FINAL REPORT

B4C – Biomass for Conversion

Pyroneer Gasification Technology Development

ForskEL project 2010-1-10445

ForskVE project 2010-1-10565

May 2014 (revised May 2015)
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1. Project details (10445 & 10565)

Project title	B4C - Biomass for Conversion
Project identification	2010-1-10445 & 2010-1-10565
Name of the programme which has funded the project	ForskEL & ForskVE
Name and address of the enterprises/institution responsible for the project	DONG Energy Power A/S Thermal Power A/S Kraftværksvej 53 7000 Fredericia
CVR (central business register)	DK 27 44 64 69
Date for submission	27th May 2014

This final report documents the results obtained during both ForskEL project 2010-1-10445 and ForskVE project 2010-1-10565. These projects has been very interlinked and has several results in common. Headline is stated in each section whether the results refer to project 10445 or 10565 or to both projects.

2. Executive summary

2.1 Project background (10445 & 10565)

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 which 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 they can be separated from the produced gas via simple separation techniques 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 salt. 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.

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

2.2 Pyroneer process overview (10445 & 10565)

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

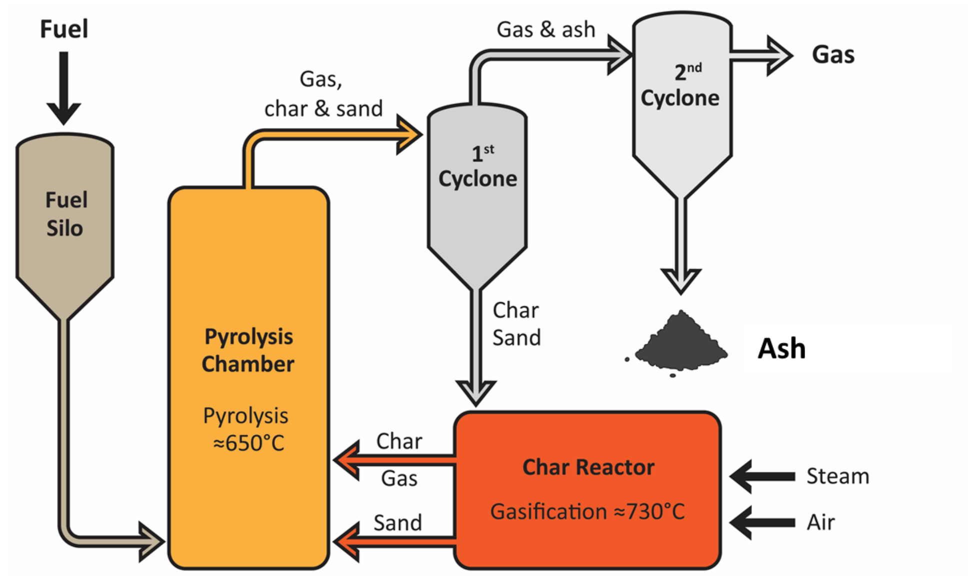


Figure 1: Simplified process flow scheme of the Pyroneer gasifier

The gasification equipment consists of mainly two connected vessels: the pyrolysis reactor and the char reactor. The straw particles are fed into the pyrolysis reactor where the temperature is circa 650°C. The straw 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.

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. Some steam can be added in order to improve the conversion without increasing the temperature. Due to the low and stable temperature, 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. Moreover, the char gas is this way somewhat cooled which means that KCl etc. that may have been partly evaporated in the char reactor is re-condensed and can therefore be efficiently separated without inserting an otherwise usual but problematic heat absorption surface prior to particle separation.

The heavier inert particles re-circulate from the bottom of the char reactor to the bottom of the pyrolysis reactor. As 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 no built in heat exchange surfaces for external heat input or output is needed.

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. Typically, the majority of the ash will be separated as flyash from the cyclone and a minor part as bottom ash. The ratio is however fuel dependent.

2.3 Project goals (10445 & 10565)

2.3.1 Design and construction of a 6MW gasifier (10445)

The aim of the B4C (Biomass for Conversion) project was to demonstrate the Pyroneer gasifier in a 12-times up-scaled version (compared to the previous largest design). This was done by designing, constructing and operating a 6MW demonstration plant at Asnaes Power Plant in Kalundborg, Denmark.

The construction of the gasifier was executed on-time and on-budget and without any safety incidents.

An overview of the gasifier specification is provided in the figure below.

Efficiency	91%
Commissioning date	2011
Operating pressure	40 $mbar_g$
Operating temperature	620-780 °C
Fuel type	Biomass / waste
Fuel storage capacity (pellets)	49 m^3
Fuel storage capacity (loose biomass)	85 m^3
Blower capacity	75 kW
Blower head pressure	780 $millibar_g$
Steam capacity (to gasifier reactor)	400 kg/h
Bed ash capacity	600 kg/h
Fly ash capacity	600 kg/h
N_2 storage capacity	18000 kg
Propane storage capacity	1000 kg (2.4m^3)

Figure 2: Pyroneer 6MW gasifier specification

The learnings from the building and operation of the 6MW plant will provide the reference design data for the first full-scale gasifier, which – at this early stage - is envisioned at a scale of 50-70MW.

2.3.2 Evaluation of key design challenges (10565)

The gasifier was first commissioned in June 2011 and further operational campaigns were carried out in 2012 and 2013. A summary of the data for all the operational campaigns is provided in the figure below. (Additional operation in 2014 is considered a part of mainly the succeeding project "Gasolution")

Operating hours blower	hours	2319
Operating hours gasification mode	hours	1393
Straw pellets	ton	1380
Loose straw	ton	643
Shea nut residue	ton	63
Sewage sludge	ton	9
Load range	MW	5-7.5
Ash produced	ton	366
Electricity produced	MWh	1578

Figure 3: Operational summary 2011 - 2013

The stable operation of the gasifier permitted a pre-identified list of technical challenges to be investigated. The table below provides an overview of the key technical challenges and the main findings from the operation of the unit.

Area	Item	Result
Up-scaling	Cyclone performance	90% efficiency of secondary cyclone proven after modification in WP3. Further investigations on-going.
	Air distribution	Stable fluidised bed behaviour in all reactors with use of sparger grid in char reactor and radial nozzles elsewhere
	L-leg performance	L-leg functioning as per design intent. No barriers to controlling circulation between the reactors
Materials	Ceramic lining	Satisfactory performance of the refractory even after numerous heat-ups and cool-downs. Only minor repairs made.
	Gas duct	No hot spots detected on gas duct joints. Heat loss from gas duct should be reduced by better insulation in full-scale plant
	Steel shell of gasifier	Corrosion tests done on steel shell of gasifier which showed no indication of degradation behind refractory
	Air nozzles	Good mixing in the fluidised bed but alternative material may be required for full-scale. Future material identified and tested
Technical solutions	Feeding system	High availability on the pellet feeding system. Key design criteria determined for full scale loose straw feeding system
	Ash handling system	A lot of experience gained in handling ash from the process. Humidification identified as suitable and necessary for full scale plant
	Start-up burner	Stable and reliable operation of the start-up burner. System can be heated up from cold within 24 hours, but can be improved for upscaled plants.
Process control	Start-up procedures	Automatic control sequence developed allowing start-up of the gasifier with minimal operator intervention
	Shutdown procedures	Safe shutdown of the gasifier demonstrated under various scenarios (gasifier trip, boiler trip, black-out)
	Impact of load changes	Data obtained on the performance of the gasifier at load variations from 83% - 125%
Process optimisation	Gas properties	Dry gas composition monitored online from 3 areas during operation. Trace elements measured by IR and GC.
	Char loss	More than 120 analyses recorded measuring the carbon content in the fly-ash from all the test campaigns.
	Ash retention	90% efficiency of secondary cyclone proven after modification in WP3. A varying additional retention is due to ash accumulating in and being drained from the bed. Further investigations on-going.

Figure 4: Overview of key technical findings

2.3.3 Future of the technology (10445 & 10565)

When biomass has been gasified it can be used for several applications all depending on the downstream gas clean-up. The figure below illustrates some of the opportunities

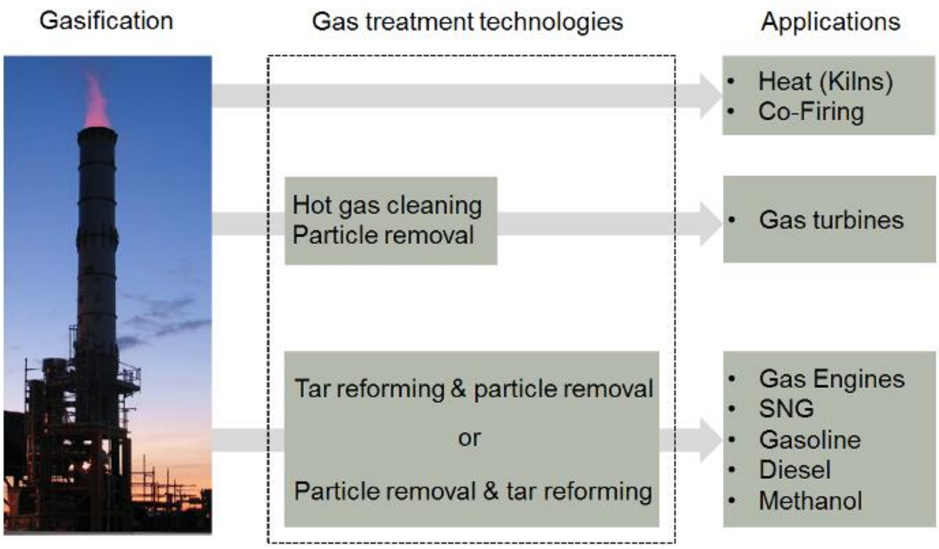


Figure 5: Illustration of opportunities with gasification

Biomass gasification is not a new technology, and at least 4-5 companies are established at the world market. These are however all mostly developed with the purpose of being able to convert woody biomass, and cannot handle the high alkaline feedstock's as straw.

The B4C project has focused on the development of the fuel flexible biomass gasifier, which can handle high alkaline agri-based residues. This fuel flexible gasifier can be the basic building block of future energy concepts.

At present the Pyroneer technology is being introduced to the market in the simplest of its intended forms, which means simple gas treatment only in the form of particle separation in a hot secondary cyclone. Hence focus is on up-scaling the 6 MW unit to a 60 MW design, and to prove that as the basic building block. The intention is to construct a 60 MW gasifier and connect it to one of the DONG Energy coal fired power stations.

Next development step is to prove the various more efficient types of gas treatment technologies, and to gradually introduce concepts where these are also included. These further building blocks will typically be developed together with various partners and suppliers, and have to be tested on the Pyroneer gas. These test will be performed within the PSO supported *Gasolution* project. The new concepts will gradually be introduced to the market as they are developed and proven.

3. Project results

3.1 Overview of work packages (10445 & 10565)

The 6MW gasification demonstration plant was built with the purpose of being able to test and verify the fundamentals of the low temperature circulating fluidised bed gasification concept and reduce the risks associated with the design and construction of a commercial scale gasifier (size range >50 MW for co-firing major biomass fuels such as straw).

From the outset, the 10445 and the 10565 projects were divided into 6 main work packages as described below.

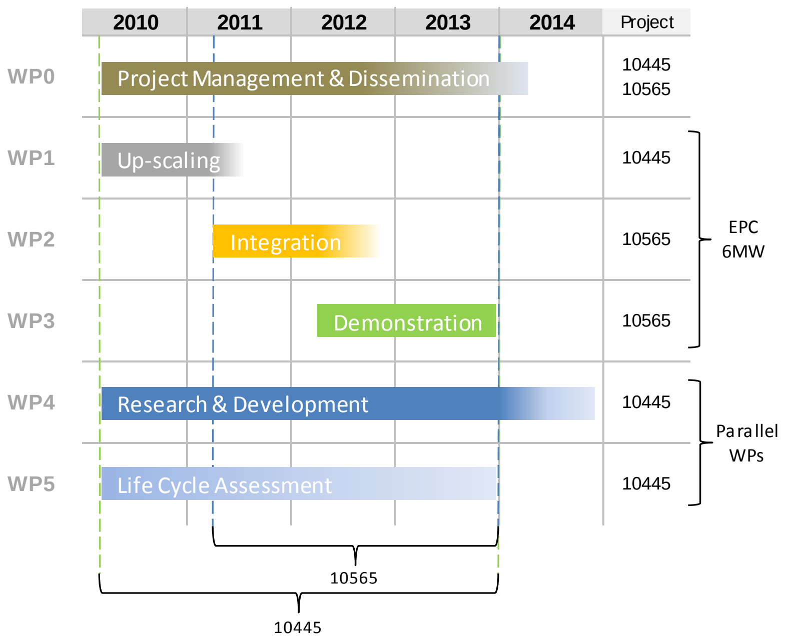


Figure 6: Work-package overview

WP0 encompassed the entire project management and administration of project 10445 and 10565 as well as dissemination of the results.

The EPC (Engineering, Procurement and Construction) of the gasifier was placed in WP1-3. The main principle was to advance through the design phases as long as the basic principles at each stage had been successfully demonstrated.

WP1 was a simple up-scaling of the gasifier where the core fluidisation and temperature control were tested. The gasifier was operated manually and the produced gas flared. (10445)

WP2 was integration where the gasifier was connected to an existing coal boiler via a gas duct and gas burned in a dedicated gas burner. The ash and fuel handling systems were also made more advanced and automated. (10565)

WP3 involved demonstration of the gasification concept via longer test campaigns doing parameter variations and testing different fuels. (10565)

WP4 looked at knowledge build up through theoretical investigations, measurements and data analysis. This involved a Ph.D. study which ended later than the main project. (10445)

WP5 included a Life-Cycle Assessment where the environmental performance of the gasifier was compared to other technologies. (10445)

3.2 WP0 Project Management and Dissemination (10445 & 10565)

3.2.1 Summary of objectives

The key objectives of WP0 were the overall B4C PSO project management and dissemination of the project results. An important element of the work package was the management of the multiple B4C consortium partners and other external stakeholders with respect to the long term development of the technology.

3.2.2 Inauguration events

In order to communicate the results of the project to the energy community and wider Danish public, two inauguration events have taken place at the 6MW demonstration plant.

1. 11/03-2011 to celebrate the finalisation of construction and commencement of operation

Construction of the 6 MW demonstration plant was started late summer 2010 and on the 11^{th} of March 2011 the construction was finalised. On this date, the former brand LT-CFB was replaced by the Pyroneer trade name. The construction period was executed 'on time' and 'on budget'. The day was celebrated together with circa 100 invited internal and external stakeholders.

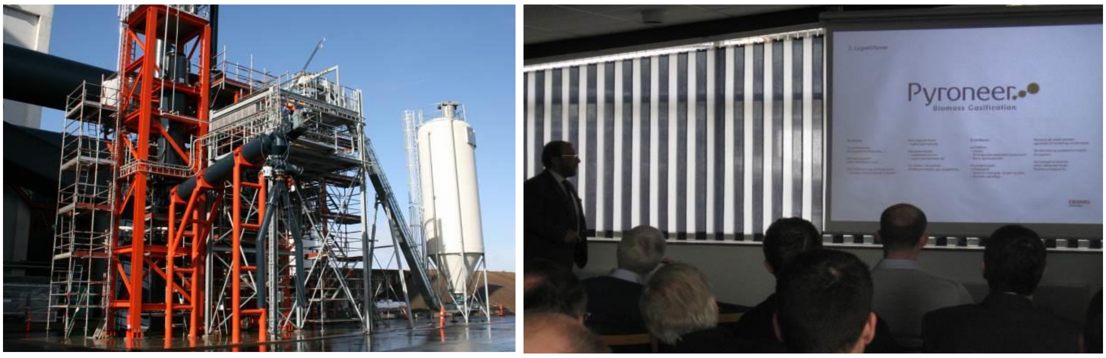


Figure 7: 1st inauguration event – March 2011

2. 01/09-2012 to celebrate the operational achievements

The gasifier was commissioned during spring 2011 and operated in various test campaigns according to the project plan. Approximately one year after initial commissioning, the gasifier was integrated with the ASV2 boiler and the first green power was produced in April 2012. On 11^{th} of September 2012, the successful up-scaling and operation of the gasifier was celebrated in a 2^{nd} inauguration event. Around 100 stakeholders and partners participated in the event. The second inauguration event marked the beginning of the commercialisation phase of the Pyroneer technology and the kick-off of an active marketing strategy. It marked the day when stakeholders finally could see that the new technology could be realised in an industrial scale.

Figure 8: 2nd inauguration event – September 2012

3.2.3 *Public presentations & conferences*

There has been a broad and sustained interest in the Pyroneer technology and the progress of the B4C project has been presented to a wide range of audiences. A summary list of the largest conferences and events is given below.

Conferences:

Nov 2013, IEA Bioenergy task 33, Gothenburg
http://www.ieatask33.org
Nov 2013, ACI Gasification Conference, London
Sept 2013, DTU International Energy Conference, Roskilde
http://www.natlab.dtu.dk/Energikonferencer/
May 2013, Gastekniske dage, Denmark
http://www.gasteknik.dk/arrangem/2013/
April 2013, European Biomass to Power Conference, Krakow
Oct 2012, SGC-Seminar, Stockholm – www.sgc.se
June 2012, European Biomass Conference, Milan
March 2012, Termisk forgasning og indpasning i naturgasnettet, ATV Seminar, Copenhagen
March 2012, Clean Coal IEA Co-firing, Copenhagen

Homepage

Further dissemination of the project aims and results has taken place through the world wide web. A homepage has been developed to promote the Pyroneer technology – www.pyroneer.com. On average, the website has received 10 hits per day from Denmark and the wider European region during the course of the project.

Movie

A small movie introducing the 6MW demonstration plant has also been produced. The movie can be found on the Pyroneer web page via the following link:
http://www.pyroneer.com/en/demonstration-plant

3.2.4 *Visitors to demonstration plant*

There has been a huge interest to see the demonstration plant resulting in access and priority being given to future commercial partners and customers. The following is a list of the types of groups that have visited the plant:

- Several Danish Authorities
- Several Danish organisations such as: DK Naturfredningsforening, Straw suppliers, Danish Industry etc.
- Chinese and Russian delegations arranged together with ENS
- Several private enterprises within the Energy sector
- Various potential customers and partners (Belgium, Chile, France, Germany, France, Finland, Sweden, UK)
- Students from DTU, Maskinmesterskolen etc.

The feedback from visiting delegations has been extremely positive and the 6MW demonstration unit is proving a highly valuable asset in the commercialisation phase of the technology.

3.3 WP1 Upscaling (10445)

3.3.1 Summary of objectives

The objective of WP1 was principally to engineer the up-scaled core gasifier system, procure the necessary equipment based on the design criteria, construct the equipment at Asnæsværket power plant and commission the gasifier to demonstrate the functioning of the process at the larger scale. Focus was on only the most necessary systems done in a simple way e.g. using pelletized fuel and flaring the gas.

3.3.2 Engineering and Construction

3.3.2.1 Engineering

In the engineering phase, a strong focus was placed on ensuring that the fundamental design criteria were well documented for future reference. In order to specify the mechanical equipment, the process design, hydrodynamic design and reactor sizing (including anticipated pressure profiles in the system) were developed using standardised work tools in excel. These were based on adapted tools from the small scale units using a mixture of empirical and theoretical design rules. These same tools will form the basis of future full-scale commercial designs.

After the finalisation of the basic mechanical design, impetus was placed on the development of the control and safety philosophy for the unit. Compared to existing commercial gasifiers, the low-temperature gasification of biomass in the Pyroneer system has some unique characteristics that required careful design of the safeguarding system. Amongst others, numerous calculations were made to investigate the explosion properties of both the biomass feedstock and the different producer gas compositions.

3.3.2.2 Construction

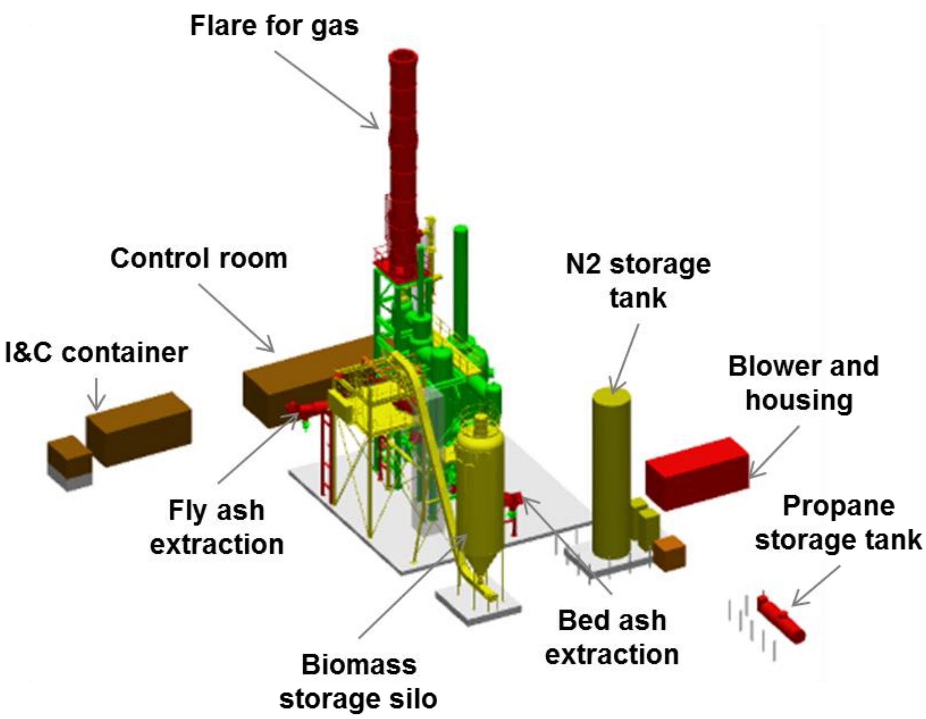


Figure 9: WP1 main plant components

In the initial up-scaling phase, the main refractory lined gasification reactors and interconnecting ducts were assembled and supported in a steel framework construction. The refractory solution was developed and installed by project partner Calderys based on their experience from other processes. A 49 m^3 biomass silo for pellets was installed with a disc mill to crush the pellets before feeding to the gasifier. The fly ash and bed ash cooled screws were installed, each with a capacity of handling 40% ash fuels (600kg/h).

The further auxiliary systems for supplying: N_2 (mainly for shut-down purging), propane (as start-up fuel), process air (as the major gasification agent); steam (for enhanced char conversion and temperature moderation) were also installed.

Figure 10: From left to right: silo installation; reactor installation; refractory installation

3.3.2.3 Control system

The safety system on the gasifier was developed according to IEC/EN 61511 / EN12952.

A full hazard and risk assessment was conducted on all of the gasifier systems including documented barrier diagrams. Various protective layers were established including:

1. Inherently safe design (where possible)
2. Process control system
3. Process shut down system (PSD)
4. Fire detection system
5. Gas detection system (CO + propane)
6. Access control
7. Personal CO detectors

A full SIL (safety integrity level) classification was carried out on all safety instrumented functions (example shown in Figure 11). The final sensor configuration was then implemented according to the defined SIL requirement.

SIF Description:	Lav temperatur i PK top
SIF Number	32
Prepared by:	SOBYJ
Approved by:	theo@ramboll.dk 21/2-2012 Final element valideres af andre
Comment:	Trip er væsentligt bedre, da blæser også stoppes på frekvensomformer, og der er overvågning af endestop og kontaktor. I sensor indgår også at forgasser køre i combustormode (mode 2). det afgøres bla. af om opstartbrænder er inde (1oo3 kobling på ventiler og flamme), som er meget bedre end 2oo3 temperatur

Common cause failure rates	Percent
β-Sensor	5%
β-Solver	0%
β-Final Element	5%

Diagnostic Coverage	Percent
DC-Sensor	0%
DC-Solver	0%
DC-Final element	0%

		1			2			3				HFT
Subsystem	Architecture	KKS	Description	PFD	KKS	Description	PFD	KKS	Description	PFD	PFD Subsystem	MAX SIL
Sensor	2oo3	23RAA10CT055A	Temperatur	5,58E-03	23RAA10CT065A	Temperatur	5,58E-03	23RAA11CT001A	Temperatur	5,58E-03	4*PFD^2+beta*PFD	3
		23CRA10_AI	AI Siemens	5,00E-05	23CRA10_AI	AI Siemens	5,00E-05	23CRA10_AI	AI Siemens	5,00E-05		4
		-	-	0,00E+00	-	-	0,00E+00	-	-	0,00E+00		4
		-	-	0,00E+00	-	-	0,00E+00	-	-	0,00E+00		4
	Result 1oo1			5,63E-03			5,63E-03			5,63E-03	4,08E-04	3
	Incl DC										4,08E-04	
Solver	1oo1	23CRA10_CPU	CPU Siemens	1,90E-04	-	-	0,00E+00	-	-	0,00E+00	PFD	3
		23CRA10_BUS	Bus Siemens	1,00E-05	-	-	0,00E+00	-	-	0,00E+00		3
		-	-	0,00E+00	-	-	0,00E+00	-	-	0,00E+00		3
	Result 1oo1			2,00E-04			0,00E+00			0,00E+00	2,00E-04	3
	Incl DC										2,00E-04	
Final element	1oo2	23CRA10_DO	DO Siemens	1,00E-05	23CRA10_DO	DO Siemens	1,00E-05	-	-	0,00E+00	4/3*PFD^2+beta*PFD	4
		23REA01AA001-Y01	Pilotventil	1,70E-03	23REA01AN001-Q71	Maksimalafbryder	4,76E-04	-	-	0,00E+00		2
		23REA01AA001MS01	Aktuator AVID	2,58E-03	-	-	0,00E+00	-	-	0,00E+00		3
		23REA01AA001KA01	Ventil Keystone	3,30E-03	-	-	0,00E+00	-	-	0,00E+00		2
	Result 1oo1			7,59E-03			4,86E-04			0,00E+00	4,56E-04	2
	Incl DC										4,56E-04	
System	PFD system										1,06E-03	
	PFD incl DC										1,06E-03	
	SIL (PFD)										2	
	Result (SIL)										**SIL 2**	

Figure 11: SIL classification of low temperature safety function

The DCS configuration for the gasifier is shown in Figure 12. Two control stations were located in the control room (one for operation and one for engineering). An additional operating station was located in the main control room of the power station (for remote operation). Furthermore, the system can be accessed remotely from any computer on the DONG network.

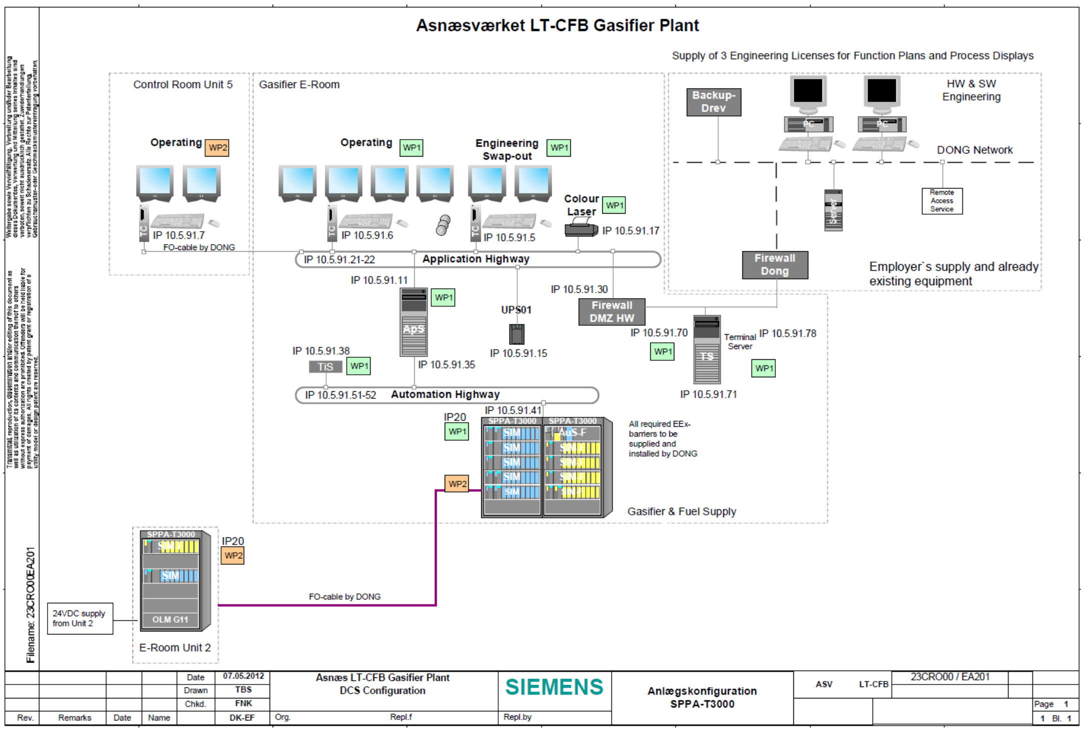


Figure 12: DCS configuration

The gasifier was designed with four state-dependent modes which each have a set of unique interlocks and permissives which must be valid before the operator can change from one operating mode to another. Once the permissives for each operating mode have been granted then the sequences are fully automatic with no operator intervention required.

The four main operating modes are as follows:

1. Cold start-up
2. Hot re-start
3. Inerting
4. Leak test

- “1” and “2” leading to normal operation

In addition to the main operating modes, a number of additional automatic sub-sequences were designed to operate various non-continuously operating functions. These are listed below:

1. Start-up burner control
2. Product gas support burner operation
3. Dosing silo filling
4. Pellet feeding
5. Cyclone ash removal
6. Bottom ash removal
7. Gas sampling system operation

The gasifier has multiple closed loop controllers which monitor and adjust the process without the requirement for the operator to manually intervene. These control loops are used to, for example, maintain the operating temperature in the reactors within a 2 °C range.

The closed loop controllers are listed below:

1. L-bend level control
2. Pyrolysis reactor temperature incl. slope control
3. Char reactor temperature incl. slope control
4. Gasifier load control
5. Pellet load controller
6. Seal air for fuel feed system control
7. Blower pressure control
8. Start-up burner load and temperature control
9. Product gas support burner load control

All data obtained during the operation of the gasifier is logged and accessible for post-operation process analysis.

3.3.3 Operational campaign

The operational overview from the first test campaign on the gasifier is shown in the table below.

Operating hours, blower	Hours	460
Operating hours in gasification mode	Hours	240
Availability	%	70
Straw pellets gasified	Ton	240
Ash produced (dry)	Ton	20
Electricity produced (all gas flared)	MWh	0

Figure 13: Data for operational campaigns in WP1

3.3.4 Key learnings

- *Stable operation of the gasifier:* The most important observation from the WP1 operational campaign was that the gasifier could be heated up and operated with stable temperatures in both the pyrolysis reactor and char reactor. This proved that the general up-scaling design, based on the smaller units, had been successful.

- *Start-up:* In two out of three of the earlier smaller scale units, the entire system could simply be heated up by means of electrical tracing located under the insulation on the outside of the unlined stainless steel reactors. The 6MW scale gasifier required a start-up philosophy more similar to the one applied for the earlier also refractory lined 500 kW plant. For the 6 MW plant this is based on a 1MW start-up burner exhausting into the pyrolysis reactor as heat input to the system. This was used to heat up the circulating bed material which transported the heat from the pyrolysis reactor to the char reactor. A key requirement for this modified start-up philosophy was the need to ensure safety in the system when going from combustion mode to a reducing environment when explosive gas mixtures can become a real issue. The WP1 operation showed that the process could be heated up stably and safe using this philosophy.

- *Ash handling:* One thing that had been underestimated in the scaled-up design was the ability to handle the ash from the gasifier in dry conditions. The system that had been designed was based on the assumption that the ash would be heavy enough to fall downwards under gravity and settle in the big bags. Due to the extremely light particles from the gasifier cyclone (Essentially 100% below 100 microns), this proved not to be the case and lead to the requirement to install a humidifier downstream the cooled screw in WP2.

- *Combustibility of the gas:* The stable flame observed from the flare stack gave a positive indication on the combustibility of the Pyroneer gas and the stability of the process.

Figure 14: flaring of gas from the first operational campaign

- *Ash quality initial results:* An important aspect of the Pyroneer gasification process is the sustainability aspect which also comes from re-application of the ash back to farmlands. Multiple analyses from the first test campaign were carried out on the ash produced in the process to determine the levels of heavy metals and Poly Aromatic Hydrocarbons (PAH) in the ash. All of the levels were well below the limitations set by the Danish government for re-application of the ash onto farmland. More details of the nutritional value of applying bio-ash from the Pyroneer process onto farmland are provided in section 3.4.4 and 3.5.4.

Mg/kg (dry basis)	PAH	Cd	Cr	Hg	Ni	Pb
Period 1	4.6	<0.05	28	<0.0020	4.8	4.4
Period 2	5	<0.05	17	<0.0020	4.5	2.4
Limits to be meet for straw ash	12	5	100	0.8	60	120

Figure 15: PAH and heavy metal content in Pyroneer fly ash from straw

3.4 WP2 Integration (10565)

3.4.1 Summary of objectives

The main objective of WP2 was to construct the required 100 m gas duct and install the burner in the unit 2 boiler at ASV to enable combustion of the producer gas.

The cost of WP2 represented a substantial percentage of the total project cost. This meant that the actual investment was only approved after the up-scaling of the gasifier had been confirmed as successful and the gas proven combustible in the first test campaign.

3.4.2 Design

3.4.2.1 Mechanical design and construction

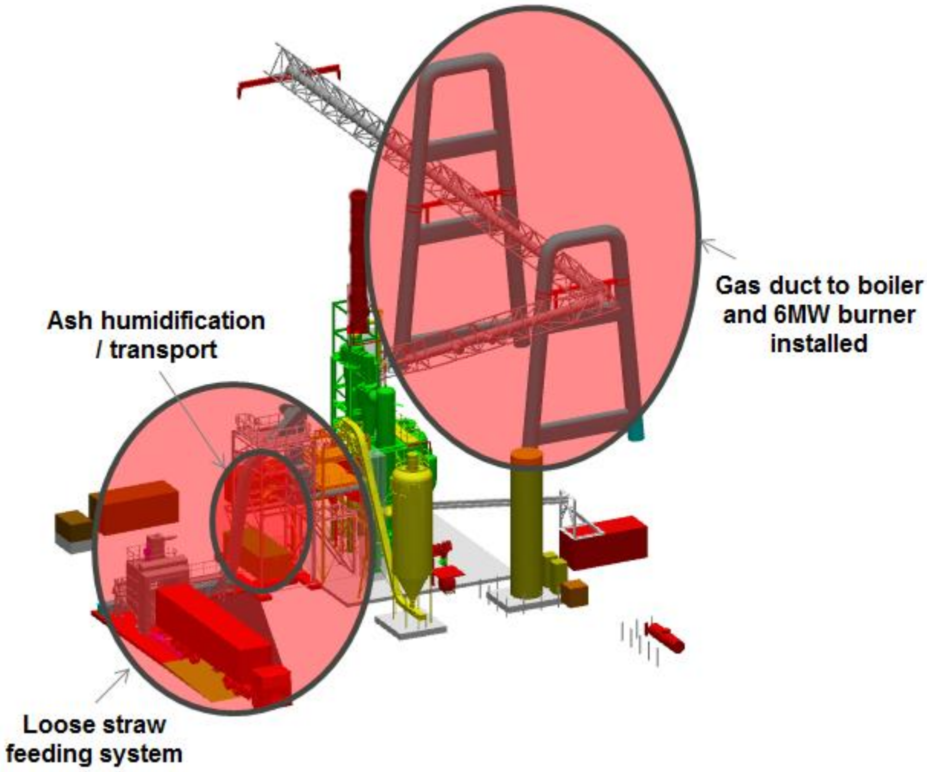


Figure 16: WP2 main plant components added

In the integration phase, a refractory lined gas duct was installed on the plant to connect the gasifier to the ASV unit 2 coal-fired boiler. The duct was manufactured from carbon steel with an internal refractory consisting of two layers: a hard face erosion protection layer and a soft insulating layer. The design of the refractory was developed within the project by project partner Calderys. The outer diameter of the duct was circa 700 mm and manufacturing was completed in lengths of 2.4 m which were then welded together. The total length of the gas duct was circa 100m. The duct was installed in a custom built rack supported on existing supports at the power plant.

It was necessary to carry out a modification on the boiler to install the 6MW burner to combust the gas produced in the Pyroneer process. Several tubes on the boiler side wall were cut to make the opening for the burner. Thereafter, an interfacing flange was installed to which the burner was mounted. The gasification gas flows tangentially through the burner where it is mixed with combustion air taken from the main boiler combustion air system. A diesel fired support flame was also installed in the burner to ensure stable burner operation during start-up of the gasifier.

Figure 17: Modifications to the boiler

In a commercial gasification plant, the use of pellets has a significant negative impact on the overall plant economics. An additional important aspect of WP2 was therefore to add an additional biomass handling system to process loose straw. After assessing the CAPEX and OPEX costs of different commercially available systems, a walking floor trailer system was selected. The system allows biomass to be offloaded from trailers onto a transport conveyor which transports it to the existing biomass feeding equipment.

A fly-ash humidifier and container handling system (on weighing scales) were also installed to ease handling of the fine particle size fly ash captured by the secondary cyclone.

3.4.2.2 Control system

In WP2 additional automatic sub-sequences and closed loop controllers were added for the new loose straw feeding system which are listed below.

1. Receiving station filling sub-sequence
2. Receiving station dosing sub-sequence
3. Hot swap between fuels sub-sequence
4. Loose straw load controller
5. Loose straw dosing silo level controller

This enabled fully automatic control over changing from pelletised to loose biomass (and vice versa) with the gasifier remaining fully online. One of the most challenging aspects of gasifying biomass is the inhomogeneity of the fuel. The additional flexibility of changing from one fuel handling system to the other had therefore a positive contribution to the overall reliability of the gasifier.

Another important aspect of the control system was the integration of the gasifier safeguarding to the existing boiler to ensure shut-off of the gasifier in the event of a boiler trip. The entire operation philosophy was also modified to avoid the use of the flare during start-up and shut-downs of the gasifier. This was an important design concept to prove due to the high impact on the ability to obtain the environmental permits for a future full-scale gasifier.

In addition, many small modifications were made to the existing control loops to refine the ability of the gasifier to be placed in automatic control without the need for operator intervention.

3.4.3 Operational campaign

WP2 operation was mainly on loose straw and all gas was burned in ASV unit 2.

Operating hours, blower	Hours	868
Operating hours in gasification mode	Hours	462
Availability	%	76
Straw pellet	Ton	252
Loose straw	Ton	583
Ash produced (humidified)	Ton	100
Electricity produced	MWh	669

Figure 18: Data for operational campaigns in WP2

3.4.4 Key learnings

- *Feeding loose straw:* The operational campaign highlighted clearly how much more challenging it is to handle loose straw (where foreign bodies and objects were not efficiently removed) compared to pellets where the pelletising process ensures more homogenous biomass properties including the absence of large stones etc.. The lower density of the loose straw also proved challenging for the final feed screw which had been originally designed for the higher density of crushed pellets. Modifications were made to the final feed screw to increase the capacity but stones still caused blockages on the common feed screw. In future plants, a stone trap will be critical to ensure that foreign bodies do not cause reliability problems in the gasifier feed system.

- *Mechanical-physical properties of different fuels:* One of the most interesting learnings from the campaign was the difference in behaviour of the loose straw compared to the pelletised biomass that had first been tested in the unit. This can be further seen from the comparison of the product gas compositions (dry basis – measured in the gas duct of the gasifier) between the two fuel types. This is shown in Figure 19. These results have shown the importance of the mechanical-physical properties of the biomass on the overall gasifier operation.

	CO (vol. %)	H_2 (vol. %)	CH_4 (vol. %)	CO_2 (vol. %)
Straw pellet	12.3	6.9	4.5	17.9
Loose straw	14.9	5.0	4.8	18.9

Figure 19: Dry gas composition comparison between straw pellets and loose straw

- *Efficiency of cyclone:* The installation of the gas duct also allowed iso-kinetic sampling of the dust content in the gas for the first time. This indicated that the overall efficiency of the cyclones was not as high as had been seen in the 100kW pilot plant and which they were designed for. This had already been identified as one of the key up-scaling challenges in the design phase of the project. High efficiency cyclones are extremely important for two reasons. Firstly, a high efficiency primary cyclone ensures that char from the pyrolysis is captured for further conversion in the char reactor. Secondly, a high efficiency secondary cyclone is critical in order to protect the boiler from the corrosive ash compounds found in the feedstock and also in order to retain and recirculate the nutrients.

  The analysis of the cyclone efficiencies led to the decision to install new cyclones before the operation of the unit in WP3 to ensure that the full efficiency of the gasifier could be demonstrated.

- *Refractory performance:* In WP2, regular monitoring of the refractory performance was carried out by DONG and project partner Calderys using infra-red imaging techniques and physical inspections. The temperature scans showed no indication of hot spots. Furthermore, the scans revealed the high difference on heat loss when operating the gasifier in summer and winter. This is shown in Figure 20 below.

  The physical inspections were used to monitor the size and development of any cracks in the hard-face layer. No signs of problematic slagging were revealed during the inspections.

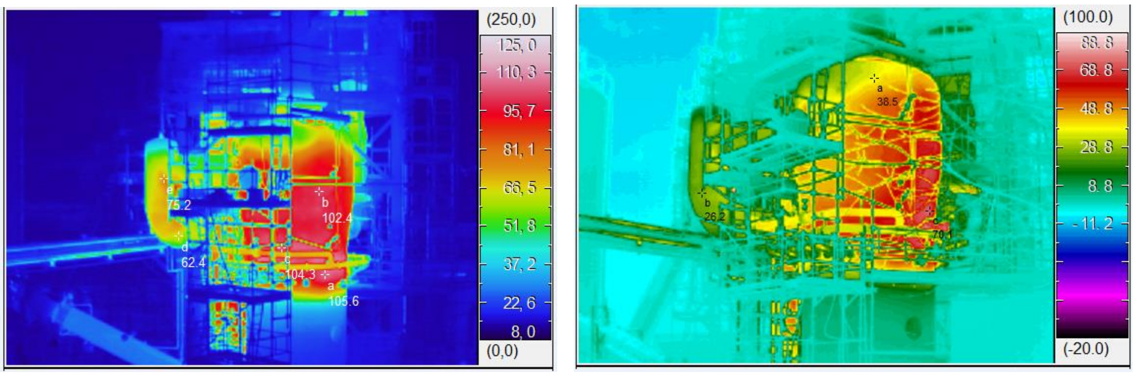


Figure 20: Surface temperature of the gasifier in June (left) and November (right)

- *Stable combustion of gas in boiler:* The combustion characteristic of the product gas burner was monitored via two flame eye detectors and shown to be very stable once the gasifier was in steady operation. This meant that the support burner (fired by diesel) could be switched off within a few hours of going into gasification mode.

- *Sand addition requirements:* After operating the gasifier for the longer operational period in WP2, it was concluded that there was limited or no requirement to add sand during the operation of the unit. No problems with agglomeration was encountered.

- *Ash handling and usage:* The 100 tonnes of ash from the WP2 test campaigns were was distributed on the fields of Bregentved Estate as a part of the INSURANCE project (Combined soil carbon sequestration and crop nutrient supply using thermal conversion technology residuals) funded by the Willum Foundation. Of the 100 tonnes, 20 tonnes were used in a detailed study to determine how the farmland reacts to different concentrations of potassium, phosphorous and carbon in the Pyroneer ash. As a continuation of the study, the amendment of ash has been repeated the following year.

Figure 21: Pyroneer ash study at Bregentved Estate

3.5 WP3 Demonstration (10565)

3.5.1 Summary of objectives

The main objective of WP3 was to build up the operational hours on the gasifier and assess the impact of the new cyclones that were installed as a result of the learnings in WP2. Further improvements were made into the automatic operation and control of the gasifier. In the demonstration phase, modifications were also made to improve the reliability of the data obtained from the operational campaigns in order to further develop an understanding of the process and assess the overall gasifier performance.

The gasifier was also used as a future marketing tool during the WP3 demonstration phase with numerous visits from suppliers and potential future partners and customers.

3.5.2 Design

3.5.2.1 Mechanical design and construction

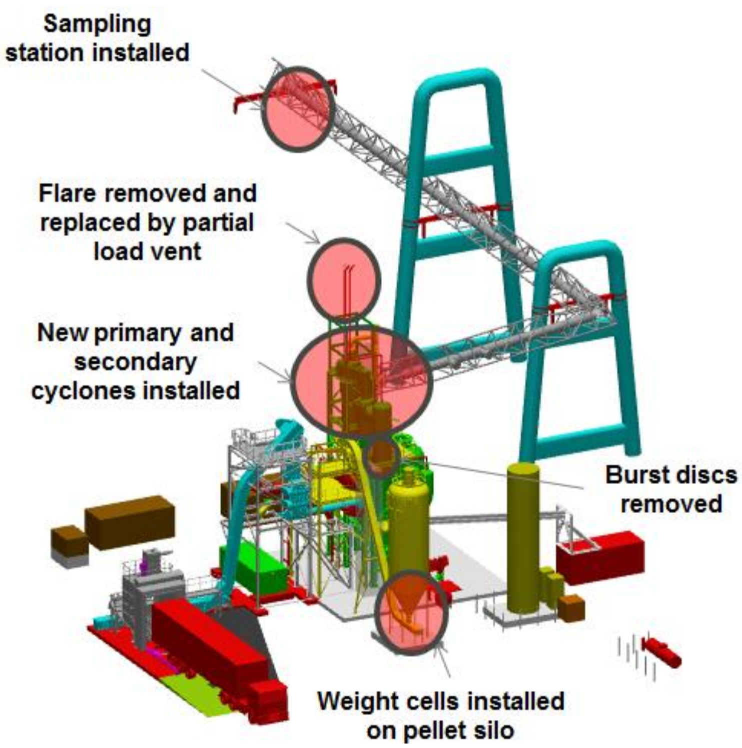


Figure 22: WP3 main construction systems

In the demonstration phase, new cyclones were installed on the unit due to lower than anticipated performance with the original design identified in WP2. The new cyclones installed were larger in size than the original cyclones which meant raising the height of the pyrolysis reactor and L-leg and modifying the connection to the gas duct.

Figure 23: Installation of two new cyclones

The flare system that had been installed to combust the gas during the initial up-scaling phase was also removed and replaced with a partial load vent. This was based on a shut-down analysis which showed that the boiler could be used to depressurise the gasifier, even under black-out conditions. This means that for future commercial plants, the additional CAPEX of a full load flare is no longer required with a partial load flare sufficient (estimated 10% full design gas flow capacity).

Multiple small modifications were also made on the gasifier. For example, weight scales were installed on the pellet silo to assist in the mass balance calculations which assess the gasifier's performance. Furthermore, all burst discs on the gasifier core reactor system were removed based on the outcome of a study to re-assess the explosion consequences. A sampling station was also installed on the straight length of the gas duct for measuring instruments to allow permanent iso-kinetic analysis of the particles downstream the secondary cyclone and measurement of the product gas trace elemental composition via online optical methods and offline GC methods.

3.5.2.2 Control system

In WP3, the sequence was developed to allow cold start-up of the gasifier without the need for operator intervention. In Figure 24, an example of a cold start-up is provided. The straw pellet flow rate together with the temperatures in the pyrolysis and char reactors are all shown for the beginning of the operational campaign in November 2013. The automatic cold start-up sequence was used to heat up the different parts of the gasifier until the normal operating temperatures was reached. The entire start-up was made in about 24 hours (constrained by the requirement to control the heat-up of the refractory lining).

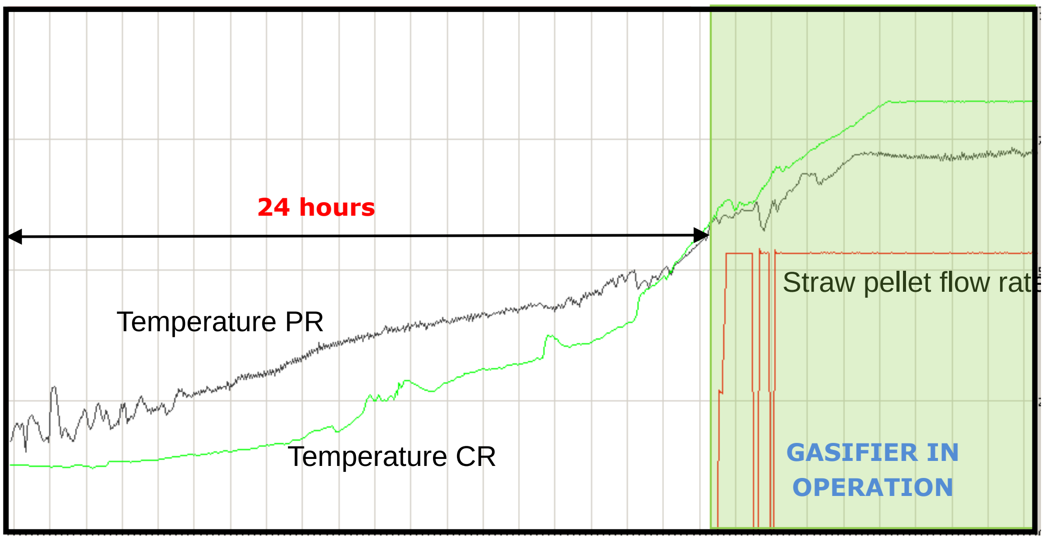


Figure 24: Cold start-up graph

In Figure 25, an example of a warm re-start is provided. The straw pellet flow rate together with the temperatures in the pyrolysis and char reactors are all shown initially during steady state operation. At 02:00, the fuel feeding system tripped due to a piece of metal in the fuel silo. This caused the gasifier to trip with a resulting decrease in the reactor temperatures. At 07:45, the problem with the fuel feeding system was resolved. The automatic hot start-up procedure was then initiated. The fuel feeding started shortly after and the gasifier was back at normal operating temperature one hour later.

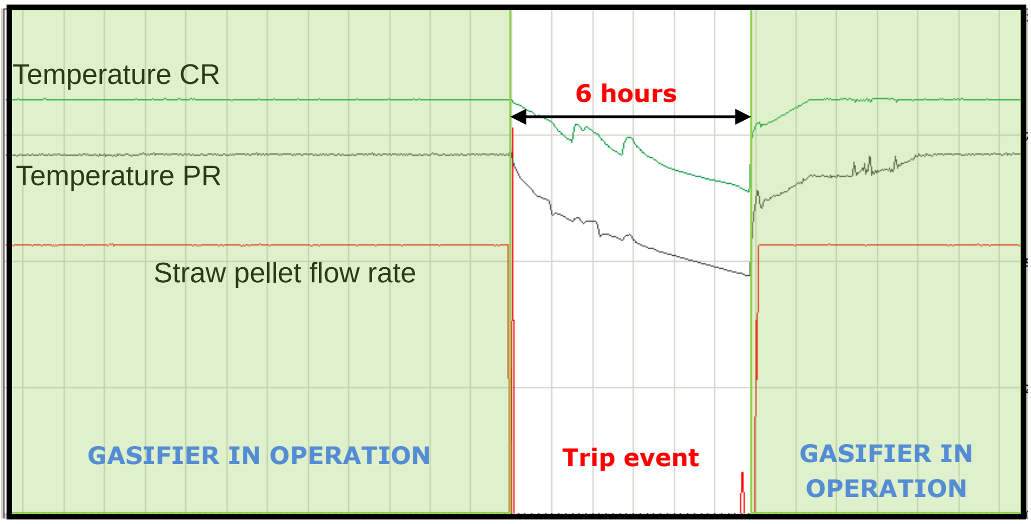


Figure 25: Warm re-start graph

3.5.3 Operational campaign

Main data for the operational campaigns for WP3 performed in 2013:

Operating hours, blower	Hours	991
Operating hours in gasification mode	Hours	691
Straw pellets	Ton	888
Loose straw	Ton	60
Shea nut residue	Ton	63
Sewage sludge	Ton	9
Ash produced (humidified)	Ton	245
Electricity produced	MWh	909

Figure 26: Data for operational campaigns in WP3

During the operational campaigns in WP3, a high reliability was seen for the gasifier as shown in the below figures. As has previously been discussed, the main cause of downtime was foreign objects delivered as contained in the biomass.

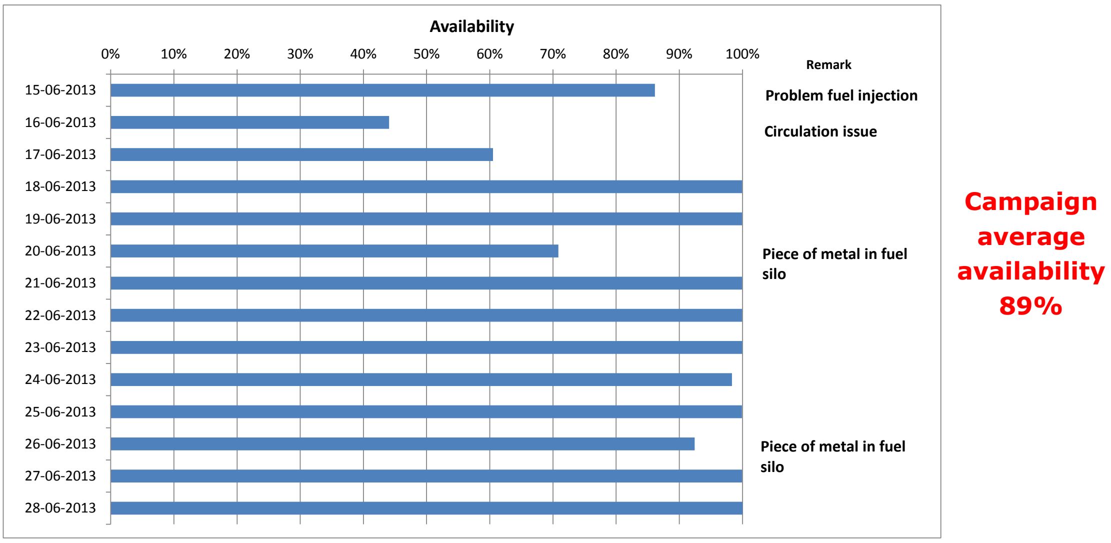


Figure 27: Availability of the gasifier, June 2013 campaign

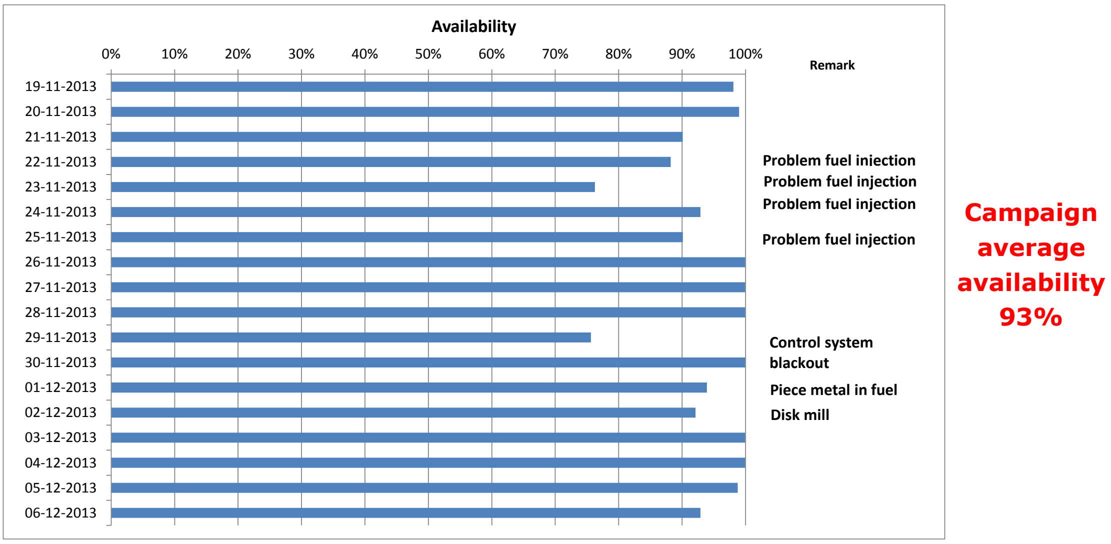


Figure 28: Availability of the gasifier, November 2013 campaign

The stable operation allowed numerous parameter tests to be undertaken to further refine the impact on performance of different variables with the end goal of obtaining the highest possible efficiency.

During the final operational campaign in November 2013, a key goal was to test the gasifier with other biomass fuels. A total mass of 63 tonnes Shea nut residue (sourced from Aarhus Karlshamn) were gasified within two days of operation. The system showed robust transition from straw to shea and back again and stable operation. Furthermore, a blend of straw pellets and dried sewage sludge (sourced from Bjergmarken Renseanlæg, Roskilde) were gasified in another 2 day period showing also robustness of the process towards high ash fuels.

3.5.4 Key learnings

- *Refractory performance:* During the maintenance inspections in between the WP3 operational campaigns, minor repairs were required on the refractory. These were carried out by project partner Calderys. Despite the number of operational hours being only in the 2000 range, the frequency of heat-ups and shut-downs has far exceeded that expected in commercial operation of the gasifier. It is during these temperature changes that cracking of the erosion resistant hard face can occur. There were no signs of neither depositions due to slagging nor disintegration of the refractory due to CO or alkaline penetration.

- *Nutritional value of ash:* The Pyroneer ash has been shown to have K values in the range 5-8% and P values of up to 1% when gasifying straw. The theoretical value of the ash with respect to the content of K and P will depend on the price of conventional fertilizers. The plant availability is a matter of debate but if one assumes an availability comparable to commercial fertilizers then the straw ash could represent a value of up to 340 DKK per dry ton (2010/11 prices, assuming 5 wt% K and 0.35 wt% P in the dry ash and 6 DKK/kg K and 11 DKK/kg P). There are some uncertainties related to this value since the plant availability is dependent on the origin of the fuel (e.g. agricultural residues like straw or waste fractions like sewage sludge).

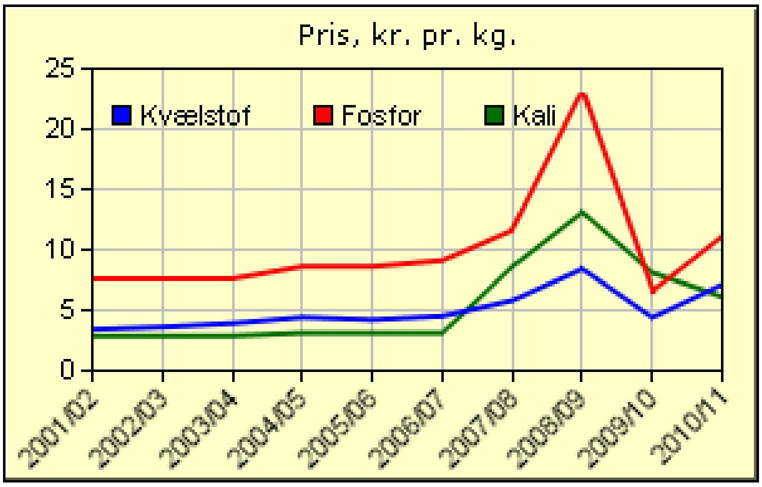


Figure 29: Conventional prices of fertilisers in Denmark over the last 10 years

The potential value of the residual carbon - to improve soil structure and further potential benefits - is presently hard to place a price on, as the potential large benefits on soil quality still needs verification. However, preliminary studies suggest a positive influence on biomass root development and soil water retention, which in particular is in poor sandy types of soil. Results also shows that the carbon from the

ash is very stable in the soil, and the carbon content can therefore be increased much more, than when tilling down straw, as this is not stable in the soil. Hence, the potential is not only improving the soil quality but also carbon **sequestration**.
The majority of the ash produced from the 6MW plant has been used as farmland fertilizer at Bregentved Estate and for lab scale tests within the INSURANCE project funded by the Willum Foundation.

- *Manning of the gasifier:* In the operational campaigns in WP3, extremely stable operation of the gasifier was obtained with periods of up to 130 hours without any trips or disturbances. This meant that the manning requirement on the gasifier was very low with just one operator required for managing fuel and ash deliveries and taking samples. Support from the core engineering and design team was carried out via remote log-in with the local power station operations team being responsible for the monitoring and control of the gasifier.

- *Bottom ash handling:* A key learning was obtained with regards handling of the bottom ash from the gasifier. In order to keep the installation cost down, only one bottom ash screw was installed. These cooling screws are vulnerable to blockages (especially if small pieces of refractory come off). If a blockage occurs, then it is advantageous to have an isolation valve between the screw and the process so that the blockage can be removed whilst the unit is online. During one of the heat-up periods, such a blockage occurred which resulted in the requirement to stop for emptying out the bed material to repair the screw before start-up could be resumed.

- *Use of different fuels:* In the final test campaign, several other fuels were tested in the gasifier (shea nut residue and a blend of straw pellets and sewage sludge). The typical product gas composition on a dry basis for the operation on straw pellet, shea nut residue and a blend of straw pellet and dried sewage sludge pellets is shown in Figure 30. The different gas compositions observed during the operation with straw pellets for WP2 and WP3 reflect the changes in process parameters used when operating the gasifier.

	CO (vol.%)	H_2 (vol.%)	CH_4 (vol.%)	CO_2 (vol.%)
Straw pellet	14.5	8.5	4.5	18.9
Shea nut	9.6	13.2	2.1	19.4
Sludge and straw	10.5	8.5	3.5	19.2

Figure 30: Product gas composition for different fuels

3.6 WP4 Process Research and Development (10445)

3.6.1 Summary of objectives

Objective of WP4 was to:

- Plan the 6MW operation campaigns performed in WP1-3
- 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

A part of the work was done within a Ph.d. project at Risoe-DTU.

3.6.2 Data analysis and process development

An extensive amount of data are stored in the DCS from all the 6MW campaigns. During and after each campaign some of these data are analysed. Due to limited resources, a priority has been made to focus the analysis on the most important subjects after each campaign. The focus areas has been within:

- 6MW optimisations
    - Gas quality
    - Efficiency
    - Availability
- Upscaled design references
    - Test of different fuels
    - Simulation tests of different reactor sizes

Before each campaign, a thorough operation plan has been made which specifies the parameter variations, measurements and samples needed to produce data and build up know-how for the area in focus.

3.6.3 6 MW test campaign November 2013

The following highly compressed presentation of test results gives an overall impression of the results obtained from the November 2013 campaign, i.e. from Nov 21 to Dec 12 2013, which was the last of the test campaigns within the reported project.

Besides the choice of fuels, which was straw pellets, sheanut residue fibers, and thermally dried sewage sludge, a number of further operational parameters such as fuel-, air- and steam flow rates were varied. All of the variations contribute more or less to variations in the calculated performance data.

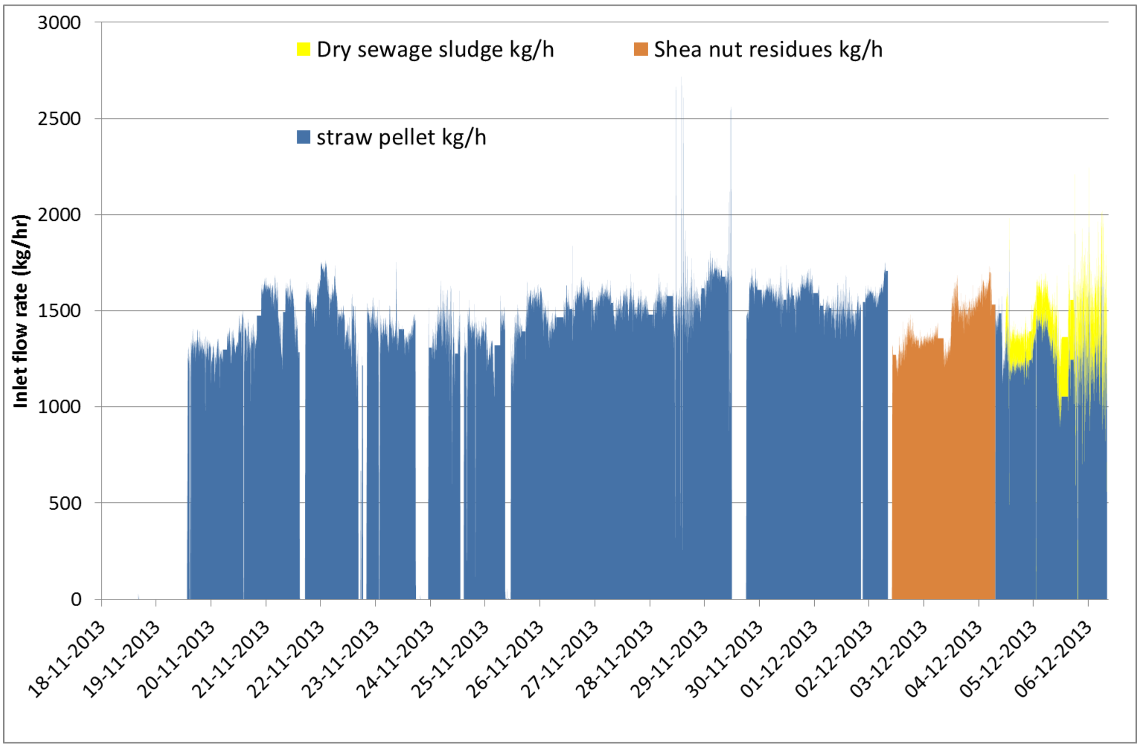


Figure 31: Stable operation of the gasifier (November 2013)

Blue: Straw pellets – Orange: Shea – Yellow: Sewage Sludge

3.6.3.1 Fuel

For 6MW optimisation, it could be to evaluate the fuel stability and correspondence between DCS set point and actual fuel flow. Figure 32 shows that the actual fuel flow was a little lower than the DCS set point. Such a difference is quantified and data and DCS set points are adjusted accordingly after the campaign.

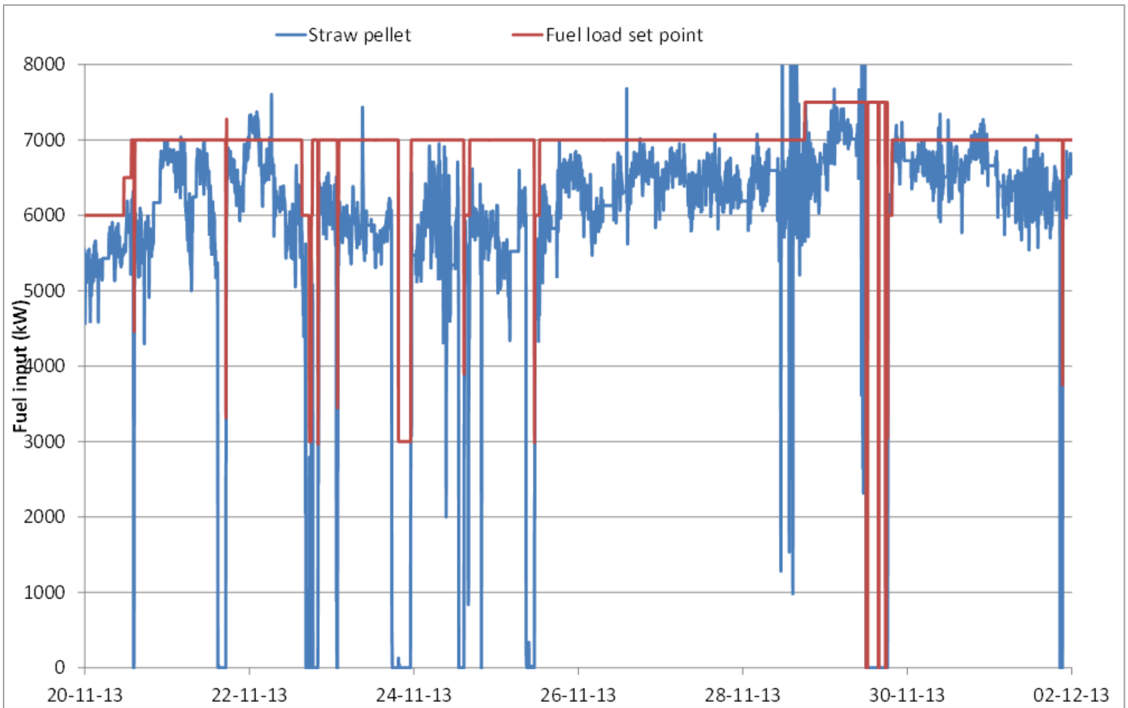


Figure 32: November 2013, 6MW campaign fuel input data

For upscale reference, the campaigns include testing of new fuels. The Pyroneer process are capable of converting a wide range of different fuels but time for testing were limited so fuels have been chosen carefully. Most important selection criterion was that fuels must be directly relevant as reference for commercial projects within a short horizon. Focus was on fuels that are cheap and available in large enough quantities to feed several large gasifiers.

Straw pellets
Straw pellets (alone) were used in the first and the last part of this operation campaign and as a backup fuel when running on sludge and shea.
Supplier was Storkedal who also supplied during the last operation period in. Based on analysis done earlier of pellets from same supplier the below values were entered in the DCS:

Moisture content	11.2	% (a.r.)
Ash content	7.3	% (dry)
Heating value (calculated)	15.2	MJ/kg

Figure 33: Analysis of straw pellets from Storkedal

Sewage sludge pellets
Mixtures of (same) straw pellets and sewage sludge pellets. The sludge pellets are from Roskilde wastewater treatment plant. Main parameters of interest is:

Moisture content	11.0	% (a.r.)
Ash content	41.0	% (dry)
Heating value (calculated)	9.6	MJ/kg

Figure 34: Analysis of sewage sludge pellets from Bjergmarken

Two different ratios was tested for ~24 hours each:

1) Straw pellets / sludge pellets: 1380 / 100 kg/h ~6 MW
2) Straw pellets / sludge pellets: 1140 / 444 kg/h ~6 MW

Shea nut residue pellets
A test was made on shea pellets. Manufacturer was Aarhus Karlshamn and supplier was Storkedal (as for the straw pellets). Main parameters of interest is:

Moisture content	11.0	% (a.r.)
Ash content	6.3	% (dry)
Heating value (calculated)	15.9	MJ/kg

Figure 35: Analysis of shea pellets

Startup fuel
As startup fuel will mainly be used char coal briquettes based on wood. Anticipated amount used ~1 ton.

3.6.3.2 Results

Due to the high number of parameter variations, it is generally optimistic to expect precise results (including mass and energy balances) because of insufficient time for achieving fully steady state. However, it has been attempted to increase the quality of the results by carefully planning the best order of changing the parameters, by focussing mainly on the hours before the time of parameter changes and by leaving out data collected within the following most transient periods.

It should also be noticed that the results is derived from complicated model calculations wherein a number of assumptions has to be made, in order to estimate e.g. the amount of water vapour and tar components in the product gas.

The gasifier efficiency has been calculated as:

$$Efficiency = \frac{Thermal\ and\ chemical\ energy\ product\ gas + thermal\ and\ chemical\ energy\ ash\ and\ char\ in\ product\ gas}{Energy\ input\ fuel}$$

The gasifier ash retention is calculated as:

$$Ash\ retention = \frac{Ash\ accumulation + Ash\ in\ fly\ ash\ stream}{Ash\ inlet}$$

Notice here that "Ash accumulation" is the part of the total ash stream that could instead be drained as bottom ash and that "fly ash" is the part separated by the secondary cyclone.

Figure 36 & Figure 37 shows the average calculated energy balance and the ash mass balance for all of the November 2013 test campaign.

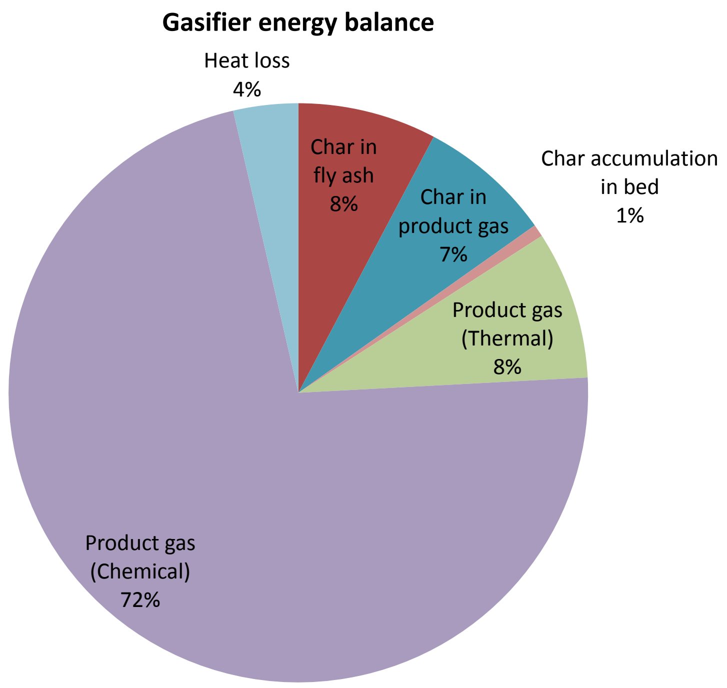


Figure 36: Gasifier energy balance during operation periods (November 2013)

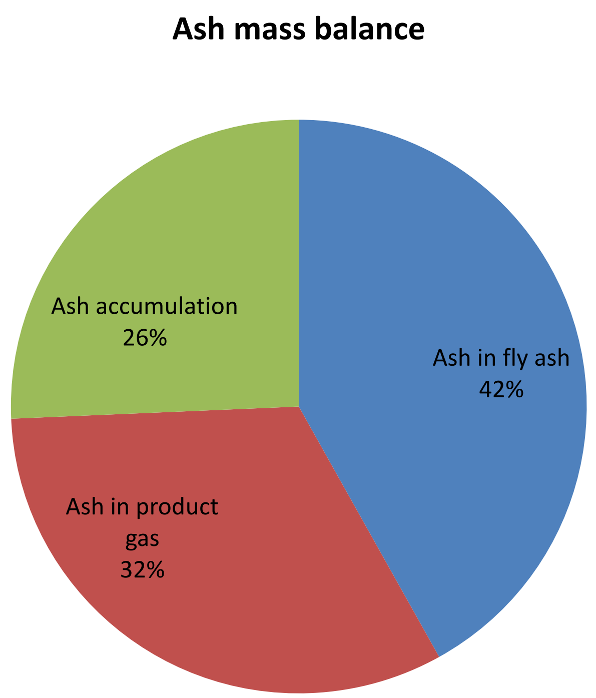


Figure 37: Calculated average ash balance during the operation periods (November 2013)

When evaluating the energy and mass balance components seen in Figure 36 & Figure 37 it should be noticed that the aim of the campaign was mainly to investigate the impact of the various separate parameter settings rather than a complete optimisation of all performance data within each of the test conducted. Moreover, the implementation of several planned solutions to counteract some well-known performance limitations was postponed to later tests campaigns.

E.g. the overall campaign average gasifier efficiency of 88 % seen in Figure 36 spans over figures of up to 94 % and both of these numbers are in spite of a relatively high (overall campaign) surface loss of 4 % which can be reduced by better insulation and which will surely also be reduced just due to scaling up the gasifier.

Moreover, the energy efficiency as well as the calculated (overall campaign) total ash retention of only 68 % (seen in Figure 37) is impacted negatively due to postponing planned solutions that will positively affect the function of both of the cyclones and probably especially the secondary cyclone. Even without these planned improvement, the highest total ash retention achieved was 85 %.

The above mentioned better than overall campaign average maximum figures is the averages within the full partial tests with constant parameter settings (typically lasting at least 24 hours) and of course even better (but also worse) figures can be found if looking down into all of the many model calculations performed within each of the partial test periods.

The extend of model calculations performed is visible from the many data points in Figure 38, which is only for the November campaign tests conducted on straw. Figure 38 also shows a clear influence on the amount of unconverted char from the fuel flow rate. Hence, the relative amount of unconverted char increases from approximately 5 % to more than 10 % of the fuel flow rate when the fuel flow rate was increased from the low load figure of approximately 1000 kg/hour to the (very) high fuel load level of 2700 kg/h. Other varied parameters are also influencing but it is clear that one way of prioritising energy efficiency is by avoiding a high load, and - on the other hand - the production of “biochar” could be prioritised simply by overloading the gasifier.

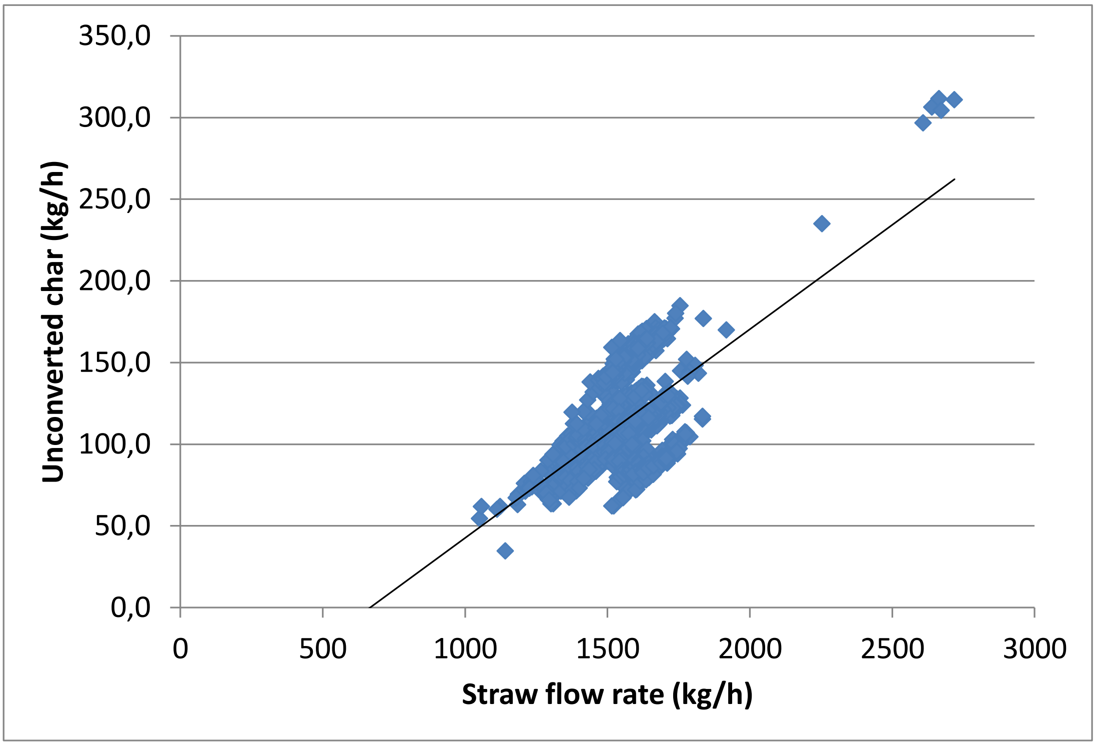


Figure 38: Unconverted char as a function of the straw pellet flow rate (November 2013)

3.6.3.3 Boiler impact

In the project, it was planned to examine the impact on the boiler caused by co-firing of straw-based gasification gas. Here, it was desired to examine the chemical conditions as a result of deposition and corrosion with a special focus on the description of the inorganic chemistry. Due shortened test runs and delayed progress in the development of the chemical model, these issues were not investigated in the project.
However, it should be noted that visual observations were made – These inspections did not indicates any negative impacts on the boiler or by-products (ash).

3.6.4 Ph.d. project: Ash chemistry

The B4C project included a Ph.D. project investigating deeper into the ash chemistry within the Pyroneer process. This study has contributed greatly by giving new knowledge about the chemical behaviour of alkali, chlorine and sulphur from it enters with the fuel, goes through the pyrolysis and gasification before solid state ash is separated from the gas. Agglomeration has also been studied both theoretically and experimentally.

The Ph.d. study started in July 2011 and will be finalised in 2015. This will be later than the rest of the project. Main investigations and conclusions has however been achieved already and a draft of the Ph.D. thesis are shown in appendix 1.

The entire Ph.d. thesis will be available by end of 2015 from DTU publication database at www.orbit.dtu.dk

3.7 WP5 LCA Sustainability (10445)

3.7.1 Summary of objectives

The main objective of WP5 was to carry out a full life-cycle assessment (LCA) of the Pyroneer gasifier. This was executed by developing a life-cycle model that looked at a number of impact categories relevant for the assessment of sustainability including:

- Net global warming impact per energy unit produced
- Emissions of key air pollutants e.g. NO_x, SO_x and particles (PM10)
- Environmental assessment of eutrophication
- Environmental assessment of acidification

After the model has been developed, the goal was to benchmark the Pyroneer technology with other comparable conversion technologies. To this extent, two comparative studies were made which are elaborated on further below:

1. Gasification of straw compared to direct straw combustion and fossil fuel combustion
2. Gasification of miscanthus compared to direct miscanthus combustion and anaerobic digestion of miscanthus

3.7.2 LCA of straw gasification

This study assessed the environmental performance of straw gasification for electricity production and compared it with that of alternatives such as straw-fired electricity production and fossil fuel-fired electricity production. Compared with direct burning of straw, using the Pyroneer gasification technology reduced the environmental impacts per kWh by 50, 38, 58 and 70% for the impact categories global warming, non-renewable energy use, acidification and respiratory inorganics, respectively. Compared with natural gas as a conventional energy source, straw gasification reduced global warming impact by 85 % and almost eliminated the use of non-renewable energy. There was, however, an increase in acidification and respiratory inorganics.

The relative performance of straw gasification versus fossil fuel references does not change with varying assumptions about whether or not a facility for combined electricity and heat production or only electricity production was used. The contribution to acidification and respiratory inorganics impacts of straw gasification for electricity production was mainly related to the downstream combustion process, where emissions of various air pollutants such as nitrogen oxides, sulphur dioxide, carbon monoxide and particulate matters are created, and which might be further optimized.

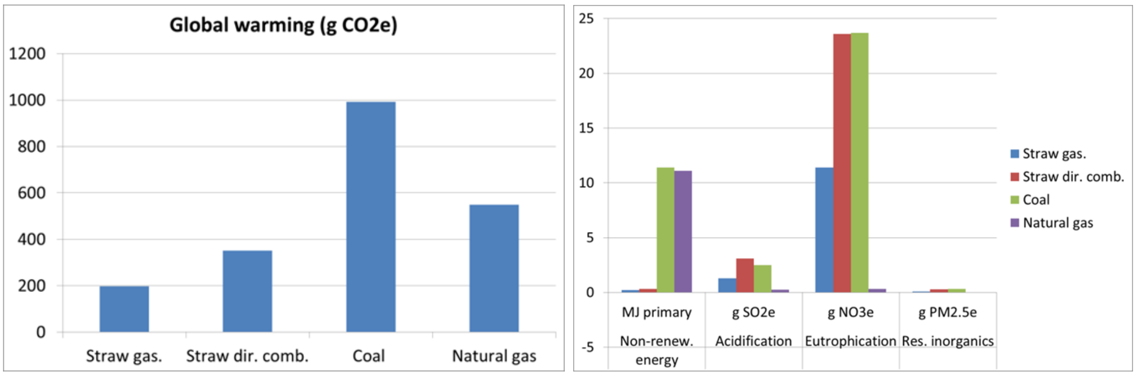


Figure 39: LCA – Environmental assessment – Basis: Production of 1 kWh electricity

The results of the study were published as detailed below:

Nguyen T. L.T., Hermansen J. E., Nielsen R. G. Environmental assessment of gasification technology for biomass conversion to energy in comparison with other alternatives: the case of wheat straw.
Journal of Cleaner Production 53 (2013) 138-148;
http://dx.doi.org/10.1016/j.jclepro.2013.04.004.

According to straw gasification the main conclusion in the article is:
"The production of electricity from straw based on gasification technology appears to be more environmentally friendly than straw direct combustion in all impact categories considered", Source: **Nguyen et.al.; Journal of Cleaner Production 53 (2013) 138-148**

3.7.3 LCA of miscanthus gasification

An alternative feed-stock to straw for the Pyroneer technology could be the perennial energy crop, miscanthus. Perennial energy crops e.g. willow and especially miscanthus have recently received large attention as a potential source of renewable energy. The giant C4 grasses of the genus Miscanthus stand out as promising candidates for future bioenergy crop, owing to their high yield, low resource inputs, high carbon sequestration capacity and potentially low environmental impact as compared to more conventional annual crops used for bioenergy.

However, the growing of miscanthus does consume land which is a limited resource, so the possibility of land use change needs to be accounted for. Thus, the environmental performance of biomass gasification for electricity production based on miscanthus was assessed and compared with direct combustion and anaerobic digestion of miscanthus as well as the use of natural gas, using a life cycle approach. In the assessment, two aspects were included which have opposite effects on the environmental performance of energy production from miscanthus: the carbon sequestration in the soil on the one hand and the indirect land use change following the occupation of land (iLUC) on the other hand.

It was found that the production of 1 kWh of electricity from miscanthus through gasification would lead to a global warming potential of 25 g and 301 g CO_2e, without and with iLUC consideration, respectively. The production of electricity from miscanthus based on gasification technology appears to be the best option for environmental sustainability compared to other alternatives like direct combustion and anaerobic digestion, in all impact categories considered, except for non-renewable energy use where anaerobic digestion performs best. The comparison with natural gas showed that using miscanthus as an alternative energy source reduced global warming by approximately 45 %, but increased acidification, eutrophication and respiratory inorganics. Interestingly, despite making a huge contribution to the global warming impact of electricity production from miscanthus, the iLUC-related emissions were not of sufficient magnitude to counterbalance the emission savings from the substitution of biomass as a low carbon energy source for natural gas in power plants.

The results of the study are published (Life cycle environmental performance of miscanthus gasification versus other technologies for electricity production): *"T.L.T. Nguyen, J.E. Hermansen / Sustainable Energy Technologies and Assessments 9 (2015) 81-94."*

4. Utilisation of project results (10445 & 10565)

All the knowhow related to this specific gasification technology is owned by Pyroneer A/S, which is a 100% owned subsidiary of DONG Energy. The results from the project is directly used to up-scale the technology from the 6 MW unit to a commercial size in the range of 50-100 MW. DONG Energy is in the process of converting fossil fuel power stations to biomass, and in this respect the Pyroneer technology plays an important role.

Pyroneer is however also teaming up with partners that can market, deliver and service this technology on the global market. In this respect Pyroneer is already in close dialog with potential partners, and there is on ongoing discussion with several potential customers.

In order to protect such a business IPR is an important part, and the Pyroneer team continuously tries to develop and patent various intelligent solutions related to the technology. The demonstration plant is an important assets used to verify that the various ideas is actually worthwhile to pursue.

5. Project conclusion and perspective

5.1 Key achievements obtained (10445 & 10565)

The project has made it possible to upscale and test the Pyroneer process with a factor of 12 from 500kW to 6MW, which is close to commercial interesting size. Thereby securing the continuation of the technology development. The hands-on experience gained from the operation of the 6MW, together with the scientific investigations, has made it possible to further upscale and optimise the process.

The project has followed the original project schedule with the division of the 6MW construction and testing into 3 phases. This division has proven successful, because it has made it possible to keep things as simple as possible and maintain focus on the most important subjects. Everything cannot be foreseen in a development project of this complexity and duration, but this project setup has facilitated sufficient flexibility to overcome unforeseen challenges. Also the setup allowed a simple first approach, which made it possible to acquire the first results quite fast after project start up.

One of the major project achievements has therefore been to deliver good results fast and finish the project within time and within budget.

Another major reason why the project has been a success is the good and productive cooperation between the partners in the project. It has been very value creating to bring together people with knowledge and experience from the whole range from basic scientific research to daily, on-site, mechanical maintenance. All partners has contributed constructively to the design and construction of the 6MW plant, to performing tests, measurements and analysis of data and to look wider into the future to make sure upscaled plants are as environmentally friendly and sustainable as possible.

5.2 Future technology development (10445 & 10565)

5.2.1 Upscaling

Both CAPEX and OPEX optimisations are important when upscaling and commercialising a technology like this. CAPEX and risk of investment are closely linked and a high CAPEX will delay or terminate the investment decision of the first upscaled plants. OPEX and business case are closely linked as cumulated expenses over such a plants lifetime and payback time is dominated by the OPEX contribution.

CAPEX of upscaled plants has been reduced within this project, mainly because the experience gained has made it possible to design some of the reactors relatively smaller and smarter than the 6MW. Also the work with the safety philosophy, has made it possible to build safe upscaled plants simpler and cheaper.

OPEX of upscaled plants are made up by primarily fuel, manning and auxiliaries. A robust and efficient control philosophy has been developed within this project, which allows for a minimum of manning to run the process thereby greatly reducing the cost for manning. Use of auxiliaries has also been reduced, mainly amount of N_2. Fuel consumption is therefore the main constituent of OPEX. Efficiency has been increased and further possibilities has been identified for upscaled plants, which will decrease the fuel expense with several percentage points. Main possibility for OPEX decrease is however to be able to utilise very cheap fuels in the process, which can reduce the fuel cost with up to several factors. This has also been proved possible, and further tests will be done on specific cheap fuels with commercial aim, to continue the development of an optimised fuel flexible process.

5.2.2 Gas upgrading and stand-alone applications

The setup with co-firing of Pyroneer biomass based gasification gas into a modern existing coal fired power plant boiler for efficient production of combined heat and power has been proven and demonstrated with the 6MW setup at Asnaes Power station. This setup will be further optimised, upscaled and commercialised. It is a robust and simple setup, where gas cleaning can be limited to involve only hot cyclones for the separation of ash and gas. Power station sites typically also allows for good infrastructure, so that large gasifiers can be built and operated with different cheap biomass and waste fractions.

Different setups involving upgrading of the gas quality does however also offer promising possibilities, including establishing new heat and power capacity based on cheap biomass and waste fractions. The 6MW plant will in the near future also be used for testing filtration of the gas, so it can be used in e.g. gas fired boilers, and also tar cracking to enable e.g. gas utilisation in engines.

6. Annual export of electricity (10565)

During WP1 in 2011 all gas produced from the 6MW plant was flared, and no electricity was produced. In WP2 and WP3 all gas produced was burned in Asnaes unit 2 and electricity was produced.

A summarise of the total amount of electricity delivered to the grid within the project:

WP2 – 2012	669 MWh
WP3 – 2013	909 MWh
Total	1578 MWh

Figure 40: Electricity produced from 6MW plant

7. Economy (10445 & 10565)

Both projects (10445 and 10565) was delivered on-time and on-budget and fulfilled the technical objectives set.

The overall economy for the projects is shown below. Total economy for both projects was 90 MDKK, hereof 35 MDKK was received as PSO support from the ForskEL and ForskVE programmes.

Project	DONG Energy	DFBT	Calderys	DJF	DTU	Total	Hereof PSO support
10445	41.302	895	2.126	1.089	4.006	49.418	24.000
10565	39.064	895	788	-	-	40.747	11.000
Total	80.366	1.790	2.914	1.089	4.006	90.165	35.000

DKKx1.000

Figure 41: Economy for 10445 and 10565 projects (as applied for)

8. Appendix 1: Ph.D project abstract - Ash Chemistry (10445)

Ph.D. project title: Ash Chemistry in Circulating Fluidized Bed
Ph.D. student: Vikas Narayan, CHEC / DTU
Supervisors: Peter Arendt Jensen and Ulrik Birk Henriksen, Risoe-DTU

8.1 Introduction

Gasification of herbaceous based fuels poses a large potential for power generation. Herbaceous fuels however, contain high amounts of alkali metals which get volatilized at high temperatures and form salts of low melting points and thus condense on pipelines, reactor surfaces and cause de-fluidization. The Low Temperature Circulating Fluidized Bed Gasifier[1,2], is designed to minimize ash sintering and deposit problems and most potassium and chlorine are simply retained in a separate biomass ash stream. In this way a fuel-gas with low alkali content and a relatively high calorific value is produced that can be used for power production by use of a boiler.

As shown in Figure 1.1, the LT-CFB process consists of two reactors. The biomass fuel enters the first reactor which is the pyrolysis chamber. The fuel is pyrolysed at around 650^{0}C due to good thermal contact with mainly re-circulated sand and ash particles from the char reactor. The heat for the pyrolysis reaction is thus provided mainly by the sand bed particles and some re-circulated char and ash particles. The residual char, pyrolysis gases and inert particles are led to the primary cyclone, which separates char and inert particles to a bubbling bed char reactor. In this reactor, the char is exposed to air to undergo partial combustion and gasification, at temperatures typically around 730°C. Some steam or water may also be added in order to improve the conversion of char and limit the reactor temperature.

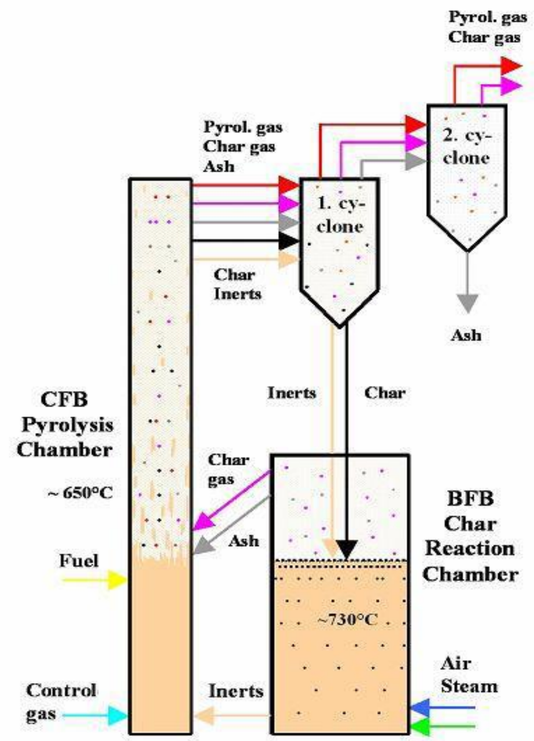


Figure 1.1: LT-CFB flow diagram[1,2]

The exit stream out of the pyrolysis chamber has a lower temperature compared to the temperature in the char reactor. Consequently, alkali species and other ash components are present in the solid phase and only small amounts get carried off with the product gas while most is separated in the cyclones. Moreover, the relatively low temperatures in the process limit the tendencies of de-fluidization in the system.

8.2 Objectives of the PhD Study

The aim of the PhD project is to study the behavior of alkali metals, Cl, S and biomass ash in a Low Temperature Circulating Fluidized Bed System. The focus of the study is on release of ash species with exit gas from the reactor system, ash transformation and bed de-fluidization.

8.3 Study of ash chemistry in the LTCFB Gasifier

8.3.1 Measurements on particle emissions and ash species in LT-CFB Gasifier

To understand the behavior of alkali and ash in LTCFB reactors, available test data from runs made on 100 kW plant at Risø and 6 MW plant at Kalundborg (Pyroneer Gasifier), were analyzed by a preliminary mass balance. It was seen from the mass balance analysis that, the data were not sufficient to give a good understanding of the ash behavior in the system or to provide information on the concentration of ash species in the Product gas. It was therefore suggested to have direct measurements done on the product gas. The main aim of the measurements was to measure the concentration of K, Cl and S in the exit gas.

Thus, measurements were made on the 100 kW LTCFB gasifier at Risø and on the 6MW LTCFB gasifier at Kalundborg. In addition to the gas phase measurements, bed material and cyclone ash samples were also collected and analyzed for the composition of the inorganic elemental species within the same. Mass balance calculations were thus made using the above results. The fuel used for all the plant runs was Danish Wheat Straw.

8.3.2 Observation and Results from the measurements in the LTCFB Gasifier

Table 1.1: Dust Load in product gas in the various Plant runs made in Risø and Kalundborg (from selected plant runs with good performance of cyclones)

	Dust Load, g/Nm^3
Risø (100kW Plant)	8-11
Kalundborg (6MW Plant)	20-30

As can be seen from Table 3.1, the dust loading in the product gas leaving the LTCFB gasifier for the 100 kW plant at Risø was 8-11 g/Nm$^{3.}$ In the 6 MW plant at Kalundborg, the particle concentrations were found to lie within the range of 20-30 g/Nm^3.The ash content of the collected samples were also analyzed using TGA. The TGA analysis of the cyclone ash collected from the secondary cyclone bottoms and the dust samples in the exit gas showed that the samples were reasonably similar. Both the samples were found to contain about 35-40% char and 45-50% ash, with low percentage of volatiles (5-6%).

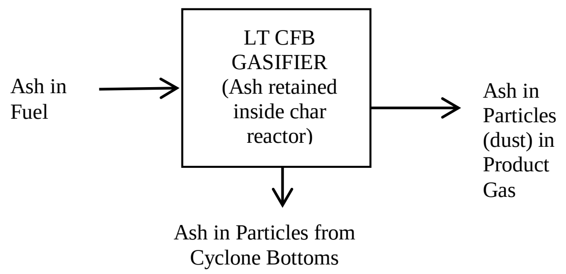


Figure 1.2: Distribution of ash in the LTCFB system

An overall ash balance on the LTCFB system is shown in Figure 1.2.

Table 1.2: Fraction of ash in the fuel released with the dust in the product gas and the fraction retained within the secondary cyclone ash in the various Plant runs made in Risø and Kalundborg.

% in Product gas	% in Cyclone	% Unaccounted
8-10 %	40-50 %	40-50%

It was seen that about 8-10% of the total ash in the fuel was found as dust in the product gas and 40-50% retained in the cyclone bottoms. The rest was retained within the system leading to accumulation of ash within the gasifier system. To develop a preliminary understanding on the behaviour of the inorganic species within the LTCFB gasifier, an overall mass balance of the inorganic elemental species within the LTCFB system was done.

Table 1.3: Results of mass balance from measurements at Kalundborg (from 29-06-2012,3:07 to 29-06-2012, 12:00)

1.	Element ,i	Si	K	S	Cl	Ca
2.	Fraction in cyclone ash	0.85	0.62	0.18	0.45	0.47
3.	Fraction accumulated in bed material (inside char reactor)	-0.18	-0.21	-0.009	-0.01	-0.16
4.	Fraction in product dust	0.07	0.07	0.03	0.09	0.08
5.	Unaccounted	0.27	0.55	0.79	0.48	0.62
6.	Sum total output	1.00	1.00	1.00	1.00	1.00

Table 1.3 shows the fraction of the major inorganic elemental species in the fuel that got collected in the secondary cyclone ash, in the dust particles in exit gas, in the bed material samples taken out for analysis and the fraction that got accumulated within the reactor, during plant runs at Kalundborg. Rows 1, 2 and 3 in Table 1.3 (the mass fractions determined from the samples analyzed during the plant runs) are based on the measured values whereas values in row 5 are the unaccounted mass fractions of the species calculated by closing the mass balance.

It can be seen from Table 1.3 that the mass balance closed poorly for most of the species. One of the main issues with the closure of the mass balance can be observed to be the uncertainty of the measured values for the accumulation of the species within the reactor. Bed material samples taken for analysis may be non-representative of the bed material inside the system. Though the accumulation of the species within the char reactor was uncertain, an analysis on the release of the ash forming species in the dust particles in the exit gas and that retained in cyclone ash could still be made. It can be seen from Table 1.3 that 60% of K in the fuel was retained in the cyclone ash along with Cl (45%) and Si (85%) which indicates the possibilities of presence of chlorides and silicates in the cyclone ash. Similar trends were observed in the dust particles in the exit gas. About 7-8% of K and Ca, 7% of Si, 10 % of Cl and 3% of S, present in the fuel leaves the reactor with the exit gas dust particles. A high fraction of Cl (50%) and S, (80%) were found to be unaccounted for the mass balance (Table 1.3). The unaccounted mass fractions could be due to the non-measured concentrations of S and Cl in the gaseous form (HCl or methyl chlorides). The sulphur may appear as reduced gas phase species COS, H_2S or as SO_2.

A study on the composition of the major inorganic elemental species in the secondary cyclone ash and in the exit dust particles further showed that the samples were reasonably similar, as shown in Table 1.4. The remaining fractions in the cyclone ash and dust (not shown in the Table) included char (as also evident from the TGA analysis).

Table 1.4: Composition of the inorganic elemental species in secondary cyclone ash and dust samples in exit gas collected during plant runs in Kalundborg (from 29-06-2012,3:07 to 29-06-2012, 12:00)[3]

	Si (mass%)	K(mass%)	Ca(mass%)	S(mass%)	Cl(mass%)
Secondary Cyclone Ash	13.0	6.4	2.3	0.3	1.1
Dust	6.7	4.8	2.5	0.3	1.4

As can be seen from Table 1.4, both the cyclone ash and the dust particles in exit gas were found to be mainly dominant in Si (7 -15%), K (5 -6%) and Ca (2 – 2.5%). Cl (1-1.5%) and S (0.2-0.3%) were present in lower amounts.

A study on the molar ratios of the inorganic elemental species in the samples analyzed further explained the behaviour of the species in the system.

Table 1.5: Molar ratios of the inorganic elemental species in the secondary cyclone ash and dust in exit gas collected during plant runs in Kalundborg (from 29-06-2012,3:07 to 29-06-2012, 12:00)

	Secondary Cyclone Ash				Dust in Exit Gas		
	K/Cl	K/Si	K/S		K/Cl	K/Si	K/S
Molar Ratio	5.2	0.4	18.6		3.2	0.5	12.4

Table 1.5 shows the molar ratios of the inorganic elemental species in the secondary cyclone ash and dust particles in exit gas collected during the plant runs in the 6MW LTCFB Gasifier at Kalundborg. It can be seen from Table 1.5 that the molar ratios of K/Cl (5.2) is high. This indicates that K was present in substantial amounts in other forms apart from being bonded to Cl.

The tar in the exit gas was also collected during the plant runs at Risø and analyzed for the inorganic elemental composition. It was seen from the analysis[3] that the tar present in the product gas contained very low amounts (< 0.004% by mass) of K, Ca, Si, Cl, S and other inorganic elemental species. The above results indicate a low release of the major inorganic elements with tar in the gasifier during the above plant runs.

Furthermore, the exit gas was also analyzed for the presence of methyl chlorides[4] to confirm the presence of Cl in gaseous forms. The analysis of the exit gas showed consistent presence of methyl chlorides which were in the range of 90-100 ppm. The amount of Cl in the exit gas thus measured was about 15% of the Cl present in the fuel. The presence of gaseous Cl in the exit gas as seen above (which were not included in the mass balance results shown in Table 1.3), could thus also partially explain some of the unaccounted fractions of Cl (70-80%) observed in the mass balance results explained earlier.

8.3.3 Conclusions

To study the overall ash distribution and behaviour of the inorganic elemental species within the LTCFB system, particle sampling measurements were made on the exit Product gas leaving the LTCFB Gasifier.

There were exit gas particle measurements made at Risø and Kalundborg and dust particles, secondary cyclone ash and bed material samples from the gasifier were collected and analyzed with respect to the inorganic elemental composition. It was seen from the measurements made on the LTCFB gasifier, that of the total ash that enters the system, 40 -50% of the ash was retained in the cyclone bottoms and a lower amount (8-10%) was released as dust in the product gas. A mass balance calculation was performed on the inorganic elemental species within the LTCFB system. It was seen from the mass balance results that about 50-60% of K, 30-40% of Ca and 50-80% of Si in the fuel were retained in the cyclone ash. About 30-40% of Cl in the fuel was also found to be retained in secondary cyclone ash. About 7-10% of K and Ca and 10% of Cl and Si, present in the fuel were released with the exit gas dust particles. It was also seen that high fractions of Cl and S (60-80%) were unaccounted in the mass balance results which could be due to the unmeasured concentrations of Cl and S in gaseous form. Cl could be present as methyl chlorides or HCl and S as COS or H2S. 15% of Cl in the fuel was found to be present as methyl chlorides (90-100 ppm). A study on the composition of the cyclone ash and dust particles in the exit gas further showed that the samples were reasonably similar. Both the cyclone ash and the dust particles in the exit gas were found to be mainly dominant in Si (7-15%), K (5-6%) and Ca (2–2.5%). Cl (1-1.5%) and S (0.2-0.3%) were present in lower amounts. The properties of the inorganic elements in cyclone ash and dust were further studied by observing the molar ratios of the elements within them. The molar ratios of K/Cl were found to be high in secondary cyclone ash and dust (3-5) which indicated that K is present in other forms apart from chlorides. It was also seen that the tar present in the product gas contained very low amounts (<0.004% by mass) of K, Ca, Si, Cl, S and other inorganic elemental species. This thus shows that the amount of K and other inorganic species present in tar in the LTCFB gasifier are low.

8.3.4 Future Work

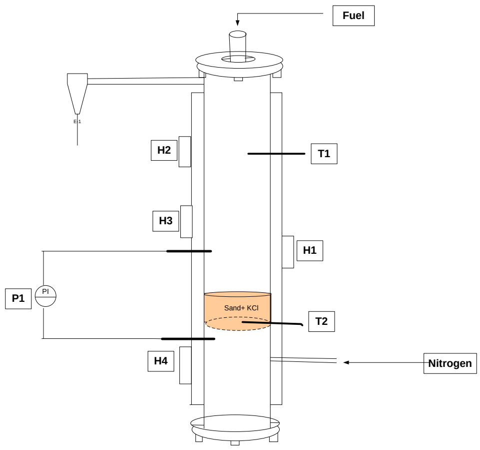
Based on the above analysis and literature studies, efforts towards developing an understanding on the mechanism of transformation and release of the inorganic elements within the LTCFB system are being made. A simplified model that can describe the behaviour of ash species in the LT-CFB system is being developed.

8.4 De-Fluidization studies

8.4.1 Experiments on De-Fluidization of bed material samples from Pyroneer Gasifier

A major problem often encountered in fluidized beds is bed agglomeration, which may result in total de-fluidization, leading to unscheduled downtime and additional costs. The above problems are found to be critical in fluidized bed combustion and gasification of biomass fuels which have high ash and alkali contents.

The main aim of this study was to understand the agglomeration and de-fluidization behaviour of alkali rich ash (bed-material) samples obtained from the 6 MW Pyroneer Gasifier, under non-oxidizing conditions. To begin with, experiments were first performed with Sand-K mixtures with varying K concentrations (results are shown in Table 4.1).



Symbol	Description
T1, T2	Thermocouples
P1	Pressure Indicator
H1,H2,H3,H4	Heating Elements

Figure 1.3 Fluidized Bed Set up for De-fluidization studies

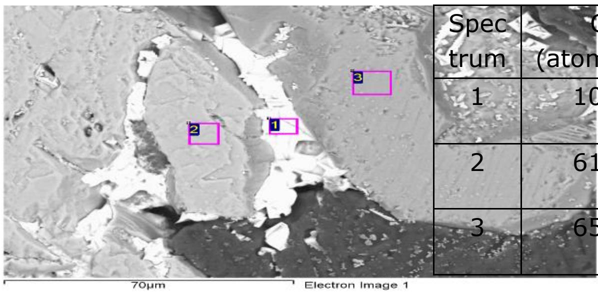
Table 1.6 De-fluidization temperatures of Sand+ KCl and Sand+ K_2CO_3 mixtures

Sand + KCl		Sand+ K_2CO_3	
Potassium content%	De-fluidization temperature,^{0}C	Potassium content %	De-fluidization temperature,^{0}C
2	766	1.5	737
4.5	762	4.5	732
6.5	756	6.5	728

The experiments were performed in a pilot scale fluidized bed set up as shown in Figure 1.3. The samples were fed from the top and fluidized using Nitrogen gas. The fluidization behaviour was studied by using the pressure drop trends measured across the bed as shown. The set up was electrically heated and the temperatures increased at a constant rate (by approximately 10^{0}C/min) during the experiments. The temperatures were measured just above the distributor plate and in the freeboard as shown. The operating velocities of the fluidizing gas (U) were maintained at 1.2 times the minimum velocity of the gas required to fluidize the particles (the minimum fluidization velocity, (U_{mf})). De-fluidization in the system was indicated by a sudden drop in the pressure, and the temperature at which it occurred is defined as the de-fluidization temperature.

8.4.2 *Observations and Results from the De-fluidization experiments*

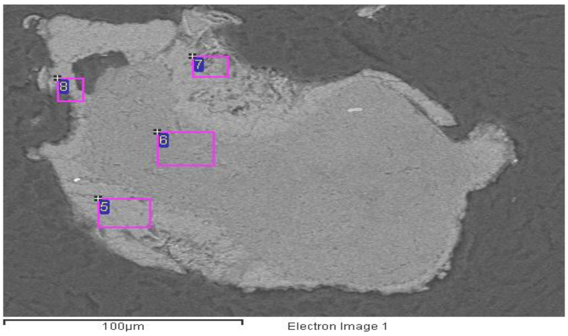
The results obtained for Sand+KCl and Sand+K_2CO_3 mixtures are shown in Table 1.6. As can be seen from Table 1.6, Sand+KCl mixtures were de-fluidized at about 760 ^{0}C and Sand+K_2CO_3 mixtures, at about 730 ^{0}C. The de-fluidization temperatures decreased with increase in K concentrations. Figure 1.4 shows the SEM analysis of the de-fluidized samples of Sand+KCl mixtures.



Spectrum	O (atomic%)	Si (atomic%)	Cl (atomic%)	K (atomic%)
1	10.4	1.4	40.2	48.1
2	61.0	24.1	0.0	7.5
3	65.6	34.4	0.0	0.0

Figure 1.4 SEM image and analysis of the de-fluidized samples of Sand+KCl mixtures.

The SEM image of Sand+KCl mixtures show pure KCl (spectrum 1) in between sand particles (spectrums 2.3). This shows that there was no reaction between KCl and the sand particles. The agglomeration could be initiated by the melting of KCl which acts as glue between the sand particles (melt induced agglomeration).



Spectrum	O (atomic%)	Si (atomic%)	K (atomic%)
5	64.7	23.4	11.9
6	66.2	33.1	0.7
7	65.4	20.2	14.4
8	69.3	20.0	10.7

Figure 1.5 SEM image and analysis of the de-fluidized samples of Sand + K_2CO_3 mixtures

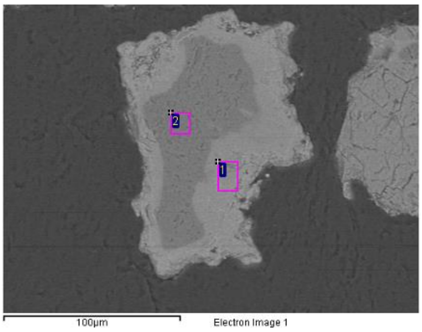
The SEM image of Sand+K_2CO_3 show two distinct phases as can be seen from Figure 1.5. The inner phase (spectrum 6) is rich in Si, which is surrounded by a coating layer (spectrum 5, 7, 8) rich in K and Si. This thus shows that K_2CO_3 reacts with silica in sand to form eutectic melts of K silicates. The K silicate melts form a coating layer on the surface of sand particles, which being sticky, binds to other particles forming agglomerates (coating induced agglomeration).

The de-fluidization experiments were then performed on ash (bed material samples) obtained from the Pyroneer Gasifier. The ash samples contained, 3.2%, 4.2% and 4.7% K respectively. The results of the above experiments are shown in Table 1.7.

Table 1.7 De-fluidization temperatures of bed material samples from Pyroneer Gasifier

%K	De-fluidization temperature,^{0}C
4.7	780
4.3	785

As can be seen from the Table, the De-fluidization temperatures of 4.3% K was about 785 ^{0}C and for 4.7% K was 780 ^{0}C . The SEM images of the de-fluidized samples of ash particles are shown in Figure 1.6.



Spectrum	O (atomic %)	Mg (atomic%)	Si (atomic%)	Cl (atomic%)	K (atomic%)	Ca (atomic%)
1	57.7	0.9	28.0	0.2	8.3	3.8
2	64.2	0.0	35.8	0.0	0.0	0.0

Figure 1.6 SEM image and analysis of the de-fluidized ash (bed material) samples

As seen from the SEM image, similar to the Sand+K_2CO_3 mixtures, the ash samples contained two distinct phases with the inner ash layer (spectrum 2 - dominant in Si) is surrounded by a coating layer (spectrum 1) dominant in K, Ca, Mg and Si. This indicates the reaction between alkali species K, Ca and Mg with Si forming a coating layer of eutectic melts of silicates around the bed particles, which being sticky bind to other particles forming agglomerates. It can be seen that de-fluidization takes place at higher temperatures in case of bed material samples (about 780^{0}C) as compared to the Sand+K_2CO_3 mixtures (about 730^{0}C), though in both cases, the mechanism of agglomeration is the same (coating induced agglomeration). One of the reasons could be due to the presence of Ca, Mg and Cl in the bed material samples (which were not present in Sand+K_2CO_3 mixtures) which could shift the formation of the eutectic melts to higher temperatures.

8.4.3 Future Work

Based on the above analysis and literature studies, further efforts towards developing an understanding on the mechanism of de-fluidization of ash samples under non-oxidizing conditions are being made. Thermodynamic modelling studies are also being done as an effort to improve understanding in this regard.

8.5 References

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