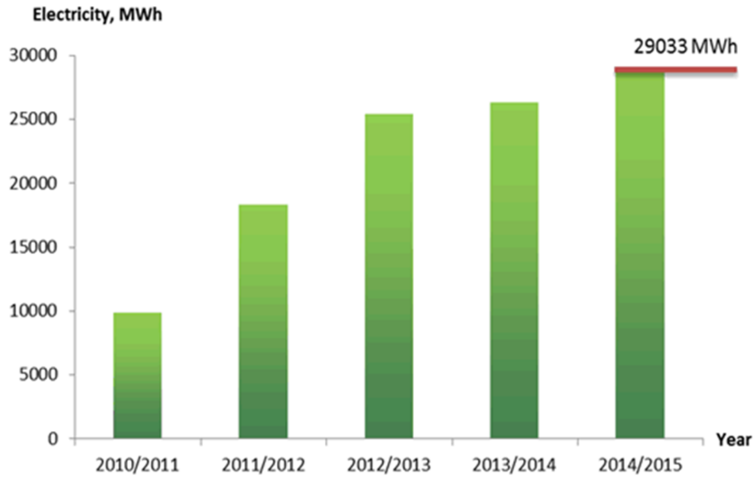


Figure 19 Sessional production increase at Skive Fjernvarme

Production has increased around 16% after the installation of the new tar reformer and around a factor three since the beginning of the cooperation between the project partners. Details of project results hare describe in the previous chapter.

Haldor Topsøe A/S has received a number of requests for tar reforming catalysts, reactors and complete gasification based plants involving tar reforming, none has, however, materialized into business such as paid studies or actual projects. The main barriers for further deployment of the technology are the current oil and gas prices, which has put an effect stop to all larger biomass gasification based prospect, and increased business and employment resulting from the project results cannot be expected before the energy marked and policy becomes more favorable for investors and plant owners.

The project has received considerable national and international attention and the operation at Skive Fjernvarme Værk is recognized in the gasification community as one of the best if not the best running reference for combined heat and power production based on biomass gasification in a fluid bed gasifier.

The project has been presented on numerous occasions nationally and internationally (See Annex for details), and the presentation "Clean" and "Dirty" Tar Reforming of Biomass Gasification Gas - an operational point of view by Winnie Eriksen at the International Freiberg Conference in Dresden (Radebeul), Germany 2014 won a best presentation reward. Moreover, several national and international delegations have visited Skive Fjernvarme Værk to see the plant and learn about their experience, and the project and it results have been described in three publications (See Annex for details).

Inventions has continuously throughout the project been filed as IP, and at present one patent has been granted, two are published and are under examination, while another two are prepared for submission. The patents cover the process, reactor internals, catalyst, and operation of the tar reformer (See Annex for details).

The project result can contribute significantly to the future energy policy objectives, where electrification is going to be the predominant energy source and biomass is intended for gas production and subsequent production of liquid fuels. The project has contributed with demonstrating and improving a robust and reliable gasification technology and downstream gas conditioning prior to power, heat, and potentially liquid fuel production, which can be based on conventional, existing, and commercialized technologies.

1.7 Project conclusion and perspective

The project has been very successful in relation to the design construction a, installation and operation with MEGA monolith and reactor internals and the barrier for commercialization of this new technology has been reduced significantly. A number of smaller issues has been identified during operation relating to the integration with the gasifier and carrier over of dust through the transfer line as well as an opportunity to operate with a continues regeneration of the catalysts. These issues have been addressed in patent application, but must be demonstrated in a larger scale plant. Technically the project has lifted the technology to a level were a broad technical deployment can be pursued.

The main barriers for further deployment of the technology are the current oil and gas prices, which has put an effect stop to all larger biomass gasification based prospect like E.On in Malmø and Gobigas II in Gothenburg.

The perspective of expanding heat and power production with production of chemicals or fuels like gasoline is highly challenged by the economy of scale in the plant. Technically, there are no obstacles, but it will be very difficult to establish an economic viable production in small scale. Typically, a factor 3 – 4 premium has to be paid for the raw fuel production cost compared to conventional oil and gas based fuels.

Table 3 Estimated raw production cost for a range of fuels from a typical 200 MW biomass gasification based production site

Fuel	*SNG*	*Gasoline*	*DME (Diesel)*
Estimated production cost	~5 DKK/m^3	~5 DKK/l	10 DKK/l

This can only be realized with a 10 – 15 years complete tax exception on the product from a biomass gasification based production.

Annex

List of references:

Publications:

1. Jens Utoft; *Skive har styr på forgasning*; Kraftvarme NYT; 2015, 135, pp. 28 - 29
2. Jens Utoft; *Succes for EUDP-projekt på Skive Fjernvarme*; Kraftvarme NYT; 2015, 139, pp. 24 - 26
3. B. Voss, J. Madsen, J. Bøgild Hansen, K. J. Andersson; *Topsøe tar reforming in Skive: the tough get going*; The Catalyst Review; May 2016, pp 7 - 14

Patents:

1. EP 2640683 B1 Process for the preparation of gaseous synfuel
2. WO 2016096868 A1: Process and systems for regeneration of tar reformer catalyst
3. WO 2014195165 A1: Monolithic catalyst for tar reactor
4. Application in progress: IDF 2114 Continuous regeneration system for tar reforming
5. Application in progress: IDF 2113 Tar Reforming arrangement

Presentations by Tage Meltofte Skive Fjernvarme:

1. Fjernvarmeindustriens årsmøde den 11. september 2013 på Grundfos
2. Energipolitisk åbningsdebat den 3. oktober 2013 på Christiansborg
3. Indlæg på VETEC den 9. oktober 2013 på Teknologisk Institut i Taastrup
4. Temadag om fremtidens energikilder den 20. oktober 2013 ved Dansk Fjernvarme
5. Temadag om grønne gasser den 12. juni 2014 i Kultur Center Limfjord
6. Besøg af Klima, energi og bygningsudvalget den 2. september 2014
7. Besøg af Skive Byråd den 4. marts 2015
8. Seminar "midt.energistrategi" den 25. marts 2015
9. Besøg af Energistyrelsen den 4. september 2015
10. Seminar om termisk forgasning den 17. november 2015 på Force Technology Brøndby

Presentations by Haldor Topsøe A/S:

1. Plenary talk: Going green with chemicals and fuels Sustainable at a premium or not? Martin Skov Skjøth-Rasmussen, 17th Nordic Symposium on Catalysts, Lund, 14 June 2016
2. Invited presentation: Going green with chemicals and fuels Sustainable at a premium or not?, Martin Skov Skjøth-Rasmussen, Workshop on Challenges and Opportunities for Sustainable Production of Chemicals and Fuels beyond the Shale Gale, UCSB, Santa Babara, February 2015
3. Presentation: Production of new clean (green) fuels
   from gasification processes, Martin Skov Skjøth-Rasmussen, 6th International Freiberg Conference, Dresden Radebeul, May 2014
4. Invited presentation: Biomass gasifier – Gas conditioning and conversion, Martin Skov Skjøth-Rasmussen, SGC International Seminar on Gasification, Malmö October 2014
5. The role of alkali in heterogeneous catalysis for gas cleaning in stationary and mobile applications, Klas J. Andersson, ACS National meeting 2015, Denver, CO, USA
6. "Clean" and "Dirty" tar reforming of biomass gasification gas, Klas J. Andersson, AIChe spring meeting 2013, San Antonio, TX, USA
7. Tar reforming of biomass gasification gas, Klas J. Andersson, Europacat 2013, Lyon, France
8. Options for tar reforming in biomass gasification, Klas J. Andersson, International Freiberg Conference 2012, Cologne, Germany
9. "Clean" and "Dirty" Tar Reforming of Biomass Gasification Gas, Winnie Eriksen, International Freiberg Conference 2014, Dresden Radebeul, Germany
10. Present and future opportunities downstream gasifiers, Klas J. Andersson, International Freiberg Conference 2015, Hohhot, China
11. Fra biomasse til benzin, Temadag om biogas, forgasningsgas og gas til transport, Winnie Eriksen, Temadag om grønne gasser i Skive Danmark, 12. juni 2014
12. Topsoe Activities Downstream Gasifiers, Presentation Poul E.Højlund Nielsen and Klas J. Andersson 8th International Freiberg Conference June 12-16, Cologne 2016