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Biomass based energy intermediates boosting biofuel production

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Publishable Summary

The overall objective of Bioboost project is to investigate various de-central biomass pre-treatment processes to optimize, high energy density carriers which can be utilized in large scale applications for synthesis of transport fuel and chemicals or directly in small scale combined heat and power (CHP) plants. Fast pyrolysis (FP), Catalytic pyrolysis (CP) and Hydrothermal Carbonization (HTC) are there different pre-treatment process investigated under this project. Each pre-treatment process produces a range of energy carriers from liquids to solids and/or their mixtures as slurry/paste.

This deliverable mainly focuses on the utilization of solid energy carrier in heat and power production via combustion. Pyrolysis char (supplied by KIT) and HTC-Coal (supplied by AVA-CO_2) were investigated with in this work package. Combustion tests were performed at lab scale and pilot scale combustion facility at IFK, University of Stuttgart. Both co-firing and mono-firing combustion tests were performed. Combustion tests were focused on the investigation and evaluation of combustion performance, stability and emission behaviour at different thermal shares of the Bioboost fuels. A comparative evaluation is done with respect to the hard coal (mono) firing scenario. Fly ash and deposit samples were also collected during the combustion test. In addition fuel feeding/handling issues were also evaluated.

- Combustion test with Pyrolysis Char (PC-dry)

Combustion test were performed with various thermal shares of pyrolysis char (PC-dry). As a reference mono-firing of coal and pyrolysis-char has been performed. The co-firing shares were chosen to represent the range of existing practice of co-firing straw, as straw was the original biomass source used for the production of char. The results from PC-dry combustion experiments showed that co-firing in small shares can be technically possible. However issues related to chlorine are still critical and needs careful consideration. The experiences from straw co-firing are transferable for the pyrolysis char (PC-dry) because the content of critical in-organic elements like potassium (K) and chlorine (Cl) remains similar or higher in the char.

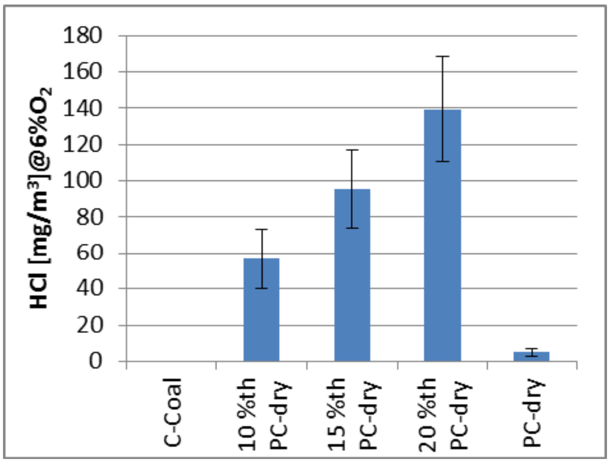


Figure: HCl [mg/m^3] concentration in flue gas at various thermal share of Pyrolysis Char (PC-dry)

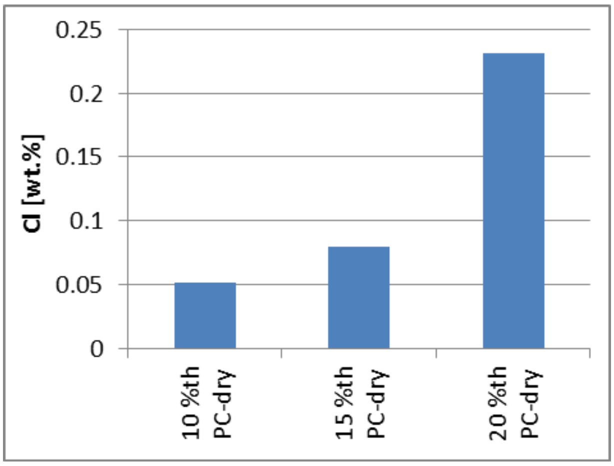
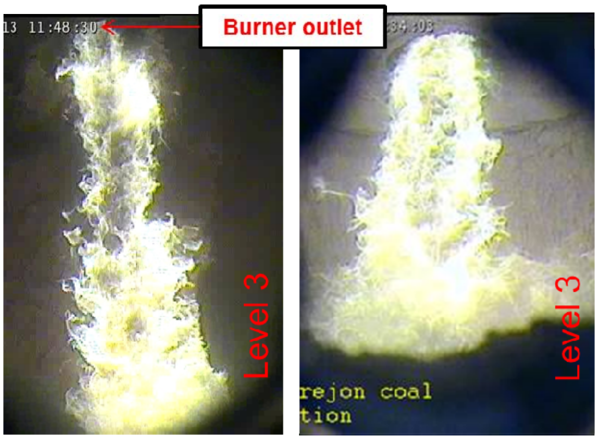


Figure: Chlorine (Cl) [wt.%] content in fly ash at various thermal share of Pyrolysis Char (PC-dry)

- Combustion test with HTC-Coal

HTC-Coals are new range of secondary biomass solid fuel, in combustion practices. A range of co-firing shares were chosen including mono-firing of HTC-Coal. As expected, properties of HTC-Coal vary significantly with the source biomass material so HTC-BT (spent grains from brewing, Biertreber) and HTC-BW (household kitchen waste, Biowaste) shows different challenges. HTC-BW has higher amount of ash and lower heating value in comparison to HTC-BT. Chlorine is also significantly present in HTC-BW. HTC-BW showed acceptable combustion performance only during co-firing while technically; both mono-firing and co-firing is possible with HTC-BT. However, burner design and modification, fuel-N to NOx formation and reduction related issues, fly ash quality and phosphorous utilization issues and milling safety issues are some areas which possibly need further understanding and clarification for large scale utilization.

HTC-Coal showed some fundamental difference in combustion behaviour in comparison to the reference hard coal. The HTC-Coal particles take longer time to combust and create a very long flame and different temperature profile in comparison to reference coal. The different combustion behaviour is expected to impact aspects of burner and boiler design. More R&D work is necessary to understand the combustion behaviour of HTC-Coals including long term continuous combustion tests. The comparison of HTC-Coal combustion behaviour with brown/lignite coal and other biomass fuels (e.g. torrefied wood) should be considered in the further work.



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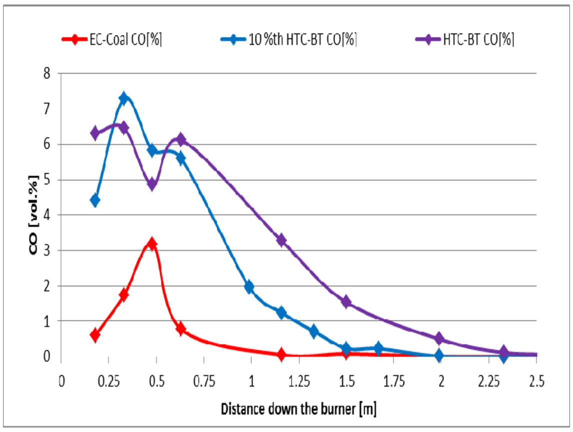

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1. Introduction

This report is deliverable ‘D6.2 Solid Energy Carrier Combustion’ prepared within the European Project’ Biomass based energy intermediates boosting biofuel production.’ Bioboost is 3.5 year project supported by the European Commission with in 7th Framework Programme.

The overall objective of Bioboost project is to investigate various de-central biomass pre-treatment processes to optimize, high energy density carriers which can be utilized in large scale applications for synthesis of transport fuel and chemicals or directly in small scale combined heat and power (CHP) plants. Fast pyrolysis (FP), Catalytic pyrolysis (CP) and Hydrothermal Carbonization (HTC) are there different pre-treatment process investigated under this project. Each pre-treatment process produces a range of energy carriers from liquids to solids and/or their mixtures as slurry/paste.

This deliverable mainly focuses on the utilization of solid energy carrier in heat and power production via combustion. Pyrolysis char (supplied by KIT) and HTC-Coal (supplied by AVA-CO_2) were investigated.

The pyrolysis char produced in pilot scale plant at KIT during fast pyrolysis of straw was supplied to University of Stuttgart within the frame work of Bioboost project. The pyrolysis char is here after referred as PC-dry.

HTC-Coal was produced by hydrothermal carbonization of wet residual biomass and supplied to IFK, University of Stuttgart by AVACO_2. HTC-Coal from two different sources were supplied, namely from spent grains from brewing (Biertreber) and from household kitchen waste (Biowaste). The HTC-Coal produced from spent grains (Biertreber) is here after referred to as HTC-BT and from Biowaste is referred to as HTC-BW.

The received fuels were analyzed according to standard fuel analysis method. Combustion tests were performed in lab and pilot scale pulverized fuel combustion facility at IFK, University of Stuttgart. Both mono-firing and co-firing tests were performed. A hard coal was used as the reference coal.

The focus of the combustion test is to investigate the combustion behaviour and performance of the fuel. The emission behaviour, boiler aspect like deposition and corrosion and the quality of residues i.e. fly ash were assessed. In addition, aspects of fuel handling and feeding were also briefly discussed.

The report is divided into 3 main parts:

1. Combustion test of Pyrolysis Char (PC-dry)
2. Combustion test of HTC-Biertreber (HTC-BT)
3. Combustion test of HTC-Biowaste (HTC-BW)

PC-dry and HTC-BW were combusted in 20 kW lab scale pulverized fuel combustion facility while HTC-BT was combusted in 500 kW pilot scale pulverized fuel combustion facility. The fuels were received as powder therefore decided for pulverized fuel combustion.

2. Combustion facility

The combustion facilities discussed here are pulverized fuel combustion facility. Each combustion facility is briefly discussed in the following chapters.

2.1. 20 kW pulverized fuel combustion facility (BTS)

Figure 1 shows the schematic outline of 20 kW PF combustion facility (lab scale). It is a down fired atmospheric drop tube furnace. The combustion chamber (furnace) is electrically heated ceramic tube of 0.2 m of internal diameter and a length of 2.5 m. A certain temperature profile can be maintained inside the combustion chamber by external electric heating. The electrical heating zones are divided in 5 zones. Each zone can be established at certain temperature. For the combustion test discussed here, the upper zone T1 and T2 was around 1300 °C, T3 was around 1200 °C and T4 and T5 was kept around 1100 °C. The temperature was so chosen to have a similar temperature profile as observed in coal fired pulverized fuel combustion facility. The pulverized fuel/fuel blend with combustion air is injected into the combustion chamber through the burner mounted at the top. A screw feeder was used to meter and feed the fuel/fuel blend continuously. As the fuel enters the heated furnace zone it ignites to create a stable flame and the combustion product is extracted at the end of the furnace, and gradually cooled along the flue gas path. A temperature profile can also be maintained in the flue gas path by external heating. A bag house candle filter at the end of the flue gas path collects the fly ash generated during the combustion.

The oil-cooled gas sampling probe that can move along the central axis, facilitate the extraction of flue gas at different location inside the combustion chamber. The flue gas is extracted at the end of combustion chamber (2.5 m down the burner) and O_2, CO_2, CO, SO_2, NO and NO_x are continuously measured.

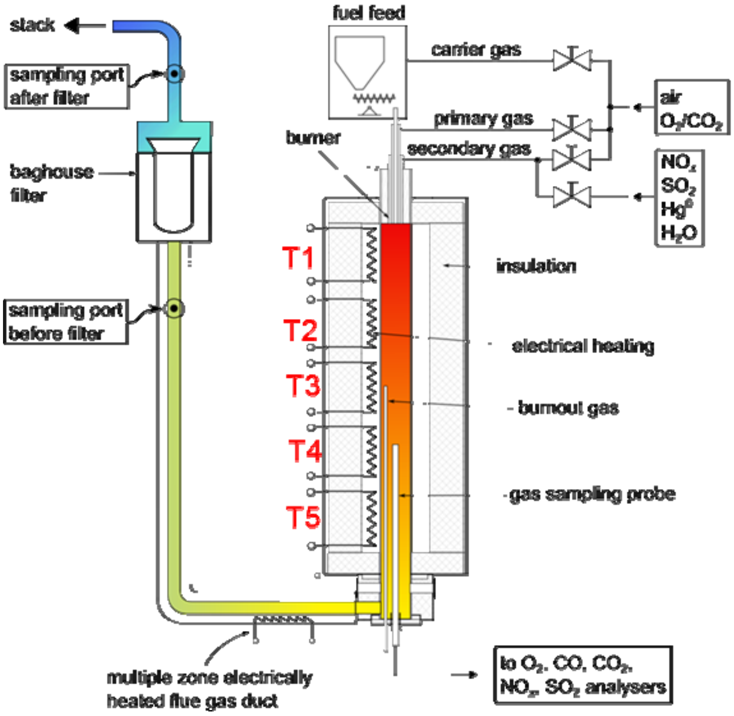

Figure 1: Schematic outline of pulverized fuel combustion facility (20 kW) at IFK

Moreover, the gas profile at different location inside the flue gas can also be measured. The oil cooled probe also facilitates the collection of fly ash from different location inside the combustion chamber. It also helps to place the deposit sampling probes at desired location inside the combustion chamber.

2.2.500 kW pulverized fuel combustion facility (KSVA)

Figure 2 shows the schematic outline of 500 kW pulverized fuel (PF) combustion facility (pilot scale). It is down fired atmospheric combustion facility for pulverized fuels such as coals, biomasses and other pre-treated solid combustibles. The test facility is optimized for investigation of pulverized fuel combustion processes and allows the characterization of different kinds of fuels at staged and un-staged combustion conditions. It also simulates the flue gas side of a power plant including flue-gas cleaning with a high-dust SCR catalyst, an electrostatic precipitator (ESP) and a bag-house filter (FF) Dependent on the test requirements, every of those flue gas cleaning devices can be by-passed or used. Combustion air is provided by a forced draught (FD) fan while an induced draught (ID) fan ensures the transport of the flue-gases through the flue-gas system towards the stack.

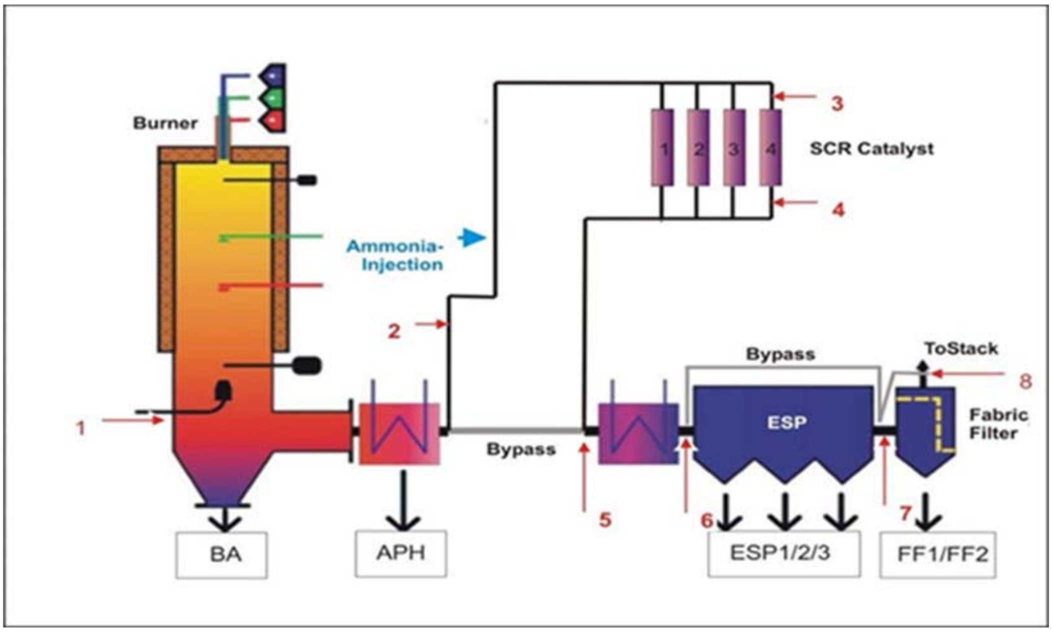

Figure 2: Schematic outline of pulverized fuel combustion facility (500 kW) at IFK

The combustion chamber consists of six cylindrical segments with a total length of 7.000 mm and an inner diameter of 800 mm. Refractory lining covers the inner surface of the upper four segments of the combustion chamber to a distance of 4.000 mm from the burner. Numerous measurement openings are integrated into the reactor wall.

The reactor is 1st heated with the pilot gas flame. The solid fuel and combustion air is then injected gradually through the main burner mounted at the top. Once the proper flame is established the gas flame is totally closed. The flame than maintains the temperature profile inside the combustion reactor and along the flue gas path.

The flue gas is sampled continuously from L25 (see

Annex 5) and O_2, CO_2, CO, SO_2, NO and NO_x are measured. The flue gas concentration and temperature at various locations inside the furnace can also be measured through the openings at different levels.

3. Combustion test of Pyrolysis Char (PC-dry)

PC-dry refers to the char produced from fast pyrolysis of straw. Table 1 shows the properties of PC-dry and the C-Coal. The lower heating value (LHV) is reported here is 'as analyzed' (an), ash is reported as 'water free' (wf) and rest are reported as 'water ash free' (waf).

Table 1: Composition and Heating Value of PC-dry and C-Coal

Fuel	**LHV**	**W**	**A**	**V**	**Cfix**	**C**	**H**	**N**	**S**	**Cl**
	[MJ/kg, an.]	[%, an.]	[%, wf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]
PC-dry	21.2	2.9	30.1	21.2	78.8	86.1	3.56	0.87	0,25	0.91
C-Coal	27.9	0.31	11.03	42.3	57.7	77.5	5.09	1.51	1.09	--

As the product is the char fraction of pyrolysis, the amount of volatiles is very low. It is also characterize by high amount of ash. The amount of chlorine (Cl) is also significantly high as expected because straw is known to content significant amount. While, sulphur (S) is relatively low.

The coal is Columbian hard coal and is a reference fuel for the co-firing. The nitrogen (N) and sulfur (S) content in coal is higher in comparison to PC-dry.

Silicon oxide (SiO_2) accounts for the majority of the ash oxide composition of PC-dry. The amount of potassium oxide (K_2O) is also significantly high. While in coal, silicon oxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) are main ash oxides. The respective ash composition (as oxides) is shown in Annex 1.

Three co-firing shares namely; 10 $\%_{th}$, 15 $\%_{th}$ and 20 $\%_{th}$ of PC-dry ($\%_{th}$ indicates % of thermal energy) were combusted in 20 kW PF facility along with mono-firing of PC-dry and C-Coal. Low co-firing shares were chosen because the experience reported from most straw combustion studies [1] are mostly for very low shares (typically not exceeding 10 $\%_{th}$). The total flue gas volume (as calculated form the respective fuel/fuel blends composition) is 11.5 m^3N/h during all combustion cases. The excess O_2 was around ~3% at the end of the combustion chamber during all combustion cases.

3.1.Fuel handling and feeding

Pyrolysis-char (dry) as received was in form of fine powder. For co-firing, individual fuels (PC-dry + C-Coal) were manually mixed before feeding. Homogeneous mixing was assured by mixing smaller quantities. Respective fuel (mono-firing) /fuel blend (co-firing) was fed through the screw feeder. Homogeneous and stable feeding was achieved during all combustion cases. No specific problems regarding small scale feeding.

3.2. Combustion behaviour

A stable flame was maintained during all combustion cases with excess O_2 of ~ 3 % for all cases. The O_2 and CO_2 measured during various combustion cases of PC-dry are shown Annex 10. The CO measured as the end of the combustion chamber is shown in Figure 3. It shows that the CO concentration is very low (below 20 ppm) for all co-firing case. The CO values during coal mono-firing were even lower. It indicates acceptable burnout was achieved for both mono-firing (coal) and co-firing cases. The CO level during PC-dry mono combustion was significantly higher. Higher fluctuations in CO and frequent CO peaks observed during PC-dry mono-firing indicated poor combustion performance. Poor performance may be related with properties of pyrolysis char e.g. like higher ash content, particle size etc.

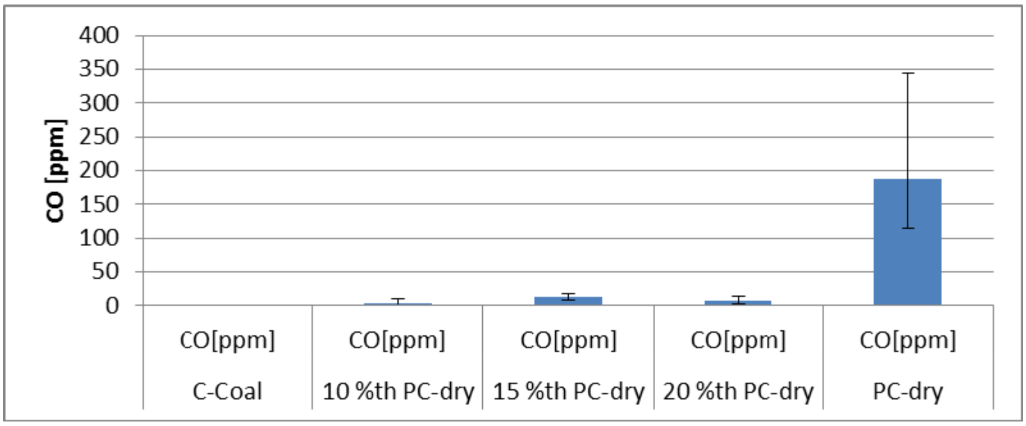

Figure 3: Average CO concentration [ppm] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of PC-dry (co-firing) and PC-dry (mono-firing)

3.3. Emission

NO_x (calculated as NO_2), SO_2 and HCl emissions are discussed in this section. The emission concentration is presented as mg/m^3 @ 6 % O_2 to compare with the national or regional emission limits. NO_x and SO_2 concentration measured at the end of the furnace i.e. 2.5 m down the burner while HCl was measure in the flue gas path before filter is considered as emission values. These are the concentration measured before any emission control measures. NO_x and SO_2 were continuously measured by standard flue gas analyzer. HCl was measured by wet chemical method.

A conversion factor as % is also discussed along with absolute emission values. For example, the NO_x conversion is calculated as measured NO_x during respective combustion case divided by theoretical maximum $NO_{x,}$ assuming all fuel-N (fuel-nitrogen) is converted to NO_x. The HCl conversion and the SO_2 conversion are calculated analogically as the NO_x conversion.

3.3.1. SO_2 emission

Figure 4 shows the SO_2 concentration measure at the end of furnace (2.5 m) for various thermal shares of PC-dry. The SO_2 emission from coal is significantly higher in comparison to PC-dry and so does the amount of fuel-S (fuel-sulfur) (almost 4 times higher) in coal. Up to 20 $\%_{th}$ PC-dry the SO_2 emission is comparable to coal mono-firing case. The SO_2 emission is expected to decrease with increase share of PC-dry due to decreasing fuel-S. Increasing share of PC-dry is also expected to increase sulfur retention in ash due to increase of sulfur capturing species like calcium (Ca) and potassium (K).

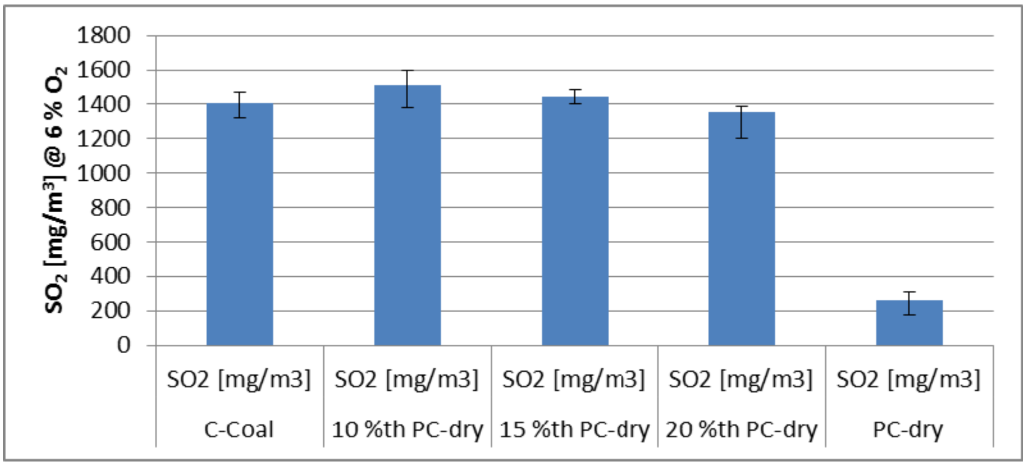

Figure 4: Average SO_2 concentration [mg/m^3 @ 6 % O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of PC-dry (co-firing) and PC-dry (mono-firing)

3.3.2. NO_x emission

Figure 5 shows the NO_x concentration measure at the end of furnace (2.5 m) for all the combustion cases. The NO_x emission from coal and PC-dry is almost similar. However, fuel-N is almost 2 times higher in coal in comparison to PC-dry. The NO_x conversion for coal is in average ~25 % while for PC-dry is almost 50 % in the combustion condition and combustion facility discussed here. The higher NO_x conversion for PC-dry indicates that the fuel-N from PC-dry is more susceptible to form NO_x.

NO_x is slightly higher during co-firing in comparison to both mono-firing cases. The fuel-N in flue blend decreases with increasing share of PC-dry while the NO_x conversion slightly increases.

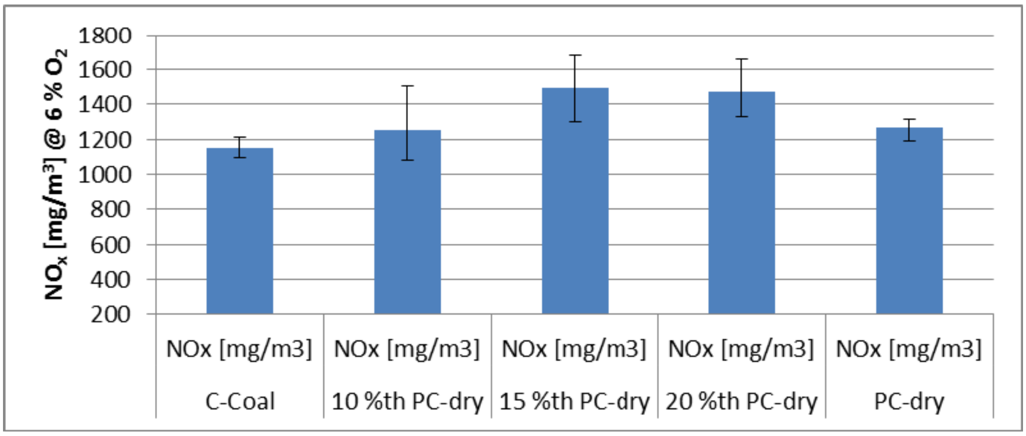

Figure 5: Average NO_x concentration [mg/m^3 @ 6 % O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of PC-dry (co-firing) and PC-dry (mono-firing)

For all cases NO_x emission is higher than accepted limit values. NO_x control strategy should be implemented. Primary NO_x reduction measures like staging is likely to be an attractive option.

3.3.3. HCl emission

Figure 6 shows the HCl concentration measured at the flue gas path (200-300 °C) before filter at various thermal shares of PC-dry. Despite of significant different of fuel-Cl among coal and PC-dry HCl concentration was almost negligible for both mono-firing cases. Lower HCl during coal can be related to the negligible fuel-Cl (fuel-chlorine) in coal.

While in case of PC-dry, fuel-Cl is significantly high. The maximum HCl concentration assuming all fuel-Cl converted to HCl is around 800 mg/m^3. It apparently indicates that fuel-Cl from PC-dry has not been released as HCl. The chlorine apparently remained in ash as probably as KCl. The retention of chlorine in ash is widely discussed issues for many other biomass related fuels and critical issue regarding corrosion and fly utilization.

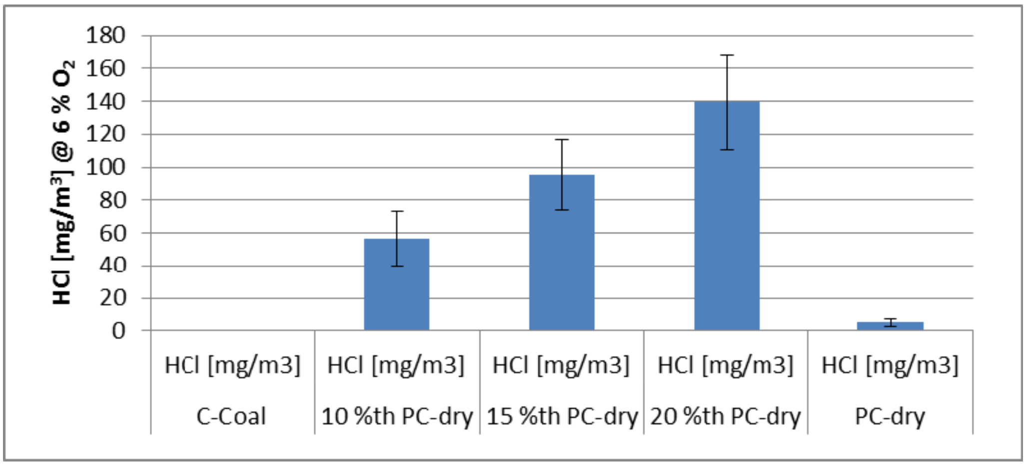

Figure 6: Average HCl concentration [mg/m^3 @ 6 % O_2] measured in the flue gas path before filter (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of PC-dry (co-firing) and PC-dry (mono-firing)

During co-firing cases HCl was significantly higher in comparison to both reference coal and PC-dry. HCl increases with increasing share of PC-dry which can be co-related to the increasing amount of fuel-Cl.

The chlorine in PC-dry is expected to be as potassium chloride (KCl) and released as gaseous KCl during combustion. Sulfation reaction according to reaction 1 is expected to be limited during mono-firing, due to low amount of fuel-S (fuel-sulfur) resulting lower SO_2 concentration in flue gas. Lack of sulfation limits the release of Cl as HCl. This can possibly explain why negligible HCl was measured during PC-dry mono-firing case despite of significant higher amount of fuel-Cl.

$$2KCl + SO_2 + 0.5O_2 + H_2O \rightarrow K_2SO_4 + 2HCl \qquad R1$$

However, during co-firing significantly higher SO_2 promotes the sulfation of KCl to release HCl. So, higher HCl concentration is measured during co-firing.

Moreover, certain minerals like aluminosilicate (like, kaolinite) commonly present in coal are also discussed to react with KCl to release chlorine according to reaction 2. But in most biomass fuel like straw (or here PC-char) no aluminosilicate minerals are present.

$$2KCl + \text{aluminosilicate} \rightarrow \text{K-aluminosilicate} + HCl \qquad R2$$

In summary both reaction 1 and 2 increase the release of chlorine as HCl and in lack of these reaction chlorine will end in the fly ash as KCl. The choice of coal composition is of great concern for co-firing. Coal rich in sulfur and aluminosilicate ash is preferable to co-combust with chlorine rich biomass fuels.

Chlorine released as HCl in flue gas can be easily removed during flue gas cleaning while chlorine as KCl in fly ash may create serious concerns regarding corrosion (heat exchanger surfaces) and fly ash utilization. The issues related to chlorine will be discussed further also in further sections.

3.4. Deposit and Corrosion

The ash composition of PC-char indicates it as problematic regarding ash deposition. The amount of potassium and silicon is expected to increase the tendency of molten deposit formation. Formation of low melting potassium silicates and increased deposition tendency in various biomass fuels has been reported in many studies. The sintering temperature of PC-dry ash is significantly low; 670 °C (see Annex 4).

Figure 7 shows un-cooled deposit collect at 1.5 m down the burner during combustion of PC PC-dry (mono-firing). The black particles on the surface are un-burnt particles. The deposit mass collected over the ceramic surface was very loose and sandy. The loose sandy deposit is apparently quartz (SiO_2) particles.

The quartz was the heating medium/bed material used during the pyrolysis process. High amount of quart (SiO_2) appear to be mixed with PC-dry char. These quartz parties are almost un-reactive and significantly dilute the deposit mass to appear loose and sandy.

The BSE image of the deposit cross section shows the ceramic probe surface to be almost clean indicating no any molten particles. However, low melting potassium silicates are expected to form. The dilution effect from unreactive quartz seems dominant in PC-dry un-cooled deposit. Some quartz particles seem to be bridged together. The bridge contains specially potassium and silicon and apparently molten so able to bridge the individual particles.

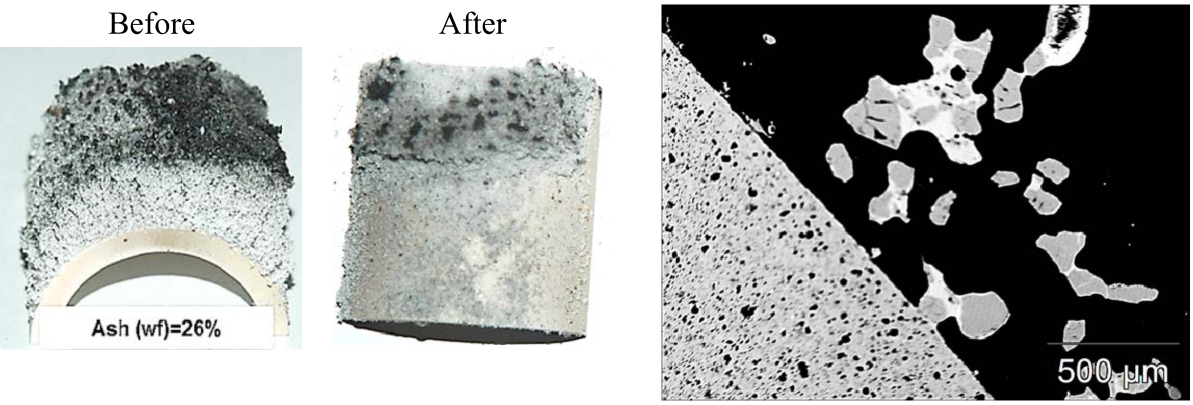

Figure 7: The uncooled deposit sampled at 1.5 m down the burner during PC-dry mono-firing, sample surface before and after brushing. The BSE image of the deposit sample cross-section (right)

Figure 8 shows un-cooled deposit collect at 1.5 m down the burner during combustion of 20%th. PC–dry (co-firing). Deposit is still loose and sandy but comparatively less in comparison PC-dry mono-firing. Loose and sandy deposit can be easily removed but ceramic surface still have a thin brownish layer. The BSE (Backscattered electrons) image of the deposit cross-section shows a layer of molten/fused deposit mass on the ceramic surface.

The issues related to deposition due to formation of low melting alkali silicates and issues related to corrosion e.g. condensation of alkali chloride on heat exchanger surfaces both can be an critical issues for PC-dry. While co-firing such fuels, the choice of coal is also a major factor. Coals rich in aluminosilicate minerals (like kaolinite) are found effective to capture gas phase potassium species as potassium–aluminosilicate, which has very high melting. Potassium chloride is efficiently captured by aluminosilicate releasing HCl (see reaction 2). Therefore, reduces the risk of potassium chloride condensation on heat exchanger surfaces or as fly ash particles. Moreover, sulfation of alkali chlorides also releases chlorine as HCl; therefore coal with significant amount of sulphur can be advantageous. The sulfation reaction is discussed earlier see reaction 1. Potassium sulfate (K_2SO_4) is less corrosive in comparison to potassium chloride (KCl).

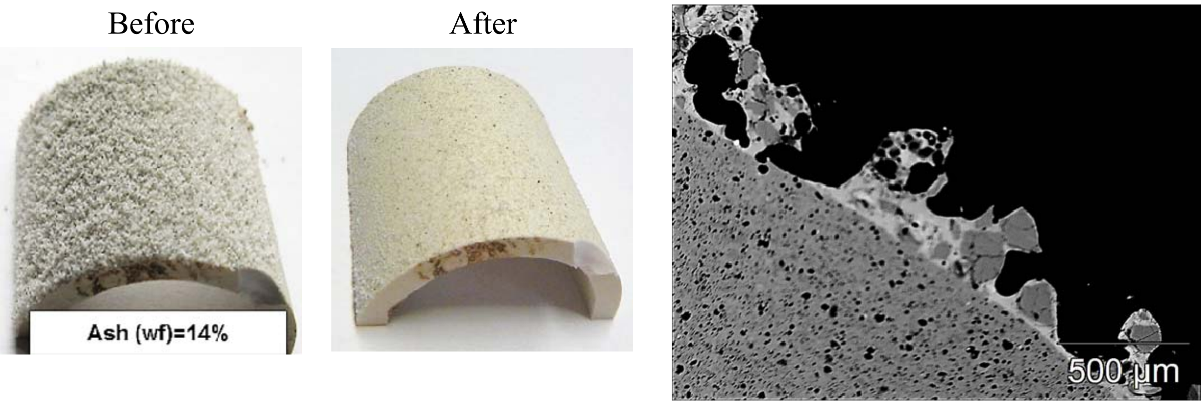
Before
After

Figure 8: The uncooled deposit sampled at 1.5 m down the burner during 20 $\%_{th}$ PC-dry co-firing, sample surface-before and after brushing. The BSE image of the deposit sample cross-section (right)

3.5.Fly Ash

Silicon, aluminium and iron are major elements present in coal ash while silicon, calcium and potassium are major elements present in PC-dry. The composition of co-firing ashes varies according to their respective mass ratio during co-firing. Fly ash sample was from the candle filter at the end of the flue gas path collected during each combustion cases. Figure 9 shows the composition of fly at various thermal shares. In general, as expected calcium and potassium increases with increasing share of PC-dry while aluminium and iron decreases. The silicon was also expected to be higher in co-firing ashes because of higher silicon content in PC-dry ash, but it was slightly lower. This is possibly related to the sampling error or sample in-homogeneity.

Fly ash from coal is mostly utilized for concrete and construction industries. Various standards exist to categorize the suitability of fly ash for specific kind of utilization. Table 2 summarizes some criteria (chemical requirement) for fly ash utilization in cement/concrete industry.

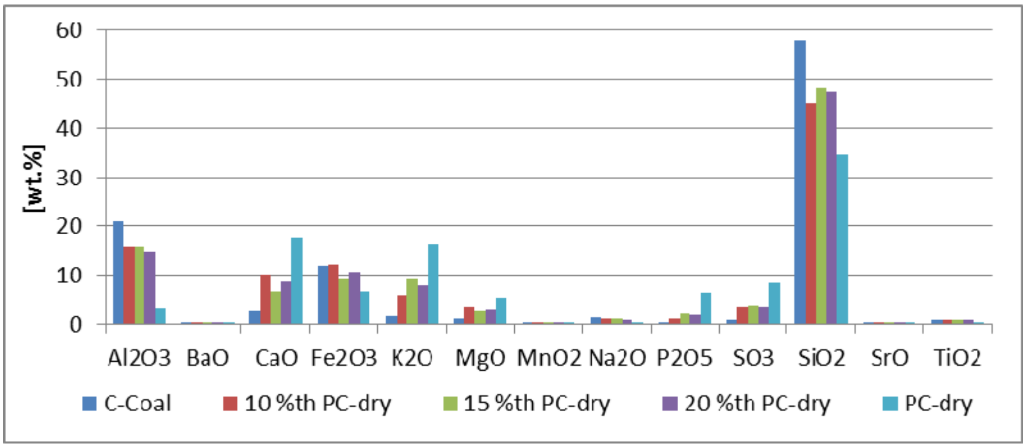

Figure 9: Composition of fly ash [wt.%] collected during coal (mono-firing), various thermal shares of PC-dry (co-firing) and PC-dry (mono-firing)

It clearly indicates that, co-firing of fuels like PC-dry would influence the fly ash utilization criteria. Especially, total alkali content and chlorine content in fly ash will be critical. The total alkali content will exceeds the values above 10 $\%_{th}$ PC-dry.

Table 2: Chemical requirements for fly ash utilization (EN 450-1)

	% (by weight)
Loss of Ignition/un-burnt carbon	<5-9 %
Chloride (Cl^-)	<0.1 %
SO_3	<3 %
CaO (reactive)	<10 %
SiO_2+Al_2O_3+Fe_2O_3	>70 %
Total alkali (calculated as Na_2O)	<5 %
P_2O_5	<5 %
MgO	<4 %

The fly ash collected by the candle filter ash was also analyzed for chlorine content. **Figure 10** shows the amount of chlorine present in fly ash at various thermal shares of PC-dry. The amount of chlorine in fly ash is increasing with increasing share of PC-dry. The HCl concentration was also observed to increase with increasing share of PC-dry (see Figure 6) for the co-firing cases. It indicates that during co-firing some of the chlorine from fuel is released as HCl while some part goes to ash. In case of PC-dry mono-firing the HCl in flue gas was negligible (see Figure 6). It means most of the chlorine ends up in the fly ash. The chlorine in fly ash collected during PC-dry mono-firing was significantly high.

It is difficult to make a mass balance for fuel-Cl among various cases and was not the focus during these tests. To make the proper mass balance for chlorine, uncertainties like the actual amount of fuel-Cl in the respective blend, uncertainty associated with the collection of candle filter ash and possible sample inhomogeneity and HCl in flue gas should be carefully assed.

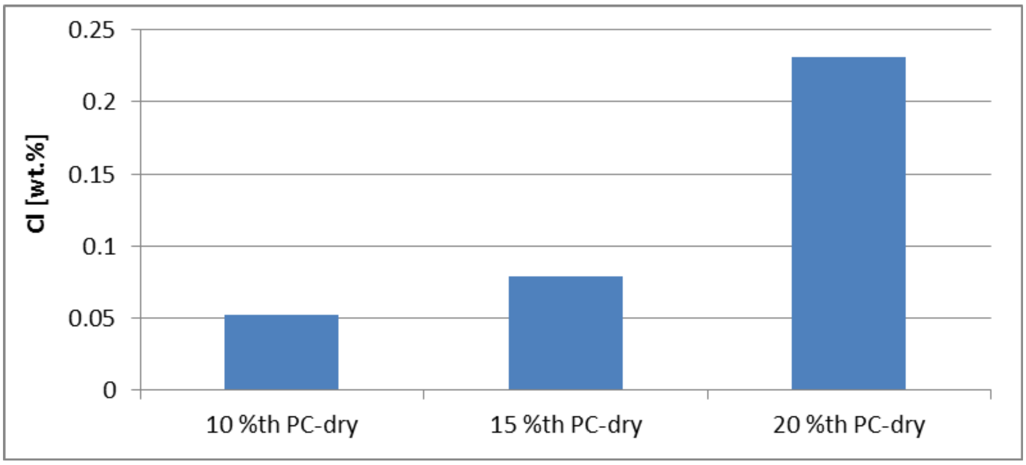

Figure 10: Chlorine (Cl) [wt.%] in fly ash at various thermal shares of PC-dry

3.6. Summary

Different thermal shares of PC-dry were co-combusted with coal. Different issues regarding the co-firing of PC-dry in existing coal firing power plants were discussed. Mono-firing in pulverized fuel boilers is not recommended for PC-dry due to its properties like, high ash and chlorine content. During mono-firing, aspects such as fuel handling/feeding, combustion stability/burnout and emission (NO_x & SO_2) do not show a significant or considerable shift from the reference coal case. The combustion and emission behaviour may be different in real-scale combustion systems where the flame itself establishes the temperature profile; however, the general comparative trend in reference to coal is expected to remain similar.

Concerns related to chlorine were identified as a major challenge for PC-dry co-firing. Chlorine impacts HCl emissions fly ash quality, and deposit/corrosion issues. Chlorine remaining as alkali salt (KCl) is more problematic in comparison to HCl emission. Alkali chloride (KCl) can condense on heat exchanger surfaces and/or is retained in fly ash. Alkali chloride is a very corrosive salt and raises issues with critical material wastage (e.g. super-heater corrosion). It will drastically reduce boiler efficiency and availability.

The maximum co-firing share is most probably limited by chlorine issues. The negative impact of chlorine [2] can be minimized by choosing a suitable quality of coal. Considerable amount of sulphur and certain ash compositions (e.g. alumino-silicate ash) are preferable coal qualities regarding biomass co-firing [1]. Both will help to keep chlorine out in flue gas as HCl. The experience from straw firing can be beneficial and transferable also for PC-dry. Problems discussed for raw straw are also the problems for pyrolysis char from straw.

Milling is also an important aspect in pulverized fuel combustion systems. This has not been covered during this work as the fuels were received as powder. Milling issues should also be considered for commercial scale utilization scenario. The chlorine related corrosion issues and fly ash quality issues need further insight.

From the experimental results obtained during this work and various studies [1] on straw firing and PC-dry is technically possible to co-fire at low thermal shares (below 10 $\%_{th}$) in existing pulverized coal fired power plants.

4. Combustion test of HTC-Biertreber (HTC-BT)

HTC-BT refers to the HTC-Coal produced by hydrothermal carbonization of spent grains from brewery industry. Table 3 shows the properties of HTC-BT and the Coal. The lower heating value (LHV) is reported here is ‘as analyzed’ (an), ash is reported as ’water free’ (wf) and rest are reported as ‘water ash free’ (waf).

Table 3: Composition and Heating Value of HTC-BT and EC-Coal

Fuel	LHV	W	A	V	Cfix	C	H	N	S	Cl
	[MJ/kg, an.]	[%, an.]	[%, wf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]
HTC-BT	25.9	2.43	7.07	71.8	28.2	66.4	7.04	3.28	0.48	0.006
EC-Coal	26.5	2.53	12.2	35.8	64.3	80.9	5.30	1.69	0.65	0.009

HTC-BT has lower amount of ash and slightly lower heating value in comparison to coal. Significant amount of nitrogen (N) is present both sulphur and chlorine are slightly lower. Table 3 shows the fuel properties of HTC-BT combusted at 500 kW facility; mono-firing case. HTC-BT was received from AVACO$_2$ (as powder) in different batches. The composition of HTC-BT for co-firing is shown in Annex 3. HTC-BT was the HTC coal extensively tested in the frame work of ‘Bio-Boost’ project.

HTC-BT ash is significantly rich in phosphorous oxide (P_2O_5) in comparison to coal. Calcium oxide (CaO) and silicon oxide (SiO_2) are other major ash oxides. The ash oxide composition is presented in Annex 2.

Three co-firing tests namely; 10 $\%_{th}$ HTC-BT, 20 $\%_{th}$ HTC-BT and 40 $\%_{th}$ HTC-BT was performed. Mono-firing of HTC-BT and EC-Coal was also performed. Staging tests were performed for 10 $\%_{th}$ HTC-BT co-firing and HTC-BT mono-firing case.

For co-firing test in 500 kW facilities HTC-BT and Coal were individually transported to the burner and mixed. The adapted feeding system for HTC-BT powder will be discussed later. Table 4 shows the feeding rate of both fuel and total combustion air for respective combustion cases.

Table 4: Fuel [kg/h] and combustion air [m^3N/h] for respective un-staged combustion cases

	Coal	10 $\%_{th}$ HTC-BT	20 $\%_{th}$ HTC-BT	40 $\%_{th}$ HTC-BT	HTC-BT
Coal [kg/h]	40	36	31	24	--
HTC-BT [kg/h]	--	5	10	20	46
Total Air (dry) [m^3N/h]	318	307	305	308	303

Total combustion air is divided into carrier air, primary air and secondary air. Fuel is transported by carrier air to the burner were primary and secondary air is mixed separately at different locations. The burner set-up was same for all combustion cases. The flue gas concentration was continuously recorded at end of the combustion chamber (L25, See Annex 5). The excess O_2 level at the end of the combustion chamber was kept around ~3 % (λ=1.15) for all individual un-staged combustion cases. The fuel gas and temperature was also measured at various levels in the combustion chamber down the burner. The staging test was focused on NO_x behaviour. The staging parameters will be discussed later.

4.1.Fuel handling and feeding

The HTC-BT was received as fine powder. The particle size analysis of fuel as received measured using malvern particle size analyzer showed that 50 % of particles were below 39 µm i.e. d50. The d90 was around 86 µm. The HTC-BT particles were slightly coarser in comparison to coal but are in particle size range expected to handle by pulverized fuel burner. A screw type feeder was adapted for feeding HTC-BT powdered fuel. The basic concerns of modification were regarding feeding safety issues mostly arising from the risk of low temperature ignition. Previous in-house experience (at IFK) of feeding lignite coal was the reference for adaptation.

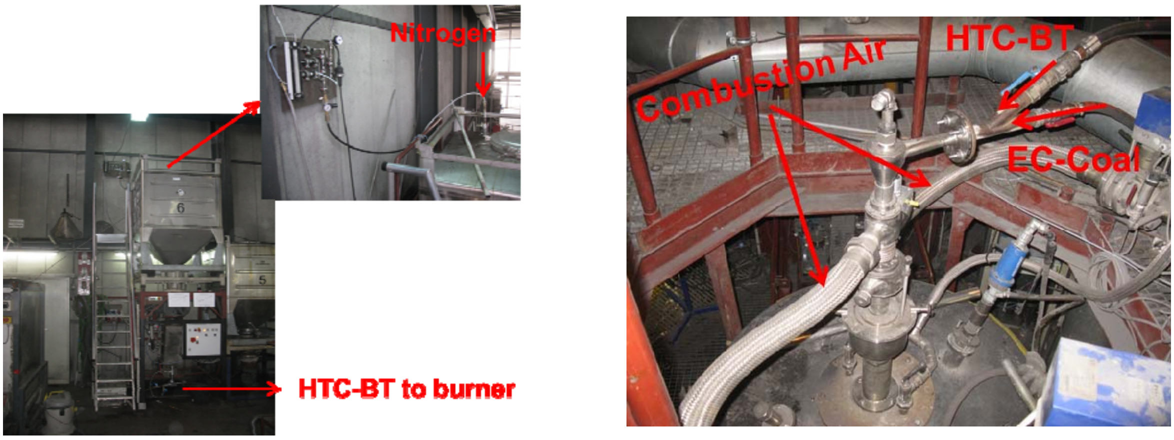

Figure 11: Feeding adaptations for HTC-BT feeding at 500 kW pulverized combustion facility (KSVA) HTC-BT feeding arrangement (left) and burner mounted on the top (right)

The photographs (Figure 11) shows the feeding arrangements for HTC-BT during the combustion test discussed here. The HTC-BT was fed through a separate screw feeder and mixed with coal just before the burner. Over pressure of N_2 was maintained over the HTC-BT container to avoid any associated fire risk during feeding. Owing to higher amount of volatiles and lower ignition temperature of HTC-BT this safety feeding method was adopted. After feeder, HTC-BT was carried to burner with carrier air (room temp.).

4.2.Combustion Behaviour

A stable flame was maintained during all combustion cases with excess O_2 of ~ 3% for all cases. The O_2 and CO_2 measured during various combustion cases of HTC-BT are shown Annex 11. The CO measured as the end of the combustion chamber is shown in Figure 12 . It shows that the CO concentration decreased with increasing share of HTC-BT. It indicates more complete combustion of HTC-BT in comparison to coal in the tested combustion system (as measured at the end of the combustion chamber).

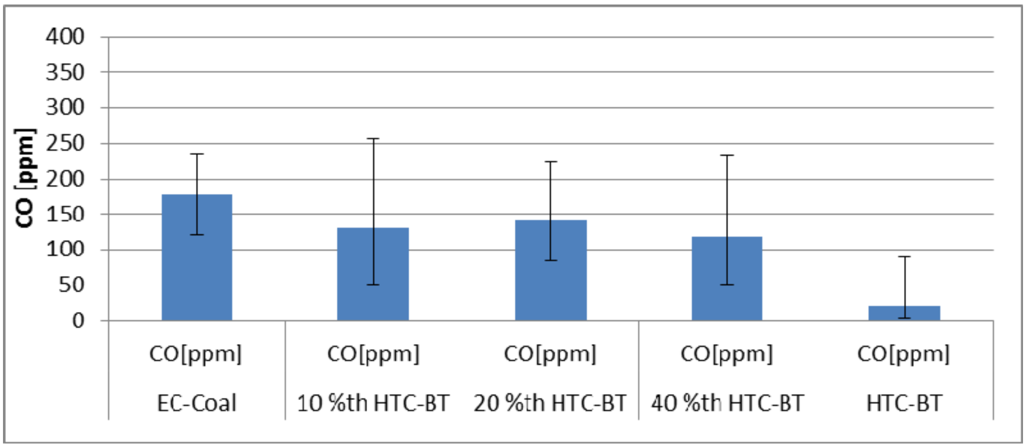

Figure 12: Average CO concentration [ppm] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of HTC-BT (co-firing) and HTC-BT (mono-firing)

A noticeable difference was observed from the visual observation of flames. These different was more significant for mono-firing case. HTC-flames were thinner, longer (up to L8-9) and dense/intense certain distance down the burner mouth while coal flame was shorter (up to L5-6), dense and intense directly from the burner mouth). The change in flame form and shape is probably related properties of HTC-BT, like high amount of volatiles. Black clouds were observed in the flame zone during HTC-BT combustion during visual observation of flame. The black clouds are speculated to be soot formed during early stage of combustion (de-volatization or pyrolysis) but no analysis has been performed regarding soot formation in HTC-BT flames during this study. A dedicated study is necessary to understand the combustion behaviour and steps of HTC-Coal, so far there are no any literature available regarding the combustion properties and behaviour of pulverized HTC-Coal flames.

The influence on flame is also observed in wall temperature of the combustion chamber. The wall temperature measured at near burner zone during HTC-BT combustion was lower in comparison to coal flames. The flue gas temperature profile also showed similar results (see Figure 13, right). Figure 13 shows the photograph of HTC and Coal flame (a) and the wall temperature measured at L4, L8 and L26 for various combustion cases. The temperature measured at the furnace end (L26) is between 750-800 °C for all cases. The temperature at L8 decreases gradually with increase in share of HTC-BT. Moreover, with increasing share of HTC-BT the difference in temperature between L4 and L8 increases. For coal flame L4 and L8 are almost similar while for HTC-BT case L8 is around 100 °C higher in comparison to L4. Beside wall temperature, the flue gas temperature was also measured at different levels.

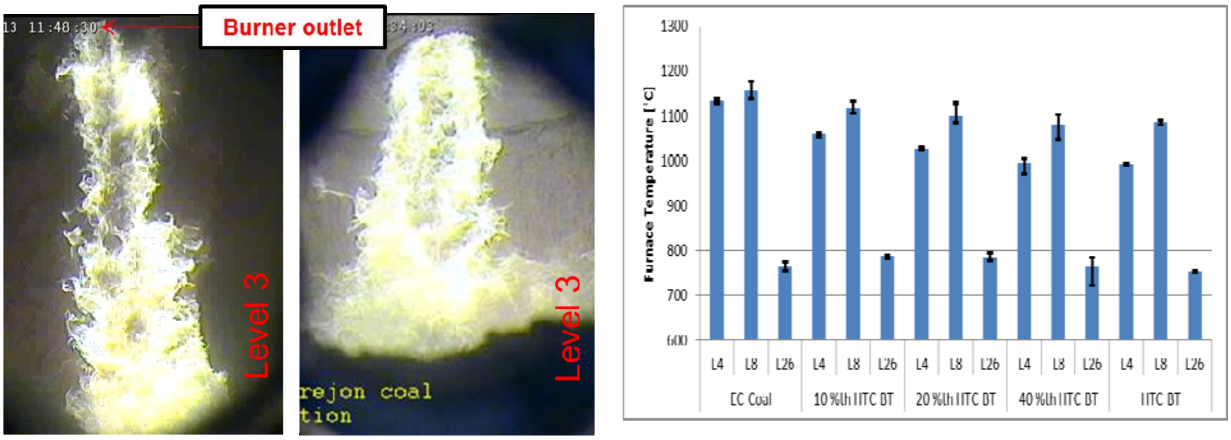

Figure 13: a: Flame photograph, HTC-flame (left) and coal flame (right) b: Wall temperature at level L4, L8and L26 during coal (mono-firing), various thermal shares of HTC-BT (co-firing) and HTC-BT (mono-firing) various combustion cases

It is clear that HTC-BT has a stable and good combustion behaviour as a solid fuel, even better that coal while considering combustion efficiency (>99 % for HTC-BT and ~98 % for coal, see

Annex 6), unburned carbon (see,

Annex 6) and CO level (see, Figure 12) measured at the end of combustion chamber.
However, in comparison to coal, HTC-BT takes longer time to combust (longer flames, see Figure 13 a), higher and longer CO rich zone in the upper boiler i.e. longer CO oxidation time (see Figure 14, right). At 10 $\%_{th}$ HTC-B, the CO profile seems more near to HTC-BT than to coal. However, the temperature profile is still similar to that of coal.
Due difference in combustion and flame behaviour, different temperature and heat transfer is expected for HTC-BT in comparison to coal which probably needs consideration for burner and boiler design and/or modification to combust HTC-coal.

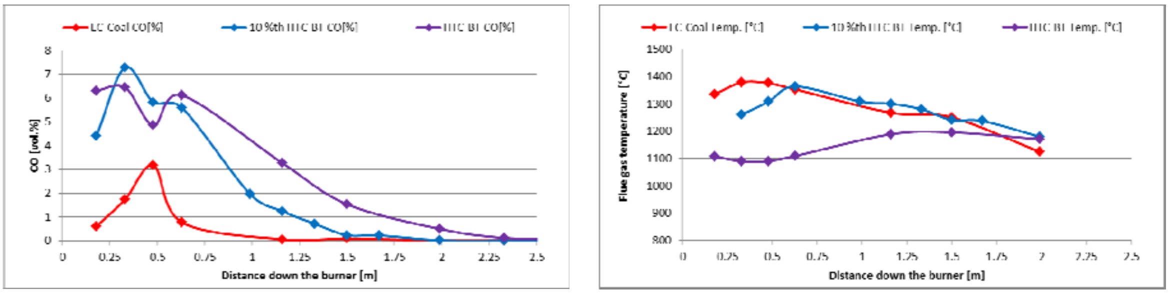

Figure 14: CO [vol.%] (left) and flue gas temperature [°C] (right) along the furnace center line during coal, 10 $\%_{th}$ HTC-BT (co-firing) and HTC-BT combustion (mono-firing)

4.3.Emission Behaviour

NO_x (calculated as NO_2) and SO_2 emissions are discussed in this section. The emission concentration is presented as mg/m^3 @ 6 % O_2 to compare with the national or regional emission limits. NO_x and SO_2 concentration measured at the end of the furnace (L 25) while filter is considered as emission values. These are the concentration measured without any emission control measures. NO_x and SO_2 were continuously measured by standard flue gas analyzer.

A conversion factor as % is also discussed along with absolute emission values. For example, the NO_x conversion is calculated as measured NO_x during respective combustion case divided by theoretical maximum NO_x, assuming all fuel-N is converted to NO_x. The SO_2 conversion is calculated analogically as the NO_x conversion.

4.3.1. SO_2 emission

As expected the SO_2 emission decreased for co-firing and HTC-BT mono firing cases. In comparison to coal the fuel-S input also decreases with increasing share of HTC-BT. Figure 15 shows the SO_2 emission during various combustion cases.

Due to low amount of sulfur capture species in coal ash (like Ca), most fuel-S is expected convert as SO_2 while for HTC-BT high amount of calcium in ash is expected to retain some sulphur in ash resulting lower SO_2 emission. Increased capture of SO_2 during HTC-BT can be conformed from calculated SO_2 conversion rate. SO_2 conversion rate is ~100 % for coal and ~60 % for HTC-BT during mono-firing cases.

HTC-BT showed lower SO_2 emission apparently because of lower fuel-S and higher capture in ash. However, the decrease of SO_2 is not linear to the increase of thermal share of HTC-BT therefore only with these results it is difficult to state the effect HTC-BT share on SO_2 emission reduction.

For both mono-firing and co-firing cases, SO_2 values do not meet the emission requirement and requires SO_2 control methods. Common method adopted in many coal firing plants, like lime-stone dosing can be one of the solutions. Due to high self-capture of SO_2 in HTC-BT ash and lower fuel-S, the lime stone dosing will probably reduce with increasing share of HTC-BT.

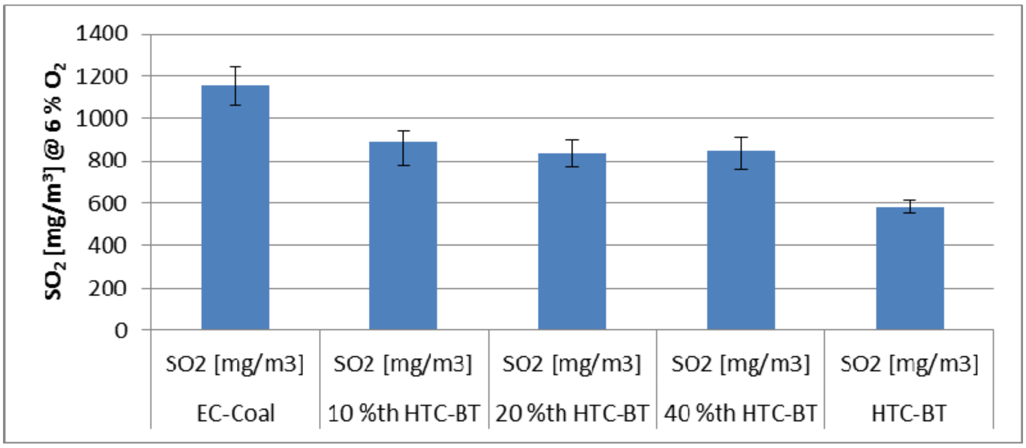

Figure 15: Average SO_2 concentration [mg/m^3 @ 6 % O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of HTC-BT (co-firing) and HTC-BT (mono-firing)

4.3.2. NO_x emission

Figure 16 shows the NO_x concentration measured during various combustion cases. NO_x emission does not show a specific and clear trend in respect to the thermal share. The fuel-N content is almost 3 times higher in comparison to the coal. With increasing share of HTC-BT lower fuel-N input is expected. The average NO_x values during co-firing are significantly higher in comparison to both mono-firing cases. It is clear that NO_x emission cannot be co-related with the fuel-N input alone. Formation of NO_x is a complex phenomenon depending on various factors of combustion parameter and the combustion system itself.

The interesting observation here is very low NO_x emission for HTC-BT (see Figure 16). Despite 3 time's higher fuel-N input, the NO_x values even more than 3 times less in comparison to coal. The HTC-BT flames appear to have a self-staging effect. Most of the fuel-N in HTC-BT is expected as volatile nitrogen and it is known that the NO formation by volatile-N is highly influence by local combustion conditions like temperature and reducing/oxidizing zone. Lower temperature of HTC-flames in the near burner and locally very reducing atmosphere (due to higher CO levels) both possibly hinders the oxidation of released volatile-N to NO. In this combustion system, the NO_x conversion for coal is in average ~12 % while for HTC-BW is very low <5 % in average. However, the NO_x conversion was higher for co-firing cases.

The NO_x conversion for HTC-BT is apparently also related to the type and form of association of nitrogen species in fuel matrix and their evolution during the combustion process. The explanation for the results is not still clear and further work is necessary for detail understanding.

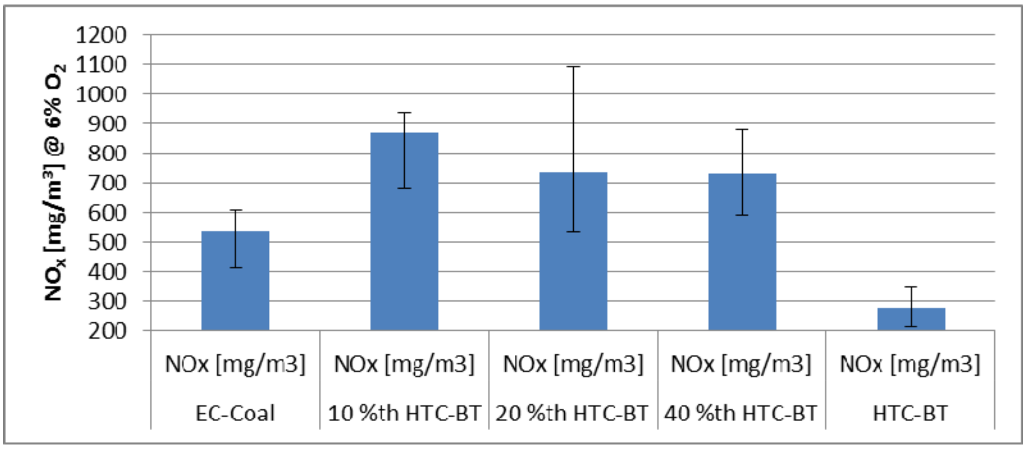

Figure 16: Average NO_x concentration [mg/m^3 @ 6% O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of HTC-BT (co-firing) and HTC-BT (mono-firing)

The NOx values are higher than limit values for all the combustion cases. Staging is common method applied by coal fired boilers to meet the NO_x emission limit requirements. The principle of staging is to create a reduction zone by air deficit in the burner to restrict the formation of NO in near burner zones and the further air is applied some distance down the burner to complete the combustion and to keep the desired excess O_2 level. Due to lower burner lamda (air-fuel ratio) poor burnout, different temperature distribution, high CO and material and corrosion issues and slagging problems with certain coals, are expected limitation of staging. However, staging is proved to be efficient for NO_x reduction especially with volatile-N. Staging combustion tests performed during this work and its impact on NO_x emission values will be briefly discussed below.

Staging test was carried out for 2 different combustion cases, $10\%_{th}$ HTC-BT (co-firing) and HTC-BT (mono-firing). Table 5 shows the fuel and combustion air feed rate during staged case. For all cases the burner lamda was kept 0.9 while the rest burn-out air was supplied between L10 and L11 (approx. 2 m down the burner). The total lamda was 1.15 and the excess O_2 around 3 % at the end of the combustion chamber for all staged combustion cases.

Table 5: Fuel [kg/h] and Combustion air [m^{3}N/h] for respective staging combustion cases

	10 %$_{th}$ HTC-BT	HTC-BT
Coal [kg/h]	36	--
HTC-BT [kg/h]	5	46
Burner air (dry) [m^{3}N/h]	245	248
Burn-out [m^{3}N/h]	68	68

Figure 17 shows the comparison of NO_x emission measured during respective un-staged and staged cases. For 10 %th HTC-BT case (co-firing), staging shows a clear reduction in NO_x emission as expected. NO_X emission measured at the end of the combustion chamber was around 40 % lower in comparison to un-staged case.

But for HTC-BT case, the NO_x emission increased while staging. It is completely opposite than expected. The explanation of this completely un-expected behaviour of staging during HTC-BT mono-firing case probably lies on the near burner combustion behaviour of HTC-BT as discussed earlier. Volatile-N from HTC-BT probably takes longer residence time to reduce to N_2 in HTC-BT flames. The burn-out air probably creates the oxidation atmosphere before the reduction is finished and volatile-N instead oxidized to NO_x.

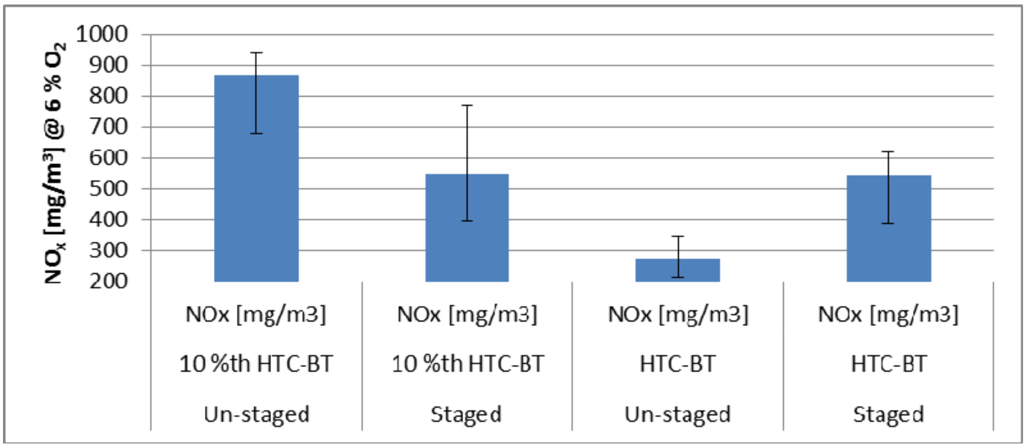

Figure 17: Average NO_x concentration [mg/m^3 @ 6 % O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during 10 %$_{th}$ HTC-BT (co-firing) and HTC-BT (mono-firing), un-staged and staged combustion tests

The burn-out air injection position that works efficiently for coal and for lower shares of HTC-BT probably is not efficient for HTC-BT (mono-firing). No combustion tests were performed with the staging probes at other positions. Therefore, it is difficult to explain satisfactorily based only on the results obtained from the combustion test performed during this project. So far no any combustion test studies are available in literature. More data and combustion tests are required for better understanding.

The current evaluation shows that probably lower temperature (near flame zone), longer reduction zone and slow combustion progress formation reduces the amount of NO_x emission during HTC-BT mono-firing. While air staging in such flame showed opposite result (i.e. increase in NO_x) due to oxidizing zone created before completion of volatile nitrogen species reduction.

4.4.Deposit and Corrosion

HTC-BT has significantly lower amount of alkali components (K and Na), sulfur and chlorine in comparison to conventional biomass fuels and lower or comparable to coal. Deposit and corrosion risk associate to these elements are not expected to be a serious issues.

Phosphorous is another element that is significantly present in HTC-BT ash. With certain high phosphorous fuels, phosphates formation is discussed as possible source to form molten deposits. But only the alkali phosphates are discussed to have low melting temperature and create deposit problems. In HTC-BT most of the phosphorous are expected to be in fuel as calcium phosphate or forms calcium phosphate during combustion which is very stable and high melting phosphate with no significant role in formation of molten deposit. The ash fusion test from the lab ash showed the initial sintering temperature of around 950 °C and fluid temperature of 1450 °C, a comparable figure to coal ash fusion temperatures (see Annex 4).

The deposit samples collected over the un-cooled ceramic probe also did not indicate serious deposition issues on visual observation. Loose mass of particles were sampled on the deposition probe and can be easily removed from the ceramic surface.

Figure 18 shows the BSE image of the cross-section of the deposit sample. The deposit samples were collected at L11 (temperature 1050 °C-1100 °C). The coal deposit samples showed mostly individual non spherical particles mostly silicates or alumino-silicates (see Element map, Annex 9). These particles are known not to pose or initiate any deposition risk. The sample surface is almost clean indicating no evidence of molten or semi-molten deposit particles.

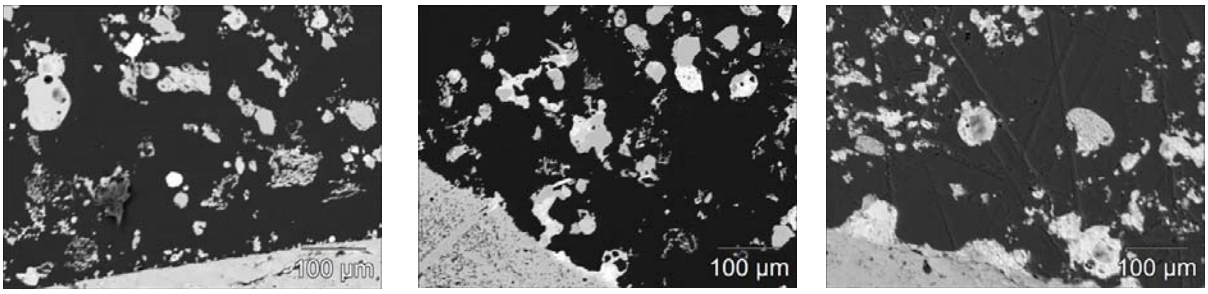

Figure 18: The BSE image of un-cooled deposit sample cross-section; Coal (right), 10 $\%_{th}$ HTC-BT (middle) and HTC-BT (right)

The HTC-BT deposit particles are mostly smaller and spherical in size. Particles are mostly rich in calcium and phosphorus (see element map, Annex 9). Some of these particles seem to be molten while approaching the surface as some of them seemed to be glued to the sample surface. Its shows some evidence of molten particles and possible sintering in comparison to coal deposits. The co-firing deposits are somehow in middle. Some particles seems glued to the sample surface and shows some deposit particles bridging. In general, none of the deposit samples are expected to posse serious risk.

From the ash composition and deposit sample observation in general HTC-BT is speculated not to have major deposit and corrosion related issues.

4.5.Fly ash

During combustion test ash collected in each ash separation unit (see Figure 2) was collected and completely weighted after certain collection time. The sample from each ash separation unit was collected and analyzed for un-burnt carbon and major ash oxides. The results and evaluation from 10 $\%_{th}$ HTC-BT (co-firing) and HTC-BT (mono-firing) will be discussed briefly. Figure 19 shows the amount of ash [wt.%] collected in different ash collection units during 10 $\%_{th}$ HTC-BT (co-firing) and HTC-BT (mono-firing).

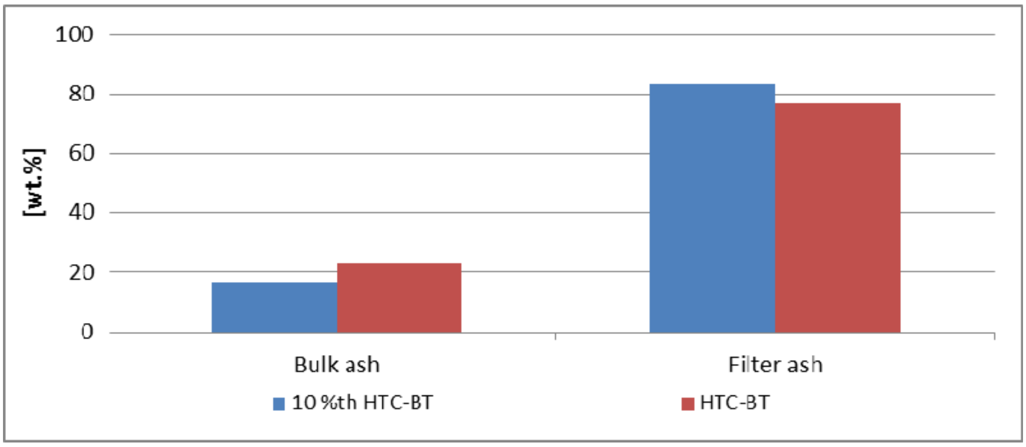

Figure 19: The amount of ash [wt.%] collected in different ash collection units during 10 $\%_{th}$ HTC-BT (co-firing) and HTC-BT (mono-firing)

The ash collected in bottom hopper (BH) and in air preheater (APH) is mostly due to gravity separation. The fly ash particles that are not carried by the flue gas flow are collected here. This fraction is considered as bulk ash in further discussion. The fly ash particles carried with the flue gas flow are separated either by Electro Static Precipitator (ESP) or by Fabric filter (FF). Both ash fractions are considered here as filter ash. For both combustion cases the amount filter ash was higher than bulk ash. 83 % of the total ash collected was filter ash for 10 $\%_{th}$ HTC-BT (co-firing) while for it was 77 % for HTC-BT (mono-firing).

Fly ash is also saleable out-put product for many coal firing power plants. Utilization in cement and concrete industry are common fly ash utilization pathway for many coal firing power plants. Fly ash composition should meet certain regulatory guidelines for utilization. HTC-BT combustion in existing coal firing power plants will change the composition of fly ash.

Table 6: Chemical requirements for fly ash utilization (EN 450-1)

	% (by weight)
Loss of Ignition/un-burnt carbon	<5-9 %
Chloride (Cl^-)	<0.1 %
SO_3	<3 %
CaO (reactive)	<10 %
SiO_2+Al_2O_3+Fe_2O_3	>70 %
Total alkali (Calculated as Na_2O)	<5 %

P_2O_5	<5 %
MgO	<4 %

Regarding composition elements like total alkali (K_2O+Na_2O), calcium oxide (CaO), phosphorous/phosphate, sulfur/sulphate, chlorine/chloride are of concern to meet utilization standards. Table 6 summarizes some criteria (chemical requirement) for fly ash utilization in cement/concrete industry.

Figure 20 shows some the composition of some critical ash oxides in fly ash regarding chemical requirements for fly ash utilization. The fly ash were collected during 10 $\%_{th}$ HTC-BT (co-firing) and HTC-BT (mono-firing) at various fly ash collection units as discussed earlier.

High amount phosphorous present in HTC-BT would be a major concern. Though the content is almost within acceptable limit at 10 $\%_{th}$ HTC-BT (co-firing) with increasing share of HTC-BT it would go out of the range.

For HTC-BT (mono-firing) the phosphorous content (as P_2O_5) is far above the acceptable limit. Moreover, phosphorous is valuable resources, the recovery of phosphorous should be considered in case of HTC-BT mono-firing. The fly ash utilization perspective has only been briefly discussed here to point out the expected critical issues.

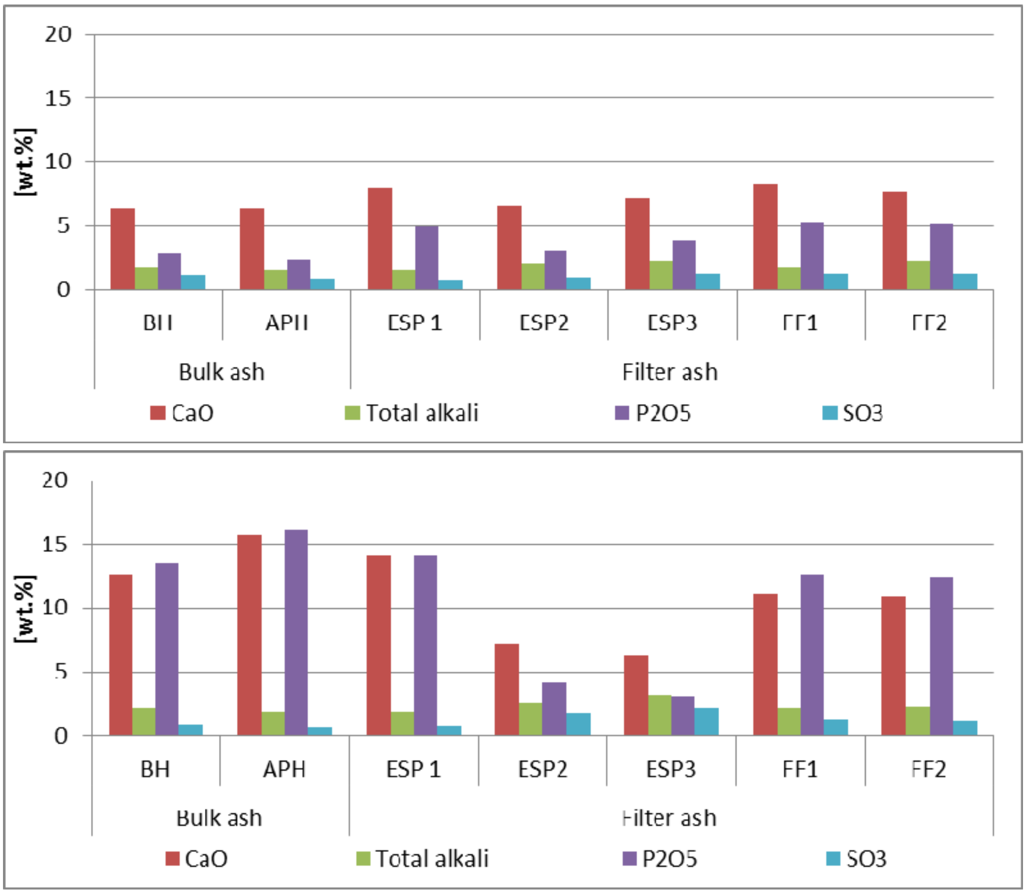

Figure 20: The composition of some critical ash oxides in fly ash regarding chemical requirements for fly ash utilization: 10 $\%_{th}$ HTC-BT (co-firing), above and HTC-BT (mono-firing), below

4.6.Summary

In general, both co-firing and mono-firing of HTC-Biertreber (HTC-BT) shows no significant problems with fuel handling/feeding and combustion performance in comparison to coal. However, HTC-BT flame appears very different with regard to shape/size and the combustion progress in near burner zones. Due to the difference in flame and combustion progress and/or behaviour, different temperature and heat transfer is expected for HTC-BT which probably needs consideration for burner and boiler design and/or modification.

The SO_2 emission was lower with HTC-BT. The lower sulphur content and higher possibility SO_2 capture in HTC-BT ash, as expected SO_2 emission decreased with increasing share of HTC-BT. The fuel-N to NO_x conversion in HTC-BT shows an interesting behaviour. Despite very high fuel-N, HTC-BT (mono-firing) shows significantly lower emission values in comparison to coal. The lower NOx emission is expected due to self-staging effect of long HTC flame. For co-firing cases, the NO_x emission was higher in comparison to coal and the staging results showed that the NO_x emission can be reduced.

Deposit and corrosion is not expected to be a major challenge due to lower amount of critical elements like alkalis, chlorine and sulphur in HTC-BT. Some minor concerns relate the role of phosphorous on deposition was observed. Phosphorous is also a concern regarding fly ash quality. The recovery of phosphorous from HTC-BT ash is a potential area of interest regarding fly ash utilization.

Milling is also an important aspect in pulverized fuel combustion systems. This has not been covered in this work package as the fuels were received as powder. Milling issues should also be considered for commercial scale utilization scenario. The lower ignition temperatures of HTC Coals were identified as a possible risk associated with milling and fuel handling.

So far no other studies on combustion behaviour of HTC Coal are available in open literature. This work is probably among the 1st of such studies. Technically, both mono-firing and co-firing of HTC-BT is possibly. The lab and pilot scale studies identified some areas of concerns. However, further technical data and understanding is still necessary for commercial scale combustion.

5. Combustion test of HTC-Biowaste (HTC-BW)

HTC-BW refers to the HTC-Coal produced by hydrothermal carbonization of household bio waste. Table 7 shows the properties of HTC-BW coal. The lower heating value (LHV) is reported here is ‘as analyzed’ (an), ash is reported as ’water free’ (wf) and rest are reported as ‘water ash free’ (waf). The reference coal was similar as discussed earlier section (see Table 3 for coal analysis)

Table 7: Composition and Heating Value of HTC-BW

Fuel	LHV	W	A	V	C-fix	C	H	N	S	Cl
	[MJ/kg, an.]	[%, an.]	[%, wf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]
HTC-BW	18.3	7.0	17.6	78.0	21.9	60.8	6.35	1.41	0.18	0.17

HTC-BW has higher amount of ash and lower heating value in comparison to Coal. Significant amount of chlorine is also present in HTC-BW. Probably chlorine is present in water-insoluble form and is not removed during the process. Packing and plastics fractions in house-hold waste can be possible chlorine sources.

Composition of HTC-Coal varies with the type/composition of feedstock to the hydrothermal carbonization process. The difference in properties of HTC-BT and HTC-BW is basically related to their respective feed-stock. The similarity among HTC-Coal would be high volatiles and lower C-fix. While the amount of ash and components like N, S and Cl are expected to vary significantly with the variation of feed-stock.

Three co-firing shares namely; 10 $\%_{th}$, 20 $\%_{th}$ and 50 $\%_{th}$ of HTC-BW was combusted in 20 kW PF facility along with mono-firing of HTC-BW and reference Coal. The combustion facility is already discussed. For co-firing, individual fuels (HTC-BW + EC-Coal) were manually mixed before feeding. The total flue gas volume (as calculated form the respective fuel/fuel blends composition is 11.5 m^3N/h during all combustion cases. The excess O_2 was around 3 % at the end of the combustion chamber during all combustion cases.

5.1.Fuel handling and feeding

The HTC-BW was received as fine powder. The particle size analysis of fuel as received measured using malvern particle size analyzer showed that 50 % of particles were below 52 µm i.e. d50. But d90 was around 1000 µm. It indicates considerable fraction of larger size particles is present in the HTC-BW powder in comparison to HTC-BT powder.

A screw type feeder was used during all combustion cases, no any specific concerns are encountered during the small scale feeding test runs (max. 2 kg/h for HTC-BW mono-firing). At large scale feeding some consideration on fuel transport and feeding should be considered, owing to higher volatiles in HTC type fuels and expected lower ignition temperature.

5.2. Combustion behaviour

The flue gas composition was continuously measured at the end of the furnace during all combustion cases. Stable flame and acceptable combustions were achieved during all combustion cases. The O_2 and CO_2 measured during various combustion cases of HTC-BW are shown Annex 12.

Figure 21 shows the CO concentration measured at the end of furnace during various combustion cases. The CO concentration measured at the end of the furnace was fairly below 40 ppm for all co-firing cases and coal mono-firing case. Average CO level of around 100 ppm was measured during mono-firing of HTC-BW. The fluctuation of CO was also higher and CO peaks were frequently measured during mono-firing of HTC-BW which is possibly related to the burning of larger particles. Considerable fraction, approx. 25 % of particles were above 100 µm and particles even up to 1000 µm are expected form the particle size analysis of HTC-BW powder as received.

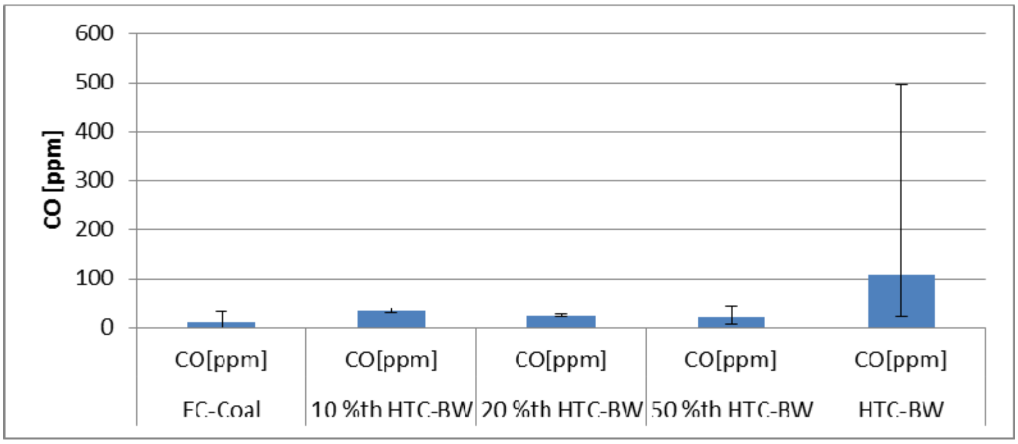

Figure 21: Average CO concentration [ppm] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of HTC-BW (co-firing) and HTC-BW (mono-firing)

5.3. Emission

NO_x (calculated as NO_2) and SO_2 emissions are discussed in this section. The emission concentration is presented as mg/m^3 @ 6 % O_2 to compare with the national or regional emission limits. NO_x and SO_2 concentration measured at the end of the furnace (L 25) while filter is considered as emission values. These are the concentration measured without any emission control measures. NO_x and SO_2 were continuously measured by standard flue gas analyzer.

A conversion factor as % is also discussed along with absolute emission values. For example, the NO_x conversion is calculated as measured NO_x during respective combustion case divided by theoretical maximum $NO_{x,}$ assuming all fuel-N is converted to NO_x. The SO_2 conversion is calculated analogically as the NO_x conversion.

5.3.1. SO_2 emission

Figure 22 shows the SO_2 concentration measured during various combustion cases. The SO_2 emission decreases with increasing share of HTC-BW. The SO_2 emission can be directly co-related with the amount of fuel-S in the respective fuel or fuel blend. Lower the amount of fuel-S lower SO_2 emission is expected. SO_2 emission is also influenced by the availability of sulphur capturing species in the respective fuel/fuel blend ash. Earth alkalis e.g. calcium is expected to capture SO_2 and reduce SO_2 emission. Significant amount of calcium is present in HTC-BW in comparison to coal, with increasing share of HTC-BW, theoretically more SO_2 will be captured in ash. The SO_2 conversion factor shows~ 99 % for coal almost and ~70 % for HTC-BW. The lower SO_2 conversion factor for HTC-BW probably indicate higher self-capture of SO_2 in ash. The composition of HTC-BW ash i.e. significant amount of calcium also supports this fact.

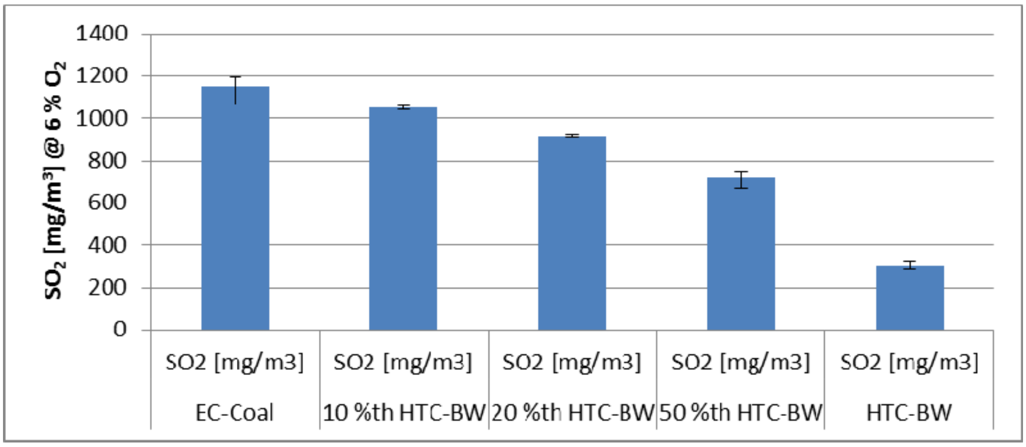

Figure 22: Average SO_2 concentration [mg/m^3 @ 6 % O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of HTC-BW (co-firing) and HTC-BW (mono-firing)

For co-firing shares and coal combusted during this test, it is clear that SO_2 control measure is necessary to be implemented. Even higher share HTC-BW (up to 50 $\%_{th}$) was not enough to reduce SO_2 to meet the emission limit values. SO_2 values during mono-firing of HTC-BW appear to meet the emission limit. As discussed earlier the lower SO_2 emission for HTC-BW is basically relates to lower fuel-S content and partly it is expected to be retained in ash.

5.3.2. NO_x emission

Figure 23 shows the NO_x concentration measured during various combustion cases. NOx emission does not show a specific and clear trend in respect to the thermal share of HTC-BW. The fuel-N content in HTC-BW is slightly lower in comparison to the coal; it means with increasing share of HTC-BW lower fuel-N input is expected. The average NOx values during co-firing are in general slightly higher in comparison to both mono-firing cases. It is clear that NO_x emission cannot be co-related with the fuel-N input alone, though it is generally stated that around 80 % of NO_x emission are resulting from fuel-N and rest from N_2 from combustion air. Formation of NO_x is a complex phenomenon depending on various factors of combustion parameter and the combustion system itself.

In the combustion system tested during this work, the NO_x conversion for coal is in average ~27 % while for HTC-BW it's around ~20 % in average. The lower NO_x conversion was also observed for HTC-BT and is discussed earlier. The lower NO_x conversion for HTC type solid fuels is probably related to the type and form of association of nitrogen species in fuel matrix and their evolution during the combustion process.

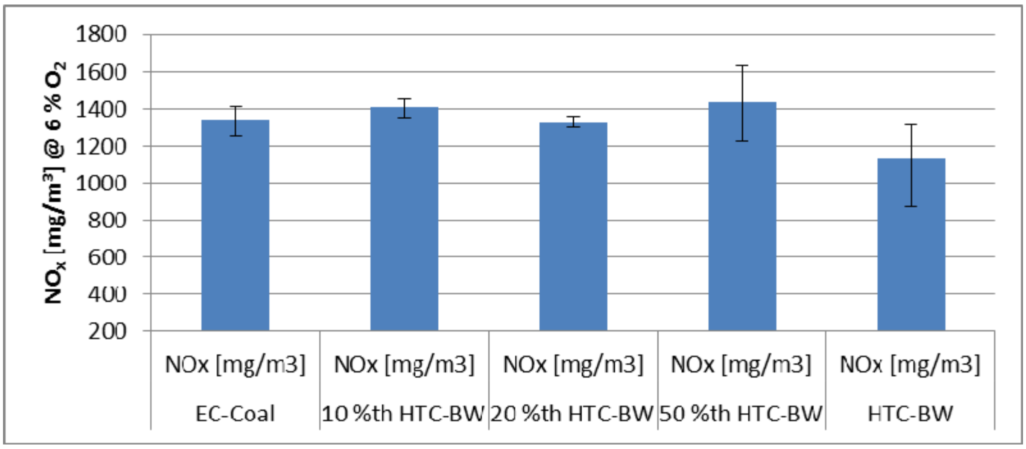

Figure 23: Average NO_x concentration [mg/m^3 @ 6 % O_2] measured at the end of furnace (error bar indicating respective maximum and minimum) during coal (mono-firing), various thermal shares of HTC-BW (co-firing) and HTC-BW (mono-firing)

For all combustion cases NO_x emission is significantly higher and NO_x control measures are required. Primary NO_x control measures like staging can be implemented.

The fuel-N to NO_x conversion/formation behavior of HTC type's fuel and the impact of staging on reducing NO_x formation on these kinds of fuels are further research interest, both from scientific research and industrial application point of view.

5.4.Deposit and Corrosion

Deposit and corrosion are related to boiler operation issues. Increased risk of deposit and corrosion will eventually decrease the boiler efficiency and availability. Mainly, slagging and fouling tendencies of fuels are related to the deposition behaviour.

The deposits formed on radiative section (such as furnace walls) of the boiler are considered are slagging deposits. Formation of low melting ash is considered to increase the slagging tendencies during combustion. The deposit formed in the convective section of boiler (such as heat exchanger surfaces) is considered as fouling deposits. The hot flue gas comes in contact with the relatively cooler boiler pipe surfaces and the condensable species forms the fouling deposits. Fouling is mostly related to volatile alkali species (like K, Na) present in fuel.

Indices have been used to predict and compare the slagging/fouling tendencies. Both slagging and fouling indices used the bulk composition of ash to predict the slagging behaviour of various fuels. Based on these indices, the fuels are categorized as low, medium and high slagging/fouling inclination fuel. These indices were basically derived and based on experience from coal combustion.

Table 8: Slagging and Fouling indices, where B = (Fe_2O_3+CaO+MgO+Na_2O+K_2O) i.e. sum of basic ash oxides [wt.%] and A = (Al_2O_3+SiO_2+TiO_2) i.e. sum of acidic ash oxides [wt.%] and S^d = sulfur content [wt.%, wf]

		Low	Medium	High
Slagging Index (R_s)	(B/A)*S^d	<0.6	0.6-2.0	2.0-2.6
Fouling Index (F_u)	(B/A)*(Na_2O+K_2O)	<0.6	0.6-40	>40

The slagging index for both EC-Coal and HTC-BW are in a range indicating low slagging tendencies. The fouling index indicates low fouling tendencies for coal while medium fouling tendencies for HTC-BW. However, these conventional indices were developed for coal which very low amount of phosphorous. HTC-BW ash might have completely different characteristics than predicted by these conventional indices.

In recent years, modified indices have also been proposed for biomass type fuels (mostly woody biomass fuels). Indices have been proposed to predict the shrinkage start temperature (SST) from the molar ratio of [(Si+P+K)/(Ca+Mg)]. The components in numerator of the index are species expected to increase the melting tendencies while the components in denominator of the index are species which are expected to decrease the melting tendencies. Therefore, lower the ratio higher shrinkage temperature is expected. SST temperature basically represents the temperature at which certain ash is expected to start to show melting tendency and are defined from standard ash fusion test. The shrinkage start temperature for HTC-BW is around 870 °C slightly higher in comparison to conventional woody biomass fuels but lower in comparison to most bituminous type coal.

For biomass fuel, K-release index can be an indicator for fouling tendencies. In biomass significant amount of potassium and chlorine is expected resulting formation of gaseous potassium species (like KCl) during combustion. Increased possibility of potassium in gas phase can mean elevated fouling tendencies. Some potassium might also end up as potassium sulphate depending on amount of fuel-S and/or availability of $SO_{x.}$ Both, alkali sulfates and alkali chloride salts are corrosive species present in ash and are related to fireside-corrosion issues. Chlorides are highly corrosive in comparison to sulfates. The ratio 2S/Cl is common indicator used to categorize the corrosion risk for biomass fuels. Molar ratio larger than 8 are expected to pose low corrosion risk while ratio lower than 4 is expected to pose high corrosion risk. The molar ratio of 2S/Cl for HTC-BW is lowers than 4. It probably indicates that the chlorine and related corrosion issues need special attention especially in mono-firing of HTC-BW.

5.5.Fly ash

Fly ash is also saleable out-put product for many coal firing power plants. Utilization in cement and concrete industry are common fly ash utilization pathway for many coal firing power plants. Fly ash composition should meet certain regulatory guidelines for utilization. Co-firing HTC-BW in existing coal firing power plants will possibly change the composition of fly ash. Table 6 summarizes some criteria (chemical requirement) for fly ash utilization in cement/concrete industry.

Elements like total alkali, calcium/calcium oxide, phosphorous/phosphate, sulfur/sulphate, chlorine/chloride will be of general concern. All of them, except sulfur/sulphate, are expected to increase with increasing share of HTC-BW. Figure 24 shows the composition of fly ash collected during coal mono-firing, co-firing (various thermal shares of HTC-BW) and mono-firing of HTC-BW. The variation of aluminium, calcium, iron and phosphorous is significant.

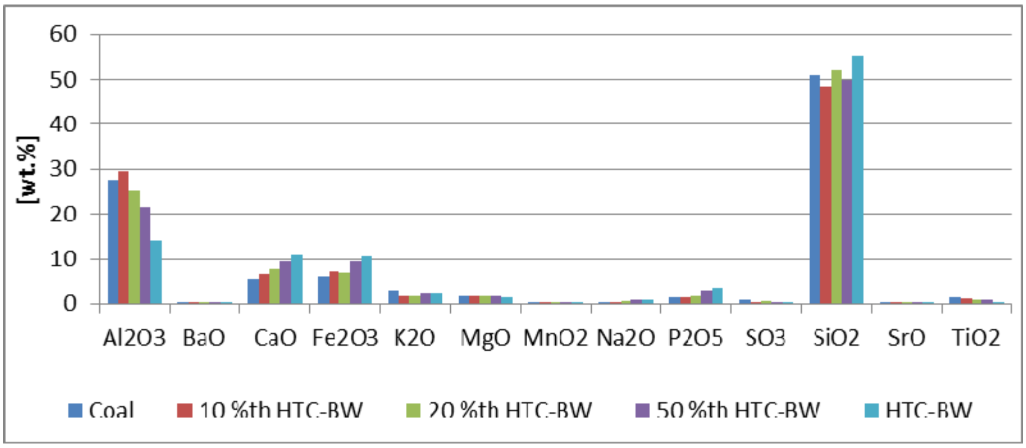

Figure 24: Composition of fly ash collected during coal (mono-firing), various thermal shares of HTC-BW (co-firing) and HTC-BW (mono-firing)

5.6. Summary

Different thermal shares of HTC-BW were co-combusted with coal. In case of co-firing, fuel handling/feeding, combustion stability/burnout do not show significant/considerable shift from the reference coal case. The mono-firing of HTC-BW does not show proper combustion. The CO level at the end of combustion chamber was higher and fluctuating. This is probably relating to higher ash amount and the larger fuel particles in HTC-BW.

The SO_2 emission decreases with increasing share of HTC-BW. The decreasing sulfur content and increasing sulfur capturing species like calcium in ash with increasing share of HTC-BW reduces the SO_2 emission. The NO_x emission is almost similar or slightly higher during co-firing.

The HTC coal produced from house hold bio-waste has considerable amount of chlorine. Hydrothermal carbonization (HTC) process is a wet process. In most biomass, chlorine is mostly present as soluble alkali salts and expected to be removed during the HTC process. The significant amount of chlorine in HTC-BW possibly implies that chlorine in household bio-waste is in the insoluble form. The composition of ash and ash fusion temperatures indicates that deposit and corrosion issues need further investigation. The changes on fly ash quality are expected due to different ash composition of HTC-BW.

From the experimental results obtained during this work, HTC-BW it is technically possible to co-fire at low to moderate thermal shares. However, HTC-Coal is new type of solid fuel for the combustion utilities more research and development work and long term combustion tests are still necessary to characterize the combustion behaviour of these kinds of fuels.

Literatures

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Annex

Annex 1: Ash composition of PC-dry and C-Coal

Ash Oxides [wt.%]	PC-dry	C-Coal
Al_2O_3	0.63	14.4
BaO	0.06	--
CaO	4.89	2.1
Fe_2O_3	0.29	15.3
K_2O	13.2	1.4
MgO	1.94	1.1
MnO_2	0.06	
Na_2O	0.18	1.7
P_2O_5	2.49	0.1
SO_3	1.97	1.8
SiO_2	68.5	59.7
SrO	0.02	--
TiO_2	0.09	0.8

Annex 2: Ash composition of HTC-BT and EC-Coal

Ash Oxides [wt.%]	HTC-BT (mono-firing)	EC-Coal
Al_2O_3	7.6	26.9
BaO	0.1	0.2
CaO	14.6	5.0
Fe_2O_3	6.4	5.9
K_2O	4.6	1.4
MgO	3.3	1.5
MnO_2	0.2	0.1
Na_2O	0.4	0.4
P_2O_5	22.9	1.1
SO_3	1.1	1.4
SiO_2	38.4	54.6
SrO	0.0	0.2
TiO_2	0.4	1.4

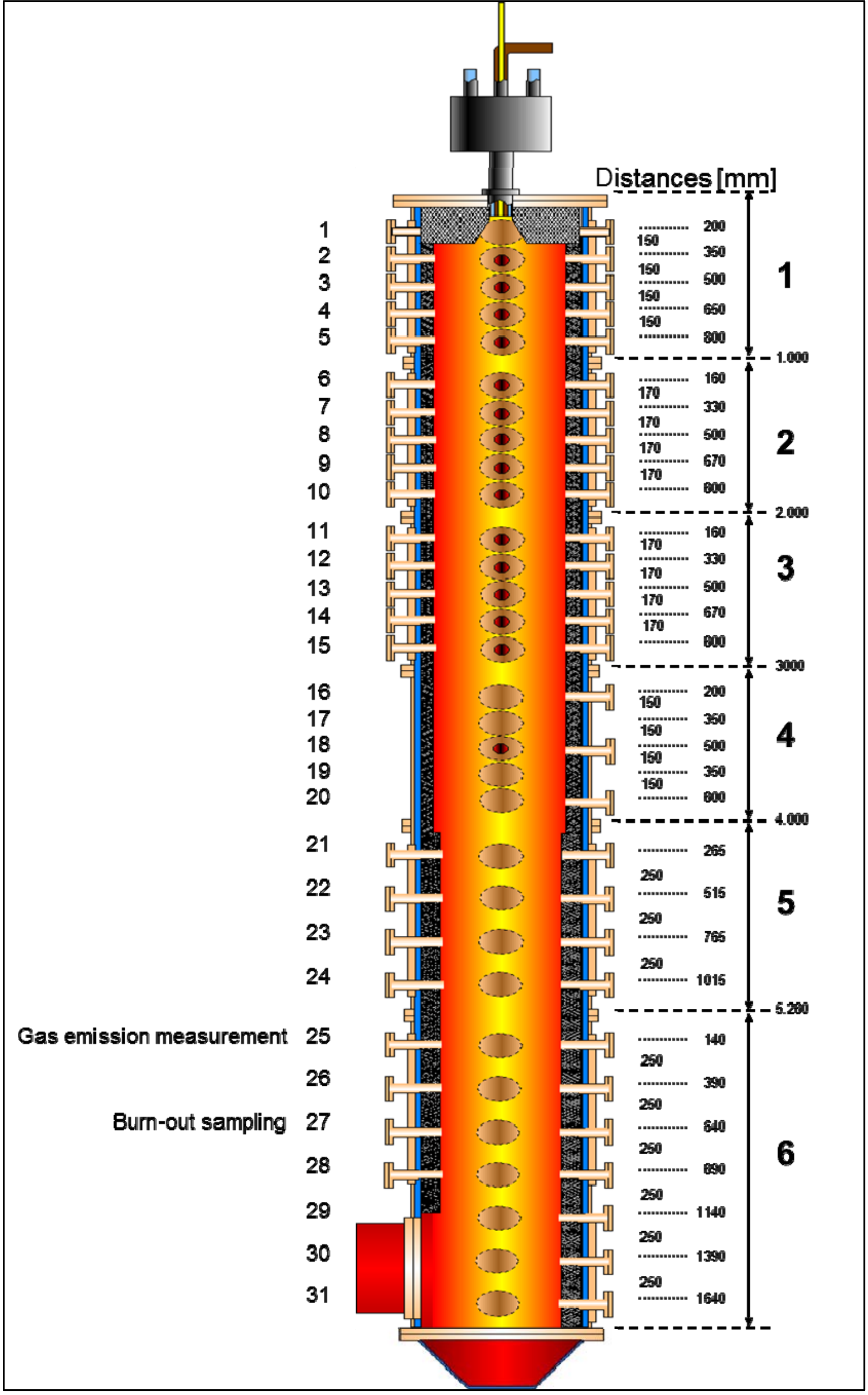
Annex 3: Fuel and ash composition of HTC-BT

Proximate analysis	**HTC-BT (co-firing)**	**HTC-BT**
Moisture [%, an]	1.96	1.25
Volatiles [%, waf]	69.1	66.2
Ash [%, wf]	4.01	9.45
Fixed C [%, waf]	30.9	33.8
Ultimate analysis		
C [%, waf]	70.1	69.4
H [%, waf]	7.36	6.45
N [%, waf]	3.86	3.83
S [%, waf]	0.44	0.28
Ash oxides [wt.%]		
Al_2O_3	0.6	5.0
BaO	0.1	0.1
CaO	18.3	19.8
Fe_2O_3	7.1	7.9
K_2O	4.0	0.8
MgO	3.0	2.5
MnO_2	0.2	0.2
Na_2O	0.3	0.5
P_2O_5	23.2	19.7
SO_3	1.0	1.2
SiO_2	42.2	41.8
SrO	0.1	0.2
TiO_2	0.1	0.3

Annex 4: Ash Fusion temperature (lab ash, 550°C) of Bioboost fuels

	PC-dry	**HTC-BT**	**HTC-BW**	**Coal**
Sintering Temperature [°C]	670	950	870	980
Softening Temperature [°C]	850	1200	1190	1310
Spherical Temperature [°C]	1020	1380	1230	1340
Hemispherical Temperature [°C]	1090	1440	1290	1440
Fluid Temperature [°C]	1200	1450	1310	1460

Annex 5: Sketch of 500 kW PF combustion reactor (KSVA)



Annex 6: Combustion efficiency [%] and un-burned carbon [%], calculated from burn-out sample

	EC-Coal	10 $\%_{th}$ HTC-BT	20 $\%_{th}$ HTC-BT	40 $\%_{th}$ HTC-BT	HTC-BT
Ash Content in Fuel (γ_{ash}, fuel)	12	11	10	8	7
Ash-in burn-out ash (γ_{ash}, bur-out sample)	87.0	92.9	91.7	87.3	98.8
Carbon- in burn-out ash (γ_C, burn-out sample)	12.6	6.4	7.5	11.6	0.7
Combustion Efficiency[%]	97.9	99.0	99.0	98.7	99.9
Unburned Carbon[%]	1.8	0.8	0.8	1.1	0.1

Combustion efficiency [%] = { (1-$\gamma_{ash, fuel}$/$\gamma_{ash, bur\text{-}out\ sample}$)/(1- $\gamma_{ash, fuel/100}$)}*100

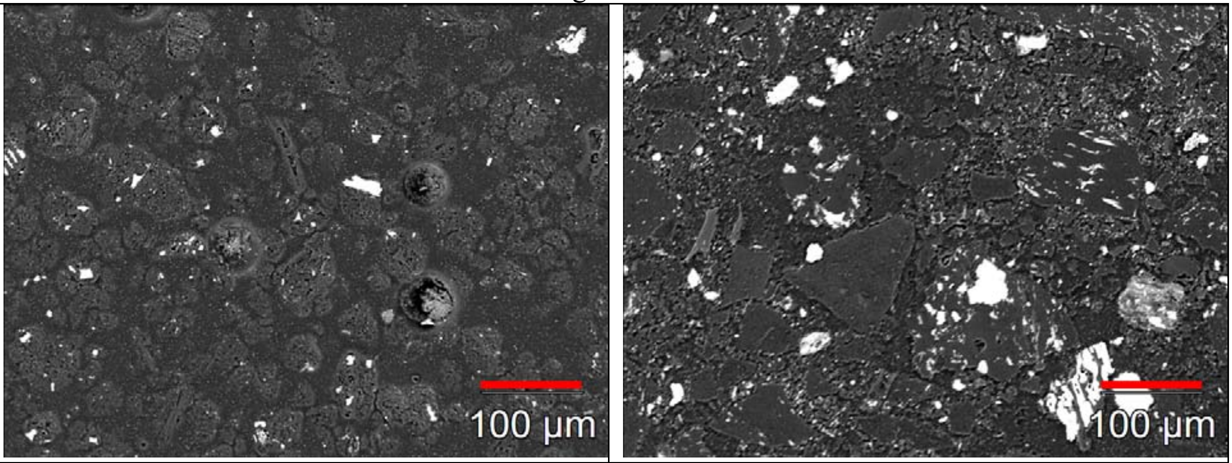
Unburned carbon [%] = ($\gamma_{ash, fuel}$/$\gamma_{ash, bur\text{-}out\ sample}$)* $\gamma_{C, burn\text{-}out\ sample}$

The burnout ash was collected at the end of the combustion chamber (L27) during each combustion case.

Annex 7: Ash composition of HTC-BW and EC-Coal

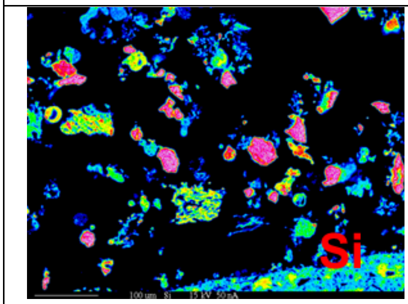
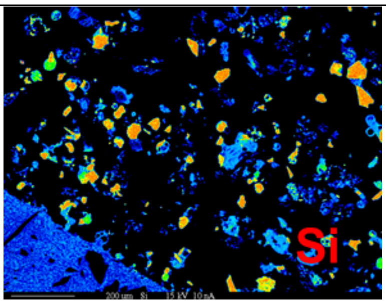
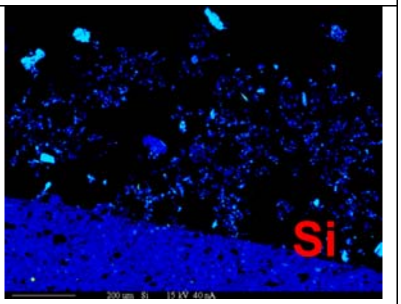
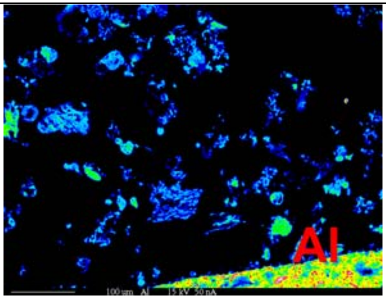
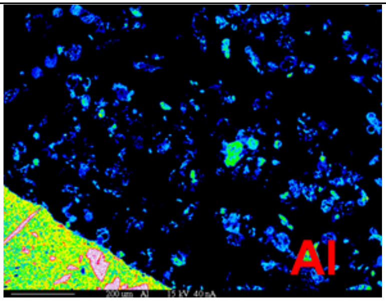
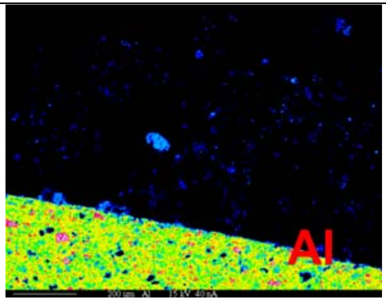
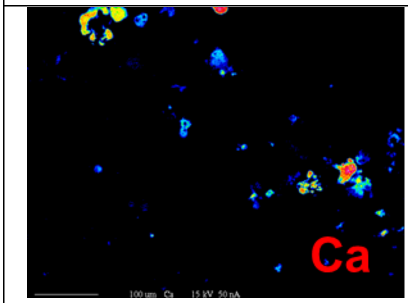
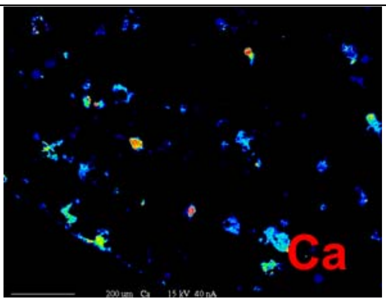
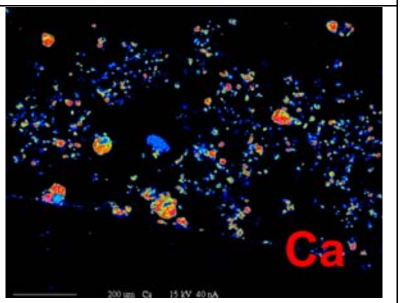
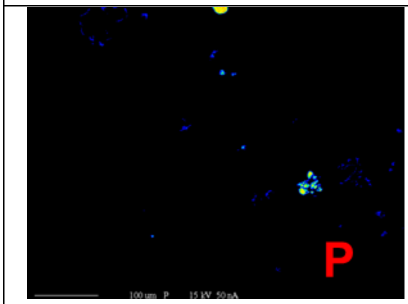
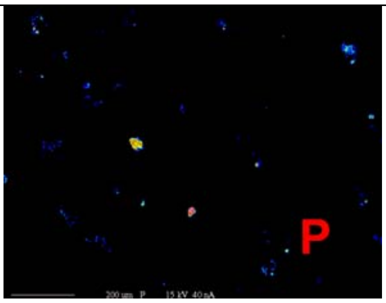
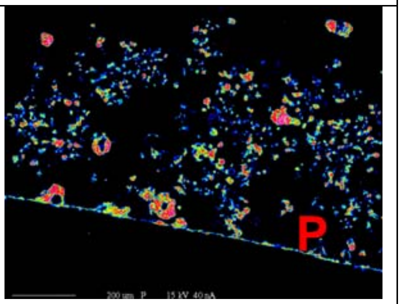
Ash Oxides [wt.%]	**HTC-BW**	**EC-Coal**
Al_2O_3	10.2	26.9
BaO	0.1	0.2
CaO	10.8	5.0
Fe_2O_3	10.8	5.9
K_2O	2.3	1.4
MgO	1.3	1.5
MnO_2	0.2	0.1
Na_2O	0.9	0.4
P_2O_5	3.3	1.1
SO_3	1.8	1.4
SiO_2	57.8	54.6
SrO	0.0	0.2
TiO_2	0.5	1.4

Annex 8: BSE Image of HTC-Fuel and Coal

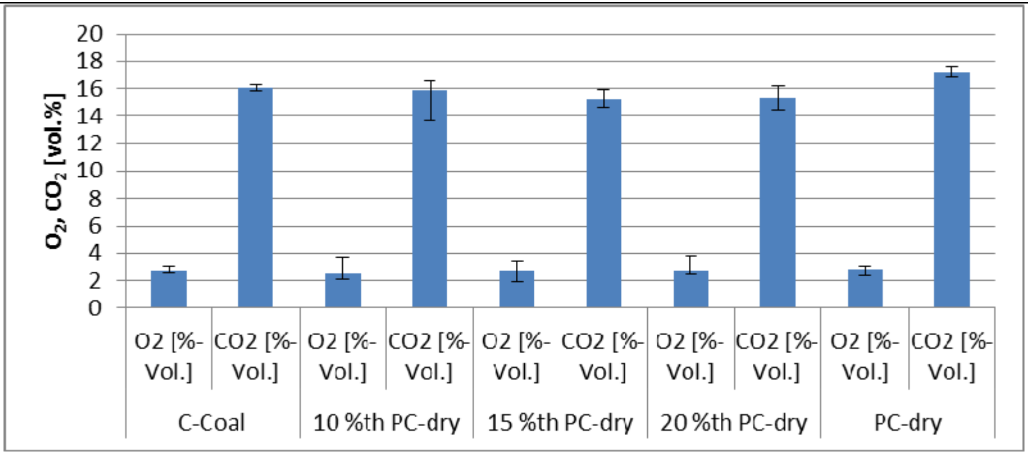


The bright particles are ash/mineral particles while the dark particles are the coal carbon matrix.

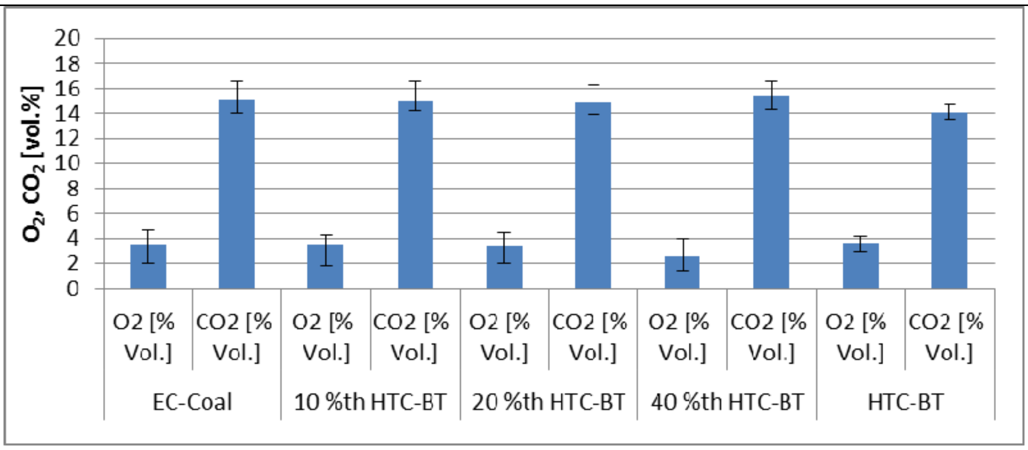
Annex 9: Element maps of uncooled deposit sample cross-section

EC-Coal	10%th HTC-BT	HTC-BT
		
		
		
		

Annex 10: O_2 and CO_2 concentration [vol.%] at the end of combustion chamber during various PC-Char combustion tests



Annex 11: O_2 and CO_2 concentration [vol.%] at the end of combustion chamber during various HTC-BT combustion tests



Annex 12: O_2 and CO_2 concentration [vol.%] at the end of combustion chamber during various HTC-BW combustion tests