FINAL
REPORT

GASOLUTION

– Enables efficient power and gas production

ForskEL 2011 – PSO project 10730

Applicant: DONG Energy A/S

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1. Project details

Project title	GASOLUTION – Enables efficient power and gas production
Project identification	ForskEL project 10730 - Gasolution
Name of the programme which has funded the project	ForskEL 2011
Name and address of the enterprises/institution responsible for the project	DONG Energy Thermal Power A/S Kraftværksvej 53 7000 Fredericia
CVR (central business register)	DK 27 44 64 69
Date for submission	4th August 2015

This final report documents the results obtained during ForskEL 2011 project 10730 Gasolution.

2.   Executive summary

2.1   Project background

Biomass represents a broad range of fuels from very expensive wood pellets to less expensive fractions, such as straw and manure fibres. Most existing coal CHP facilities can utilise wood pellets with only minor modifications. Therefore, there is a huge worldwide demand for wood pellets that has driven up the cost of this fuel.

Biomass from fast growing energy crops, such as miscanthus, willow, and especially agricultural residues, such as straw and manure fibres, constitute potentially much more low-priced alternatives but often have a high content of ash and salts (alkali). This limits the potential for today's direct co-firing with coal due to associated corrosion problems. During the last 20 years, DONG Energy has been at the forefront of the co-firing technology. However, a technical limit has now been reached as straw is allowed to account only for a maximum of 10% of the fuel input to any coal boiler. Furthermore, the actual and further planned major decrease of using coal will limit the use of straw.

A low-temperature gasifier can be used to convert such low-priced and troublesome biomass fractions into a gas that after simple dust separation by e.g. just a hot secondary cyclone, can be used in existing power plants with less technical constraints. Gasification of coal and wood has been performed for decades, but gasification of high-alkali biomass fractions for efficient electricity production has never been commercially proven. Traditional CFB gasifiers typically operate at a temperature around 800-900 °C in order to obtain sufficient carbon conversion. These gasifiers by consequence can not be operated with straw without severe bed agglomeration or the expensive use of additives.

These challenges have been solved by the development of a gasification technology that, even with a low operating temperature (around 700 °C), is able to maintain a high efficiency. The low operating temperature keep most of the ash components below the melting point and avoid bed agglomeration. Furthermore, the fact that the ash components remain in a solid but not sintered state means by using simple separation techniques they can be separated from the produced gas and reused as fertiliser on farmlands. With the gasifier, 95% of the energy content contained in the feedstock can typically be made available in the produced gas.

The Pyroneer[1] gasification technology is designed for problematic biomass and waste products with high content of ash and salts. In its simplest form, the technology converts the biomass into a hot, tarry, low-ash, combustible gas, while nearly all of the potassium and phosphorus, etc. in the feedstock are separated from the gas before it is burned.
A part of the e.g. 5 % energy loss will be in the form of unconverted char, which also adds to the soil improving value off the separated ash.

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[1] Formally known as LT-CFB (Low Temperature Circulating Fluidised Bed)

2.2 Pyroneer process overview

In Figure 1 a simplified process flow scheme of the Pyroneer gasifier is shown.
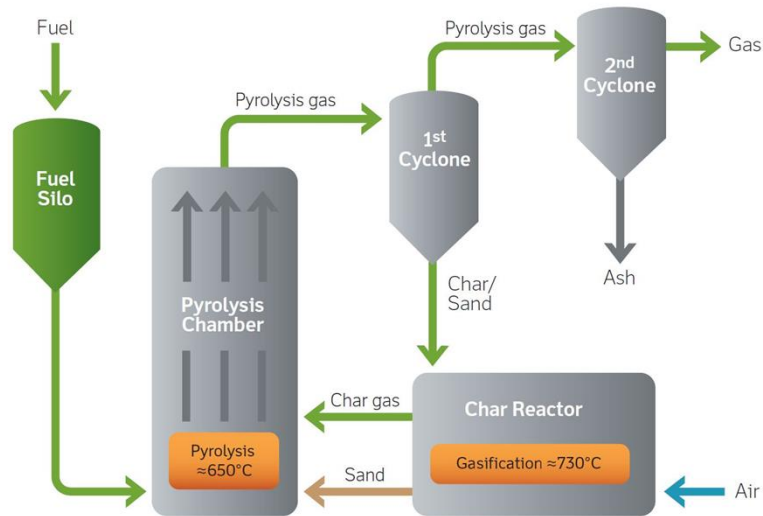
Figure 1: Simplified process flow scheme of the Pyroneer gasifier

The gasification equipment consists of two connected vessels: the pyrolysis reactor and the char reactor. The biomass in the form of pellets or coarse dust are fed into the pyrolysis reactor where the temperature is approx. 650 °C. The biomass is rapidly pyrolysed due to contact with the re-circulated bed of sand, ash and char. Due to the low temperature and short retention time, only light tars with the least problematic PAHs are formed.

After the pyrolysis has taken place the residual char, pyrolysis gases and inert particles are blown upwards to the primary cyclone, which separates the residual char and inert particles. These separated particles are fed into a bubbling bed char reactor where the char is gasified using mainly air at a temperature of approximately 730 °C. Steam can be added in the char reactor in order to control the temperature and improve the conversion. Due to the low and stable temperature in the char reactor, limited ash melting takes place, and the use of additives to avoid bed agglomeration is not necessary.

The produced char gas and fine particles leave the top of the char reactor and enter the pyrolysis reactor where the volume addition contributes to the high velocity in the upper section of the pyrolysis reactor. The heavier inert particles re-circulate from the bottom of the char reactor to the bottom of the pyrolysis reactor. By consequence, the heat released due to the mainly exothermic reactions in the char reactor is consumed by the mainly endothermic processes in the pyrolysis reactor. Thereby there is no need of external heat input.

Ash particles may re-circulate several times until they are sufficiently small to escape through the primary cyclone. The secondary cyclone is designed to remove the finer ash particles from the producer gas. A coarser ash stream can be drained from the bottom of the gasifier with the bed material. The majority of the ash will be separated as flyash from the 2nd cyclone and a minor part as bottom ash. The ratio is however fuel dependent.

2.3 Project goals

The purpose of the present project was to develop and demonstrate a more advanced gas-cleaning concept, which will allow the gas from the Pyroneer gasifier also to be used in non-

dust tolerant applications as gas boilers, Heat Recovery Steam Generators (HRSG) and gas turbines and ultimately for combined production of power, liquid fuels or SNG in a polygeneration concept. This can be illustrated with the two development tracks depicted below.
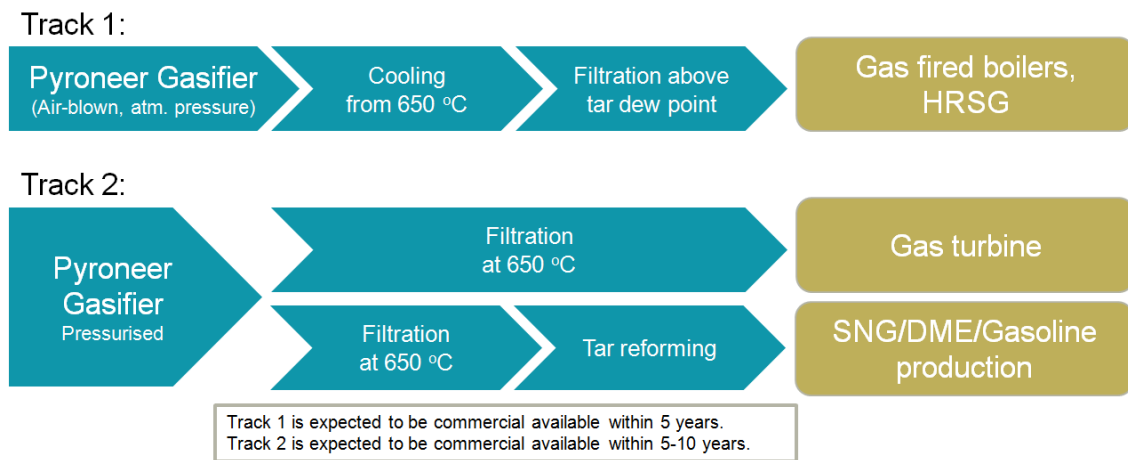
Figure 2: Illustration of the two gas cleaning tracks, this project will investigate

Track 1: Is mainly adapting and demonstrating existing technologies, and to identify a "simple gas cleaning" solution that could be commercialised already at project end.

Track 2: Is mainly developing new concepts and to identify solutions that could be demonstrated in coming projects.

2.3.1 Operation summary

The gasifier was first commissioned in June 2011 and further operational campaigns were carried out in 2012 - 2014. Table 1 below summarize the data of all operational campaigns (as is August 2014).

Table 1. Operational summary 2011 - 2014

Operating hours blower	hours	2825
Operating hours gasification mode	hours	1599
Straw pellets/loose	ton	2000
Alternative fuels (e.g. shea nut, sewage sludge)	ton	190
Load range	MW	4,5-7,5
Ash produced	ton	~ 400
Electricity produced	MWh	1824

3. Project results

3.1 Overview of work packages

Fulfilment of track 1 implies an identification and demonstration of the most effective method to clean the gas from the Pyroneer gasifier.

The cleaning of the gas was expected to be at a level, where the gas can be used in industrial gas boilers and HRSGs (WP2). Long-term demonstration of the identified concept was supposed to be performed on the 6MW gasification demonstration facility in Kalundborg, and to provide the needed confidence for a later commercial implementation (WP4). In order to design both the cooler and filter (WP3), detailed knowledge on the gas composition, both with respect to organic tars and inorganic impurities was needed (WP1). Correlation and knowledge between feedstock, operating conditions and gas composition was also generated. These findings were important for track 2, where simulation and process design lay the foundations for future pressurised concepts (WP5).

The findings from track 2, was a detailed insight in pressurised opportunities with the Pyroneer gasifier, combined with promising concepts where the gas from the Pyroneer gasifer directly can be used in a gas turbine, or through a tar reformer used for production of SNG/DME or Gasoline (WP6).
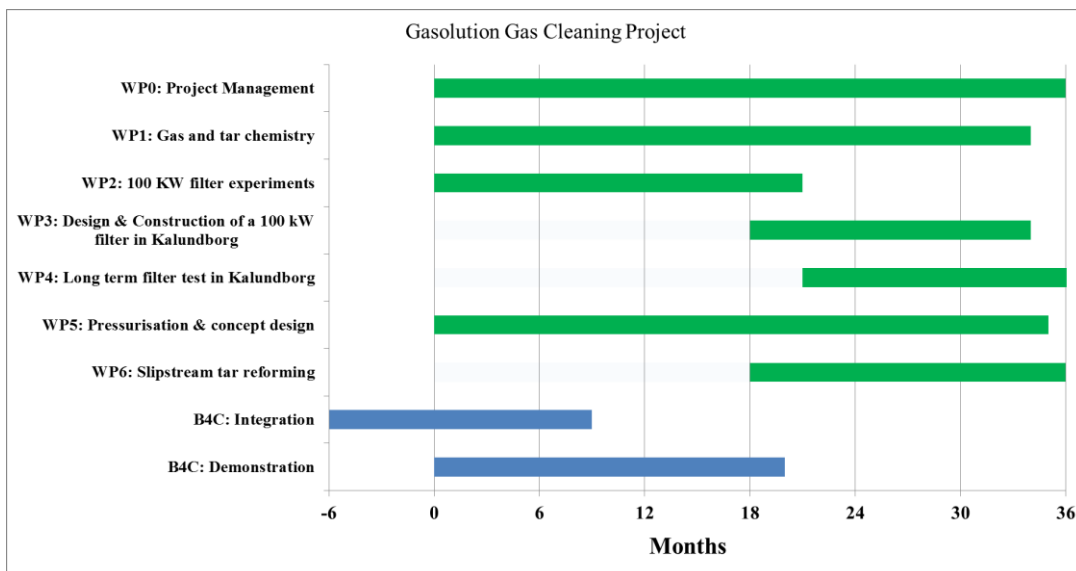
Figure 3: Work-package (green) overview including the in parallel project B4C (blue)

Project start date: March 2012

WP0 covered the entire project management and administration including cooperation and coordination between the partners as well as dissemination of the results.

WP1 was to obtain a detailed understanding about the gas and tar chemistry on a high academic level. Primarily the 100 kW gasifier located at Risø was used to generate experimental data. The tests at Risø was verified by measurements carried out at the 6 MW gasifier.

WP2 was to test bag house filters after cooling the gas to take advance of the low tar dew point of the gas. Filtration by using ceramic candle filters avoiding the need of cooling was also tested. On the background of these tests a design layout for long time testing at the 6 MW gasifier was carried out.

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WP3 was to design, procurement and construction of 100 kW slipstream filter in Kalundborg fuel silo for challenging biomasses, new equipment for gas and dust analysis. The common infrastructure to support WP4 and WP6 was established in WP3.

WP4 was intended to cover the long-term operation of filter and tar reformer at the 6 MW gasifier in Kalundborg. This included test of new fuels and improving of various operation parameters. Filter and tar reformer test was not carried out due to cancellation of the project.

WP5 established a gasifier model based on the data from the 6 MW gasifier. This model has formed the basis for studies including aspects of upscaling, reactor design and optimised operation of the gasifier. Later on the gasifier model has been upgraded to cover pressurised design and O_2-blown gasification.

WP6 The mobile tar reformer unit constructed by HTAS&DTI was installed and connected to a slipstream from the 6 MW gasifier. The purpose of using the tar reformer is to convert tar into synthesis gas and hereby removing the risk of fouling.
No tar reforming tests were carried out before the project was shut down.

3.2 WP0 Project Management
3.2.1 Summary of objectives
The project management work package had three major focus areas:
- Project agreement
- General project management
- Revision of project plans

3.2.1.1 Project agreement
During the first months of the project the project agreement among the project partners was worked out. The agreement addressed the rules of dissemination and use, including intellectual property rights management, and settlement of internal disputes. The final signed cooperation agreement was distributed to the partners primo October 2012.

3.2.1.2 General project management
According to normal practice, the project started with a kick-off meeting, several progress meetings per year. Technical meetings in limited groups were arranged on demand.

3.2.1.3 Revision of project plans
As an integrated part of the project administration was the technical progress of project regularly reviewed and the project plan was revised according to this, including risk analysis and budget revisions.

In January 2014 a revision of WP3 & WP4 was proposed and approved. Major changes was:
- A smaller filter unit installation – savings in CAPEX (WP3)
- More test hours – A rise in OPEX (WP4)

This revision did not make any changes in the overall budget and no changes in the budgets for the individual partners. Activities concerning pressurisation and filter installation was scheduled for the summer 2014.

In October 2014 DONG Energy decided to put their gasification activities on hold including mothballing of the 6 MW Pyroneer Gasifier. Consequently, it was decided to stop the Gasolution project.

3.3 WP1 Gas and tar chemistry

3.3.1 Objectives

The focus of the work package was on tar characterization and analysis of compounds that could be harmful for the applied catalyst such as sulfur and chlorine compounds. Various methods and measurement techniques were applied for the in-depth characterization of the compounds.

A minor part of the work package aimed at collecting and reviewing results from previous studies on pressurized operation of gasifiers with special focus on the produced tars and characterization of the tar fraction. The literature study is attached to the report and can be found as **Appendix 1B**.

The measurements were done in several experimental campaigns in the period of 2012 March to 2014 July, at both Campus Risø, DTU using the 100 kW LT-CFB gasifier and at Asnæsværket, Kalundborg using the 6 MW Pyroneer gasifier. Sampling methods and analysis techniques were the same at both locations. Detailed description of all equipment and measurement methods can be found in **Appendix 1A**.

The main objective of the project work package was to quantify and characterize tars in the producer gas of the LT-CFB process and elaborate on tar and critical compound formation. The experiments aimed at

- determining the amount of total tars and producer gas heating values
- characterizing phenolics and polycyclic aromatic hydrocarbons (PAHs)
- comparison of offline and *in-situ* measurements
- characterization of chlorine and sulfur compounds
- determination of water and ammonia content in the producer gas.

3.3.2 Main findings

Detailed description of the found results and mentioned references can be found in **Appendix 1**.

3.3.2.1 Total tar

The amount of total tars was measured with two different methods. Gravimetric tar determination was based on the evaporation of acetone from the sampled gas using a Petersen column and weighing the flasks after solvent evaporation. The concentration of gravimetric tar was 32.68 and 28.51 g/m^3 in the sampled gas in October, 2012. The higher heating value of the collected tars was also determined during both measurement campaigns. The tar heating values were measured at 28.6 and 28.8 MJ/kg, in the case of the 2012 October measurements, whereas 25 MJ/kg was measured for the water phase and 27 MJ/kg was measured for the non-water phase in the second tar determination. Approximately 95% of the water phase was the water content. The measured heating values are comparable, however the second method showed slightly lower values.

3.3.2.2 Characterization of phenolics and PAHs with special focus on phenol and naphthalene

Phenolics were analyzed from the collected samples with the Petersen column. More than 40 compounds were found and identified and they were grouped into compound classes. The created compound classes were acids, nonaromatic ketons, phenols, indane-based derivatives and naphthols. Several phenols, methyl-, ethyl- and allylphenols were identified with different substitutional patterns. A significant presence of indane-based derivatives appeared as well in the sample fraction with elemental compositions of $C_9H_{14}O$ and $C_9H_{16}O$. A family of dihydroxy-benzenes and substituted analogues and a whole family of methylated naphthalenols (Figure 4) were found in the more polar phase of components.

resorcinol - dihydroxy-benzene   2-methyl-1-naphthalenol
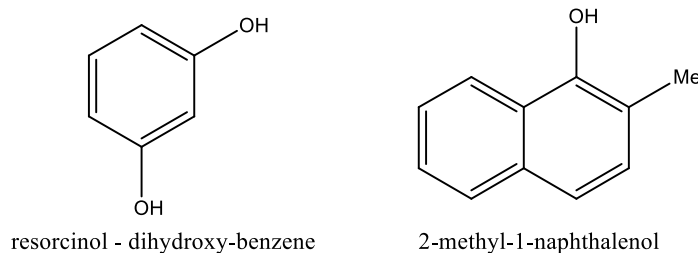
Figure 4. Structure of a dihydroxy-benzene and a naphtalenol compound

Optical measurements were done as well, and the UV absorption spectroscopy measurements [1] have shown a strong UV absorption of PAH/tar compounds in 200-300 nm where phenol was found as the main component. The calculated phenol concentration in the non-diluted gas was 416 ppm. The phenol concentration was also calculated from the UV cross-stack measurements and resulted at 7000 ppm. That is about 17 times higher of that obtained in the gas extraction measurements. This large difference may be explained by that the major part of phenol is probably removed in the tar-trapper and/or the gas extraction system by condensing tar compounds or particles. In Table 2, the concentrations of phenol and naphthalene in ppm as well as their summation in g/m^3 are presented for the three different analysis, extraction, *in-situ* (one section) and *in-situ* (three sections) and also the concentrations obtained by sampling with the Petersen column followed by GC-MS analysis [2]. In general, the GC-MS analyses showed the lowest results for phenol and naphthalene concentrations. The analysis of the UV extraction measurements and the UV *in-situ* three sections analysis are of a factor of 1.7 higher but still in the same order of magnitude. The gravimetric measurements measure the amount of total tar in the product gas show an average mass concentration of 30 g/m^3. Given the uncertainties in both methods, the value is in the same range as the 35.4 g/m^3 calculated for the one section model of the UV *in-situ* measurements. This means, if the one section model is correct, almost all tars of the product gas at 300°C are in the form of phenol and naphthalene. This, however, is contradictory to the GC-MS analysis, stating that phenol and naphthalene are only minor species. In addition, it would mean that the majority of tars in the product gas are either lost in the processing and cooling (e.g., in filters or due to condensations) or converted to heavy tars, which cannot be identified by GC-MS.

That leaves two options:

1. processing changes gas composition (e.g., by conversion, filtering, condensation)
2. flawed measurements (either UV or sampling)

Table 2. Comparison of different phenol and naphthalene values obtained from different measurements including measurement temperatures

Technique	Temperature (°C)	Phenol concentration (ppm)	Naphthalene concentration (ppm)	Sum of both (g/m^3)
UV extraction	150	360	30.5	1.77
UV in-situ (1 section)	300	7700	1000	35.4
UV in-situ (3 sections)	300	400	100	2.10
GC-MS 1	25	203	16.9	0.885
GC-MS 2	25	226	15.8	0.963

An attached manuscript (**Appendix 1C-1, not to be published**) focuses on the most significant aromatic compounds in the tar fraction produced by the LT-CFB at Campus Risø, DTU: phenol and naphthalene [5]. The two compounds were measured using a UV absorption and a separate GC-MS analysis. It was necessary to sample the aromatic compound after the HGC (hot gas flow cell) and determine the compound concentration that serves as a reference for the optical measurements. This was done with the Petersen column. Afterwards, the concentration of the aromatic in the acetone was analyzed with GC-MS and the mean concentration of aromatic in nitrogen during the sampling time could be calculated. The major results of this article were temperature dependent absorption cross-sections for phenol and naphthalene at around 20°C, 150°C, 300°C and 500°C. The results were obtained to quantify these compounds in biomass gasification. Especially high temperature processes, but also atmospheric research can benefit from these results, and make a step ahead towards online tar analysis.

3.3.2.3   Chlorine and sulfur compounds

The role of simple chlorinated organic compounds with special focus on methyl chloride (MeCl) associated with gasification or combustion is rarely discussed. The combustion of MeCl gives rise to HCl in the flue gas whereas upgrading of the producer gas may require a significant reduction of the MeCl concentration; hence concentration of MeCl in the producer gas should observed.
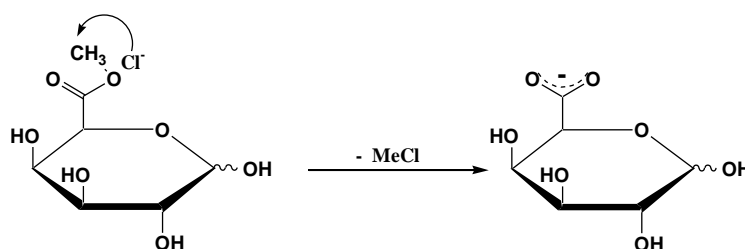
Figure 5. Formation of methyl chloride from pectin components

The abiotic formation of methyl chloride from biomass has previously been studied in detail and the widespread plant component pectin apparently acts as methyl donor (Figure 5). This reaction may result in complete volatilization below 300 °C. The formation of MeCl from pectin components has been addressed in two publications (**Appendix 1C-2 and 3-not to be published**). A fundamental study on MeCl formation from apple pectins was prepared in order to determine the optimal reaction temperature and time; and study the kinetics of the reactions between alkali metal chlorides and pectin [6]. Another study investigated the release of chlorine and sulfur from six different biomasses at torrefaction conditions [7]. Analysis of the released gas showed that MeCl is the main Cl compound in the gas phase.
An analytical method for methyl chloride in producer gas has also been developed and successfully applied to producer gases from LT-CFB gasifiers. Gaseous samples have been studied including the determination of methyl chloride (Table 3) especially during the experimental campaign of 2012 October. Similar values of methyl chloride concentrations were measured at the two sites, at the LT-CFB, at Campus Risø and at the Pyroneer gasifier.

Sulphur is a minor, but still significant component in biomass, amounting to 1100 ppm in dry wheat straw. Sulphur should be regarded as a critical component for several reasons: (1) combustion gives rise to SO_2 in the flue gas; (2) the sulphur compounds should be considered as poisons to metal catalysts. Sulfur compounds H_2S and COS appear in the window between C_2 and C_3 hydrocarbons in the GC-MS chromatograms and can be detected with high selectivity. The concentration was estimated for H_2S and COS at 34 and 28 ppm, respectively (Table 3). SO_2 was not observed in the producer gas.

Table 3. Methyl-chloride, H2S and COS concentrations in the producer gas at two locations, LT-CFB at Campus Risø, DTU and at the Pyroneer gasifier site

Date of sampling	04/10/ 2012	04/10/ 2012	04/10/ 2012	29/11/ 2012	29/11/ 2012	29/11/ 2012
Sampling place	LT-CFB	LT-CFB	LT-CFB	Pyroneer	Pyroneer	Pyroneer
Amount of MeCl (ppm)	106	96	90	91	119	134
Amount of H$_2$S (ppm)	34			0		
Amount of COS (ppm)	28			40		

H$_2$S can be regarded as a primary product whereas no direct route to COS is apparent. The reaction between CO and H$_2$S was investigated using a DIN 53436 oven and H$_2$S could quantitatively be transformed into COS at 600 °C. Based on literature survey this is unexpected and may indicate that surface promoted reactions play a significant role in this reaction.
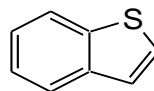
Benzene   Thiophene   Benzothiophene

Figure 6. Structures of benzene, thiophene and benzothiophene

In addition, sulphur is present in S-heteroaromatics, such as thiophene and benzothiophene (Figure 6). The estimated amount of thiophene was approximately 1.2 ppm. No thiophene was observed however in the chromatogram of the Pyroneer gas samples. Benzothiophene has in a similar way properties close to naphthalene and can likewise be determined from the PAH analysis. Benzothiophene was estimated to have a concentration of 0.5 ppm in the LT-CFB producer gas (in 2012 October).

Besides the GC-MS measurements, optical experiments were also performed to measure Cl- and S-compounds in the producer gas. During the measuring campaigns in 2012 the content of HCN was measured at 700±20 ppm and no S-compounds (OCS or H$_2$S) or Cl-compounds (CH$_3$Cl, HCl) were detected by IR measurements. The reasons for no found Cl-compounds may be due to 1) their low concentration in the producer gas (below 500 ppm/150 ppm), 2) low resolution (2cm^{-1}) used and 3) by condensed tar components (dew point above 130°C).

3.3.2.4   Water, ammonia determinations and N-compounds in the gas

The optical measurement results were compared from 2012 June and October. The gas extraction measurements in October showed significantly higher water content (33 %) in the producer gas compared to that in June (20.6 %). 550 cm cross-stack measurements resulted in a water content of 33 % that is in very good agreement with the gas extraction measurements. This supports the conclusion that there is no water condensation in the gas extraction system.

Optical measurements [10] were performed at the Pyroneer gasifier and the NH$_3$ contents were compared to those obtained by the Petersen column and determination based on a series of reactions [11] (see **Appendix-1A**). Gas extraction measurements and the IR absorption spectra were used for NH$_3$ determination. The main results showed an ammonia concentration of 0.4 % (v/v) and a HCN concentration of 245 and 350 ppm at two measurement days of the same experimental campaign (2014 June). If gas extraction measurements are compared to those obtained with cross-stack measurements, some differences are found. The ammonia

concentration in the *in situ* measurement was higher (0.55 % (v/v)) than that of the gas extraction one. This higher NH_3 concentration may indicate that a part of the NH_3 (about 24% of the *in situ* value) was trapped by probably condensing acids/tars (with dew points above 150 °C) in the tar trapper.

The measurements from the gas bobbled through the Petersen column fluctuated significantly and the average level was well below the simultaneous NH_3-N measurements performed by the spectroscopic measures. As the impinger measurements are on dry, tar free basis, the values should be higher than those from the spectroscopic assessments (0.4-0.5 % v/v, wet basis), but this was not the case (average 0.17 %v/v, dry tar-free basis). The possible explanation for the fluctuations as well as the consistent underestimation has been identified as condensation in the piping system leading from the main Pyroneer producer gas pipe to the impingers.

The GC-MS analyses of the producer gas revealed the formation of two groups of nitrogen compounds, namely a series of simple N-heteroaromatics, indoles and quinolones (Figure 7 and Figure 8). The concentrations of indole, scatole and carbazole were estimated at 2.6, 5.1 and 1.2 mg/m^3, respectively (2012 October). Thus, the indoles add up to 9.8 mg/m^3.

Indole   Scatole   Carbazole
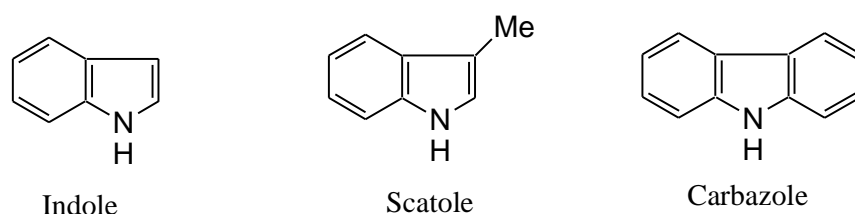
Figure 7. The chemical structure of indole, skatole and carbazole

The parent quinolines were traced in the same analysis. The concentration was estimated in a similar way to 4.7 and 2.9 mg/m^3, for quinolone and iso-quinoline, respectively (2012 October). Thus, the parent quinolines add up to 7.7 mg/m^3.

Quinoline   iso-Quinoline
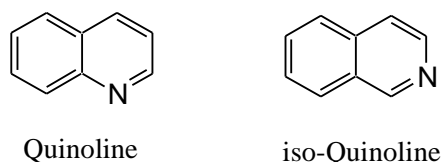
Figure 8. The chemical structure of quinoline and iso-quinoline

The systematic formation of the parent structures is surprising. However, the formation of the indoles is tentatively assigned a controlled degradation of tryptophan and/or its metabolites. The parent quinolines will typically require some condensation reaction followed by dehydrocyclization e.g. a Skraup reaction. An open structure, namely the benzyl cyanide (Figure 9) was present in an amount 6.6 mg/m^3, comparable to that of indoles. It should be noted that indole and benzylcyanide have the same elemental composition, C_8H_7N.
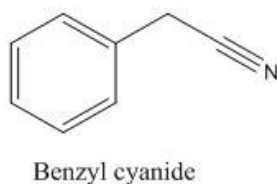
Benzyl cyanide

Figure 9. The structure of benzyl cyanide

*References for Chapter 3.3 are listed in **Appendix 1** (Tar chemistry report – WP1).*

3.4 WP2 100kW filter experiments

3.4.1 Summary of objectives

One of the challenges with the biomass approach is to clean the gas leaving the biomass gasifier. Gas from biomass gasifiers contains both dust and tars, and both components are serious challenges for the downstream equipment such as gas turbines, and catalytic reactors. This project will test, demonstrate and identify the optimum **solutions** and concepts for **gas** cleaning:

Track 1:

Pyroneer Gasifier (Air-blown, atm. pressure) → Cooling from 650 °C → Filtration above tar dew point → Gas fired boilers, HRSG

Track 2:

Pyroneer Gasifier Pressurised → Filtration at 650 °C → Gas turbine

Filtration at 650 °C → Tar reforming → SNG/DME/Gasoline production

Track 1 is expected to be commercial available within 5 years.
Track 2 is expected to be commercial available within 5-10 years.

Figure 10: Gasolution, project description

As illustrated above, the first step is filtration of the Pyroneer gas (possible after cooling) at a temperature above the tar dew point.

This chapter describes the set-up and test of a bag house filtration system including a gas cooler operating at temperature at approximately 350 °C.

Next step was to test a filtration system based on ceramic candle filters, able to operate at 600 – 650 °C avoiding the need of a gas cooler.

The knowledge and experience generated in task WP 2 supported the propositions for further work in WP 1 (gas and tar chemistry) and should form the foundation of WP 3 (Design and construction of a 100kW filter in Kalundborg).

3.4.2 Objective

Following successful filter installation and system modification, three test runs were planned with the following objectives:

- June 2012 test run (bag house filter):
  o Filter performance test including establishing a filter cake
  o Test and approval of the developed hot gas filter probe
  o Measuring particle base load
  o Test of tar measuring system
  o Initial tests of optical measuring methods
- October 2012 test run (bag house filter):
  o Determination of filter efficiency
  o Tar measurements
  o Further test of optical measuring methods
  o Test of several alternative analytic detection methods (see below)
    ▪ This part will be reported separately in WP1
  o Post test filter inspection and evaluation
    ▪ Including investigation of the collected filter particles
- November 2013 test run (ceramic candle filters):
  o Determination of filter efficiency
  o Particulate matters
  o Tar measurements
  o Electron microscopy (SEM and EDS analysis)

Prior to the above two test runs, a pre-test run has been carried out in March 2012 to test and support the development of a hot gas filter probe. In the same test run, gasifier operation and sampling was trained.

3.4.3 Conclusion and main findings

A hot gas bag house filter was established and equipped with filter bags designed for a maximum temperature of 370 °C. Later on the filter house was equipped with ceramic candle filters and tested at approx. 600 °C

The filter system was tested during three test runs. Operation of the bag house filter and the candle filter was smooth with no technical problems.

During the test runs with bag house filters, efficiencies between 90 and 99 % were measured. These values were lower than expected and it is questioned if the particle measurements did provide the correct values.

The particles collected from the filter were tested for tar contamination – no detectable amounts of condensed tars were found.

The full load gas flow was determined to be 37 Nm^3/h. The basis particle load was determined to be 11-15 g/Nm^3.

The amount of gravimetric tars was determined to 30 g/m^3, having a higher heating value of approx. 29 MJ/kg.

3.4.4 Design:

3.4.4.1 Filter characteristics

The filter house is installed with 7 filter bags made of woven glass textile and coated with a special inorganic coating, it is able to resist 371 °C (700 F) continuously, and up to 427 °C for short durations

The filter bags are cleaned via a pulse blowback system blowing nitrogen through each filter bag at 2.5 bar. When and how often is up to the gasifier controllers.

Figure 11: Spray cooler (left) and filter house (right) prepared for tracing

3.4.4.2 Modification of filter house

The filter house was modified and equipped with explosives flap, connected to the outlet. A N_2 system was added to the pressure cleaning system.

Subsequently, the filter house has been equipped with heat tracing and insulated with Kaowool high temperature ceramic blanket insulation to keep the filter at operating temperature. Furthermore dead-end pipes got additional insulation to prevent cold spots and tar condensation.
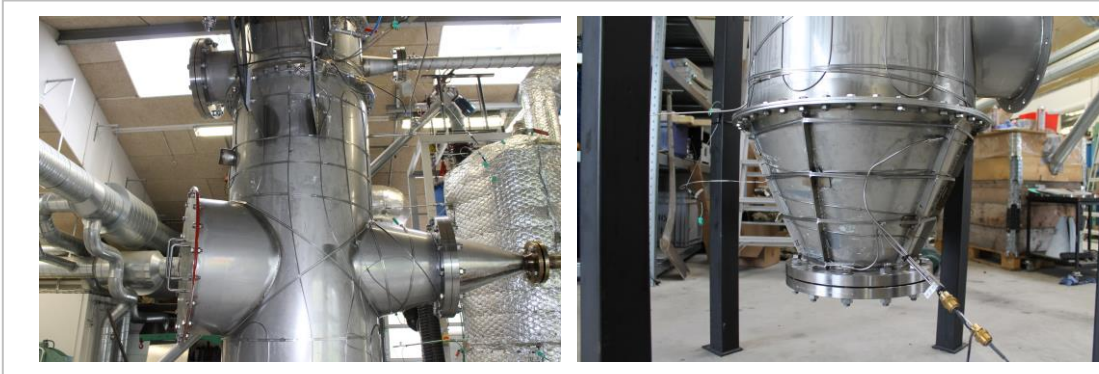
Figure 12: Filter house equipped with heat tracing

Left: Upper part of filter house - Right: Lower part with heat tracing.

3.4.4.3 Particle measurements

A special hot gas filter probe and connection system was developed.

Figure 13: Left: Hot gas filter probe installation - Right: Connection for hot gas filter probe

3.4.4.4 Cooler

To cool down the gas to an operation temperature around 300 °C, a wet spray cooler was installed before the bag house filter. Using a wet spray cooler is a simple and cheap solution for cooling down the tar containing gas while avoiding surface temperatures below the tar dew point.

Principles: Water is spayed through a two-phase nozzle producing droplets of water in the hot gas. While the water droplets evaporate, the evaporative energy of the water will cool down the hot gas to the desired temperature. As the gas to be cooled is hot and burnable N_2 is used as atomizing gas. Controlling the gas temperature is done by adjusting the flows of water and nitrogen.

Figure 14: Spray cooler.

Source: ERA-net report – Tar removal from low-temp. gasifiers.

3.4.4.5   Flare

To assure a good burn-out, the flaring system has been optimized prior to the filter exp.
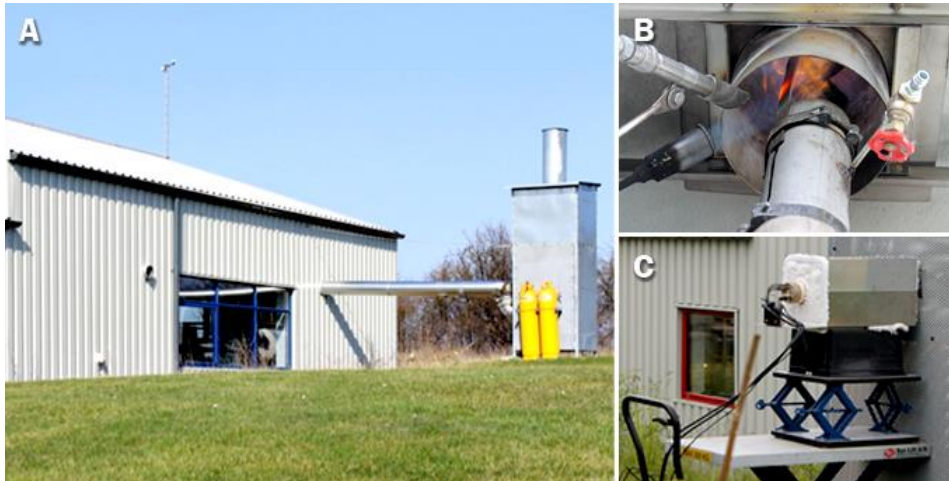
Figure 15: Flare unit.

A: Location of flare unit outside experimental facility. B: Support burner and flare details.
C: Experimental setup for optical measurements
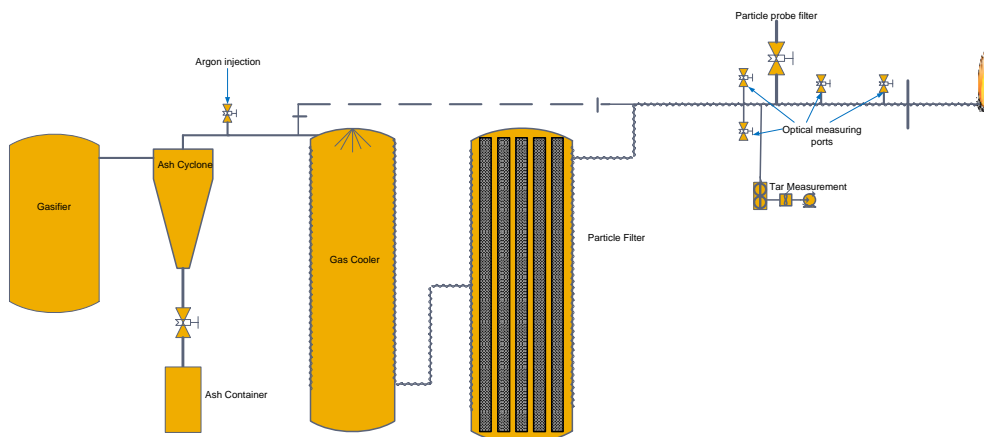
Figure 16: Experimental setup

3.4.5 Post test inspection at the bag house filter

To clarify if the filter had a leak and to further investigate it, the bag house was inspected after the test run. The following will be the sum of discoveries made.

All filter bags were intact and seemed unharmed. They were all covered with an almost uniform filter cake layer with an average thickness of 15.3 mm. The inner walls of the bag house were covered in lumps of 1-3 mm thick solids. The top part of the bag house (above the filters) was pretty clean, ½ mm black dust were present on all surfaces.

The most interesting discovery was that cleaning the filters was not as easy as expected. It was believed that the pulse blowback system was able to clean the filters, if initiated enough times. But this inspection proved otherwise: After 3 complete blows only a few lumps of filter cake were blown off as pictured in Figure 17.

Figure 17: Left: Filters before pulse blow. Right: Filters after 3 pulse blows

To get the last particles off the filters, they needed to be dismantled from the bag house, and cleaned by using a knife. Three reasons to why the particles were so difficult to remove were guessed:

- The particles had agglomerated due to moisture during the weeks of stand-still with an open bag house.
- Tar condensed on the particles made them agglomerate.
- The pulse blowback system was inefficient.

3.4.6 Post test inspection at the candle filters

As expected Soxhlet extraction showed no measurable Soluble Organic Fraction (SOF) since the gas was not cooled before the filter system. Gas chromatography analysis did not show significant amounts of PAH's either.

SEM-EDS analysis showed rather large content of carbon and oxygen and some inorganic elements like potassium and chloride.
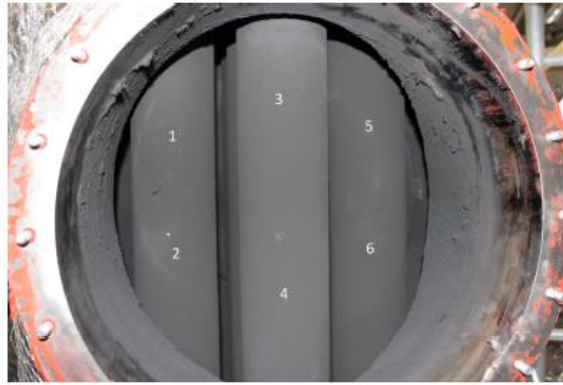
Figure 18: View of filters before back flush through side opening of filter house.

Scanning electron microscopy (SEM) was used together with energy dispersive X-ray spectroscopy (EDS) to analyse the structure and chemical composition of the particular matter.
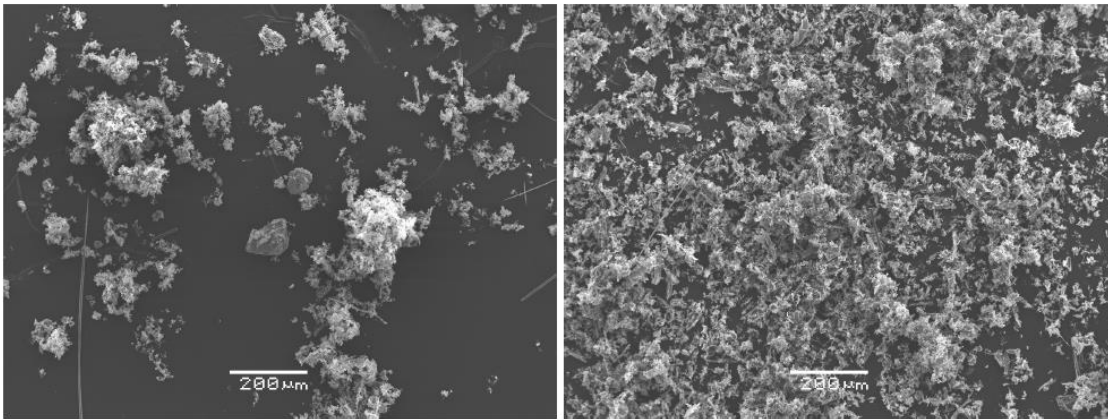
(a) Sample 3.

(b) Sample 5.

Figure 19: SEM - Overview images from sample 3 and 5
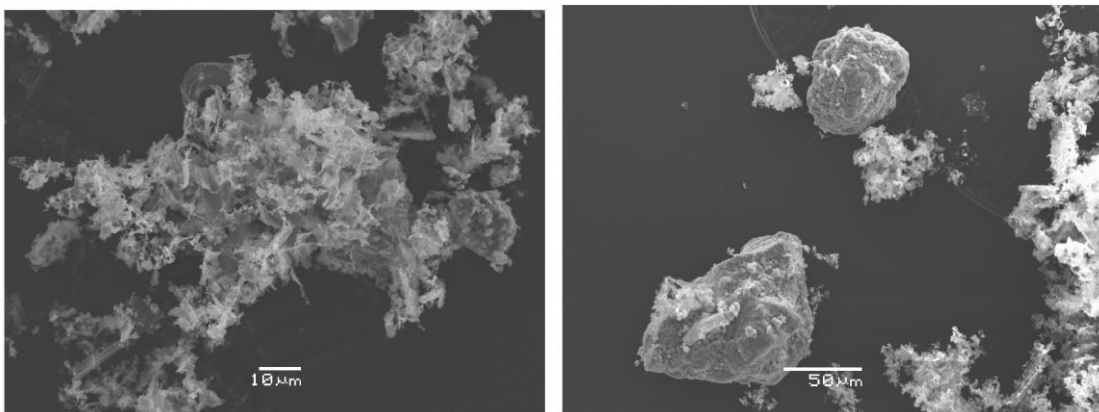
Figure 20: SEM images from sample 3
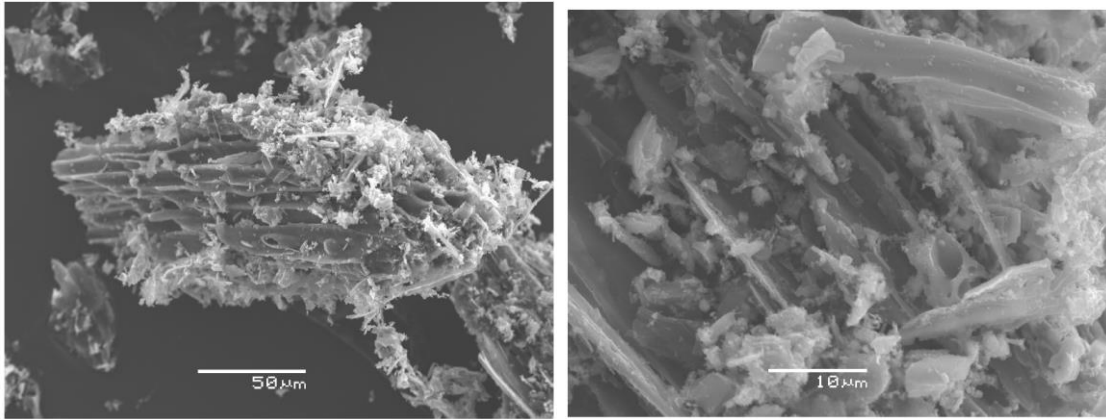
Figure 21: SEM images from sample 5

3.5 WP3 Design and construction of a 100 kW filter in Kalundborg

3.5.1 Summary of objectives

The aim of WP3 was to design, procure and construct a filter able to filter a hot-side stream of the gas produced by the 6MW Pyroneer gasifier in order to verify filter performance and design, lifetime of filter candles, etc. Based on the results obtained in WP2, the filter should be designed to operate in a temperature window of say from 600°C to 650°C and handle a gas flow equal to approx. 100 kW.

After filtration, the filtered gas was returned to the gas duct by an ejector.

The common infrastructure (piping, valves, heat tracing, ejectors, housing etc.) to support WP4 and WP6 was established in WP3.
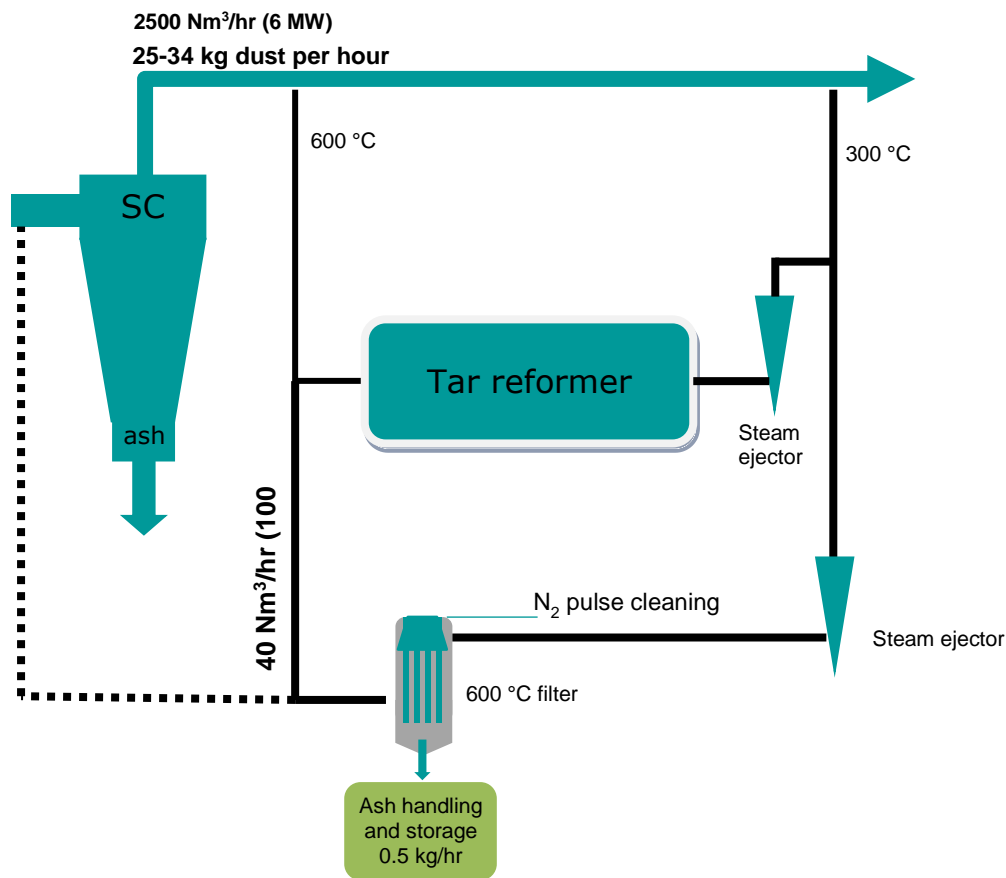
Figure 22: Illustration of the expected slipstream filter unit and tar reformer unit

A fuel silo suitable for handling of challenging biomasses and high temperature measuring equipment was developed and installed.

Piping infrastructure including high temperature valves, heat tracing, ejectors, housing and supporting N₂ and steam was installed.

1. **Installation of new silo**
2. **Establishment of tar reformer**
3. **Improved ash handling system**
4. **Organisation**

3.5.2 Installation of new silo
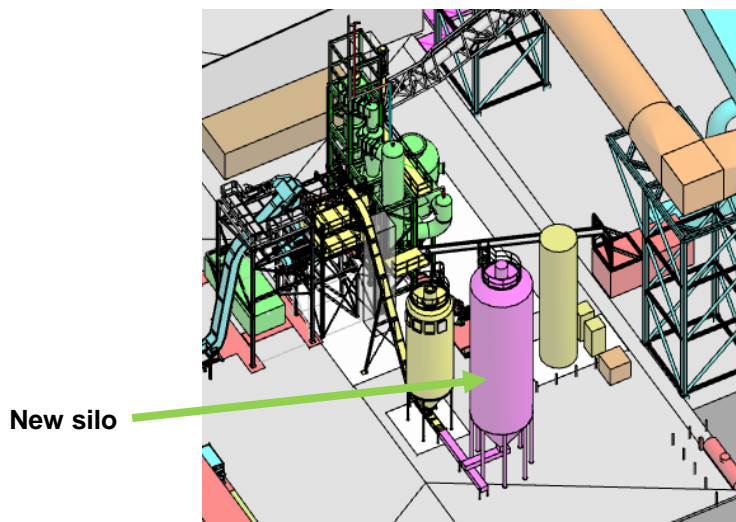
New silo ⟶

Figure 23: Installation of new silo

New fuel silo of 150 m³ is established next to the existing ones, in order to lower fuel costs.

Time schedule

- Foundation work for the new silo: 25 February – 14 March, 2014
- Installation of silo on foundation: 17 March - 28 March, 2014
- Cold test of silo: 31 March – 4 April, 2014
- First operating campaign: 22 April - 15 May, 2014 (Week 17-20, 2014)

In the beginning of 2014 a new and larger fuel silo was installed on the 6 MW plant. The size of the new was silo was three times the original fuel silo (Figure 23: yellow silo to the left of the new silo). Installation of a larger silo did make it possible to have a more flexible fuel delivery, less than once a day compared to three times a day with the small silo.
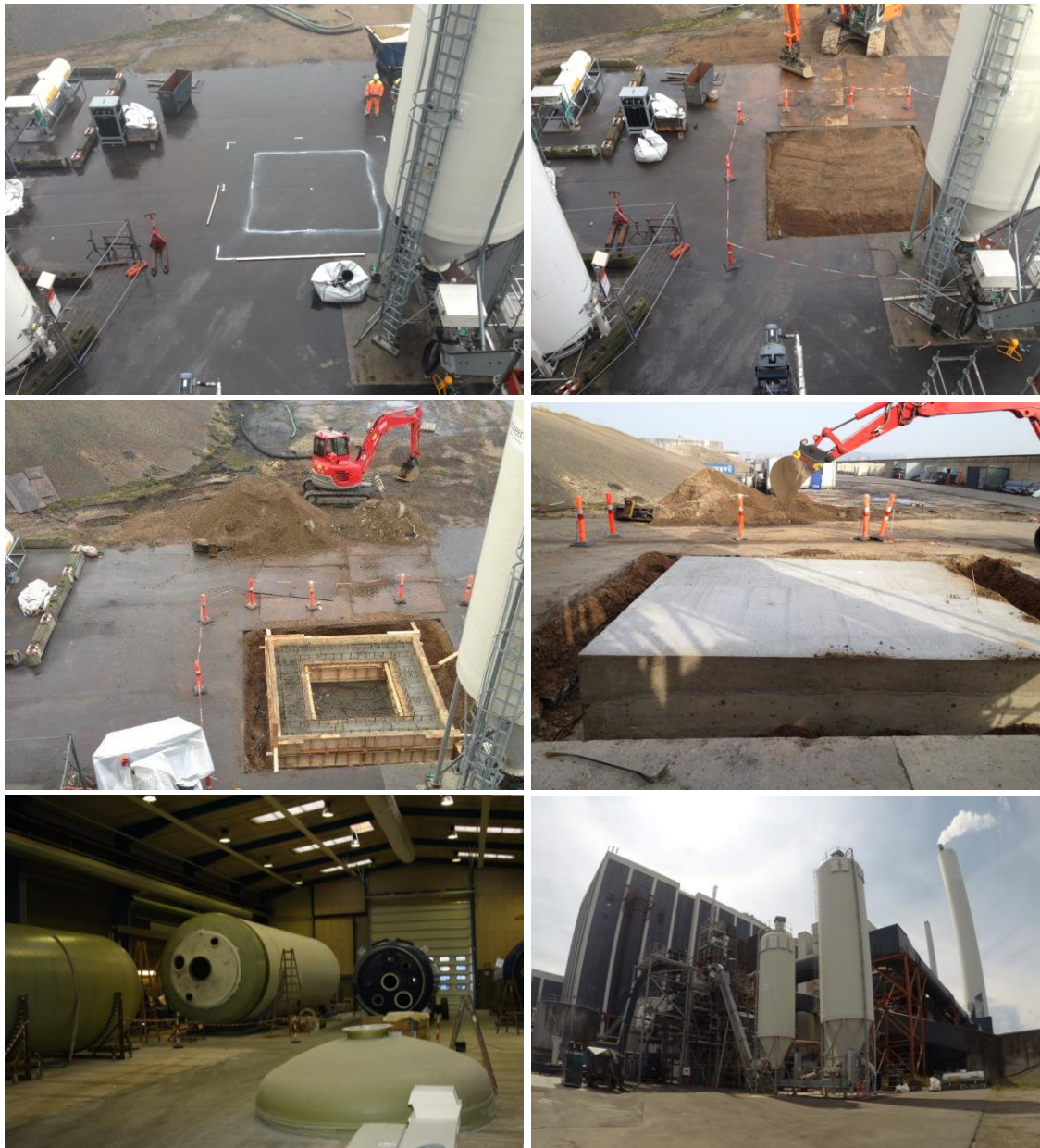
Figure 24: Installation of a new 150 m³ fuel silo

The new silo was designed for handling pulverized material making it possible to use cheap fuels. The possibility to use cheap, pulverized fuel did lowering the OPEX significantly and make it possible to run cost neutral and by this make a big incentive to continued test operation of the gasifier.

3.5.3 Establishment of tar reformer

With the aim of reform the tars in a slip stream of the raw gas test equipment from Haldor Topsoe was moved from Skive to the Pyroneer Gasifier.

Establishment:
- Additional piping connected to the existing gas channel
- A new platform for measuring equipment
- Two on top containers for housing tar reformer and gas filter
- New power and steam supplies for test containers

Time schedule

- Equipment arrives at site: 13 March
- Installation of containers: 17 March
- Installation of plat form: 24 March – 28 March
- Installation of equipment: 31 March – 11 April
- Cold test: 14 April – 16 April
- First operating campaign: 22 April - 15 May (Week 17-20, 2014)

**Access plat form (for valves etc.)
Established on existing rack for
flue gas (level 14)**

Access ladder

**2 containers installed
next to the rack**
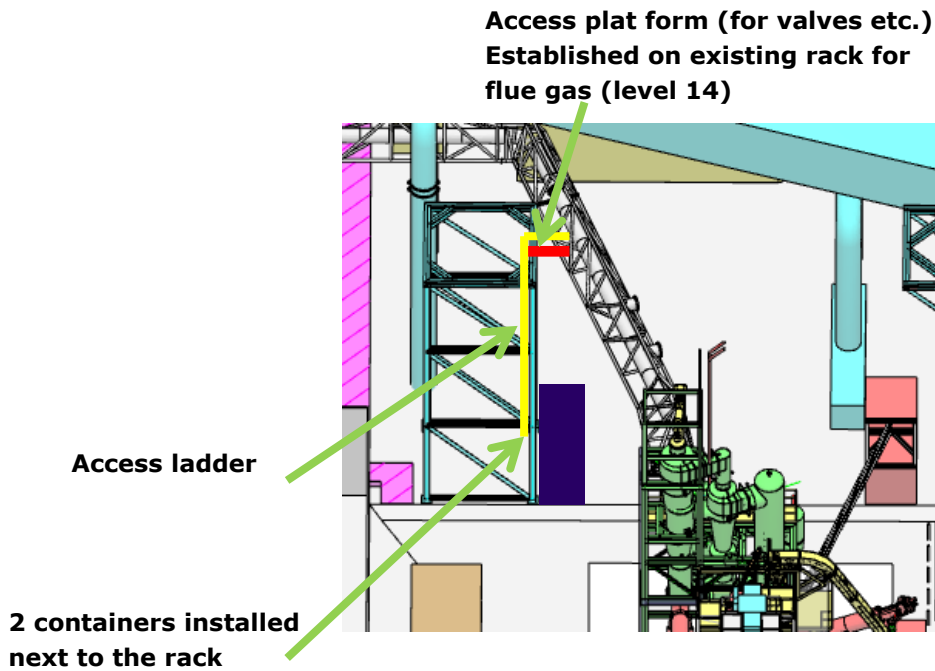
Figure 25: Tar reformer installation
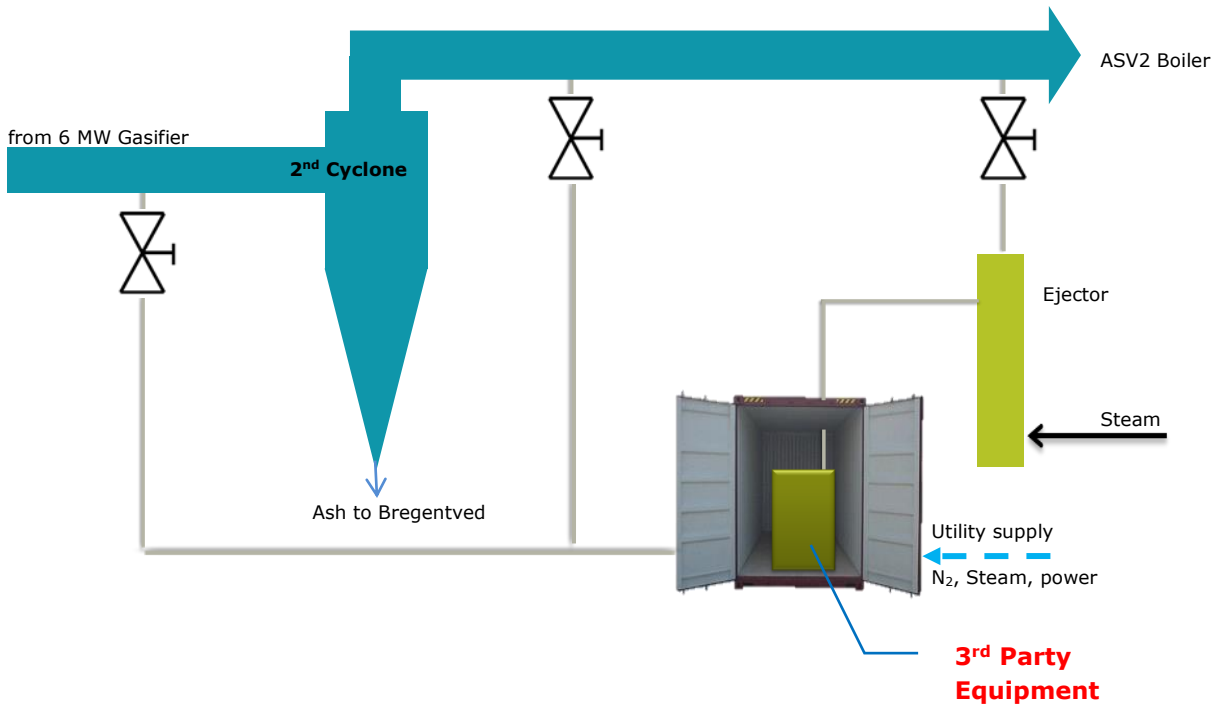
Figure 26: Tar reformer installation with container solution
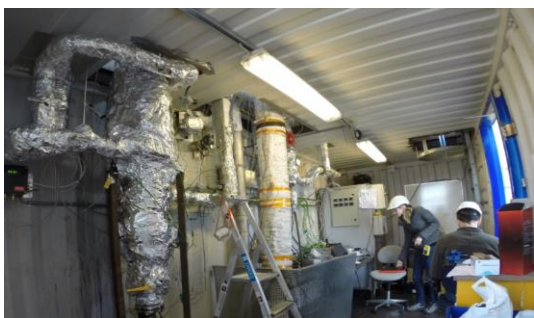
Figure 27: Pictures: Tar reformer installation

3.5.4 Improved ash handling system

To eliminate dust problems from ash handling the ash handling is changed from open containers to closed containers with filter and ventilation.

Time schedule

- Installation of blower and filter: 7 April – 11 April
- Receive new ash containers: 11 April
- Installation of plat form: 24 March – 28 March
- Installation of equipment: 31 March – 11 April
- Cold test of system: 15 April – 16 April
- First operating campaign: 22 April - 15 May (Week 17-20, 2014)
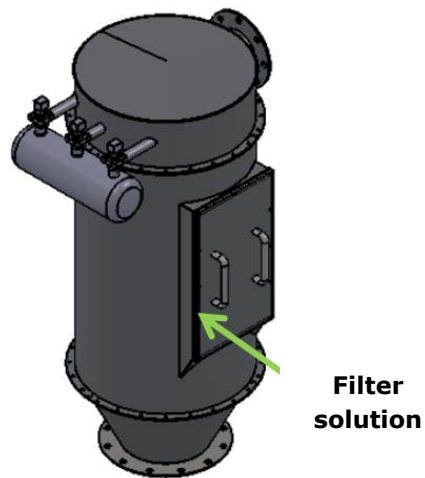
Figure 28: Improved ash handling

3.6 WP4 Long term filter test in Kalundborg

3.6.1 Summary of objectives

Objective of WP4 was to:
- Plan the 6MW operation campaigns for filter tests and tar reformer (WP6)
- Make sure data is retrieved, measurements are done and samples are taken
- Analyse data and samples
- Report results and build up know-how
- Enhance the 6MW plant and give inputs to design of up-scaled plants

Three test campaigns were carried out during 2014:
- **Week 17-20, 2014 (April)**
- **Week 25-28, 2014 (June)**
- **Week 35-37, 2014 (August)**

In this chapter, the following abbreviations will be used:
- PR: Pyrolysis Reactor
- CR: Char Reactor
- IR: Intermedia Reactor
- SC: Secondary Cyclone

3.6.2 Week 17 – 20, 2014 (March/April)

This chapter gathers results and experiences from the Pyroneer 6 MW operation campaign done in week 17 to 20, 2014.

This is the third operation with the 6 MW Pyroneer demo gasifier at Asnæs Power plant after the refurbishment of the two cyclones. This is also the first operation period after the installation of the new fuel silo that allows for feeding the gasifier with alternative and cheap fuels, such as loose shea nut residues and beet seeds (Danish "roefrø"). Modifications to the fly ash container were made in order to reduce dust nuisance and get more reliable data. In addition, the HTAS tar reformer unit used at the Skive gasifier has been installed at ASV and will be commissioned during this operation period.

The previous operation period was in week 46-49, 2013. After two weeks of operation with straw pellet, two 48 hours tests were made on pelletized shea nut and blends of straw pellet and sewage sludge. The gasifier was also operated with a low bed mass in order to partially reproduce the design of a large scale gasifier. The operation period was very successful in terms of availability. Detailed mass and heat balance calculations were performed. It was concluded that the calculations are based on a large number of assumptions and that the results are subject to a high uncertainty. The dust flow rate and contents as well as bed material composition are crucial data with respect to mass balance calculations. Based on the level of information available, it was observed that the gasifier efficiency was on average lower than expected. Recommendations were made in order to adapt the process parameters to the low bed mass and improve the char conversion.

In this operation period the fuel will be:
- Beet seeds (Danish "Roefrø")
- Straw pellet for a short period
- Loose shea nut residues

Beet seeds have an ash and moisture content and a potassium content close to the one found in straw. It is also a fuel significantly cheaper than straw. Operating with this fuel will therefore make it possible to achieve data that are representative for an up-scaled gasifier operated on straw, but at a lower cost. Shea nut residue is a promising fuel as it cannot be used directly in a conventional boiler. It is also a fuel which produces a high char yield during the pyrolysis. This char is also very reactive with steam. This allows for getting good data operating the char reactor with a high steam addition and therefore a high velocity, which is

relevant in the context of the validation of the up-scaled design. In addition, this fuel is also much cheaper than straw, which allows the large reduction of the cost of the operation of the demo plant.

3.6.2.1   Objectives

There were four main objectives set up for this operation period which will be further commented on in the Results section:

1) Potassium balance data
      a. Better data must be produced to make more accurate potassium mass balances by getting good samples of fuel, cyclone ash, dust in the gas and bed material
2) Reference data for upscaling
      a. Measuring gas composition with emphasis on NH3 and HCN to give input to calculations of NOx emission from gas burner
      b. Achieve more data at different conditions for investigating char reactor performance
3) Operation of the gasifier with high efficiency
      a. Operation of the gasifier with a high temperature in PR, CR and IR
      b. Operation with high steam addition to increase char conversion
4) Test of new fuels: Beet seed and loose shea nut
      a. Demonstrate operation on these new and cheaper fuels with the new fuel silo

3.6.2.2   Results and action plan

The operation of the gasifier in April 2014 led to agglomeration after about 14 hours of operation with beet seeds. The gasifier had been at full temperature for about 9 hours. The gasifier was manually tripped due to the disturbance of the fluidization due to agglomeration of the bed in the char reactor.
The various attempts to restart the plant were unfruitful. It was decided to stop the operation as the CR refractory required refurbishment.

During the emptying of the bed material and the inspection of the CR it was found out that agglomerates were present in the CR-IR duct. In addition, a large piece of the refractory wall had fallen in the bed. Different documents have been written / completed in order to analyse the data from the campaign and limit the risk for agglomeration during future campaigns.

There are several hypothesis that can explain the agglomeration.
- During the operation, the feeding of the fuel was unstable (cf. Figure 29). Due to a faulty control loop, the fuel flow rate to the gasifier, calculated based on the evolution of the weight silo, increased continuously for about 5 hours. The error was then detected, and the fuel load set point was set back to its initial value. The fuel load varied significantly. At 8:30 on April 25th, the calculated fuel flow rate dropped to a very low value. It is likely that it was due to a fuel bridging in the bottom of the new silo. This was followed to a drop of the air flow rate to the char reactor. Generally, the air flow rate to the char reactor bed varies significantly as well and reach at several periods the flow rate corresponding to minimum fluidization (gas velocity of 15 cm/s). The variation of the gas flow rate and the low gas velocity in the bed may have disturbed the fluidization of the bed, leading to the appearance of dead areas in the bed and hot spots.
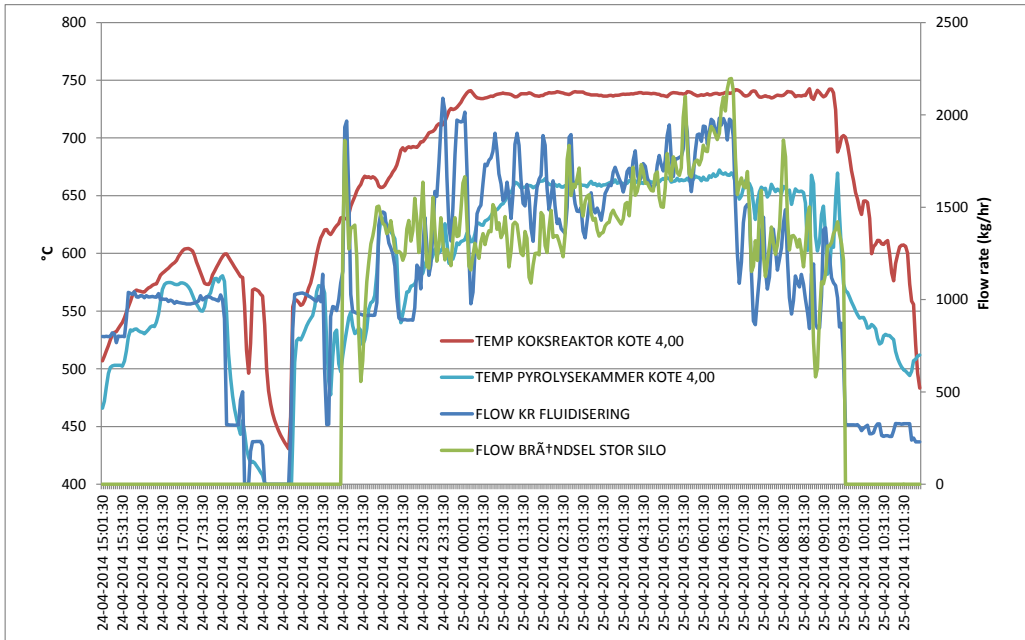
Figure 29: Fuel and gas injection of the CR bed and temp. in the CR and PR

(April 25th 2014)

- During the emptying and the inspection of the char reactor after the shut-down, a number of agglomerates were found, mostly located in the CR-IR duct and therefore blocking the sand circulation. It was also noted that a large piece of refractory had fallen from the wall (cf. Figure 30 and Figure 31). It is possible that this large piece has disturbed the fluidization of a part of the bed, which could have led to hot spots and agglomeration. Generally, the refractory was found to be in a bad state and required refurbishment. This may have been due to the fast temperature increase observed in December 2012 when a small flow rate of air was added to the char reactor bed during shut down, while the CR bed still comprised char.

Figure 30: Piece of refractory in the CR bed

Figure 31: Refractory wall in CR (May 2014)

- The agglomeration occurred after operation with beet seeds. This fuel was used for the first time in a Pyroneer gasifier. It was observed that the Na, K and Cl content is generally high. Phase equilibrium calculations show that the presence of NaCl and KCl in the ash may entail the decrease of the sintering temperature.
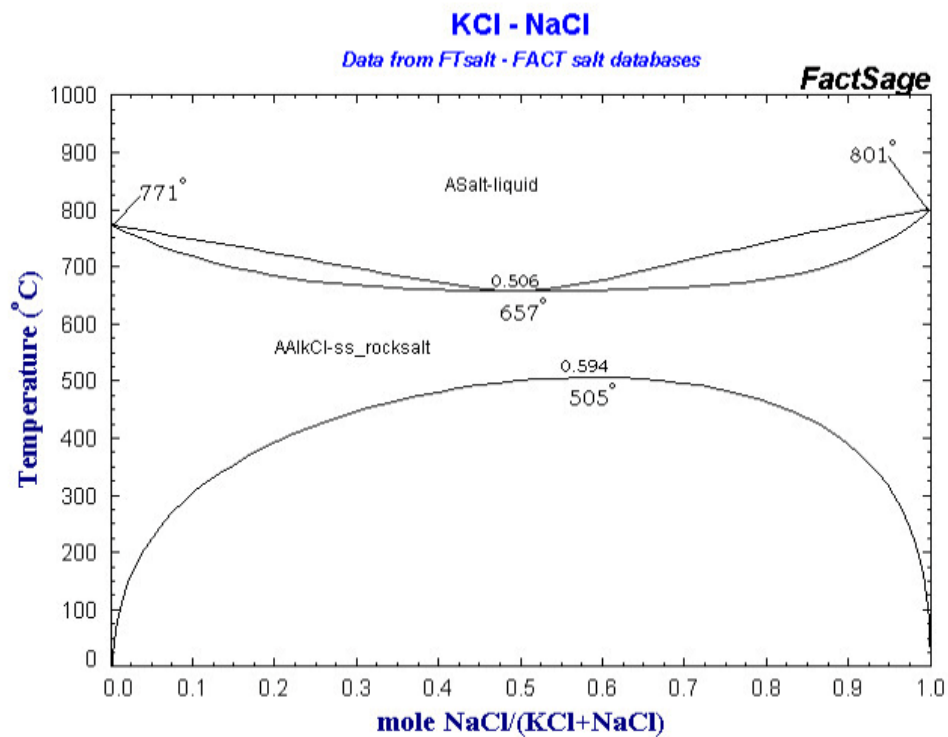
Figure 32: Equilibrium phase diagram for NaCl and KCl

3.6.2.3 Conclusion and recommendations for the June 2014 Campaign

There are several hypothesis that could explain why the agglomeration occurred.

- Before the trip, the fuel addition to the gasifier was varying significantly. According to the data from the control system, no fuel was fed to the gasifier for a short moment. This led to a variation of the air flow rate to the char reactor which may have disturbed the fluidization of the bed.
- The gasifier was emptied and the char reactor inspected. A large piece of refractory had fallen down. This may have disturbed the fluidization and induced agglomeration.
- The beet seeds that were used during operation contain a large content of Na, Cl and K. the special composition of the ash from that fuel may imply a decrease of the temperature at which agglomeration starts.

Based on this analysis, different modifications have been implemented, both related to the control system and to the reactor and equipment design.

No further tests confirming the hypothesis that the special beet seed composition resulted in the agglomeration are planned. Given the low commercial potential of a Pyroneer unit operated on beet seeds, it was decided not to operate the Pyroneer gasifier on beet seeds.

3.6.3 Week 25 – 28, 2014

This chapter gathers results and experiences from the Pyroneer 6 MW operation campaign done in week 25 to 28, 2014.

This is the second operation of the 6 MW gasifier after the installation of the new fuel silo allowing the feeding of alternative fuels. This is the 4th campaign with the new set of cyclones. The previous campaign resulted in bed agglomeration during the operation with beet seeds, after a few hours of operations, which therefore resulted in a very low availability.

Several actions have been taken in order to limit the risk of agglomeration during the campaign:

- Refurbishment of the char reactor lining. It was decided to lower its diameter in order to increase the velocity at nominal load and to give more flexibility in terms of fuel load so that the reactor design envisioned for the large-scale unit could be validated.
- Modifications have been made regarding the control of the fuel feeding from the big silo in order to limit the variation of the fuel input.
- Modifications have been made in the control system in order to ensure a high velocity if the fuel input drops. The N_2 is not accounted in the flow rate calculated for minimum fluidization velocity.
- It was decided to avoid using beet seeds as a fuel.

In this operation period the fuel will be:

- Straw pellet
- Loose shea nut residues

In addition, modifications to the fly ash container were made in order to reduce dust nuisance and get data that are more reliable. Furthermore, the HTAS tar reformer unit used at the Skive gasifier has been installed at ASV and will be commissioned during this operation period.

It is crucial that the gasifier availability of the gasifier is high during this campaign. In addition, improvements must be made in relation with the accuracy of the mass and heat balance calculations. It is critical that a high K retention can be proven. Furthermore, a high gasifier efficiency must be proven. It is therefore necessary to improve the mass and heat balance calculations. Dust flow rate and composition will be measured. The fuel flow rate input assessment will improve thanks to the weight cell signal. It will also be possible to sample bed material to assess the char and ash contents.

3.6.3.1 Objectives

There were five main objectives for this operation period:

1) Potassium balance data
   a. Better data must be produced to make more accurate potassium mass balances by getting good samples of fuel, cyclone ash, dust in the gas and bed material
2) Reference data for upscaling
   a. Measuring gas composition with emphasis on NH3 and HCN to give input to calculations of NOx emission from gas burner
3) First test of loose shea nut residue
   a. Demonstrate operation on this new and cheaper fuel with the new fuel silo
4) Commissioning of new tar reformer system
   a. Fault finding and correction and achieve first tar reforming results

3.6.3.2 Results

3.6.3.2.1 Campaign overview

Table 4: Mass of fuel gasified during the June 2014 campaign

Straw pellets	Loose Shea
tons	tons
181	119

- About 246 MWh electricity was produced by combusting the Pyroneer gas in ASV2.
- About 43.9 tons ash was produced during the campaign.
- The campaign resulted in about 206 operating hours in gasification mode.
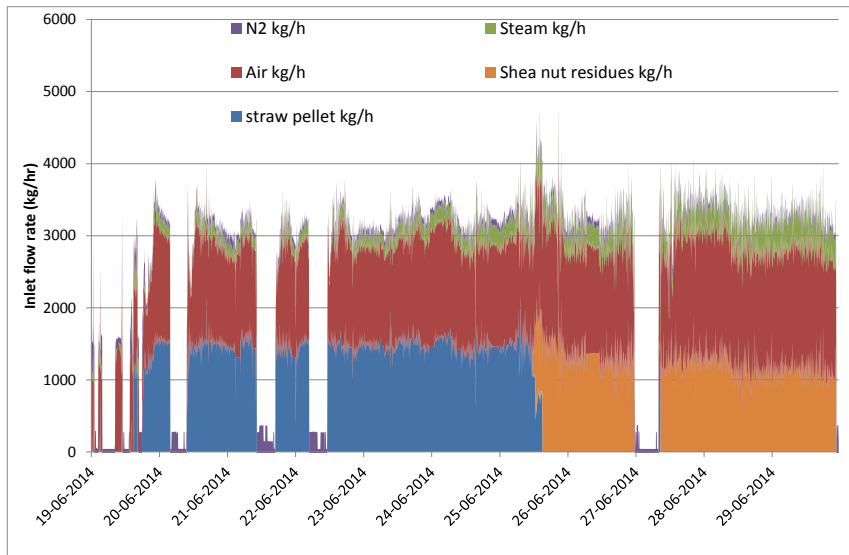
Figure 33: Mass input to 6 MW gasifier in June 2014
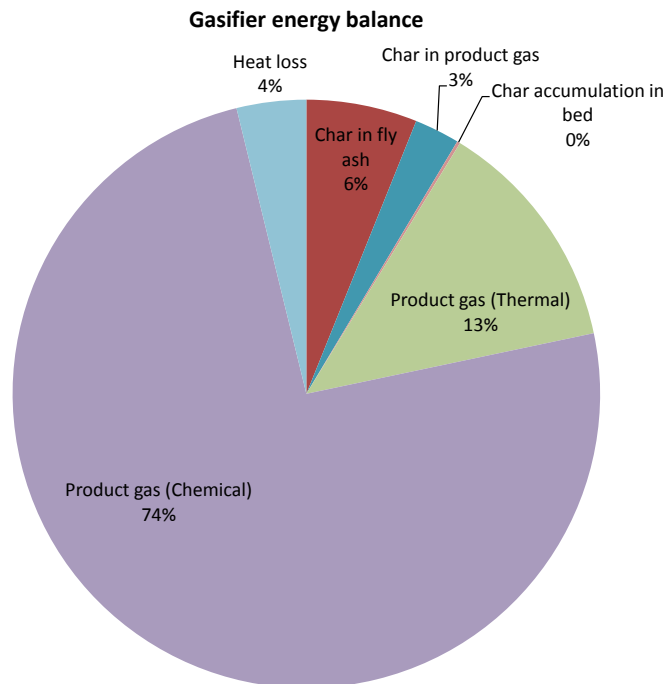
Figure 34: Gasifier energy balance during operation periods (June 2014)

3.6.3.2.2   Reaching Objectives and Success criteria

Below the objectives and success criteria as set up in the operation plan are evaluated for the campaign.

1) Potassium balance data
    a. Better data must be produced to make more accurate potassium mass balances by getting good samples of fuel, cyclone ash, dust in the gas and bed material.

Evaluation:

- SC ash was sampled regularly. The elemental composition of the ash has been measured using the XRF equipment available at DTU Lyngby.
- Few fuel samples are available from the campaign. The ash content was measured at Risø and the ash composition using the XRF equipment.
- A few bed samples are available from the June 2014 campaign. The composition was also measured using the XRF analyser.
- No dust samples could be obtain during the campaign. The evaluation of the dust concentration in the product gas from the mass balance calculations have been compared to the transmission signal in the gas duct.

Table 5: Elemental composition of the fuel ash (June 2014)

		Straw 23-06	Straw 24-06	Straw 25-06	Shea 25-06	Shea 26-06
Na	mass%	0.5	0.8	0.5	0.6	0.1
Mg	mass%	1.5	1.5	1.7	4.1	3.7
Al	mass%	1.1	0.6	1	1.1	1.5
Si	mass%	20.6	9.9	18.7	3.9	5
P	mass%	1.5	1.2	1.6	2.5	3.1
S	mass%	2	2.9	2.2	0.7	0.7
Cl	mass%	3.1	3.5	2.3	1.7	1.4
K	mass%	17.8	18.9	17.4	29	37.1
Ca	mass%	8.6	14.4	11.3	5.1	3.4
Ti	mass%	0.1	0.1	0.1	0.1	0.2
Fe	mass%	0.6	0.3	0.5	0.6	0.9
C	mass%	1	1	1	1	0
O	mass%	41.5	45	41.6	49.7	42.9
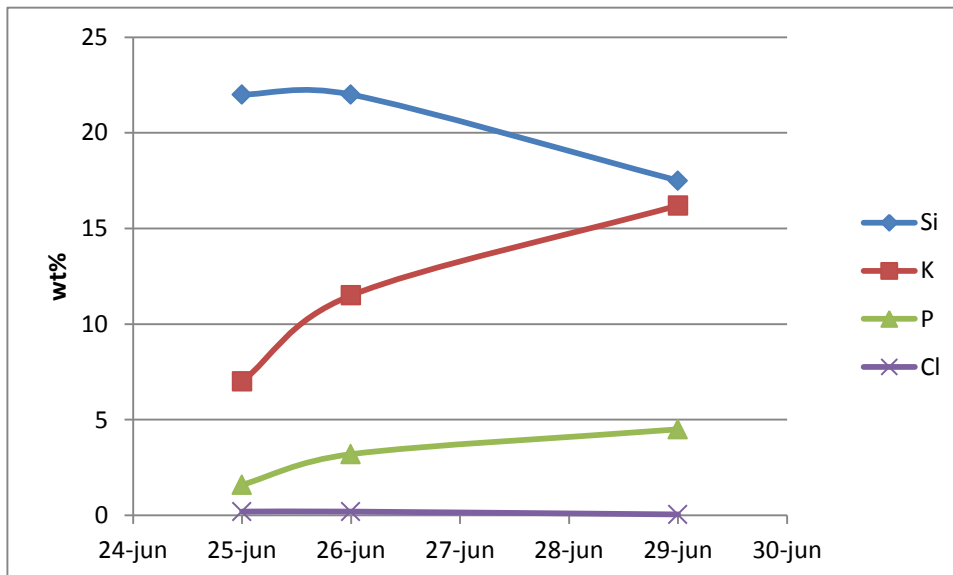
Figure 35: Si, K, P and Cl measured contents in bed material

Ash mass balance
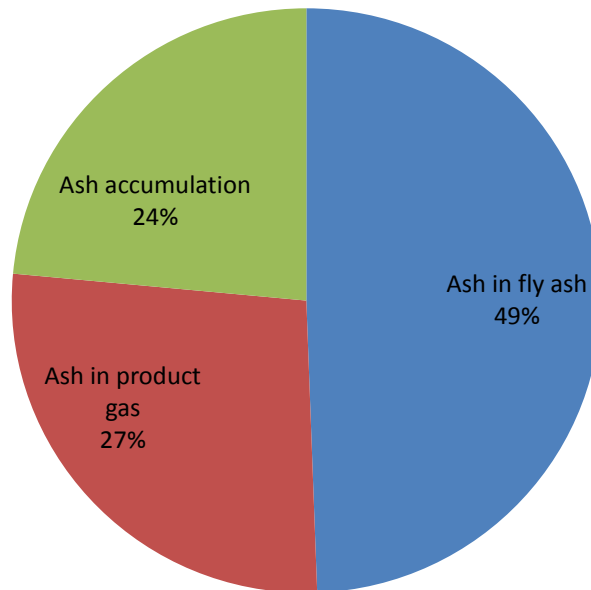
Figure 36: Calculated average ash balance during the operation periods (June 2014)

Table 6: Calculated fraction of the K inlet accumulated in the bed material

	25-jun	26-jun	29-jun
kg K in bed	504	828	1166
K from fuel (kg)	1930	2489	3751
fraction K inlet	0.26	0.33	0.31

It can be observed that the K content in the bed material increases with time (cf. *Figure 35*) which reflects the accumulation of ash in the bed.

2) Reference data for upscaling
   a. Measuring gas composition with emphasis on NH_3 and HCN to give input to calculations of NO_x emission from gas burner

Evaluation:
- The NH_3 and HCN has been measured using different methods while the gasifier was operated on straw
- Two optical methods have been used.
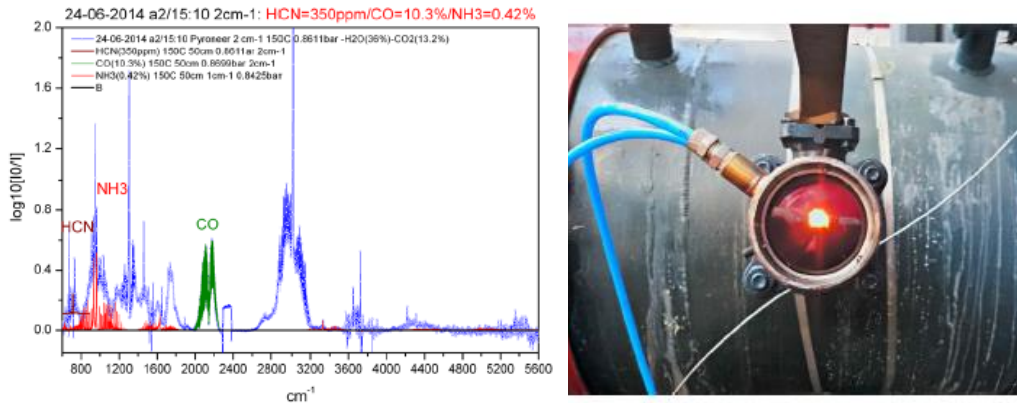
Figure 37: Typical absorption spectrum / Test setup (June 2014)

The description of the methods and the results are available Appendix 3

- The product gas was sampled using a gas pipette and the ammonia content measured by Risø.
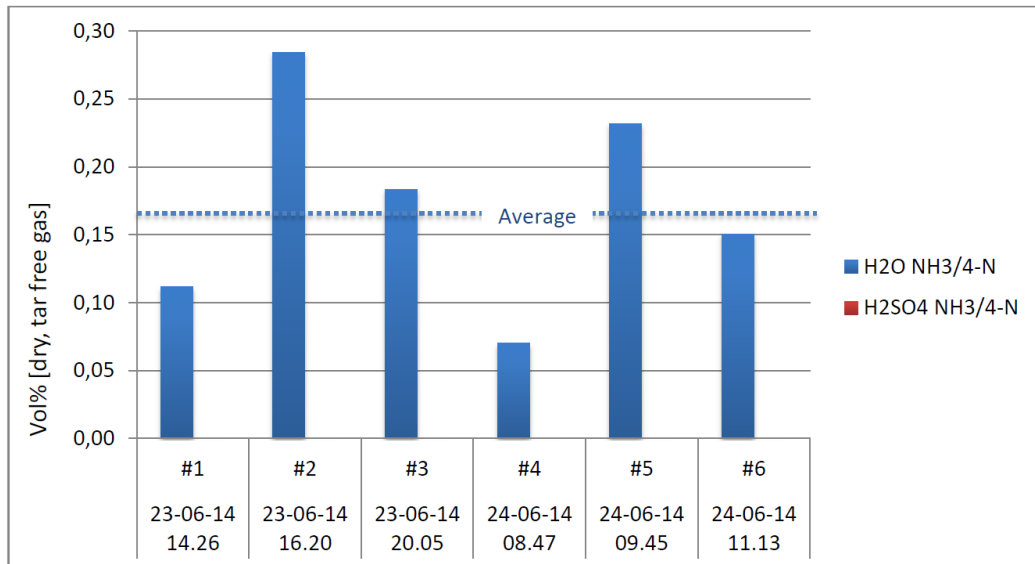
Figure 38: Results from measurements - Risø (June 2014)

More details to be found in Appendix 4.

- The results from the different methods are not in agreement. Hence, additional data and investigations are required to be able to assess the fraction of the N contained in the fuel that is present in the product gas in the form of NH_3 or HCN.

- The optical measurements have been compared with the mass and heat balance calculations using a typical N content in the straw. It shows that in order to match the measurements, about 90% of the N contained in fuel must be present in the product gas in the form of NH_3.

Based on the measurement of the N content in the fly ash from the November 2013 campaign, it can be assumed that a negligible content of the N from the fuel is contained in the cyclone ash. By using the measurements form the N content in straw from the previous operation campaigns, it is possible to compare the model calculations with the measurements.

The composition from the straw pellet from November 2013 has been used in the calculations. By assuming that 90% of the N content is converted in NH_3 and the 10% remaining converted into HCN, the NH_3 and HCN concentrations on a wet basis in the product gas calculated for a stable operation period are respectively 0.43% and 320 ppm. The measurements are therefore very much in line with the calculations.

3) First test of loose shea nut residue
   a. Demonstrate operation on this new and cheaper fuel with the new fuel silo.

Evaluation:
- The unit was operated for three different sets of parameters with loose shea as a fuel.

4) Commissioning of new tar reformer system
   a. Fault finding and correction and achieve first tar reforming results

Evaluation:
- Due to the outage of the plant, no gas was sent to the tar reformer. However, the system was tested and is supposedly ready for the next campaign.

3.6.3.3 Conclusions and plans for future campaigns
Based on the analysis of the results, several remarks can be made:
- The plant was operated with a high efficiency, both with straw and loose shea.
- The operation of the tar reformer could not be started. This should be seen as a high priority during the next campaigns.

3.6.4 Week 35 – 37, 2014

This chapter gathers results and experiences from the Pyroneer 6 MW operation campaign planned to take place in week 35 to 37, 2014.

This is the second campaign for the 6 MW gasifier after the repair and modification of the ceramic lining in the char reactor. Also second campaign with the new fuel silo and with loose shea as main fuel.

Last campaign in week 25-28 2014 was very successful and proved stabile operation with loose shea from the new silo (e.g. new record of 106 hours without trips) and data showed that efficiency and stability could be maintained at a high level with the new char reactor design at a broad fuel load. No agglomeration was encountered during operation even though up to 16% potassium was measured in the bed material.

Some problems was encountered with the center screw in the new silo which got bend and damaged the bottom of the silo. The repair of this caused a longer outage. During restart of the gasifier too high temperatures was encountered in the cyclones and due to the high potassium content in the bed material the primary cyclone particle outlet got blocked. The gasifier had to be cooled down in order to remove this and the campaign therefore had to be ended. The shea ash produced from the secondary cyclone had a tendency to self-ignite which made it more difficult to handle. Probable cause of this was most likely insufficient cooling and humidification.

Focus in week 25-28 was mainly on efficiency and the target of >90% was achieved. Ash retention was however lower than anticipated and varying. This was therefore main objective for the week 35-37 campaign.

3.6.4.1   Objectives and Success criteria
There were three main objectives for this operation period that were prioritised in the below order:

1) **First tests with tar reformer system**
   Most systems on tar reformer system was commissioned during week 25-28 campaign and objective for this campaign is to make first tests with full system including dust filter, tar reformer and gas analysis equipment. Tests will show how much of the tar is re-formed and the resulting gas composition.
   a. Success criteria is to achieve >100 operating hours for the dust filter + tar reform-er + gas analysis equipment

2) **Ash retention**
   The main feature of the Pyroneer concept is that most of the fuel ash can be retained and not send to the boiler. More measurements and data are needed to prove that a high ash retention can be reached and maintained. Primary focus is potassium reten-tion.
   a. Success criteria is >85% potassium retention
      To prove this; potassium balances must be set up for at least 3 periods of mini-mum 24 hours duration
   b. SC ash system operation and SC ash buffer level must be optimised to achieve highest possible secondary cyclone efficiency. Also a good ash quality with re-gard to handling must be achieved.
      Success criteria is to find a new set point for ash screw +rotary valve +humidifier +water addition which gives a high secondary cyclone efficiency and at the same time secures that the ash is not so dry that it self-ignites or creates dust nuisanc-es nor that it is so wet that it cannot easily be emptied out of containers.
   c. L-valve operation must be optimised to achieve highest possible primary cyclone efficiency. Focus is ash retention and on minimizing dust amount send to the boiler. Success criteria is therefore to find the set point for height in L-valve that gives the lowest dust amount in the gas evaluated on the online dust sensor. Similarly the setting for the trim valves on the L-valve air must be optimised.

3) **Reference data for upscaling**
   The June 2014 campaign gave data on straw firing suitable for evaluating NO_x emission from a gas burner. At least one more data point on shea (high N content) is needed to be able to model NO_x emission from future plants and fuels with different N content. More data is also needed to refine the design of the char reactor in upscaled plants. Results from the earlier campaigns has shown that long continuous periods (>24 hours) are needed between parameter changes before new stable conditions are reached.
   a. Measuring gas composition with emphasis on NH_3 and HCN to give input to cal-culations of NO_x emission from gas burner when operating on loose shea
      i. Success criteria is at least one good, reliable measurement with both tech-niques: Wash bottles and Optic (done by Risoe – KT/DTU)

b. Operate the gasifier at different loads to vary the bed velocity and the freeboard retention time to achieve comparable data for upscaling.
   i. Success criteria is continuous operation for >24 hours with 2 different fuel loads and 2 different freeboard retention times and bed velocities

The plant should be kept in operation as stable and for as many operation hours as possible in the 3 week operation period. Long periods with stable operation between parameter changes are prioritised so that good data can be secured.

Startup and first operating hours will be done on straw pellets because the external storage needs to be emptied (~20 tons). After that the rest of the campaign will be on loose shea. Straw pellets are used as backup in case of minor problems with the loose shea system.

3.6.4.2 Results

3.6.4.2.1 Overveiw

After 10 hours of operation with straw followed by 21 hours of continuous operation on loose shea the gasifier has tripped at 1pm. Before the trip, the temperatures and circulation was very stable.

The trip was due to a high temperature measured in IR. That temperature was a consequence of a disturbance of the circulation, which lead to a drop of the temperature in PR. The gas flow rate to the IR and CR-IR duct increased and so did the temperatures, which increased very fast in CR, IR and CR-IR duct.

It was decided to discontinue the test campaign. The data to fulfil the above objectives was not obtained and the analyse phase was dedicated to analysing the trip that lead to the outage of the 6 MW unit during the August 2014 campaign.

3.6.4.3 Analysis and results

3.6.4.3.1 Analysis of the operation before the trip

- During the operation with loose shea, the temperatures in the various parts of the process were very stable. As shown in Figure 39, the temperatures in CR and PR are stable and close to the chosen set point.
- The fuel input to the gasifier calculated based on the evolution of the fuel weight in the silo, is varying. Consequently, the flow rate of fluidizing gas to the char reactor is varying as well.
- The bed mass when the operation with shea started was about 4000 kg. Based on the operation during the June 2014 campaign, the bed mass set point was set to 2400 kg. Hence, the IR bed extraction system was used to decrease the bed mass. On September 4th at 5 o'clock in the morning, the bed mass set point was reached while the mass was still decreasing. It was therefore decided to add sand to the gasifier in order to stabilize the bed mass.
- Because of the decrease of the bed mass, the gas flow rate to the IR bed continuously increased during the operation in order to maintain a constant solid circulation.

It has been observed that the level of H_2 in the CR gas was significantly lower than what was observed in June 2014 during the operation with loose shea for similar steam to air ratios. Based on the gasifier model calculations, it was estimated that about 20% of the steam added to the gasifier was reacting with char, against 40% during the June campaign with shea.

Fuel composition measurements (ash and moisture contents and ash composition) and possibly char reactivity measurements will be conducted to assess the fuel that was used during the operation.

The table at the bottom of the figure:

...	SIGNAL TAG	DESIGNATION	RANGE LOW	RANGE HI	CURSOR 1	CURSOR 2	Y DIFF	UNIT	LAST
	23RAA10FP945A,,XQ02	dP PK FRIBORD	0.0000	25.0000				mbar	-1.0419
	23RAA20FL901A,,XQ23	MASSE KOKSREAKTOR	0.0000	10000				kg	2747
	23REC21FF001,,XQ01	FLOW KR-MR KANAL FLUIDIS...	0.0000	130.0000				kg/h	4.9323
	23REC20FF001,,XQ01	FLOW KR FLUIDISERING	0.0000	2200				kg/h	330.2859
	23REC30FF001,,XQ01	FLOW MR FLUIDISERING	0.0000	400.0000				kg/h	28.0787
	23RAA10CT955A,,XQ01	2oo3 TEMP PYROLYSEKAMME...	600.0000	700.0000				°C	580.4204
	23RCB80FF001,,XQ14	FLOW STOR SILO (dW VÆGT)	0.0000	2500				kg/h	-0.9338

Figure 39: The trip 1#3

3.6.4.3.2   Analysis of the trip

- The trip occurred at 13:09 on September 4th due to a high temperature in IR. It can be seen that a high temperature in CR and in the CR-IR duct was also observed (cf. Figure 40).
- The trip was due to a drop of the circulation at about 13:01, as seen in Figure 40.
- Before the drop of the circulation, the temperature and pressure profiles in the char reactor, intermediate reactor and pyrolysis reactor were not showing any disturbance.
- The stoppage of the circulation could be due to a blockage in the L-valve, in the bottom of CR, in the CR-IR duct or in the IR-PR duct. As shown in Figure 40, the level in the L-valve, in IR and in PR tend to decrease when the circulation stops. This tends to show that the disturbance of the circulation is due to a blockage in the CR-IR duct or at the bottom of the char reactor.
- The fast rise of the gas flow rate to IR or to the CR-IR duct is not responsible of the blockage by changing the direction of the gas flow, since the blockage of the circulation happens before.
- The trip occurred about 20 minutes after a large increase of the gas addition to the char reactor consecutive to a rise of the fuel load to the gasifier. This fast rise of the gas flow rate is followed to a fast decrease of the fluidization

air. This may have disturbed the stability of the fluidization of the char reactor.

- It was noted that due to the high set point for the steam to air ratio to the CR-IR duct, steam condensation probably occurs before the gas mixture reaches the nozzles below the CR-IR duct. The water condensation can significantly disturb the gas distribution among the nozzles and entail disturbance of the circulation.

After the trip, the maximum temperature in the bed (cote of 3m, in the middle of the bed) stays at the same level for a long period, while the other temperature measurements are decreasing fast. This may be due to the low fluidizing gas flow rate during the inerting of the gasifier.
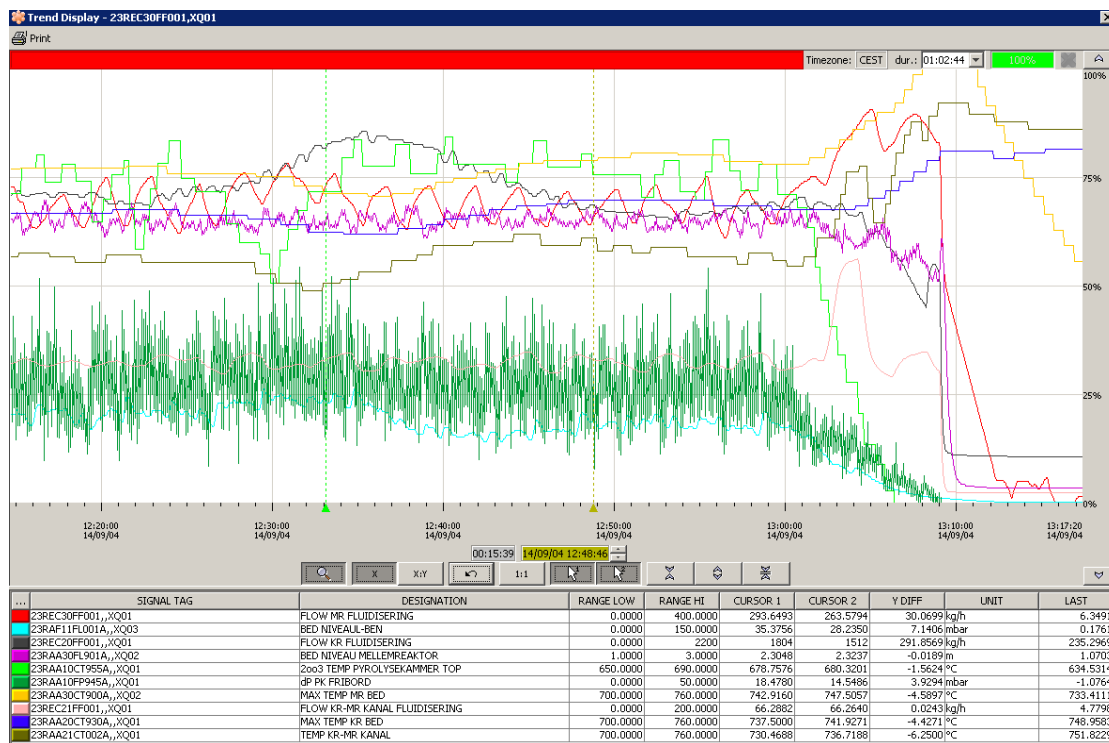
Figure 40: The trip 2#3

Figure 41: The trip 3#3

3.6.4.3.3 Post-test inspection

- During the inspection, it was observed that the CR bed was transformed into a massive and very hard agglomerate.
- The same observation was made during the inspection of the IR using a borescope.
- The high concentration of steam in the bed may affect the melting point of some compounds in the bed material and induce agglomeration at low temperature. (See text-box below, Figure 42)

K₂0-Si0₂

The phase-equilibrium relations in the system
K_2O-SiO_2 were first inferred from the study of the
ternary system H_2O-K_2SiO_3-SiO_2 by Morey and Fenner
(1917), who found the hydrate, $K_2O \cdot 4SiO_2 \cdot H_2O$,
but did not prepare the anhydrous tetrasilicate itself.
The compound $K_2O \cdot 2SiO_2$ was first prepared by Morey
(1914). The results of the study of the the system
$K_2O \cdot SiO_2$-SiO_2 by Kracek, Bowen, and Morey (1929,
1939) are shown in figure 4 and the invariant points are
given in table 4. Evidence that no orthosilicate exists
was given by Morey and Fenner, but it was not conclusive
and more study is needed. Potassium metasilicate,
$K_2O \cdot SiO_2$, melts at 976 °C and crystallizes
readily. The melt retains CO_2 tenaciously and is hygroscopic.
**When melted in an atmosphere of steam,
water is taken up, the melting point is lowered, and
on cooling, the melt crystallizes with evolution of steam,
giving an excellent second boiling point. Potassium
disilicate, $K_2O \cdot 2SiO_2$, melts at 1045°C, crystallizes
readily, and has an enantiotropic inversion at 594°C.
Potassium tetrasilicate, $K_2O \cdot 4SiO_2$, melts at 770° C, has
a reversible inversion at 594°C, and is very difficult to
crystallize**. Potassium silicate glasses richer in SiO_2
than the disilicate are more difficult to crystallize than
the corresponding sodium silicate glasses, and both glass
and crystals are very hygroscopic.

Figure 42: K_2O-SiO_2 Phase-equilibrium[2]
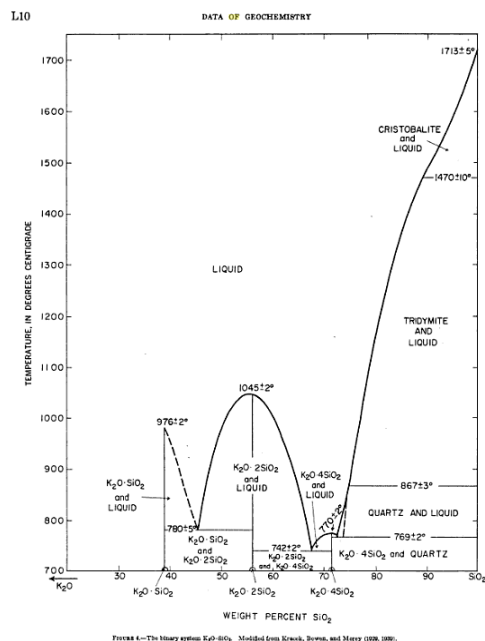
Figure 43: K_2O-SiO_2 Phase-equilibrium – phase diagram[2]

[2] Source: Data of Geochemistry, Sixth edition,1964; Chapter L: Phase-equilibrium Relations of the Common Rock-forming Oxides Except Water (George W. Morey)

3.7 WP5 Pressurisation and concept design

3.7.1 Summary of objectives

Based on the analysis of the data generated at the 6 MW unit in Kalundborg, a gasifier model has been developed. It allows for describing the reactions taking place in the different reactors of the Pyroneer process and to calculate the properties of the different streams. This model has had various applications, in the context of upscaling projects, optimisation of the reactor design and optimisation of the operation of the gasifier.

The gasifier model has then been upgraded to be applied to pressurized design and O_2-blown gasifier in order to enlarge the range of applications of the Pyroneer gas.

Different development routes have been identified, and the model has then been extended so that it includes the gas cleaning steps and the downstream application of the Pyroneer gas.

3.7.2 Development of a gasifier model for atmospheric gasification

3.7.2.1 General description - reproduction of the operation data of the 6MW

A large part of the work consisted of developing a model that could reproduce the reactions taking place in the different reactors. The model was developed in Excel based on the experimental data from the 6 MW gasifier. It has been constantly updated and upgraded with the new data generated and the additional knowledge from the operation of the demonstration plant. Each modification of the model has been documented.

The first part of the development consisted in reproducing the gas composition from the char reactor. A mixture of air and steam is added to the bottom of the char reactor in order to gasify the char separated by the primary cyclone. This gasification reaction is exothermic, which implies the increase of the bed material temperature. The hot bed material is then transferred back to the pyrolysis reactor in order to ensure the endothermic pyrolysis of the fuel. Typically, the temperature in the char reactor is comprised between 720 and 750°C while the temperature in the pyrolysis reactor is comprised between 630 and 690°C. Different reactions are considered in the model to describe the char gasification. However, at the conditions applied in the reactor, thermodynamic equilibrium is not reached. Figure 44 shows the comparison between the calculated dry composition of the gas from the char reactor against the experimental measurement of the dry gas composition measured on site. A very large gap can be observed between the model calculations and the experimental data. Hence, a modification must be implemented to the model. Some parameters have been used to reflect the deviation from the equilibrium. The fitted calculations can be seen in Figure 45.
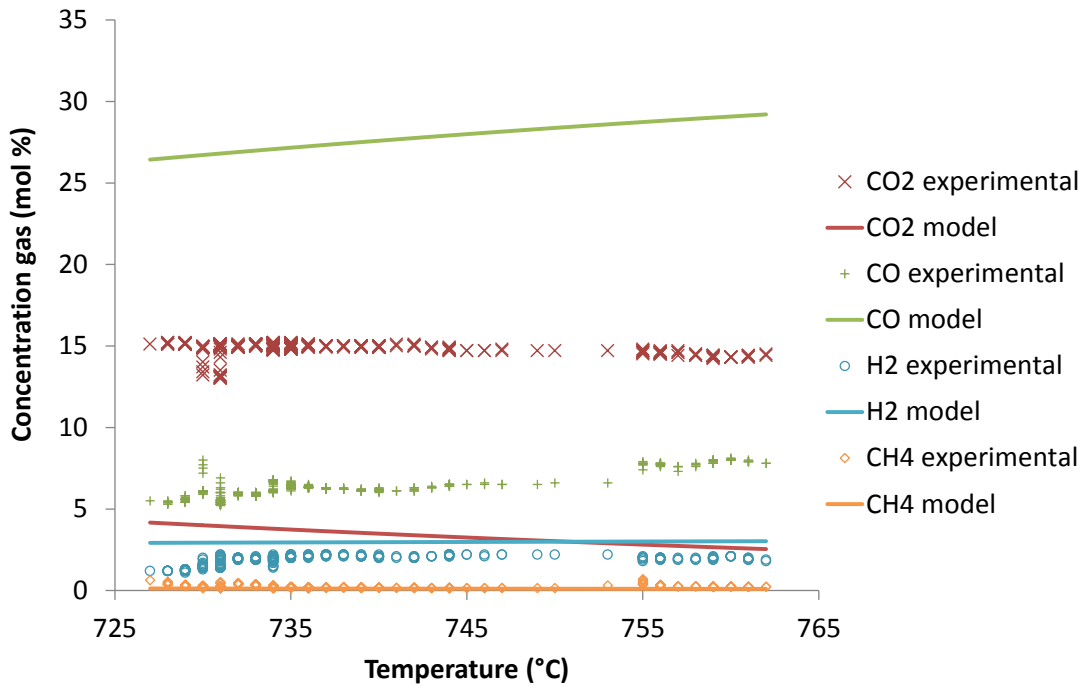
Figure 44: Comparison between the calculated and the measured dry gas composition

(If equilibrium is assumed)

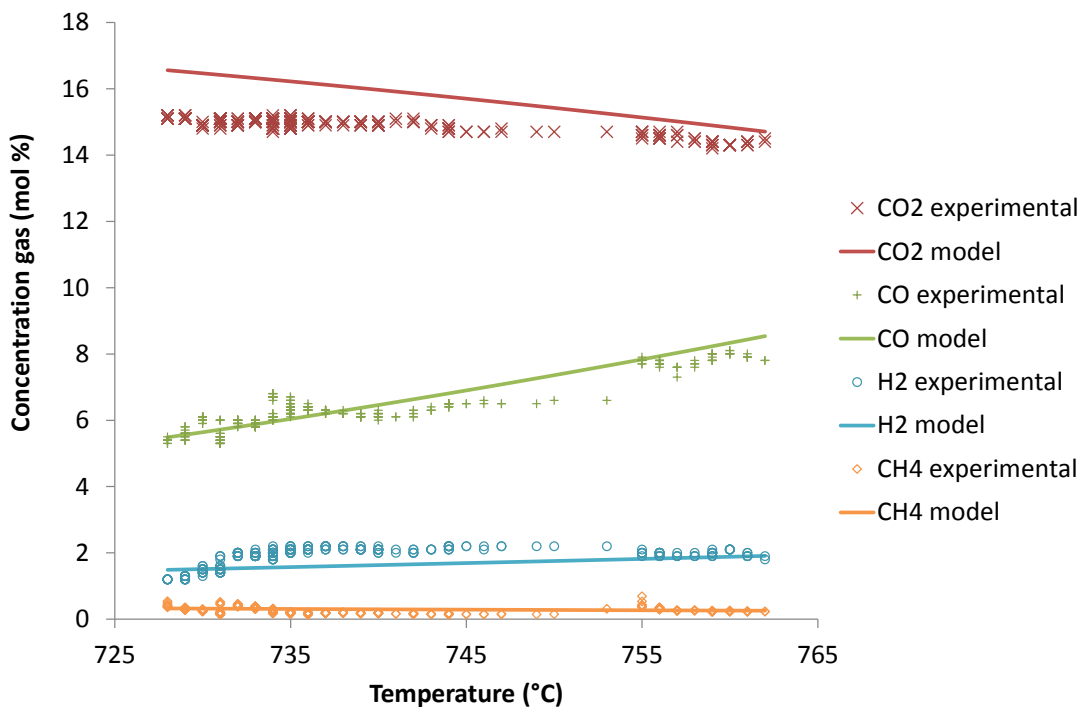*Figure 45: Comparison between the calculated and the measured dry gas composition*

(By fitting model parameters)

Based on the analysis of the data from the different campaigns, the model has later on been improved so that it can reproduce the experimental data over the range of experimental conditions applied in the reactor. However, this analysis was still ongoing when the project was stopped.

The detailed analysis of the reaction between char and the gasifying agents has led to a better understanding of the reaction taking place. Since the efficiency of the unit is largely depending on the high conversion of the char, this analysis has contributed in increasing the efficiency of the unit by optimizing the operating conditions. This increase of the efficiency has a very positive impact in terms of business case for a large scale Pyroneer gasifier.

The modelling of the gas from the char reactor was followed by the study of the composition of the gas from the pyrolysis of the fuel as a function of the temperature as well as the char and tar yields. Detailed mass and energy balance calculations were required for this study in order to reproduce accurately the data from the demonstration unit. In addition, the identification and quantification of the tar compounds in the product gas. Hence, the results from Gasolution WP1 were extensively used in the development of the model.

The model has been used for each of the operation campaign in order to analyse the performance of the gasifier and to identify the effect of the variation of process parameters. The uncertainties relying in the calculations from the model have been described and documented. Additional measuring devices were implemented from a campaign to the other in order to limit these uncertainties.

The demonstration unit has been operated with different fuels. Based on the analysis of the operation data, the model has been developed for these different fuels. A fuel library has been implemented in the model in order to change easily the fuel used in the calculations.

The model has been developed making sure it was user friendly. The inputs and outputs are clearly indicated and documentation has been written.

3.7.2.2   Main applications of the model
- The data analysis has also allowed to assess the performance of the cyclones at the demonstration unit. It was observed that the separation efficiencies were lower than expected. It was therefore decided to purchase new cyclones in order to increase the efficiency and ash retention performances.
- The model has been applied for the data analysis of the 100 kW unit located at Risø for different fuels.
- The model is based on a large number of inputs representing the conditions at which the gasifier is to be operated. The calculations also rely on a number of assumptions that have been documented. The model then allows for calculating the complete mass and heat balance of the different streams for given process conditions. The model has therefore been extensively used for upscaling projects of the gasifier.
- Based on the mass and heat balance, the model has been used to design the reactors based on design rules. These design rules have been modified based on the analysis of the data and the optimisation of the operation of the plant. The design of the char reactor has especially been modified based on the conclusions from the study of the char reactivity.
- The mass and heat balance combined with the design of the reactors and equipment led to the evaluation of the CAPEX of a large scale unit. The results were generally used for business case analysis and market evaluation.

3.7.3 Potential development route of Pyroneer V2.0

Figure 46 describes the potential routes for the development of Pyroneer.
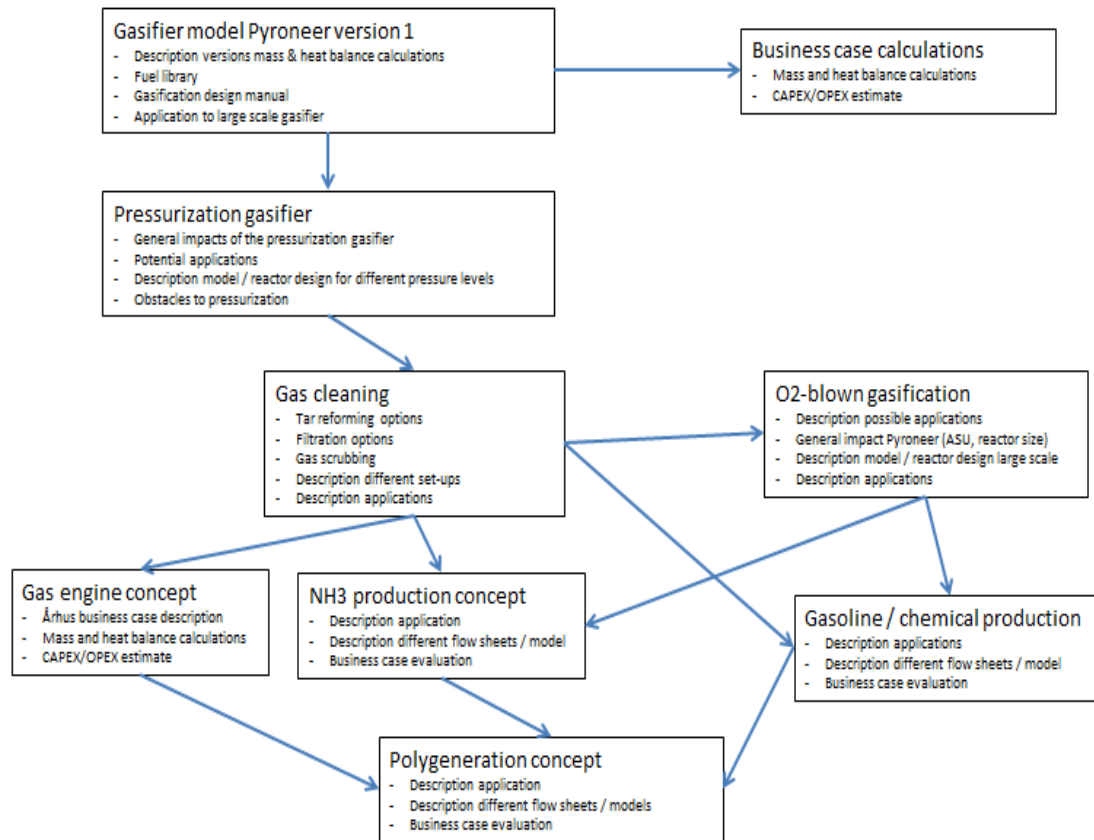
Figure 46: Potential development routes for Pyroneer

- Pyroneer version 1 corresponds to the atmospheric gasification that can be used directly for co-firing.
- A business case of a stand-alone Pyroneer unit in the context of a specific industrial project, for steam, district heating and power production has been analysed. The results showed a very positive business case that showed the potential of the Pyroneer technology.
- Many applications for the product gas require to pressurize the gasifier. The required level of the pressurization depends on the application considered.
- The applications corresponding to Pyroneer version 2 require to remove the dust and to reform the tar compounds present in the product gas. Hence, the relevant system must be evaluated and designed. This work is done in connection with Gasolution WP1, WP2 and WP6.
- One of the applications of the product gas after it has been cleaned is the power and heat production with gas engines. This possibility is especially relevant for stand-alone units. The advantage of the use of gas engines is the high electrical efficiency, especially for small scale units for power production. This development route is therefore promising. A business case has been made and analysed.
- The production of NH_3 from the product gas is a relevant application to the product gas. It is compatible with air-blown gasification. However, experimental data are required to confirm the feasibility of the process.

- The product gas after cleaning can be used to produce gasoline or chemicals through catalysed reactions. The chemical production from gasification is being studied in various research groups. Many of the applications considered require that the gas is N_2-free. Hence, O_2-blown gasification would be necessary. The synthesis is taking place at high pressure. SNG is a possibility that is already experimented on a large scale in the context of the GoBiGas project in Sweden. Other synthesis are tested at the Güssing and Oberwacht plants in Austria. Fisher Tropsch processes for diesel synthesis are tested. Alcohols, SNG and purified H_2 production are also experimented on a lab scale. Similar assumptions can be applied to the Pyroneer to investigate the potential of Pyroneer version 2. It should be noted though that the gas produced at Güssing is N_2-free.
- Based on this analysis, the poly-generation concept can be studied. It consists of producing power and steam when the demand is high and chemicals when the demand is lower. One of the main drawbacks of such concept is the high CAPEX required to produce both chemical and power.

3.7.4 Development of pressurized gasification model

The model developed for atmospheric conditions based on the data from the demonstration unit has then been upgraded so it can be applied to pressurized conditions. The modelling has been made based on assumptions from the literature on pressurized gasification processes. The influence of the pressure on the tar composition, gas composition, char yield and char reactivity has been especially studied.

The model can be used to size reactors assuming design rules similar to the ones developed for atmospheric gasification are applied. The reactor inner design has been studied for four different pressure levels that correspond to different potential applications for the gas. Based on the design and on the pressure level, the required thickness of the walls in the reactors and ducts can be determined.

The main mechanical obstacles from the pressurization of the gasifier have been identified and analysed.

- The feeding of the fuel to a pressurized vessel requires a specific design. Briquetting solutions are already available and compatible with the feeding of straw.
- The ash extraction system also needs to be designed so it is compatible with a pressurized operation of the gasifier.
- The decrease of the size of the vessels allowed by the pressurization must be compatible with the required solid circulation. The heat demand in the pyrolysis reactor is little affected by the rise of the pressure. Hence, it must be ensured that the solid circulation is not affected by smaller reactors and narrower ducts. This shows that the design rules applied to the atmospheric gasification must be adapted for high pressure gasifier in order to ensure unproblematic operation.
- The primary cyclones must also be designed for a high separation efficiency despite the lower dimensions from the high pressure. The design must be studied in collaboration with cyclone manufacturers.

3.7.5 Development of O_2-blown gasifier

Potential applications to the product gas require that the gas is N_2-free. The most obvious one is the production of synthetic natural gas. In order to study the potential and obstacles from this version of the process, the gasifier model has been adapted so that it can be applied to O_2- blown gasifier.

- The different commercial options available for the production of O_2 have been analysed. The suggested option depends on the size of the gasifier, linked to the O_2 requirement, and the required purity of the O_2 produced.
- The model allows for calculating the mass and heat balance of a Pyroneer gasifier for a given fuel load and pressure at the outlet of the gasifier. The properties of the product gas are especially interesting in the context of the downstream application of the gas.
- Based on the mass and heat balance calculations, the pressure profile in the gasifier is calculated. In addition, using the atmospheric gasifier design rule, the reactor design can be studied.

The main obstacles and challenges entailed by the use of O_2 instead of air to fluidize the reactors have been identified.

- The design rules of the main reactors must be adapted to the use of O_2.
- The explosion protection philosophy must be updated.

3.7.6 Gas cleaning

3.7.6.1 Tar reforming

The tar contained in the product gas is mainly problematic because of the high dew point temperature. This dew point temperature can be estimated based on the tar composition. Large molecules contained in the tar entail the increase of the dew point. The applications considered in Figure 46 require to cool down the gas to a temperature lower than the product gas dew point. It is therefore required to remove or convert the tars contained in the product gas.

The tar content in the Pyroneer product gas represents a very significant fraction of the gas heating value. Hence, removing the tar by scrubbing the gas is not a viable option for Pyroneer. It must therefore be investigated how to convert the tar by using a reformer. The tar reformer implemented at ASV was supposed to be used to test the action of a catalyst developed by Topsøe on the Pyroneer gas as a function of the temperature. Unfortunately, no data were obtained before the project was stopped. Traditionally, the tar reformer is operated at higher temperature. In addition, the tar composition and content in the Pyroneer gas is very different from the one observed in commercial processes. The efficiency of the catalyst is therefore uncertain in the absence of experimental data.

The increase of the temperature by oxidizing partially the product gas has been investigated. Experiments were performed at the 100 kW unit at Risø that show that the partial oxidation of the product gas allow for elevating the gas temperature and reducing drastically the tar content in the gas. The temperature increase would allow for using conventional tar reformer processes to convert the remaining tar.

The tar reforming entails a pressure drop and therefore requires the pressurization of the gasifier compared to Pyroneer version 1 where the gas is sent to a boiler.

3.7.6.2 Filtration

Despite the presence of two cyclones in series to separate the ash and sand from the gas, dust is still present in the product gas. In the applications described in Figure 46, extensive dust removal is a requirement.

The catalyst that was to be tested at the 6 MW unit was not dust compatible, which is why a filter was implemented upstream the reformer. Other commercial catalyst operating at high-

er temperature are dust compatible. Hence, the filtration step could occur downstream the tar reformer, at low temperature, which would allow for limiting the cost of the filter.

The results from Gasolution WP2 on the 100 kW unit show that filtration of the gas at high temperature is possible. However, this step is very CAPEX intensive and has not been proven over long time tests.

3.7.6.3   Scrubbing

The filter must for most of the applications considered be combined with a scrubber to remove the residual impurities present in the gas. The temperature applied in the scrubber will affect the water content in the gas. For many applications, such as the use of gas engines, a minimum heating value in the gas is required. Hence, the water scrubbing is a way to increase the heating value to make it compatible with gas engine combustion. Experience from other gasification technologies show that the scrubbing of product gas from gasification is not unproblematic.

3.7.7   Modelling of Pyroneer version 2

Based on various assumptions, the gas cleaning steps have been implemented in the gasifier model. The tar reforming reactions have been assuming different cases, depending on the extent of the reactions taking place in the reformer. The gas composition after the scrubber has been modelled assuming that the gas is saturated with water at the chosen temperature. The heat produced or extracted in the different steps of the process are considered in the model. The gas composition after each step of the process can therefore be estimated by the gasifier model. Commercial simulators have then been used to model other unit operations in order to ensure accurate calculations. The power, steam, heat and chemical production can therefore be determined. CAPEX and business case analysis can then be studied using these tools.

3.8 WP6 Slip Stream Tar reforming by HTAS/DTI pilot

The overall goal for the tar reformer is to convert the tar molecules in the gasification gas into synthesis gas. This has at least two great advantages; first of all having tars in the gas introduces a risk of fouling the downstream process, by reforming the tar this risk is eliminated. As a side effect, the tar is transformed into synthesis gas, which may be utilised. Tar molecules are in this context considered to be any aromatic compounds, including benzene, which does not contain impurities such as O, S or N.

The tar composition in the Pyroneer gasification gas is slightly different from most other biomass gasifiers. As the main difference this gas contains a large amount of oxygenates and a relatively low amount of tar molecules. The aim of this study was to address the issues in having oxygenates in the gas stream and finding an industrial applicable solution for removing them from the gasification gas.

3.8.1 Construction, installation and initial testing of tar reforming setup

3.8.1.1 Design of setup

Although some key components could be re-used from a previous EUDP project the whole setup still had to be re-designed to fit the system properties in Kalundborg and the space in the container.

The setup consisted of a pilot reactor and a filtration unit as the two primary parts, both of these were constructed in a previous EUDP project taking place in Skive. The pilot reactor is an approx. three meter long special high temperature steel alloy tube, in which the tar reforming catalyst is placed. The reactor is heated by eight heating elements attached to the reactor, as seen in Figure 48. In the filtration unit, the raw gas is filtrated using a candle filter placed in a filter house, see Figure 47. Upstream the reformer, an automatically controlled high temperature needle valve was placed in order to control the gas flow rate and a filter blow back tank was used to clean the filter. Both of these were also used in the previous EUDP project however, the blow back tank system had to be significantly modified to fit in the container and to account for the significantly lower pressure of the supplies gas of the Pyroneer gasifier compared to the gasifier in Skive. A safety release valve was added to the filter blow back system to prevent any system pressure build-up in case both valves releasing the N_2 from the tank would be prevented from closing simultaneously. Furthermore, a constrictor was placed on the N_2 inlet to the tank to ensure a slower filling of the filter blow back tank.

Figure 47: Filter element (right) and filter-house (left).

Figure 48: Pilot reactor with visible heating elements.

The left photo is from when the setup was constructed in Skive. The right photo is from when the reactor was tested in Taastrup prior to the field test in Skive in the previous EUDP project.

A drawing of the main components of the system incl. differential pressure transmitters can be seen in Figure 49 and a PID diagram of the system incl. valves, pressure gauges etc. can be seen in Figure 50.
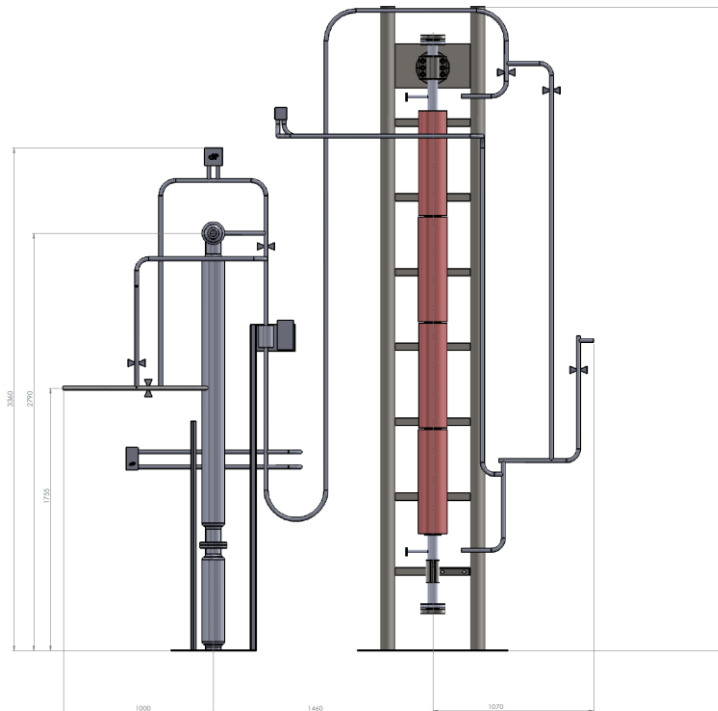
Figure 49: Drawing of main components: Filtration unit (left) and reactor (right)
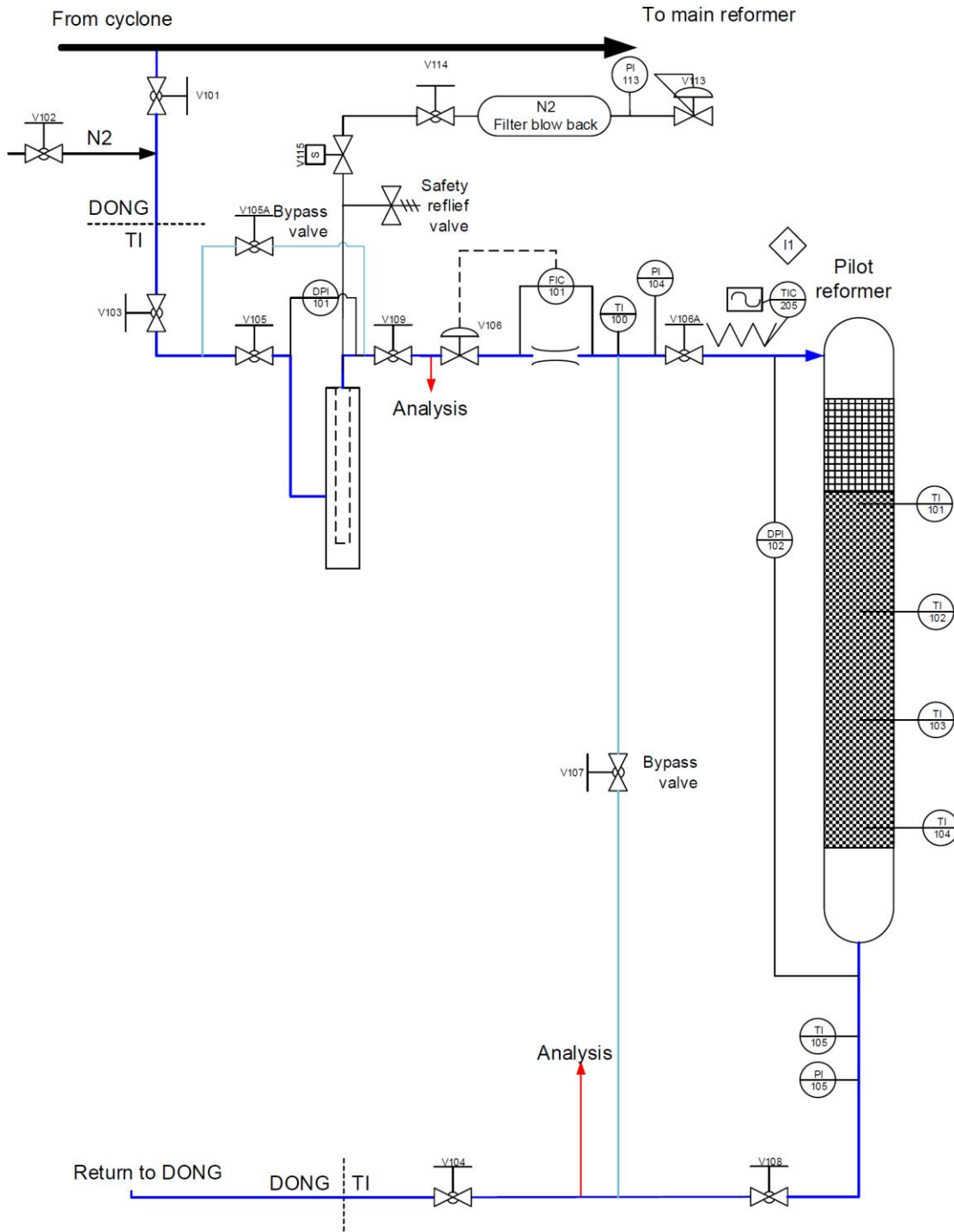
Figure 50: PID of system incl. valves, pressure gauges, temperature controllers etc.

3.8.1.2 Construction and installation

The filtration unit and reactor was shipped directly from Skive to ASV in Kalundborg and placed inside the containers before the construction of the setup began. All piping had to be re-done and all valves needed to be replaced. Furthermore, the filter blow back system had to be modified, see Figure 51. All piping with gasification gas was traced to min. 250 °C and insulated in order to prevent tar condensation. A lot of effort was put into preventing cold spots and optimizing the piping with respect to both length and angle. The finished system can be seen in Figure 52 and Figure 53.

Figure 52: System inlet (left), filtration unit (middle) and needle valve (right)

Needle valve

Figure 51: Filter blow back system

Figure 53: Filtration unit (left), reactor (middle) and system outlet (right)

3.8.1.3 Safety and pressure test

The whole system was pressure tested to ensure that it met the necessary safety requirements. Furthermore, several safety protocols were made incl. a requirement to wear a personal gas detector when entering the container.

3.8.1.4 Initial testing

The whole system was flow tested using N_2 gas. The flow was successfully controlled and varied using the needle valve. The system was also successfully tested using the steam ejector and it was shown that it was possible to have a stable gas flow for days due to the need valve being able to quickly adjust the flow when necessary.

The filter blow back system, which cleans the filter quickly releasing a tank full of N_2, was tested in both N_2 flow and in gasification gas. It was clearly seen that the pressure drop over the filter increased over time as expected when using gasification gas and furthermore, it was seen that one "shot" of N_2 was enough to clean the filter i.e. reset the pressure drop over the filter to the initial starting value.

No gasification gas was passed through the reactor during the test campaigns due to unfortunate circumstances although severe effort was made from all participating partners. In order for obtaining meaningful results, a gas supply with a stable gas composition is necessary before gas can be sent through the reactor and thus over the catalyst. The Pyroneer gasifier needs to run for approx. 24 hours to obtain stable gas composition and then it is necessary to measure the gas composition thoroughly before sending gas through the reactor. These measurements are needed in order to have sufficient before-data to get proper information out of the measurement of the gasification gas after having passed through the reactor.

3.8.1.5 Catalyst testing

In previous projects, we have shown that it is possible to remove tar molecules from the gasification gas by steam reforming. The main challenge on the pyroneer gas is to remove the oxygen containing compounds – the oxygenates. The classical route for treating oxygenates is to do hydrodeoxygenation(HDO), which in example is employed for upgrading biooils. The chemistry is simply to supply a hydrogen molecule and produce water. In this case we are fortunate to have hydrogen present in the gasification gas, which enables the reaction without adding anything.

The test strategy for the pilot test at the Pyroneer plant was to test a "normal" tar reforming catalyst initially to investigate the properties of this catalyst regarding HDO. If the tar forming catalyst was not able to reach satisfactory conversion, a completely new catalyst was to be tested. This new catalyst was to be based on a classic hydrotreating. At HTAS a few experiments on this catalyst were conducted showing, that it was possible to hydrodeoxygenate simple oxygenates, such as phenol and cresol. The stability of the tested catalyst was, however, relatively poor. This was possibly caused by the fact that the carrier was not suited for these process conditions. A modified carrier was under development.

3.8.1.6 Gas analysis
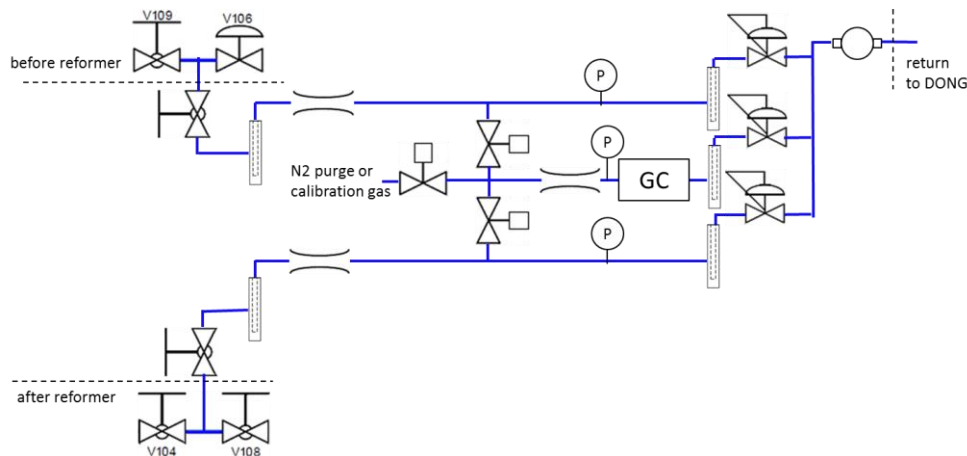
Figure 54: Diagram of the gas analysis system

The gas analysis system is shown schematically in Figure 54. The main component is a gas chromatograph (GC), which measures the gas composition before and after the tar reformer. Automated valves switch between these gas lines or a 3rd line with calibration gas or purge gas. For quantitative analysis it is important that the gas pressure in the system is constant. The system was designed to be operated at 400 mbar(a), which was below the lowest pressure that was expected after the tar reformer. The pressure was maintained by using back-pressure regulators with captured vent, with both the outlet and the vent connected to a vacuum pump.

For the initial tests it was decided to use a Global Analyser Solutions Compact GC (Figure 55).

Analysis of H_2, CO, CO_2 and N_2 was done with a thermal conductivity detector (TCD) after separation on CP-U-Bond and Molsieve 5A columns with Rt-QBond pre-columns at 60 °C.

Analysis of hydrocarbons was done with a flame ionisation detector (FID) after separation on an Rtx-1 column at 140 °C. The applied conditions allowed the separation of prioritised oxygenates (mainly phenols and furans) as well as the expected reaction products (C2-C4 components and aromatics up to naphthalene).

The sampling system was prepared for operation at temperatures up to 300 °C, but a lower temperature was used during the initial tests because the maximum inlet temperature of the Compact GC is 140 °C. Tar traps at the inlet of the analysis system were operated at 135 °C in order to prevent condensation of tars inside the GC.

Figure 55: Gas analysis system with Compact GC

3.8.1.7   Decommissioning

Decommissioning took place 2nd December 2014 apart from the filtration unit and reactor, which will remain on site until spring.

4.   Utilisation of project results

Pyroneer A/S is a 100% owned subsidiary of DONG Energy. Pyroneer A/S owns all the knowhow related to this specific gasification technology. The results from the project aims to develop the Pyroneer gasification technology to a broader scope by make a cleaning of the raw gas by using filtration and later on tar reforming. Based on the experiences gained in the Gasolution project a big step is made forward to use gasification gas in a gas turbine and the route has been shown to make biomass into liquid fuels by using gasification of biomass in connection with cleaning technologies.

In parallel, the project has produced background to up-scale the technology from the 6 MW unit to a commercial size in the range of 50-100 MW. First step has been to prove the liability of the technology and make green electricity in a conventional power plant.

DONG Energy is in the process of converting fossil fuel power stations to biomass, and in this respect, the Pyroneer technology was intended to play an important role.

Despite the technological success and the good business case, the market situation has unfortunately made it necessary to mothball the technology and suspend further development so far.

5.   Project conclusion and perspective

5.1   Key achievements obtained

5.1.1   WP 1 – Gas and tar chemistry

Chemical analyses were performed on the producer gas of the 100 kW test gasifier and the 6 MW gasifier in Kalundborg. The aim of the analyses was to characterize tar compounds in the producer gas and get a deeper understanding of the tar composition and reactions.

The analysis were mainly focused on the gas from the 100 kW test gasifier. Measurements were able to track critical components track critical components for the later processing of the producer gas that may have crucial importance for catalysts. Measurements presented supplementing support of GC-MS and UV determinations of phenol and naphthalene that is very promising for accurate and reliable future online gas analysis. Using GC-MS analysis, more than 40 compounds were found and identified in the producer gas of the 100 kW test gasifier and characterization of phenolics and PAHs were performed. Comparisons of water, ammonia, and "critical component" contents were made using optical techniques and GC or GC-MS measurements.

5.1.2   WP 2 - 100 kW filter experiments

A hot gas filter system was established and equipped with hot gas filter bags (370 °C) and subsequently equipped with ceramic candle filters (600 °C). Both filter systems showed an overall satisfactory performance.

The particles collected from the filter were tested for tar contamination – no detectable amounts of condensed tars were found.

5.1.3   WP 3 – Design and construction of a 100 kW filter in Kalundborg

Design and construction of infrastructure and equipment for filter and tar reforming were established.

A fuel silo suitable for handling of challenging biomasses and high temperature dust measuring equipment was developed and installed.

To support WP4 and WP6 the common piping infrastructure including high temperature valves, heat tracing, ejectors, housing and supporting N_2 and steam was installed and tested.

5.1.4   WP 4 – Long term filter test

A total of five test campaigns of 460 hours each were anticipated to be carried out in WP4.

Before the Gasolution project was closed three test campaigns were completed as described in chapter 3.6.2 – 3.6.3.

During these campaigns, two new fuels (beet seeds and loose shea residues) were tested. The system for tar reforming (and particle filtration) was initially tested but unfortunately not tested during the three campaigns who were completed before the Gasolution project was closed.

5.1.5   WP 5 – Pressurisation and concept design

In WP 5 a study how the design of the Pyroneer gasifier can be converted into a pressurised design was carried out. Based on a gasifier model atmospheric gasification, a gasifier model able to compare pressurised with non-pressurised operation was develop.

A roadmap of how the pressurised gasifier can be developed and explain what kind of concepts the future development was established to provide the technical basis to decide whether and how the Pyroneer track 2 should be developed in subsequent projects.

5.1.6   WP 6 – Slipstream tar reforming by HTAS/DTI pilot

The tar reformer from a previous EUDP project in Skive was redesigned and installed in a separate container system. The system was initially tested next to a test of the GC gas analysis system.

No tar reforming data were obtained before the Gasolution project was closed.

5.2 Future technology development

Due to the situation of taking the Pyroneer technology to stand-by the future technology development awaits clarification of Pyroneers future role.

6.   Economy

The project was delivered on-time and on-budget and fulfilled the technical objectives set with the exceptions mentioned in the present report.

The overall economy for the projects is shown below. Total budget for project was 39.5 MDKK, hereof 20 MDKK was granted as PSO support from the ForskEL programme.

	DONG Energy	Haldor Topsøe	DTU CHEC	DGC	DTI	TOTAL
Total per partner	27,834	3,450	4,978	1,081	2,146	39,498
PSO-support	11,488	1,502	4,978	639	1,393	20,000
						DKK x 1,000

Figure 56: Budget for the Gasolution project (as applied for)

	DONG Energy	Haldor Topsøe	DTU CHEC	DGC	DTI	TOTAL
Total per partner	18,718	1,310	4,978	643	2,146	27,796
PSO-support	7,617	576	4,978	380	1,393	14,944
						DKK x 1,000

Figure 57: Economy for the Gasolution project (as spent)