TUHH
Technische Universität Hamburg

IUE

Technische Universität Hamburg
Institut für Umwelttechnik und Energiewirtschaft

Final Report

Mobilization of Corn Cobs as Energy Source and Improvement of Heat Generators Concerning Environmental Impacts

funded under Az. 33897/01 and 33897/02 by Deutsche Bundesstiftung Umwelt

sponsored by
DBU
Deutsche
Bundesstiftung Umwelt
www.dbu.de

Natasa Dragutinovic, Isabel Höfer, Martin Kaltschmitt, Djordje Djatkov, Milan Martinov

Hamburg den 4/26/2021

06/02

Projektkennblatt
der
Deutschen Bundesstiftung Umwelt

Az	**33897/01**	Referat	**24/0**	Fördersumme	**123.988 €**

Antragstitel **Mobilization of Corn Cobs as Energy Source and Improvement of Heat Generators Concerning Environmental Impacts**

Stichworte Energie, halmgutartige Biomasse, Maisspindel, Emission, Verbrennung

Laufzeit	Projektbeginn	Projektende	Projektphase(n)
2 Jahre 7 Monate	**15.03.2018**		

Zwischenberichte halbjährig

Bewilligungsempfänger
Technische Universität Hamburg
Institut für Umwelttechnik und Energiewirtschaft
Eissendorfer Str. 40
21073 Hamburg

Tel 040 428 78 3008
Fax 040 428 78 2315

Projektleitung
Martin Kaltschmitt

Bearbeiter
Natasa Dragutinovic
Isabel Höfer
Djordje Djatkov
Milan Martinov

Kooperationspartner
Fakultät für Technische Wissenschaften (Faculty of Technical Sciences) Novi Sad, Serbien

Termoplin Mladenovac, Serbien

Objective and rationale of the project

Main objective of the proposed project is to investigate possibilities to reduce negative environmental impact when using corn cobs as a fuel for combustion in common small facilities to generate heat energy for households in Serbia.

Presentation of the work steps and the applied methods

The work tasks are summarized in three applied scenarios:
- I: Corn cobs are to be collected from farm storage and combusted in heating facility in traditional way.
- II: After collecting, corn cobs are to be crushed prior to combustion in automated heating facility.
- III: After collecting, corn cobs are grounded and pelletized prior to combustion in automated heating facility. Additives and fuel blending are applied with the aim to improve fuel properties.

Combustion experiments take place in selected units, during which emissions of CO, NO_x, organic gaseous carbons (OGC)), particulate matter (PM), as well as energy efficiency and thermal capacity of the combustion unit were monitored. After initial measurement of the emissions appropriate primary measures for emission reduction and for the improvement of energy efficiency are suggested and implemented, followed by repeated combustion trails and measurement of emissions and efficiency. Assessment of environmental aspects is performed through energy and greenhouse gas balances, whereas profitability assessment through software BiomasaPro and selected economic parameters.

Results and Discussion

Two experimental setups were constructed in Serbia (in Mladenovac – Termoplin, and in Kula, Terming) and one in Hamburg (TUH). Results from the combustion trials in Serbia can be summarized as follows:

- **Automatic boiler Termoplin TK**. When using corn cob pellets and after combustion chamber modification, CO emissions were in line with the EN 303-5 class 4 requirements (< 500 mg/m^3) and PM emission (143 mg/m^3) was in line with class 3 requirement (< 150 mg/m^3). Efficiency > 75 % is also met (class 3). When using crushed corn cobs and after the installation of the fireclay mantel, CO and organic gaseous carbon (OGC) emissions are in line with class 3 (CO < 3,000 mg/m^3 and OGC < 100 mg/m^3), whereas PM emissions and efficiency are outside the standard requirements.
- **Automatic boiler Terming Ozone agro 25**. After introducing secondary combustion air and a fireclay cylinder in the combustion chamber, emissions from corn cob pellet combustion at nominal load decreased. CO emissions met the class 4 requirements (< 1,000 mg/m^3), but PM emissions were above class 3 requirements (< 150 mg/m^3). Efficiency values were in line with class 5 (> 89 %). Emissions are partial loads (50 % and 30 %) are higher than at nominal load.
- **Manual boiler Terming TIG P**. After modifications CO emissions are reduced more than 5-fold, being in line with the requirements of class 3 for manually-fed units (< 5,000 mg/m^3). PM emission is reduced almost 3-fold and is close to the class 3 requirement (< 150 mg/m^3). Efficiency is improved from 40 % to > 50 %.

Project goals were partially achieved. The reduction of PM emissions remains an open question.
From the experiments at the Hamburg University of Technology (TUH) following conclusions can be made:

- **Automatic boiler Terming Ozone agro 25**. Blending of corn cob pellets with wood pellets has an effect on emission reduction but not enough to meet the emission limit values. In some blends emissions of CO are in accordance with EN 303-5 class 5 (< 500 mg/m^3), whereas PM emissions are higher than standard requirements. Corn cob grits are not adequate fuel for small-scale combustion without secondary treatment. The emissions are outside of the acceptable range, even with additives.
- **Pellet oven Austroflamm Polly 2.0.** Blending of corn cob pellets with wood pellets has an effect on emission reduction, but emission limit values are met only when minor shares of corn cob pellets are present (up to 25 wt. % corn cobs). Additivation of corn cob pellets with kaolin prior to pelletization can reduce both CO and PM emissions, but not enough to meet the standard requirements. The combination of fuel blending and additivation of corn cob pellets with kaolin should be further investigated.

All three scenarios achieved high values of energy indicators, showing that the values of total energy input are low and that it is possible to increase transport distances or apply fuel preparation. All three scenarios are sustainable with savings of 98 % for the whole cob, 91 % for crushed, and 84 % for pellets. Investing in the construction of heat generators is economically viable for all options. In the case of reconstruction, scenario with whole cobs is mostly viable, whereas other two pathways are not.

Promotion and Presentation

During the course of the project results were presented at Central European Biomass Conference in Graz 2020 and Winter Seminar of Farmers Association Klub 100P+ in Kopaonik. At the moment of finalizing of the report (December 2020), one original research paper is accepted for publication, and one is in preparation. Additional papers are planned and underway.

Conclusion

Low-cost primary measures are effective up to a certain point. CO emissions have been reduced in most cases and are in accordance with emission limit values. Due to the fact that the sole use of corn cob pellets in automatically-fed small-scale units results in increased PM emissions which do not meet the emission limit values, energetic utilization of corn cob pellets in small-scale automatically-fed units in an environmentally acceptable is possible only in certain fuel blends. It could be recommended to blend agro pellets with higher quality wood pellets and to further investigate the application of kaolin. In case of whole and crushed cob combustion, it is possible that the achievement of such ambitious goals is attainable only in large units with flue gas treatment. All investigated options met the sustainability criteria. Investment options for heat generator construction are profitable for all fuel types, whereas reconstruction is not.

Table of Contents

Nomenclature

Symbols in Latin alphabet

CO	Carbon monoxide concentration in the flue gas	mg/m^3
PM	Total particulate matter emission	mg/m^3
NO_x	Nitrogen oxide concentration in the flue gas	mg/m^3
OGC	Organic Gaseous Carbon concentration in the flue gas	mg/m^3
NPV	Net Present Value	€
IRR	Internal Rate of Return	%
PP	Payback Period	Year(s)
NG	Natural gas price	$c€/Sm^3$
MC	Moisture Content	wt. %
LHV	Lower Heating Value	MJ/kg
KEA	Cumulative energy demand	MJ/t_{DM}
KEA_H	Cumulative energy required for production	MJ/t_{DM}
KEA_N	Cumulative energy required for use	MJ/t_{DM}
KEA_E	Cumulative energy required for disposal	MJ/t_{DM}
KEA_T	Cumulative energy required for transport	MJ/t_{DM}
E_T	Energy for transport of whole, crushed or pellets of corn cob	MJ/t_{DM}
E_E	Electricity for crushing, grinding, pelleting and combustion	MJ/t_{DM}
E_P	Energy for packaging	MJ/t_{DM}
ER	Energy ratio	MJ_p/MJ_f
NET	Net Energy Gain	MJ/t_{DM}
E	Total emissions from the fuel production before energy conversion	gCO_{2eq}/MJ
e_{ec}	Emissions from the extraction or cultivation of raw materials	gCO_{2eq}/MJ
e_l	Annualized emissions from carbon stock changes caused by land-use change	gCO_{2eq}/MJ

e_p	Emissions from processing	gCO_{2eq}/MJ
e_{td}	Emissions from transport and distribution	gCO_{2eq}/MJ
e_u	Emissions from the fuel in use	gCO_{2eq}/MJ
e_{sca}	Emission savings from soil carbon accumulation via improved agricultural management	gCO_{2eq}/MJ
e_{ccs}	Emission savings from CO_2 capture and geological storage	gCO_{2eq}/MJ
e_{ccr}	Emission savings from CO_2 capture and replacement	gCO_{2eq}/MJ
EC_h	Total greenhouse gas emissions from heat generation	gCO_{2eq}/MJ
S	GHG emission saving	%
$EC_{F(h)}$	Emissions of fossil fuel comparator	gCO_{2eq}/MJ
d	Diameter of the nozzle	m
$\dot{V}_f$	Volumetric flow in the entry nozzle	m^3/s
v_f	Velocity of the flue gas at the measurement point (filter)	m/s
$\dot{V}_m$	Measured sampled volume flow under the conditions at the gas meter	m^3/s
h_f	Humidity content of the sampled volume flow under the condition at the measurement point (filter)	vol.%
h_m	Humidity content of the sampled volume flow under the gas meter conditions	vol.%
T_m	Sampled volume flow temperature during measurement at the gas meter	K
T_f	Temperature of the sampled volume flow at the measurement point (filter)	K
p_f	Absolute pressure of the sampled volume flow at the measurement point (filter)	Pa
p_m	Absolute pressure of the sampled volume flow during measurement at the gas meter	Pa
h_i	Volumetric share of moisture	-
$p_{H2O}(t)$	Saturation pressure of the water vapor at the given temperature	Pa

c_{PM}	PM volumetric concentration in dry gas at standard conditions and at the reference oxygen content	mg/m^3
m	Mass of the PM collected on the filter	g
V_{ref}	Volume of the flue gas under standard conditions	m^3
T_{ref}	Standard temperature	273,15 K
p_{ref}	Standard pressure	101325 Pa
O_m	Average measured oxygen content	vol. %
O_{ref}	Reference oxygen content	vol. %
Q_B	Chemical (fuel) energy input into the system	J
B	Fuel flow	kg/s
P	Thermal capacity	kW
$\dot{m}_1$	Mass flow of water though the water circuit	kg/s
c_1	Specific heat capacity of water	J/kgK
T_O	Temperature of the incoming cold water	°C
T_I	Temperature of the outgoing cold water	°C
Symbols in Greek alphabet		
η_E	Energy efficiency index	%
η_h	Annual efficiency of heat generator	%
φ_i	Relative humidity	%
λ	Excess air coefficient	-
η_B	Thermal efficiency	%

Abbreviations

AAS	Atomic Absorption Spectrometry
BA	Bottom Ash
FA	Fly ash
CO	Carbon monoxide emission
DIN	Deutsche Institut für Normung (German Institute for Standardisation)
dm	Dry matter
EDS	Electron Dispersive Spectroscopy
e.g.	Exampli gratia (for example)
ELV	Emission Limit Values
EN	European Standard (Europäische Norm)
FTS	Faculty of Technical Sciences
FU	Functional Unit
HEPA	High Efficiency Particulate Air
IC	Ion Chromatography
i.e.	Id est (in other words)
ISO	International Organization for Standardization
IUE	Institute for Environmental Technology and Energy Economy (Institut für Umwelttechnik und Energiewirtschaft)
KAO	Kaolin
LCA	Life Cycle Assessment
MgO	Magnesium oxide
NO_x	Nitrogen oxide emissions
OGC	Organic Gaseous Carbon
PM	Particulate matter
PM10	Particulate matter with aerodynamic diameter <10 µm
PM2.5	Particulate matter with aerodynamic diameter <2.5 µm

ppm	Parts per million
PM	Total particulate matter emission
SEM	Scanning Electron Microscopy
TUHH	Technische Universität Hamburg – Hamburg University of Technology
Vol.%	Volumetric share in percentage
XRD	X-Ray Diffraction

1 Summary

Main objective of the proposed project is to investigate possibilities to reduce negative environmental impact when using corn cobs as a fuel for combustion in common small facilities to generate heat energy for households in Serbia.

The work tasks are summarized in three possible pathways. Scenario I investigates corn cob combustion in heating facility in traditional way after the collection from farm storage. Scenario II includes additional step of corn cob crushing prior to combustion in automated heating facility. Scenario III includes, besides grinding as initial fuel processing step, densification through pelletizing prior to combustion in automated heating facility. Additives and fuel blending are applied with the aim to improve pellet properties. Combustion experiments took place in selected manual and automated units, during which emissions of CO, NOx, organic gaseous carbons (OGC)), particulate matter (PM) were monitored, as well as energy efficiency and thermal capacity. After initial measurements appropriate primary measures for emission reduction and for the improvement of energy efficiency are suggested and implemented, followed by repeated combustion trails and measurement of emissions and efficiency. Assessment of environmental aspects is performed through energy and greenhouse gas balances, whereas profitability assessment through software BiomasaPro and selected economic parameters. Two experimental setups were constructed in Serbia (in Mladenovac - Termoplin, and in Kula - Terming) and one in Hamburg (TUH).

According to the results from combustion trials project goals of emission reduction were partially achieved. The reduction of PM emissions remains an open question. After combustion chamber modifications in all tested units in Serbia (two automatic and one manual boiler) CO emissions were reduced and mostly in line with emission limit values from EN 303-5, whereas PM emissions were usually higher than emission limit values. Combustion experiments at the Hamburg University of Technology (TUH) with one automatic boiler and one pellet oven have shown that blending of corn cob pellets with wood pellets has an effect on emission reduction but not enough to meet the emission limit values. In blends where minor shares of corn cob pellets are present (up to 25 wt. % corn cobs) CO emissions were in accordance with EN 303-5 class 5 (< 500 mg/m^3), whereas PM emissions were higher than standard requirements. CO and PM emissions from corn cob grit combustion could not meet the emission limit values, even with additives. According to the results from combustion experiments with the pellet oven, additivation of corn cob pellets with kaolin prior to pelletization can reduce both CO and PM emissions, but not enough to meet PM standard requirements. All three scenarios achieved high values of energy indicators, showing that the values of total energy input are low and that it is possible to increase transport distances or apply fuel preparation. All three scenarios met the sustainability criteria. Investing in the construction of heat generators is economically viable for all options. In the case of reconstruction, scenario with whole cobs is mostly viable, whereas other two pathways are not.

Low-cost primary measures are effective up to a certain point. CO emissions have been reduced in most cases and are in accordance with emission limit values. Due to the fact that the sole use of corn cob pellets in automatically-fed small-scale units results in increased PM emissions which do not meet the emission limit values, energetic utilization of corn cob pellets in small-scale automatically-fed units in an environmentally acceptable is possible only in certain fuel blends. It could be recommended to blend agro pellets with higher quality wood pellets and to further investigate the application of kaolin. In case of whole and crushed cob combustion, it is possible that the achievement of such ambitious goals is attainable only in large units with flue gas treatment.

2 Background and aim

2.1 Background

Natasa Dragutinovic, Isabel Höfer, Djordje Djatkov, Milan Martinov, Martin Kaltschmitt

The problem of deteriorating air quality in Serbia, specifically air pollution resulting from the emission of particulate matter (PM) and sulphur dioxide (SO_2) is becoming more serious year by year and a cheap and easy to implement solution is urgently needed. During the winter 2019 / 20 most of urban settlements in Serbia in particular and in the Balkan region in general were dealing with the severe problem of poor air quality, to a certain part due to (increased) air-born pollutant emissions from stationary combustion sources. These emissions can be traced back to large lignite-powered power plants (without an adequate de-sulfurization treatment) and a large number of small-scale emitters. This is in line with the Serbian Environmental Protection Agency (Figure 2.1) stating that the biggest overall source of particulate matter (PM) emissions are stationary sources like e.g. district heating and single-unit combustion appliances below 50 MW.

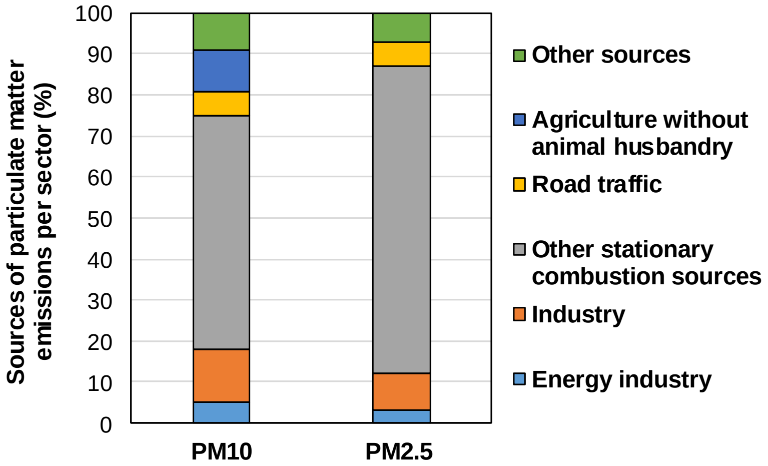


Figure 2.1 Main sources of particulate matter emissions in Serbia in 2019 (adapted from (Knezevic et al. 2019))

The number of installed solid fuel combustion units have been increasing dramatically in recent years (Figure 2.2). Since 2005, when the first pellet units have been manufactured in Serbia, interest towards the use of wood pellets in burners, boiler, and furnaces has been growing. According to (Glavonjic et al. 2017) the production of pellet units increased by 60 % between 2013 and 2015 with the consequence that the market share of pellet units grow from 5 % in 2013 to 7 % in 2015. This trend is expected to continue in the years to come, which would most certainly result in increased particulate matter (PM) emissions at least from wood fired combustion devices.

The production of wood pellets combustion units in Serbia is mostly realized by medium and large-scale manufacturer (Figure 2.3). Some of them focus on the delivery to international markets (EU and non-EU countries) and for design modernization (e.g., pellet burners for boiler reconstruction). Micro-companies mainly concentrate on the manufacturing of kitchen stoves and household appliances. These units for solid fuels are primarily used for cooking purpose and secondarily for room (space) heating. Efficiencies of kitchen stoves range between 60 and 90 %, whereas pellet boilers show efficiencies above 90 % in some cases.

Previous studies on Serbian heating units (Huelsmann und Kaltschmitt 2015) have shown that these devices are related to technological characteristic values clearly less promising compared to devices available within the EU due to the valid environmental legislation. These design drawbacks become especially evident in the case of the combustion of crop residues due to the problematic fuel properties of these types of solid biomass. Such less promising fuel properties compared to e.g. wood fuel become noticeable within the higher ash content, the higher alkali, S, and Cl contents, the lower ash-melting temperatures etc.

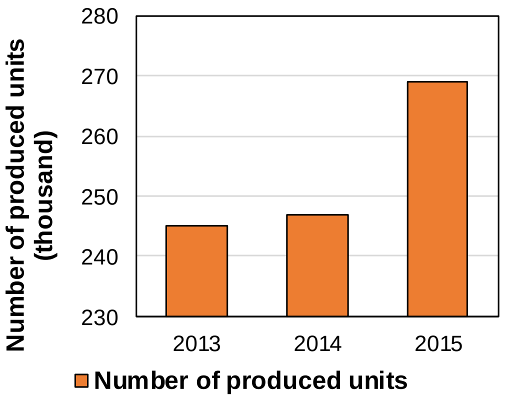


Figure 2.2 Development of the biomass combustion unit production sector in Serbia (adapted from (Glavonjic et al. 2017))

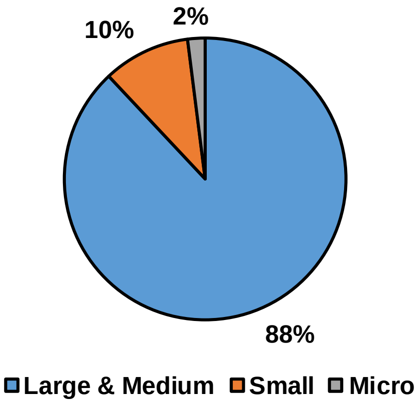


Figure 2.3 Share / distribution of production of combustion units in Serbia between large, small, and micro-sized manufacturers in 2015 (adapted from (Glavonjic et al. 2017))

An overview of Serbian, EU, and German legislative regarding emission limit values (ELV) is given in Table 1.1.

Table 2.1 Selected emission limit values (ELV) relevant for automatic small-scale combustion units for biomass

	EN 303-5						BImSchV	RS Regulation 2016		TA Luft
Conditions	0 °C 10 % O_2 1013 mbar						0 °C 1013 mbar 13 % O_2	0 °C 1013 mbar 13 % O_2		11 % O_2
Fuel	Manually-fed unit Biogenic fuel			Automatic units			Straw	Firewood / wood pellets	Wood Briquettes / pellets	cereals, grasses, miscanthus
Capacity	≤ 50 kW						≥4 ≤ 1000 kW	≥4 kW		≤ 1 MW
Class	3	4	5	3	4	5	-	old	new	-
	mg/m³			mg/m³			mg/m³	mg/m³		mg/m³
CO	5,000	1,200	700	3,000	1,000	500	400	4,000	800	250
PM	150	75	60	150	60	40	20	150	60	50
OGC	150	50	30	100	30	20				
NO_x	-	-	-	-	-	-	(inst. Ab 31.12.2014) 500	-	-	500
Efficiency*	0.75	0.83	0.89	0.75	0.83	0.89				

*calculated according to EN 303-5 for 25 kW nominal capacity

Emission limit values (ELVs) from EN 303-5 class 3 being the strictest requirement from this standard is similar / in accordance with German regulation on emissions from newly installed small-scale combustion devices. Compared to that, Serbian regulation for emissions from small-scale newly installed combustion unit issues limit values is closer to class 4 from EN

303-5, and less strict than German BImSchV, especially regarding particulate matter (PM) emission limit values.

Combustion devices characterized by an insufficient environmental performance and a very low efficiency can be improved typically through the implementation of a better design and control system. Such a development can be stimulated by the introduction of regulations that set clear requirements for testing procedures as well as emission limit values (ELV) for various pollutants emitted by these devices. In this respect an important approach can be to harmonize the technological differences between available devices on the Serbian and the EU-market (Glavonjic et al. 2017). It is also necessary to support the development of critical infrastructure, such as accredited national laboratories and quality testing systems for devices in accordance with standards.

In order to resolve issues mentioned above, more sophisticated combustion technology and fuel-upgrading measures should be applied. However, this causes additional operating and investment costs, mostly unaffordable for the average user of solid biofuels in Serbia, which could typically only invest in cheap technical solutions. Therefore, the motivation for this report is to identify and develop low-cost solutions for an environmentally friendly utilization of corn cobs as a solid fuel in small-scale combustion devices. A possibility to improve the fuel properties of corn cobs is by applying primary fuel-upgrading measures (e.g., fuel processing – pelletization, use of additives).

Against this background, the main objective of this report is to investigate possibilities to reduce negative environmental impact when using corn cobs as a fuel for combustion in commonly used small scale combustion facilities used for the provision of heat for households in rural Serbia. Further objective is to develop necessary procedures to mobilize and increase utilization of this type of fuel in a sustainable way, which subsume more efficient, but low-cost solutions for storage, processing, packaging, transport, manipulation and combustion as well.

2.2 Project aim and description

Natasa Dragutinovic, Isabel Höfer, Djordje Djatkov, Milan Martinov, Martin Kaltschmitt

The overall project being behind this report is divided into two project phases: first one taking up a majority of resources and lasting for 18 months, and the second one lasting for additional 6 months.

In the first project phase, based on the overarching goal of minimizing negative environmental impacts from the energetic use of corn cobs as a solid fuel in small scale combustion devices, several possible pathways are analyzed. Figure 2.4 presents the three options to be investigated within this project.

The first option subsumes storage of corn cobs at the farm premises and a subsequent combustion in the traditional way for heating of own residential rooms. Corn cobs are not processed, but stored in hovel prior to combustion. The used combustion facility shows a simple design with manual stoking and no automatic control of the overall combustion process. This will be the reference scenario and results obtained for other scenarios will be compared with it, in order to determine if certain measures allow for the reduction of an environmental impact.

The second option presents an improved approach and includes fuel processing through size reduction (crushing) to enable an automatic feeding of the fuel into the combustion device. This option subsumes cases when corn cobs are (1) either utilized for own needs within the same farm, or (2) traded within the same rural community. If such a fuel is planned to be delivered to another biomass user, packaging, transport and storage prior to utilization need to be considered. The respective combustion facility is equipped with a “classical” excess air ratio control.

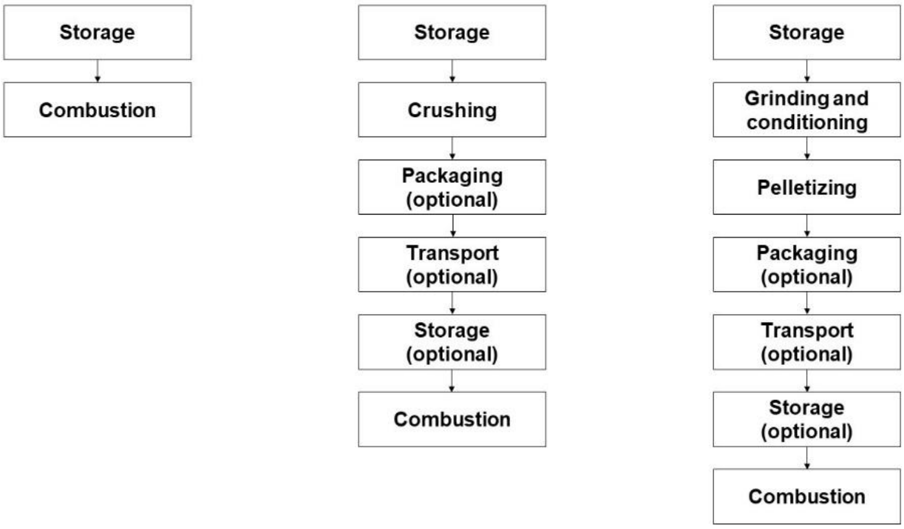


Figure 2.4 Investigated options of corn cobs processing and utilization

The third option is similar to the second one, but the fuel processing includes corn cob grinding and pelletizing. Since bulk density of the fuel is significantly increased due to such a mechanical treatment, this option enables shipping the fuel via to longer distances by taken economic constraints into consideration and the utilization of these fuel pellets by biomass users in other municipalities, regions, etc. However, this form of corn cobs as a fuel could be used on site or within the same community, if the goal is to reduce environmental impact. This could be achieved if the combustion properties are improved, e.g. by blending with wood or admixing with slagging inhibitors, such as mineral additives.

Based on the main project goals and the three options discussed above, the specific goals are proposed and discussed below.

- The first specific goal is to investigate fuel crushing and processing. For this purpose, the crushing procedure for corn cobs using crushers available in rural communities is tested. Appropriate manipulation and stoking of corn cobs should be enabled. Particle size distribution analysis should be performed as well. With this aim, samples of corn cobs are to be collected from representative farms using standard sampling procedures. The processing of the samples should be in accordance with the various options. Within this project goal, all potential costs and incomes / savings, that are consequence of investment and operation of a heating facility that uses corn cobs as a fuel, are collected.
- The second goal is to investigate the emissions and efficiency of using corn cobs as a solid biofuel in small-scale heat generators. Two types of market-available combustion devices are selected for further investigation: first corresponding to the traditional way of corn cobs combustion (e.g., cooking ovens and stoves), whereas second should allow for automation process and control of the combustion and to use both fuel forms (crushed and pelletized). During the combustion, emissions and parameters relevant for energy-efficiency calculation are measured in line with limits and guidelines defined within the EN 303-5. If the obtained results should belong to any of the three classes defined within the EN 303-5, the examined heating facilities are declared as acceptable. After conducting the combustion trials, deficiencies of tested heat generators that cause technical problems and negative environmental impacts are evaluated. The heating facilities are subsequently qualitatively and quantitatively assessed with regard to whether certain fuel processing measures or heating facility adaption measures contribute to the reduction of the environmental impact.

Appropriate measures are defined and suggested to industrial partners to alter the constructional and operational concept of their combustion devices.

- The third goal is the analysis of the environmental burden, conducted through Life Cycle Assessment (LCA) method by a development of representative models of the defined options. These models should include the entire life cycle of corn cobs as a solid fuel, by involving: transport, manipulation, storage, processing, combustion, etc. These options are analyzed with respect to environmental impact related to climate change (i.e. GHG emissions). Such a LCA analysis give an insight whether certain measures cause increased environmental impact, possibly due to additional energy inputs (direct) or material consumption (indirect). These results should be the basis to suggest which of the investigated options has the least negative influence to the environment.
- The fourth and final goal is it to assess the profitability of investment in heating facilities using corn cobs as a solid biofuel to be conducted by the application of the calculator and decision-making tool named BiomasaPro (Martinov et al. 2011). The calculator is designed to be used by potential biomass users.

In the second phase of the project, the planned scope is extended to include combustion of processed corn cobs in the form of pellets within an 8 kW pellet oven. This includes also the measurement of the resulting emissions, including online measurement of the particulate matter related to mass and number size distribution, as well as detailed subsequent laboratory analysis of the solid combustion residues. This extended analysis should give a better insight into the effect of selected fuel-related primary measures for the particulate matter (PM) mitigation in small-scale units when using crop residues as fuels.

The heating facilities are subsequently qualitatively and quantitatively assessed with regard to whether certain fuel processing measures or heating facility adaption measures contribute to reduction of the environmental impact.

3 Fuel processing

Fuel processing encompasses four tasks:

- Testing of corn cob crusher,
- Collection and processing of corn cobs,
- Selection and adaptation of heat generators, and finally
- Inventory of economic parameters.

These various tasks are presented in separate sub-chapters, each describing applied method, followed by results and discussion. Certain tasks are performed at two locations: (1) Serbia and (2) Germany. The results for these sub-packages are categorized according the location of the experimental setup.

3.1 Testing of corn cob crusher

Djordje Djatkov, Milan Martinov

3.1.1 Methodology

For this experiment, the forms B and C according to Figure 3.1 were used. The production of grits is only the final phase of comminuting as a final preparatory step for pelletization. Crushed form used as a fuel, means partial reduction of length, whereby, its length should be same as diameter or about 1.5 of diameter.

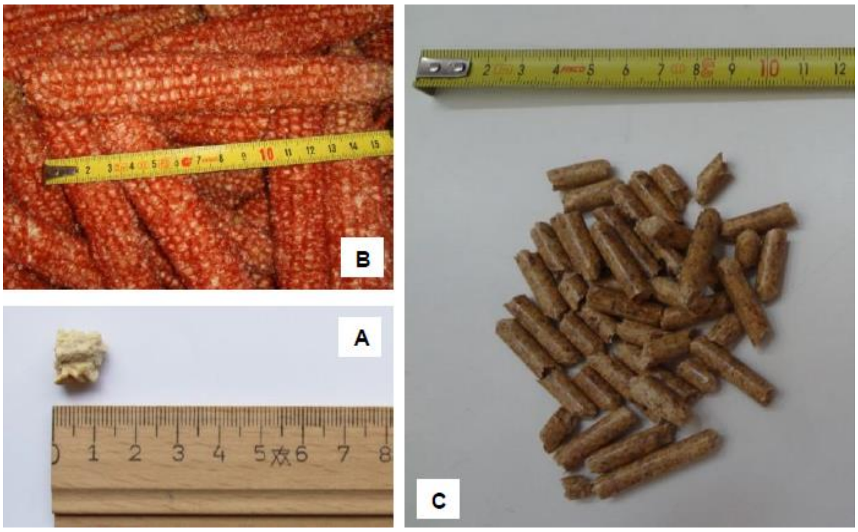


Figure 3.1 Different product formats and sizes A: cobs grits; B: loose cobs; C: pellets

Figure 2.2 presents the schematic of the used crusher and Figure 2.3 shows the preparatory steps for the crushing process (left) and crushed corn cobs (right).

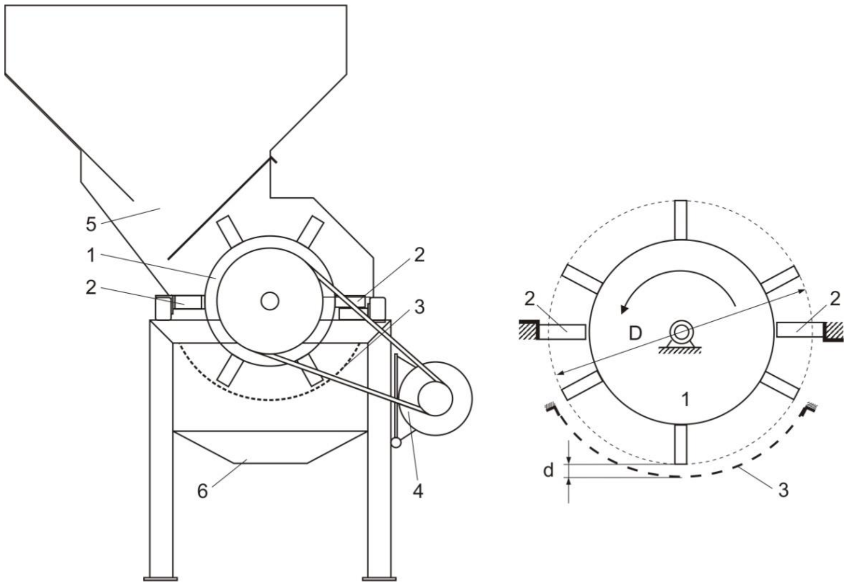


Figure 3.2 Scheme of corn cobs crusher: 1 – drum with six lines of spirally situated knives, 2 – stationary comb like knives, 3 – screen, 4 – belt drive, 5 – inlet hopper with dozing slider, 6 – outlet hopper

Particle size distribution of crushed material was performed using laboratory sieves. Screens' mashes from 0.63 to 40 mm were used with a mash step ratio R5 (fifth root of ten, ≈ 1.6). For the openings up to 6.3 mm woven cloth screens in accordance with DIN 4185, part 1, were used. Sieves diameter were 200 mm. For openings 10, 16, 25, and 40, perforated plates, in accordance with DIN 4185, part 2, were used, and sieve diameter were 400 mm. Longer particles were measured manually and selected into two groups: 40 to 63 mm and longer. For the particle length group up to 6.3 mm, as a representative value were taken middle of neighboring mash dimension. For further groups a manual measuring of particle sizes was performed, the median has been calculated and used as a representative value of the group. Samples were of minimum 4 L, in accordance with DIN CEN/TS 15149-1, and balance accuracy 0.1 g.

3.1.2 Results

Results are presented in the diagram for log-normal distribution (Figure 2.4), according to DIN 66144, and for particle size distribution used method of calculation and presentation defined by (Batel 1971).

Figure 3.3 Preparation for testing (left) and examples of crushed cobs (right)

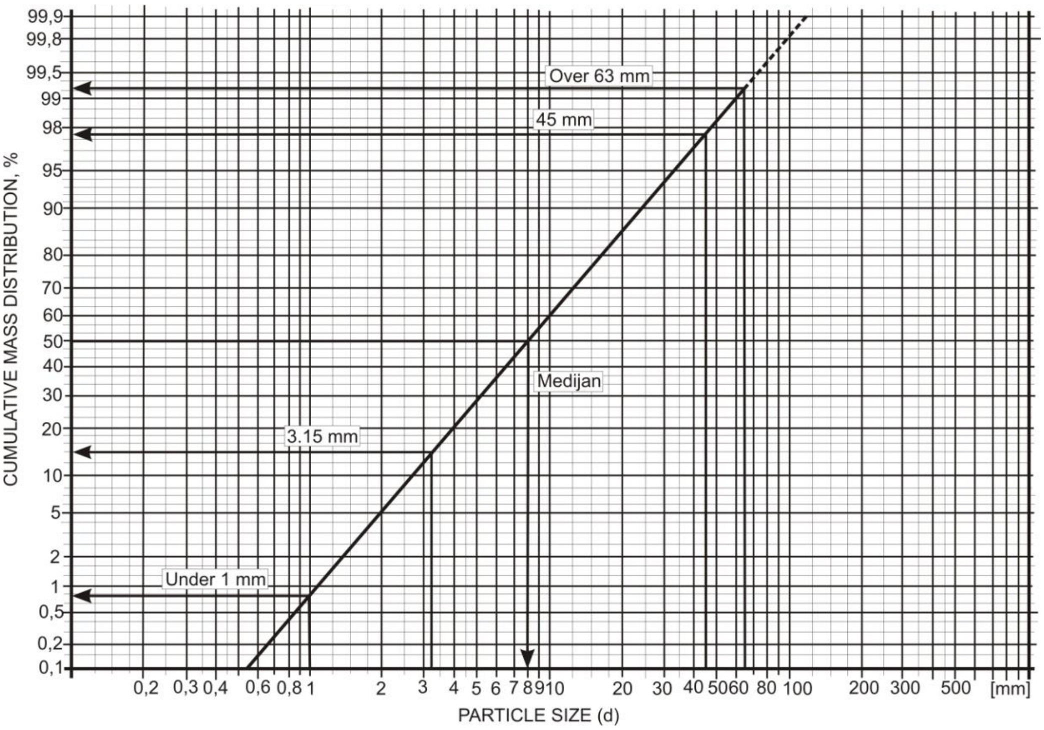


Figure 3.4 Example of particle size distribution, test No. 15

Selected results of the crushing tests are presented in Table 3.1, whereas an overview of the corn cob properties before and after crushing is given in Table 3.2.

Table 3.1 Results of crushing test (selected some of total 19)

No.	Drum PTO, min^{-1}	Distance to knives d, mm	Second stationary knifes	Share, % 3.15-45 mm	< 1 mm	> 63 mm	Median, mm	Coefficient of correlation
4	520	20	yes	85	0.8	0.5	7.5	0.89
8	520	30	yes	84	0.7	0.8	8.0	0.87
15	420	20	no	84	0.8	0.8	8.0	0.89
19	520	40	no	86	0.5	3.0	11.0	0.83

Obtained particle size distribution of crushed maize cobs fully corresponds to size classes of wood chips P45 and G50, in accordance with DIN CEN/TS 14961 and ÖNORM M 7133, respectively.

Table 3.2 Measured dimensions before crushing and bulk density of maize cobs

	Cobs' dimensions, mm	
	Median	SD
Length	186.2	20.8
Max. diameter	27.1	1.6
Length middle point diameter	25.2	1.1
	Bulk density, kg m^{-3}	
	Median	SD
Non crushed	104	8.9
Crushed	227	14.2

3.2 Collection and processing of corn cob samples

Processing of corn cobs was performed at two locations: (1) Serbia and (2) Germany. Methods and results are categorized according to the locations and project partner performing the respective tasks.

3.2.1 Location 1 (Serbia)

Djordje Djatkov, Milan Martinov

Corn cob pellets for the combustion trials were procured in ready-to-use form from one of the biggest manufacturer of pellets in Vojvodina, located in Stari Slankamen. For the collection and transport of pellets a special, big volume trailer was used Figure 3.5.

Figure 3.5 Trailer for the collection and transport of corn cobs for pelletizing

Figure 3.6 Pelletizing of corn cobs in Serbia

As Figure 3.6illustrates, crushing, milling and separation of dust were performed as preparatory steps for pelletizing. Cooling and additional removal of dust fraction through sieving are performed after pelletization.

Corn cob pellets were collected (purchased) in their processed form from the manufacturer.

3.2.2 Location 2 (Germany)

Natasa Dragutinovic, Isabel Höfer, Martin Kaltschmitt

3.2.2.1 Methodology

Ground corn cob feedstock (3-5 mm particle size) was procured from a German company dealing in manufacture, collection, process, and trading of biomass. From this feedstock, further processing of corn cobs was investigated through pelletizing of corn cob grinds:

1. In their pure form,
2. With additives (kaolin and magnesium oxide (MgO)),
3. With additives (kaolin and magnesium oxide (MgO)), and starch as a binder.

During pelletizing mineral additives can be easily added to the feedstock. Additives such as kaolin and magnesium oxide are used to mitigate particulate matter generation and ash melting behaviour (Kaltschmitt et al. 2016), (Schmitt), (Steenari und Lindqvist 1998). Alumina-silicate-based additives such as kaolin have been proven to contribute to the reduction of particulate matter (PM) emissions from the combustion of woody biomass (Huelsmann et al. 2019), (Höfer und Kaltschmitt 2017), (Gollmer et al. 2019) as well as to improve problematic ash melting behavior and minimize other ash-associated problems during combustion such as ash deposition, fouling and corrosion (Steenari und Lindqvist 1998).

The effect of mineral additives on the selected physico-mechanical properties and ash melting behaviour of corn cobs pellets, which in turn affect fines content of the pellets and consequently fine PM formation and emissions were investigated experimentally and statistically.

Pelletizing was conducted in two series of experiments with full factorial design. In both series, a full factorial design with three two-level factors was prepared using commercially available software. In the first series the moisture content (18 to 20 wt. %), the additive type (kaolin-MgO), and the additive content (0 to 2 wt. %) were varied. Within the second series, the starch content (used as a binder) (2 to 4 wt. %), the additive type (kaolin-MgO), and the additive content (0 to 2 wt. %) were used.

After the production each pellet batch was left to cool down overnight and stored. Pellets have been sampled from the produced batch and the physical-mechanical properties (according to ISO 17225-6: mechanical durability, bulk density, ash content, moisture content, and higher heating value) have been assessed with the methods shown in Table 3.3.

Table 3.3 Overview of material analysis methods

Property/Process	Method/standard	Corn cob grind	Corn cob pellets
Sampling	EN 14778	X	X
Sample preparation	DIN EN ISO 14780	X	
Elemental composition	DIN EN 15104, DIN EN 15290	X	
Particle size distribution	mesh sizes: 6.3 – 4.0 – 2.0 – 1.0 mm DIN EN ISO 17827-2	X	
Moisture content	ISO 18134-2	X	X
Ash content	ISO 18122	X	X
Bulk density	ISO 17828	X	X
Mechanical durability	ISO 17831-1		X
Higher heating value	Bomb calorimeter, isoperibolic IKA		X

In order to statistically evaluate the influence of independent variables (factors) on the mechanical durability and bulk density of pellets (responses) experimental series were evaluated comprehensively with a commercially available software (SPSS Software | IBM 2020). Where assumption for parametric tests were met (normal distribution of residuals, equality of variance and no outliers), regression analysis was used (i.e., analysis of variance (ANOVA)). Mathematical models used during this regression describe the main effect and interaction of independent variables (input parameters) on the output variables (response variables), using linear equations (for main effects) and higher-order equations for interaction effects (quadratic, cubic etc.). In certain cases, after the transformation of input data the normal distribution of residuals was met and appropriate parametric tests were performed.

In such a regression analysis (and ANOVA) linear or higher-order mathematical functions (quadratic, cubic etc.) are used to describe the main influences of the input (parameter) on the output variables (responses), as well as their interactions (quadratic model and higher). Quality of fit of the proposed model has been estimated based on F-values and associated p-values of the overall model and individual model terms. Lack of fit tests (F-value) compares pure error with the residual error. Significant difference tests were performed at α-value of 0.05 with a confidence level being 95 %. If probability p is below α, null-hypothesis is rejected and there is strong evidence that the alternative hypothesis is true. Then the effect of the parameter is deemed statistically significant. The determination coefficient R^2 is used to evaluate the acceptability of the investigated model: the model is generally regarded as adequate if $R^2 > 0.95$.

If ANOVA assumptions are not meet in case of three parameters full-factorial design, non-parametric tests were applied. In this case the requirements of non-parametric tests (Welch ANOVA, Mann-Whitney U test, Kruskal-Wallis) were tested and, where appropriate, these tests were applied (Field 2018). Non-parametric tests do not assume that the data come from a distribution that can be fully described by two parameters, such as mean and standard deviation (in normal distribution). In most non-parametric tests, data are ranked. That means that response values are converted to their ranks in the overall data set.

Welch ANOVA is an alternative to classic ANOVA. This approach does not require the assumption of homogeneity of variances. But normally distributed data are needed.

Man-Whitney U-test is the non-parametric equivalent to parametric two sample t-test, and does not require normal distribution of residuals.

Kruskal-Wallis H-test is the non-parametric equivalent to one-way analysis of variance (ANOVA), also called ANOVA on ranks. This method compares the equality of medians for two or more independent samples of each or different sample sizes, also not requiring normal distribution of residuals.

3.2.2.2 Results

Experimental findings can be summarized as follows:

- Pellet properties such as moisture content, ash content, heating value, N-, and S-content from both experimental series are in accordance with threshold values given by the respective non-wood pellet standard ISO 17225-6.
- Without binder, only pellets with MgO can reach the durability threshold limit and only in certain cases. This is possibly due to thermal stability and uniform heat distribution within the biomass pellet during pelletizing of MgO-additivized feedstock, originating from high heat-conducting capacity of MgO and resulting in the formation of solid bridges in pellets through lignin glass transition.
- After the addition of a binding agent, the mean value of all additivized corn cobs pellets with low amounts of starch (< 4 wt. %) can reach durability requirements of the respective ISO fuel standard for non-wood pellets, damping the effect of powdery inert material such as additive on the fuel mechanical properties.
- The bulk density threshold limit was reached without exceptions in both experimental series. Values of bulk density from all produced pellets (with and without additive, with and without binder) are in accordance with the threshold values of the respective ISO standard (> 600 kg/m^3).

- Bulk density is negatively influenced by starch as a binding agent.

Results from statistical analysis can be summarized as follows:

- Mechanical durability is significantly affected by the type of added additive (to support an environmentally sound combustion) and the amount and type of the added binding agent.
- Type of additive affects mechanical durability of corn cob pellets; without the binder only corn cob pellets with MgO as additive could reach the mechanical durability requirements (and only in certain cases).
- Moreover, there is a statistically non-significant but observable interaction between additive type and additive content.

Thus, the quality of agro pellets can be in line with the requirements of respective ISO fuel standard even when mineral, powdery materials (e.g. an additive) are applied. This requires the addition of a binding agent to improve the durability of the produced pellets.

The results from this work package will be included in an original research paper.

3.3 Selection and adaption of heat generators

Similar to the previous chapter, the selection of heat generators used in combustion trials was performed at two locations. Methods and results are organized according to the location and the project partner responsible for combustion trials at the location.

3.3.1 Location 1 (Serbia)

Djordje Djatkov, Milan Martinov

3.3.1.1 Methodology

Combustion units were selected taking into consideration the three investigated options (described in chapter 2.2). A heat generator with manual fuel-feeding has been chosen to investigate option I and II with unprocessed and crushed corn cobs, whereas a modern combustion unit with automated-fuel feeding was selected to investigate option III.

3.3.1.2 Results

Three typical boilers for biomass have been selected to be tested:

- **Termoplin**. From the manufacturer Termoplin an underfeed boiler, developed for wood chips, fruit pits (bones), but also tested with crushed corn cobs was investigated. Type TK-25 with a nominal thermal power of 29 kW (Figure 3.7) has been selected. This one is also suitable for the combustion of pellets.
- **Terming**. From this manufacturer two boilers have been tested: Ozon 25 (Figure 3.8) with a nominal thermal power 25 kW, aimed for agro pellets, and a low-cost, batch boiler (TIG-P) aimed for combustion of whole cobs (Figure 3.9).

Performed adaptations for both are presented in chapter 3.

Figure 3.7 TK-25 with nominal capacity 29 kW

Figure 3.8 Terming Ozone agro with automated fuel-feeding

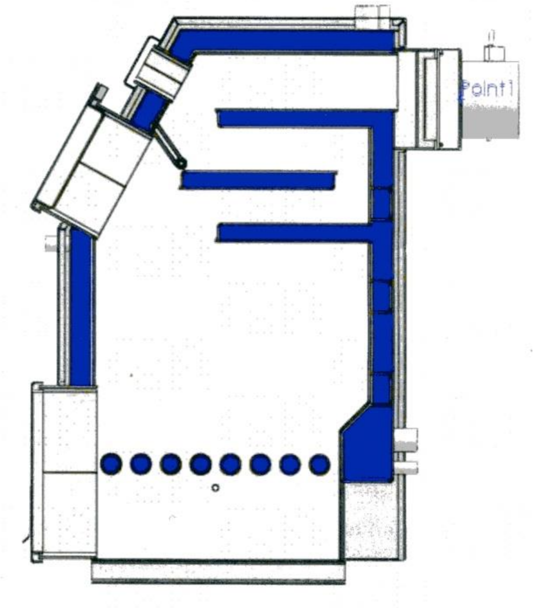


Figure 3.9 Terming TIG-P with manual fuel-feeding

Figure 3.10 Pelletoven Austroflamm Polly 2.0

3.3.2 Location 2 (Germany)

Natasa Dragutinovic, Isabel Höfer

3.3.2.1 Methodology

For the investigation of option III with pelletized corn cobs two modern combustion units with automated fuel-feeding were selected, with the aim to compare the state-of-the-art combustion units, subsequently efficiencies and emissions in Serbian and German conditions.

3.3.2.2 Results

TUHH selected the following combustion plants:

- **Terming**. The boiler of the Serbian manufacturer "Terming Kula" was selected as a suitable small-scale biomass boiler for the combustion of corn cob pellets (Figure 3.8). The same appliance tested also by the Faculty of Technical Sciences. The combustion device "Ozone agro" has 25 kW nominal heat capacity. This oven can operate with minimum of 30 % partial load and is a "multi-fuel boiler" (i.e., it can use different types of biomass as fuel, including agro pellets). The system is also equipped with a moving grate, an automatic fuel supply (with three speeds), and an air supply in two stages. This moving grate facilitates the use of fuels with a higher ash content, such as agro pellets, and at the same time prevents sintering of the grate ash. This plant was chosen on the basis of the moving grate, the favorable price and the already performed and successfully completed preliminary tests in Serbia. The furnace is a representative example of small-scale biomass plants in Serbia.
- **Austroflamm**. The boiler "Polly 2.0" from the company Austroflamm is an automated single-room combustion plant (Figure 3.10). This pellet stove has a tilting grate. Therefore, it is expected that the stove will also be able to use agro-pellets with a higher ash content.

3.4 Inventory of economic parameters

Djordje Djatkov, Milan Martinov

3.4.1.1 Methodology

The necessary data for the economic estimation calculations are given in Table 3.4.

Table 3.4 Properties and purchase prices of assessed fuels

Fuel	Natural gas	Coal	Wood logs	Wood chips	Wood pellets	Whole CC	Crushed CC	CC pellets
MC, % (*w.b.*)	–	24.0	20.0	20.0	8.0	7.5	7.5	8.9
LHV, MJ kg^{-1}	9.3^{a}	4.6	4.0	4.0	4.7	4.4	4.4	4.3
Purchase price, € t^{-1}	30.2^{b}	115	105	75	180	30	100	140

CC: corn cobs; MC: Moisture content; w.b.: wet based; LHV: Lower heating value; ^{a}kWh Sm^{-3}; ^{b}€c Sm^{-3}.

The overview of parameters used for the calculations is given in Table 3.5.

Table 3.5 Technical data, investment and operating costs of assessed heating appliances

Appliance	Base-case option	TIG-P	TK-25	Ozon 25
Power, kW	24	30	29	25
Stoking	A	M	A	A
Fuel	Natural gas	Whole CC	Crushed CC	CC pellets
Annual efficiency, %	90	55^{a,b}	60	90^{d}
Lifespan, a	20	12^{a,b}	12^{c}	15^{d}
Investment cost, €	550	680	2,100	2,580
Transport cost, €	0	0	121	0
Installation/testing, €	200	150	200	150
Maintenance, €	20	50^{b}	50	50
Material costs, €	20	50	50	100^{d}

A: automatic; M: manual; CC: Corn cobs; ^{a}Coal: 60%, 10 a; ^{b}Wood logs: 50%, 15 a, 0 €; ^{c}Wood chips: 15 a; ^{d}Wood pellets: 92%, 18 a, 50 €.

3.4.1.2 Results

The obtained economic performances are presented in the Table 3.6.

Table 3.6 Profitability assessment

Whole corn cobs		NPV$_1$ – NPV$_2$, €	Viable
CC	W logs	–8,707	YES
CC	Coal	–6,978	YES
CC	NG	–4,105	YES
CC+HA	NG	–4,751	YES

Crushed corn cobs		$NPV_1 – NPV_2$, €	Viable
CC	NG	4,714	NO
CC	W chips	1,625	NO
Corn cob pellets		$NPV_1 – NPV_2$, €	Viable
CC	NG	5,666	NO
CC	W pellets	315	NO

NPV: Net present value; HA: Heat accumulator; CC: Corn cobs; W: Wood; NG: Natural gas.

Detailed inventory of economic performances is presented within the paper titled “*Profitability of corn cob utilization as a fuel in small residential heating appliances*” to be found in the Appendix A of this report.

The obtained results are on the lower level for the use of corn cobs. This is mainly due to the relatively low price of natural gas and firewood.

4 Measurement of emissions and technical assessment – Location 1 (Serbia)

Djordje Djatkov, Milan Martinov

Combustion trials make up the core of the project and include measurement of selected airborne emissions, as well as testing of the proposed measures for the reduction of negative environmental impact from the combustion of corn cob.

Results are organized according to the location and project partner performing the tasks. Tasks are performed at two locations by the project partners (1) in Serbia by Faculty of Technical Sciences and Termoplin (in Kula and Mladenovac) and (2) in Germany by Hamburg University of Technology (in Hamburg). Description of methods and experimental setups are presented in two chapters (chapter 0 and chapter 0), according to the location and project partner performing the tasks.

In this chapter the experimental trials performed by the Faculty of Technical Sciences with industrial project partner Termoplin will be explained. Therefore, the experimental setup and methodology is described in the first, followed by the results from the combustion experiments. Faculty of Technical Sciences conducted experiments at two locations, first being in Mladenovac, at the location of Termoplin company, and the second one in Kula, at the location of the company Terming ATI.

4.1 Methodology and Experimental setup

Faculty of Technical Sciences used renewed existing measuring equipment as well as newly acquired appliances. Gas analyzer TESTO 350 S was renewed (electricity supply system and measuring cells for NO_x (nitrogen oxide)) was used for gaseous pollutant emission monitoring (Figure 4.1).

Furthermore, the device TESTO 380 with measuring sensors for PM, CO, O_2, temperature and pressure and draught of the flue gas was used (Figure 4.2). The core part of the TESTO 380 is the emission analyzer TESTO 330-2 LL. In connection with the TESTO 380, the simultaneous measurement of particulate matter (PM) is possible.


Figure 4.1 The existing device *TESTO 350 S* for NO_x measurement


Figure 4.2 The newly purchased TESTO 380 for CO, O_2 and PM measurements

Testing stands were planned and defined by project team members of the Faculty of Technical Sciences and constructed by manufacturers: Termoplin (Figure 4.3 and Figure 4.4) and ATI Terming (Figure 4.5 and Figure 4.6). Except the repair and purchase of new devices for measurement of emissions, in both firms (at both locations) new scales for mass measurement and calorimeters (heat meters) used for measurement of generated heat energy and thermal power of the investigated boilers were installed, in order to determine energy efficiency of the boilers and installed power.

Figure 4.3 Testing stand in firm Termoplin, Mladenovac

Figure 4.4 Experimental setup in Termoplin

Figure 4.5 Testing stand in Terming, Kula

Figure 4.6 Experimental setup in Terming, Kula

The testing method was based on following standards (now adapted as national ones, SRPS EN):

- EN 303-5 Heating boilers – Part 5: Heating boilers for solid fuels, hand and automatically stocked, nominal heat output of up to 500 kW – Terminology, requirements, testing and marking.
- CEN/TS 15883 Residential solid fuel burning appliances – Emission test methods.

- EN 13284-1 Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method.
- EN 303 Heating boilers – Test code for heating boilers for atomizing oil burners.

Testing methods are defined in details in these standards, and within the project activities strictly followed.

4.2 Results

In the following text the results from the testing of two different combustion test stands (with "Termoplin" and "Terming") using different combustion appliances will be presented. Combustion tests have been conducted by Faculty of Technical Sciences in cooperation with project partners.

4.2.1 Termoplin

On the location of Termoplin production site boiler unit TK-25 with automatic, under fired fuel-feeding has been tested. This boiler is aimed to be used with different fuels, such as wood chips, wood and agro pellets, fruit pits, as well as granulated materials of various origin. However, as alternative, wood logs can also be used. The last possibility makes the reconstruction of utilization of this boiler complicated, especially for using corn cob pellets, and crushed cobs.

Nominal installed thermal capacity is P_n = 29 kW. In this combustion unit measurement with two fuels, corn cob pellets (moisture content about 9 %) and crushed cobs (length of pieces one to two diameters, moisture content about 8 %) were performed. Schematic presentation of boiler is given in Figure 4.7, and view of combustion test stand in Figure 4.8.

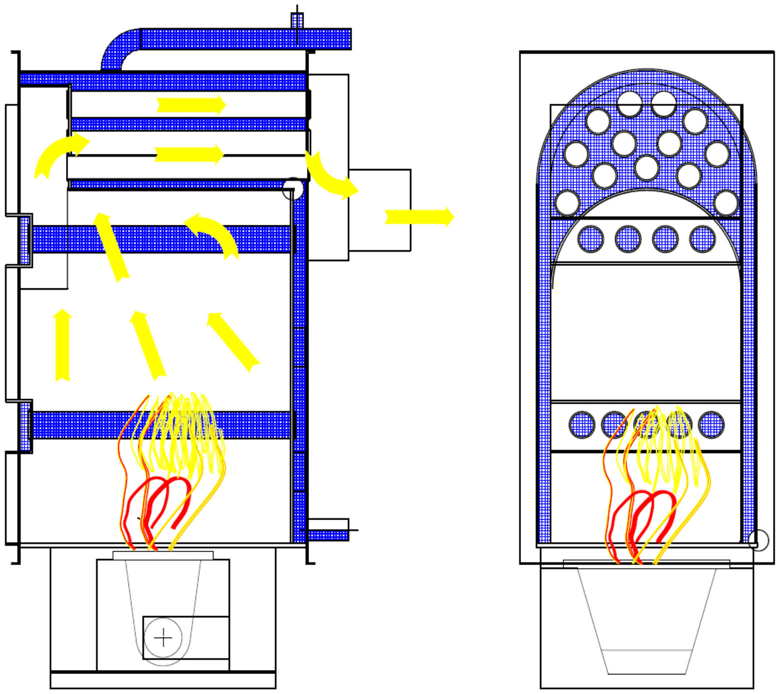


Figure 4.7 Schematic of the boiler TK—25

Figure 4.8 Combustion test stand in Termoplin

Figure 4.9 Exhaust gas ventilator installed in TK-25

Natural drought (vacuum) was used at the beginning and was later replaced with exhaust gas ventilator, as shown in the Figure 4.9. Heat exchanger with an air-heater was installed as a heat sink (thermal energy consumer).

The boiler has single stage combustion, with only primary air. Furthermore, water-cooled tubes, which are part of the heat exchanger, are situated above the lower part of combustion chamber. Their function is also to serve as a grate when using wood logs as a fuel.

The obtained measuring results are as presented in Table 4.1 and Table 4.2 , for two types of fuel forms.

Table 4.1 Emissions from the combustion of corn cob pellets in TK-25

No.	CO	OGC*	PM	*η*
		mg/m^3 for 10 % O_2		%
1	2,683	188	247	71.6
2	2,731	98	272	69.5
3	3,273	76	314	64.5
4	2,964	87	307	66.5
5	2,473	56	308	70.8
6	2,787	26	294	67.3
Average	2,819	89	290	68.4

*OGC – organic gaseous carbon

Table 4.2 Emissions from the combustion of crushed corn cobs in TK-25

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O$_2$			%
1	10,194	1,712	324	50.5
2	11,468	2,300	264	60.1
3	13,679	1,828	347	61.3
4	12,482	2,362	335	58.8
5	15,670	2,095	358	61.4
6	13,160	1,475	392	57.5
Average	12,776	1,962	337	58.3

*OGC – organic gaseous carbon

The emissions of both CO and particulate matter (PM) are several times higher than the emission limit values (ELVs) in the EN 303-5. The obtained results are not meeting given emission limit values, except the emissions of organic gaseous carbon (OGC) when using corn cob pellets as a fuel.

When comparing the emissions from corn cob pellets and crushed corn cobs, it is evident that combustion of pellets results in lower emissions of both CO and particulate matter (PM). CO emissions as well as organic gaseous carbon (OGC) emissions from the combustion of pellets are in line with the class 3 from EN 303-5 (CO < 3,000 mg/m^3 and OGC < 100 mg/m^3). However, even when using pellets, particulate matter (PM) emissions are almost double of the limit value of 150 mg/m^3 for class 3.

In the case of crushed corn cobs, emissions of CO are almost 4 times higher than the CO emission limit value of 3,000 mg/m^3 for class 3, whereas particulate matter (PM) emissions are more similar to those from corn cob pellet combustion. Organic gaseous carbon (OGC) emissions are more than 10-fold higher than allowed values from class 3 (< 100 mg/m^3).

From the above results, it can be estimated that the most efficient measure for CO emission reduction is automatic feeding of fuel, which eliminated the user interference and disruption of combustion process due to loading of the fuel. Regarding particulate matter (PM) emissions, the need for additional improvements (both fuel- and combustion unit-related) become evident.

4.2.1.1.1 Implemented improvements

The main idea was to enable two stage combustion, introducing secondary combustion air in hot zone, enable an improved mixture of flue gases, after primary combustion, and prolong residence time within the hot zone. Therefore above the water tubes half cylindrical fireclay mantel has been situated (Figure 4.10). By frequency control can be adjusted inlet of secondary air, which is heated in the tubes inside of mantel. Thus, it is possible to adjust excess air ratio, also by control of exhaust gases ventilator, whereby share of primary air was between 55 and 60 %.

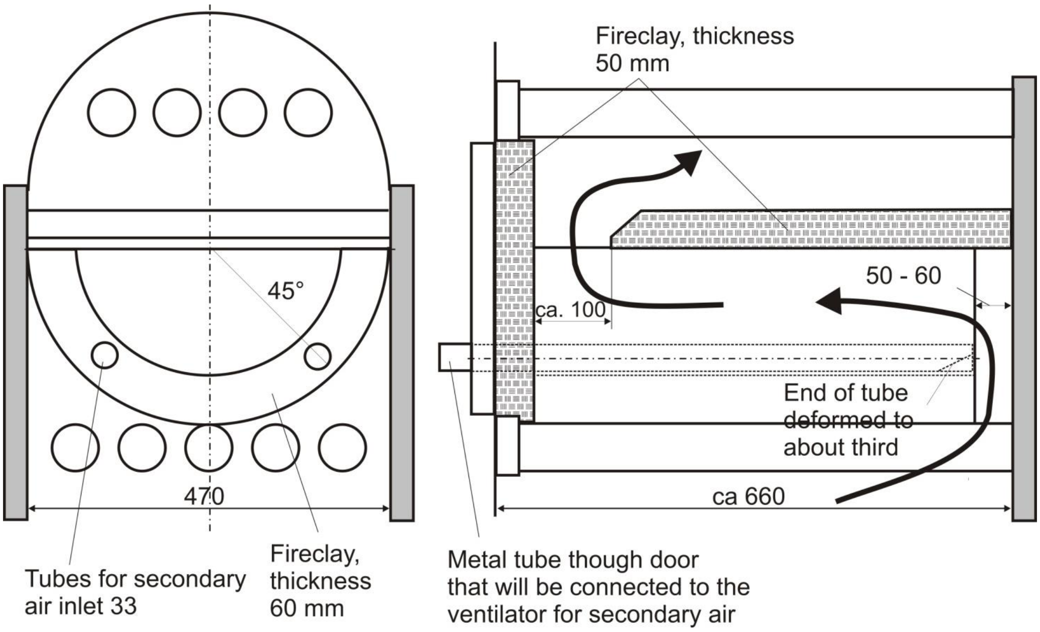


Figure 4.10 Schematic of the cylindrical fireclay mantel

In the Figure 4.11 till Figure 4.13 steel made moulds for fireclay mantel are presented. The respective costs will increase very roughly by 25 to 30 %.

Figure 4.11 Steel mould – side view

Figure 4.12 Steel mould – top view

Figure 4.13 Steel mould for the fireclay mantel

The obtained emission results and the energy efficiency values are presented in Table 4.3 and Table 4.4.

Table 4.3 Emissions from the combustion of corn cob pellets after the installation of the fireclay mantel

No.	CO mg/m^3	OGC[*] for 10 % O_2	PM	η %
1	854	26	112	78.6
2	736	18	156	77.4
3	1,157	34	189	79.2
4	946	39	145	78.3
5	734	26	127	76.1
6	862	28	125	77.3
7	1,236	32	121	75.0
8	863	18	165	79.4
Average	933	28	143	77.7

[*]OGC – organic gaseous carbon

After the installation of the improved measures in the combustion chamber, CO emissions from the combustion of corn cob pellets were reduced almost three times, meeting the requirements of the stricter class 4 from the EN 303-5 (< 1,000 mg/m^3). Similar effect can be observed for organic gaseous carbon (OGC) emissions. Average value of particulate matter (PM) emissions of 143 mg/m^3 is in line with the requirements of the EN 303-5 class 3 (< 150 mg/m^3). Efficiency value of > 75 % is also met.

After the installation of the fireclay mantel CO and organic gaseous carbon (OGC) emissions from the combustion of crushed corn cobs are in line with class 3 (< 100 mg/m^3). However, particulate matter (PM) emissions and efficiency are just below the standard requirements.

Table 4.4 Emissions from the combustion of crushed corn cobs after the installation of the fireclay mantel

No.	CO mg/m^3	OGC[*] for 10 % O_2	PM	η %
1	3,654	86	178	73.4
2	2,587	102	175	71.5
3	2,693	65	188	72.1
4	2,763	88	129	70.9
5	2,512	68	196	73.2
6	3,235	79	167	70.2
7	2,865	98	192	72.3
Average	2,901	84	175	71.9

[*]OGC – organic gaseous carbon

4.2.1.1.2 Discussion

These results are for both fuels much better, but still not good enough to meet the requirements of the standard.

To sum up, the installation of the fireclay mantel in the boiler TK-25 clearly led to the improvements in the combustion process, as evident from the emissions and efficiency parameters. In the case of corn cob pellet combustion, it is enough to place the emissions and energy efficiency values in line with the standard requirements. Even tough implemented measures led to the reduction of CO emission by almost tenfold when using crushed corn cobs as fuel, particulate matter (PM) emissions and energy efficiency are still not meeting the EN 303-5 requirements.

4.2.2 Terming

The second test stand was located in the town of Kula, on the production site of the company “Terming”. Corn cob pellets used for this round of experiments are the same as in previous case. Whole cobs consist partly of crushed cobs; its moisture content was about 10 %.

Combustion experiments were performed using two different units, the first one being an automatically feed boiler “Ozone agro 25”, and the second one manually fired furnace “TIG P”.

4.2.2.1 Automatic feeding boiler Ozone agro 25

This, for Serbian conditions high tech pellet boiler is especially designed for agro pellets from crop residues (dominantly wheat and soybean straw). The installed thermal capacity is P_n = 25 kW. This unit is also a single stage combustion boiler (i.e., only primary air). A cross section of this boiler indicating the realized air flow is presented in Figure 4.14.

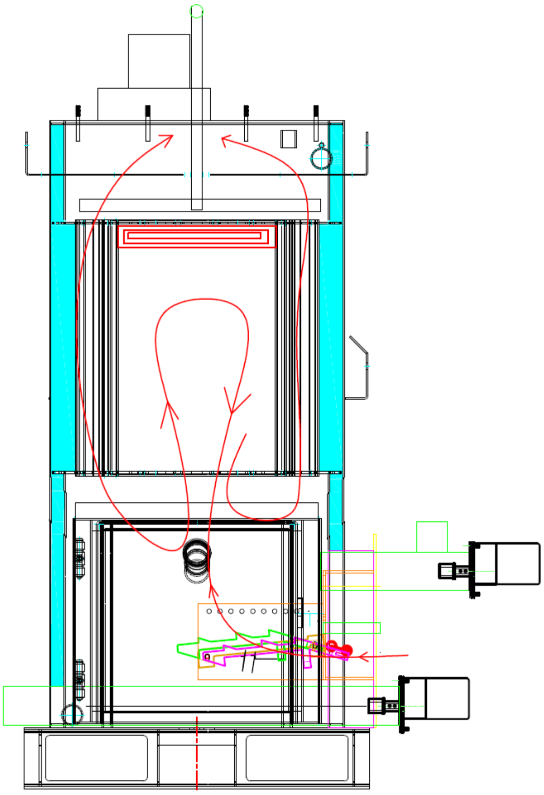


Figure 4.14 Schematic of the boiler Ozone agro 25

Table 4.5 Emissions from the combustion of corn cob pellets in Ozone agro 25

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O_2			%
1	2,485	63	280	91.5
2	2,861	52	243	92.1
3	2,136	49	216	90.8
4	1,365	33	227	89.8
5	1,375	78	312	87.8
6	1,423	68	212	90.4
7	1,408	97	235	88.9
Average	1,865	63	246	90.2

*OGC – organic gaseous carbon

The results from the initial combustion trials without any modifications are presented in Table 4.5. According to this, CO and organic gaseous carbon (OGC) emissions from the combustion of corn cob pellets within the Ozone agro 25 are in line with class 3 of EN 303-5 (CO < 3,000 mg/m^{3}and OGC < 100 mg/m^3). Compared to that, the level of particulate matter (PM) emission is rather high. Efficiency is in line with the strictest EN 303-5 class 5 (> 89 %).

4.2.2.1.1 Implemented Improvements

Figure 4.15 shows the construction of the boiler after improvements. The idea behind these improvements is to introduce secondary combustion air in the extension of the burner (grate) and before the added fireclay cylinder. This cylinder is installed with the aim to emulate secondary combustion chamber to enable stable high temperatures, to promote turbulence and to mix the combustion products and the secondary combustion air as well as to prolong the residence time of the combustion products in the combustor before reaching the heat exchanger. Figure 4.16and Figure 4.17 illustrate these improvements implemented within the combustion chamber.

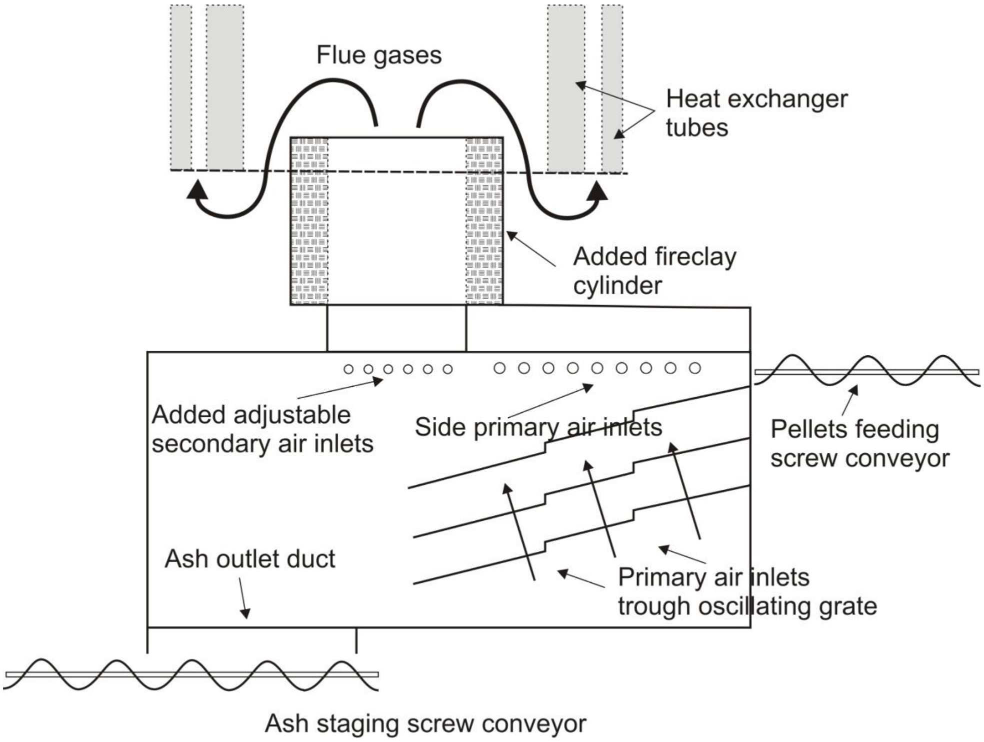


Figure 4.15 Schematic of the improvements on the Ozone agro 25 boiler

Figure 4.16 Clay insert mounted above the grate

Figure 4.17 Fireclay insert during combustion

The results of measurements of the improved automated pellet boiler Ozone 25 agro are shown in Table 4.6t ill Table 4.8. Table 4.6 presents the results during full load operation (i.e., at maximal thermal power of 25 kW). Table 4.7 and Table 4.8 show results for partial load of boiler operation (30 % and 50 %) aiming to determine the level of expected increased emissions for a lower power range. It should be noted that only this boiler Ozone 25 agro enables power regulation (i.e., operation at partial load) due to more sophisticated fuel/air dosing regulation.

Table 4.6 Emissions from the combustion of corn cob pellets after the installation of the clay insert in Ozone agro 25 at nominal load

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O$_2$			%
1	982	38	148	90.1
2	895	42	164	93.0
3	870	25	157	94.2
4	839	27	118	89.8
5	1,055	21	183	93.7
6	809	33	192	91.7
7	656	23	196	89.9
8	1,149	18	154	91.6
Average	907	28	164	91.8

*OGC – organic gaseous carbon

At the nominal load of 25 kW the CO emissions are in accordance with class 4 (< 1,000 mg/m^3). Even though the installation of the fireclay mantel and the introduction of the secondary air brought improvements, particulate matter (PM) emissions are still high, just above the emission limit values (ELVs) of EN 303-5 class 3 (< 150 mg/m^3).

Table 4.7 Emissions from the combustion of corn cob pellets after the installation of the clay insert in Ozone agro 25 at 50 % load

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O$_2$			%
1	1,568	64	198	84.2
2	1,457	67	205	86.3
3	1,596	62	187	80.1
4	1,358	63	174	81.8
5	1,425	60	188	82.4
6	1,543	65	196	83.1
Average	1,491	64	191	83.0

*OGC – organic gaseous carbon

At the 50 % load the CO emissions increased when compared with emission at nominal load. But still they are in accordance with class 3 (< 3,000 mg/m^3), whereas particulate matter (PM) emissions are also higher than at nominal load. The latter was expected. But nevertheless, this is not in line with any emission limit values (ELVs) from the given and valid standards.

Table 4.8 Emissions from the combustion of corn cob pellets after the installation of the clay insert in Ozone agro 25 at 30 % load

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O$_2$			%
1	2,852	85	187	72.3
2	2,645	73	193	76.6
3	2,378	92	197	74.5
4	2,832	87	194	71.7
5	2,387	95	183	72.5
6	2,845	74	192	73.6
7	2,460	81	205	72.9
Average	2,628	84	193	73.4

*OGC – organic gaseous carbon

Similar to in the previous case of combustion at 50 % load, the emission from the combustion at minimal load are higher compared to those at nominal load. More specifically, they are the highest ones. Still CO emissions are in accordance with EN 303-5 class 3 (< 3,000 mg/m^3), whereas as expected particulate matter (PM) emissions are too high.

4.2.2.1.2 Discussion

Before the installation of the proposed improvements, the CO emissions from the combustion of corn cob at nominal load within the Ozone 25 agro boiler were in line with class 3 (< 3,000 mg/m^3), whereas particulate matter (PM) emissions were too high. Efficiency values were in line with class 5 (> 89 %).

After the implementation of the proposed measures to modify (modernize) the combustion chamber by introducing secondary combustion air and "secondary combustion chamber", emissions from the combustion at nominal load decreased, more specifically CO emissions meet the class 4 requirements (< 1,000 mg/m^3), but particulate matter (PM) emissions were just above the class 3 emission limit values (< 150 mg/m^3). Efficiency values were in line with class 5 (> 89 %). As expected, emissions at partial loads (50 % and 30 %) are higher than at nominal load. In both cases, CO emissions meet the class 3 requirements (< 3,000 mg/m^3). Particulate matter (PM) emissions are not in line with the requirements of the standard.

Although the modifications brought substantial improvements in the quality of the combustion process and therefore contributed to emission reduction, further measures need to be taken into consideration. These include potentially the introduction of a lambda probe, the modernization / improvement of the control system, fuel-related measures etc.

4.2.2.2 Manual stoking batch type of boiler TIG P

This is a simple solution of boiler construction, aimed for the combustion of diverse fuels, from wood logs to straw and others. It is also the cheapest appliance. Installed heat capacity is P_n = 24 kW. Results of the preliminary testing are presented in theTable 4.9.

Table 4.9 Emissions from the combustion of whole corn cobs in TIG P

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O$_2$			%
1	21,567	2,442	322	44.8
2	23,659	1,445	440	36.8
3	22,452	2,014	529	44.2
4	22,364	1,834	496	44.8
5	26,257	2,569	469	35.7
6	27,579	1,836	499	36.4
7	27,881	1,587	522	41.5
8	18,852	1,879	457	39.7
Average	23,826	1,951	467	40.5

*OGC – organic gaseous carbon

Based on the results from preliminary testing of the TIG P boiler, none of the investigated parameters meet the requirements of the EN 303-5 standard. CO emissions are more than 4 times higher than the respective emission limit values for class 3 for manually-fed units (< 5,000 mg/m^3), whereas particulate matter (PM) emissions are almost double the emission limit values for class 3 for manually-fired units (< 150 mg/m^3). Organic gaseous carbon (OGC) is more than 12 times higher than the respective emission limit values for class 3 for manually-fed units (< 150 mg/m^3).

4.2.2.2.1 Implemented improvements

A control of primary air intake by the implementation of a Burdon tube was introduced. A new flap for secondary combustion air, with manual adjustment of the position, was also installed. Moreover, on the inside of the combustion chamber, a fire clay wall (fireclay elements) has been introduced, aimed to support ignition of primary combustion compounds (Figure 4.18). The costs for reconstruction are assessed with the result that the boiler price might increase roughly by about 20 %.

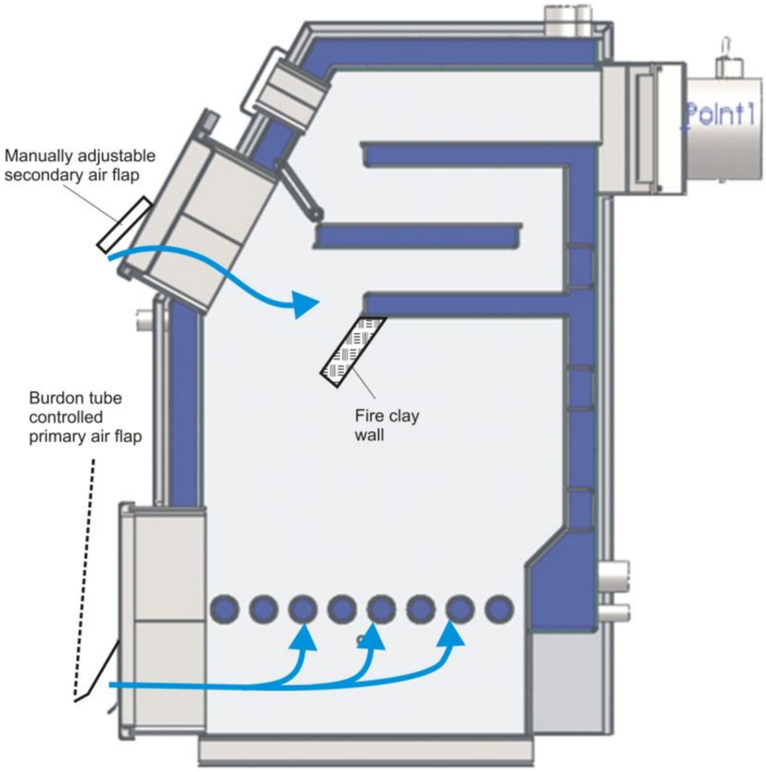


Figure 4.18 Schematic of the boiler TIG P with improvements

The results of the emission and efficiency measurements after the boiler reconstruction are presented in Table 4.10.

Table 4.10 Emissions from the combustion of whole corn cobs after the improvements in TIG P

No.	CO	OGC*	PM	η
	mg/m^3 for 10 % O$_2$			%
1	4,659	231	126	51.6
2	5,237	368	187	55.8
3	3,697	158	159	52.3
4	4,588	198	187	49.1
5	3,675	265	136	52.9
6	5,776	312	148	48.7
Average	4,605	255	157	51.7

*OGC – organic gaseous carbon

After the modification of the boiler TIG P, emissions are reduced for all considered pollutants. CO emissions are in line with emission limit values for manually-fed units, class 3 (< 5,000 mg/m^3). Organic gaseous carbon (OGC) and particulate matter (PM) emissions are still outside this standard.

4.2.2.2.2 Discussion

Before the combustion unit modification, emissions from the combustion of whole corn cobs in the TIG P boiler were many times higher than the limits and requirements given in EN 303-5, whereas efficiency was lower than the requirements of the standard.

After the modification of the boiler TIG P, average CO emissions are reduced more than 5-fold, being in line with the standard requirements for manually-fed units class 3 (< 5,000 mg/m^3). Efficiency is also improved by increasing from 40 % to > 50 % on average. Organic gaseous carbon (OGC) emissions are reduced as well more than 7-fold (from 1,900 mg/m^3 on average, to 255 mg/m^3 on average. Nevertheless, they still do not meet the EN 303-5 requirements. Most problematic parameter, particulate matter (PM) emission, is reduced almost 3-fold and is quite close the emission limit value for class 3 in EN 303-5 (< 150 mg/m^3), on average. This is somewhat of a surprise, taking into consideration the value of CO emission and the results from the measurement trials with other combustion units.

4.2.3 Conclusions

Considering the three investigated units (KTK-25, Ozone 25 agro, and TIG P) and corresponding emissions before and after the proposed measures, expected improvement has been partly achieved. CO emission seem to be more easily reduced by controlling combustion air and the introduction of fireclay elements in the combustion chamber. Thus, the requirements for complete combustion such as long-enough residence time of volatiles, high temperatures, and mixing (turbulence) of combustion products with oxygen are facilitated. The still unsolved problem is the considerable reduction of particulate matter (PM) emissions.

After the installation of the improved measures in the combustion chamber of first investigated unit, automatic boiler KTK-25, average CO emissions from the combustion of corn cob pellets were reduced almost three times, meeting the requirements of the class 4 from the EN 303-5 (< 1,000 mg/m^3). In parallel, average value of particulate matter (PM) emissions of 143 mg/m^3 have been measured being in line with the requirements of the EN 303-5 class 3 (< 150 mg/m^3). Efficiency value of > 75 % is also met (class 3).

In the other combustion unit (Ozone 25 agro) secondary combustion air and “secondary combustion chamber” were introduced. After these improvements, emissions from the combustion at nominal load decreased. CO emissions met the class 4 requirements (< 1,000 mg/m^3), but particulate matter (PM) emissions were just above the class 3 emission limit values (< 150 mg/m^3). Efficiency values at nominal load were in line with class 5 (> 89 %). Emissions at partial load (50 % and 30 %) have been higher than at nominal load. In both cases the measured emissions met the class 3 emission limit values for CO emissions (< 3,000 mg/m^3). But, the measurement result have not been in line with the particulate matter (PM) emission limit values on average.

In the last investigated unit (TIG P), after the modification of the boiler average CO emissions are reduced more than 5-fold, being in line with class 3 for manually-fed units (< 5,000 mg/m^3). Efficiency is also improved but not in line with standard requirements, increasing from 40 % to > 50 %, on average. Particulate matter (PM) emissions are reduced almost 3-fold and thus just above the acceptable emission limit values for class 3 in EN 303-5 (< 150 mg/m^3), on average.

5 Measurement of emissions and technical assessment – Location 2 (Germany)

Natasa Dragutinovic, Isabel Höfer, Martin Kaltschmitt

Combustion experiments are performed in two phases, differing in the following aspects: (1) the combustion unit and respective capacity, and (2) measurement performed during combustion.

All experiments are realized at the combustion test stand, according to EN 303-5 under full load.

- In the first phase, during combustion in a 25 kW boiler, gaseous and particulate matter (PM) emissions are monitored, as well as the energy conversion performance (energy balance) of the overall process. Samples of bottom ash from the ash container, fly ash from the combustion chamber walls, and particulate matter (filter) are collected and analyzed in the laboratory for crystalline phases and elementary composition.
- In the second phase, combustion experiments are performed with an 8 kW pellet oven. Besides discontinuous particulate matter sampling mentioned in the first project phase, in this second phase also the particle size and number distribution were recorded.

These different phases are described in detail below. This is also true for the experimental setup for the combustion experiments at TUHH and the applied methodology. The results are presented and discussed in the subsequent chapter.

5.1 Methodology

A detailed description of the methodology for each step of the investigation, as well as an overall measurement plan, are outlined below.

5.1.1 Materials

Corn cob pellets used within the experiments as a solid biofuel have been produced from corn cob grits cultivated in Germany. Wood pellets used in the combustion trials have been purchased from two different dealers in Germany.

The three feedstock samples (corn cob grits, wood pellets 1 and 2) have been analyzed for elementary composition in the laboratory of TUHH based on the methods from DIN EN 15104, DIN EN 15289, DIN EN15290, and DIN EN 15297.

5.1.2 Phase one Experimental setup

In the combustion tests of the first project phase, the boiler "Ozone agro" with 25 kW capacity (ATI Terming Kula, Serbia) was integrated at the existing test stand in TUHH's technical center. The schematic illustration of the test bench is shown in Figure 5.1.

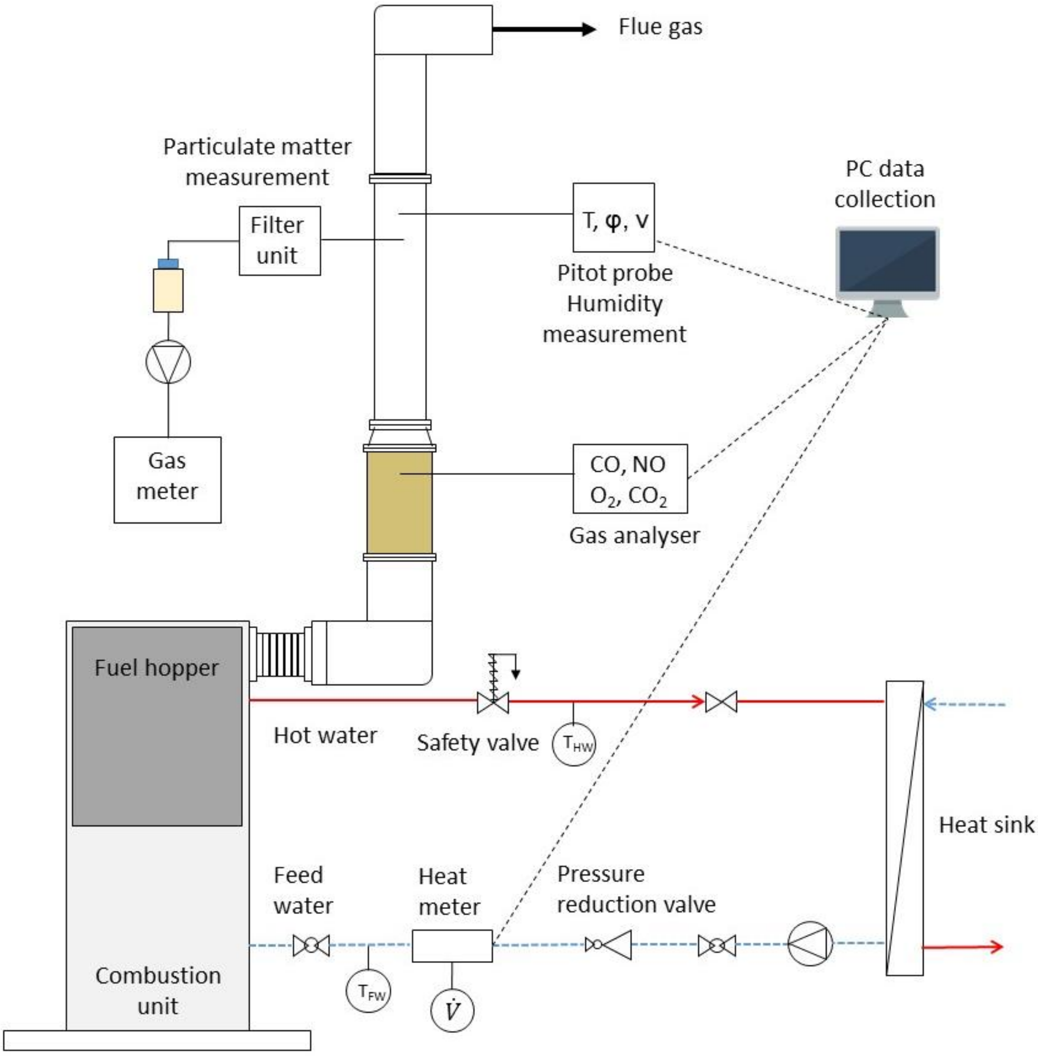


Figure 5.1 Test stand

Fuel consumption (energy input) was determined by weighing the fuel before (input) and after (leftover) the combustion experiment. On the energy output side, a heat meter (Sontex Superstatic 789) is installed and connected to a computer with a M-Bus (Relay GmbH), enabling online heat transfer data monitoring using a commercial available software (Relay GmbH). These two data sets are used to calculate the thermal capacity and efficiency (Appendix B). Water circuit of the boiler heat exchanger is operating at a pressure level of below 3 bar. The water circuit is connected to the cooling system of TUHH. The water flow of the cooling circuit is ca. 1.1 m^3/h. Efficiency is calculated in accordance with EN 303-5.

Fuel is fed into the combustion chamber from the fuel hopper (capacity 75 kg) (Figure 5.2), connected to the burner through automatically controlled screw-feeder with adjustable speed control. Combustion air is fed using a single fan with adjustable speed control (3 speeds) distributed as primary air from the bottom of the moving grate. Additionally, a share of the combustion air is blown into the combustion chamber through holes on the burner sides. Approximately half of the overall moved air is introduced through the grate and the rest through these holes on the burner sides into the combustion area. Ash from the moving grate is actively removed from the combustion chamber into a separate ash container using an ash screw feeder. The temperature inside the combustion chamber is monitored with a flexible immersion probe type K, class 1 (Testo 925, measurement < 1,300 °C). Above the burner, gaseous combustion products are passing through the heat exchanger, in which turbulators are installed to enable a better mixing of combustion products and pre-heated air.

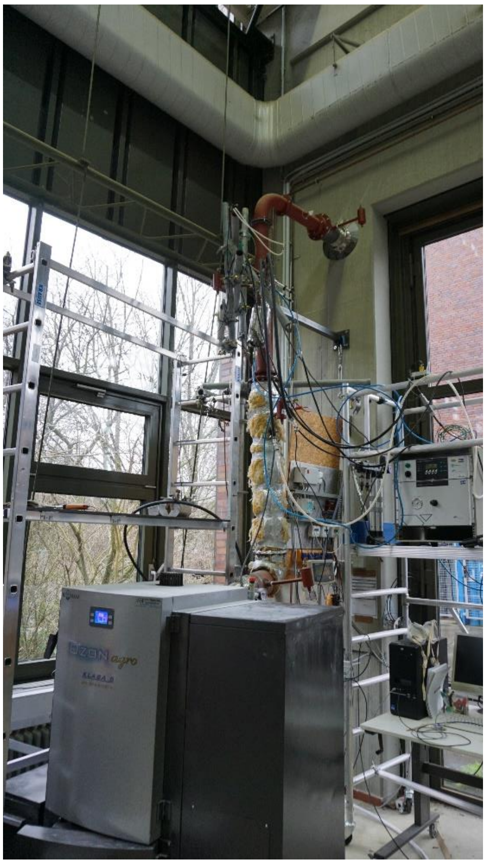


Figure 5.2 Combustion test stand at the Hamburg University of Technology

Figure 5.3 Corn cob granulate and pellet fuels **(top);** moving grate and ash removal screw **(middle)**; filter unit for PM sampling and conditioned filter before sampling **(bottom)**

After the heat exchanger the flue gases are passing through the chimney. Here, additional measurement points are installed. Pressure and temperature are continuously measured online at different points in 10 s intervals and monitored online (TracerDAQ software). Flue gas velocity (differential pressure) is monitored using a pitot tube and Testo 440 dp. Gaseous emissions such as CO_2, CO, NO_x and O_2 concentrations are continuously measured using gas analyzer Wöhler 550 in 10 s intervals and monitored online (Wöhler software). Flue gas moisture content is measured semi-continuously in (Testo 440 dp).

5.1.2.1 Particulate matter and ash sampling

Particulate matter (PM) content is discontinuously sampled according to iso-kinetic method using a Paul Gothe titanium sampling probe with a filter unit (according to VDI 2066-1) (Figure 5.3). Before the measurement four quartz filters (Macherey-Nagel QF – 10, diam. 4.5 cm), four plane filter holders and coarse PM filter holder are conditioned at 160 °C for 1 h and cooled down in the desiccator for at least 8 h. Three conditioned filters are used for measurements whether the fourth one is used for blank value determination (error). During sampling the filter unit, equipped with a titanium nozzle and probe which enables iso-kinetic sampling of the flue gas, is heated to 160 °C in order to maintain approximately the same temperature as in flue gas and to prevent any condensation of the gaseous species. After entering the sampling probe through the selected nozzle, sampled gas is passed through the isolated, heated filter unit. After the filter unit, a silica gel station removes the moisture from the sampled flue gas and at the end of the measurement train is a pump (Carpanelli) with a gas meter (GMT BK – G4T). Each particulate matter sampling duration lasted 5 to 15 min depending on the loading of the filter. Volumetric flow of the sampled gas (affected by the pressure drop due to the filter loading) was kept constant by regulating the vacuum pump flow. The volumetric flow of the sampled gas at the gas meter is calculated based on actual conditions during the respective combustion experiment (i.e., temperatures at the sampling point (filter) and at the gas meter, pressures at both points, and humidity at both mentioned points). Particulate matter (PM) measurements have been performed in triplicates for each experiment. After the sampling filters and filter holders were heated again to 160 °C for 1 h, kept for another 8 h in the desiccator and weighed. The load of the particles in the sampling probe was divided between each of the PM samples proportionally, based on each sampling duration.

After each combustion experiment, bottom ash from the grate, fly ash from the combustion chamber walls, and particulate matter (PM) samples are taken. Fly ash includes air-borne particulate matter entrained from the grate and / or released in gaseous form but condensed and finally deposited on the walls or bottom of the combustion chamber and / or the heat exchanger.

5.1.2.2 Laboratory analysis of solid residue samples

The three sampled fractions of ash samples are investigated in the laboratory.

- All three ash fractions are investigated for elemental composition.
- Bottom ash (BA) and fly ash (FA) samples are investigated additionally for crystalline phases with powder X-ray diffraction (XRD).

Analysis of elemental composition. Determination of elemental composition of bottom ash and particulate matter (PM) samples are performed using two methods. The concentrations of K, Na, Ca, Al, Fe and Mn are determined after microwave-assisted acid digestion of the sample with aqua regia and the atomic absorption spectroscopy (AAS). Ion chromatography (IC) is used for measuring the water-soluble portions of SO_4^{2-}, Cl^-, and PO_4^{3-}.

Contents of SO_4^{2-}, Cl^-, and PO_4^{3-} were determined using IC (ICS-90 Dionex). Samples (0.05 g) are filled with 10 mL of double distilled (ultrapure) water, shaken for 1 h at 150 min^{-1}, and afterwards filtered with a mesh size of 0.45 µm.

For the determination of K, Na, Ca, Al, Fe, und Mn, bottom ash samples (0.1 g) are firstly digested in a multi-step pressurized microwave with aqua regia and nitric acid. In the initial step aqua regia (8 mL) is added to the sample, consisting of three parts HCl (32 %) and one part HNO_3 (65 %). Samples are then treated in the microwave oven (Anton Paar Microwave Digestion System Multiwave GO) for 30 min at 500 W and additionally for 15 min at 1,000 W, possibly reaching temperatures of 230 °C and a pressure level of up to 20 bar. Another 6 mL of HNO_3 is added after the sample is cooled down. After this step, the sample is treated again in the microwave oven for another 20 min at 1,000 W, possibly reaching temperatures up to 260 °C and pressures up to 30 bar. Because silicates are not digested through this process, digested samples are filtered using filter paper and filled up to 50 mL with distilled water. After this sample preparation, the content of Na, K, Ca, Mg, Fe, Al and Mn is determined using AAS (Analytik Jena ContrAA 700).

Analysis of crystalline phases. In order to investigate the possible reactions taking place in the ash during combustion, X-ray diffraction analysis (XRD) (model Siemens D500) is used to identify crystalline phases in the ashes. The bottom ash sample is directly placed in a holder and loaded in the diffractometer, in range 20 to 63 ° in 2θ with scan speed of 1 s.

5.1.3 Phase two Experimental Setup

In the second project phase the boiler is substituted with the state-of-the art pellet oven, model Polly 2,0 (Austroflamm) (Figure 5.4).

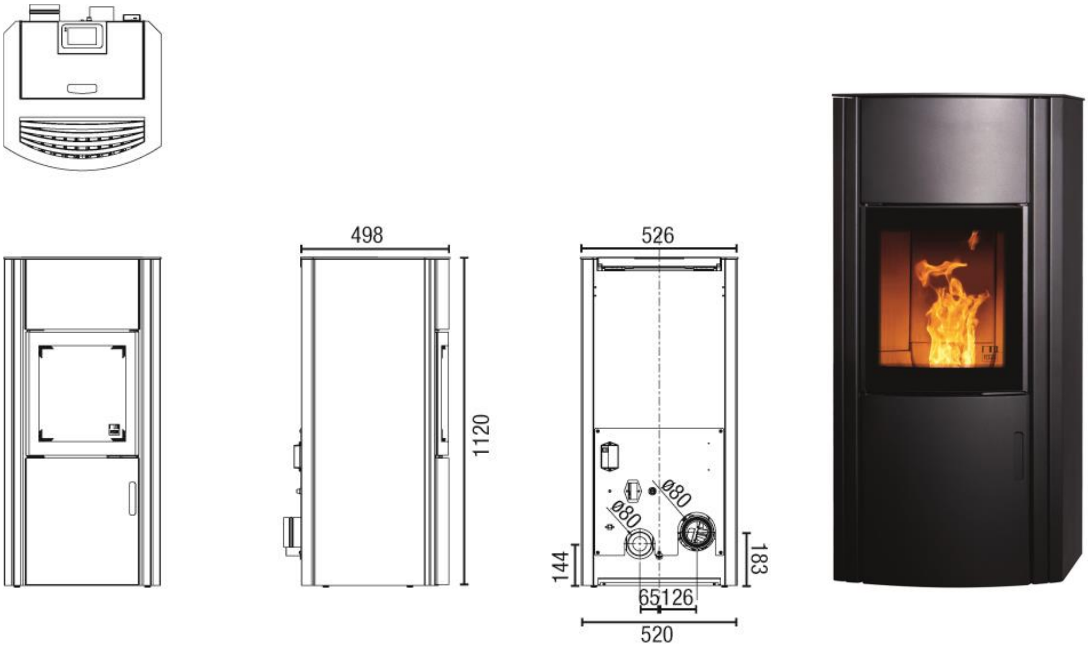


Figure 5.4 Scheme of the Polly 2.0 pellet oven (left) and photo of a Polly 2.0 pellet oven (right)

Primary heat transfer mode is radiation; thus, heat exchanger (gas / water) and water distribution circuit do not exist. Therefore, also the possibility of direct online measurement of heat transfer and thermal capacity is not possible. Thus, the efficiency is calculated in accordance with EN 303-5/EN 304 – Indirect method. Fuel consumption (energy input) was determined by weighing the fuel before (input) and after (leftover) the combustion experiment. The temperature of the flue gas was used to calculate the heat output.

The pellet oven Polly 2.0 is a commercially available oven for wood pellets, equipped with a flip-grate and a ceramic cup burner. The presence of self-cleaning grate should enable the combustion of agro pellets and/or pellet blends with higher ash content and lower melting points. The pelletized fuel is fed into the combustion chamber from the fuel hopper (capacity 25 kg). This feeding is automatically controlled. Combustion air is distributed as primary air from the bottom of the moving grate. Ash from the cup burner is actively removed from the combustion chamber using a flip-grate on hinges, into a separate ash container underneath.

An overview of the most important operational and technical parameters of the combustion unit is given in Table 5.1.

Table 5.1 Technical and operational parameters of the Polly 2.0 pellet oven

Nominal thermal output	7,8 kW
Partial-load thermal output	2,4 kW
Degree of effectivity	90,7 %
Flue gas temperature at nominal load	206 °C
Flue gas temperature at partial load	115 °C
CO content at nominal load	47 mg/m^3
CO content at partial load	173 mg/m^3
Flue gas mass flow at nominal load	4,9 g/s
Flue gas mass flow at partial load	3 g/s
Capacity of filling tank	25 kg
Min./max. pellet consumption	0,6 – 1,9 kg/h

Above the burner gaseous combustion products are passing through directly into the chimney pipe and from here into the chimney, where measurement points are installed (Figure 5.1) (for detailed description see chapter 5.1.2).

5.1.3.1 Particle size number and mass distribution

Beside above mentioned sampling and measurement methods (see chapter 5.1.2), in the second phase particulate matter (PM) distributions are sampled and analyzed using a system consisting of:

- Sampling of the flue gas using a two-step dilution system (Dekati Fine Particle Sampling (FPS) 4000 Module)
- TSI NanoScan (10 to 420 nm) and TSI OPS (0.3 to 10 µm) devices for PM for number, mass and surface size distribution.

First step of the particle number and size distribution measurement is the sampling of the flue gas using a two-step dilution system (Dekati Fine Particle Sampler 4000 (FPS-4000)). The Dekati Fine Particle Sampler samples the flue gas with an in-stack method using a perforated sampling probe, after which the sampled gas is mixed with pre-heated dilution air also at 160 °C (Figure 5.5 and Figure 5.6). The perforated sampling tube is heated with a controllable external heating element at 160 °C. Pre-heated air is compressed to 3 bar, filtered using a high efficiency particulate air (HEPA) filters and dried in silicagel before entering the mixing module. After the primary dilution the ejector diluter is introduced, further diluting the sample to the concentrations appropriate for the detection limits of the subsequent analysis methods (Figure 5.7). The combination of primary diluter and ejector diluter amount to the total dilution of the sample. In this measurements total dilution ratios 100 to 200 were used. The total dilution ratio and temperature of the primary diluter are adjusted online using a FPS VI1.3 software. Volumetric flow of the sampled flue gas was approximately 0.8 L/min. After passing through the software of the Dekati Fine Particle Sampler, diluted sample gas is split into 6 sub-streams.

Figure 5.5 Sampling probe with heated primary dilution air (FPS manual full 5.8)

Figure 5.6 Control system of the FPS (FPS manual full 5.8)

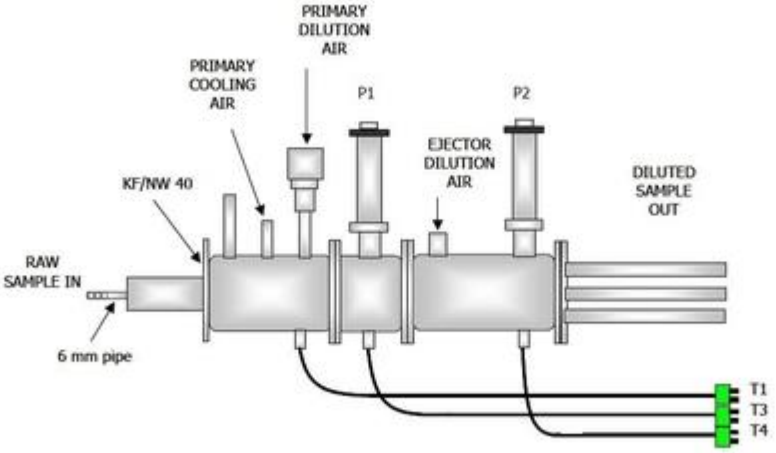


Figure 5.7 Schematic of the sampling probe and two-dilution steps (FPS manual full 5.8)

TSI measurement train consists of two devices: TSI NanoScan Scanning Mobility Particle Sizer (SMPS) and TSI Optical Particle Sizer (OPS) model 3030. The NanoScan is a portable analytical instrument measuring nanoparticle size distributions and concentrations. NanoScan consists of following parts:

- Inlet conditioner is used to remove larger particles which can potentially cause clogging and which are likely to have multiple charges. To ensure optimum resolution over the entire operating size range, a cyclone with an approximately 500 nm cutpoint is used on the inlet of the NanoScan.
- The aerosol charger charge each particle. This charge per particle must be known to calculate the particle diameter from electrical mobility. Unipolar charger is used which increases nanoparticle counting efficiency
- Electrical mobility, or the ability of a particle to traverse an electric field, is a method to measure particle size, because it can be directly measured and is a first principle function of size. Electrical mobility is typically measured by using a Differential Mobility Analyzer (DMA).
- Downstream of the Differential Mobility Analyzer, the number of particles in each size bin is measured using an isopropanol-based Condensation Particle Counter (CPC) providing measurements at high and low concentrations using a working fluid acceptable in workplace environments. Condensation Particle Counter (CPC) measure particle concentration by counting single particles resulting in a high level of accuracy and excellent performance at low concentrations.

The Model 3330 Optical Particle Sizer (OPS) operates on the principle of single particle counting (Figure 5.8). The Optical Particle Sizer (OPS) uses a laser and a detector to detect particles passing through a sensing volume illuminated by the laser. The flow rate being sampled into the instrument is 1.0 L/min and additionally there is 1.0 L/min of sheath flow. Sheath flow keeps the particles well focused across the laser light and also prevents the optics from getting contaminated. Beam shaping optics focus the laser light and convert that to a fine sheath with maximum intensity across the particle beam. The viewing volume is created by the intersection of the laser sheath and the particle flow. Particles pass through the beam and light scattered by the particles is picked up by an elliptical mirror and focused onto the photodetector. The intensity of the flash is used to count and size the particles. This measurement device provides resolution over the size range of 0.3 to 10 µm. The maximum particle size that can be counted is 10 µm. Particles above 10 µm will be counted but not sized.

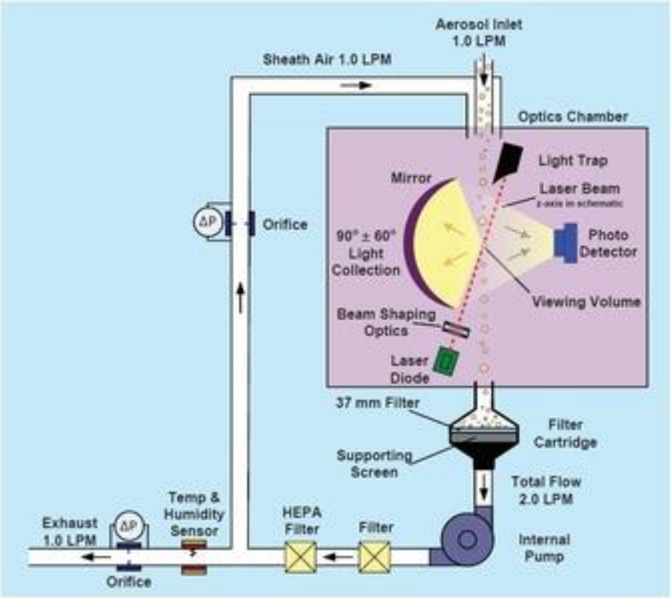


Figure 5.8 Schematic of Optical Particle Sizer (OPS) (TSI OPS Operation and service manual)

5.1.3.2 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM / EDS)

In addition to the same methods applied in the first phase of the combustion trials (chapter 5.1.2), Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-Ray Spectroscopy (EDS) were used to analyze the morphology and surface elementary composition of selected ash samples. Using these methods, particle (ash) surface morphology on a micro level, and elemental composition of selected areas can be investigated, allowing for better understanding of processes taking place in the ash, as well as better understanding of PM formation.

Representative samples of bottom ash (BA) and particulate matter (including filters) (PM) were homogenized and mounted on carbon tapes which were then mounted on top of sample tabs. Particulate matter including quartz fiber filters were cut to fit size of the sample holder and mounted on carbon tapes mounted on top of sample tabs. List of solid combustion residue samples from each combustion series is given in Table 5.2.

Table 5.2 List of samples analyzed with SEM / EDS; from each experiment bottom ash and particulate matter sample was analyzed

Series	Sample
Blends of corn cob pellets and wood pellets	Abbreviation
100 wt. % wood pellets	WP
50 wt. % wood pellets 50 wt. % corn cob pellets	50%CCP
100 wt. % corn cob pellets	CCP
Corn cob pellets with additives	Abbreviation
99 wt. % corn cobs pellets 1 wt. % kaolin	CCP 1KAO
98 wt. % corn cobs pellets 2 wt. % kaolin	CCP 2KAO
99 wt. % corn cobs pellets 1 wt. % magnesium oxide	CCP 1MgO
98 wt. % corn cobs pellets 2 wt. % magnesium oxide	CCP 2MgO

Samples were coated with ca. 7-8 nm gold to provide a conductive surface and loaded into the Zeiss Supra 55 VP FEG-SEM with Variable Pressure Mode (VP-Mode), EDS, WDS und EBSD. Operational parameters used were electron high tension (EHT) of 5 kV and Aperture size of 10 µm.

5.2 Measurement plan

Below the measurement plans are described.

5.2.1 Phase one

Here the effect of primary measures such as fuel processing (pelletizing) and fuel blending, as well as certain combustion unit modification steps, are investigated in a 25 kW boiler. Combustion trials were organized and performed in two series of experiments, which are presented in the following text. In addition to this, the used abbreviations are defined which are to be used during the subsequent presentation of the results.

5.2.1.1 Blends of corn cob pellets and wood pellets

There are three reasons for blending commercially available wood pellets with corn cob pellets produced in the lab. Firstly, by blending the agro fuels with standardized wood pellets, the quality of the agro fuel is improved in comparison with pure agro pellets (and the resulting airborne emissions are consequently (most likely) reduced). The second reason is the limited availability of corn cob pellets (research scale pellet mill). Therefore, first experiments with such a “new” fuel (corn cobs) with the aim of optimization were performed by blending corn cob pellets with wood pellets. Lastly, preliminary experiments performed only with corn cob pellets resulted in so excessive CO emissions that the available equipment could not measure its concentration in the flue gas (> 5,000 ppm). The overview of the experimental series is given in Table 5.3. Pure wood pellets have been regarded as reference fuel.

Table 5.3 Experiments from the series “Blends of corn cob pellets and wood pellets” including abbreviations

Fuel	Abbreviation
100 wt. % wood pellets	WP
87.5 wt. % wood pellets 12.5 wt. % corn cob pellets	12.5CCP
75 wt. % wood pellets 25 wt. % corn cob pellets	25CCP
50 wt. % wood pellets 50 wt. % corn cob pellets	50CCP
100 wt. % corn cob pellets	CCP

5.2.1.2 Corn cob grinds and additives

In order to facilitate the energetic use of corn cobs with minimal processing efforts and with minimized investments and enable its use in boilers with automatic fuel-feeding, the crushed corn cob material is combusted without additives as a reference case in this series. In subsequent experiments, it is mixed with additives to investigate the effect of the applied additives on the particulate matter (PM) and carbon monoxide (CO) emissions. Kaolin and magnesium oxide in 1 wt. % and 2 wt. % have been used as additives (Table 5.4).

Table 5.4 Experiments from the series “Corn cob grits and additives” including abbreviations

Fuel	Abbreviation
100 wt. % corn cobs grit	CCG
99 wt. % corn cobs grit 1 wt. % kaolin	CCG 1KAO
98 wt. % corn cobs grit 2 wt. % kaolin	CCG 2KAO
99 wt. % corn cobs grit 1 wt. % magnesium oxide	CCG 1MGO
98 wt. % corn cobs grit 2 wt. % magnesium oxide	CCG 2MGO

5.2.2 Phase two

The effect of primary measures such as fuel blending and additivation on the particle size distribution and the properties of ash fractions of particulate matter are investigated. Combustion trials were organized and performed in several series of experiments, which are presented in the following text. First two experimental series are analogue to those in the phase one, whereas third series includes the combustion of upgraded corn cob pellets with starch. Starch has been used to improve mechanical properties of the pellets (reduce fine content and increase mechanical durability). In all three series, pellets have been sieved with 4 mm sieve before loading them in the fuel hopper to remove fines that might cause disruptions with the combustion in the pellet oven. The abbreviations are defined which are to be used in the latter chapters.

5.2.2.1 Blends of corn cob pellets and wood pellets

Fuel blending (i.e., blending agro pellets with standardized wood pellets in defined ratios) improves the quality of fuel in comparison with pure agro pellets. This in turn minimizes potential operational issues such as blockage of air-feeding, ash sintering, and most importantly reduces particulate matter (PM) emissions due to reduced fuel ash and fine content. In addition, due to their low cost and availability in agricultural regions agro pellets are comfortable and affordable for consumers in agricultural regions. The overview of the experimental series is given in Table 5.5. Pure wood pellets have been regarded as reference fuel. All experiments have been performed twice (two replications).

Table 5.5 Experiments from the series “Blends of corn cob pellets and wood pellets” including abbreviations

Fuel	Abbreviation
100 wt. % wood pellets	WP
87,5 wt. % wood pellets 12,5 wt. % corn cob pellets	12.5%CCP
75 wt. % wood pellets 25 wt. % corn cob pellets	25%CCP
50 wt. % wood pellets 50 wt. % corn cob pellets	50%CCP
100 wt. % corn cob pellets	CCP

5.2.2.2 Corn cob pellets with additives

This option includes full fuel processing, starting with particle size reduction, mixing with additives (prior to pelletization), and pelletization. Results from additivized pellet combustion have been compared with the results from pure corn cob pellet combustion (without additives). Kaolin and magnesium oxide in 1 wt. % and 2 wt. % have been used as additives (Table 5.6). All experiments have been performed twice (two replications).

Table 5.6 Experiments from the series of "Corn cob pellets with additives" including abbreviations

Fuel	Abbreviation
100 wt. % corn cobs pellets	CCP
99 wt. % corn cobs pellets 1 wt. % kaolin	CCP 1KAO
98 wt. % corn cobs pellets 2 wt. % kaolin	CCP 2KAO
99 wt. % corn cobs pellets 1 wt. % magnesium oxide	CCP 1MgO
98 wt. % corn cobs pellets 2 wt. % magnesium oxide	CCP 2MgO

5.2.2.3 Corn cob pellets with additives and binder

This option includes full fuel processing, mixing with additives (prior to pelletization) and binder, and pelletization. In order to cover the full range 0 till 2 wt. % kaolin as additive, pellets using 0,5 wt. % and 1,5 wt. % kaolin (with 2 wt. % starch as binder) have been produced (Table 5.7). This series has been performed once.

Table 5.7 Experiments from the series of "Corn cob pellets with additives and binder" including abbreviations

Fuel	Abbreviation
98 wt. % corn cobs pellets 2 wt. % starch	CCPB
97.5 wt. % corn cobs pellets 2 wt. % starch 0.5 wt. % kaolin	CCPB0.5KAO
96.5 wt. % corn cobs pellets 2 wt. % starch 1.5 wt. % kaolin	CCPB1.5KAO

5.3 Operational parameters and settings used during the combustion tests

Below the operational setting used in the respective combustion experimental series' are presented and explained.

5.3.1 Phase one

5.3.1.1 Blends of corn cob pellets and wood pellets

The settings of the combustion device used for these investigations in the first set of experiments were chosen based on manufacturers input as standard settings for wood pellets (Table 5.8). However, air- and fuel-feeding have been fine-tuned in order to minimize the pollutant emissions and keep the heat load (heat output) as stable as possible. Therefore, in some cases variations caused instable regime and corresponding increase in emissions.

In the second series of experiments, air-feeding was kept constant. In parallel, other parameters have been fine-tuned in order to keep the thermal output constant.

Table 5.8 Operational parameters used in the combustion of blends of corn cob and wood pellets

Fuel	Heating value kWh/kg	Air-feeding (P1/P2/P3)* V	Feed speed g/min.	Duration of the movement s	Loading of the burner s
SERIES1					
WP	4.8	85/90/95	410	1	30
12.5CCP	3.6	n.a.	500	0.5	30
25CCP	4.6	95/100/105 - 105/110/115	400	1	30
50CCP	4.2	95/100/105 - 105/110/115	380	1	30
CCP	3.8	85/90/95 - 95/100/105	390	1	30
SERIES 2					
Fuel	Heating value kWh/kg	Air-feeding (P1/P2/P3) V	Feed speed g/min.	Duration of the movement s	Loading of the burner s
WP	4.8	85/90/95 - 80/85/90	465/390	1	30
12,5CCP	4.8	65/70/75 - 50/50/50	440/460	1	30
25CCP	4.8	85/90/95 - 65/70/75	410/465	1	30

*P1/P2/P3 – power settings of the air-feeding fan in Volts

5.3.1.2 Corn cob grinds and additives

The most important difference in this series is the fuel-feeding parameters adjusted to the bulk density of the corn cob grinds (Table 5.9). In the first series of experiments, the air- and fuel-feeding were fine-tuned to keep the emissions at minimum and the heat load constant. However, this results in the end in an instable operation and in increased airborne emissions. Therefore, in the second series, the air-feeding was strictly kept constant and the heating value was adjusted in the control system, as well as fuel-feeding, in order to meet the heat load of 25 ± 2 kW.

Table 5.9 Operational parameters used in the combustion corn cob grinds with additives

Fuel	Heating value kWh/kg	Air-feeding (P1/P2/P3)* V	Feed speed g/min	Duration of the movement s	Loading of the burner s
SERIES 1					
CCG	3.9	95/100/105	300	0.5	50
CCG 1MGO	3.2	85/90/95	330	0.5	50
CCG 2MGO	3.5	80/85/90	300	0.5	50
CCG 1KAO	5.2	90/95/100	330	0.5	50
CCG 2KAO	5.6	80/85/90	350	0.5	50
SERIES 2					
Fuel	Heating value kWh/kg	Air-feeding (P1/P2/P3) V	Feed speed g/min	Duration of the movement s	Loading of the burner s
CCG	4.3	80/85/90	330	0.5	50
CCG 1MGO	3.9	80/85/90	330	0.5	50
CCG 2MGO	3.6	80/85/90	330	0.5	50
CCG 1KAO	5.8	80/85/90	330	0.5	50
CCG 2KAO	5.6	80/85/90	350	0.5	50

*P1/P2/P3 – power settings of the air-feeding fan in volts

5.3.2 Phase two

Below the operational settings of the Polly 2.0 pellet oven used in the respective combustion experimental series' are presented and explained. From the user standpoint, following parameters can be adjusted in the control system of the pellet oven: quality of the pellet fuel (1-best, 3-worst), target temperature (C), and power level (1-low, 5-nominal capacity).

5.3.2.1 Blends of corn cob pellets and wood pellets

Operational parameters used during combustion of blends of wood and corn cob pellets are given in Table 5.10

Table 5.10 Operational parameter from the combustion series "Corn cob and wood pellets"

Fuel	Target temperature °C	Power level -	Pellet quality -
WP	30	5	1
12,5CCP	30	5	1
25CCP	30	5	1
50CCP	30	5	1
CCP	30	5	1

5.3.2.2 Corn cob pellets with additives

Operational parameters used during combustion corn cob pellets with and without additives are given in Table 5.11.

Table 5.11 Operational parameters used in the combustion series "Corn cob pellets with additives"

Fuel	Target temperature °C	Power level -	Pellet quality -
CCP	30	5	1
CCP 1MGO	30	5	1
CCP 2MGO	30	5	1
CCP 1KAO	30	5	1
CCP 2KAO	30	5	1

5.3.2.3 Corn cob pellets with additives and binder

Operational parameters used during combustion corn cob pellets with and without additives are given in Table 5.12.

Table 5.12 Operational parameters used in the combustion series "Corn cob pellets with additives and binder"

Fuel	Target temperature °C	Power level -	Pellet quality -
CCPB	30	5	1
CCPB0.5KAO	30	5	1
CCPB1.5KAO	30	5	1

5.4 Results

Below the results from feedstock analysis and two experimental series are presented and discussed in detail.

5.4.1 Fuel

Results

An overview of the elementary composition of the solid biofuels used in the combustion trials is presented in Table 5.13. In the case of corn cob grits also trace elements in the fuel have been determined. C contents of corn cobs and wood pellets are ca. 49 wt. % and 50 wt. %, respectively. H contents of all analyzed samples ranges from ca. 6.7 to ca. 7.8. wt. %, whereas N content ranges from <0.10 to 0.25 wt. %. S contents of corn cobs and woody pellets are 0.1

and <0.2 wt. %, respectively. Ash forming elements such as K can be found in corn cobs in the concentrations of ca. 0.77 wt. % whereas in wood samples the concentrations are more than 10 times lower, from ca. 0.04 to 0.06 wt. %. Chlorine content of corn cobs is ca 0.37 wt. %, whereas it is <0.05 wt. % in both wood pellet samples.

Table 5.13 Elementary composition of fuels used in combustion experiments

Element	Corn cob	Wood pellets 1	Wood pellets 2
	wt. $\%_{dm}^{*}$		
C	48.879	50.000	50.000
H	7.769	6.700	6.600
N	0.108	0.250	<0.110
S	0.108	<0.210	<0.210
O	40.229	42.897	43.172
K	0.766	0.058	0.043
Na	0.006	<0.02	<0.020
P	0.019	<0.013	<0.013
Mg	0.019	0.016	0.019
Ca	0.006	0.076	0.104
Al	0.001	0.003	0.006
Cl	0.367	<0.050	<0.050
Si	0.019	<0.020	0.056
	mg/kg_{dm}^{*}		
Zn	14	$<100^{**}$	
Cu	4.70	$<10^{**}$	
Cr	<0.5	$<10^{**}$	
Cd	<0.2	$<0.5^{**}$	
Pb	<0.5	$<10^{**}$	

*dm - dry matter; **literature values from (Verma et al. 2012)

Discussion

When comparing elementary composition of selected fuels, corn cobs are characterized by a higher H content in average, whereas wood pellets have typically more C in the fuel. Characteristically high Cl and K content of corn cobs, in comparison to wood, is observed, making this fuel more challenging for combustion purposes. Ca content is distinctively higher in wood than in corn cobs, Si content is similar in first two samples, being three times higher in the third one, which could be due to presence of impurities in the wood such as soil and sand.

Content of Cl at 0.37 wt.% in this study is higher than 0,01 wt.% (as received) reported by (Krugly et al. 2014) for corn stalk pellets. Same can be said for S; here it was determined to be 0.11 wt.%, whereas (Krugly et al. 2014) assessed it at 0.028 wt.%. This can be explained by different cultivation practices, soil conditions, as well as difference in analytical methods. Content of heavy metals, more specifically, Zn at 14 mg/kg is comparable with values of 19.5 mg/kg reported by (Brunner et al. 2011), whereas copper concentration in our case at 4.7 mg/kg is lower than 11.8 mg/kg reported by (Brunner et al. 2011). Lead in our case is lower than the detection limit, whereas in the study by (Brunner et al. 2011) it was 0.5 mg/kg.

5.4.2 Combustion Phase one

Combustion experiments have been performed at the location of Hamburg University of Technology using Ozone 25 agro boiler. Below are the various results presented. Therefore, this part of this report is divided into subchapters based on experimental series. Here the emissions of CO and particulate matter (PM) are presented and discussed, as well as elementary composition of different ash fractions and crystalline phases in the ash. Finally, the energy efficiency of the process is discussed. Specifics of each combustion series and associated challenges and remarks are described in the respective sections.

5.4.2.1 Blends of corn cob pellets and wood pellets

5.4.2.1.1 Emission indicators and energy efficiency

Results

Emissions and efficiency. All values of emissions pollutants refer to standard conditions (0 °C, 1,013 mbar) and are related to 10 % O_2 and dry flue gas (according to EN 303-5). Average results from two replication are given in Table 5.14. Combustion experiments with blends of 50CCP (50 % corn cob pellets) and CCP (pure corn cob pellets) were performed only once, whereas the combustion experiments with all the other blends were performed twice.

Table 5.14 Average values of selected parameters from the combustion series “Blends of corn cob pellets and wood pellets”

	CO	NO	PM	Tfg[**]	Thermal capacity	Efficiency
	mg/Nm^{3}[*]			°C	kW	%
WP[a]	282±237.5	66±28	67±11.5	145±4.5	25±0.6	83±0.1
12.5CCP	189±0	80±0	164±0	125±12	25±0.4	95±5
25CCP	1326±1295.5	63±43	171±27	150±0.5	27±0.8	90±2.6
50CCP	3,627	110	349	153	31.8	98.5
CCP	6,750[***]	115	263	132	28.7	66.7

[*](dry gas, 0 °C, 1,013 mbar, 10 % O_2); [**]temperature of the flue gas, [***]calculated value

[a]for the list of abbreviations see Table 5.3

Table 5.15 gives an overview of average temperatures in the combustion chamber (in the center of the chamber, on the side of the burner).

Table 5.15 Average temperature in the combustion chamber and calculate excess-air from the series “Blends of corn cob and wood pellets”

Abbreviation	Temperature °C	Excess air -
WP[a]	515	5±2.2
12.5CCP	489	3±0
25CCP	679	6±4.2
50CCP	651	2.2
CCP	512	1.7

[a]for the list of abbreviations see Table 5.3

Discussion

CO Emissions. During initial combustion tests with pure corn cob pellets emissions of CO were 10-fold higher than with wood fuels. This could be traced back to fuel properties and fine-tuning of air-feeding used during this first combustion series to keep the heat output constant and minimize emissions. During each combustion experiment parameters such as lower heating value (LHV), air and fuel-feeding as well as air distribution between primary and secondary combustion air were adjusted. This turns out to be counterproductive. After mixing corn cob pellets with grade A1 pellets from a commercial trader the CO emissions considerably improved.

The values of CO emissions measured during the initial tests from the combustion of corn cob pellets were too high for the available equipment. In order to estimate this value anyway, corn cob pellets mixtures with wood were produced and combusted. Based on these values a regression analysis of the results has been performed. Based on the regression results with *R*-square of 0.59 the CO emission from the combustion of pure corn cob fuel was estimated at approximately 5.4 g/Nm^3.

Such a correlation between the CO emissions and the share of agro pellets in the blends with wood pellets are reported by (Juszczak und Lossy 2012). Following their findings, the CO emission increase is directly proportional with the share of agro pellets within the fuel blend. Therefore, the blends with > 50 wt.% wood pellets are more favorable from a CO emission reduction point of view. The calculations performed here have shown a Pearson coefficient of 0.77 between the content of corn cobs and CO emissions (Figure 5.9 and Figure 5.10).

The CO emissions measured in the first replication series from experiments with pure wood pellets and two blends (with 12.5 wt.% corn cob pellets and with 25 wt.% corn cob pellets) are in line with emission limit values (ELV) of 303-5 class 3 (< 3,000 mg/m^3). This is also true for the Serbian emission limit values ELV for old appliances (< 4,000 mg/m^3). Pure corn cob pellets without additional measures cannot comply with CO emission limit values, neither in Serbia nor in Germany.

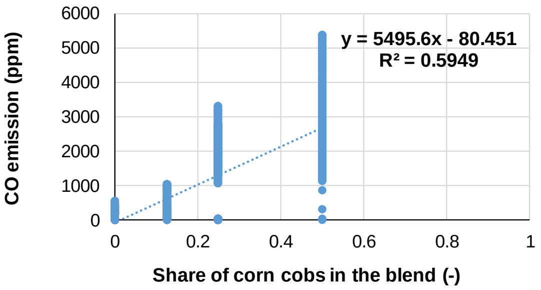


Figure 5.9 Regression analysis for CO emissions vs. corn cob share in the blend

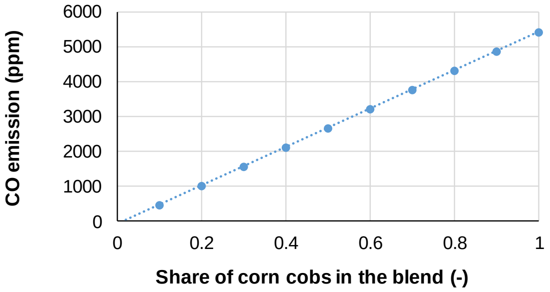


Figure 5.10 Predicted values of CO emission from pure corn cob combustion

A reduction of CO emission was observed in the second series of experiments, where air-feeding was kept constant. In the second experimental series constant thermal output was achieved by fine-tuning the fuel-feeding and heating value of the fuel, whereas air-feeding was kept unchanged throughout the experiment and set at the optimal values determined in previous series of experiments. In this case, blends of wood pellets with corn cob pellets are in line with the CO emission limit values from strictest class 5 in EN 303-5 (< 500 mg/m^3), the CO emission limit values from Serbian regulation for new units (< 800 mg/m^3), and in line with German BImSchV requirement (< 400 mg/m^3).

The optimal values of air-feeding have been shown to be 75/80/85 to 85/90/95. The deviations below and above this value result in the strong variations in the emissions and heat load, also preventing stationary process. This has been the most influential parameter on the CO emissions.

CO/CO_2 ratio of the first combustion series remained below 0.1 and ranged 0.0022 and 0.03, indicating complete combustion. Compared to that in the second series it varied significantly in the range between 0.0012 and 0.13.

NO_x Emissions. Since there are no emission limit values (ELV) published for small-scale combustion appliances, in comparison with ‘TA Luft’ emission limit values (ELV) all the experimental values of NO_x emissions comply with the requirements. Also NO_x emission limit value of 0.5 g/m^3 which is only applicable during type-testing (BImSchV), is met.

PM Emissions. For the particulate matter (PM) emissions a considerable difference can be observed when the share of corn cob pellets becomes dominant in the mixtures. All particulate matter (PM) emissions from the first series are ≤ 349 mg/m^3, even though the air-feeding was fine-tuned in order to minimize emissions. In the second series air-feeding was lowered and kept constant during entire burning phase resulting in no considerable changes in particulate matter (PM) emissions. The higher emission with 12.5 wt.% seem to be an outlier. Therefore, it seems that the previous setting was better suited for pellet blends. These values are reported for 10 % O_2 content, whereas the regulation BImSchV and Serbian regulation require reporting on a 13 % O_2-basis. However, even in this case the emissions would not comply with the requirements of the given standards. Therefore, the particulate matter (PM) emissions are identified as a crucial and critical parameter to be addressed to reduce negative environmental impact of small-scale combustion devices.

Stronger air-feeding dilutes the flue gas. Additionally, it also causes cooling of the combustion chamber and entrains the particulate matter (PM) from the grate so it becomes air-born.

Combustion efficiency. Combustion trials using blends of wood and corn cob pellets are characterized by highest efficiency values. The mean values of all combustion experiments were ca. 90 % meeting the strictest requirement of class 5 of the EN 303-5 (> 89 %), or at least class 4 (> 83 %). Only the combustion with pure corn cob pellets could not meet the efficiency requirements of any class, being well below 75 % (class 3). This could be possibly traced back to under-optimal combustion process (low combustion chamber temperatures). Since the combustion of pure corn cobs were among the first experiments performed, the optimal control of the process might not been given (by the user and the boiler control system).

Blending of wood pellets with agro pellets is feasible from the technical standpoint. Such a procedure would cause neither process disruptions nor reductions in efficiency.

5.4.2.1.2 Ash analysis

Results

Neither sintering nor deformation of the grate ash could be observed from the samples and from the inspection of the combustion chamber after the experiments. Therefore, no problems of this sort should be expected or experienced; but long-term monitoring studies are required to confirm this assumption (photographic representation of ash samples from this combustion series are given in the Supplementary Material).

Distribution of elements in different ash fractions. Distribution of ash-forming elements in three ash fractions (bottom ash, fly ash, particulate matter) are given in Figure 5.11 - Figure 5.15 and discussed below. Major bottom ash components (and similarly for fly ash) from the combustion of wood pellets are CaO, K_2O, MgO, and Fe_2O_3, whereas bottom ash from the combustion of corn cob pellets is dominated by K_2O, and the bottom ash samples from the combustion of fuel blends lie somewhere in between the previous two: ca. 20 to 30 wt.% of bottom ash is comprised of K_2O, followed by CaO, MgO, Al_2O_3 and Fe_2O_3. Fly ash from the combustion of wood pellets have the same composition as bottom ash, whereas fly ash from corn cob pellet combustion is mostly composed of K, chlorides, and sulphates. In the fly ash samples from the fuel blends (12.5 wt. %, 25 wt. %, and 50 wt. %) increased chlorine contents, in comparison with bottom ash from wood pellet combustion, are identified. Particulate matter samples from wood pellet combustion are dominated by sulphates and chlorides, whereas PM from corn cob combustion consists mostly of K and chlorides. Major PM components in PM samples from fuel blend combustion were K, chlorides, and sulphates.

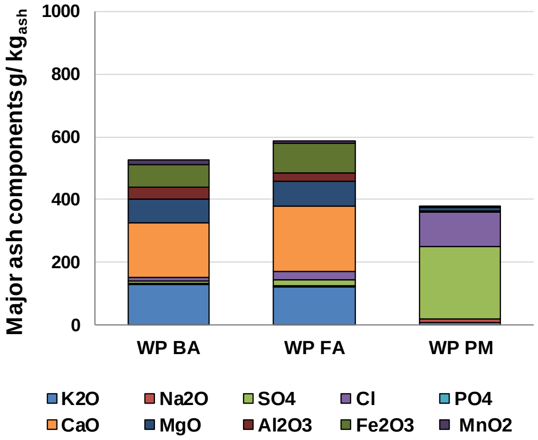


Figure 5.11 Major elements in samples ash fractions from the combustion of pure wood pellets; BA – bottom ash, PM – particulate matter

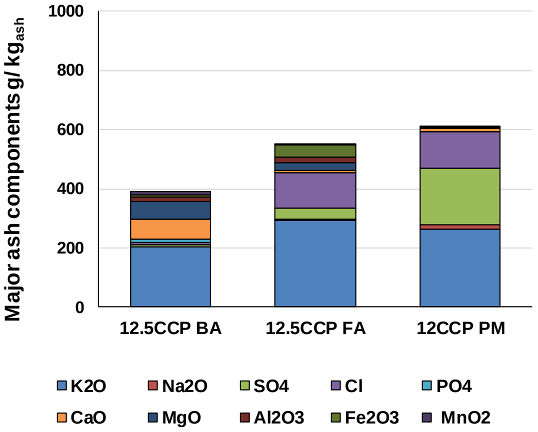


Figure 5.12 Major elements in samples ash fractions from the combustion of 12.5% corn cob pellets in blend with wood pellets; BA – bottom ash, PM – particulate matter

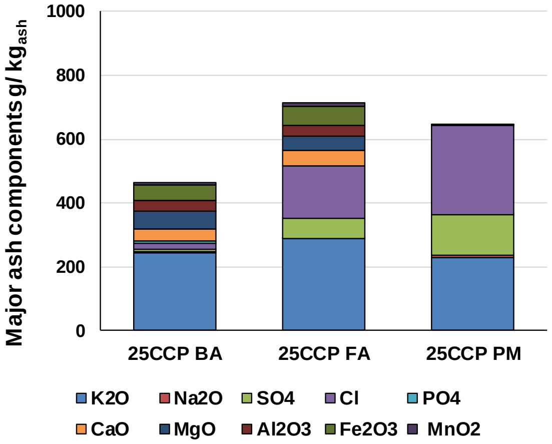


Figure 5.13 Major elements in samples ash fractions from the combustion of 25% corn cob pellets in blends with wood pellets; BA – bottom ash, PM – particulate matter

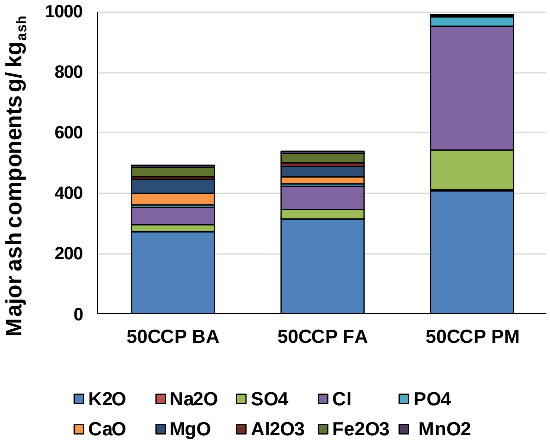


Figure 5.14 Major elements in samples ash fractions from the combustion of 50% corn cob pellets in blends with wood pellets; BA – bottom ash, PM – particulate matter

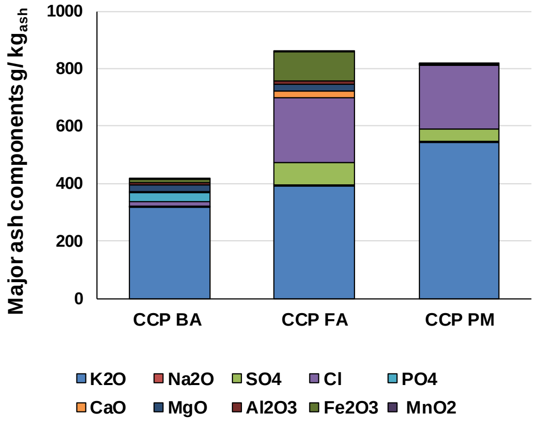


Figure 5.15 Major elements in samples ash fractions from the combustion of corn cob pellets in blends with wood pellets; BA – bottom ash, PM – particulate matter

Crystalline phases. An overview of the crystalline phases identified in the samples of grate (bottom) ash and fly ash is given in Table 5.16. In combustion tests with fuels where wood is the dominant component (wood pellets and 12.5 wt.% corn cob pellets), Ca-based species such as Ca-silicates, Ca-carbonates, and Ca-oxides are found. Different Mg-species such as silicates and salts have been identified across all samples. On the other hand, in pure corn cob ash only K-salts have been identified (KCl and K_3PO_4, K_2SO_4). In addition to this, KCl and $CaCO_3$ have been found in most samples.

Table 5.16 Crystalline phases in the ash samples of the experimental series “Blends of corn cob and wood pellets”

Crystalline phase	WP[a]	12.5CCP	25CCP	50CCP	CCP	Literature
$KAlSiO_4$	BA	BA			BA	(Dragutinovic et al. 2019), (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
$MgCO_3$	BA	BA				
CaO	FA	FA				(Olanders und Steenari 1995), (Boström et al. 2012), (Vamvuka et al. 2009), (Febrero et al. 2015); (Du et al. 2014), (Kaknics et al. 2017)
Ca_2SiO_4	FA					(Olanders und Steenari 1995), (Boström et al. 2012), (Ma et al. 2016), (Febrero et al. 2015); (Du et al. 2014), (Kaknics et al. 2017)
MgO	FA					(Huelsmann et al. 2019), (Hülsmann 2018), (Olanders und Steenari 1995), (Boström et al. 2012)
$CaCO_3$		BA		BA FA		(Huelsmann et al. 2019), (Wang et al. 2014), (Hülsmann 2018), (Olanders und Steenari 1995), (Vamvuka et al. 2009); (Du et al. 2014), (Kaknics et al. 2017), (Yao et al. 2016)
KCl		FA	FA	BA FA TA	FA	(Huelsmann et al. 2019), (Boström et al. 2012), (Xiao et al. 2011), (Ma et al. 2016); (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
$Ca(Mg,Al)(Si,Al)_2O_6$		FA				(Boström et al. 2012)

$CaSiO_3$	FA	BA			(Olanders und Steenari 1995), (Boström et al. 2012); (Dragutinovic et al. 2019)
$Mg_2P_2O_7$		BA	FA		
K_2SO_4		FA		BA	(Huelsmann et al. 2019), (Olanders und Steenari 1995), (Boström et al. 2012); (Du et al. 2014), (Kaknics et al. 2017), (Yao et al. 2016)

[a]for the list of abbreviations see Table 5.3

Discussion

Black color of sampled particulate matter (PM) indicates the presence of soot and incomplete combustion. Typically, this is in accordance with high CO emissions. In some cases of incomplete combustion, unburned hydrocarbons can be found both in the bottom ash and in the fly ash (combustion chamber wall deposits).

The one white-colored particulate matter (PM) filter in the case of 50CCP combustion is somewhat surprising, but underneath the white top-layer, a dark-colored layer of possibly soot and unburned material can be observed.

Distribution of elements in different ash fractions. The composition of bottom ash samples is in accordance with previous studies, where CaO and SiO_2 have been identified as major wood ash components (Huelsmann et al. 2019), (Misra et al. 1993), (Demirbas 2004), and K_2O and SiO_2 as major components of bottom ash from crop residues combustion ((Vassilev et al. 2010), (Dragutinovic et al. 2019). The unidentified species in bottom (and fly) ash could be the products of incomplete combustion, originating from hydrocarbon matrix decomposition.

Similar composition of bottom and fly ash in some experiments (e.g. for wood pellets and 50 wt. % corn cob pellets) indicates that there was entrainment of the bottom ash from the grate into the flue gas flow, subsequently depositing on the combustion chamber walls (fly ash). Composition of fly ash from the combustion of fuel blends is in accordance with the previous study by (Verma et al. 2012), where stabile oxides Al_2O_3, SiO_2, Fe_2O_3, and CaO were the major components of fly ash from crop residue combustion, possibly generated through solid-particle pathway during thermos-chemical conversion. The remaining share is assumed to be comprised of SiO_2 and soot. The increase in CaO content in the fly ash of pure corn cob pellets (CCP) are possibly due entrained with the flue gas (Brunner et al. 2011), (Verma et al. 2012). In comparison with bottom ash composition, fly ash samples have increased shares of sulfates and chlorides, possibly released in the form of gaseous form during thermos-chemical conversion reactions and subsequently condensed and deposited on the chamber walls and other surfaces. This is evident in the fly ash of pure corn cobs (CCP), where sulfates can be found in increased amounts and could be traced back to combustion chamber wall deposits (Niu et al. 2016).

In the particulate matter (PM) only the presence of K_2O could be detected with our methods, taking into consideration the elements (species) investigated. It is probable that the large unidentified share is composed of soot, but this was not investigated within this study. This assumption is supported by high emissions (CO and particulate matter (PM)) and the black color of all three ash fractions (see Supplementary Material). The increased concentrations of sulfates and chlorides in the particulate matter (PM) from the combustion of 12.5CCP blends are due to a higher content of S and Cl in crop residues than in wood (Brunner et al. 2011), (Dragutinovic et al. 2019), (Hülsmann 2018). During combustion alkali chlorides are becoming air-borne through the solid-gas-particle pathway, contributing to corrosion and PM formation (Höfer und Kaltschmitt 2017), (Boman 2005), (Boström et al. 2012). Alkali salts are major particulate matter forming species, contribution to approx. 95 wt.% in particulate matter (PM) composition (Johansson et al. 2003), (Brunner et al. 2011).

Crystalline phases. The presence of KCl and $CaCO_3$ indicates low temperatures in the combustion chamber (< 600 °C) being in accordance with the measured values (mentioned above). Lower temperatures prevent the sintering and melting of crop residue ashes. However, this is also preventing a complete combustion. The 3-*T* (temperature, turbulence, residence time) rule (e.g. (Kaltschmitt et al. 2016)) is not met in this case, since temperatures in the combustion chamber are not sufficiently high for complete devolatilisation and oxidation. One reason for low temperatures within the combustion chamber could be the inappropriate (unadjusted) air-feeding.

5.4.2.1.3 Corn cob grit with additives

In this experimental series, the option II (with additional measures) is investigated (Figure 2.4). Thus, the bulky fuel such as whole corn cobs are processed, producing corn cob grits (grinds) which can be used in automatically-fed combustion systems (boilers), creating a more efficient combustion process with minimal investments into the fuel upgrading. The second primary measure investigated in this experimental series is the application of additives. Additives are a primary measure to prevent pollution formation and emission, which has been proven effective in the combustion of wood fuels (Khalil et al. 2012), (Huelsmann et al. 2019), (Wolf et al. 2005), (Carroll und Finnan 2015), (Fournel et al. 2015), (Wang et al. 2012b). Results from this combustion series are presented below.

5.4.2.1.4 Emission indicators and energy efficiency

Results

Emissions and efficiency. All values of emissions pollutants refer to standard conditions (0 °C, 1,013 mbar, 10 % O_2 and dry flue gas) (EN 303-5). In the Table 5.17 average values from two replications are given. Specific results are discussed in the following paragraphs.

Table 5.17 Average values from selected combustion parameters from the experimental series “Corn cob grits with additives”

	CO	NO	PM	T_{fg}**	Thermal capacity	Efficiency
		mg/Nm3*		°C	kW	%
CCG[a]	4985±4542.5	125±10.5	970±41.5	142±22	32±0	65±0
CCG 1MGO	7482±4625	117±1	818±51.5	128±20.5	26±0.4	83±0.4
CCG 2MGO	2806±1304	129±15	724±74	121±13.5	25±0	80±0
CCG 1KAO	3252±3251.5	56±55.5	488±60.5	121±0	29±1.8	78±2.3
CCG 2KAO	1670±108.5	134±1.5	510±17.5	131±0	28±0.2	91±5.1

*(dry gas, 0 °C, 1013 mbar, 10 % O_2); **temperature of the flue gas

[a] for the list of abbreviations see Table 5.4

On overview of the average temperatures in the combustion chamber during combustion experiments is found in Table 5.18.

Table 5.18 Average temperature value in the combustion chamber from the experimental series “Corn cob grit with additives”

Fuel	Temperature °C
CCG[a]	410
CCG 1MGO	440
CCG 2MGO	490
CCG 1KAO	525
CCG 2KAO	570

[a]for the list of abbreviations see Table 4.4

Discussion

CO Emissions. Based on the results from the first combustion series**,** carbon monoxide (CO) emissions from the experiments with crushed corn cobs are higher by a factor of more than 5 in comparison with the combustion of pelletized fuel. Only the trials with 2 wt.% kaolin could meet the EN 303-5 class 3 requirement (< 3,000 mg/m^3).

The difference in the CO emissions become apparent when comparing two combustion series. In the series 1 air feeding was manually handled in order to compensate for the high emissions and to achieve constant thermal output, whereas in the second series the air-feeding was adjusted to the most adequate values (based on previous experiments) and kept constant. Constant heat output was achieved by adjusting fuel-feeding and heating value parameter in the boiler control system.

The reduction of CO emission in the second combustion after stabilizing the combustion air feeding series is quite significant. Based on these observations it can be concluded that the control system need fine-tuning and upgrading and there is a strong need that the control system is adequately adjusted to the respective fuel properties. Thus a more flexible combustion system would significantly improve the combustion quality and reduce the respective emissions. The CO emissions from all trials are in line with class 3 EN 303-5 (< 3,000 mg/m^3), some even with class 5 from EN 303-5 (< 500 mg/m^3).

NO$_x$ Emissions. In comparison with the German regulation ‘TA Luft’ emission limit values all experimental values of NO$_x$ emissions comply with these requirements. Emission limit value of 0.5 g/m^3 only applicable during type-testing (BImSchV) is met.

PM Emissions. After using 1 wt.% kaolin particulate matter (PM) emissions have dropped for > 50 wt.%, whereas using 2 wt.% kaolin particulate matter (PM) emission reduction is around 46 %. Based on current results the combustion trials with 1 wt.% kaolin is preferable.

In almost all experiments entrainment of the bottom ash into the gaseous phase in observed, originating most probably from the corn cob grit combustion (particles formed through solid-particle pathway) by the entrainment of powdery and inert additives (especially magnesium oxide) into the gaseous phase with the combustion air and flue gas flow.

Based on the comprehensive analysis of CO and particulate matter (PM) emissions, even after the improvements achieved through the stabilization of the air-feeding, the heating unit investigated here is not well-equipped for the combustion of crushed corn cobs. The effect of kaolin as additive is evident. However, still the particulate matter (PM) emissions are not meeting the emission limit values from EN 303-5.

Combustion efficiency. The combustion efficiencies from this series with corn cob grinds are lower than in the combustion series with pellets. Difficulties in maintaining stabile and constant thermal capacities have characterized this series. In order to control the thermal power, fuel and air-feeding have been manipulated manually, most probably disturbing combustion under stationary conditions. This could have led to a too short residence time of the solid fuel on the grate and thus to incomplete combustion (On overview of the average temperatures in the combustion chamber during combustion experiments is found in Table 4.18.). The efficiency values are mostly in accordance with class 3 (> 75 %), two in accordance with class 4 (> 83 %), and one with class 5 (> 89 %). The experiments with pure corn cob grinds again had the lowest efficiency, not meeting the requirements of the standard (< 75 % for class 3).

However, these were the first experimental trials. The operation of the boiler when using corn cob grinds as a solid fuel was optimized in subsequent trials. It is expected that the efficiency of combustion under real conditions could meet the requirements of class 3 (> 75 %). Moreover, since the amount of fly ash entrained from the grate is considerable, the deposition of fly ash on the surfaces of heat exchanger tubes might cause a reduction in heat transfer efficiency.

Moreover, although the combustion of grounded corn cobs is feasible and no ash melting issues have been registered, there has been sintering of the bottom ash and it is expected that during long-term operation serious problems could arise.

5.4.2.1.5 Ash analysis

Results

In the case of corn cob grinds without additive some agglomeration of the ash and formation of ash clumps are observed (photographic representation of ash samples from this combustion series are collected in a table in the Supplementary Material.). However, this did not cause problems due to moving grate preventing long residence times and sintering. During long-term operation this could lead to disruptions and malfunctions in the boiler. After additivation, no sintering of the ash in the combustion chamber is observed.

Distribution of elements in different ash fractions. Composition of bottom ash, fly ash (ash entrained from the grate and deposited on the combustion chamber walls and surfaces), and particulate matter (PM) for each corn cob pellet type from the second series of experiments (replication 2) are illustrated in Figure 5.16 till Figure 5.20 and discussed below.

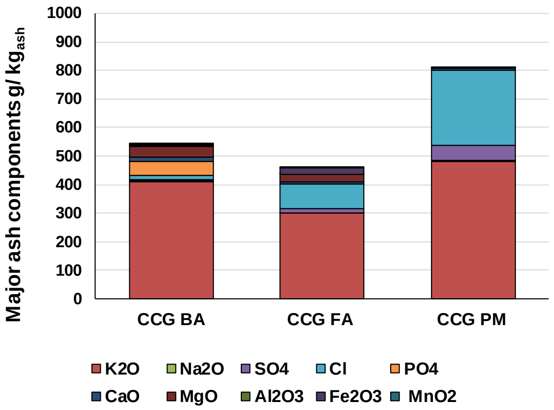


Figure 5.16 Major elements in samples ash fractions from the combustion of corn cob grit without additives; BA – bottom ash, PM – particulate matter

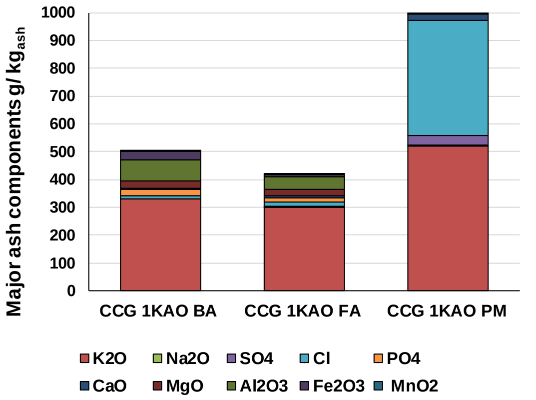


Figure 5.17 Major elements in samples ash fractions from the combustion of corn cob grit with 1 wt. % kaolin; BA – bottom ash, PM – particulate matter

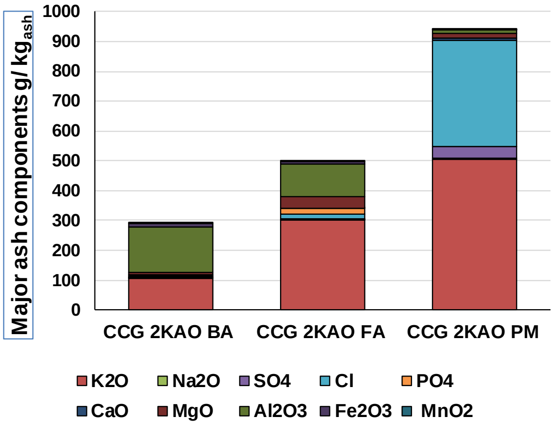


Figure 5.18 Major elements in samples ash fractions from the combustion of corn cob grit with 2 wt. % kaolin; BA – bottom ash, PM – particulate matter

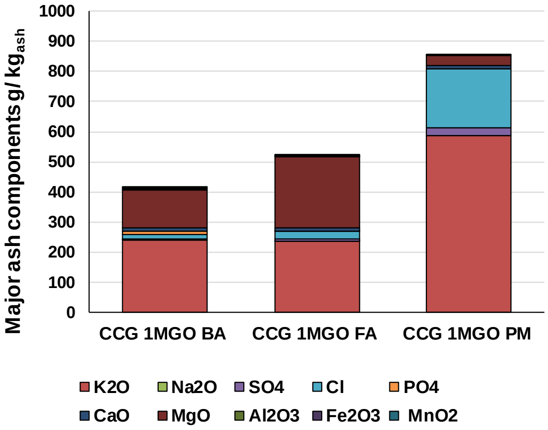


Figure 5.19 Major elements in samples ash fractions from the combustion of corn cob grit with 1 wt. % MgO; BA – bottom ash, PM – particulate matter

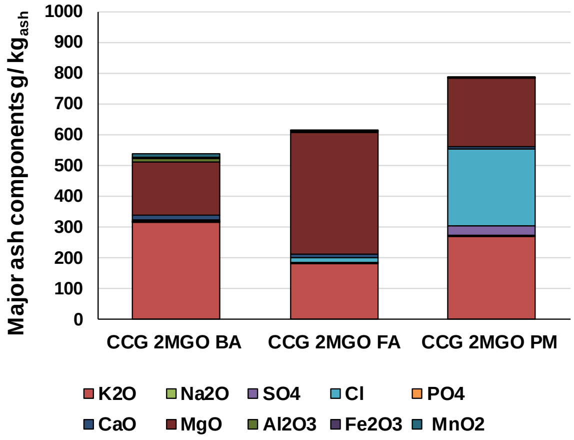


Figure 5.20 Major elements in samples ash fractions from the combustion of corn cob grit with 2 wt. % MgO; BA – bottom ash, PM – particulate matter

Crystalline phases. Overview of crystalline phases, identified in the samples of grate (bottom) ash and fly ash, is given in Table 5.19. KCl was identified in almost all samples of bottom ash and fly ash, followed by MgO. K-Al-silicates such as $KAlSiO_4$, $KAlSi_2O_6$, $KAlSi_3O_8$, as well as K_3AlO_3 were identified in bottom and fly ash samples with kaolin.

Table 5.19 Crystalline phases in the ash samples of the experimental series “Corn cob grit with additives”

Crystalline phase	CCG[a]	CCG 1 MGO	CCG 2MGO	CCG 1 KAO	CCG 2 KAO	Literature
KCl	FA	BA FA	FA	BA FA	BA FA	(Huelsmann et al. 2019), (Boström et al. 2012), (Xiao et al. 2011), (Ma et al. 2016); (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
SiO_2		FA			BA	(Du et al. 2014), (Yao et al. 2016)
$2CaO\cdot Al2O_3\cdot SiO_2$				FA	BA	
$KAlSiO_4$				BA	BA FA	(Dragutinovic et al. 2019), (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
$KAlSi_2O_6$					FA	(Yao et al. 2016)
$KAlSi_3O_8$		FA				(Vassilev et al. 2013a)
K_2MgSiO_4	BA				FA	
$Ca_2Al_2SiO_7$				BA		
K_3AlO_3		BA	BA FA			
MgO	BA FA	BA FA	BA FA		FA	
$MgCl_2$		FA	FA	FA		(Vassilev et al. 2013a)
$MgCO_3$			BA	FA		(Vassilev et al. 2013b), (Kalembkiewicz et al. 2018)
$Ca_3Al_2O_6$	BA					
$CaCl_2$		BA				(Vassilev et al. 2013b), (Vassilev et al. 2013a)

[a]for the list of abbreviations see Table 5.4

Discussion

Black color of the ash indicates the presence of unburned matter, in accordance with the efficiency values from the respective experiments, which show somewhat lower level of thermal efficiency.

Distribution of elements in different ash fractions. The crucial element in the formation and emission of particulate matter is potassium (K). It is usually expressed in its oxide form (K_2O) identified to be the main component of all bottom ash samples. In cases where kaolin was used as an additive, alumina is present in large concentrations both in the bottom and in the fly ash (due to additivation). The same can be concluded for cases with MgO addition. It is challenging to make conclusions about the enrichment of K in the bottom ash samples, since there is a dilution effect due to an increase in the ash content and the mineral nature of the additives. The reduction of K concentration in the ash sample with 2 wt.% kaolinite could be attributed to over-dosing of the fuel with additives and/or an analytical error, as well as sampling errors.

The entrainment of additives, especially MgO, from the bottom ash into fly ash is supported by high concentration of MgO in this ash fraction. This underlines the need to modify the mechanisms of the additive / fuel contact, since homogenizing ground corn cobs with powdery additive does not bring the desired effect. It is necessary either to introduce the additive into the combustion chamber in a different manner or mix it with the fuel prior to processing (e.g. before pelletizing). The effect of additivized pellets in combination with the optimal combustion process parameters will be investigated in the subsequent study.

The composition of particulate matter (PM) samples is almost entirely accounted for, and is made up mostly from K, S, and Cl species. This is in accordance with previous findings (Niu et al. 2016), (Vassilev et al. 2013a), (Brunner et al. 2011). Exception can be observed in the case of 2 wt.% MgO addition, where a large share of PM is composed of Mg. This could be due to the fine particle nature of the MgO additive, making it light and easily air-borne, as well as due to increase air-feeding. In this experiment, it is possible that large amounts of bottom ash were carried away with the flue gas, since the compositions of bottom and fly ash as well as particulate matter (PM) are similar.

Crystalline phases. In the ash samples from the combustion experiment without additives the most common potassium species, KCl, is found in the fly ash, in accordance with the solid-gaseous-particle pathway and previous studies (Nunes et al. 2016). When kaolin was used as an additive, K-Al-silicates are formed, in accordance with previous studies (Gollmer et al. 2019), (Höfer und Kaltschmitt 2017). In the trials with kaolin K-Al-silicates are found both in bottom and fly ash samples, indicating the entrainment of the ash from the grate into the gaseous phase. Ash samples from trials with MgO as an additive also show the presence of KCl both in the bottom and in the fly ash. In this case, KCl was partially volatilized and condensed, since the temperature were not high enough for full devolatilization, or the residence time was too short. MgO and other Mg-species (e.g. Mg-chloride) could be found in the ash. Ca and Mg are naturally found in the biomass in the form of chlorides (Shao et al. 2012).

5.4.3 Combustion Phase two

5.4.3.1 Blends of corn cob pellets and wood pellets

5.4.3.1.1 Emission indicators and energy efficiency

Results

Emissions and efficiency. All values of emissions pollutants refer to standard conditions (0 °C, 1,013 mbar) and are related to 10 % O_2 and dry flue gas (according to EN 303-5). Average values of emissions and efficiency indicators from the two replications are found in Table 5.20.

Table 5.20 Combustion indicators from the „Blends of corn cob pellets and wood pellets"

	CO	NO	PM	Thermal capacity	Efficiency
		mg/Nm^{3*}		kW	%
WP[a]	241	152	39 ± 0.5	5.7 ± 0.4	92.6 ± 0.1
12.5CCP	342	157	88 ± 1.6	6.1 ± 0	93.3 ± 0.1
25CCP	538 ± 107	165 ± 2.6	120 ± 0.5	5.7 ± 0.1	92.7 ± 0.6
50CCP	725 ± 342	160 ± 5.5	184 ± 0.3	5.1 ± 1.2	92.8 ± 0.3
CCP	2040 ± 1114	170 ± 31.5	463 ± 5	7 ± 0.2	92.4 ± 0.1

[*] dry gas, 0 °C, 1013 mbar, 10 % O_2

[a] For the list of abbreviations see Table 5.5

Particle size distribution. Total mass and number concentrations from the combustion of fuel blends are presented in Table 5.21. Ultra-fine fractions $PM_{0.1}$, $PM_{0.5}$, and PM_1 make up for almost 100 % of the overall particulate matter (PM).

Table 5.21 Summary of particle size distribution measurements the combustion of fuel blends

	Total number concentration 1/cm³	Total mass Concentration ug/m³
CCP[a]	2.26E+06	3,692
50CCP	8.27E+05	368
25CCP	2.87E+06	2,045
12.5CCP	6.42E+05	909
WP	4.49E+06	1,616

[a]For the list of abbreviations see Table 5.5

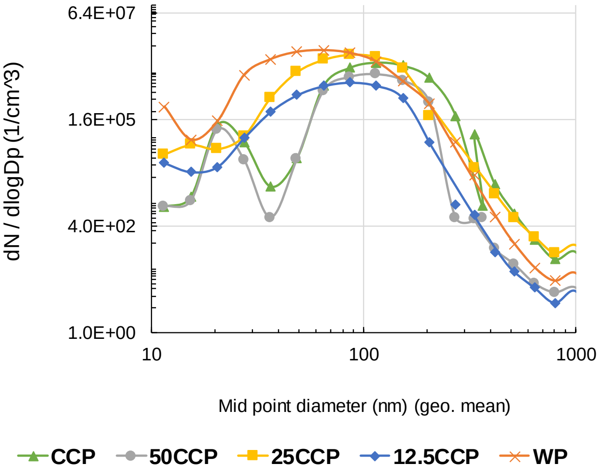


Figure 5.21 Number size distribution of particles from the combustion of fuel blends

Discussion

CO Emissions. The increase in carbon monoxide emissions with the increasing corn cob pellet share in the blends is evident with 0.98 Pearson correlation coefficient. According to current emission values, combustion of wood pellets and blends of 12.5 wt.% of corn cob pellets within wood pellets are in line with the strictest requirements of EN 303-5 (500 mg/m^3) and BImSchV. (400 mg/m^3), whereas the emissions from other blends are in line with class 3 or class 4 from the standard.

A study by (Brunner et al. 2011) reported average CO values of 15.6 mg/Nm^3 (related to 13 vol.% O_2 and dry flue gas), whereas NO emissions were on average 240 mg/Nm^3. There is significant room for improvement regarding the potential for CO emission reduction (i.e. to reach a full oxidation of all fuel components). However, the CO emission values are lower in our experiments than previously reported. A study by (Verma et al. 2012) indicate CO emissions from the small-scale wheat straw pellet combustion to be in some cases 500 mg/Nm^3. This is in general in line with our measurements. (Roy und Corscadden 2012) reported CO emission being ca. 2,000 mg/Nm^3 from the combustion of hay briquettes. This is also in accordance with our results. CO emission values of >1,000 mg/Nm^3 are characteristic of manual heating units. These CO emissions might result from low combustion temperature, poor mixing of the unburnt components with combustion air and / or too short residence time. In our experiments excess air coefficient ranged between 2.2 and 2.4 (calculation) during combustion of pure corn cob pellets. These relative high values could have been the reason for low temperatures in the combustion chamber resulting in high CO emissions. A study by (Schmidl et al. 2011) measured the CO emissions from the combustion of triticale pellets in a multi-fuel 40 kW boiler under full load conditions in a stationary phase to be 78 mg/Nm^3 (13 vol.% O_2). This is lower than the values from our study. (Carvalho et al. 2013) reported average CO emissions of ca. 100 mg/MJ during the combustion of maize (in comparison to ca. 330 mg/MJ limit value according to ENE 303-5). The CO emissions from our study correspond to 640 mg/MJ; i.e., they are higher. (Krugly et al. 2014) reported CO emission from the combustion of corn stalk pellets to be ca. 5.2 g/kg; our CO emissions could be expressed as 9.8 g/kg on average.

NO_x Emissions. As in previous cases, all NO emission values are in accordance with ‘TA Luft’ and ‘BImSchV’ emission limit values (ELV).

PM emissions. Even the combustion of wood pellets resulted in particulate matter emissions higher than emission limit values from BImSchV. Compared with the emission limit values from EN 303-5, the three fuel blends wood pellets, blends with 12.5 wt.% corn cob pellets and blends with 25 wt.% corn cob pellets meet the requirements of class 3 (≤ 150 mg/m^3). Emission values from the other blends are higher than these values. Based on this, only the combustion of up to 25 wt.% corn cob pellets in fuel blends would be in line with the regulatory requirements. This allows for a strongly limited fuel flexibility within the heating period and does not allow an independence from the wood pellet market.

According to a study by (Brunner et al. 2011) total particulate matter (PM) emissions from the combustion of corn cobs after the multi-cyclone were ca. 92 mg/Nm^3; the PM1 emissions contribute with 90.7 mg/Nm^3 to the total particulate matter (PM) emissions. (Roy und Corscadden 2012) reported ca. 180 mg/Nm^3 emission of particulate matter (PM) from the combustion of hay briquettes. (Schmidl et al. 2011) reported PM emissions from the combustion of triticale pellets in a multi-fuel boiler during full load combustion and stationary phase to be 183 mg/Nm^3 (13 vol.% O_2); these results are comparable to our values. (Johansson et al. 2003) measured mass concentration of particles from the combustion of wood pellets and briquettes between 34 and 240 mg/Nm^3. (Zeng et al. 2016) investigated the fuel blends of pinewood, Miscanthus, and straw. He found out that increasing the straw share in the blends coincides with the increase in total particulate matter (PM) emissions, but not with CO emission increase (due to the geometry of the boiler designed for agro fuels lower emissions were achieved using agro fuels than with wood fuel). The optimal blend share was found to be 70 wt.% wood with 30 wt.% Miscanthus. They also found that in real-life conditions the blend of 50 wt.% wood with 50 wt.% Miscanthus meet the requirements (emission limit values) of the EN 303-5 standard. (Carvalho et al. 2013) reported total particulate matter (PM) emissions from the boiler when burning maize of ca. 90 mg/MJ (in comparison with emission limit value of ca. 133 mg/MJ). Emissions of particulate matter (PM) from corn cob pellet combustion in our study in relation to input fuel energy are 143 mg/MJ on average. This is somewhat higher compared to the values from the study mentioned above, but within a similar order of magnitude. (Verma et al. 2012) reported particulate matter (PM) emissions from agro pellet combustion in small-scale units to range from 13.8 for reed canary grass pellets to 657.7 mg/Nm^3 for sunflower husk pellets. Authors attribute low Si content of sunflower husks as potential cause of high emissions due to a lack of silicates to facilitate alkali sorption in the bottom ash. Total particulate matter (PM) emissions from the combustion of corn stalk pellets has been reported by (Krugly et al. 2014) with 88 g/kg whereas the particulate matter (PM) emissions from the combustion of corn cob pellets on average in our experiment were 2.2 g/kg.

Particle size distribution. Total number concentrations of particles from fuel blend combustion range between $6\cdot10^5$ and $4.5\cdot10^6$ 1/cm^3. The trend of increasing particulate matter mass concentration with increasing corn cob pellet share is observable and reasonably correlated (Pearson coefficient 0.72).

Particle number size distributions from the combustion of pellet blends have modes ranging from 80 nm to 120 nm (Figure 5.21). Mode of particle number distribution from wood pellet combustion is found at ca. 80 nm with the value of $8\cdot10^6$ 1/cm^3. The trend of increasing particle mode diameters size follow the increasing share of corn cob pellets in the fuel blend, ending at ca. 120 nm with $4\cdot10^6$ 1/cm^3 for the mode middle point diameter for particles from the combustion of corn cob pellets. The number concentration values for the emissions from the combustion other fuel blends fall in between these two values. In the PM number size distributions from the combustion of 50 wt. % corn cob pellets (50CCP) and corn cob pellets

(CCP) a second mode in the nucleation and Aitken region are observed, possibly indicating nucleation, as in (Krugly et al. 2014), (Lamberg et al. 2011).

The the presence of ultra-fine particles in the PM from wood pellet combustion is in line with the results of SEM imaging (see next chapter 5.4.2.1.2), where the particulate matter sampled on the filter was in the range <200 nm, made up of network of uniform-sized particles, whereas the particulate matter from corn cob combustion was made of two distinct particle sizes (networks).

Previous studies reported different patterns of mass and number size distributions from the combustion of biomass.

In a study by (Brunner et al. 2011) particle size distribution measurement after the multi-cyclone using a low-pressure impactor (related to 13 wt. % O_2 content and dry flue gas) revealed a unimodal distribution with a distinct mode between 125 and 250 nm, which is in line with our results from corn cob pellet combustion. In the same study total PM mass emission amounted to 90.7 mg/Nm^3. (Bäfver et al. 2011) reported a unimode particle number size distribution from the combustion of wood pellets in a modern pellet oven with mode at ca. 100 nm and concentration at ca. 10^8 1/ cm^3. Most of the particles were found in the fine particle size range (<1 µm). (Verma et al. 2012) reported the particle sizes from wood pellet combustion ranged between 300 nm and 1.2 µm in diameter with the majority of the particles between 300 and 900 nm in diameter. (Johansson et al. 2003) measured mass concentration of particles from combustion of wood pellets and briquettes of 34 to 240 mg/Nm^3, which were dominated by submicron particles with a maximum size in the range 80 to 200 nm. The number concentrations from domestic heating devices varied between $1.4 \cdot 10^7$ and $13 \cdot 10^7$ particles per Nm^3 with unimodal distribution and mode at 80 to 300 nm, which is in line with our measurement of PM number size distribution from wood pellet combustion.

Bimodal distribution of particulate matter mass and / or number size from the combustion of biomass was reported in several investigations. (Krugly et al. 2014) reported bimodal number size distribution from the combustion of corn stalk pellets; one mode being in the range of 0.017 to 0.03 µm, reflecting nucleation, and a second one between 0.26 and 0.64 µm, reflecting accumulation. Mass size distribution from the same study revealed a unimodal distribution with a peak at 0.5 µm. (Lamberg et al. 2011) reported the particulate matter number distribution as bimodal, with Aitken modes and accumulation modes. (Sippula et al. 2009) measured a bimodal PM mass distribution with (1) fine mode at 0.1 to 0.2 µm, and (2) coarse mode at ca. 3 µm, but an unimodal PM number size distribution with geometric mean particle sizes from 96 to 147 nm (after the filtration units). In another study (Sippula et al. 2017) measured a bimodal particle mass size distributions with a fine particle mode (d_p[1] < 1 µm) ranging from 0.1 to 0.2 µm and coarse particle modes (d_p 1–10 µm) at 5.1 µm.

The size distribution patterns are reported to depend on many factors, including sample conditioning, combustion devices and techniques, as well as combustion conditions. Some of the influencing factors could be flue gas residence time and temperature in the burner, the load of the fuel, the air excess ratio, as well as type, composition, and geometry of the fuel (Krugly et al. 2014). Even tough for each of our experiment the operating parameters were kept the same (load, air and fuel-feeding rates), some conditions such as slight weather changes (atmospheric temperature and pressure) could not be influenced.

---

[1] d_p - particle diameter, also used instead of d_a – Aerodynamic diameter (d_a) is defined as the diameter of a unit density sphere (1 g/cm^3) having the same settling velocity (due to gravity) as the particle of interest of whatever shape and density (Kaltschmitt et al. 2016.)

Energy efficiency. Efficiencies of the combustions processes in this series are always above 75 %; i.e. all requirements of EN 14785 are fulfilled. Efficiency values are in line with literature findings. (Carvalho et al. 2013) reported efficiency between 79 and 91 % when combustion agricultural residues in a 15 kW pellet oven. Specifically, when using maize as a fuel the combustion efficiency was reported to be ca. 83 to 89 %.

5.4.3.1.2 Ash analysis

Results

An overview of photographs of ash and particulate matter samples can be found in Supplementary Material. Ash samples from woody pellet combustion are characterized by dark color, whereas after combustion of the fuel blend with 12.5 wt. % corn cob, even some unburned pellets and charcoal were found in the grate residue. Moving towards blends with a higher share of corn cob pellets, the ash amounts increase and the ash color becomes more light grey; this trend is present both in bottom / fly ash samples as in particulate matter samples. The bottom ash from the combustion of corn cob samples is characteristically green / turquoise in color, mixed with light grey (as already known from the previous laboratory-scale experiments).

In the combustion trials with corn cob pellets there were no issues regarding sintering of the ash, although this could become a major problem during long-term combustion in real conditions.

Distribution of elements in different ash fractions. Average distributions of most important ash-forming species from two series (replications) are given in the Figure 5.22 till Figure 5.26. For the list of abbreviations see Table 5.5.

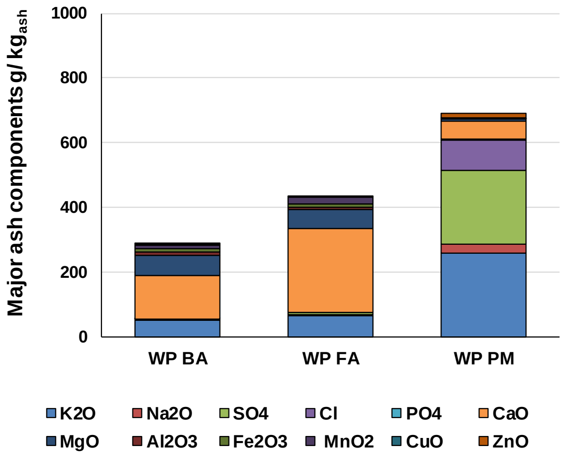


Figure 5.22 Average values of major ash-forming species in different ash fractions from the combustion of pure wood pellets; BA – bottom ash, PM – particulate matter

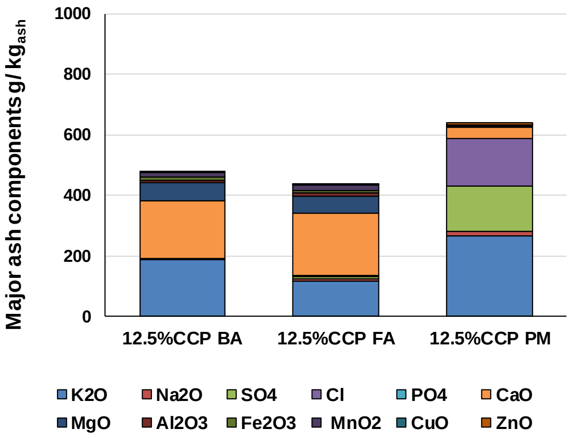


Figure 5.23 Average values of major ash-forming species in different ash fractions from the combustion of 12.5 wt. % corn cob pellets; BA – bottom ash, PM – particulate matter

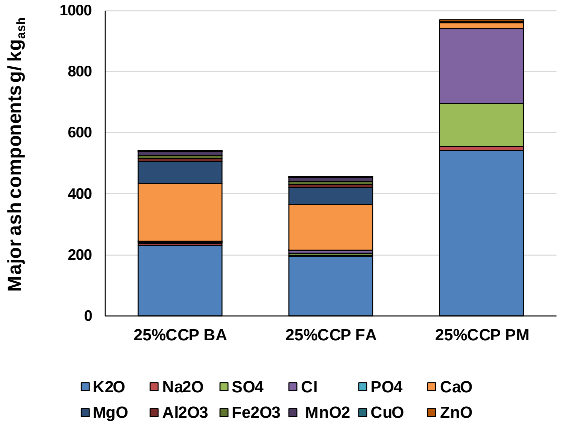


Figure 5.24 Average values of major ash-forming species in different ash fractions from the combustion of 25 wt. % corn cob pellets; BA – bottom ash, PM – particulate matter

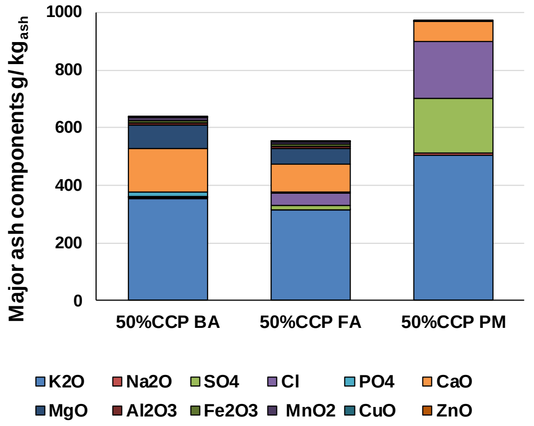


Figure 5.25 Average values of major ash-forming species in different ash fractions from the combustion of 50 wt. % corn cob pellets; BA – bottom ash, PM – particulate matter

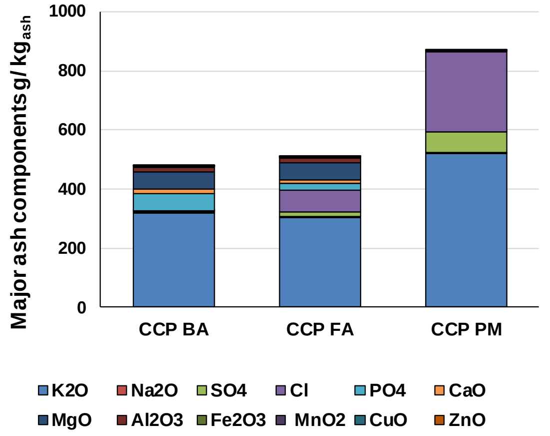


Figure 5.26 Average values of major ash-forming species in different ash fractions from the combustion of pure corn cob pellets; BA – bottom ash, PM – particulate matter

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM / EDS). The results of SEM imaging of selected samples from this combustion series (see Table 5.2 for the list of analyzed samples) are presented and discussed in the following paragraphs (Figure 5.27 till Figure 5.44) and the results from EDS measurements can be found in (Table 5.22). Abbreviation BA in the figures refers to bottom ash, whereas PM refer to particulate matter. Bottom ash samples where corn cob pellets are dominant share the filament structure, possibly remains of the cell structure wall, whereas wood pellet ash has undistinctive powdery ash with some clusters. Particulate matter samples from blends where corn cob pellets are dominant share the same characteristic structure of two interlocking networks of agglomerations.

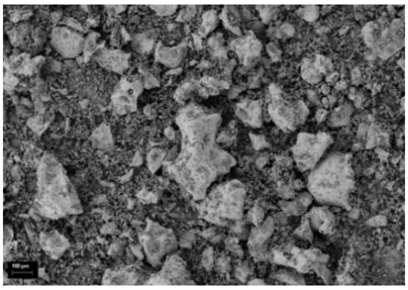


Figure 5.27 SEM image of WP BA

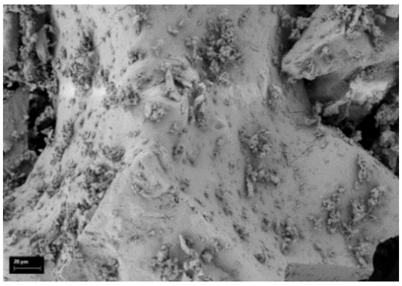


Figure 5.28 SEM image of WP BA

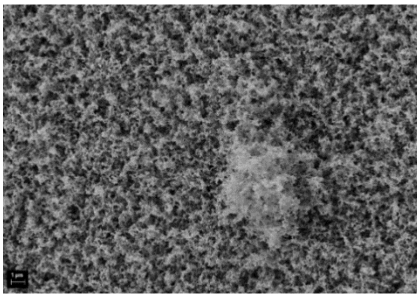


Figure 5.29 SEM image of WP PM

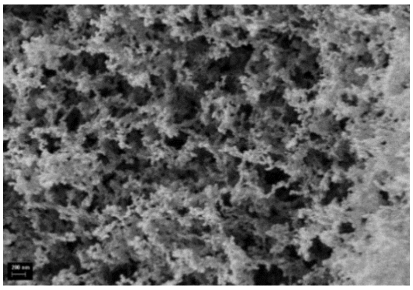


Figure 5.30 SEM image of WP PM

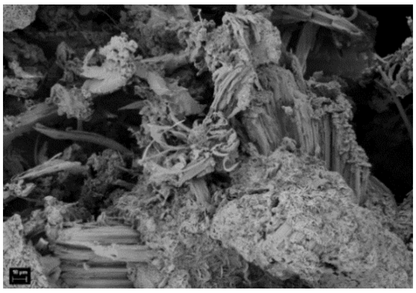


Figure 5.31 SEM image of 50 CCP BA

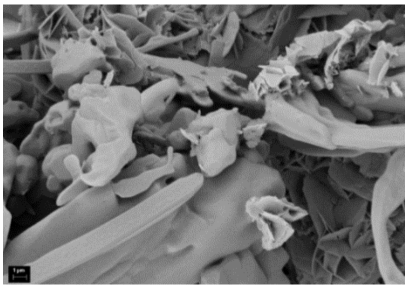


Figure 5.32 SEM image of 50 CCP BA

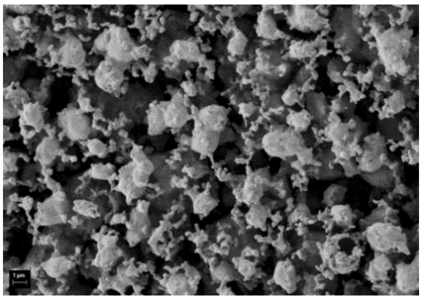


Figure 5.33 SEM image of 50 CCP PM

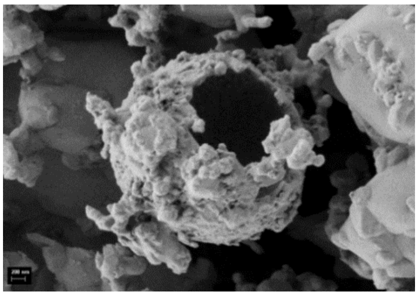


Figure 5.34 SEM image of 50 CCP PM

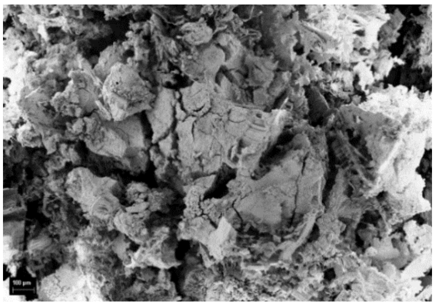


Figure 5.35 SEM image of CCP BA

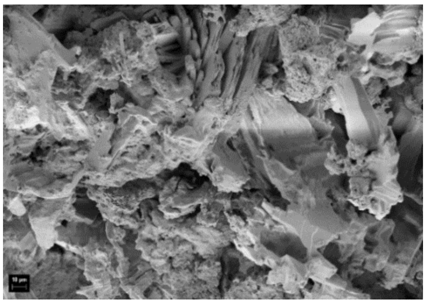


Figure 5.36 SEM image of CCP BA

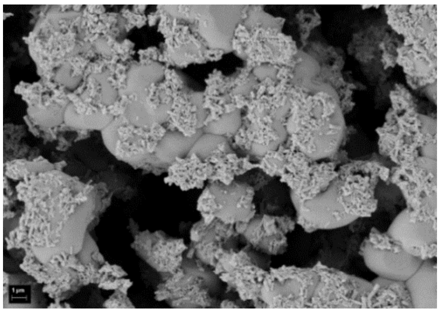


Figure 5.37 SEM image of CCP PM

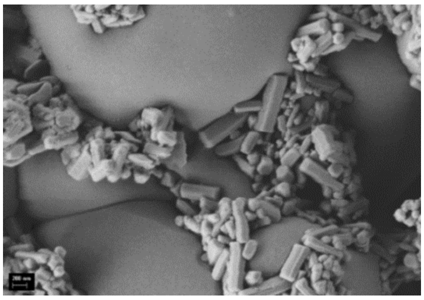


Figure 5.38 SEM image of CCP PM

EDS analysis was used to scan surfaces and spots in selected bottom ash and particulate matter samples from this series (for the list of selected samples see Table 5.2) for elementary composition; the summary of results is given in Table 5.22. The images indicating the scanned regions are given in Figure 5.39 till Figure 5.44. Major elements in the bottom ash from wood pellets combustion are Ca, Si, Co, and O, whereas elements in the bottom ash from corn cob pellet combustion are K, C, and O. Particulate matter composition is similar across the experimental series, consisting of K, S, C, O, and Cl.

Table 5.22 Composition of solid residues from “Blends of corn cob pellets and wood pellets” analyzed with EDS

element (norm, wt. %)	WP[a] BA[b]		WP PM		50CCP BA		50 CCP PM			CCP BA		CCP PM		
	1*	2**	1*	2**	1*	2**	1**	2**	3*	1*	2**	1*	2**	3*
K	5.9	5.5	19.1	22.2	32.9	36.2	57.4	36.1	43.1	28.3	19.5	35.9	36.0	35.0
Na	0.2	0.2								0.1	0.3			
Ca	21.6	21.6			4.3	1.5				1.2	1.9			
Mg	3.1	3.2			0.7	0.4				1.7	4.9			
Si	11.0	10.4	1.1		1.5	0.8				2.3	7.0	0.2		0.6
Al	0.9	1.0			0.2	0.2				0.5	1.0	0.1		0.1
P	1.8	2.3			1.3	0.7				2.0	3.1			
S			4.2					13.0	6.6			3.8	3.7	3.4
C	13.5	12.6	53.6	53.5	16.1	16.3		15.7	14.7	19.5	18.5	18.5	16.9	19.9
O	38.1	39.1	14.5	15.9	42.9	44.1		26.8	12.3	44.1	42.0	15.5	18.0	15.5
Cl			7.7	8.4	0.2		42.6	8.4	23.3	0.4	0.9	26.0	25.5	25.4
Fe	1.5	1.4												
Mn	2.6	2.5												

*surface **spot

[a] For the list of abbreviations see Table 5.5

[b] BA – bottom ash, PM – particulate matter

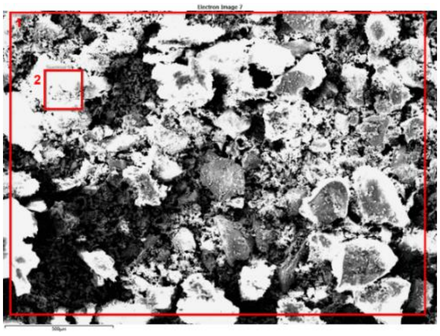


Figure 5.39 WP BA with scanned regions

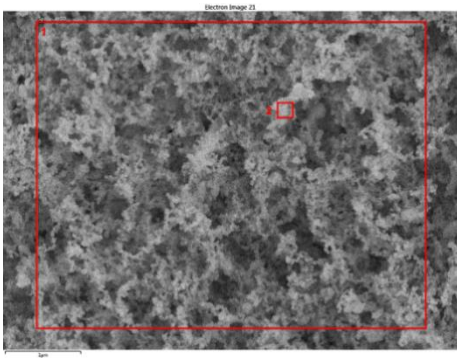


Figure 5.40 WP PM with scanned regions

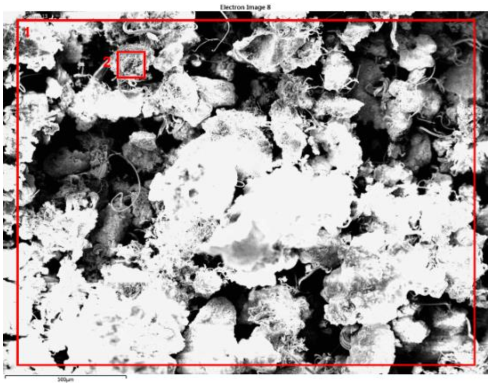


Figure 5.41 50 CCP BA with scanned regions

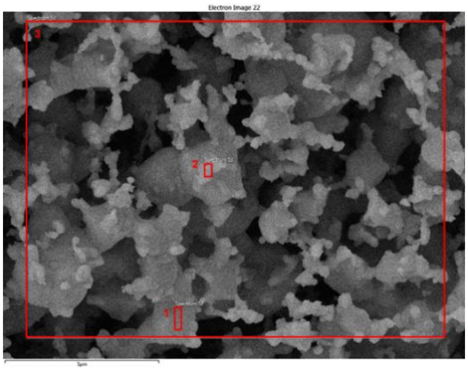


Figure 5.42 50 CCP PM with scanned regions

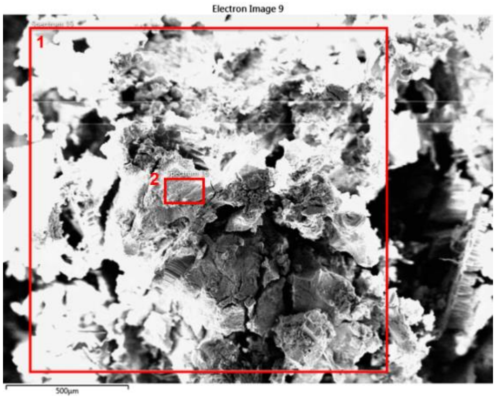


Figure 5.43 CCP BA with scanned regions

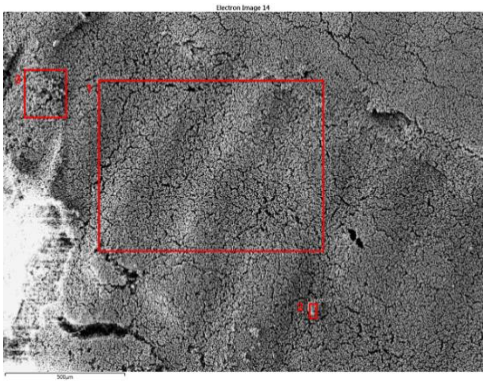


Figure 5.44 CCP PM with scanned regions

Crystalline phases. The overview of most important crystalline phases detected in the bottom and fly ash samples from the two replications are presented in Table 5.23.

Table 5.23 Major crystalline phases from the combustion of “Blends of corn cob pellets and wood pellets”

Crystalline phase	WP[a]	12,5%CCP	25%CCP	50%CCP	CCP	Literature
SiO_2	BA[b] FA	BA FA	BA FA	FA		(Yao et al. 2016), (Vassilev et al. 2013a), (THY et al. 2006), (Boström et al. 2012), (Höfer und Kaltschmitt 2017) ,
$CaCO_3$	BA FA	FA	BA FA	FA	BA	(Huelsmann et al. 2019), (Wang et al. 2014), (Hülsmann 2018), (Olanders und Steenari 1995), (Vamvuka et al. 2009), (Du et al. 2014), (Kaknics et al. 2017), (Yao et al. 2016)
C	BA FA	BA FA	FA	FA		
KCl				BA FA	BA FA	(Huelsmann et al. 2019), (Boström et al. 2012), (Xiao et al. 2011), (Ma et al. 2016); (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
Al_2O_3		BA				(Höfer und Kaltschmitt 2017), (Hülsmann 2018)
MgO				BA		(Boström et al. 2012), (Höfer und Kaltschmitt 2017)
$2K_2CO_3{\cdot}3H_2O$					BA FA	
$K_5P_3O_{10}$					BA	
$CaMn_{14}SiO_{24}$		BA	BA	BA		(Sarenbo et al. 2009)
NaCl				BA		(Hülsmann 2018)
$Ca_3Al_2O_6$	FA					(Hülsmann 2018)

[a] For the list of abbreviations see Table 5.5

[b] BA – bottom ash, PM – particulate matter

Discussion

The black color of all ash samples including particulate matter from wood pellet combustion possibly indicates the presence of to soot and other unburned hydrocarbons. Although there were no issues with ash deformation during corn cob pellet combustion, a clear tendency toward agglomeration is evident form the photographs and known from previous studies (Dragutinovic et al. 2019). Therefore, the possible sintering of bottom ash during long-term real-life operation cannot be excluded.

Distribution of elements in different ash fractions. As with previous experiments in the 25 kW boiler (section 5.4.2), the main components of bottom ash from wood pellet combustion are CaO, K_2O, and MgO. The same composition is observed for the bottom ash and the fly ash, indicating grate ash entrainment. Only ca. 30 wt.% of grate ash can be accounted for with major elements, indicating that the other unaccounted share is possibly carbon (soot) and unburned hydrocarbons as well as the other major ash component silica. Carbon presence is corroborated by the dark color of the sampled particulate matter in the case of wood pellet combustion. Moving away from wood towards crop residues in the fuel blends, it can be noticed that K-species' and chlorides' concentration increase steadily, reaching maximum value with bottom ash from pure corn cob pellet combustion. The reverse trend is observed for CaO and sulfate concentrations. Phosphates are detected in larger amounts only in corn cob bottom ash, and in minor concentrations in fly ash of the same fuel. Since the pellet oven used here is not constructed for agro pellets and other herbaceous fuel characterized by a high ash content, large amounts of grate ash were entrained with the flue gas and deposited on the combustion chamber walls, as well as carried away with the flue gas.

In general, particulate matter composition has been well accounted for, in most cases almost 100 wt.%, except in the case of pure wood pellets and 12.5 wt.% corn cob pellets. The composition of particulate matter from wood pellet combustion is mostly comprised of K_2O or similar K-species, most probably K-salts, in accordance with high sulfate and chlorides concentrations in the particulate matter. There is also CaO identified in the particulate matter, possibly from the coarser fraction of PM formed through solid-particle pathway. It is expected that the rest (the unidentified matter) is made of soot and other products of incomplete combustion. The increased concentrations of sulfates and chlorides in the particulate matter (PM) from the combustion of 12.5CCP blends are due to a higher content of S and Cl in crop residues than in wood (Brunner et al. 2011), (Dragutinovic et al. 2019), (Hülsmann 2018). During combustion alkali chlorides are becoming air-borne and go through the solid-gas-particle pathway, contributing to corrosion and particulate matter formation (Höfer und Kaltschmitt 2017), (Boman 2005), (Boström et al. 2012). Alkali salts are major particulate matter forming species, contribution to approx. 95 wt.% in particulate matter (PM) composition (Johansson et al. 2003), (Brunner et al. 2011). The unidentified species in bottom and fly ash could be the products of incomplete combustion.

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM / EDS). SEM image of wood pellet bottom ash (Figure 5.27) shows its heterogeneous nature, where fine powdery particles are dispersed between the larger clusters. Under larger magnification of SEM (Figure 5.28), the smooth surface of the ash is visible. No signs of sintering or melting of the ash can be observed. The uniform structure of the particulate matter from the combustion of wood pellets are evident from SEM image in Figure 5.29, where the ultrafine structures in the nm range dominate the particulate matter (Figure 5.30), also visible under larger magnification. Most primary particles are with average diameter of <100 nm, in some cases agglomerating and forming clusters of several μm in size. Similar findings were reported in previous studies, (Boman et al. 2004) reported that ca. 90 wt. % of total particulate matter from wood combustion in made from PM_1 particles. (Sippula et al. 2009) reported that the fine particles from wood combustion mainly consisted of agglomerates of few primary particles characterized by a compact.

In comparison with SEM images of bottom ash from wood pellet combustion, SEM images of bottom ash samples from 50CCP (50% corn cob pellets) fuel blend combustion (Figure 5.31 and Figure 5.32) show different structure and appearance. The filament structure from the biomass cells is evident under both magnifications and some crystalline structures can be observed (as reported in (Anukam et al. 2017). The ash is comprised of two distinct ash types: fine powdery ash from wood pellets, and filament ash from crop residues. In the particulate matter SEM images (Figure 5.33 and Figure 5.34) distinct structure can be observed: larger polyhedral structures and spherical particles on average 1 μm in size, on which smaller square-prism-shaped particles, on average 200 nm in size, are adsorbed and agglomerated.

The SEM images of corn cob bottom ash are presented in Figure 5.35 and under larger magnification in Figure 5.36. The remnants of biomass cell structure are visible in the images. Based on SEM imaging, no sintered or molten phases in the corn cob ash can be observed, but as seen in photo archive from the experimental trials (see Supplementary Material), the characteristic greenish ash color and some weak agglomerations in the ash were indeed present. (Yao und Xu 2016) reported a beginning of the melting of corn cob ash at 600 °C and an inhomogeneous nature of the ash at this temperature. In the SEM images of particulate matter from corn cob pellet combustion (Figure 5.37 and Figure 5.38) distinct structures among particulate matter samples are observed. Larger particles form primary agglomerations (networks), on which secondary agglomerations of smaller square-prism-shaped particles are adsorbed (Figure 5.38). Ash grains with filament structure from the combustion of corn cobs have been previously reported in literature, as well as smaller particles suspended on top of larger ones due to condensation, nucleation etc.((Wang et al. 2012a), (Jin et al. 2017)).

According to EDS results, bottom ash from the combustion of woody biomass is dominated by the elements Ca, O and Si, probably forming CaO and Ca-silicates (Figure 5.39). Furthermore, there is ca. 13 wt.% of carbon in the scanned bottom ash region, which indicates the presence of carbonates and / or incomplete combustion. This is in accordance with results from wet chemical analysis and XRD, where SiO_2, $CaCO_3$ and $Ca_3Al_2O_6$ have been identified.

As indicated by EDS surface and spot scans, particulate matter from wood pellet combustion containing mostly K, S, C, O, and Cl, has uniform structure and composition, probably consisting of KCl and K_2SO_4, and K_2CO_3, and soot of unburned hydrocarbons (Figure 5.40), in line with previous findings (Sippula et al. 2009). Besides alkali salts, carbon was identified in the particulate matter. This is in accordance with wet chemical analysis, where almost 30 wt.% of particulate matter was unaccounted for, possibly due to presence of soot and carbonaceous products of incomplete combustion, although this was not analytically determined. Methods applied in wet chemical analysis were used to determine to composition of selected elements, but not carbon. The presence of carbonaceous matter in PM is in accordance with previous studies regarding wood pellet combustion ((Huelsmann et al. 2019), (Schmidl et al. 2011), (Boman et al. 2004)). Soot was reported to be one of the main components of particulate matter from residential wood combustion (due to incomplete combustion with low temperatures in small scale units) (Sippula et al. 2009), (Roy und Corscadden 2012).

According to EDS, bottom ash sample from the combustion of blend of 50 wt. % wood and 50 wt. % corn cob pellets (50CCP BA) is a mixture of alkali and earth alkali (oxides) and contains ca. 15 wt. % carbon. There is no S detected in the scanned region of the ash and Cl is present in small quantities (0.2 wt. %). Spot scan of fibrous ash section identified elements K, O, and C. Carbon is possibly present in the form of alkali- and earth alkali-carbonates, whereas the rest consists of mostly K_2O and CaO (Figure 5.41). This is in accordance with results from wet chemical analysis and XRD, where SiO_2, $CaCO_3$, C, and MgO and some phosphates were detected.

The EDS scan of particulate matter sample from the combustion of blend of 50 wt. % wood and 50 wt. % corn cob pellets (50CCP BA) reveals major elements being K, S, C, O and Cl (region 3^* in the Table 5.22). According to calculations where KCl is preferably formed, followed by K_2SO_4, and eventually K_2CO_3, surface scan composition corresponds to ca. 49 wt.% KCl, 34 wt.% K_2SO_4, and ca. 14 wt.% of soot, in summary accounting for 97 wt.% of particulate matter. Spot scans reveal that bigger agglomerations creating a primary network are made of KCl (region 1 in the Table 5.22), whereas the secondary network particles are made of > 50 wt.% K_2SO_4, followed by ca. 18 wt.% KCl, ca. 9 wt.% soot, and ca. 4 wt.% K_2CO_3 (region 2 in the Table 5.22) (Figure 5.42). The presence of KCl in this scanned section is attributed to the penetration of X-Rays into the deeper layer of the sample, thus scanning also the underlying KCl network. This is in contrast with findings from wheat straw combustion by (Nielsen 2000), where K_2SO_4 formed sponge-like structures, on top of which angular particles of KCl were adsorbed. However, it seems that the association of S in biomass influences the condensation structures formation. In (Jin et al. 2017) deposits from corn stover combustion were different than in the case of wheat straw combustion; this was linked to major association of S in organic form in corn stover, whereas higher fraction of S might occur as sulfates in wheat straw, even though these two crop residues contain same amount of total S in the biomass.

EDS scans of bottom ash from pure corn cob pellet combustion reveal composition made of mostly K, C, O, and some Si, indicating that K_2O and K-silicates are major ash-forming species, besides fixed and unburned carbon (Figure 5.43). This is in line with XRD findings, where $CaCO_3$, K_2CO_3, phosphates, and KCl have been identified.

Particulate matter scan reveals the similar composition as in previously mentioned particulate matter: K, Cl, S, C, and O making up the entirety of particulate matter composition (Figure 5.44). Calculation analogue to the one in the previous paragraph reveals that ca. 54 wt.% of scanned region is made of KCl, followed by ca. 17 wt.% K_2SO_4, and soot (ca. 18 wt.%). These species amount to > 90 wt.% of ash. The rest could be Al_2O_3 and Al_2SiO_5, accounting for 1 to 2 wt.% of the scanned region. This is in line with results from wet chemical analysis, where ca. 25 wt.% of particulate matter is made of Cl^- and ca. 50 wt.% of K_2O. Although there is a difference in K content from the two methods, there is a tendency of increasing the K and Cl contents in particulate matter with the increasing share of corn cob pellet in the blends, but not proportionally to the corn cob pellet share in the blend. Therefore, it could be the case that the true content of K in the particulate matter is closer to 50 wt. % (as in chemical wet analysis), and that with EDS there has been deviation in K content in the particulate matter, due to sampling, randomness, combustion conditions, etc. S content determined by EDS (ca. 3 to 4 wt.%) is smaller than the one detected with IC (ca. 7 wt.%) (see Figure 5.26), but the major elements and trends are the same and in similar contents in both methods. Also, it should be noted that the elementary composition with wet chemical analysis AAS and IC were expressed in oxide terms, not on the elementary basis. Filament structure of corn cob ash was reported in literature by (Wang et al. 2012a), where K-containing phosphates where linked to this structure. Secondary agglomerations were linked to K_2SO_4, in line with our findings.

In summary CaO is possibly a major species in blends where wood pellets are dominant, whereas K_2O is major oxide species in corn cob pellet. Particulate matter from all experiments has comparable composition and is made of KCl, K_2SO_4 and K_2CO_3.

Crystalline phases. Silica and calcite have been found in almost all bottom ash and fly ash samples, which is expected in samples from the combustion of blends where wood pellets are dominant, since wood ash is rich in CaO ((Misra et al. 1993), (Demirbas 2004), (Demirbas 2005)). Alumina and magnesia are expected crystalline phases in ash samples from the combustion of wood pellets; this is also in accordance with previous literature results ((Huelsmann et al. 2019), (Höfer und Kaltschmitt 2017). The presence of C is fitting with the dark color of ash samples and associated with the products of incomplete combustion such as soot etc.

KCl is the main crystalline phase detected in fly ash samples, which is also in accordance with previous findings and the results of elementary composition, since K-salts are the main particulate forming matter, making up to 95 wt.% of particulate matter (Johansson et al. 2003).

5.4.3.2 Corn cob pellets with additives

5.4.3.2.1 Emission indicators and energy efficiency

Results

Emissions and efficiency. All values of emissions pollutants refer to standard conditions (0 °C, 1,013 mbar) and are related to 10 % O_2 and dry flue gas (according to EN 303-5). Average values of emissions and efficiency indicators from the two replications are shown in Table 5.24.

Table 5.24 Combustion indicators from „Corn cob pellets with additives”

	CO	NO	PM	Thermal capacity	Efficiency
	mg/Nm^{3*}			kW	%
CCP[a]	2040 ± 1114	170 ± 31.5	462 ± 3.5	7 ± 0.2	92.4 ± 0.1
CCP 1%MGO	3391 ± 583	187 ± 12.5	997 ± 27.6	6.7 ± 0.2	91.5 ± 0.9
CCP 2%MGO	4622 ± 2916	192 ± 36.3	1160 ± 6.9	6.4 ± 0.5	89.8 ± 0.8
CCP 1%KAO	873 ± 150	176 ± 13.8	358 ± 2.9	7.1 ± 0.1	93.2 ± 0.3
CCP 2% KAO	920 ± 412	171 ± 10.4	538 ± 31	7.1 ± 0.1	91.6 ± 1.6

*dry gas, 0 °C, 1013 mbar, 10 % O_2

[a]For the list of abbreviations see Table 5.6

Particle size distribution. Total PM emissions with MgO as additive were too high for the particle size distribution measuring equipment available to us. Even though the measurement train is equipped with fine particle sampler (FPS) module for flue gas dilution which enables dilution ratios up to 200, no reliable and plausible measurement of the PM emissions with MgO were feasible, PM emissions were still too high for the subsequent particle size measurement devices. Since kaolin proved to be better additive for the reduction of PM emissions based on previous results, only particle size distributions of PM emissions from the combustion trials with kaolin were measured and presented here. Total mass and number concentrations from the combustion of corn cob pellets with kaolin are presented in Table 5.25 and the number size distributions in Figure 5.45.

Table 5.25 Summary of particle size distribution measurements the combustion of corn cob pellets with additives

	Total number concentration number/cm^3	Total mass concentration ug/m^3
CCP[a]	2.26E+06	3,692
1KAO	1.92E+06	368
2KAO	2.68E+06	2,045

[a]For the list of abbreviations see Table 5.6

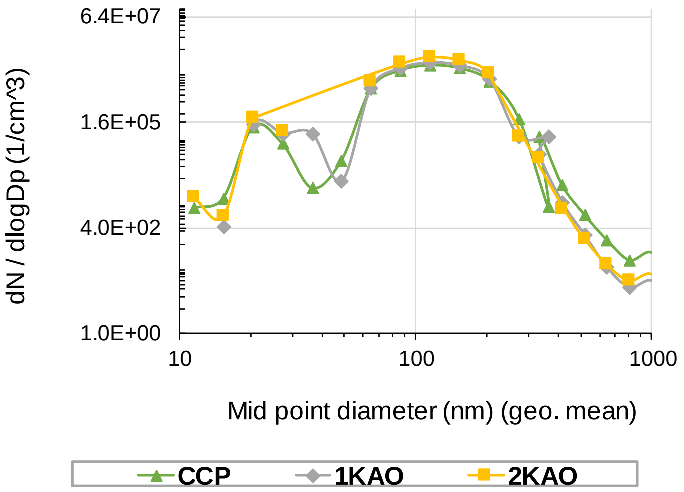


Figure 5.45 Number size distribution of particle emission from the combustion of corn cobs with additives

Discussion

CO Emissions. A reduction in emission values of ca. 54 to 58 wt.% has been observed with the addition of kaolin. Emission values from the experiments with kaolin are in line with class

4 (1,000 mg/m^3), whereas emission values from the combustion of pure corn cob pellets are in line with class 3 of EN 303-5 (3,000 mg/m^3). Although the CO emissions are reduced with kaolin as additive, they still do not meet the requirements of BImSchV. Kaolin has been proven to be effective in reducing CO emission during combustion of wood fuels (Huelsmann et al. 2019), (Hülsmann 2018), (Gollmer et al. 2019), (Mack et al. 2020). Also (Kallio und Oravainen 2011) reported a decrease in CO emissions from the combustion of mixed pellets (straw and peat) in a 60 kW moving grate burner after the addition of kaolin.

NO_x Emissions. As in previous cases, all NO emission values are in accordance with 'TA Luft' and 'BImSchV' emission limit values (ELV).

PM Emissions. A reduction of particulate matter emissions of ca. 22 wt.% are recorded when using kaolin as an additive. Nevertheless, the emissions of particulate matter are still higher compared to the legal requirements.

MgO as an additive has not shown any improvement, on the contrary. The possible reason for increased particulate matter emissions with MgO is the inert mineral nature of the additive: since MgO is inert mineral material that increased the ash content of the biomass, it has prevented the contact of other active ash components (such as e.g. KCl and silicates) and prevented subsequent reactions in the ash, practically forcing the volatile species such as KCl into the gaseous phase and preventing the formatting of K-silicates in the ash (which have been detected in pure corn cob ash and which could cause sintering). The presence of KCl in the particulate matter is expected and confirmed, whereas no presence of MgO has been detected in the particulate matter, eliminating the possibility that the entrainment of grate ash from the combustion chamber into the particulate matter could have caused increase in particulate matter emissions.

As with CO emission reduction, previous studies support the reduction of particulate matter emission through the use of kaolin as an additive (Huelsmann et al. 2019), (Hülsmann 2018), (Gollmer et al. 2019), (Mack et al. 2020). For example, (Carroll und Finnan 2015) investigated the addition of kaolin to herbaceous biomass pellets and discovered that 4 wt.% kaolin does indeed significantly reduce PM_1 emissions ($p<0.01$) in Miscanthus and tall fescue pellets (with Miscanthus over 50 % and with tall fescue pellets over 40 % from 300 mg/m^3 to 200 mg/m^3). (Tissari et al. 2008) reported the reduction of PM_1 emissions during oat combustion with kaolin addition: from 0.49 g/kg to 0.29 g/kg, in line with our findings. Our total PM emissions using isokinetic sampling and a filter unit amounted to ca. 2.2 g/kg from corn cob pellet combustion and with 1 wt. % kaolin it was reduced to 1.6 g/kg.

Energy efficiency. Average thermal efficiencies of all experiments are above 75 % and in line with standard requirements of ISO 14785. From this point of view, additivation of the fuel should not be problematic.

Particle size distribution. The majority of the particles are found in the accumulation region (< 0.5 µm) with the mode around 100 nm. The distribution of PM in the ultra-fine region has remained similar after the application of 1 wt. % kaolin; a smaller mode in the nucleation and Aitken region can be observed (Figure 5.45). Kaolin seems to have influenced the formation of ultra-small particles (<100 nm). These findings for PM samples with and without additives are in line with the results of Scanning Electron Microscope (SEM) imaging (see chapter 5.4.3.2.2), where particle sizes in the ultra-fine (<100 nm) and fine (< 1 µm) regions were identified. Energy Dispersive X-Ray Spectroscopy (EDS) scans revealed similar composition of all PM samples (with and without kaolin). There is an exception in the composition of PM after using kaolin to this due to the presence of K-Al-silicates.

According to the study by (Tissari et al. 2008), particle number distribution from the combustion of oats at nominal load was $11 \cdot 10^{14}$ particles per kg of fuel (1/kg) (which corresponds to $2 \cdot 10^{8}$ 1 / cm^{-3}), whereas this number was increased to $13 \cdot 10^{14}$ particles per kg of fuel when kaolin was used as additive with unimodal distributions; geometric mean diameter being 52 nm and 41 nm respectively. In our case, total number decreased after 1 wt. % kaolin and increased after 2 wt. % kaolin addition. In the same study by (Tissari et al. 2008) mean mass diameters from oat combustion before and after addition of kaolin were determined to be 177 and 385 nm (due to shift of the mean diameter to higher sizes), which is in line with our results. Based on the results of the study by (Tissari et al. 2008), both total number and mass distributions of fine particles increased when using kaolin as additive in the combustion of oats. Moreover, a clear coarse particle mode was identified in the particle size measurements from the combustion of wood with kaolin, indicating that certain amounts of kaolin were entrained from the bottom ash into the flue gas during combustion. This is in line with the results of our SEM / EDS analysis, where K, Al, and Si were detected in PM from the combustion of fuel with kaolin (see chapter 5.4.3.2.2).

(Huelsmann et al. 2019) reported the reduction of PM_1 (ultrafine) mass emissions after the addition of kaolin during combustion of wood pellet with kaolin. However, this study also reported the increase in number of particles after kaolin addition to the fuel.

5.4.3.2.2 Ash analysis

Results

The ash melting behavior was improved after the use of additives, since all samples are powdery in nature and no traces of sintering have been observed. The additivized bottom ash samples all show a white color. Even though bottom and fly ash samples from the combustion of samples with kaolin were white, the particulate matter samples from the combustion of corn cob pellet with kaolin are black (selected photographs of the ash samples from the combustion of corn cob pellets with additives are presented in the Supplementary Material).

Distribution of elements in different ash fractions. Average concentrations of major ash-forming elements from the two combustion series (replications) are given in Figure 5.46 till Figure 5.49.

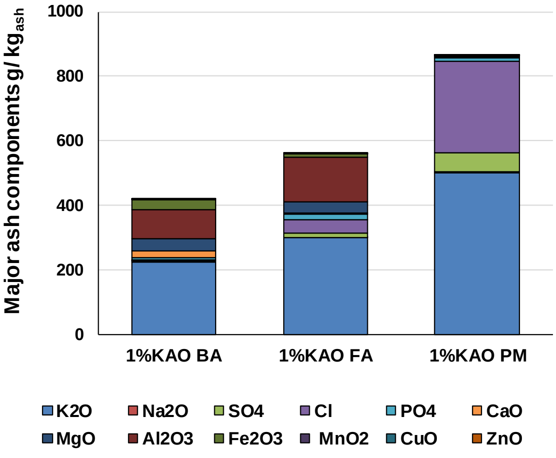


Figure 5.46 Average values of major ash-forming species in different ash fractions from the combustion of corn cob pellets with 1 wt. % kaolin; BA – bottom ash, PM – particulate matter

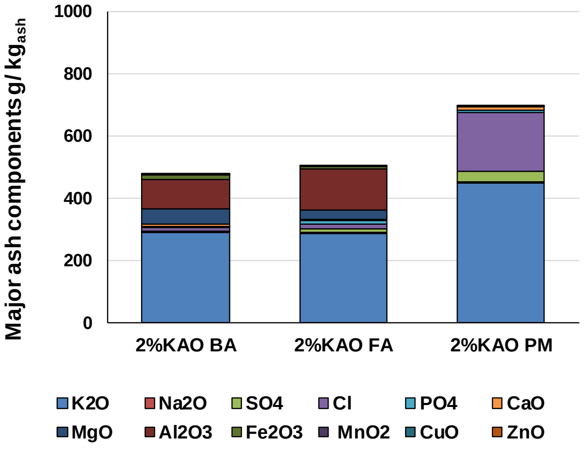


Figure 5.47 Average values of major ash-forming species in different ash fractions from the combustion of corn cob pellets with 2 wt. % kaolin; BA – bottom ash, PM – particulate matter

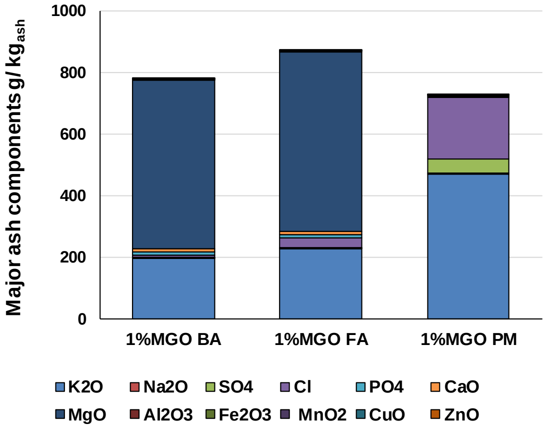


Figure 5.48 Average values of major ash-forming species in different ash fractions from the combustion of corn cob pellets with 1 wt. % MgO; BA – bottom ash, PM – particulate matter

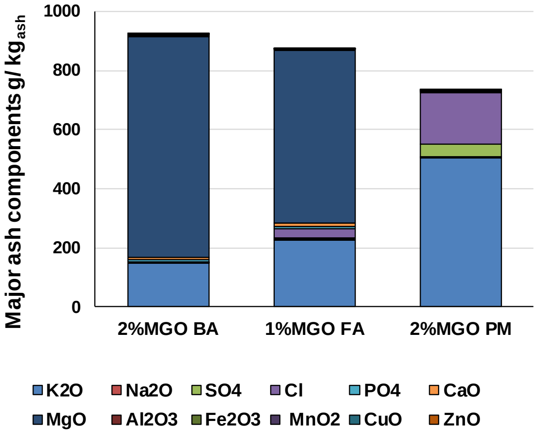


Figure 5.49 Average values of major ash-forming species in different ash fractions from the combustion of corn cob pellets with 2 wt. % MgO; BA – bottom ash, PM – particulate matter

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM / EDS). Since the morphology of bottom ash and particulate matter from the combustion of corn cob pellets are discussed in the previous chapter, in the following text only the residues from the additivized-fuels will be further elaborated (Figure 5.50 till Figure 5.57), in comparison with Figure 5.35 till Figure 5.38. Abbreviation BA represents bottom ash and PM represents particulate matter. In the bottom ash samples additivized with kaolin some crystalline structures can be observed. All the particulate matter samples, independent from presence (absence), and amount of additive but dependent from the fuel, share the same particle size and structure.

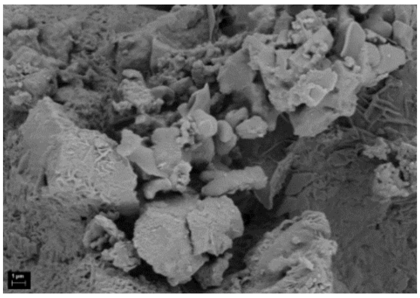


Figure 5.50 SEM image of 1KAO BA

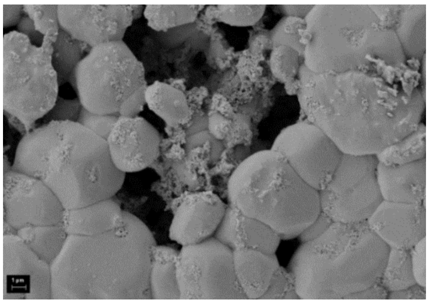


Figure 5.51 SEM image of 1KAO BA

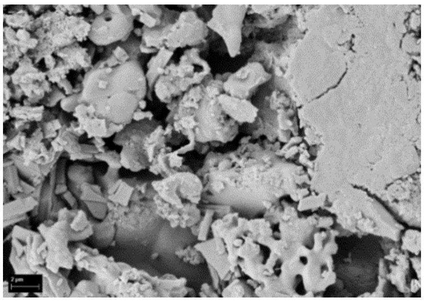


Figure 5.52 SEM image of 2KAO BA

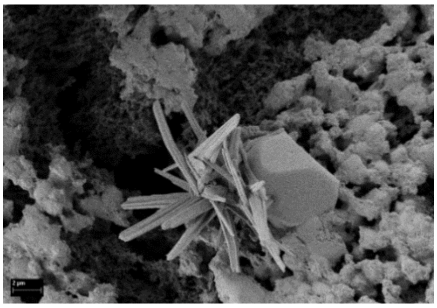


Figure 5.53 SEM image of 2KAO PM

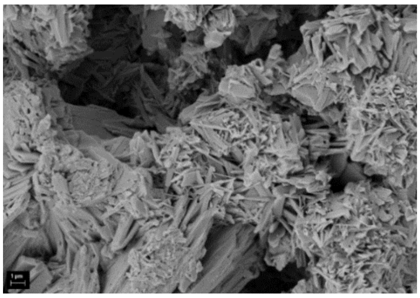


Figure 5.54 SEM image of 1MGO BA

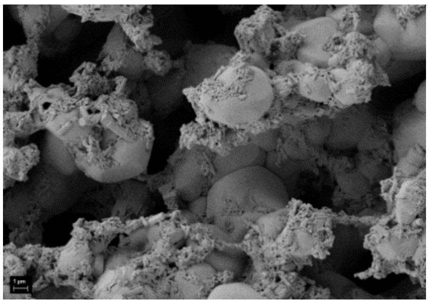


Figure 5.55 SEM image of 1MGO PM

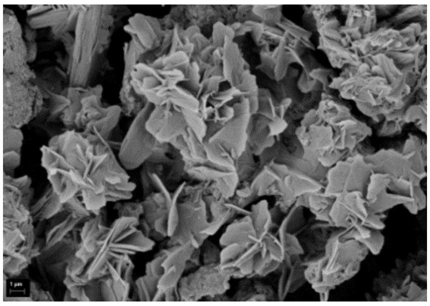


Figure 5.56 SEM image of 2MGO BA

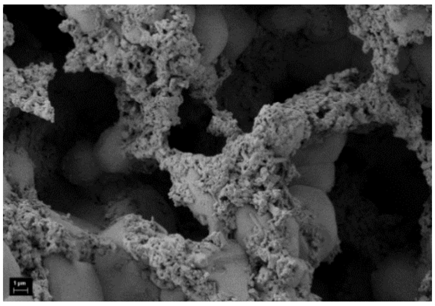


Figure 5.57 SEM image of 2MGO PM

The overview of surface elemental composition of samples from the combustion of corn cob pellets with kaolin determined by EDS is found in Table 5.26.

Table 5.26 Composition of solid residues from “Corn cob pellets with additives” analyzed with EDS

element (norm, wt. %)	1KAO[a] BA[b]			1KAO PM					2KAO BA					2KAO PM					1MGO BA		1MGO PM			2MGO BA			2MGO PM		
	1**	2**	3**	1*	2*	3**	4**	5**	1*	2**	3*	4**	5**	1*	2**	3**	4**	5**	1*	2	1**	2**	3*	1*	2**	3**	1**	2**	3*
K	16.5	21.0	21.5	38.2	39.4	54.5	35.9	59.5	23.6	15.1	23.2	19.1	20.2	26.7	24.3	45.0	46.3	40.9	26.9	29.1	58.9	45.5	43.8	20.5	18.3	17.9	54.7	52.1	39.1
Na	0.5	0.2	0.2							0.5			0.4		0.2														
Ca	5.8	2.2								3.0			1.8																
Mg	2.3	1.3	1.6						1.4	1.3	1.3	0.6	1.4						12.6	11.5				20.5	19.6	23.1			
Si	11.9	11.3	12.6		0.3		12.2		11.1	20.1	11.3	13.2	6.7	0.3	0.3				0.5	0.5				1.3	1.2	1.0			
Al	4.0	6.8	7.3				8.3		9.5	4.7	9.2	10.2	3.4												0.6				
P	2.9	1.2	1.3						0.9	0.8	1.0	1.0	1.5	1.0	0.8				0.9	0.8				0.7	0.5	0.5			
S				1.8	1.4									1.7	1.4		2.6	4.5				13.9	3.9					12.3	8.6
C	13.9	12.5	12.6	20.8	18.2				14.2	16.0	15.0	16.3	21.1	39.7	44.0	16.7	11.2	15.5	17.3	15.9			14.0	14.4	19.5	17.9			13.9
O	39.3	41.3	42.0	9.0	8.5		36.8		38.3	36.8	37.7	39.0	42.2	11.4	10.7	5.9	7.5	15.2	40.0	40.2		33.7	23.3	39.7	37.8	39.1		27.3	22.1
Cl				30.2	32.2	45.6	6.8	40.5	0.4		0.7		0.7	19.3	18.3	32.4	32.4	23.9	0.4	0.4	41.1	6.9	15.0	0.3	0.3	0.2	45.3	8.4	16.3
Fe			1.0						0.6	1.7	0.5	0.7	0.6													0.4			
Mn	2.9	2.0																											

*surface, **spot

[a] For the list of abbreviations see Table 5.6

[b] BA – bottom ash; PM – particulate matter

The images indicating the scanned regions are given in Figure 5.58 till Figure 5.63. The results of additivized fuel ashes are compared with results from the combustion of corn cob pellets without additives, given in Figure 5.43 till Figure 5.44.

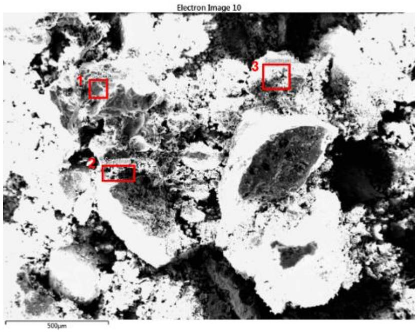


Figure 5.58 1KAO BA with scanned regions

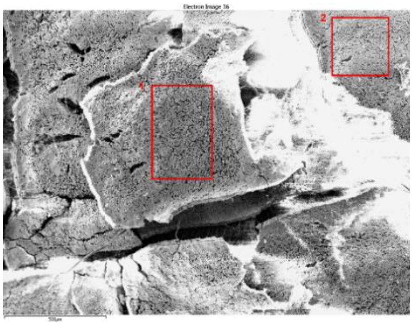


Figure 5.59 1KAO PM with scanned regions -1

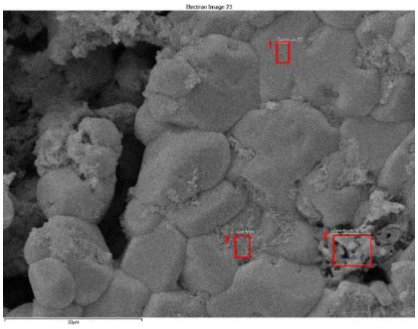


Figure 5.60 1KAO PM with scanned regions -2

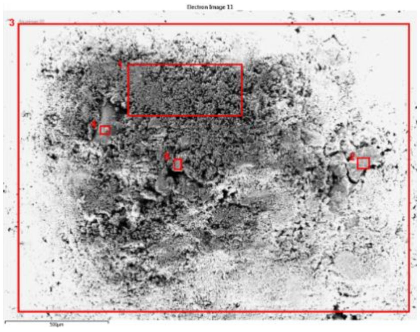


Figure 5.61 2KAO BA with scanned regions

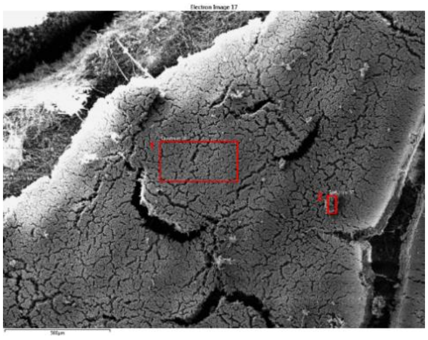


Figure 5.62 2KAO PM with scanned regions – 1

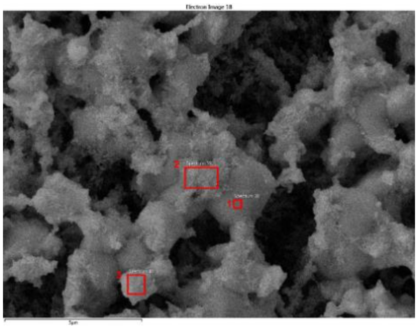
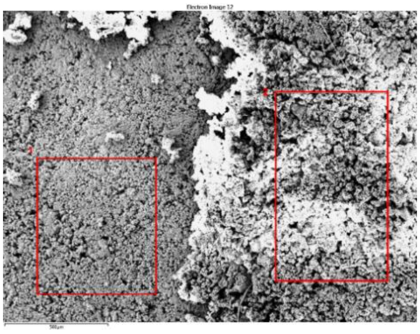


Figure 5.63 1KAO PM with scanned regions -2



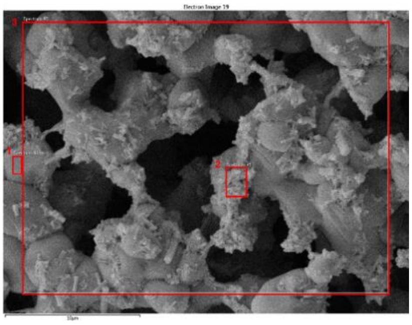


Figure 5.64 1MGO BA with scanned regions

Figure 5.65 1MGO PM with scanned regions

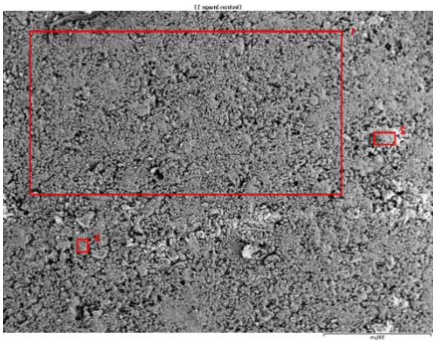


Figure 5.66 2MGO BA with scanned regions

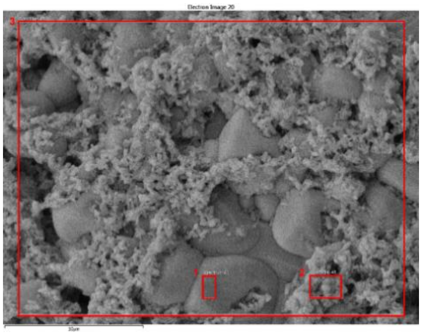


Figure 5.67 2MGO PM with scanned regions

Crystalline phases. An overview of major crystalline phases found in the bottom and fly ash samples from the combustion of additivized corn cob pellets can be found in Table 5.27.

Table 5.27 Major crystalline phases in bottom and fly ash samples from the combustion of "Corn cob pellets with additives"

Crystalline phase	1KAO[a]	2KAO	1MGO	2MGO	CCP	Literature
$KAlSiO_4$	BA	BA FA				(Dragutinovic et al. 2019), (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
MgO		BA	BA FA	BA FA		(Huelsmann et al. 2019), (Hülsmann 2018), (Olanders und Steenari 1995), (Boström et al. 2012)
KCl	FA	FA	BA FA		FA	(Huelsmann et al. 2019), (Boström et al. 2012), (Xiao et al. 2011), (Ma et al. 2016); (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)
$2K_2CO_3·3H_2O$					BA FA	(Du et al. 2014), (Mlonka-Mędrala et al. 2020)
$K_2Mg_2(SO_4)_3$			BA			
$CaCO_3$					FA	(Du et al. 2014), (Mlonka-Mędrala et al. 2020), (Huelsmann et al. 2019), (Wang et al. 2014), (Hülsmann 2018), (Olanders und Steenari 1995), (Vamvuka et al. 2009); (Kaknics et al. 2017), (Yao et al. 2016)

[a] For the list of abbreviations see Table 5.6

Discussion

The effectiveness of additives in the increase of ash melting behavior is evident from the powdery nature of all bottom ash samples. Even though there was no sintering or ash deformation during combustion of corn cob pellets without additives in the pilot-scale experiments, the application of additives should be considered for the long-term utilization of corn cob pellets, to ensure prevention of ash sintering. The black color of PM samples from the combustion of corn cobs with kaolin are probably caused by soot, which will be discussed in the next section.

Distribution of elements in different ash fractions. The distribution of elements in the particulate matter samples does not seem to change after additivation. Due to dilution of ash after additivation no conclusions can be made about the sorption of alkalis in the bottom ash and results of elementary composition must be evaluated comprehensively with the results from XRD analysis, SEM / EDS etc.

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy (SEM / EDS). Crystalline structures possibly representing the beginning or crystalline growth in the bottom ash sample with 1 wt.% kaolin can be observed in Figure 5.50. When using higher amount of kaolin as additive, no differences in the bottom ash structure can be noticed (Figure 5.52), and among the particulate matter sample additional crystalline phases are observed among the network of agglomerations (Figure 5.53).

In the particulate matter samples, the characteristic structure of primary and secondary agglomerations (same as in the previous combustion series, see chapter 5.3.2.1) is observed (Figure 5.51). Therefore, also the chemical composition of particulate matter samples with and without kaolin is expected to be similar.

According to EDS, bottom ash of fuels additivized with kaolin (Figure 5.58 till Figure 5.61) are comprised of C, O, Al, Si, and K. Silicon makes up ca. 12-20 wt. % of the bottom ash (increasing with increasing additive content). Species such as K_2CO_3 and oxides (K_2O) are mixed with K-Al-silicates. XRD results support these findings: in bottom ashes of fuels additivized with kaolin $KAlSiO_4$, Ca-phosphates, Na-Al-phosphates, have been found. EDS identified Cl only in minor amounts. Results from wet chemical analysis are in line with EDS findings: K content according to EDS ranges 16-24 wt. % whereas with AAS K_2O content was found to be 23-29 wt. %, Al with 4-10 wt. % whereas Al_2O_3 with AAS was found to be ca. 9 wt. %. The same follows for other major elements.

EDS surface scan of particulate matter with 1 wt. % and 2 wt. % kaolin show the main elements C, O, S, Cl, and K (Figure 5.59 and Figure 5.60), whereas focused spot scans (Figure 5.60 and Figure 5.63) help identify larger spherical and hexagonal network structures as KCl, on top of which two distinct groups of agglomerations or "secondary" network layer seems to be formed. Different spot scans reveal: 1) one group formed of KCl and K-Al-silicates (4** under 1KAO PM in the table Table 5.26), 2) smaller groups formed from K_2SO_4 as with other particulate matter samples. Calculation of possible K distribution in the particulate matter in one of the groups in the secondary layer (as in 4^{**} under 1KAO PM in the table Table 5.26), where priority has been given to KCl formation followed by the formation of $KAlSiO_4$ has shown that ca. 14 wt. % is taken up by KCl, whereas $KAlSiO_4$ makes up >48 wt. % of the agglomerations scanned in this section (agglomeration of second layer of particles adsorbed on top of bigger network). The entrainment of K-Al-silicates from the grate ash in the flue gas and subsequent particulate matter seems possible. The presence of silicates (K-Al-silicates) in the particulate matter with 1 wt. % kaolin (Figure 5.60) could originate from the entrainment of the bottom ash into the flue gas and the chimney.

K content in particulate matter ranges from 25-45 wt. % with 2 wt. % kaolin to ca. 40-50 wt. % with 1 wt. % kaolin. This is in line with ca. 50 wt. % K_2O (1 wt. % kaolin) and 45 wt. % K_2O (2 wt. % kaolin) from wet chemical analysis using AAS. S content with EDS is lower than with AAS (1.5 – 4.5 wt. % vs 3.3.-5.9 wt. %), as observed in other samples. Total chlorine ranges of 19-32 wt. % with 2 wt. % kaolin and 6-45 wt. % with 1 wt. % kaolin identified with EDS cover the chloride concentrations determined using AAS (19 wt. % with 2 wt. % kaolin and 29 wt. % with 1 wt. % kaolin). It should be noted that with EDS total chlorine is determined and some spot scans were focused specifically on KCl.

To summarize, results support the thesis that major species in the bottom ash are K_2O, followed by are K-Al-silicates in fuel with kaolin. Phosphorus is found in all bottom ash samples, therefore alkali- and earth alkali-phosphates are possibly present in the ash, whereas no S or Cl are found in the bottom ash samples. Carbon is present in both bottom ash and particulate matter, probably in the form of carbonates. Ca, Mg, and Fe are expected to be found in the form of oxides and silicates. Particulate matter from all experiments has comparable composition and is made of KCl, K_2SO_4 and K_2CO_3.

Crystalline phases. K-Al-silicates identified in the ash using XRD are the products of kaolin decomposition into meta-kaolinite and subsequent reactions with K-species in the ash, in accordance with previous studies (Gollmer et al. 2019), (Höfer und Kaltschmitt 2017). Similarly, as in previous results, KCl has been identified as major K-species in corn cob ash samples, both bottom and fly ash (ash entrained from the grate and deposited on the combustion chamber walls). Ca-carbonates with melting point 825 °C (European Chemicals Agency 14.12.2020) have also been detected in the fly ash sample of corn cobs, together with K-carbonates. Other crystalline phases include alkali- and earth alkali-phosphates and sulphates.

5.4.3.3 Corn cob pellets with additives and binder

5.4.3.3.1 Emission indicators and energy efficiency

Results

Emissions and efficiency. All values of emissions pollutants refer to standard conditions (0 °C, 1,013 mbar) and are related to 10 % O_2 and dry flue gas (according to EN 303-5). Emissions and efficiency indicators from the combustion series of corn cob pellets with kaolin and starch are found in Table 5.28.

Table 5.28 Emission and efficiency indicators from the combustion series "Corn cob pellets with kaolin and binder"

	CO mg/Nm3*	NO	PM	Thermal capacity kW	Efficiency %
CCPB[a]	2,434	163	609±27.4	8.5	91.1
CCPB0.5KAO	2,236	149	559±32.2	7.5	90.8
CCPB1.5KAO	357	161	317±16.2	7.8	93.2

*dry gas, 0 °C, 1013 mbar, 10 % O_2

[a]For the list of abbreviations see Table 5.7

Particle size distribution. Total mass and number concentrations from the combustion of fuel blends are found in Table 5.29 and the particle number size distribution are illustrated in Figure 5.68.

Table 5.29 Summary of particle size distribution measurements the combustion of corn cob pellets with additives and binder

	Total number concentration #/cm^3	Total mass concentration ug/m^3
CCPB[a]	2.10E+04	80
CCPB0.5KAO	1.07E+04	37

[a]For the list of abbreviations see Table 5.7

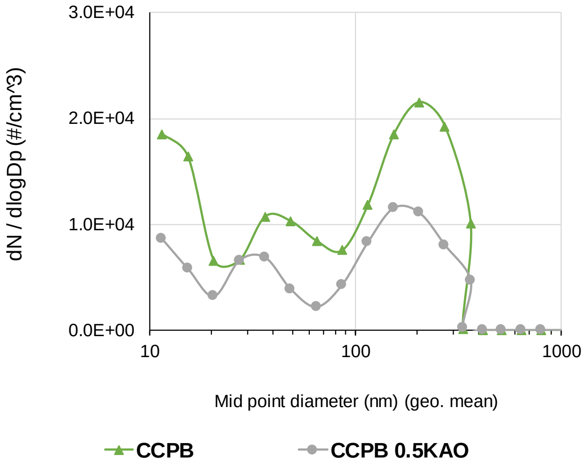


Figure 5.68 Number size distribution of particle emission from the combustion of corn cobs with additives and binder

Discussion

CO Emissions. After addition of 1.5 wt. % of kaolin a ca. 89 wt. % reduction in CO emissions is recorded, being the largest CO reduction value from all experiments with kaolin. Since no reduction was detected with 0.5 wt. % kaolin, and a reduction in CO emissions with 1 wt. % kaolin was recorded in previous combustion series, it can be assumed that the optimal kaolin share is in between 1 wt. % and 2 wt. %, possibly being 1.5 wt. %. Furthermore, since a reduction in CO emissions has been recorded even when starch was used as binder (to improve mechanical properties of pellets), it can be assumed that starch is not hindering the combustion process or promoting the formation of pollutants.

NO$_x$ Emissions. As in previous cases, all NO emission values are in accordance with 'TA Luft' and 'BImSchV' emission limit values (ELV).

PM Emissions. Both experiments with kaolin have resulted in the reduction in PM emissions, in comparison with non-additivized fuel. With 0.5 wt. % kaolin ca. 10 wt. % reduction in PM emissions are recorded, whereas with 1.5 wt. % a ca. 48 wt. % PM reduction is achieved. As with CO emissions, the presence of binder in the pellets does not seem to hinder combustion, nor does it promote the formation of particulate matter. The share of kaolin of 0.5 wt. % seems to bring modest improvements, whereas the share of 1.5 wt. % brought about the biggest improvements out of all experiments with kaolin. Therefore, based on current results and when focusing on PM emission reduction as main goal, the optimal share of kaolin would be between 1 wt. % and 2 wt. %, possibly being 1.5 wt. % kaolin. The detailed investigation for the verification of the attained results is needed.

Energy efficiency. Efficiency values are in line with the EN 14785 standard requirements (≥75 %), whereas the thermal capacities range 7-8.5 kW. Based on current results, the addition of kaolin and starch as binder (in these amounts) should not negatively influence the combustion efficiency and heat generation.

Particle size distribution. The significant differences in the particle size distributions after using binder and kaolin are the reduction in total mass and number concentrations. Bimodal distribution including a first mode in the nucleation and Aitken region, and a second mode in the agglomeration range (100-500 nm) is analogue with previous experiments. In comparison with particle size distribution before binder addition the position of number concentration peaks from the combustion of corn cobs with binder has remained in the same range, although moved slightly to the larger size (ca. 200 nm). The position of the peak with the addition of 0.5 wt. % kaolin has also moved to the bigger size at ca. 180 nm.

5.4.3.3.2 Ash analysis

Results

Photographs of ash samples from the combustion trials using corn cob pellets with binder and kaolin are found in a table in Supplementary Material. Bottom ash sample from the combustion of corn cob pellets with binder and without kaolin is characteristic in color, formed of small non-sintered agglomerations. As with previous samples, no issues regarding ash melting behavior have been observed after binder has been used as pelletizing aid. In some bottom ash samples from additivized fuel whole unburned pellets have been observed.

A difference between the color of particulate matter sampled on the filters with time can be observed in all three cases, where first PM samples are light in color and probably contain more mineral matter, towards darker PM samples which could contain more carbonaceous matter.

Distribution of elements in different ash fractions. Concentrations of major ash-forming elements in three ash fractions from the combustion of corn cobs with binder and kaolin are found in Figure 5.69 till Figure 5.71.

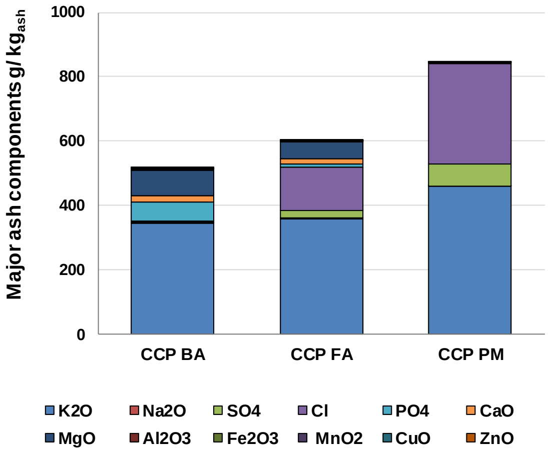


Figure 5.69 Major ash-forming species in different ash fractions from the combustion of corn cob pellets with binder; FA – fly ash, PM – particulate matter

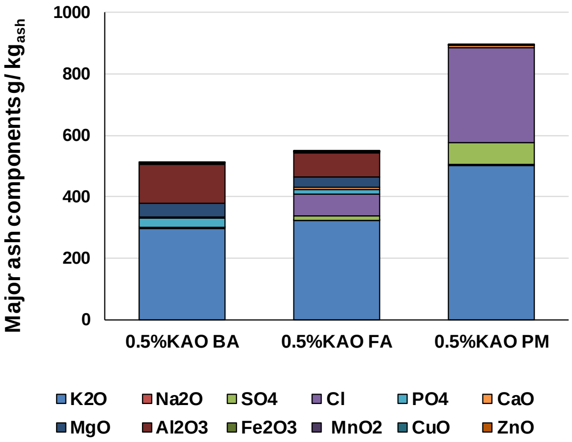


Figure 5.70 Major ash-forming species in different ash fractions from the combustion of corn cob pellets with binder and 0.5 wt. % kaolin; BA – bottom ash, PM – particulate matter

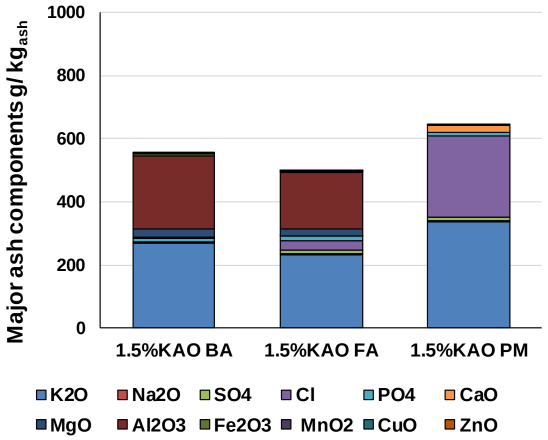


Figure 5.71 Major ash-forming species in different ash fractions from the combustion of corn cob pellets with binder and 1.5 wt. % kaolin; BA – bottom ash, PM – particulate matter

Crystalline phases. An overview of major crystalline phases identified using XRD in the bottom and fly ash samples from the combustion of corn cob pellets with binder and kaolin are found in Table 5.30. For comparison purposes the crystalline phases identified in the ash samples of corn cob pellets without binder are also listed in the same table.

Table 5.30 Major crystalline phases in the ash samples from "Corn cob pellets with additives and binder"

Crystalline phase	CCPB[a]	0.5%KAOB	1.5%KAOB	CCP	Literature
$Mg_2P_2O_7$	BA				
$K_2CO_3 \cdot 1.5H_2O$	BA				
$KAlSiO_4$			BA FA		(Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a), (Dragutinovic et al. 2019)
$CaCO_3$				BA	(Huelsmann et al. 2019), (Wang et al. 2014), (Hülsmann 2018), (Olanders und Steenari 1995), (Vamvuka et al. 2009); (Du et al. 2014), (Kaknics et al. 2017), (Yao et al. 2016)
$Ca_3Al_2O_6$		BA			(Hülsmann 2018)
KCl	FA	BA FA	FA	FA	(Huelsmann et al. 2019), (Boström et al. 2012), (Xiao et al. 2011), (Ma et al. 2016); (Du et al. 2014), (Yao et al. 2016), (Vassilev et al. 2013a)

[a]For the list of abbreviations see Table 5.7

Discussion

Distribution of elements in different ash fractions. The higher concentrations of alumina in the ash samples from additivized fuel can be traced back to kaolin. Lower sulphate concentrations in the particulate matter with 1.5 wt. % kaolin indicated possible S sorption in the ash using kaolin, mentioned in previous studies (Dragutinovic et al. 2019). No proof of K sorption in the bottom ash can be found based on elementary composition due to dilution of ash samples with mineral matter.

Crystalline phases. K-Al-silicates were identified in the samples of ash from the combustion of corn cob pellets with 1.5 wt. % kaolin, but not in the samples with 0.5 wt. % kaolin, which could indicate that the amount of 0.5 wt. % kaolin is not enough to bind the potassium in silicate form and prevent its release into the gaseous phase. This is supported by the fact that KCl is detected in both bottom and fly ash samples from the combustion of corn cob pellets with 0.5 wt. % kaolin. KCl is also found in ash samples from corn cob pellet combustion trials, both with and without binder. K-carbonates and Mg-phosphate have furthermore been identified.

5.5 Conclusions

In the following paragraphs general observations, conclusions and recommendations based on the experimental investigation are discussed.

5.5.1 Advantages

Phase one (boiler). There were neither issues with grate ash slagging nor with blockages of air-feeding due to large contents of ash. Corn cobs have been reported to have somewhat better ash melting behavior than other crop residues (e.g. wheat straw) along with lower ash content (Dragutinovic et al. 2019). After application of additives in combination with moving step-grate and active ash removal system, possibility of issues due to problematic ash behavior are completely eliminated. Therefore, in this regard the investigated combustion unit does not require any additional modification and is completely adjusted to the energetic utilization of crop residues. The same can be said for combustion of fuels with large ash contents. By having a moving grate and an active ash removal system problems associated with high contents of ash are avoided. This should be the case for other herbaceous fuels, not only corn residues.

During the combustion experiments significant amounts of entrained grate ash were observed to be deposited on the combustion chamber walls / surfaces and heat exchanger surfaces. If used regularly, according to the manufacturers instruction, the problems of ash deposition and corrosion should be minimized.

After keeping the air-feeding constant CO emissions have been reduced 28-times when using corn cob grits as fuel. Particular matter (PM) emissions have also been reduced after stabilizing the air-feeding. However, the control system should be more adjusted to the new fuel.

Phase two (pellet oven). No issues with sintering or slagging of ash were observed due to self-cleaning grate. Some minor agglomerations of grate ash were found in the ash box. Even the increased ash content in crop residues which was further increased with additives did not block the combustion air feeding system because the combustion unit was automatically cleaned by every 50 minutes, as programmed by the manufacturer. Self-cleaning included flipping of the grate and rinsing of the combustion chamber with fresh air.

5.5.2 Challenges and limitations

The difference in particulate matter emissions from the two tested combustion units can be explained in part by construction differences, of special importance is the moving grate, which prevents sintering of the ash but promotes the entrainment of the ash into the gaseous phase. This phenomenon of increasing PM emission with moving grates was previously reported by (Sippula et al. 2017).

Phase one (boiler). As a general impression, the construction of the combustion unit is not adequate for ground corn cobs as fuel. Air-feeding proved to be critical parameter influencing emissions. The challenge in this parameter setting was to adjust them to the “new fuel”. Initially, after reaching the stabile burning phase, the emission measurements were initiated with a gas analyzer and during this phase the air feeding rate (fan power) was fine-tuned, in order to minimize the emissions of CO, which turned out not to be the solution to the challenge of keeping the output steady. Another possibility to influence the air feeding is the handle under the grate, where the operator (consumer) can roughly regulate the distribution of primary and secondary air (more primary / less secondary, half primary / half secondary, less primary / more secondary). Correct operation and behavior of the consumer is critical to both CO and particular matter (PM) emission, as studied previously (Mack et al. 2019). It was concluded that during the ignition phase primary air inlet should be dominant, whereas immediately after reaching burning the primary air should be minimized in order to enable pyrolysis conditions in the primary combustion chamber (on the grate), minimize the temperature and prevent ash melting and sintering. In this phase (stabile stationary combustion) the secondary air should be the main source of oxygen for volatiles in the secondary combustion chamber, e.g. before heat exchanger, to promote full oxidation.

Ash deposition was detected on the heat exchanger surfaces and was promoted with increased air flow, additive content in the fuel, and properties of the fuel (ash). The deposition of fly ash is associated with corrosion and decrease in efficiency of heat transfer. (Carvalho et al. 2013) reported the decrease of 10% in boiler efficiency after 110 h of operation due to fly ash deposition on the heat exchanger. Another study with corn cobs (Brunner et al. 2011) reported considerable deposition on heat exchanger surfaces during corn cob combustion. In the ash fractions, volatile K-salts have been found, confirming the corrosive nature of the fly ash. This issue needs to be further addressed.

Since bulk densities of corn cob pellets and corn cob grit are considerably different, also fuel-feeding had to be adjusted. Another challenge was the constancy of heat output, which was monitored by the heat meter. During each experiments the value in control system of the boiler was set to 25 kW which was overreached in almost all cases. For the modification of this issue the fuel-feeding rate had to be reduced, as well as heating value parameter in the control system.

During some experiments the condensation on the surfaces of the heating unit was observed due to slow heating up of the boiler or due to thermal bridges in the corners of the combustion chamber.

In some cases, especially in the experimental series with corn cob grits the overshooting of the thermal capacity was the rule. The fuel and air feeding as well as lower heating value (LHV) were entered into the control algorithm in the same method as in other experimental series. However, possibly due to small particle size of the fuel, powdery inert mineral nature of the additive, and the non-adapted fuel-feeding system stabile and stationary combustion was challenging. The strong variations were observed from the heat meter output, where it was noticed that although process was continuous, the constant thermal capacity was not achievable in most cases.

Based on current results the effectiveness of applying additives on the CO emissions is not observable, on the contrary. In the case of particulate matter (PM), they seem to show more promise. The effect of additives can be observed using 1 and 2 wt. % of kaolin. The possibilities for emission reduction and increase in efficiency when using corn cob are only if grounded cobs (corn cob grit) should be further processed (pelletized). Otherwise the use of grounded corn cobs in small-scale units could not be advised due to high emissions.

The reduction of particulate matter (PM) emissions have been proven most challenging and possibly require the combination of both combustion chamber design modernisation, as well as low-cost measures such fuel-upgrading, in order to meet the strict emission limit requirements.

Issues with fuel-feeding, air-feeding and stabile thermal power need to be addressed as priority. The utilization of alternative agro pellets needs to be recognised by the control system and making the control system more flexible to the requirements of the agro-fuels. In the current engineering solution user / consumer has the possibility to adjust: 1) lower heating value of the fuel, 2) fuel feeding speed, and 3) fan speed / power. The adjustments of the unit parameters are found based on experience of the installation technician and the user. Therefore, the education (briefing) of the user is essential in order to operate the unit in the most efficient and conscious way.

Phase two (pellet oven). Entrainment of the grate ash with combustion air and flue gases was evident, deposition of entrained ash was detected on the chamotte surfaces inside the combustion chamber as well as outside in the base of the flue gas duct. Thus, the particulate matter emissions are increased.

As a user, there is no possibility to manipulate fuel- or air-feeding, possibly adjusting the control system to the properties of the new fuel (corn cob pellets or pellets with additives). As an adjustable parameter user can choose between three pellet qualities.

5.5.3 Recommendations

Regarding the combustion unit modification, suggestions to further investigate the possibilities to improve combustion chamber are following:

- Boiler:
    - creation of CO curves vs. O_2 content (excess air ratio) curves, based on which the control system can be optimized for each new fuel,
    - installation of the excess air sensor (lambda sensor): in order to monitor the combustion process quality, information regarding air supply and concentration of O_2 (CO_2) are crucial,
    - lining of the combustion chamber with chamotte (fireproof) material in order to enable high temperatures in the combustion chamber,
    - installation of the physical barrier – differentiation between primary and secondary combustion chamber. Flue gasses are crossing into the secondary chamber before reaching the heat exchanger – this way the residence time of the flue gases is prolonged, and turbulence is secured.
    - Introduction of a secondary air in the newly designed secondary combustion chamber,
    - Adjustment of the control system algorithm to include alternative fuels and their average properties. In this case user should be able to add new fuels and their properties critical for combustion, such as LHV, bulk density, particle size, ash

From the aspect of fuel-related measures, it can be concluded that fuel processing is essential in order to energetically utilize corn cobs in small-scale units. The focus is to reduce the amount of fines present in the fuel, which is directly associated with emissions of particulate matter:

- Boiler:
    - Blending of wood pellets and corn cobs pellets is an effective measure to decrease both CO and PM emissions. However, none of the fuel blends can meet the emission limit values without additional measures.
    - Corn cob grits are not adequate fuel for the combustion in small scale units, even with additives.
- Pellet oven:
    - Blending of wood pellets and corn cobs pellets is an effective measure to decrease both CO and PM emissions. However, in order to keep the emissions under the limit values, corn cobs can be added to the fuel blend in minor shares (up to 25 wt. %).
    - Additivation of the corn cob pellets with kaolin does reduce both CO and PM emissions. However, additional secondary measures such as cyclones are required to meet the emission limit values.

- The combination of fuel blending (with wood pellets) and additivation of corn cob pellets with kaolin should be investigated as measure to increase the share of corn cobs in fuel blends and thus alleviate economic burden and promote the utilization of locally sourced biomass.

6 Assessment of environmental aspect

Djordje Djatkov, Milan Martinov

6.1 Methodology

6.1.1 Material

Corn cobs were sampled in a pellet production plant Fer Komerc DOO from Slankamen. The moisture content of cobs was 8.45 %, the ash content was 1.13 %, and the lower calorific value was 17.21 MJ/kg (*d.b.*). The bulk densities of cobs, crushed cobs and pellets were about 200 kg/m^3, 300 kg/m^{3}and 700 kg/m^3 *w.b. (wet basis)*, respectively. Corn cob samples were used to conduct analyses of moisture and ash content and calorific value, and these results were used for the purposes of balancing energy and GHG emissions.

Three options of using corn cobs as a fuel for combustion in small heat generators were analysed. Each of these options implies a different form of corn cob usage, and thus different requirements for processing, transport and storage, as well as different types of heat generators. These options are described in chapter 2.2.

6.1.2 Data for calculation of energy and GHG balances

Table 7.1 provides transport data for all three options, which were further used to calculate the respective energy and GHG balances.

Table 6.1 Transport data for all three scenarios

Parameter	Unit	Value	References
Emissions for diesel[1]	gCO_{2eq} MJ^{-1}	93.9	(Giuntoli et al. 2015)
Truck consumption	MJ t^{-1} km^{-1}	0.811	(Giuntoli et al. 2015)
Mass to be transported[2]	t	14	(Anonymous 2019a)
Mass to be transported	t	20	(Anonymous 2019a)

[1] Emissions from the transport and refining of oil, and the transport and combustion of diesel fuel. [2] Option I considers the transport of whole cob from farmers, which has a lower bulk density than cob from seed centers, which is considered in option II and III.

The transport distances considered for option I range from 0 to 100 km, with an intermediate step of 20 km. In option II and III, the transport distance during the delivery of the whole cob to the production plant is 80 km.

Data on the energy required for processing corn cobs (crushing / grinding and pelleting) are given in Table 6.2. Moreover, the table shows the emission factor for the electricity mix in Serbia, as well as the efficiency of energy transformation.

Table 6.2 Corn cob processing data

Parameter	Unit	Value	References
Electricity for preparation[1]	kWh t_W^{-1}	20	(Miranda et al. 2018)
Electricity for pelletizing	kWh t_W^{-1}	80	(Miranda et al. 2018)
Emission factor for electricity	gCO_{2eq} MJ^{-1}	275.3	(Anonymous 2015)
Efficiency of energy transformation	–	0.535	(Vlada Repuplike Srbije)

[1] Electricity for crushing and grinding corn cobs. W: wet mass.

For option II and III, the possibilities to pack the crushed cobs and pellets are considered. For the crushed cob, the possibility of packing in jumbo bags that can hold about 300 kg of crushed cob is considered, while for pellets, packing in 15 kg bags is assumed. The jumbo bag is made of polypropylene fabric (PP), and the bags are made of LDPE (low density polyethylene). Table 6.3 provides data on GHG emissions and energy required for the production of these materials.

Table 6.3 Energy and emissions for PP **&** LDPE

Parameter	Unit	Value	References
Energy for PP	MJ kg^{-1}	83	(Thiriez und Gutowski 2006)
Emission factor for PP	$kgCO_{2eq}$ kg^{-1}	1.95	(Anonymous 2011)
Mass of jumbo bag[1]	kg	1.5	–
Energy for LDPE	MJ kg^{-1}	73.1	(Thiriez und Gutowski 2006)
Emission factor for LDPE	$kgCO_{2eq}$ kg^{-1}	2.06	(Anonymous 2011)
Mass of bag[1]	g	38.15	–

[1] Measured value.

Since option II and III consider automated combustion devices, these ovens require electricity for the fuel and air dosing systems. The electricity required to combust one ton of dry mass-based pellets in a 48 kW thermal power generator is 24.6 kWh (Anonymous 2019b). Option I considers the use of a simple heat generator without control of the combustion process; i.e., in this case no electrical energy is needed. The assumed annual efficiency of the heat generator in option I is 65 %, due to the fact that it is a device without control of the combustion process, and for option II and III 80 %, because it is an automated device with control of the combustion process (Martinov et al. 2011).

Emissions of GHG that occur during the combustion of corn cobs, except CO_2, were 0.24 gCO_{2eq} MJ^{-1} according to (Giuntoli et al. 2015).

6.1.3 Energy balance

Methods in accordance with the VDI guideline 4600 (1997) were used to implement the energy balance. According to VDI 4600 cumulative energy demand (*Kumulierter Energieaufwand – KEA*) is defined as the total primary energy required for production (index *H*), use (index *N*) and disposal (index *E*) of material and nonmaterial goods. The equation for calculating *KEA* can be summarized according to equation (1).

$$KEA = KEA_H + KEA_N + KEA_E \tag{1}$$

The purpose of this parameter is to provide as much information as possible for the optimal design and production of economic goods in accordance with environmental compatibility. The concept of this method is not to prescribe every detail, so the possibilities of the methodology are open; i.e., this method does not set system boundaries, so it is up to the user to determine it. Cumulative energy demand can be expressed as total primary energy, but is more often specified by mass, volume, area, final energy. In this paper, *KEA* is specified by dry matter (DM) of the cob (MJ/t_{DM}).

According to the above, the general term for total energy input (KEA_T) for the preparation and use of corn cobs for combustion can be defined according to equation (2).

$$KEA_T = E_T + E_E + E_P \tag{2}$$

with

E_T energy for transport of whole, crushed or pellets of corn cob in MJ/t_{DM},

E_E electricity for crushing, grinding, pelleting and combustion in MJ/t_{DM}

E_P energy for packaging in MJ/t_{DM}.

In addition to calculating the total energy input of KEA_U, analyses of energy balance were performed using the terms for energy ratio (*ER*, in MJ_p/MJ_f), net energy gain (*NEG*, in MJ t_{DM}^{-1}) and energy efficiency index (η_E).

The energy ration (*ER*) (equation (3)) is defined as the ratio of the energy value of the output (product) and the total energy used in the production of that product; i.e., this indicator shows what share of input energy is transformed into useful output energy. This index enables an understanding of the influence of inputs expressed in energy units in the production of products (biomass) (Ortiz–Cañavate und Hernanz 1999).

The net energy gain (*NEG*) (equation (4)) shows the net profit, more precisely the difference between the energy of the product and the energy invested in its production.

LHV is the lower calorific value based on dry mass in MJ/t_{DM}.

$$ER = \frac{LHV}{KEA_T} \tag{3}$$

$$NEG = LHV - KEA_T \tag{4}$$

$$\eta_E = \frac{LHV - KEA_T}{LHV} \tag{5}$$

6.1.3.1 Greenhouse gases emissions balance

GHG emission balances, for all three options, were determined in accordance with the RED method. The general expression for calculating GHG emissions from the production and use of biomass fuels before generating thermal energy according to this method can be calculated according to equation (6).

$$E = e_{ec} + e_l + e_p + e_{td} + e_u - e_{sca} - e_{ccs} - e_{ccr} \tag{6}$$

With

e_{ec} – emissions from the extraction or cultivation of raw materials,

e_l – annualised emissions from carbon stock changes caused by land-use change,

e_p – emissions from processing,

e_{td} – emissions from transport and distribution,

e_u – emissions from the fuel in use,

e_{sca} – emission savings from soil carbon accumulation via improved agricultural management,

e_{ccs} – emission savings from CO_2 capture and geological storage,

e_{ccr} – emission savings from CO_2 capture and replacement,

E – total emissions from the fuel production before energy conversion in gCO_{2eq} MJ^{-1}.

Emissions from the production of machinery and equipment are not taken into account. e_l and e_{ec} are not considered because corn cob is a by-product of corn grain production to which the resulting emissions are attributed. Also, emission savings (e_{sca}, e_{ccs}, e_{ccr}) are not relevant here.

Emissions from the production and use of biomass fuels in the generation of thermal energy are calculated using equation (7).

$$EC_h = \frac{E}{\eta_h} \tag{7}$$

With

EC_h total greenhouse gas emissions from heat generation in gCO_{2eq} MJ^{-1}

η_h annual efficiency of heat generator in %.

6.1.3.2 Assessment of GHG emissions savings

GHG emission savings are calculated according to equation (8). The fossil fuel comparator for biomass used for heating purposes is 80 gCO_{2eq} MJ^{-1} according to the RED Directive. The emission saving parameter describes whether the use of a certain type of fuel is sustainable. Specifically, for biomass, the sustainability criterion is 70 % from 2021, or 80 % from 2026 if it is used to generate heat.

$$S = \frac{EC_{F(h)} - EC_h}{EC_{F(h)}} \tag{8}$$

with

S GHG emission saving in %,

$EC_{F(h)}$ emissions of fossil fuel comparator in gCO_{2eq} MJ^{-1},

6.2 Results

6.2.1 Energy balance

Table 6.4 shows results of the energy balance for the three scenarios, as well as the share of each phase in the total value of energy used in the chain of preparation and use of corn cobs as fuel. The energy needs are shown only for the longest transport distances. In cases when variations are considered, for the whole cob 100 km, and for crushed and cob pellets the distance from the production plant to the consumer is 300 km.

Table 6.4 Energy balance for whole, crushed and corn cobs pellets

	Whole CC		Crushed CC		CC pellets	
	MJ t_{DM}^{-1}	%	MJ t_{DM}^{-1}	%	MJ t_{DM}^{-1}	%
Energy input						
Energy for transport	81.1	100.0	308.5	29.8	308.5	22.1
whole[1]	81.1	100.0	65.5	6.3	65.5	4.7
crushed/peller[2]	nr	nr	243.0	23.5	243.0	17.4
Energy for crushing	nr	nr	147.0	14.2	147.0	10.5
Energy for pelletizing	nr	nr	nr	nr	588.0	42.2
Energy for packaging	nr	nr	415.0	40.1	185.9	13.3
Energy for combustion	nr	nr	165.8	15.9	165.8	11.9
Total (KEA_T)	81.1	100.0	1,036.3	100.0	1,395.2	100.0

[1] Energy for transporting corn cobs from source to production plant or consumer

[2] Energy for transporting crushed or corn cobs pellets from the production plant to the consumer. nr: not relevant

The value of total energy used is the lowest for the whole cob, and the highest for the cob pellets, about 81 and 1,395 MJ t^{-1}, respectively. Energy used in transport represents a significant share of the energy balance for all three forms of fuel. For the whole cob, it represents the total energy used, while for crushed and pellets, it has a share of about 30 % and 22 %, respectively. In the case of crushed cobs, a large share in the energy balance has the energy used for packaging, about 40 %, while in the case of pellets, the share of energy for packaging is smaller and amounts to approximately 13 %.

Figure 6.1 shows the used energy for three scenarios, *i.e.* for whole, crushed and pellets of corn cob. It is noticed that for pellets, the largest share in the energy balance has the pelleting process, followed by the energy for transport to the end user.

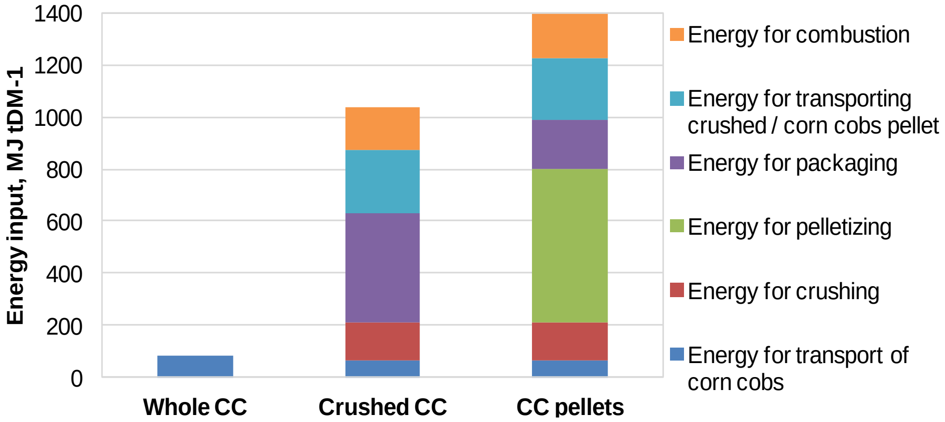


Figure 6.1 Energy input for all three scenarios per parameter

The impact of transport distance on total energy input for the three scenarios is given in Figure 6.2 till Figure 6.4. For the whole cobs, by increasing the transport distance by 20 km, as a result, about 16 MJ t^{-1} more of energy is used, while the scenario with crushed cobs and pellets with increased transport distance by 50 km, used energy increases by about 40 MJ t^{-1}. The exception in the scenario with crushed cobs and pellet is in the case when the transport distance is equal to zero, then the total energy input is reduced by the value of energy required for packaging. The reason for not taking energy into account for packaging is that if the fuel is used at the place where it is processed, it is not necessary to pack it.

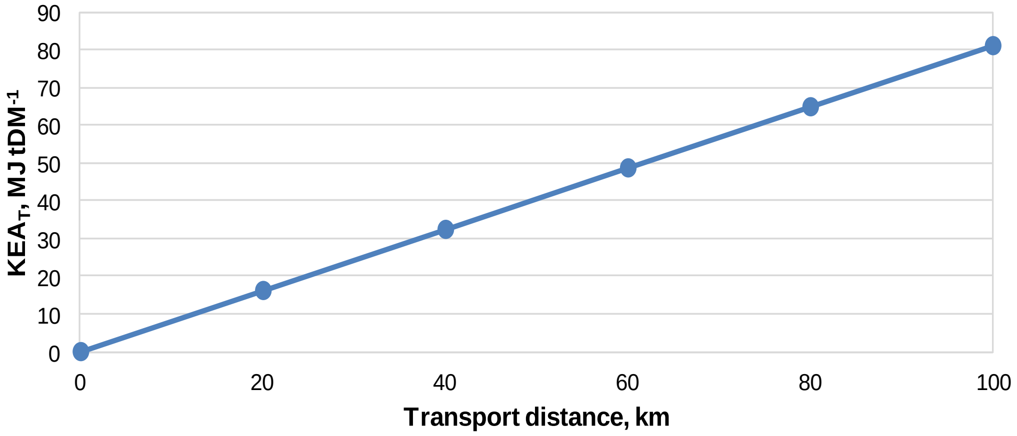


Figure 6.2 Impact of transport distance on total energy input for whole corn cobs

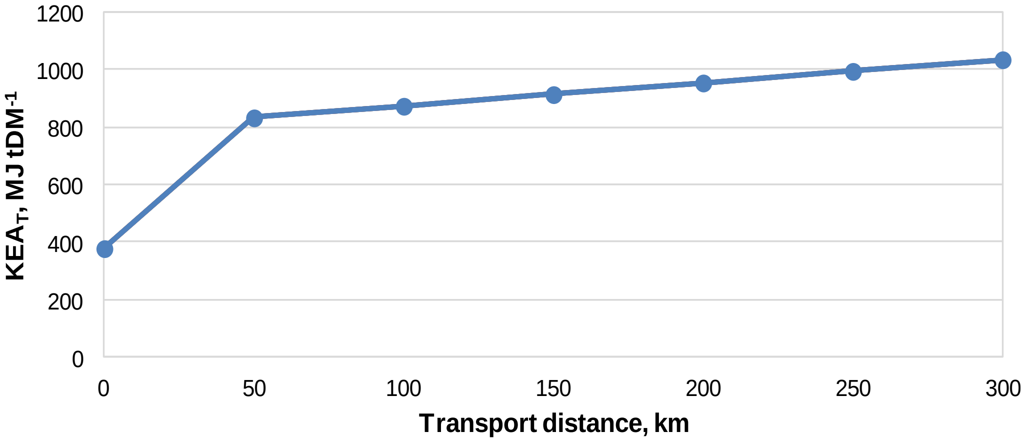


Figure 6.3 Impact of transport distance on total energy input for crushed corn cobs

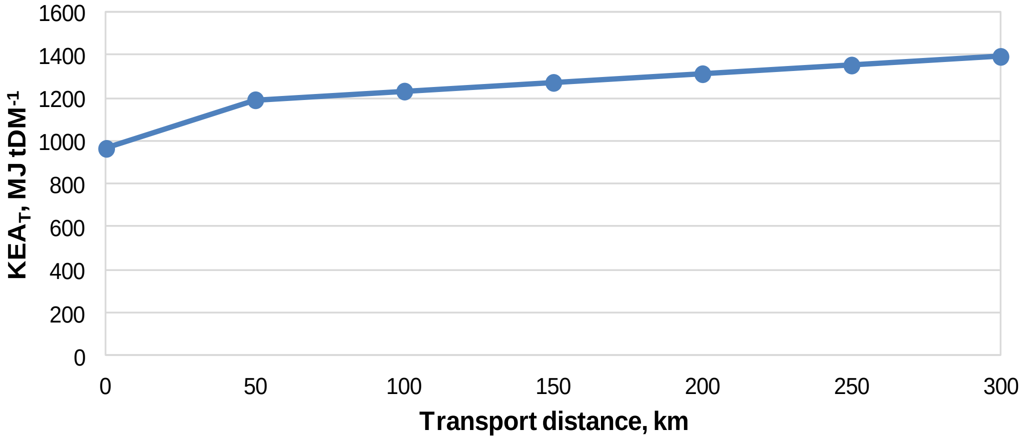


Figure 6.4 Impact of transport distance on total energy input for corn cobs pellets

Figure 6.2-Figure 6.4 shows the values of energy indicators for all three scenarios. ER is high for the whole cobs scenario, and low for the crushed cobs and pellets. Reason for that is that the value of the used energy for the crushed cob is 13, and for the pellet of the cob 17 times higher than the used energy for the whole cob. NEG is highest for the whole cob, and the lowest for the pellet, because this indicator represents the difference between the fuel energy and the energy used. The value of the energy efficiency index for all three scenarios is high and exceeds 90 %. It shows that the share of net energy in the total energy of fuel (Table 6.5).

Table 6.5 Comparative presentation of energy indicators

Parameter	Unit	Whole CC	Crushed CC	CC pellets
Energy ratio	MJ_p/MJ_f	212.2	16.6	12.3
Net Energy Gain	MJ t_{DM}^{-1}	17,126.9	16,171.7	15,812.8
Energy Efficiency Index	%	99.5	93.9	91.9

6.2.2 GHG emissions

A comparison of the results of the greenhouse gas emission balance only for the longest transport distances is given in Table 7.5. The values are based on the lower calorific value for dry mass, *i.e.* GHG emissions are specified per MJ of dry mass of whole, crushed and pellets of cob.

Like the energy balance, the emissions have the lowest value for the whole cob, and the highest for the pellets. Transport has a significant share in the emissions balance for all three scenarios. In Scenario III (cob pellets), the pelletizing process has the largest share in GHG emissions, around 50 % of total emissions.

Emissions that occur during the operation of the boiler, *i.e.* electricity for the boiler, have a significant share in total emissions of about 26 % and 14 %, for crushed cob and pellets respectively.

Table 6.6 Greenhouse gas emission balance

	Whole CC		Crushed CC		CC pellets	
	gCO_{2eq} MJ^{-1}	%	gCO_{2eq} MJ^{-1}	%	gCO_{2eq} MJ^{-1}	%
Transport	0.5	71.4	1.9	35.2	1.9	18.8
whole[1]	0.5	71.4	0.4	7.4	0.4	3.9
crushed/peller[2]	nr	nr	1.5	27.8	1.5	14.9
Crushing	nr	nr	1.3	24.1	1.3	12.9
Pelletizing	nr	nr	nr	nr	5.0	49.5
Packing	nr	nr	0.6	11.1	0.3	2.9
Appliance work	nr	nr	1.4	25.9	1.4	13.9
Combustion	0.2	28.6	0.2	3.7	0.2	2.0
Total (E)	0.7	100.0	5.4	100.0	10.1	100.0
EC_h[3]	1.1		6.8		12.6	

[1]Emissions for the transport of corn cobs from the source to the production plant or consumer. [2]Emissions for the transport of crushed or corn cobs pellets from the production plant to the consumer. [3]Total greenhouse gas emissions from thermal energy generation. nr: not relevant.

Figure 6.5 shows the share of GHG emissions for individual phases for all three scenarios. It can be seen that in the scenario with the whole cob, the emissions from transport have the largest share, while in the scenario with the crushed cob, a significant share of emissions come from the crushing, transport and operation of the boiler. In scenario III, the pelleting phase is dominant in relation to the other phases in the emission balance.

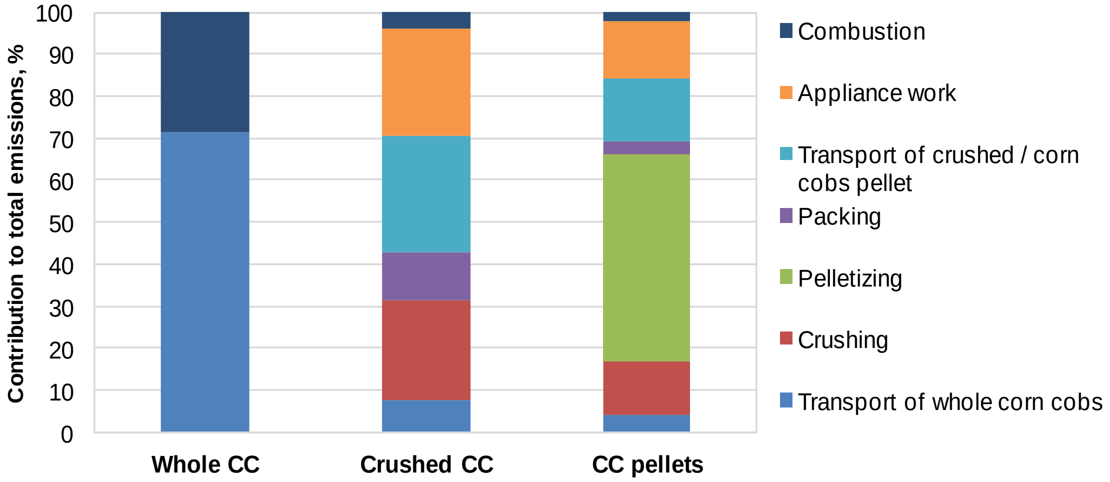


Figure 6.5 Contribution of GHG emissions from different phases in total balance for analyzed scenarios

Total emissions for the whole cob, 0.7 gCO_{2eq} MJ^{-1}, are significantly lower than in Giuntoli et al. (2015) for harvest residues in bulk density greater than 0.2 t m^{-3}, which also includes corn cobs, and amount 4.0 gCO_{2eq} MJ^{-1}. The reason for this is that Giuntoli et al. (2015) considered a transport distance of 500 km, and a transport distance of 100 km was used in this calculation. The same source determined the emissions for straw pellets, which were 8 and 10 gCO_{2eq} MJ^{-1}, for the typical and default value, respectively, while in this example the emissions for corn cob pellets are 10.1 gCO_{2eq} MJ^{-1}, which is almost identical to the default values for straw pellets.

The impact of transport distance on total GHG emissions, as well as emissions generated by heat generation (EC_h) for the three scenarios is given in Figure 6.6 till Figure 6.8. E and EC_h for the whole cob increase linearly and with the increase of the transport distance by 20 km they are higher by about 0.1 and 0.2 gCO_{2eq} MJ^{-1}, respectively. For scenarios with crushed cobs and pellets, the increase in E and EC_h, with an increase in the transport distance by 50 km, is about 0.3 gCO_{2eq} MJ^{-1}, for distances from 50 to 300 km, while this is not the case when the transport distance is 0 km. The reason for that is the same as in the subchapter "Energy balance", *i.e.* emissions from packaging are not taken into account.

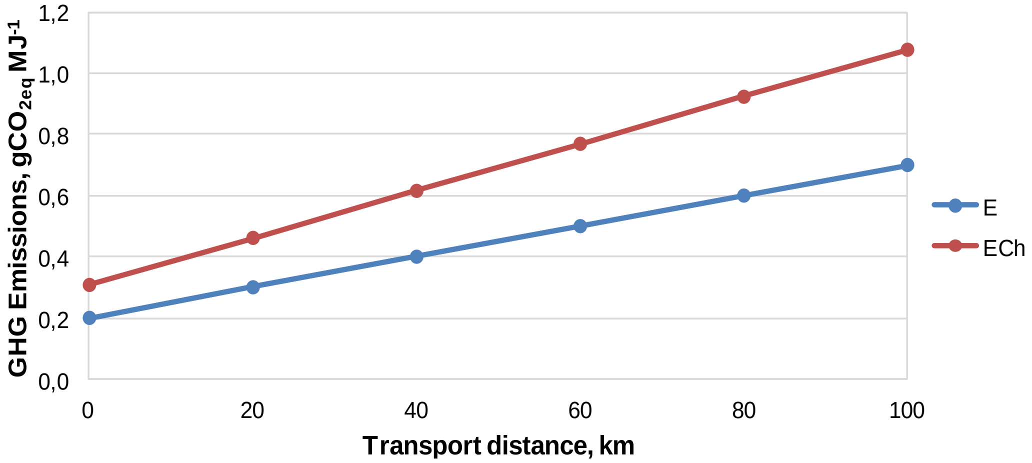


Figure 6.6 Influence of transport distance to GHG emissions for whole corn cobs

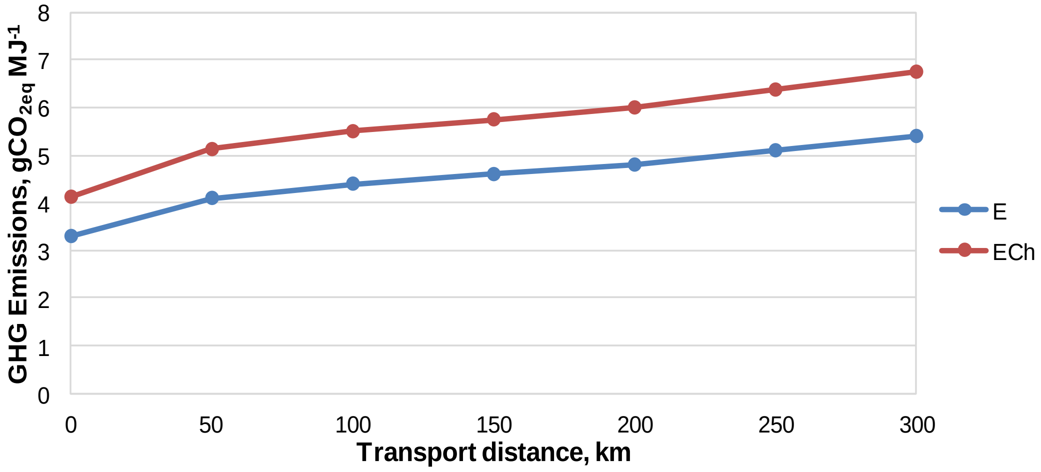


Figure 6.7 Influence of transport distance to GHG emissions for crushed corn cobs

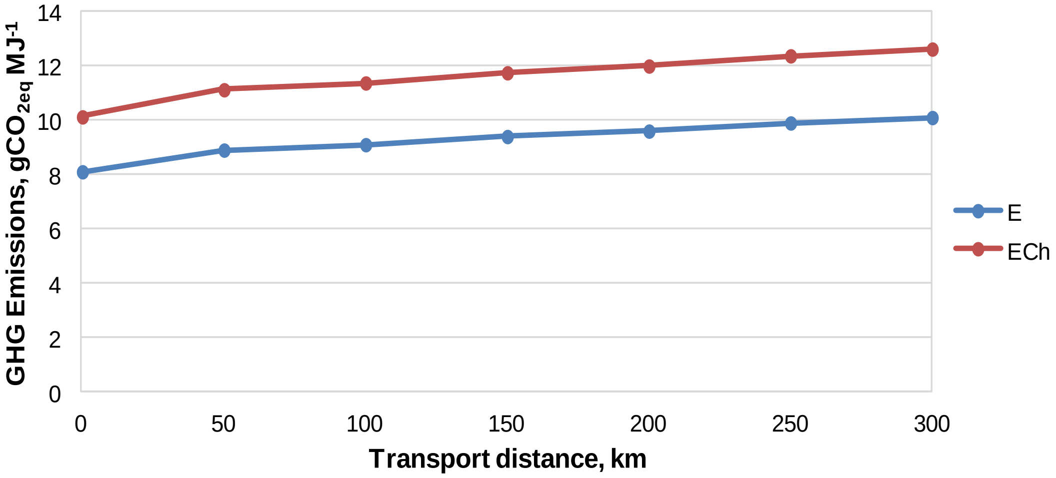


Figure 6.8 Influence of transport distance to GHG emissions for corn cobs pellets

6.2.3 GHG emission savings

Greenhouse gas emission savings for the longest transport distances are shown in Table 6.7 for three scenarios. The fossil fuel comparator has the same value for all three scenarios because it is a fossil biomass comparator used for heating.

Table 6.7 GHG emission saving

Parameter	Unit	Whole CC	Crushed CC	CC pellets
EC_h[1]	gCO_{2eq} MJ^{-1}	1.1	6.8	12.6
$EC_{F(h)}$[2]	gCO_{2eq} MJ^{-1}	80.0	80.0	80.0
S[3]	%	98.6	91.5	84.3

[1] Total greenhouse gas emissions from heat generation. [2] Emissions of fossil fuel comparator. [3] GHG emission saving.

Figure 6.9 shows the achieved emission savings and sustainability criteria, which are defined in the RED Directive, and amount to 70 % for the period from 2021 and 80 % from 2026.

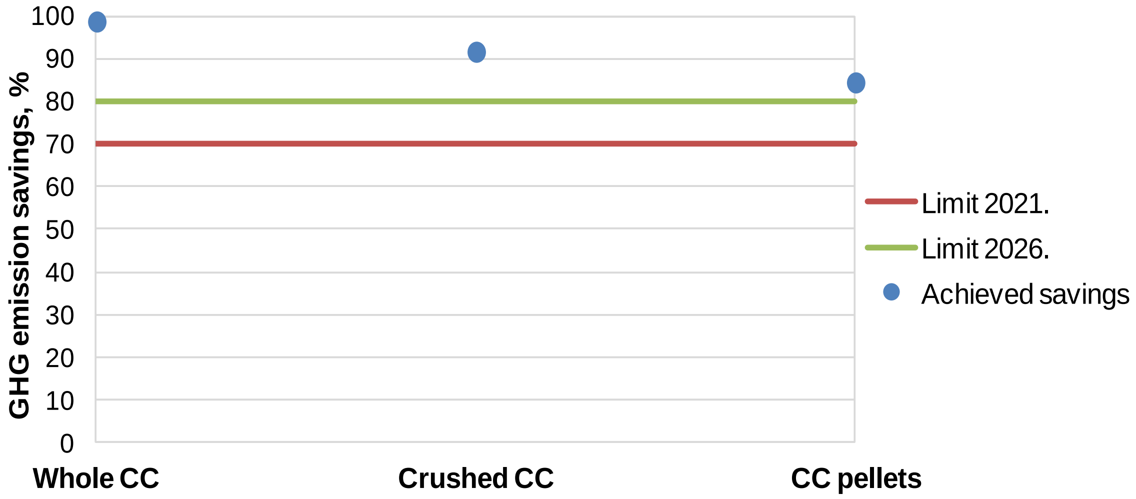


Figure 6.9 Achieved savings and limit values according to the RED Directive

All three scenarios meet the sustainability criteria. With about 84 % the pellet has the lowest emission saving value, while the whole cob with about 98 % has the highest. High values of savings are also for crushed cobs, more than 10 % of the values defined as sustainability criteria for the period from 2026.

The largest transport distances to which the whole, crushed and pellets of corn cobs would remain sustainable, *i.e.* meet the sustainability criteria according to the RED Directive, are given in Table 6.8. For the whole cob, the transport distance from the source to the consumer was considered, while for the crushed cob and pellet, the transport distance from the production plant to the consumer was additionally considered.

Table 6.8 Transport distances to which the scenarios would remain sustainable according to RED

Limits	Whole CC	Crushed CC[1]	CC pellets[1]
70 %	3,180 km	3,170 km	2,150 km
80 %	2,100 km	1,850 km	850 km

[1] Transport distance from the production plant to the consumer.

The difference in the obtained values for the maximum transport distances, for the whole and crushed cob is only 10 km, in the case of 70 % of the saved GHG emissions. The reason for this, although the crushed cob causes higher emission values due to crushing, packaging and boiler operation, is that in scenario I (the whole cob) the mass transported by the truck is 14 t, and for scenarios II and III it is 20 t. Also, the difference in the distance between the crushed cobs and pellet, for both sustainability criteria, is about 1,000 km.

6.2.4 Conclusions

All three scenarios achieved high values of energy indicators, which shows that the values of total energy input are low and that it is possible to increase transport distances or apply an additional phase of fuel preparation.

From an environmental point of view, all three scenarios analysed are sustainable. The highest values of savings were achieved for the whole cob by about 98%, then crushed by about 91 %, and the lowest by pellets with about 84 %. For all three scenarios, the increase in transport distance does not affect the assessment of the sustainability of the considered environmental aspect.

7 Assessment of socio-economic aspects

Djordje Djatkov, Milan Martinov

7.1 Methodology

Profitability assessment of investment in heating facilities that use corn cobs as a fuel was conducted by application of the calculator and decision-making tool named *BiomasaPro (Martinov et al. 2011)*. The assessment approach behind this tool is in line with parameters, criteria and rules of the Ministry of Energy and Mining of Republic of Serbia intended for planning and construction of energy facilities.

Table 7.1 Parameters and criteria for economic assessment

Parameter	Criteria for positive assessment
Net Present Value	> 0
Internal Rate of Return (Project IRR)	Higher than discount rate
Payback Period	Shorter than project duration

For the assessment the collected data about capital costs, operational costs, investment options, fuel characteristics, heat generator characteristics, etc. were used. Table 7.1 shows the selected parameters and defined criteria for the economic assessment.

Two options and therewith two *BiomasaPro* versions were used in the assessment.

- The first subsumes *construction* of new heating systems and two pathways were directly compared, a heat generator using natural gas with one that uses biomass. In this case, positive assessment of the heat generator that uses biomass is considered if the Net Present Value (*NPV*) of all generated costs is lower than those for heat generator that uses natural gas.
- The second option subsumes *reconstruction* of old heating system that uses natural gas by new on that uses biomass. In this case, the three parameters in the table below were used for the economic assessment and if all parameters satisfied defined criteria, the investment in heating facility was considered as viable.

In both options, the three corn cob forms were considered, whole, crushed and pellets, with appropriate heat generator for the selected form.

7.2 Results

In the following two subchapters the results of scenarios *Construction* and *Reconstruction* are presented and discussed.

7.2.1 Construction

In the Table 7.2 – Table 7.4 profitability assessment results of the three considered corn cob forms are presented, namely whole corn cobs, crushed and corn cob pellets, respectively. The results show that all considered cases are viable, whereby influencing parameters on profitability were varied. This means, when considering investment in the new heating system (*construction*), all three scenarios are economically viable, even with the minimized lifespan of the equipment and the maximized maintenance and material costs, in any financing option.

Table 7.2 Profitability assessment of whole corn cobs use as a fuel, option construction

Lifespan, a Without bank loan	Maintenance, €	Material costs, €	NVP_2 - NVP_1	Viable
10	0	0	-3,922 €	YES
10	100	50	-2,793 €	YES

10	150	100	-2,039 €	YES
15	0	0	-5,630 €	YES
15	100	50	-4,079 €	YES
15	150	100	-3,045 €	YES
Bank loan 5 years for 50% of capital costs				
10	0	0	-2,997 €	YES
10	100	50	-2,135 €	YES
10	150	100	-1,561 €	YES
15	0	0	-3,963 €	YES
15	100	50	-2,876 €	YES
15	150	100	-2,151 €	YES
Bank loan 7 years for 100% of capital costs				
10	0	0	-2,314 €	YES
10	100	50	-1,639 €	YES
10	150	100	-1,189 €	YES
15	0	0	-2,888 €	YES
15	100	50	-2,088 €	YES
15	150	100	-1,556 €	YES

NVP_2 - NVP_1: difference of Net Present Values between scenario for whole corn cobs (NVP_2) and scenario for natural gas (NVP_1)

Table 7.3 Profitability assessment of crushed corn cobs use as a fuel, option construction

Lifespan, a	Maintenance, €	Material costs, €	NVP2 - NVP1	Viable
Without bank loan				
10	0	0	-3,404 €	YES
10	100	50	-2,275 €	YES
10	150	100	-1,522 €	YES
15	0	0	-4,832 €	YES
15	100	50	-3,281 €	YES
15	150	100	-2,247 €	YES
Bank loan 5 years for 50% of capital costs				
10	0	0	-2,644 €	YES
10	100	50	-1,783 €	YES
10	150	100	-1,208 €	YES
15	0	0	-3,527 €	YES
15	100	50	-2,440 €	YES
15	150	100	-1,715 €	YES
Bank loan 7 years for 100% of capital costs				
10	0	0	-1,956 €	YES
10	100	50	-1,281 €	YES
10	150	100	-831 €	YES
15	0	0	-2,536 €	YES
15	100	50	-1,737 €	YES
15	150	100	-1,204 €	YES

NVP_2 - NVP_1: difference of Net Present Values between scenario for crushed corn cobs (NVP_2) and scenario for natural gas (NVP_1)

Table 7.4 Profitability assessment of corn cob pellets use as a fuel, option construction

Lifespan, a	Maintenance, €	Material costs, €	NVP_2 - NVP_1	Viable
Without bank loan				
10	0	0	-2,924 €	YES
10	100	50	-1,794 €	YES
10	150	100	-1,041 €	YES
15	0	0	-4,151 €	YES
15	100	50	-2,600 €	YES
15	150	100	-1,566 €	YES
Bank loan 5 years for 50% of capital costs				
10	0	0	-2,291 €	YES
10	100	50	-1,430 €	YES

10	150	100	-855 €	YES
15	0	0	-3,088 €	YES
15	100	50	-2,001 €	YES
15	150	100	-1,277 €	YES
Bank loan 7 years for 100% of capital costs				
10	0	0	-1,654 €	YES
10	100	50	-979 €	YES
10	150	100	-529 €	YES
15	0	0	-2,204 €	YES
15	100	50	-1,404 €	YES
15	150	100	-872 €	YES

NVP$_2$ - NVP$_1$: difference of Net Present Values between scenario for corn cob pellets (NVP$_2$) and scenario for natural gas (NVP$_1$)

Table 7.5 presents the results of the sensitivity analysis with aim to determine highest acceptable prices of all three corn cob forms that allow for economic profitability of the investment in new equipment (*construction*). The results show that these prices could be approximately up to 6, 3 and 2.5 times higher than actual prices on the market. Therefore, the corn cob pellets are the most sensible to price change on the market, and oppositely, whole corn cobs at least.

Table 7.5 The highest acceptable prices of the three corn cob forms that allow for economic profitability, option construction

Lifespan, a	Whole	Crushed	Pellet
	€ t^{-1}		
Without bank loan			
10	247	303	326
15	247	301	323
Bank loan 5 years for 50% of capital costs			
10	249	309	332
15	251	313	338
Bank loan 7 years for 100% of capital costs			
10	243	294	314
15	248	307	331

7.2.2 Reconstruction

In Table 7.6 the profitability assessment results of the three considered corn cob forms are presented, when considering investment in the new heating system (*reconstruction*). The results show that scenario for whole corn cobs is almost always viable, with an exception for financing option with bank loan, short equipment lifespan, and high maintenance and material costs. Other two scenarios are not economically viable, only with an exception for scenario with crushed corn cobs with no ban loan, long equipment lifespan, and low maintenance and material costs.

Table 7.6 Profitability assessment of the three forms of corn cob fuel, option reconstruction

Lifespan, a	Maintenance, €	Material costs, €	Whole	Crushed	Pellet
			Viable		
Without bank loan					
10	0	0	YES	NO	NO
10	100	50	YES	NO	NO
10	150	100	YES	NO	NO
15	0	0	YES	YES	NO
15	100	50	YES	NO	NO
15	150	100	YES	NO	NO
Bank loan 5 years for 50% of capital costs					
10	0	0	YES	NO	NO
10	100	50	YES	NO	NO

10	150	100	NO	NO	NO
15	0	0	YES	NO	NO
15	100	50	YES	NO	NO
15	150	100	YES	NO	NO
Bank loan 7 years for 100% of capital costs					
10	0	0	YES	NO	NO
10	100	50	YES	NO	NO
10	150	100	NO	NO	NO
15	0	0	YES	NO	NO
15	100	50	YES	NO	NO
15	150	100	NO	NO	NO

In the Table 7.7 varied fuel prices of corn cob forms and natural gas are presented, which enable zero profitability (NPV = 0) when considering replacement of old heating system with natural gas by biomass. Prices higher than those actual on the market are marked green and lower with red.

Table 7.7 Fuel prices that allow for zero profitability, option reconstruction

Lifespan, a	Whole € t^{-1}	NG c€ Sm^{-3}	Crushed € t^{-1}	NG c€ Sm^{-3}	Pellet € t^{-1}	NG c€ Sm^{-3}
Without bank loan						
10	🟩 117	🟥 9	🟥 58	🟩 40	🟥 41	🟩 53
15	🟩 150	🟥 2	🟩 120	🟥 26	🟥 112	🟩 36
Bank loan 5 years for 50% of capital costs						
10	🟩 104	🟥 12	🟥 34	🟩 47	🟥 12	🟩 61
15	🟩 139	🟥 5	🟥 99	🟩 31	🟥 87	🟩 42
Bank loan 7 years for 100% of capital costs						
10	🟩 86	🟥 17	nr	🟩 57	nr	🟩 73
15	🟩 104	🟥 13	🟥 32	🟩 48	🟥 10	🟩 61

NG: Natural gas; nr: not relevant.

7.2.3 Assessment of social aspects

From the aspect of social availability/acceptability corn cob pellets are at least available form for the average user. The practice of pelletizing of crop residues is not common and is usually performed per request, for consumers with bigger capacities.

On the other hand, crushed and pelletized corn cobs are more acceptable by users that require comfort and could be potentially used even in the suburban area.

Finally, whole, unprocessed corn cobs are more acceptable by users in typical rural areas such as farms and in villages due to their wide availability since the corn is the most commonly cultivated crop. The low-price is the of waste crop residues is the deciding factor influencing potential users.

8 Final consideration and outlook

Natasa Dragutinovic, Isabel Höfer, Djordje Djatkov, Milan Martinov, Martin Kaltschmitt

8.1 General conclusions

With the overarching aim of minimizing negative environmental impacts from the energetic use of corn cobs as a solid fuel in small scale combustion devices several possible pathways are analysed in this project.

Under first specific goal fuel processing was investigated, and the results showed that obtained particle size distribution of crushed maize cobs fully corresponds to size classes of wood chips P45 and G50, in accordance with DIN CEN/TS 14961 and ÖNORM M 7133, respectively. Produced corn cob pellets with additives and starch as a binder are in line with the requirements of ISO 17225-6 for non-wood pellets with regards to fuel properties.

During testing and improvement of heat generators, three experimental setups were used for combustion trials, two in Serbia (in Mladenovac and in Kula) and one in Hamburg, at the premises of TUHH. In Serbia two manually fed units were tested and one automatically fired unit, whether in Hamburg one automatically-fed multi-fuel boiler was tested.

Results from the combustion trials in Serbia by Faculty of Technical Sciences (FTS) and Project partner Termoplin can be summarized as follows:

- Mladenovac (automatic boiler Termoplin TK):
  - When using corn cob pellets as fuel and after the modification of the combustion chamber, CO emissions were in line with the requirements of the class 4 of EN 303-5 (< 500 mg/m^3). Average value of particulate matter (PM) emissions of 143 mg/m^3 is in line with the requirements of the EN 303-5 class 3 (< 150 mg/m^3). Efficiency value of $> 75\%$ is also met (class 3 from EN 303-5).
  - When crushed corn cobs are used as fuel after the installation of the fireclay mantel, CO and organic gaseous carbon (OGC) emissions are in line with class 3 (CO $< 3{,}000$ mg/m^3 and OGC < 100 mg/m^3). However, particulate matter (PM) emissions and efficiency are just outside the standard requirements.
- Terming Ozone agro 25:
  - After installing the proposed measures by introducing secondary combustion air and a fireclay cylinder in the combustion chamber, emissions from the combustion of corn cob pellets at nominal load decreased. CO emissions met the class 4 requirements ($< 1{,}000$ mg/m^3), but particulate matter (PM) emissions were just above the class 3 emission limit values (ELVs) from EN 303-5 (< 150 mg/m^3). Efficiency values were in line with class 5 (> 89 %). As expected emissions are partial loads (50 % and 30 %) are higher than at nominal load. In both cases CO emissions meet the class 3 emission limit values (ELVs) ($< 3{,}000$ mg/m^3). Particulate matter (PM) emissions are not in line with the requirements of the standard.
- Terming TIG P:
  - After the modifications, average CO emissions are reduced more than 5-fold, being in line with the requirements of class 3 for manually-fed units ($<5{,}000$ mg/m^3). Efficiency is also improved, increasing from 40 % to > 50 %, on average. Most problematic parameter, particulate matter (PM) emission, is reduced almost 3-fold and is quite close the emission limit values (ELVs) for class 3 in EN 303-5 (< 150 mg/m^3), on average.

The expected improvement concerning emissions of pollutants has been partly achieved. The, problem left to resolve is reduction of particulate matter (PM). It seems that this cannot be obtained without after treatment, like utilization of multi cyclone. However, these interventions can cause significant increase of boiler costs.

From the experiments at the Hamburg University of Technology (TUHH) following conclusions can be made:

- Terming Ozone agro:
    - Air-feeding is the critical parameter affecting emissions. After stabilizing the air-feeding the emissions of CO and PM were reduced in both investigated experimental series.
    - Blending of fuel can reduce emissions but not enough to meet the emission limit values. In blends of corn cob pellets with wood pellets the emissions of CO are in accordance with EN 303-5 class 5 emission limit value (< 500 mg/m^3), whereas particulate matter (PM) emissions are still higher than emission limit values.
    - Corn cob grits are not adequate fuel form for small-scale combustion. The emissions are outside of the acceptable range, even with the application of additives.
- Austroflamm Polly 2.0:
    - Blending of corn cob pellets with wood pellets can reduce emissions, but emission limit values are met only when minor shares of corn cob pellets are present in the blend (up to 25 wt. % corn cobs). By blending locally sourced corn cob pellets with high-quality wood pellets certain savings can be achieved, as well as reduction of pollutant emissions.
    - Additivation of corn cob pellets with kaolin prior to pelletization can reduce both CO and PM emissions, but not enough to meet the standard requirements.
    - The combination of fuel blending (with wood pellets) and additivation of corn cob pellets with kaolin should be investigated as measure to increase the share of corn cobs in fuel blends and thus alleviate economic burden and promote the utilization of locally sourced biomass.

Assessment of environmental impact has shown that all three scenarios achieved high values of energy indicators, which shows that the values of total energy input are low and that it is possible to increase transport distances or apply an additional phase of fuel preparation. From an environmental aspect, all three scenarios analysed are sustainable. The highest values of savings were achieved for the whole cob by about 98 %, then crushed by about 91 %, and the lowest by pellets with about 84 %. For all three options, the increase in transport distance does not affect the assessment of the sustainability of the considered environmental aspect.

Profitability assessment of using corn cobs as energy source has shown that in the case of construction, all three options are economically viable, even with the minimized lifespan of the equipment and the maximized maintenance and material costs. In the case of reconstruction, the results show that option I using whole corn cobs is almost always viable, with an exception for financing with bank loan, short equipment lifespan, and high maintenance and material costs. Other two pathways are not economically viable, with the exception of option II with crushed corn cobs with no ban loan, long equipment lifespan, and low maintenance and material costs.

Taking into consideration the overall and specific project goals and the achieved results, it can be concluded that low-cost measures are effective in the case of corn cob combustion, up to a certain point. The CO emissions have been reduced in most investigated cases and are in accordance with emission limit values. However, in order to meet the strict requirements of the international standard for small-scale combustion units regarding particulate matter (PM) emissions, it is necessary to further modernise the equipment and upgrade the fuel. In case of whole and crushed corn cob combustion, it is possible that the achievement of such ambitious goals is attainable only in large combustion units with flue gas treatment systems.

Due to the fact that the sole use of corn cob pellets in automatically-fed small-scale units results in increased particulate matter (PM) emissions, the energetic utilization of corn cob pellets in small-scale automatically-fed units in an environmentally acceptable way (in line with standard requirements and emission limit values) is possible only in fuel blends. Thus, it could be recommended to blend these agro pellets with higher quality wood pellets, partially alleviating the economic burden, using local available fuel source and mitigating the particulate matter (PM) emissions. Another promising possibility is to further investigate the application of mineral additives, specifically kaolin, in combination with fuel blending.

8.2 Outlook

Against this background, and in order to promote more environmentally conscious energetic utilization of locally-sourced biomass in Serbia different actions could be recommended and further investigated.

Uncontrolled utilization of waste biomass in small-scale units in household in rural, suburban, as well as in urban households should be replaced with controlled, modernized and monitored small-scale heating units. Crop residues as such should only be used as fuel in their processed form in automatic heating units in combination with higher quality fuels.

A questionnaire for residents of rural, suburban, and urban settlements regarding their habits and activities in the field of heat provision and use of solid fuels should be conducted, so that a better insight into the consumer (user) behaviour is achieved. The mapping of the consumer behaviour is a basis and a helpful tool when designing framework and scenarios, as well as measures for reducing negative environmental impact and planning the energy provision and air quality monitoring programs.

As a complementary tool, a mapping of pollution emissions in rural, suburban, and urban settlements should be conducted over a two-year period, covering two heating seasons. The mapping or air pollution is essential to get an overview of the sources of pollution emissions and the contribution of small-scale heating units in the total air pollution emissions, as well as dynamic of emissions during the day, on an hourly basis.

After evaluating the impact and contribution of small-scale polluters in the total air-pollution emissions by comparison with statistical data, and after considering the hourly dynamics of emissions, appropriate plans and measures should be proposed.

Literature

Anonymous (2011): Winnipeg sewage treatment program. Appendix 7: CO2 emission factors database. Winnipeg, Canada. Online verfügbar unter www.winnipeg.ca/finance/findata/matmgt/documents/2012/682-2012/682-2012_Appendix_H-WSTP_South_End_Plant_Process_Selection_Report/Appendix%207.pdf.

Anonymous (2015): Baza podataka BioGrace. Online verfügbar unter www.biograce.net/app/webroot/biograce2/content/ghgcalculationtool_electricityheatingcooling/overview.

Anonymous (2019a): Fer Komerc DOO, Slankamen, direktor Ljepoja Vlado, lični kontakt (April 2019).

Anonymous (2019b): Termoplin DOO, Mladenovac, Aleksandar Jugović dipl. inž. maš, lični kontakt (Maj 2019).

Anukam, Anthony I.; Goso, Boniswa P.; Okoh, Omobola O.; Mamphweli, Sampson N. (2017): Studies on Characterization of Corn Cob for Application in a Gasification Process for Energy Production. In: *Journal of Chemistry* 2017, S. 1–9. DOI: 10.1155/2017/6478389.

Bäfver, Linda S.; Leckner, Bo; Tullin, Claes; Berntsen, Morten (2011): Particle emissions from pellets stoves and modern and old-type wood stoves. In: *Biomass and Bioenergy* 35 (8), S. 3648–3655. DOI: 10.1016/j.biombioe.2011.05.027.

Batel, W. (1971): Einführung in die Korngrößenmesstechnik: Springer-Verlag, Berlin - Heidelberg - New York.

Boman, C. (2005): Particulate and gaseous emissions from residential biomass combustion. Umea University, Umea. Energy Technology and Thermal Process Chemistry.

Boman, Christoffer; Nordin, Anders; Boström, Dan; Öhman, Marcus (2004): Characterization of Inorganic Particulate Matter from Residential Combustion of Pelletized Biomass Fuels. In: *Energy Fuels* 18 (2), S. 338–348. DOI: 10.1021/ef034028i.

Boström, D.; Skoglund, N.; Grimm, A.; Boman, C.; Öhman, M.; Broström, M.; Backman, R. (2012): Ash Transformation Chemistry during Combustion of Biomass. In: *Energy Fuels* 26 (1), S. 85–93. DOI: 10.1021/ef201205b.

Brunner, T.; Kanzian, W.; Obernberger, I.; Theissl, A. (2011): Combustion properties of maize cobs - Results from lab and pilot scale tests. From research to industry and markets, Proceedings; ICC Berlin International Congress Center Berlin, Germany, conference 6-10 June 2011, exhibition 6-9 June 2011. In: *19th European Biomass Conference and Exhibition*, S. 944–951.

Carroll, J. P.; Finnan, J. M. (2015): The use of additives and fuel blending to reduce emissions from the combustion of agricultural fuels in small scale boilers. In: *Biosystems Engineering* 129, S. 127–133. DOI: 10.1016/j.biosystemseng.2014.10.001.

Carvalho, L.; Wopienka, E.; Pointner, C.; Lundgren, J.; Verma, V. K.; Haslinger, W.; Schmidl, C. (2013): Performance of a pellet boiler fired with agricultural fuels. In: *Applied Energy* 104, S. 286–296. DOI: 10.1016/j.apenergy.2012.10.058.

Demirbas, A. (2004): Combustion characteristics of different biomass fuels. In: *Progress in Energy and Combustion Science* 30 (2), S. 219–230. DOI: 10.1016/j.pecs.2003.10.004.

Demirbas, Ayhan (2005): Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. In: *Progress in Energy and Combustion Science* 31 (2), S. 171–192. DOI: 10.1016/j.pecs.2005.02.002.

Dragutinovic, N.; Höfer, I.; Kaltschmitt, M. (2019): Effect of additives on thermochemical conversion of solid biofuel blends from wheat straw, corn stover, and corn cob. In: *Biomass Conv. Bioref.* 9 (1), S. 35–54. DOI: 10.1007/s13399-017-0273-7.

Du, S.; Yang, H.; Qian, K.; Wang, X.; Chen, H. (2014): Fusion and transformation properties of the inorganic components in biomass ash. In: *Fuel* 117, S. 1281–1287. DOI: 10.1016/j.fuel.2013.07.085.

European Chemicals Agency (14.12.2020): Calcium carbonate - Registration Dossier - ECHA. Online verfügbar unter https://echa.europa.eu/registration-dossier/-/registered-dossier/16050/4/3, zuletzt geprüft am 14.12.2020.

Febrero, L.; Granada, E.; Patiño, D.; Eguía, P.; Regueiro, A. (2015): A Comparative Study of Fouling and Bottom Ash from Woody Biomass Combustion in a Fixed-Bed Small-Scale Boiler and Evaluation of the Analytical Techniques Used. In: *Sustainability* 7 (5), S. 5819–5837. DOI: 10.3390/su7055819.

Field, Andy (2018): Discovering Statistics Using IBM SPSS Statistics: North American Edition, 5th Edition: SAGE Publications.

Fournel, S.; Palacios, J.; Godbout, S.; Heitz, M. (2015): Effect of Additives and Fuel Blending on Emissions and Ash-Related Problems from Small-Scale Combustion of Reed Canary Grass. In: *Agriculture* 5 (3), S. 561–576. DOI: 10.3390/agriculture5030561.

FPS manual full 5.8.

Giuntoli, J.; Agostini, A., Edwards, R.; Marelli, L. (2015): Solid and Gaseous Bioenergy Pathways: Input Values and GHG Emissions.

Glavonjic, B.; Ziem, S.; Chudziak, K. (2017): Ocena tržišta drvnih goriva i uređaja na čvrsta goriva za grejanje i kuvanje u Srbiji.

Gollmer, C.; Höfer, I.; Harms, D.; Kaltschmitt, M. (2019): Potential additives for small-scale wood chip combustion – Laboratory-scale estimation of the possible inorganic particulate matter reduction potential. In: *Fuel* 254, S. 115695. DOI: 10.1016/j.fuel.2019.115695.

Höfer, I.; Kaltschmitt, M. (2017): Effect of additives on particulate matter formation of solid biofuel blends from wood and straw. In: *Biomass Conv. Bioref.* 7 (1), S. 101–116. DOI: 10.1007/s13399-016-0217-7.

Huelsmann, T.; Kaltschmitt, M. (2015): DIN-compliant testing of small-scale combustion devices. Final Report in the project Development of sustainable Bioenergy market in Serbia. PN 2011.9798.0-011.00.

Huelsmann, T.; Mack, R.; Kaltschmitt, M.; Hartmann, H. (2019): Influence of kaolinite on the PM emissions from small-scale combustion. In: *Biomass Conv. Bioref.* 9 (1), S. 55–70. DOI: 10.1007/s13399-018-0316-8.

Hülsmann, T. (2018): Feinstaubemissionen bei der Verbrennung von Holz- und Holz/Stroh-MIschpellets -Einfluss einder Brennstoffadditivierung-.

Jin, Xi; Ye, Jiaming; Deng, Lei; Che, Defu (2017): Condensation Behaviors of Potassium during Biomass Combustion. In: *Energy Fuels* 31 (3), S. 2951–2958. DOI: 10.1021/acs.energyfuels.6b03381.

Johansson, L. S.; Tullin, C.; Leckner, B.; Sjövall, P. (2003): Particle emissions from biomass combustion in small combustors. In: *Biomass and Bioenergy* 25 (4), S. 435–446. DOI: 10.1016/S0961-9534(03)00036-9.

Juszczak, M.; Lossy, K. (2012): Pollutant emission from a heat station supplied with agriculture biomass and wood pellet mixture. In: *Chemical and Process Engineering* 33 (2), S. 231–242. DOI: 10.2478/v10176-012-0020-3.

Kaknics, J.; Michel, R.; Poirier, J.; Bilbao, E. de (2017): Experimental Study and Thermodynamic Modelling of High Temperature Interactions Between Molten Miscanthus Ashes and Bed Particles in Fluidized Bed Reactors. In: *Waste Biomass Valor* 8 (8), S. 2771–2790. DOI: 10.1007/s12649-017-9828-x.

Kalembkiewicz, Jan; Galas, Dagmara; Sitarz-Palczak, Elżbieta (2018): The Physicochemical Properties and Composition of Biomass Ash and Evaluating Directions of its Applications. In: *Pol. J. Environ. Stud.* 27 (6), S. 2593–2603. DOI: 10.15244/pjoes/80870.

Kallio, M.; Oravainen, H. (2011): Agrofuels - Challenging Fuel for the Future, S. 253–260.

Kaltschmitt, M.; Hartmann, H.; Hofbauer, H. (2016): Energie aus Biomasse. Berlin, Heidelberg: Springer Berlin Heidelberg.

Khalil, R. A.; Todorovic, D.; Skreiberg, O.; Becidan, M.; Backman, R.; Goile, F. et al. (2012): The effect of kaolin on the combustion of demolition wood under well-controlled conditions. In: *Waste management & research : the journal of the International Solid Wastes and Public Cleansing Association, ISWA* 30 (7), S. 672–680. DOI: 10.1177/0734242X11427942.

Knezevic, J.; Jovic, B.; Maric Tanaskovic, L.; Jovanovic, M.; Mitrovic Josipovic, M.; Ljubicic, A. et al. (2019): Kvalitet vazduha u Republici Srbiji in 2018 - Godisnji Izvestaj - Air quality in the Republic of Serbia in 2018 - Annual report. Hg. v. F. Radovic. Serbian Environmental Protection Agency, Ministry for Environmental Protection.

Krugly, E.; Martuzevicius, D.; Puida, E.; Buinevicius, K.; Stasiulaitiene, I.; Radziuniene, I. et al. (2014): Characterization of Gaseous- and Particle-Phase Emissions from the Combustion of Biomass-Residue-Derived Fuels in a Small Residential Boiler. In: *Energy Fuels* 28 (8), S. 5057–5066. DOI: 10.1021/ef500420t.

Lamberg, Heikki; Nuutinen, Kati; Tissari, Jarkko; Ruusunen, Jarno; Yli-Pirilä, Pasi; Sippula, Olli et al. (2011): Physicochemical characterization of fine particles from small-scale wood combustion. In: *Atmospheric Environment* 45 (40), S. 7635–7643. DOI: 10.1016/j.atmosenv.2011.02.072.

Ma, T.; Fan, C.; Hao, L.; Li, S.; Song, W.; Lin, W. (2016): Fusion characterization of biomass ash. In: *Thermochimica Acta* 638, S. 1–9. DOI: 10.1016/j.tca.2016.06.008.

Mack, R.; Kuptz, D.; Schön, C.; Hartmann, H. (2020): Schwierige Pelletbrennstoffe für Kleinfeuerungsanlagen. Verbrennungstechnische Optimierung durch Additivierung und Mischung. Technologie- und Förderzentrum im Kompetenzzentrum für Nachwachsende Rohstoffe. Straubing.

Mack, R.; Schön, Cl.; Kuptz, D.; Hartmann, H. (2019): Nutzereinflüsse auf die Emissionen aus Kaminöfen. Anzünden, Lufteinstellungen, Brennstoff. TFZ. Straubing.

Martinov, M.; Đatkov, Đ.; Krstić, J.; Vujić, G.; Golub, M.; Brkić, M.; Bojić, S. (2011): Program za ocenu ekonomskih pokazatelja za energetsku primenu biomase.

Miranda, M. T.; Sepúlveda, F. J.; Arranz, J. I.; Montero, I.; Rojas, C. V. (2018): Analysis of pelletizing from corn cob waste. In: *Journal of environmental management* 228, S. 303–311. DOI: 10.1016/j.jenvman.2018.08.105.

Misra, Mahendra K.; Ragland, Kenneth W.; Baker, Andrew J. (1993): Wood ash composition as a function of furnace temperature. In: *Biomass and Bioenergy* 4 (2), S. 103–116. DOI: 10.1016/0961-9534(93)90032-Y.

Mlonka-Mędrala, Agata; Magdziarz, Aneta; Gajek, Marcin; Nowińska, Katarzyna; Nowak, Wojciech (2020): Alkali metals association in biomass and their impact on ash melting behaviour. In: *Fuel* 261, S. 116421. DOI: 10.1016/j.fuel.2019.116421.

Nielsen, H. (2000): Deposition of potassium salts on heat transfer surfaces in straw-fired boilers: a pilot-scale study. In: *Fuel* 79 (2), S. 131–139. DOI: 10.1016/S0016-2361(99)00090-3.

Niu, Y.; Tan, H.; Hui, S. (2016): Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. In: *Progress in Energy and Combustion Science* 52, S. 1–61. DOI: 10.1016/j.pecs.2015.09.003.

Nunes, L.J.R.; Matias, J.C.O.; Catalão, J.P.S. (2016): Biomass combustion systems: A review on the physical and chemical properties of the ashes. In: *Renewable and Sustainable Energy Reviews* 53, S. 235–242. DOI: 10.1016/j.rser.2015.08.053.

Olanders, B.; Steenari, B. M. (1995): Characterization of ashes from wood and straw. In: *Biomass and Bioenergy* 8 (2), S. 105–115.

Ortiz–Cañavate, J.; Hernanz, J. L. (1999): Energy Analysis and Savings. In Hadbook of Agricultural Engineering, Volume V, Energy & Biomass Engineering, ed. Kitani O, Jungbluth T, Peart R.M, Ramdani A, S. 13–42.

Roy, Murari Mohon; Corscadden, Kenny W. (2012): An experimental study of combustion and emissions of biomass briquettes in a domestic wood stove. In: *Applied Energy* 99, S. 206–212. DOI: 10.1016/j.apenergy.2012.05.003.

Sarenbo, S.; Mellbo, P.; Stalnake, O.; Claesson, T. (2009): Reacivity and Leaching of Wood Ash Pellets dehydrated by Hot Air and Flue Gas. In: *The Open Waste Management Journal* 2, S. 47–54.

Schmidl, C.; Luisser, M.; Padouvas, E.; Lasselsberger, L.; Rzaca, M.; Ramirez-Santa Cruz, C. et al. (2011): Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. In: *Atmospheric Environment* 45 (39), S. 7443–7454. DOI: 10.1016/j.atmosenv.2011.05.006.

Schmitt, Verena: Dissertation am Institut für Umwelttechnik und Energiewirtschaft an der Technischen Universität Hamburg-Harburg.

Shao, Y.; Wang, J.; Preto, F.; Zhu, J.; Xu, Ch. (2012): Ash Deposition in Biomass Combustion or Co-Firing for Power/Heat Generation. In: *Energies* 5 (12), S. 5171–5189. DOI: 10.3390/en5125171.

Sippula, Olli; Hokkinen, Jouni; Puustinen, Harri; Yli-Pirilä, Pasi; Jokiniemi, Jorma (2009): Particle Emissions from Small Wood-fired District Heating Units. In: *Energy Fuels* 23 (6), S. 2974–2982. DOI: 10.1021/ef900098v.

Sippula, Olli; Lamberg, Heikki; Leskinen, Jani; Tissari, Jarkko; Jokiniemi, Jorma (2017): Emissions and ash behavior in a 500 kW pellet boiler operated with various blends of woody biomass and peat. In: *Fuel* 202, S. 144–153. DOI: 10.1016/j.fuel.2017.04.009.

SPSS Software | IBM (2020). Online verfügbar unter https://www.ibm.com/analytics/spss-statistics-software, zuletzt aktualisiert am 01.06.2020.000Z, zuletzt geprüft am 01.06.2020.

Steenari, B. M.; Lindqvist, O. (1998): High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite. In: *Biomass and Bioenergy* 14 (1), S. 67–76.

Thiriez, A.; Gutowski, T. (Hg.) (2006): An Environmental Analysis of Injection Molding. In Proc. 2006 IEEE International Symposium on Electronics and the Environment. 195-200. Scottsdale, AZ, USA, 8-11 May.

THY, P.; JENKINS, B.; Grundvig, S.; SHIRAKI, R.; LESHER, C. (2006): High temperature elemental losses and mineralogical changes in common biomass ashes. In: *Fuel* 85 (5-6), S. 783–795. DOI: 10.1016/j.fuel.2005.08.020.

Tissari, J.; Sippula, O.; Kouki, J.; Vuorio, K.; Jokiniemi, J. (2008): Fine Particle and Gas Emissions from the Combustion of Agricultural Fuels Fired in a 20 kW Burner. In: *Energy Fuels* 22 (3), S. 2033–2042. DOI: 10.1021/ef700766y.

Vamvuka, D.; Pitharoulis, M.; Alevizos, G.; Repouskou, E.; Pentari, D. (2009): Ash effects during combustion of lignite/biomass blends in fluidized bed. In: *Renewable Energy* 34 (12), S. 2662–2671. DOI: 10.1016/j.renene.2009.05.005.

Vassilev, S. V.; Baxter, D.; Vassileva, C. G. (2013a): An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. In: *Fuel* 112, S. 391–449. DOI: 10.1016/j.fuel.2013.05.043.

Vassilev, Stanislav V.; Baxter, David; Andersen, Lars K.; Vassileva, Christina G. (2010): An overview of the chemical composition of biomass. In: *Fuel* 89 (5), S. 913–933. DOI: 10.1016/j.fuel.2009.10.022.

Vassilev, Stanislav V.; Baxter, David; Andersen, Lars K.; Vassileva, Christina G. (2013b): An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. In: *Fuel* 105, S. 40–76. DOI: 10.1016/j.fuel.2012.09.041.

Verma, V. K.; Bram, S.; Delattin, F.; Laha, P.; Vandendael, I.; Hubin, A.; Ruyck, J. de (2012): Agro-pellets for domestic heating boilers: Standard laboratory and real life performance. In: *Applied Energy* 90 (1), S. 17–23. DOI: 10.1016/j.apenergy.2010.12.079.

Vlada Repuplike Srbije: Odluka o utvrđivanju Energetskog bilansa Republike Srbije za 2019. godinu. Službenom glasniku Republike Srbije 105/2018.

Wang, L.; Skjevrak, G.; Hustad, J. E.; Skreiberg, Ø. (2014): Investigation of Biomass Ash Sintering Characteristics and the Effect of Additives. In: *Energy Fuels* 28 (1), S. 208–218. DOI: 10.1021/ef401521c.

Wang, Liang; Hustad, Johan E.; Grønli, Morten (2012a): Sintering Characteristics and Mineral Transformation Behaviors of Corn Cob Ashes. In: *Energy Fuels* 26 (9), S. 5905–5916. DOI: 10.1021/ef300215x.

Wang, Liang; Hustad, Johan E.; Skreiberg, Øyvind; Skjevrak, Geir; Grønli, Morten (2012b): A Critical Review on Additives to Reduce Ash Related Operation Problems in Biomass Combustion Applications. In: *Energy Procedia* 20, S. 20–29. DOI: 10.1016/j.egypro.2012.03.004.

Wolf, Karl J.; Smeda, A.; Müller, M.; Hilpert, K. (2005): Investigations on the Influence of Additives for SO 2 Reduction during High Alkaline Biomass Combustion. In: *Energy Fuels* 19 (3), S. 820–824. DOI: 10.1021/ef040081a.

Xiao, Ruirui; Chen, Xueli; Wang, Fuchen; Yu, Guangsuo (2011): The physicochemical properties of different biomass ashes at different ashing temperature. In: *Renewable Energy* 36 (1), S. 244–249. DOI: 10.1016/j.renene.2010.06.027.

Yao, X.; Xu, K.; Li, Y. (2016): Physicochemical Properties and POssible Applications of Waste Corncob Fly Ash from Biomass Gasification Industries of China. In: *BioResources* 11 (2), S. 3783–3798.

Yao, Xiwen; Xu, Kaili (2016): Comparative study of characterization and utilization of corncob ashes from gasification process and combustion process. In: *Construction and Building Materials* 119, S. 215–222. DOI: 10.1016/j.conbuildmat.2016.04.077.

Ye, Yalan; Jiang, Wenhao; Wang, Hongming; An, Xiang (2019): A New Method for Calculating Excess Air Ratio. In: Jason C. Hung, Neil Y. Yen und Lin Hui (Hg.): Frontier Computing, Bd. 542. Singapore: Springer Singapore (Lecture Notes in Electrical Engineering), S. 767–776.

Zeng, T.; Weller, N.; Pollex, A.; Lenz, V. (2016): Blended biomass pellets as fuel for small scale combustion appliances: Influence on gaseous and total particulate matter emissions and applicability of fuel indices. In: *Fuel* 184, S. 689–700. DOI: 10.1016/j.fuel.2016.07.047.

Appendices

A. Appendix A

http://thermalscience.vinca.rs/online-first/4035

B. Appendix B

Calculations

B.1 Calculations of emissions

Detailed description of emission calculations, as well as thermal efficiency calculations are given in Annex C.

B.1.1 Gaseous emissions

According to EN 303-5 mean values of gaseous emissions of CO_2, O_2, CO, (organic gaseous carbon (OGC)), and NO_x are calculated across the entire measurement duration at full load.

Volume concentrations of O_2, CO, CO_2 (calculated), NO, NO_x are exported form Wöhler A550 gaseous analyser (ppm) in relation to dry gas and recalculated to (mg/m^3).

B.1.2 Particulate matter emissions

Based on the volume flow and the velocity of the flue gas (measured with Pitot probe and Testo 440 dp) the nozzle diameter can be selected:

$$d = \sqrt{\frac{4 \cdot \dot{V}_f}{\pi \cdot v_f}} \tag{B.9}$$

Where d is the diameter of the nozzle (m), $\dot{V}_f$ is the volumetric flow in the entry nozzle (m^3/s), and v_f is the velocity of the flue gas at the measurement point (filter) (m/s).

In order to perform iso-kinetic sampling during PM measurement, it is necessary to calculate the volume flow of sampled volume of flue gas, with regards to the velocity of flue gas at the measurement point (filter) and the effective diameter of the nozzle (DIN EN 13284-1):

$$\dot{V}_m = \dot{V}_f \times \frac{100\% - h_f}{100\% - h_m} \times \frac{T_m}{T_f} \times \frac{p_f}{p_m} \tag{B.10}$$

Where $\dot{V}_m$ is the measured sampled volume flow under the conditions at the gas meter, $\dot{V}_f$ is the sampled volume flow under the conditions at the measurement point (filter), h_m is the humidity content of the sampled volume flow under the gas meter conditions in vol.%, h_f is the humidity content of the sampled volume flow under the condition at the measurement point (flter) in vol.%, T_m is the sampled volume flow temperature during measurement at the gas meter in K, T_f is the temperature of the sampled volume flow at the measurement point (filter) in K, p_m is the absolute pressure of the sampled volume flow during measurement at the gas meter, p_f is the absolute pressure of the sampled volume flow at the measurement point (filter).

The relative humidity of flue gas is measured using differential manometer (Testo 440 dp) and a Pitot probe in % and the values converted to volumetric ratio according to the following equation:

$$h_i = \varphi_i \times \frac{p_{H2O}(t)}{p} \tag{B.11}$$

Where h_i is the volumetric share of moisture (-), φ_i is the relative humidity in %, $p_{H2O}(t)$is the saturation pressure of the water vapour at the given temperature (Pa), and P is the absolute pressure (Pa). The saturation water vapour pressure is calculated according to Antoine equation-as follows:

$$p_{H2O}(t) = 10^{\left(5{,}11564-\frac{1687{,}537}{t+230{,}17}\right)} \tag{B.12}$$

Where t is the given temperature for which the saturation pressure is calculated in degrees Celsius and saturation pressure is calculated in bar.

Mean value of PM emission is calculated from values of three independent samples. Each sampling duration depends on the current flue gas conditions and filter loading. Sampling duration ranges 5-15 min. Total particulate matter concentration is determined gravimetrically, calculated based on mass difference of filter before and after combustion, based on the following equation:

$$c_{PM} = \frac{m}{V_{ref}} \tag{B.13}$$

Where c_{PM} is the PM volumetric concentration (mg/m^3) in dry gas at standard conditions and at the reference oxygen content, m – mass of the PM collected on the filter (Δm of the filter before and after the combustion) (g), V_{ref} – volume of dry flue gas at standard conditions (m^3) and reference oxygen content (10 vol.% acc. to EN 303-5).

Volume of the flue gas under standard conditions is calculated as follows (DIN EN 17255-1):

$$V_{ref} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_m}{p_{ref}} \times \frac{100\% - h_m}{100\% - h_{ref}} \times \frac{21\% - O_m}{21\% - O_{ref}} \tag{B.14}$$

Where O_m is the concentration of oxygen under the conditions at the gas meter, and the O_{ref} is the reference oxygen concentration.

C.2 Excess air calculation

Excess air coefficient (λ) was approximately calculated from the volumetric concentrations of O_2 and CO in the dry flue gas (vol.%) (Ye et al. 2019):

$$\lambda = \frac{21}{21 - O_2 - CO} \tag{B.15}$$

B.3 Energy efficiency calculation

B.3.1 Direct method

Energy efficiency calculations have been calculated in accordance with the following international standard:

EN 303-5: Heating boilers – Part 5: Heating boilers for solid fuels, hand and automatically stoked, nominal heat output up to 500 kW – Terminology, requirements, testing and marking.

According to this standard the test duration at full load for automatically-fed units should be >6 h. Amount of heat transferred to the water circuit is measured directly (inside the boiler circuit) or indirectly (using a heat exchanger). Heat capacity of the boiler is the mean value during the entire measurement period.

In the following text the calculation procedure based on direct method is described.

Energy input. For assessing the process efficiency chemical (fuel) energy input into the system Q_B must be taken into account, calculated based on equation:

$$Q_B = B \times LHV \tag{B.16}$$

Where B – fuel flow in (kg/s); LHV – specific lower heating value of the fuel (J/kg).

Thermal capacity. Is calculated based on the following equation:

$$P = \dot{m}_1 \times c_1 \times (T_I - T_o) \tag{B.17}$$

Where $\dot{m}_1$- mass flow of water though the water circuit (kg/s);

c_1 – specific heat capacity of water (J/kgK);

T_O – temperature of the incoming cold water (°C);

T_I – temperature of the returning (output) water (°C).

Efficiency – direct method. Thermal efficiency (η) is calculated based on direct method, as given in the equation:

$$\eta_B = \frac{P}{Q_B} \times 100 \tag{B.18}$$

B.3.2 Indirect method

Energy efficiency calculations have been calculated in accordance with the following international standards:

DIN EN 14785: Residential space heating appliances fired by wood pellets – Requirements and test methods.

According to this standard the test duration at full load for automatically-fed units should be 3 h. According to the DIN EN 14785 after the steady state is achieved for more than 30 min and the temperature of the exhaust gas is constant (+/- 5 K). If the furnace is equipped with a heat exchanger the water flow through the heat exchanger has to be adjusted so that the water temperature is 80 °C + / - 5 °C.

For the calculation of energy efficiency indirect method is used. The following procedure describes the calculations according to DIN EN 14785.

Efficiency. Combustion unit efficiency (η) is calculated according to the indirect method:

$$\eta = 100\% - (q_a + q_b + q_r) \tag{B.19}$$

Values in the parentheses represent different losses associated with the combustion process, where q_a are heating losses, q_b are chemical losses, and q_r are the losses of the exhaust gas as well as heating losses of the combustibles components in the grate ash. All losses are based on the lower heating value (LHV). Q_a, Q_b, Q_r are based on the amount of fuel.

$$q_a = \frac{Q_a}{LHV} \tag{B.20}$$

$$q_a = \frac{Q_b}{LHV} \tag{B.21}$$

$$q_a = \frac{Q_r}{LHV} \tag{B.22}$$

Where heating losses of the exhaust gas (Q_a), Chemical losses of the exhaust gas (Q_b) and finally, heating losses of the combustible components in the grate ash (Q_r) are calculated as follows:

$$Q_a = \left(T_f - T_{atm}\right) \cdot \left[\left(\frac{C_{pmd} \cdot (C - C_r)}{0.536(CO + CO_2)}\right) + \left(\frac{C_{pmH2O} \cdot 1.92(9H + M_{ar})}{100}\right)\right] \tag{B.23}$$

$$Q_b = \frac{12644 \cdot CO \cdot (C - C_r)}{0.536(CO + CO_2) \cdot 100} \tag{B.24}$$

$$Q_r = 335 \cdot b \cdot \frac{A_{dm}}{100} \tag{B.25}$$

Where T_f is the exhaust gas temperature and T_{atm} is the room temperature (K), b are the combustible components in the grate ash (wt. %), C is the carbon content of the fuel (wt. %), CO is the carbon monoxide content of the flue gas (vol.%), CO_2 is the carbon dioxide content of the flue gas (vol.%), C_r is the carbon content of the grate ash compared to the fuel (wt. %), C_{pmd} is the specific heat of dry flue gas, dependent on temperature and composition (kJ/Km^3), C_{pmH2O} is the specific heat of water, dependent on temperature (kJ/Km^3), H is the hydrogen content of the fuel (wt. %), and M_{ar} is water content of the fuel (wt. % as received), A_{dm} – ash content in the grate residue (wt. % dry mass). Combustible residues in the bottom ash b were estimated in the thermogravimetric analysis.

Further values C_{pmd}, C_{pmH2O} and C_r were calculated as followed:

$$\begin{aligned} C_{pmd} = 3.6 \cdot \Bigg(& 0.361 + 0.008 \cdot \left(\frac{T_f}{1000}\right) + 0.034 \cdot \left(\frac{T_f}{1000}\right)^2 \\ & + \left(0.085 + 0.19 \cdot \left(\frac{T_f}{1000}\right) - 0.14 \cdot \left(\frac{T_f}{1000}\right)^2\right) \cdot \left(\frac{CO_2}{100}\right) \\ & + \left(0.3 \cdot \left(\frac{T_f}{1000}\right) - 0.2 \cdot \left(\frac{T_f}{1000}\right)^2\right) \cdot \left(\frac{CO_2}{100}\right)^2 \Bigg) \end{aligned} \tag{B.26}$$

$$C_{pmH2O} = 3.6 \cdot \left(0.414 + 0.038 \cdot \left(\frac{T_f}{1000}\right) + 0.034 \cdot \left(\frac{T_f}{1000}\right)^2\right) \tag{B.27}$$

$$C_r = b \cdot \frac{A_{dm}}{100} \tag{B.28}$$

Total thermal capacity. Total thermal capacity (P_t) is calculated based on the following equation:

$$P_t = \eta \cdot B \cdot LHV \tag{B.29}$$

Where B is the hourly fuel consumption.

Thermal capacity of the water. For the calculation of the energy available with the water pumped through the heat exchanger (if installed), the following equation is used:

$$P_w = C_p \cdot M_w \cdot N \tag{B.30}$$

Where P_w is the water thermal capacity, C_p specific heat of the water, M_w is the water flow, N is the temperature increase.

Room-heating thermal capacity. The difference between total thermal capacity and the thermal capacity of the hot water produced within the heat exchanger is defined as the room-heating thermal capacity (P_{SH}):

$$P_{SH} = P_t - P_w \tag{B.31}$$