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ABSTRACT

The aim of this paper is the production of a high-quality corn cob pellet which satisfies ISO 17225-6 requirements and addresses the ash melting behavior through additives kaolin and magnesium oxide. The effects of additives on the (1) physico-mechanical properties and (2) ash melting behavior of pellets were investigated. Before statistically analyzing the effect of additives on the mechanical durability and bulk density, pelletizing was conducted in two experimental series (full factorial design). In series 1, moisture content (18–20 wt. %), additive type (kaolin or MgO), and additive content (0–2 wt. %) were varied; in series 2, binding agent content (2–4 wt. %), additive type (kaolin or MgO), and additive content (0–2 wt. %) were varied, whereas moisture content was kept constant at 20 wt. %. The effect of additives on ash melting behavior was pre-evaluated: (1) in a laboratory scale, (2) using thermodynamic equilibrium calculations, and (3) fuel indices. Results show that without a binder, only pellets with MgO can reach durability threshold class B (≥96 wt. %) from ISO 17225-6, whereas using a binder, the mean value of all pellets complies with the durability class A (≥97.5 wt. %). Results of pre-evaluation tests are in agreement regarding kaolin but not regarding MgO. Experimental results show that corn cob ash starts sintering >800 °C, melt consisting primarily of K, Si, and O, and both additives prevent sintering. FactSage predicts K sorption in the ash using kaolin, and molar (Si + P + K)/(Mg + Ca + Al) ratio predicts the improvement of ash behavior with both additives.

I. INTRODUCTION

The compaction of loose herbaceous biomass through densification processes improves handling, transport, and storage properties by providing a compact and homogeneous solid biofuel with relatively uniform fuel properties.[1–7] Such a more homogeneous fuel with defined physical-mechanical fuel properties can also typically be easily used in automatically operated combustion devices.[8,9] Automatic fuel-feeding can, compared to manually fed units, lead to clearly higher efficiencies and noticeable reductions in air-borne emissions.[10,11] Thus, densification of herbaceous feedstock[5,12–17] is currently a widely tackled area of research, motivated by increasing resource scarcity and price of wood available as a feedstock for the provision of a solid biofuel.[18] Properties of non-woody pellets such as mechanical durability, bulk density, ash, and moisture content, among others, are issued by international standard ISO 17225-6. In order to reach pellet quality threshold requirements, use of binders is necessary in some cases. Lignosulfonate, molasses, starches, etc.,[19–25] have been added to increase the pellet quality and minimize the quality variations.

Besides improving the mechanical properties of non-woody pellets through densification, ash-associated problems and high emissions of particulate matter (PM) need to be addressed through the use of additives. Additives are used to mitigate particulate matter generation and improve the ash melting behavior.[26–30] In this respect, specifically 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,[31–34] as well as to improve problematic ash melting behavior. Combining additives with binding agents could be the adequate fuel-related measure to solving different challenges associated with agrofuel combustion.[35] Ash melting behavior depends on many factors, including fuel composition, particle size and mechanical properties, combustion technology, combustion chamber temperature, etc., which need to be considered comprehensively and for each individual fuel.[36] However, there have been numerous efforts recently to pre-evalute biomass fuels and their behavior using simplified experimental, empirical, and theoretical models,[36–38] which will be applied and assessed in this study to evaluate the potential application of additives in the combustion of corn cob pellets.

TABLE I. Methods for the analysis of feedstock and pellet properties.

Procedure	Standard method
Sampling	DIN EN ISO 14778
Sample preparation	DIN EN ISO 17827
Moisture content	DIN EN ISO 18134-2
Ash content	DIN EN ISO 18122
Fuel composition	DIN EN 15104, DIN EN ISO 15290
Higher heating values (HHV)	DIN EN 18125
Mechanical durability	DIN EN ISO 17831-1
Bulk density	DIN EN ISO 17828

Moreover, the effect of mineral additives on the fuel properties of pellets is uncertain. Previous studies on corn residue densification[5,13,16,17] identified the most important parameters affecting pellets quality to be feed constituents, moisture content, particle size, conditioning temperature, binding agents, process temperature/pressing temperature, and densification equipment variables.[4,39,40] However, none of them focused specifically on the influence of mineral additives on the properties of the respective pelletized solid biofuels. Due to their properties inert mineral matter such as additives could potentially negatively influence the mechanical properties which are essential for transport, handling, and trading. In addition to this, the potential interaction of binder and additives could affect fuel properties.

The overarching goal of this study is to produce a high-quality corn cob pellet (CCP) which satisfies the pellet quality requirements of ISO 17225–6 and addresses the ash melting behavior issue (and subsequently mitigate particulate matter emissions). In addition to this, two specific goals have been proposed:

(1) assessment of the effect of selected mineral additives, a binding agent, and their interaction on the mechanical properties of corn cobs pellets, experimentally and statistically, and
(2) analysis the effect of additives on the corn cob ash melting behavior using different pre-evaluation methods.

The effect of different factors on the fuel properties of corn cob pellets are assessed based on experimental results by comparing mean values of output variables with standard requirements, whereas mechanical durability and bulk density were further analyzed statistically. In this study, the effect of additives on the ash melting behavior is assessed through different pre-evaluation methods: (1) investigation of the ash melting behavior in the muffle furnace, followed by the analysis of ash morphology and composition using scanning electron microscopy and electron-dispersive spectrometry (SEM/EDS), and identification of ash crystalline phases and reactions taking place in the ash with Powder X-Ray Diffraction (XRD), (2) thermochemical equilibrium calculations (FactSage), and (3) empirically based fuel indices.

II. MATERIALS AND METHODS

A. Feedstock analysis

Grounded corn cobs have been purchased in the spring 2019 in Germany (3.8–5.0 mm particle size). Feedstock characterization was performed according to the methods found in Table I. Additive composition is provided by the manufacturer.

B. Pelletizing

1. Design of experiment

Two series of experiments were designed, each with full-factorial two-level three-factor (Table II) using a commercially available software Design Expert.[41] Series 1 totals 48 experiments, five replicates for each experiment with additional central points (8). Series 2 considered using a starch-based binder for the improvement of pellet durability. In series 2, moisture content was kept fixed at 20 wt. % (based on results from series 1), whereas the variable binder content was introduced. Series 2 totals 24 experiments, comprising of 8 experiments for a full-factorial model.

Abbreviation list can be found in Table III.

2. Pelletizing

Before pelletizing, grounded corn cob feedstock material (8–9 wt. % original moisture content in the delivered feedstock) was first conditioned with water (to 18–20 wt. % final moisture) using a sprinkler (and additives and/or binding agent) with a precision of 0.1 g, manually homogenized using a shovel, and stored overnight (24–48 h). For each experiment, approximately 5 kg of conditioned feedstock was

TABLE II. Design of pelletizing experiments in series 1 and series 2.

	Influential variable	Investigated values		Response variable
Series 1 Design of experiment: Full-factorial two-level three-factor experiment				
1	Moisture content (wt. %)	(18–20)	1	Mechanical durability (wt. %)
2	Additive content (wt. %)	(1–2)	2	Bulk density (kg/m^3)
3	Additive type	(kaolin/MgO)		
Series 2 Design of experiment: Full-factorial two-level three-factor experiment				
1	Binder content (wt. %)	(2–4)	1	Mechanical durability (wt. %)
2	Additive content (wt. %)	(1–2)	2	Bulk density (kg/m^3)
3	Additive type	(kaolin/MgO)		

TABLE III. Labels and abbreviations of produced corn cob pellets from series 1 and series 2.

Series 1		Series 2	
Abbreviation	Full label	Abbreviation	Full label
CCP	Corn cob, 0 wt. % additive	CCP 2S	Corn cob, 0 wt. % additive 2 wt. % starch
CCP 1KAO	Corn cob, 1 wt. % kaolin	CCP 4S	Corn cob, 0 wt. % additive 4 wt. % starch
CCP 2KAO	Corn cob, 2 wt. % kaolin	CCP 1KAO 3S	Corn cob, 1 wt. % kaolin 3 wt. % starch
CCP 1MGO	Corn cob, 1 wt. % MgO	CCP 2KAO 2S	Corn cob, 2 wt. % kaolin 2 wt. % starch
CCP 2MGO	Corn cob, 2 wt. % Mg	CCP 2KAO 4S	Corn cob, 2 wt. % kaolin 4 wt. % starch
		CCP 1MGO 3S	Corn cob, 1 wt. % MgO 3 wt. % starch
		CCP 2MGO 2S	Corn cob, 2 wt. % MgO 2 wt. % starch
		CCP 2MGO 4S	Corn cob, 2 wt. % MgO 4 wt. % starch

pelletized in a Kahl 14–725 flat die pellet press (capacity approximately 5 kg/h) with a rotating roller suspension and two rotating rollers at a constant press mill die roller speed (frequency) of 50 Hz. A press die with a compression ratio 1 to 4 and 6 mm diameter was used.

3. Analysis of pellet properties and statistical analysis

After the production, each pellet batch was left to cool down overnight and stored under cool and dry conditions covered in plastic containers. Produced pellets have been analyzed according to the methods found in Table I. The mean value of each pellet property including standard deviations (Appendix B) is calculated for each experiment and compared with the DIN EN ISO 17225-6 requirements.

4. Data analysis

In order to statistically evaluate the influence of independent variables on the mechanical durability and bulk density of pellets, data from each experimental series were evaluated statistically with a commercially available software SPSS.[42] Analysis of variance (ANOVA)[43,44] was applied to test the effect of input parameters and their interaction on the response variables (selected pellet properties). In ANOVA, linear or higher-order mathematical functions are used to describe the main influences of the input on the output variables, as well as their interactions. 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. Significant difference tests were performed at an α-value of 0.05 (Appendix B). After testing the ANOVA assumptions (normality of residuals, homoscedasticity, and outliers), selected parametric tests (T-test, One-Way ANOVA, Multi-way ANOVA) were conducted. In addition, the requirements of non-parametric tests (Welch ANOVA, Mann-Whitney U test, Kruskal-Wallis) were tested, and where appropriate, these tests were applied.[43] 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, meaning that response values are converted to their ranks in the overall data set.

C. Ash melting behavior and the effect of additives

The effect of additives on the ash melting behavior of corn cob pellets are assessed using methods described in Sec. II C 1–II C 3.

1. Laboratory-scale experimental investigation

For ash sintering tests, corn cob pellet ash generated at 550 °C according to DIN EN ISO 18122 was heated in the laboratory muffle furnace following a method to ash melting behavior previously described in Refs. 45 and 46. After cooling, the (previously) molten corn cob ash from the sintering tests was analyzed using a Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDS) Analysis, using Zeiss Supra 55 VP Field Emission Scanning (FEG)-SEM with Variable Pressure Mode (VP-Mode). The ash sample was coated with an 8 nm gold layer to improve conductivity before analysis; the concentration of gold and associated peaks have been taken into consideration. Moreover, crystalline phases in corn cob pellet ash samples with and without additives generated in the muffle furnace at 550 °C, according to DIN EN ISO 18122, and at 1000 °C, according to the procedure described in Ref. 46, were investigated using powder x-ray diffraction (XRD) (Siemens D5000). Representative ash samples were taken from the crucibles, hand crushed using agate mortar and pestle, and homogenized using a glass spatula before the analysis. The investigated range was $3°–63°$ in 2θ with a scan speed of 1 s.

2. Thermodynamic equilibrium calculation

FactSage 8 software was applied to model and simulate the ash melting behavior during combustion of corn cob pellets.[47,48] For this purpose, elemental composition of corn cobs and additives [$Al_2Si_2O_5(OH)_4$ and MgO] (Table IV), stoichiometric amount of air (per kg of fuel), initial and final conditions (p,t) were used as input variables. Based on the principle of Gibbs free energy minimization after reaching the thermodynamic equilibrium, thermodynamically stable physical and chemical forms as a function of temperature, pressure, and input biomass and air composition are calculated, i.e., the composition of the multiphase system. Thermodynamic data were taken from the Fact_PS database; all calculations were performed at 1 bar ambient pressure and excess air ratio of 1 (stoichiometric air amount of 6.61 kg) in the temperature range of 400–1000 °C with 100 °C increment.

TABLE IV. Composition and selected parameters of corn cobs used for pelletizing experiments (DB—dry basis).

Parameter	Corn cob	Kaolin	MgO
		wt. $\%_{DB}$	
C	48.88		
H	7.77	1.56	
N	0.11		
S	0.11		
O	40.23	55.81	39.70
K	0.77		
Na	0.01		
P	0.02		
Mg	0.02		60.30
Ca	0.02		
Al	<0.01	20.94	
Cl	0.37		
Si	0.06	21.70	
Moisture	9.1		
Ash	2.1		
	mg/kg_{DB}		
Zn	14		
Cu	4.70		
Cr	<0.5		
Cd	<0.2		
	kg/m^3		
Bulk density	428		

3. Fuel indices

Fuel indices empirically developed for coal combustion can be used adjusted and/or combined with phase diagrams to explain the behavior of wide range of inhomogeneous biomass fuels.[49–51] Selected fuel indices, molar (Si + P + K)/(Mg + Ca + Al) and molar Si/K ratio, were calculated based on the elementary composition of the fuel and their applicability for the pre-evaluation of corn cob pellet ash melting behavior with and without additives analyzed. Molar ratio (Si + P + K)/(Mg + Ca + Al) should be a better predictor of ash melting behavior with Al-silicate based additives.[52,53]

III. RESULTS AND DISCUSSION

Results are organized according to the specific goals (Sec. I). After presenting the results of feedstock analysis, mean values of pellet properties are compared with the requirements of the international standard for non-woody pellets, for both series, respectively. Results of the statistical analysis of experimental data are afterwards shown and discussed, for both pelletizing series, respectively. In the second part of the investigation, the results from different pre-evaluation test methods for ash melting behavior are presented, compared, and discussed.

A. Feedstock analysis

The increased contents of N, K, and Cl in the herbaceous feedstock are results of fertilization (Table IV). The composition of herbaceous biomass is known to be inhomogeneous and can vary depending on the climatic conditions, soil quality, fertilizer use, cultivation practices, harvesting techniques, etc. Crop residues are known to be often contaminated with impurities such as soil particles, which further hinder energetic utilization.[54] However, even with certain variations, it is expected that corn cobs can meet the requirements of the standard. Composition of corn cobs is consistent with previous findings.[55–57]

B. Pellet properties and statistical analysis

Experimental data on response variables mechanical durability and bulk density can be found in Appendix A. Contents of N and S are calculated based on elementary composition of materials. Results are compared with the requirements of the DIN EN ISO 17225-6 standard.

1. Physico-mechanical properties of pellets from series 1 (with additives)

Table V summarizes the selected pellet properties from the series 1 in comparison with the requirements from DIN EN ISO 17225-6 (n = 2). All pellet properties with the exception of mechanical durability are in accordance with the requirements. The durability threshold according to the standard is ≥97.5 wt. % for class A pellets and

TABLE V. Summary of pellet properties from series 1 of pelletizing experiments and requirements of ISO 17225-6.

	Ash content wt. %	Moisture content wt. %	LHV MJ/kg_{ar}	Durability wt. %	Bulk density kg/m^3	N content[a] wt. %d.b.	S content[a] wt. %d.b.
CCP[b]	4.39 ± 3.73	9.1 ± 0.55	14.89 ± 0.57	97 ± 0.52	685.92 ± 3.49	0.1057	0.1057
CCP 1MGO	4.64 ± 3.8	11.9 ± 1.73	14.98 ± 0.68	97.85 ± 0.68	633.56 ± 4.38	0.1036	0.1036
CCP 2MGO	9.61 ± 4.44	9.64 ± 2.03	14.52 ± 0.53	97.7 ± 0.26	695.97 ± 24.15	0.1036	0.1036
CCP 1KAO	3.93 ± 1.96	10.9 ± 1.29	15 ± 0.16	97.55 ± 1.04	662.42 ± 29.52	0.1036	0.1036
CCP 2KAO	11.38 ± 3.05	8.72 ± 1.49	14.85 ± 0.61	97.4 ± 0.85	702.01 ± 51.25	0.1036	0.1036
CLASS A	≤6	≤12	≥14.5	≥97.5	≥600	≤1.5	≤0.2
CLASS B	≤10	≤15	≥14.5	≥96	≥600	≤2.0	≤0.3

[a]Calculated values based on the composition of corn cobs and additives, separately.
[b]For the full list of abbreviations see Table II.

≥96.0 wt. % for class B (Table V). Pellets additivized with MgO show higher durability than other experiments; the durability increases with the increasing content of MgO, whereas in the case of kaolin, trend is reversed. During pelletizing of corn cobs grits with kaolin, process control proved to be challenging due to strong temperature variations. Rapid temperature changes could be attributed to a considerable increase in friction and a subsequent heat release due to the mineral (inert) and powdery nature of kaolin clay. In some cases, when process temperature exceeded 100 °C, the process had to be stopped due to disruptions, resulting in irregular and discontinuous pellet quality. Although the limit value was reached during pelletization with MgO, this level could not be kept constant and stable for each experiment.

2. Physico-mechanical properties of pellets from series 2 (with additives and binder)

Table VI summarizes the mean values including standard deviations of selected pellet properties from the series 2 of experiments (with binders) in comparison with requirements from DIN EN ISO 17225-6 (n = 2). In this series, moisture content of the feedstock was kept at a constant level of 19 wt. %. Mean values of ash content, lower heating value (LHV), bulk density, and N- and S-content of all experimental trials are in line with the standard requirements. Average durability value after the use of 3 wt. % binding agent is improved and in accordance with standard requirements for both additives (>97.5 wt. %), which corresponds to lower content of fines and is important from the perspective of combustion quality and particulate matter emissions.

3. Statistical data analysis

The statistical analysis for each response is conducted comprehensively for both pelletizing series. Results of ANOVA analysis are found in Appendix B.

Durability. Since there was some deviation from the normal distribution of the residuals and homoscedasticity of the data, both parametric and non-parametric tests have been employed. After removal of one outlier, parameters additive type (p = 0.001) and binder content (p < 0.001) have been proven significant with probability $p < 0.05$ with ANOVA parametric tests (Appendix B). Factor additive type can explain approximately 8.5% of durability variance (partial Eta squared 0.085), whereas factor binder is responsible for almost 16% of variance (partial Eta squared 0.159). Non-parametric Kruskal-Wallis test showed no significance for binder content. ANOVA *post hoc* tests (Tukey Honestly Significant Difference (HSD), Least Significant Difference (LSD), Dunnett T3, Games-Howell) showed significant differences between groups: 0 and 2 wt. %, 0 and 3 wt. %, and 0 and 4 wt. % binder. Although the interaction between additive type and content has been proven non-significant in this range ($p = 0.059$), a difference in the behavior of two additives is evident.

Bulk density. All data fulfilled the assumptions of parametric tests; therefore, ANOVA was used, with significance $p = 0.048$ being close to the rejection zone. Therefore, the effect of binder content on bulk density is minor, but still statistically significant. This variable is responsible for approximately 8% of bulk density variation (partial Eta squared 0.077) (Appendix B). *Post hoc* tests (Tukey and LSD) have shown significant differences ($p < 0.05$) between groups containing 0 and 2 wt. %, 2 and 4 wt. %, and 3 and 4 wt. % binder. The optimal content of binder from the bulk density optimization point of view would be 2 wt. %, whereas with the further increase in binder content, the bulk density decreases. Negative influence of starch addition on the bulk density is due to swelling effect. This is not expected to be problematic in the case of corn cob pelletizing since bulk density values for pellet samples are well above the threshold limit values.

C. Ash melting behavior and the effect of additives

Results of different pre-evaluation test methods estimating ash melting tendency during combustion with and without additives are presented in the following text.

1. Experimental lab-scale investigation

Based on the results of laboratory scale muffle-furnace ash melting tests (Table VII), non-additivized corn cob pellet ash samples have shown sintering as early as 800 °C (Appendix C). In molten corn cob ash samples at 800 and 1000 °C, no crystalline phases could be

TABLE VI. Summary of pellet properties from series 2 of pelletizing experiments and requirements of ISO 17225-6.

	Ash content wt. %	Moisture content wt. %	LHV MJ/kgar	Durability %	Bulk density kg/m^3	N content[a] wt. %d.b.	S content[a] wt. %d.b.
CCP 2S[b]	4.39 ± 3.73	9.1 ± 0.55	15.6 ± 0.23	97 ± 0.52	685.92 ± 3.49	0.1057	0.1057
CCP 4S	4.64 ± 3.8	11.9 ± 1.73	14.98 ± 0.16	97.85 ± 0.68	633.56 ± 4.38	0.1036	0.1036
CCP 1KAO 3S	2.01 ± 0.02	9.64 ± 2.03	15.24 ± 0.13	97.7 ± 0.26	695.97 ± 24.15	0.1036	0.1036
CCP 1MGO 3S	2.17 ± 0.23	10.9 ± 1.29	15.05 ± 0.12	97.55 ± 1.04	662.42 ± 29.52	0.1036	0.1036
CCP 2KAO 2S	2.62 ± 0.22	8.72 ± 1.49	15.81 ± 0.98	97.4 ± 0.85	702.01 ± 51.25	0.1036	0.1036
CCP 2KAO 4S	1.82 ± 1.57	8.85 ± 0.57	15.24 ± 0.06	97.1 ± 0.14	693.99 ± 5.65	0.1014	0.1014
CCP 2MGO 2S	2.75 ± 0.58	10.64 ± 1.61	14.79 ± 0.07	98.4 ± 0	696.64 ± 51.25	0.1036	0.1036
CCP 2MGO 4S	2.99 ± 0.26	12.12 ± 0.19	14.43 ± 0	97.1 ± 0.14	608.36 ± 2.33	0.1014	0.1014
CLASS A	≤6	≤12	≥14.5	≥97.5	≥600	≤1.5	≤0.2
CLASS B	≤10	≤15	≥14.5	≥96	≥600	≤2.0	≤0.3

[a]Calculated values based on the composition of corn cobs and additives, separately.
[b]For the full list of abbreviations see Table II.

TABLE VII. Categorization of corn cob grit/pellet ash melting behavior and crystalline phases in the ash.

	Sintering grade[b]			Crystalline phase	
	Ash generation temperature (°C)				
Fuel ash[a]	800	900	1000	500	1000
CCP	6	6	6	KCl, K_2SO_4	n.a.
CCP 1KAO	2	2	2	KCl, K-Al-silicate	K-Al-silicate, SiO_2
CCP 2KAO	2	2	2	KCl, K-Al-silicate, $KAlSiO_4$	K-Al-silicate
CCP 1MGO	2–3	2–3	3	MgO	MgO
CCP 2MGO	2	2	2	KCl, MgO	MgO

[a]For the full list of abbreviations, see Table II.
[b]Sintering categorization: 1—no sintering (powdery ash), 2—small crystals or coarser particles, 3—light crust, easily broken, 4—firm crust and agglomeration, 5—sintered ash, 6—molten ash; categories 1 to 3 are considered acceptable.

identified since during cooling molten K-silicates form glassy compounds, undetectable with XRD.[42,58] KCl and K_2SO_4 are detected in 550 °C ash samples. The melting points of KCl and K_2SO_4 are 760 and 1069 °C, respectively;[59] during combustion, they are released into gaseous phase and are main components of particulate matter. The presence of KCl in an ash sample at 550 °C and its absence from the molten samples (800 °C) indicate its release into the gaseous phase in this temperature region, supported by SEM/EDS results. As shown in Figs. 1 and 2, at temperatures >800 °C, the entire surface of molten ash particle is smooth, except from occasional large pores. The formation of cavities could be the result of release of volatiles species such as KCl into the gaseous phase.[27,28,60,62] EDS results (Fig. 3) how that K, Si, and O make up almost 85 wt. % of the tested sample. This is possibly due to the presence of molten K-silicates.

Application of additives kaolin and MgO has been efficient in preventing ash sintering although kaolin showed better results. In pellets with kaolin, K-Al-silicates such as $KAlSiO_4$ are identified at both temperatures. Addition of kaolin converts the K-compound into silicates which are stable at high temperature. Kaolinite decomposes at temperatures between 450 and 600 °C and forms an amorphous mixture of Al_2O_3 and SiO_2 called meta-kaolinite, which reacts with K to stop its release and make stable K-Al silicates.[61] These results are in accordance with previous reported kaolin acting mechanisms. On the other hand, in most MgO-additivized samples, only this mineral (periclase) is detected besides KCl. This corroborates that MgO acts as a diluting agent, preventing the contact of reactive compounds and sintering of the corn cob ash.

2. FactSage calculations

Since K is the most important ash-forming from the aspect of particulate matter formation and contributes to ash melting and slag formation,[62,63] the results of FactSage calculations using Fact_PS database are discussed from the viewpoint of K distribution (fractionation) in solid, liquid, and gaseous phases after reaching the thermodynamic equilibrium.

According to the FactSage calculations with non-additivized corn cob (Fig. 4), K is mainly present in the form of solid $KCl_{(s)}$, $K_2CO_{3(s)}$, and $K_3PO_{4(s)}$ until 600 °C. At 800 °C, sylvite disappears and KCl is distributed between liquid $KCl_{(liq)}$ slag and gaseous $KCl_{(g)}$ phase. K_2CO_3 on the other hand does not form slag phase, but it is present as solid until 800 °C and is released into gaseous phase afterwards, possibly as $CO_{2(g)}$ and $K_{(g)}$. $K_3PO_{4(s)}$ is still present in solid form at 1000 °C. At this temperature, approximately 50 wt. % of all K is found in $KCl_{(g)}$.

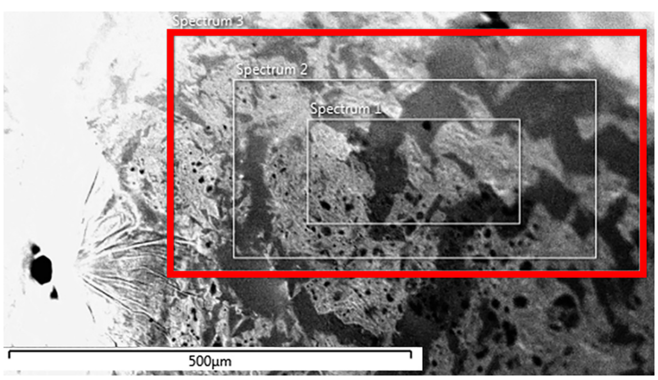

FIG. 1. SEM image of molten corn cob ash from non-additivized pellets with the EDS scanned region marked in red.

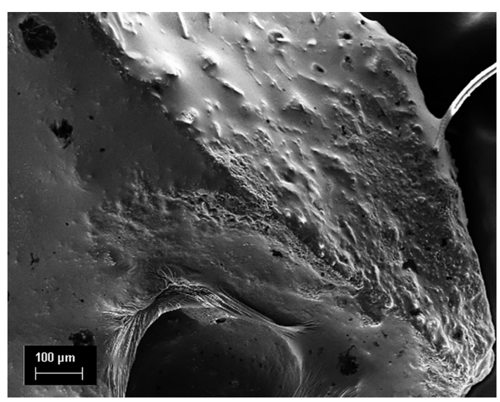

FIG. 2. SEM image of corn cob ash from non-additivized pellets.

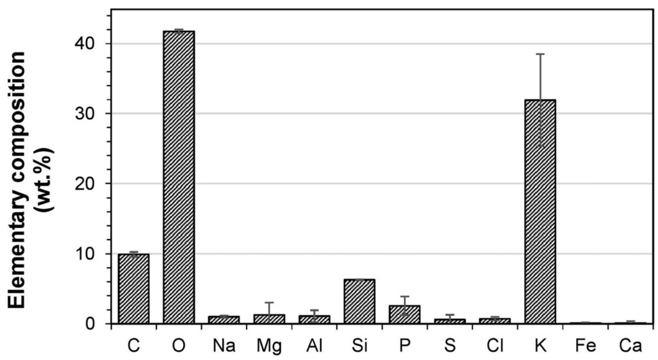

FIG. 3. Composition of molten corn cob ash from non-additivized pellets.

The appearance of liquid slag at 800 °C and the presence of KCl crystalline phase in the 550 °C are in accordance with experimental results. The prevalence of K in solid phases during combustion of biomass at temperatures <600 °C is shown in previous studies.[27,64–68] Solid KCl and K_2SiO_3 exist until approximately 800 °C;[69] solid K_2CO_3 dramatically drops and disappears at approximately 900 °C.[67] At 1000 °C, K is present either as KCl slag (liquid)[69,70] or in combination with $KCl_{(g)}$[71] in line with our findings. K_2O is reported to be the major component of slag until 1100 °C.

After the addition of 1 and 2 wt. % kaolin, release of K into the gaseous phase seems to be hindered (Figs. 5 and 6), indicating potential reduction of PM emissions during combustion. At 1000 °C, about half of K is present in solid and half in the gaseous phase with 1 wt. % kaolin, whereas less than 50 wt. % of K is released into the gaseous phase with 2 wt. % kaolin. The minimization or absence of liquid (molten) phases indicates prevention of sintering when using kaolin. The formation of high-temperature stabile K-Al-silicates such as $KAlSiO_4$ and $KAlSi_2O_6$ is predicted and is in accordance with XRD

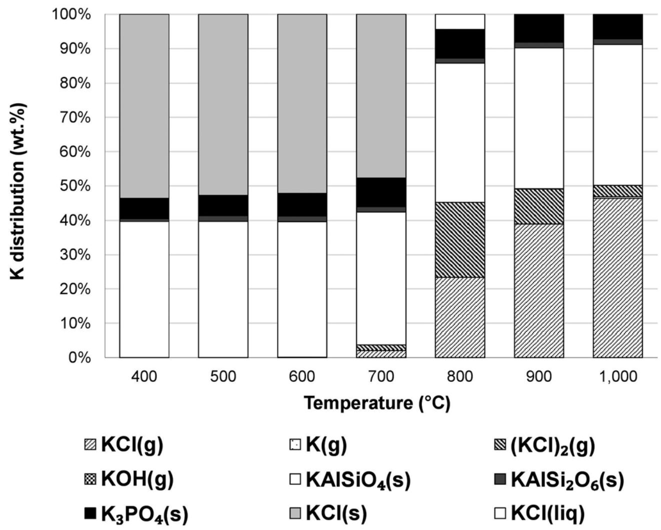

FIG. 5. K distribution during combustion of corn cob with 1 wt. % kaolin (calculation using FactSage[47]).

results and previous literature.[29,72,73] With MgO as an additive, there does not seem to be any incorporation of K in the solid phase at higher temperatures (Figs. 7 and 8). On the contrary, at 1000 °C, more than 80% of K is released into the gaseous phase. In addition to this, $KCl_{(liq)}$ slag makes up almost 40 wt. % of all K-compounds at 800 °C with 1 and 2 wt. % MgO, but this slag phase disappears at 900 °C according to FactSage calculations. This is not in line with experimental results (Table VII). Due to the fact that thermodynamic equilibrium calculations are a simplification of a complex process and are dependent on the used databases, contrasting results can appear. In this paper, results of FactSage calculations, regarding kaolin in line with experimental results, are consistent with the findings from Ref. 64.

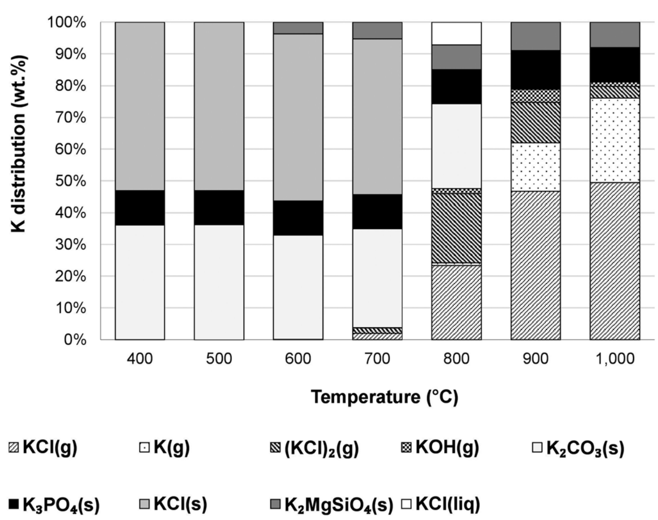

FIG. 4. K distribution during combustion of corn cob without additives (calculation using FactSage[47]).

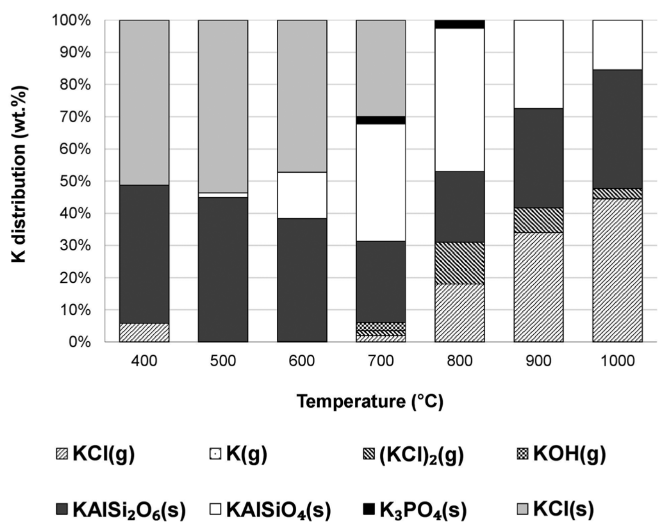

FIG. 6. K distribution during combustion of corn cob with 2 wt. % kaolin (calculation using FactSage[47]).

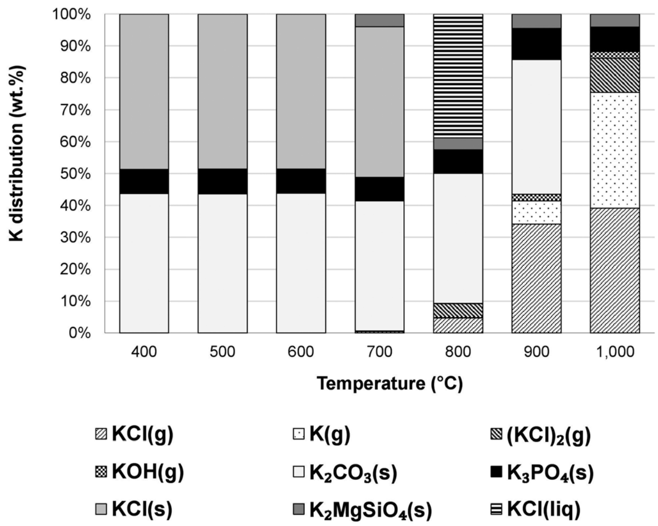

FIG. 7. K distribution during combustion of corn cob with 1 wt. % MgO (calculation using FactSage[47]).

3. Fuel indices

Empirically based fuel indices, adapted for biomass combustion, have been calculated based on elementary composition and dry fuel basis and presented in Table VIII. With the decreasing value of molar (Si + P + K)/(Mg + Ca + Al) index, the ash melting point increases.[52] Therefore, with the addition of kaolin and MgO, the corn cob pellet ash melting behavior should be improved. The previously reported value of adapted molar (Si + P + K)/(Mg + Ca + Al) index was ≈5 and >5 for herbaceous fuels and <1 for woody fuel.[52] Even though this is not in line with the value of 16 calculated in this study, the rough estimate of the problematic ash melting prediction still holds true. Higher molar Si/K ratio value points toward preferred formation of K-silicates and K sorption in the ash.[74] Based on index value of <2.5, no clear conclusions regarding K release can be drawn, according to Ref. 37, even though there is an increase in the ratio value as a consequence of kaolin addition (Si from kaolin), indicating increased K sorption in the ash and low K release.

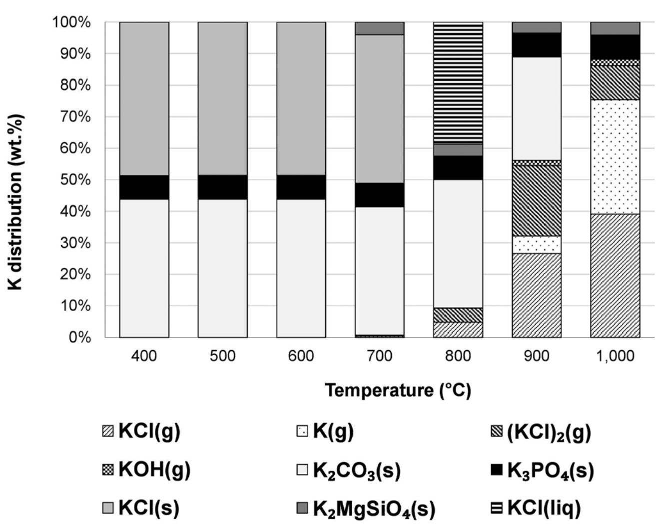

FIG. 8. K distribution during combustion of corn cob with 2 wt. % MgO (calculation using FactSage[47]).

TABLE VIII. Selected fuel indices for predicting ash behavior and pollutant emissions.

Fuel	(Si + P + K)/(Mg + Ca + Al) mol/mol	Si/K mol/mol
CCP	16.8207	0.1181
CCP 1KAO	3.1690	0.5481
CCP 2KAO	2.1532	0.9869
CCP 1MGO	0.7957	0.1181
CCP 2MGO	0.4035	0.1181

IV. CONCLUSION

The aim of this study was to produce high-quality additivized corn cob pellets and to assess the effect of additives kaolin and magnesium oxide (MgO) on the ash melting behavior in laboratory-scale conditions. Durability requirements of the international standard for non-woody pellets DIN EN ISO 17225-6 could be reached in all cases if binders are applied. From an optimization point of view, the amount of 2 wt. % binder should be sufficient to reach the desired values of class A pellets when using MgO, whereas for pellets with kaolin, minimum 3 wt. % of binder should be used. Bulk density requirements were met in all cases.

The results of three investigated pre-evaluation methods are mostly in line with each other regarding kaolin and point toward prevention of corn cob ash sintering up to 1000 °C (except Si/K ratio). Results with MgO as an additive are contrasting; it has been effective in preventing ash sintering during experimental investigation in the muffle furnace, but FactSage results do not predict K sorption in the residue ash. For validation purposes, the results from this laboratory-scale study will be compared with results from pilot-scale combustion trials using the produced pellets.

ACKNOWLEDGMENTS

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APPENDIX A: EXPERIMENTAL DATA

Tables IX and X show experimental data from pelletizing series 1 and series 2.

APPENDIX B: STATISTICAL ANALYSIS

Mean value $\bar{x}_i$ and standard deviations SD of pellet properties were calculated according to [(B1) and (B2)]

TABLE IX. Experimental data from pelletizing series 1 with additives.

Std	Run	Factor 1 Type	Factor 2 wt. %	Factor 3 wt. %	Response 1 wt. %	Response 2 kg/m^3
26	1	Kao	2	20	90.8	672.04
46	2	Mgo	1	19	98.4	701.61
11	3	Kao	2	18	92.6	658.6
27	4	Kao	2	20	82	580.64
19	5	Kao	0	20	94.6	658.6
29	6	Mgo	2	20	89.8	639.78
2	7	Kao	0	18	96.6	685.48
16	8	Mgo	2	18	99	693.54
42	9	Mgo	1	19	97.6	685.34
9	10	Kao	2	18	94.4	682.79
31	11	Mgo	2	20	98.4	701.61
5	12	Mgo	0	18	97.5	685.48
10	13	Kao	2	18	94	645.16
13	14	Mgo	2	18	98.6	701.61
14	15	Mgo	2	18	99.2	658.6
28	16	Kao	2	20	94.2	661.29
35	17	Kao	1	19	92.2	682.79
47	18	Kao	1	19	97.4	709.67
6	19	Mgo	0	18	95.6	666.66
7	20	Mgo	0	18	95.6	663.98
20	21	Kao	0	20	97.8	668
1	22	Kao	0	18	97.4	680.1
24	23	Mgo	0	20	94.6	655.91
38	24	Mgo	1	19	98.6	688.17
3	25	Kao	0	18	95.2	637.09
22	26	Mgo	0	20	97.8	696.23
39	27	Kao	1	19	95.8	642.47
30	28	Mgo	2	20	97.4	645.16
36	29	Mgo	1	19	97.8	639.78
37	30	Kao	1	19	94	655.91
45	31	Kao	1	19	96.2	639.78
33	32	Kao	1	19	93	623.65
34	33	Mgo	1	19	98	666.6
12	34	Kao	2	18	94.4	655.9
8	35	Mgo	0	18	97.4	663.98
25	36	Kao	2	20	94.2	685.48
21	37	Mgo	0	20	95.8	631.72
41	38	Kao	1	19	94.4	661.29
43	39	Kao	1	19	97.3	672.04
48	40	Mgo	1	19	98.6	655.91
40	41	Mgo	1	19	99	690.08
4	42	Kao	0	18	92.4	602.15
17	43	Kao	0	20	95.6	698.92
23	44	Mgo	0	20	94.2	620.97
32	45	Mgo	2	20	97.4	651.12
18	46	Kao	0	20	95.8	610.21
15	47	Mgo	2	18	98.6	688.17
44	48	Mgo	1	19	98	658.6

TABLE X. Experimental data from pelletizing series 2 with additives.

Std	Run	A:Additive type	B:Additive content wt. %	C:Binder wt. %	Durability wt. %	Bulk density kg/m^3
5	1	Kao	2	2	96.8	665 772
3	2	Mgo	0	2	96.4	690
4	3	Mgo	0	2	97.2	687 248
14	4	Kao	2	4	97.2	697 987
12	5	Mgo	0	4	97.6	633 557
2	6	Kao	0	2	96.8	684 564
13	7	Kao	2	4	97	690
1	8	Kao	0	2	97.6	681 879
16	9	Mgo	2	4	97.2	610
11	10	Mgo	0	4	98.4	628 188
9	11	Kao	0	4	98.4	638 926
17	12	Kao	1	3	97.6	673 826
21	13	Kao	1	3	98	714 094
7	14	Mgo	2	2	98.4	660 403
18	15	Mgo	1	3	98.8	687 248
19	16	Kao	1	3	97.4	676.51
20	17	Mgo	1	3	96.6	665 772
23	18	Kao	1	3	97.8	719 463
10	19	Kao	0	4	97	633 557
15	20	Mgo	2	4	97	606 711
6	21	Kao	2	2	98	738 255
22	22	Mgo	1	3	98	676.51
24	23	Mgo	1	3	96.8	620 134
8	24	Mgo	2	2	98.4	732 886

$$\overline{x}_i = \frac{1}{n}\sum_{i=1}^{n} x_i, \tag{B1}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x}_i)^2}{n-1}}, \tag{B2}$$

where x_i is the measured value and n is the number of experiments.

The following tables are results from ANOVA analysis of response variables mechanical durability (Table XI) and bulk density (Table XII) for both series of experiments.

TABLE XI. SPSS multi-factor ANOVA table for comprehensive durability analysis [df—degrees of freedom, F—F-statistic value, Sig.—significance level of the ANOVA test (*p*-value)].

Tests of between-subjects effects

Dependent variable: Durability

Source	Type III sum of squares	df	Mean square	F	Significance	Partial eta squared
Corrected model	168.877a	19	8.888	3.304	0.000	0.452
Intercept	552 517.042	1	552 517.042	205 355.654	0.000	1.000
Additive_type	18.887	1	18.887	7.020	0.010	0.085
Additive_content	0.480	1	0.480	0.178	0.674	0.002
Moisture_content	5.535	1	5.535	2.057	0.156	0.026
Binder_content	38.563	2	19.281	7.166	0.001	0.159
Error	204.481	76	2.691			
Total	892 420.400	96				
Corrected total	373.358	95				

TABLE XII. SPSS multi-factor ANOVA table for comprehensive bulk density analysis [df—degrees of freedom, F—F-statistic value, Sig.—significance level of the ANOVA test (p-value)].

Tests of between-subjects effects						
Dependent variable: Bulk_density						
Source	Type III sum of squares	Df	Mean square	F	Significance	Partial eta squared
Corrected model	24 525.416a	19	1290.811	0.796	0.705	0.166
Intercept	26 600 904.765	1	26 600 904.765	16 393.601	0.000	0.995
Additive_type	3197.855	1	3197.855	1.971	0.164	0.025
Additive_content	262.322	1	262.322	0.162	0.689	0.002
Moisture_content	250.084	1	250.084	0.154	0.696	0.002
Binder_content	10 241.792	2	5120.896	3.156	0.048	0.077
Error	123 320.606	76	1622.640			
Total	43 646 209.280	96				
Corrected total	147 846.022	95				

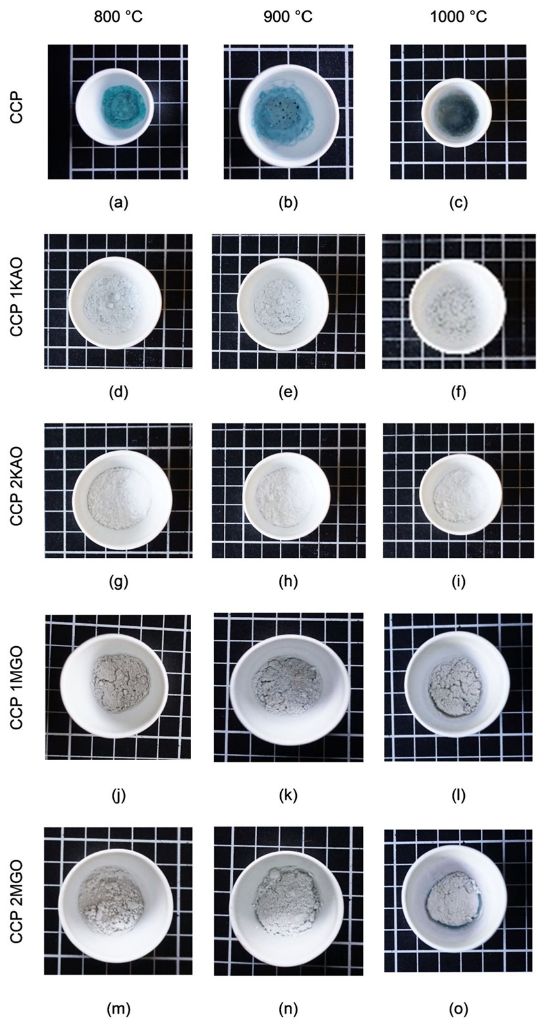

FIG. 9. Photographs of ash melting behavior of corn cob pellets.

APPENDIX C: PHOTO ARCHIVE

Figure 9 shows photographs of corn cob ash with and without additives after sintering tests.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its appendixes.

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