Obernberger I., Thek G., Brunner T., Nowak P., Mandl C., Kerschbaum M., Borjabad E., Mediavilla I., Pena D., Carrasco J. E., 2018: Next Generation Fuel Flexible Residential Biomass Heating Based on an Extreme Air Staging Technology with Ultra-low Emissions. In: Proceedings of the 26th European Biomass Conference and Exhibition, May 2018, Copenhagen, Denmark, ISBN 978-88-89407-18-9, ISSN 2282-5819, pp. 7-15 (paper DOI 10.5071/26thEUBCE2018-CP.1.7), ETA-Florence Renewable Energies (Ed.), Florence, Italy

NEXT GENERATION FUEL FLEXIBLE RESIDENTIAL BIOMASS HEATING BASED ON AN EXTREME AIR STAGING TECHNOLOGY WITH ULTRA-LOW EMISSIONS

Ingwald Obernberger¹, tel: +43 316 48130012; fax: +43 316 481300 4; email: <u>obernberger@bios-bioenergy.at</u> Gerold Thek¹, tel: +43 316 48130063; email: <u>thek@bios-bioenergy.at</u> Thomas Brunner¹, tel: +43 316 48130013; email: <u>brunner@bios-bioenergy.at</u> Piotr Nowak¹, tel: +43 316 48130022; email: <u>mowak@bios-bioenergy.at</u> Christoph Mandl¹, tel: +43 316 48130022; email: <u>mandl@bios-bioenergy.at</u> Michael Kerschbaum², tel: +43 6212 2341308; email: <u>michael.kerschbaum@windhager.com</u> Elena Borjabad³, tel: +34 975 281013206; email: <u>elena.borjabad@ciemat.es</u> Irene Mediavilla³, tel: +34 975 281013300; email: <u>irene.mediavilla@ciemat.es</u> David Peña³, tel: +34 975 281013302; email: <u>iuan.carrasco@ciemat.es</u> Juan E. Carrasco³, tel: +34 91 346 6682; email: <u>juan.carrasco@ciemat.es</u> ¹ BIOS BIOENERGIESYSTEME GmbH, Hedwig-Katschinka-Straße 4, A-8020 Graz, Austria ² Windhager Zentralheizung Technik GmbH, Anton-Windhager-Straße 20, A-5201 Seekirchen am Wallersee, Austria ³ CEDER-CIEMAT - Research Centre for Energy, Technology and Evironment, Autovía A15, salida 56, 42290 Lubia (Soria), Spain

ABSTRACT: Although present small-scale biomass boilers, in particular pellet boilers, have already reached a high technology level, still a potential for further improvements exists which shall be used to increase their competiveness on the residential-scale heating market. Increased fuel flexibility towards the utilisation of low-quality ash rich wood fuels and non-wood fuels (agricultural residues), further reduced emissions, especially in terms of particulate matter (PM) emissions, and the integration of advanced flue gas condensers to increase efficiency are seen as development targets for future residential biomass boiler technologies. With the PuroWIN technology, which has been developed by Windhager Zentralheizung Technik GmbH in cooperation with BIOS BIOENERGIESYSTEME GmbH, a concept has been introduced, which allows for an utilisation of softwood pellets and high-quality wood chips at almost zero CO, OGC and PM emissions. Within an ongoing EU funded research project, R&D work is performed to broaden the fuel range applicable as well as to improve its efficiency by the implementation of a novel flue gas condenser concept. In this paper,

intermediate results of the project are presented which show that for future biomass boilers a utilisation of various wood and non-wood fuels at almost zero CO, OGC and dust emissions and high efficiencies is possible.

Keywords: biomass, combustion, efficiency, emissions, fuel flexibility

1 INTRODUCTION AND OBJECTIVES

The fuels utilised in present residential biomass heating boilers are almost exclusively wood fuels (logwood, pellets and wood chips). From all combustion technologies applied, wood pellet boilers show the highest potential for efficient heat production at low emissions. This is mainly due to the fact that wood pellets are well characterised regarding combustion relevant fuel parameters. Thanks to normative measures narrow margins for e.g. moisture contents, ash contents and particle size are given which support an optimised boiler design and control concept. With the introduction of the PuroWIN wood chip and wood pellet boiler technology, a new milestone in residential-scale low-emission combustion of wood chips and wood pellets could be achieved. This technology shows almost zero emissions of CO, OGC and particulate matter as well as compared with other state-of-the-art technologies reduced NO_x emissions at very low excess air ratios (λ of 1.2 to 1.3) and thus high efficiencies [1].

However, the market demands for a further extension of the fuel base applicable in residential heating systems and for an increase of their efficiencies while at the same time current emission levels shall be maintained or even reduced. Against this background the EU-Horizon 2020 funded R&D project FlexiFuel-CHX (project number 654446; 01.01.2016 - 31.12.2018) has been initiated. Within this project the PuroWIN technology is further developed towards the future residential biomass heating system.

The overall objectives are:

• A significant widening of the feedstock base to be

utilised from high quality wood fuels to wood fuels in a broad quality range (e.g. wood pellets of any quality class, forest residues, wood from short rotation coppice - SRC) and non-wood fuels (e.g. agricultural or industrial residues).

- Almost zero emissions of CO, OGC and particulate matter at nominal and partial load, ultra-low HCl and SO_x emissions (especially relevant for non-wood fuels) as well as compared with other state-of-the-art technologies clearly reduced NO_x emissions.
- A further relevant increase of the thermal efficiency up to 110% (related to the NCV of the fuel) by the development of a new and fuel-flexible flue gas condensation technology in combination with the extremely low excess air ratios achievable by the PuroWIN technology (λ 1.2 to 1.3).

In order to achieve these ambitious goals a multidisciplinary international consortium has been formed consisting of the following partners:

- Windhager Zentralheizung Technik GmbH (AT): wellknown biomass conversion technology provider
- BIOS BIOENERGIESYSTEME GmbH: engineering company specialised in the development of energetic biomass conversion systems
- Evoplan AG (CH): engineering company active in the heating, cooling and air conditioning sector
- TU Munich, Institute for Material Handling, Material Flow, Logistics (DE): experts regarding logistics and transport of bulk materials
- CIEMAT Center for Energy, Environment and Technology Research (ES): recognised R&D institution also active in preparation, characterisation,

standardisation and testing of non-conventional biomass fuels

• Wuppertal Institute for Climate, Environment and Energy (DE) and Utrecht University (NL): institutions experienced in market studies and techno-economic and environmental impact assessments

2 APPROACH

2.1 Fuel flexibility

Future residential biomass boilers should be able to operate with a wide range of different biomass fuels. Thereby, fuel costs could be reduced due to a higher flexibility in fuel purchase. Moreover, an application of biomass boilers also becomes interesting for regions with low wood resources but high availabilities of non-wood feedstocks such as agricultural residues. However, the latter are often rich in S, Cl and ash forming elements (especially Si and K) and therefore, when utilising these fuels in conventional boilers, usually severe problems occur. High ash contents cause problems with the stability of the fuel bed and with de-ashing, elevated Si and K contents lead to comparably low ash melting temperatures and thus to slagging problems. Moreover, elevated K and Cl contents cause an increased release of K to the gas phase from which high levels of fine particulate emissions result, which exceed the dust emission limits for wood pellet boilers by at least an order of magnitude. Additionally, high S and Cl contents are relevant with respect to gaseous HCl and SO_x emissions and additionally bear increased risks for low temperature corrosion.

During technology development within the FlexiFuel-CHX project, special attention is paid to these problems. The aim is to achieve the objectives mentioned for a broad fuel spectrum and also to ensure high plant availabilities.

2.2 The PuroWIN pellet and wood chip boiler technology

The patented technology consists of a fixed-bed updraft gasifier directly connected with a gas burner and a hot water fire-tube boiler (see Figure 1 and Figure 2). A typical feature of fixed-bed updraft gasifiers is the formation of distinct zones in the fuel bed with charcoal combustion at high temperatures (in the bottom - see scheme in Figure 1), gasification and pyrolysis at moderate temperatures (in the central part) and fuel heating and drying at low temperatures (in the upper region). Due to this pronounced temperature profile in the fuel bed alkaline compounds released from the fuel to the gas phase during charcoal combustion are condensed and precipitated in the upper fuel bed region again and get incorporated in the grate ash [2]. Therefore, the formation of inorganic fine particles (which is dominated by the Ksalts KCl, K₂SO₄ and K₂CO₃) can be minimised. Moreover, the product gas velocities at fuel bed outlet are very low which minimizes the entrainment of fuel, ash and charcoal particles and thus coarse fly ash emissions. The product gas from the gasifier is then burned in a staged burner, facilitating an almost complete gas phase burnout at very low excess air ratios ($\lambda \sim 1.2$) resulting in almost zero emissions and high efficiencies. For example for wood pellet combustion average CO emissions of 3 mg/MJ, OGC emissions below the detection limit of the analyser as well as total dust emissions of 1 mg/MJ (all values related to the NCV of the fuel) and an efficiency

of 94% have been determined [1].

Within the project, R&D work focuses on further development regarding the fuel feeding system, the grate, the design of the gasifier regarding geometry and cooling in distinct zones, the fuel bed temperature control, the deashing system as well as the gas burner in order to make it ready for a wide fuel spectrum.



Figure 1: Basic concept of the ultra-low emission PuroWIN wood chip and pellet boiler technology



Figure 2: Cross section of the ultra-low emission PuroWIN wood chip and pellet boiler technology

2.3 Integration of a flue gas condenser

In current residential-scale biomass boiler designs, the flue gas temperature at boiler outlet usually amounts to 150°C - 180°C at nominal load. During partial load operation, the flue gas temperatures may drop as low as 75°C, which can, when firing e.g. agricultural fuels with elevated S contents, cause severe low-temperature corrosion risks due to undercutting the acid dew point or due to corrosion caused by hygroscopic salts [3]. The combination of a boiler with a flue gas condenser allows for a staged heat transfer, whereby a high flexibility regarding the design temperature at the interface between stage 1 (boiler) and stage 2 (condenser) exists. Therefore, a new fuel-flexible boiler has been developed, which shows flue gas outlet temperatures, which are during all load phases sufficiently high to prevent low-temperature corrosion (can therefore be constructed with conventional low cost steel).

Condensers applied in residential biomass

combustion systems are actually based on fire tube or water tube heat exchangers with typically wide flue gas pathways to avoid problems with blockage by ash deposit formation on the heat exchanger tubes. Therefore, heat transfer and consequently the potential for latent heat recovery are limited since condensation usually only takes place on the tube surfaces. The low particulate emissions of the PuroWIN technology bear the significant advantage that deposit formation risks become of minor relevance. Therefore, a condenser design with narrow flue gas flow channels, as it is usually applied in natural gas fired condensing boilers, is a feasible option. Such a design offers a much better heat exchange as well significantly lower differences between the as temperatures of the flue gas at condenser outlet and the return water from the heating system due to the considerably larger heat exchange surfaces available and therefore, a much higher latent heat recovery potential is given. Moreover, compared with the flue gases from conventional biomass boilers the flue gases from the PuroWIN technology show a significantly decreased oxygen content and thus a more than 5°C higher water dew point, which is one relevant factor regarding improved condensation efficiency. However, especially when utilising non-wood fuels, the acidity of the condensate is high (pH values typically between 3.5 and 4.0) which has to be considered regarding material selection and condensate neutralisation.

3 RESULTS ACHIEVED SO FAR

3.1 Test run results

During the first two project years, the PuroWIN technology has been further developed and a new flue condenser has been developed, designed and connected to the boiler. Three testing plants (nominal load including boiler and condenser: 50 kW) have been constructed and tested at three different sites (Windhager, BIOS and CIEMAT). The testing campaigns comprised test runs with reference fuels (same fuel assortments utilised at all three testing sites to check the comparability of results) and typical Central/Northern European as well as Mediterranean biomass fuels. Up to now forest residues wood chips, poplar chips (from SRC), olive stones, almond shells, miscanthus pellets and olive tree pruning pellets have been tested. In the following, test runs with the following four different feedstocks are discussed in more detail:

- Forest residues good quality (FR-GQ): a typical Central/Northern European biomass fuels in form of wood chips
- Poplar from SRC (Pop): a typical Mediterranean biomass fuel which is, however, also applicable in Central/Northern Europe; as FR-GQ this fuel has also been applied in form of chips
- Olive stones (OS): a typical Mediterranean biomass fuel
- Miscanthus pellets (Misc): a typical Central/Northern European biomass fuels in form of pellets

However, the results and trends achieved with these fuels have been comparable with those of the other fuels mentioned.

In Table I, the results of chemical analyses of FR-GQ, Pop, OS and Misc are presented.

FR-GQ (softwood chips) show typically moderate N, S, Cl, Si, K and ash contents. As Ca dominates the ash

matrix no ash melting problems are expected (Ca increases the ash melting temperatures). The moisture content of FR-GQ is significantly higher compared to the other fuels tested. Therefore, the heat recovery potential in a flue gas condenser increases. All in all, FR-GQ can be regarded as a high-quality wood fuel with no major problems to be expected and is used as a reference for the other fuels tested.

Poplar chips are characterised by increased N, S, Ca, Mg, K and ash contents. Thus, elevated aerosol emissions and increased coarse fly ash emissions have to be expected for conventional grate combustion systems. Moreover, higher SO_x and NO_x emissions will occur. Because of the high Ca content no relevant ash melting problems should be expected.

In terms of N, S and ash contents olive stones are comparable to FR-GQ but their K content is significantly higher and dominates the ash matrix. Therefore, elevated aerosol emissions must be expected in conventional grate combustion systems and also lower ash melting temperatures will occur. Moreover, due to the elevated Cl content higher HCl emissions will occur.

Table I: Results of fuel analyses of FR-GQ, Pop, OS and Misc

Explanations: M.C....moisture content; A.C....ash content; GCV...gross calorific value; NCV...net calorific value; d.b....dry basis; w.b....wet basis; SST...shrinkage starting temperature; DT...deformation temperature; FR-GQ...forest residues – good quality; Pop...poplar chips; OS...olive stones; Misc...Miscanthus pellets; mean...mean value; s...standard deviation

| | | FR-GQ | Рор | OS | Misc |
|------|------------|--------|-------|-------|-------|
| M.C. | wt.% w.b. | 26.10 | 13.60 | 12.70 | 7.63 |
| A.C. | wt.% d.b. | 0.76 | 2.45 | 0.77 | 2.28 |
| GCV | MJ/kg d.b. | 19.72 | 20.03 | 20.04 | 19.29 |
| NCV | MJ/kg w.b. | 12.94 | 15.78 | 16.00 | 16.39 |
| С | wt.% d.b. | 49.01 | 48.89 | 49.60 | 47.69 |
| н | wt.% d.b. | 6.10 | 6.24 | 6.14 | 6.11 |
| Ν | wt.% d.b. | 0.10 | 0.42 | 0.10 | 0.21 |
| S | mg/kg d.b. | 132 | 370 | 130 | 625 |
| Cl | mg/kg d.b. | 82 | 72 | 218 | 354 |
| Si | mg/kg d.b. | 499 | 189 | 42 | 4,810 |
| Ca | mg/kg d.b. | 1,550 | 7,030 | 1,230 | 912 |
| Mg | mg/kg d.b. | 285 | 764 | 129 | 548 |
| К | mg/kg d.b. | 1,030 | 2,930 | 2,430 | 4,720 |
| Na | mg/kg d.b. | 15 | 15 | 9 | 193 |
| Р | mg/kg d.b. | 138 | 637 | 71 | 490 |
| Al | mg/kg d.b. | 166 | 44 | 11 | 15 |
| Fe | mg/kg d.b. | 98 | 66 | 24 | 52 |
| Mn | mg/kg d.b. | 43 | 155 | 4 | 76 |
| Zn | mg/kg d.b. | 6 | 27 | 1 | 14 |
| SST | °C | 1,250 | 760 | 730 | 800 |
| DT | °C | >1.500 | 1.320 | 790 | 840 |

The ash content of Miscanthus is on a similar level as for poplar chips, thus also for Miscanthus pellets elevated dust emissions have to be expected for conventional grate combustion systems. The N content of the fuel is between FR-GQ and poplar chips, following, NO_x emissions should also be in-between. Miscanthus pellets are mainly characterised by comparatively high concentration levels for S, Cl, Si and K. This results in elevated SO_x and HCl emissions. Moreover, elevated aerosol emissions have to be expected for combustion conditions in conventional grate firings and low ash melting temperatures have to be expected due to the Si-K-dominated as matrix.

Poplar chips, olive stones and Miscanthus can be

characterised as so-called "difficult" biomass fuel for residential wood chips and pellet boilers.

Test runs have been performed at nominal and 30% part load operation. For OS the nominal load had to be reduced to about 32 kW due to the high pressure drop over the fuel bed (limitation of the flue gas fan). During all test runs, a stable and continuous operation without any problems regarding slag formation could be achieved. As an example, the load, O₂ and CO trends for the nominal and partial load test runs with Miscanthus pellets are shown in Figure 3.



Figure 3: Exemplary results of the full (top) and partial load (bottom) test runs with Misc

In Figure 5 the CO, TSP (=total suspended particulate matter = total dust) and PM_1 (particulate matter <1 μ m) emissions are presented.

As the data show, the CO emissions measured during the combustion of FR-GQ, OS and Misc are very low (at nominal load < 3.5 mg/MJ). Slightly elevated CO emissions occurred with poplar at nominal load (appr. 14 mg/MJ) due to the more inhomogeneous particle size and the very low bulk density, which is, however, still a low level.

The TSP emissions range from 0.8/0.5 mg/MJ (NL/PL) for FR-GQ over appr. 1 mg/MJ for Misc and 2 mg/MJ for OS to appr. 5 mg/MJ for poplar. The PM1 emissions amount to between 49% (Misc NL) and 96% (OS PL) of the TSP emissions. Thus, the TSP and PM₁ emissions are by more than a factor of 10 lower in comparison to conventional fixed bed combustion systems (see Figure 4).



Figure 4: PM₁ emissions in dependence of the aerosol forming elements in the fuel



Figure 5: CO, TSP and PM₁ emissions during the operation of the FlexiFuel-CHX testing plants with FR-GQ, Pop, OS and Misc

Explanations: mg/MJ related to the NCV of the fuel; NL...nominal load; PL...partial load; FR-GQ...forest residues – good quality; Pop...poplar chips; OS...olive stones; Misc...Miscanthus pellets

Figure 6 provides an overview of the NO_x emissions in dependence of the N content in the fuels tested for nominal and partial load. It is obvious, that the NO_x emissions increase with increasing N content in the fuel. The lower NO_x emissions during partial load operation can be mainly attributed to the higher residence time of the flue gas in the under-stoichiometric secondary combustion zone of the burner. This effect is of relevance regarding the further NO_x reduction target for the second generation testing plant (design of a Low-NO_x burner).



Figure 6: NO_x emissions in dependence of the N content in the fuel

During the test runs the excess air ratio was adjusted to $\lambda = 1.2$ at nominal load, corresponding to an average oxygen content of the flue gas of 3.5 vol% (d.b.) and to $\lambda = 1.35$ to 1.40 at partial load, corresponding to an average oxygen content of the flue gas of 5.4 to 5.9 vol% (d.b.). At such low oxygen contents high water dew points of the flue gas of about 50°C can be achieved, even when utilising such dry fuels like poplar, olive stones and Miscanthus pellets (moisture content: 7.6 to 13.6 wt% w.b. - see Table I). For comparison, for forest residues with a moisture content of about 30 wt% (w.b.), the dew point increases to 56°C. With the new condenser design it has been possible to cool the flue gas down to temperatures which were with on average 33°C (partial load) respectively 35°C (nominal load), just 3 to 5°C higher than the return temperature of the water, which has been adjusted to 30°C.

In Figure 7, the resulting boiler efficiencies, overall efficiencies and the contribution of the flue gas condenser to the overall heat produced are presented for the tests runs with FR-GQ, poplar, OS and Misc.

As it can be seen, for the dry fuels (Pop, OS and

Misc) the condenser increases the heat output at nominal load by 11% to 13%. Thus, overall efficiencies of 104 to 105% could be reached for these fuels. For the moist FR-GQ, the condenser contributes at nominal load with 15% to the heat produced and the overall efficiency increases to 107%. The total thermal efficiencies at partial load are only slightly lower. Regarding these results it has to be mentioned that for experimental reasons a measurement section has been implemented between the boiler and the condenser leading to a temperature decrease of the flue gas of about 10°C before it enters the condenser. In a real plant with a direct mounting of the condenser at boiler outlet, these energy losses would not occur and therefore the efficiencies would be even higher.





Explanations: NL...nominal load; PL...partial load; FR-GQ...forest residues – good quality; Pop...poplar chips; OS...olive stones; Misc...Miscanthus pellets



Figure 8: HCl and SO_x concentrations upstream and downstream the condenser and the corresponding precipitation rates during the test runs with Misc

As revealed from Table I, Miscanthus shows the highest S and Cl contents compared to the other fuels. Figure 8 shows, as an example, the SO_x and HCl emissions up- and downstream the condenser as well as the related precipitation efficiencies. SO_x precipitation rates between 55 and 99% have been achieved for all fuels tested (higher values for partial load) and HCl precipitation rates above 90% are realistic. Downstream the condenser average HCl-emissions of below 1.0 mg/MJ and average SO_x emissions of below 10 mg/MJ (related to the NCV of the fuel) for all fuels tested have been determined. Due to this efficient emission reduction,

no negative impact on air quality by the utilisation of S and Cl-rich fuels shall occur. The condensate however, shows a high acidity (pH values in the range of 3.5 to 4.0). Depending on regional or national regulations it might therefore be required to neutralise the condensate.

3.2 Investigation of the ash formation with a special focus on K

One main critical issue regarding fuel flexibility is related to the behaviour of ash forming elements with special respect to ash melting and K-behaviour. K is in particular of relevance, as K is the main aerosol forming element for chemically untreated biomass fuels and thus relevant regarding PM_1 emission reduction. Therefore, embedding of K in the grate ash would support the aerosol emission reduction and thus a focus has been put on the investigation of the related mechanisms.

For the investigation of the ash formation mechanisms several different methods have been employed:

- Ash sintering tests
- Thermodynamic high-temperature equilibrium calculations (TEC)
- · Lab-reactor tests
- Test runs with the gasifier

The following different ash fractions occur in fixedbed biomass conversion processes:

- Grate ashes
- · Coarse fly ashes
- Fine particulate emissions

In general, two different ash matrices have to be considered, namely the Ca-K-dominated system and the Si-K-dominated system. For the fuels utilised within the FlexiFuel-CHX project the Ca-K-dominated system is the most relevant one since it covers all wood fuels, olive stones and almond shells. In this Ca-K-dominated system, the ash formation mechanisms described in the following prevail. For Miscanthus and agro-pellets the Si-K-dominated system is of relevance, which is described later in this section. A graphical scheme of the mechanisms is presented in Figure 10.

In the Ca-K-dominated system the fuel enters the gasifier from above and on the upper layer of the fuel bed at first drying takes place. Then, in the pyrolysis zone, the fuel is quickly heated up to about 700°C. It has to be pointed out that this temperature increase takes place in a very short zone, which only amounts to some percent of the whole gasifier fuel bed height. According to [4, 5 and 6], Cl is mainly released to the gas phase at temperatures between 200 and 400°C. Since this happens in the top layer of the fuel bed, most of the Cl leaves with the product gas. This is also confirmed by element balance calculations performed which show a Cl-release of up to 97 wt%.

According to [7], about 50-75% of the S contained in biomass fuels can be organically bound in proteins. Therefore, the major part of the S-release occurs during the devolatilisation of the organic matrix, i.e. during the pyrolysis reactions in the upper layers of the fuel bed. Consequently, also for the S released in the upper part of the fuel bed the remaining residence time is assumed to be too short to undergo secondary reactions with the charcoal. Remaining inorganically bound S is retained in the ash or released at temperatures >900°C. This literature data are well in line with the S-release data

determined during the test runs (50 to 89 wt%).

K in biomass fuels can be found in the organic matrix connected to carboxyl-groups or as salt (e.g. KCl). Decomposition of carboxyl-groups starts at 300°C. However, according to literature, K-release slowly starts at 500 to 600°C and then accelerates at temperatures above 800°C [8]. Consequently, in the pyrolysis layer it is not much likely that K is released to the gas phase. Also other ash forming elements (e.g. Na) and heavy metals (Zn, Pb) are not expected to be released in the temperature range below 600°C.

After heating up of the fuel to about 700° C within a very short height of the gasifier bed, a higher zone with only marginally increasing temperatures follows. The fuel entering this zone is already depleted regarding Cl and S but still all other relevant elements (especially K) are not released. At the bottom of the gasifier charcoal burnout takes place and due to the high temperatures of more than 900°C, K is now released to the gas phase.

The K released penetrates with the product gas through the fuel bed upwards. Due to the rather long section with almost constant temperatures on a 700 to 800° C level there is enough residence time and sufficiently high temperature available for the reaction of K with the pyrolysis char and with other ash forming elements. Thermodynamic equilibrium calculations (TEC) performed for Ca-K-dominated fuels have shown, that at these temperatures K forms carbonates. Which carbonates are formed, strongly depends on the K/Ca-ratio. However, K₂Ca₂(CO₃)₃, K₂Ca(CO₃)₂ and K₂CO₃ are the most relevant ones. To further investigate this dependency, a parametric study has been performed. The results are presented in Figure 9.



Figure 9: The influence of the K/Ca ratio on the formation of K-carbonates at 700°C

<u>Explanations</u>: Parametric study performed with thermodynamic high-temperature equilibirum calculations; only solid phases are plotted; Total solid K: total of $K_2Ca_2(CO_3)_3$, $K_2Ca(CO_3)_2$ and K_2CO_3

At low molar K/Ca ratios (<<1) the surplus of Ca leads to a preferred formation of the double carbonate $K_2Ca_2(CO_3)_3$ (blue points in Figure 9). At a molar K/Caratio of 0.7 for the first time besides $K_2Ca_2(CO_3)_3$ also $K_2Ca(CO_3)_2$ (Fairchildite – green points in Figure 9) is formed. With further increasing molar K/Ca ratio $K_2Ca_2(CO_3)_3$ disappears and at molar K/Ca ratios slightly above 1 only Fairchildite is formed. With further increasing K/Ca ratio the share of Fairchildite also decreases while the share of K_2CO_3 formed (black points in Figure 9) increases. It has to be pointed out that at 700°C almost the whole K is bound in these three solid compounds as confirmed by the "Total solid K" data points, which are close to 100 wt%.

Consequently, the molar K/Ca-ratio of the fuel

determines the shares of Ca-K-carbonates and K₂CO₃ formed in the pyrolysis zone in the upper part of the fuel bed. In the following, the K-compounds move together with the fuel towards the charcoal combustion zone and the temperatures slightly start to increase and finally enter the hot charcoal combustion zone. Regarding the ash transformation processes prevailing, it must now to be distinguished between three cases, which depend on the initial distribution of K in the different carbonates and therefore the K/Ca-ratio (see also Figure 10).

- <u>Case 1</u>: molar K/Ca ratio <<1: According to TEC performed, for fuels with a very low K/Ca ratio at first K₂Ca₂(CO₃)₃ decomposes at temperatures above 750°C to K₂Ca(CO₃)₂ and CaO. Then, with further increasing temperature (>800°C) K₂Ca(CO₃)₂ decomposes to K₂CO₃, CaO and CO₂. At temperatures above 900°C K₂CO₃ starts first to melt and then to decompose to K_(g), KOH and CO₂, which are released to the gas phase.
- <u>Case 2</u>: molar K/Ca ratio around 1: In this case the transformation mechanism presented above already starts at the decomposition of Fairchildite since no K₂Ca₂(CO₃)₃ is present.
- <u>Case 3</u>: molar K/Ca ratio >>1: Since only K₂CO₃ is present from the beginning, the mechanism is reduced to the K₂CO₃ decomposition at above 900°C.

However, according to the cases explained above, at the charcoal combustion temperatures prevailing during the test runs (>900°C) no K-Ca-carbonates should be present in the grate ash. This is in contradiction with grate ash analyses (wet chemical as well as XRD). The reason for this deviation can be found in the fact, that at CO₂ partial pressures above 0.03 bar, as they prevail in and above the charcoal combustion zone) the decomposition of Fairchildite (K2Ca(CO3)2) is suppressed and instead a melt is formed [9]. Due to missing thermodynamic data this effect cannot be considered by TEC. This however also means that no K₂CO₃ is formed from the Fairchildite decomposition and therefore, also no KOH can be released to the gas phase due to K₂CO₃ decomposition. This effect is supposed to be the main reason for the efficient embedding of K in the grate ash for fuels with a K/Ca-ratio of <<1 and around 1.

For fuels with a K/Ca ratio of >>1 it has to be considered that with increasing K/Ca ratio Fairchildite formation decreases and K2CO3 formation increases. This means that the suppression of the Fairchildite decomposition loses relevance and the decomposition of K₂CO₃, which is connected to the release of KOH, gains importance. Since also K₂CO₃ has been identified in the grate ashes it is assumed that within the residence time available at high temperatures, K₂CO₃ melting and decomposition cannot be completed. K released to the gas phase in the charcoal combustion zone however, can react again with the fuel bed in the upper zone (pyrolysis zones), but with time this will lead to a K accumulation in the fuel bed and a breakthrough of K may result. Frequent de-ashing could help to mitigate this breakthrough. However, for fuels like almond shells the slightly increased K release ratios can be explained with this effect. Moreover, also the slightly increased ash sintering tendencies, observed for olive stones and almond shells are supposed to be associated to such K accumulations and the formation of K₂CO₃ melts since, as XRD analyses have shown, the sintered particles almost exclusively consist of Fairchildite and K2CO3.

It has to be pointed out that in this ash formation

mechanism Si plays no relevant role. Wood fuels, olive stones and nut shells (as the most relevant representatives undergoing this ash transformation mechanism) mainly contain Si in form of mineral impurities. As XRD analyses have shown, these impurities are not reactive enough to impede the carbonate formation mechanism.



Figure 10: Ash formation during updraft gasification for fuels with a K-Ca as well as with a Si-K-dominated ash matrix

As already mentioned, fuels such as Miscanthus and agro-pellets belong to the Si-K-dominated system. In these fuels, Si is not only present as inert mineral impurity but mainly is part of the organic fuel matrix and therefore reactive. Due to this reason, carbonate formation is suppressed by the formation of K-silicates.

The first steps regarding S, Cl and K release in the upper fuel bed region (beginning of the pyrolysis zone) remain the same as for the Ca-K-rich fuels. But then, according to TEC even at temperatures above 700°C K-silicates (e.g. K₂Si₂O₅ and K₂Si₄O₉) are formed. These compounds have the ability to keep the K in the grate ash even at high temperatures. However, they also significantly reduce the ash melting temperatures.

In extreme cases (e.g. for typical wheat straw compositions) the ash melting temperatures drop below 700°C which means that even with the application of an efficient fuel bed cooling, a constant gasifier operation could not be maintained anymore.

For such fuels, the utilisation of additives has been investigated within the FlexiFuel-CHX project. It turned out that additivation with kaolin (an alumo-silicate) leads to the formation of solid K-Al-silicates over the entire temperature range evaluated (700-1,500°C) and significantly reduces the formation of low temperature melting K-silicates. It has also been experimentally proven that kaolin additivation helps to make agricultural fuels with problematic ash melting behaviour applicable in the new boiler technology.

Due to the efficient K embedding in the grate ash (K embedding >98%) PM₁ emissions can almost be avoided.

4 CONCLUSIONS

Within the still ongoing EU-H2020-funded project FlexiFuel-CHX the PuroWIN pellet and wood chips boiler technology is further developed towards a significantly increased fuel flexibility and enhanced efficiency. The results achieved so far already show that with this new technology a broad range of different biomass fuels (loose and pelletised wood and non-wood fuels) with, in terms of combustion behaviour problematic properties, can be utilised at almost zero emission levels regarding dust, CO and OGC and also at very low HCl and SO_x emissions. Moreover, due to the operation of the PuroWIN technology at very low dust and excess oxygen contents a new condenser concept with an enhanced efficiency could be implemented. By coupling this condenser with the boiler, even with dry fuels such as Miscanthus pellets, poplar chips and olive stones overall efficiencies of 104-105% could be achieved (related to the NCV of the fuel). With forest residues an overall efficiency of even 107% could be reached. Moreover, in the condenser gaseous HCl and SO_x emissions can be significantly reduced (SO_x precipitation 55-99%; HCl precipitation 93-98%). Within the remaining project time, also other so-called difficult biomass fuels shall be tested and the overall technology shall be further improved.

A detailed investigation of the ash formation mechanisms ongoing in the fuel bed of the gasifier provided knowledge regarding the relevant K embedding mechanisms in the grate ash, which supports and explains the significant reduction of aerosol emissions compared to conventional fixed bed combustion systems. The results of the test runs and analyses show, that K gets embedded in the bottom ash by >98% for all fuels

investigated.

From this work it can be derived that a highly fuel flexible operation of residential biomass combustion plants is possible. Moreover, an operation at almost zero dust, CO and TOC emissions is possible without secondary measures. In addition, by the integration of a flue gas condenser high efficiencies and very low SO_x and HCl emissions are possible. Thus, this technological development can be regarded as future approach for residential biomass combustion and forms a new technological milestone in this field.

Future developments foreseen focus on a stepwise technological optimisation and a further reduction of NO_x emissions. The final aim of this development is a highly efficient zero-emission residential biomass heating system.

5 REFERENCES

- [1] OBERNBERGER Ingwald, MANDL Christoph, BRANDT Jürgen, 2016: Demonstration of a New Ultra-Low Emission Pellet and Wood Chip Small-Scale Boiler Technology (plenary lecture). In: Proc. of the 24th European Biomass Conference and Exhibition, June 2016, Amsterdam, The Netherlands, ISBN 978-88-89407-165, pp. 367-374, (paper DOI 10.5071/24thEUBCE2016-2BP.2.1), ETA-Florence Renewable Energies (Ed.), Florence, Italy
- [2] OBERNBERGER Ingwald, BRUNNER Thomas, MANDL Christoph, KERSCHBAUM Michael, SVETLIK Thomas, 2017: Strategies and technologies towards zero emission biomass combustion by primary measures. In: Energy Procedia, Volume 120 (2017), pp. 681-688 (paper DOI 10.1016/j.egypro.2017.07.184)
- [3] BRUNNER Thomas, REISENHOFER Erwin, OBERNBERGER Ingwald, KANZIAN Werner, FORSTINGER Michaela, VALLANT Rudolf, 2017: Low-temperature corrosion in biomass-fired combustion plants - online measurement of corrosion rates, acid dew points and deliquescence corrosion. In: Proc. of the 25th European Biomass Conference and Exhibition, June 2017, Stockholm, Sweden, ISBN 978-88-89407-17-2, ISSN 2282-5819, pp. 393-400, (paper DOI 10.5071/25thEUBCE2017-2AO.8.1), ETA-Florence Renewable Energies (Ed.), Florence, Italy
- [4] BJÖRKMAN E., STRÖMBERG B., 1997: Release of Chlorine from Biomass at Pyrolysis and Gasification Conditions, Energy & Fuels, 11, pp. 1026 - 1032
- [5] JENSEN P., FRANDSEN F., DAM-JOHANSEN K., SANDER B., 2000: Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis, Energy & Fuels, 14, pp. 1280-1285
- [6] KNUDSEN J., JENSEN P., DAM-JOHANSEN K., 2004: Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass, Energy & Fuels, 18, pp. 1385-1399
- [7] KNUDSEN N.J., JENSEN A.P., LIN W., FRANDSEN J.F.; DAM-JOHANSEN K, 2004: Sulfur Transformations during Thermal Conversion of Herbaceous Biomass. Energy Fuels 2004, 18, pp. 810-819.

- [8] van LITH S., JENSEN P., FRANDSEN F., GLARBORG P., 2008: Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 2: Influence of Fuel Composition, Energy & Fuels, 22, pp. 1598-1609
- [9] WINBO C., ROSEN E., HEIN M., 1998: Thermal Analytical Study of the Decomposition of K₂Ca₂(CO₃)₃. In: Acta Chemica Scandinavia, 1998, 52, pp. 431-434
- [10] OBERNBERGER Ingwald, 2014: Strategy for the Application of Novel Characterization Methods for Biomass Fuels: Case Study of Straw. In: Energy&Fuels dx.doi.org/10.1021/ef402249x

ACKNOWLEDGEMENTS 6

This project receives funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654446 -FlexiFuel-CHX.

LOGO SPACE

