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Influence of Kaolin and Calcite Additives on Ash Transformations in Small-Scale Combustion of Oat

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A growing interest has been observed for the use of cereal grains in small- and medium-scale heating. Previous studies have been performed to determine the fuel quality of various cereal grains for combustion purposes. The present investigation was undertaken in order to elucidate the potential abatement of lowtemperature corrosion and deposits formation by using fuel additives (calcite and kaolin) during combustion of oat. Special emphasis was put on understanding the role of slag and bottom ash composition on the volatilization of species responsible for fouling and emission of fine particles and acid gases. The ash fractions were analyzed with scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), for elemental composition, and with X-ray diffraction (XRD) for identification of crystalline phases. The previously reported K and Si capturing effects of kaolin additive were observed also in the present study using P-rich biomass fuels. That is, the prerequisites for the formation of low melting K-rich silicates were reduced. The result of using kaolin additive on the bottom ash was that no slag was formed. The effect of the kaolin additive on the formation of submicrometer flue gas particles was an increased share of condensed K-phosphates at the expense of K-sulfate and KCl. The latter phase was almost completely absent in the particulate matter. Consequently, the levels of HCl and SO₂ in the flue gases increased somewhat. The addition of both calcite assortments increased the amount of formed slag, although to a considerably higher extent for the precipitated calcite. P was captured to a higher degree in the bottom ash, compared to the combustion of pure oat. The effect of the calcite additives on the fine particle emissions in the flue gases was that the share of K-phosphate decreased considerably, while the content of K-sulfate and KCl increased. Consequently, also the flue-gas levels of acidic HCl and SO₂ decreased. This implies that the low-temperature corrosion observed in small-scale combustion of oat possibly can be abated by employing calcite additives. Alternatively, if problems with slagging and deposition of corrosive matter at heat convection surfaces are to be avoided, kaolin additive can be utilized, on the condition that the higher concentrations of acidic gases can be tolerated.

1. Introduction

The need for renewable and sustainable energy sources as an alternative for fossil fuels has become very urgent in recent years for several reasons. The major reasons are the anticipated shortage of fossil fuel, primarily crude oil, and the threat of global warming. In the general search for renewable alternatives, various agriculture crops have attracted attention. In northern Europe, for instance, firing oat for small-scale heating has recently proven to be both technically feasible and economically beneficial. Globally, 73% of oat production is used as animal feed. Thus, an eventual competition between oat for energy production and for food production will be indirect. However, the huge rise in price of agricultural products in general and cereals in particular in recent years has hampered the initial enthusiasm for this opportunity. In a report from the Organisation for Economic

Co-operation and Development (OECD) and the Food and Agricultural Organization (FAO), it is concluded that the present global cereal prices have been driven higher as the weather-related production shortfalls of the past year and dwindling global stocks have tightened supply on world markets. However, they should decline toward the end of the decade, but will probably stay substantially higher than prices observed over the past decade because of expanding food demand in developing countries as well as increased demand for cereals for energy production.³ Furthermore, estimations have shown that at an oat price per ton, below 85% of the corresponding price for wood pellets, the combustion of oat is still economically favorable.⁴ In addition to the economical competitiveness of firing oat for heating, the technical aspects are crucial. Although oat firing from an operational point of view has been demonstrated to be quite unproblematic, there are a number of issues that demands attention.

Compared to for instance wood fuel, the ash content of oat is at least ten times higher. Even if oat has proven to be most

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favorable among cereals concerning ash related problems such as slagging, the emissions of particles and acid gases is still high. Due to high concentrations of acid gases, the temperature must exceed the dew point of the flue gases in order to avoid corrosion in the boiler and the chimney. There are no limits for particle emissions from appliances smaller than 500 kW in Sweden today. Nevertheless, it is important to consider these emissions since small scale wood combustion is one of the largest sources of fine ($< 1\,\mu m$) airborne particles in Europe today.

The present investigation was undertaken in order to elucidate the potential abatement of low temperature corrosion and deposits formation by using fuel additives (calcite and kaolin) during the combustion of oat. Special emphasis was placed on chemical understanding of the role of slag and bottom ash composition on the volatilization of species responsible for fouling and emission of fine particles and acid gases.

2. Materials and Methods

2.1. Fuel and Additives. The used oat grain was locally produced in the neighborhood of Umeå, Sweden. Chemical analysis of oat grain with respect to moisture content, total ash content, and main ash forming elements is given in Table 1.

Ground calcite (CaCO₃) (Duchefa Biochemie), precipitated calcite (Riedel-de Haen), and kaolin (Al₂Si₂O₅(OH)₄) (Riedel-de Haen) were used as additives. The grain sizes of these differed markedly. Ground calcite was as expected relatively coarse with grains between 5 and 50 μ m while the grains of the precipitated calcite were much smaller, the majority less than 2 μ m. The grains of the kaolin were also relatively fine but slightly coarser and more heterogeneous in size than the precipitated calcite. To obtain good distribution and good contact between additives and fuel, the materials were mixed in a cement mixer in advance of filling up the fuel storage.

2.2. Combustion Procedure and Conditions. The experiments were performed in a horizontal feeding burner, installed in a reference boiler that currently is used for the national certification tests of residential pellet burners in Sweden. A schematic view over the experimental setup is shown in Figure 1. Besides the integrated heat exchanger, the boiler walls are also water jacketed (see C in Figure 1). The burner is constructed according to the main principles for combustion of pellets. Four combustion experiments were performed; one with pure oat grain and three with different additives, i.e. 1 wt % kaolin (oat + K), 2 wt % precipitated calcite (oat + pC), and 3 wt % ground calcite (oat + gC). The duration of the combustion experiments were between 9 and 12 h. The used fuel feeding rate varied between 2.4 and 3.0 kg/h, which corresponds to 12-15 kW. Temperature measurements in the burner were performed at two positions: in the center and at the end of the burner. The maximum measured temperatures in the burner were 1000 \pm 100 °C for T1 and 700 \pm 100 °C for T2 (see Figure 1). No significant differences in measured temperatures for the experiments with and without additives were observed.

The concentrations of O_2 and CO in the flue gases were measured continuously with electrochemical sensors. Generally, the combustion conditions were relatively stable with an average O_2 concentration in the range of 7-10% and CO < 200 ppm for all experiments except the experiment with the addition of ground calcite that had more varying O_2 , in the range of 6-15%, and somewhat higher CO emissions (<800 ppm). The concentrations of the acidic gases SO_2 and HCl were measured with Fourier transformed infrared (FTIR) spectroscopy during a period of 30 min after the combustion reached stable conditions, i.e. approximately 1 h.

2.3. Sampling of Ash, Slag, and Deposits. After each experiment, the combustion equipment was inspected with respect to slag formation in the burner and deposited boiler ash (bottom

Table 1. Fuel Characteristics for the Used Oat¹

parameter	value	parameter	value
moisture ^a	9.2	SiO_2^g	1.21
ash^b	2.8	CaO^g	0.094
C^c	43	Fe_2O3^g	0.006
\mathbf{H}^{c}	6.9	K_2O^g	0.587
N^c	1.6	MgO^g	0.201
O^d	46	MnO^g	0.005
S^e	0.14	Na_2O^g	0.007
Clf	0.06	$P_2O_5^g$	0.843
heating value ^h	18	$Al_2O_3^g$	< 0.001

^a Analysis according to SS 187170. ^b Analysis according to SS 187171. ^c Analysis according to ASTM D3178-79. ^d Analysis according to calculated values. ^e Analysis according to SS 187177. ^f Analysis according to SS 187185. ^g Analysis according to SS 028113-1. ^h (HHV) according to SS 187182. ^I The values are in weight percent dry substance (ds), except for moisture which is in weight percent and heating value which is in megajoules per kilogram ds.

ash). Slag was here defined as a material that clearly could be established as previously melted, that was larger than 3 mm, and that was separated by sieving. The amount of deposited boiler ash and slag was determined and the samples were further chemically characterized by qualitative and semiquantitative methods.

To qualitatively study the deposit formation on heat exchanging surfaces, an air-cooled temperature controlled deposition probe with an exchangeable stainless steel sample ring, was used (see A in Figure 1). The sample ring was cooled to $\sim 150~^{\circ}\text{C}$ and placed just in front of the heat exchanger tubes. The exposure time was 8-10~h for each combustion experiment. The deposits on the stainless steel plate in the upper part of the boiler (see B in Figure 1) as well as on the rear boiler wall (see C in Figure 1) were also sampled and analyzed. The plate and the sampling area of the rear wall were carefully cleaned before each combustion experiment.

2.4. Particle Sampling. To determine the particles mass size distribution, a 13-step low-pressure impactor (LPI) from Dekati Ltd. was used that size classifies particles in the range of $0.03-10\,\mu\mathrm{m}$ according to aerodynamic diameter. Aluminum foils (not greased) were used as substrates in the impactor. Isokinetic sampling was carried out in the flue gas channel, and the impactor was heated to the same temperature as the flue gases, i.e. $\sim 130~\mathrm{°C}$.

2.5. Chemical Characterization. The chemical composition of formed slag, boiler ash, deposits, and fine particles was analyzed semiquantitatively by use of scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analysis unit (EDS) and qualitatively with powder X-ray diffraction (XRD). Utilizing the so-called Rietveld technique, the XRD results were evaluated to also gain semiquantitative information of the relative content of crystalline phases. The XRD measurements were performed on ground samples, which subsequently were analyzed by SEM/EDS. Thus XRD and SEM/EDS analysis were carried out on identical samples, allowing direct comparison of the two complementing methods.

2.6. Assessment of Sintering Degree. The degree of sintering for the collected slag samples was assessed through visual (microscope) inspection and a simple strength test and classified according to the following criteria:⁵

Category 1: very lightly sintered ash that breaks at a light touch.

Category 2: slightly sintered ash that holds together at a light touch but is easily broken apart. The grain structure could still clearly be distinguished.

Category 3: sintered ash that still is breakable. Visually, it is still possible to distinguish single grains, but parts of the ash

⁽⁵⁾ Öhman, M.; Boman, C.; Hedman, H.; Nordin, A.; Boström, D. *Biomass Bioenergy* **2004**, *27*, 585–596.

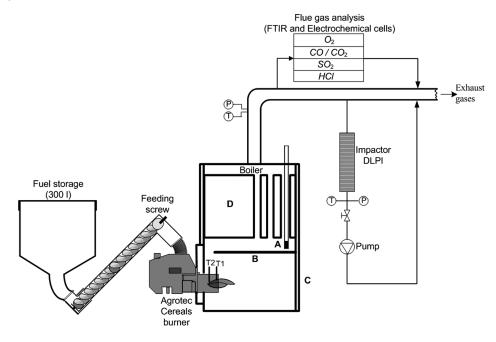


Figure 1. Schematic figure of the experimental setup. (A) air-cooled temperature controlled deposition probe, (B) stainless steel plate, (C) water jacketed boiler wall, (D) heat exchanger (water based).

Table 2. HCl and SO₂ Emissions (mg/Nm³ dg at 10% O₂) Given as 30-min Average Values with Standard Deviations

	oat	oat + K	oat + pC	oat + gC
HCl	61 ± 2	70 ± 3	52 ± 1	58 ± 5
SO_2	280 ± 20	300 ± 17	240 ± 13	210 ± 47

have structures resembling slag where melted material (glass) could be observed.

Category 4: totally sintered ash which is not breakable by hand. The ash is fused to larger lumps (slag). No individual grain structure could visually be distinguished.

3. Results

- **3.1.** Acidic Gas Emissions. The concentrations of HCl and SO_2 in the flue gases are shown in Table 2. The levels of both HCl and SO_2 were lowered when calcite was used as additive, whereas the addition of kaolin increased the HCl emissions.
- **3.2. Particle Emissions and Size Distribution.** The results from the impactor sampling are shown in Figure 2. As can be seen, the particle emissions were in all cases dominated by fine ($< 1 \mu m$) particles, and a significant reduction in mass concentration as measured in flue gases was obtained with all tested additives.
- **3.3. Ash and Slag Samples.** As shown in Table 3, the experiments with pure oat fuel and with calcite additive resulted in significant formation of slag (mainly in the burner), particularly when precipitated calcite was added. Another clear effect was the nonslagging behavior of the oat with addition of kaolin.
- **3.4.** Chemical characteristics of Ash, Slag, Deposits, and Fine Particles. The results from SEM/EDS and XRD analyses of formed boiler ash, slag, deposits, and fine particles are given in Tables 4 and 5. Slag and bottom ash were dominated by relatively refractory phosphates and silicates while the deposits on the boiler walls and the flue gas particulate matter were dominated by condensed K-phosphates, -sulphates, and -chlorides.

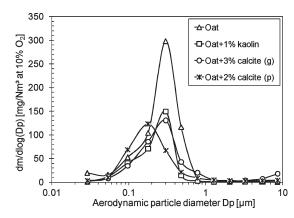


Figure 2. Particle mass size distribution.

Table 3. Slag Data

	(A) amount of slag (g)	(B) slag of ingoing fuel ash (wt %)	(C) slag of ingoing ash + additives (wt %)	(D) degree of sintering
oat	40	5		2-3
oat + K	no slag	0	0	
oat + pC	220	24	13	4
oat + gC	63	7	3	4

^a According to the classification given in section 2.5.

4. Discussion

4.1. General Comments. No true mass balance could be established since the absolute amounts of combustion residues as slag, burner and bottom ash, and deposits were not available. However, the mass content of particles in the flue gas was quantified. The following discussion is thus based on relative compositional differences and changes in the various ash fractions, obtained from the SEM/EDS and XRD results. It should also be noted that slag, as it is defined in this study, implies a material that partly has been melted and that upon cooling mainly formed crystalline phases but

as a Result of Semionantitative Refinement of the XRD Data" Table 4 Composition of Various Samples in Terms of Crystalline Phases in weight nercent.

	1	anle	Table 4. Composition of various samples in Terms	positio	10 110	v ai iou	Soam	III SIII	I CI III S	U CI	Stallin	t Hast	W III S	l ııığıa,	mencelli	of Crystannie Fliases III weight percent, as a result of Schildualitiative Refinement of the ARD Data	o amea	II SCIII	Idualiti	lative		וובווו ה	v am i	ND Da	113			
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	Oat C	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat	Oat^b	Oat	Oat	Oat
	+	+ K	+ pC	+ gC		+ K	+ bC	+ gC		+ K	+ bC	+ gC		+ K	+ bC	+ gC		$+$ κ	+ bC	+ gC		+ K	+ bC	+ gC		+ K	+ bC	+ gC
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KAISiO ₄						2				21																		
KPO ₃							3	4					,	0			92	66	13	13	25	29			<i>2</i>	9		
$\text{KPO}_3 \cdot x \text{H}_2 \text{O}$													CC	4							0	58			* * *	100		
KCI													40	11	99	57			42	19	∞		63	38	*C		09	35
CaO CaO			2	2			25	27			20	19			13	7			11	33				ţ				
CaCO ₃							7 11	23			13	18			6	S								10				
CaSO ₄ K ₂ SO ₄													17 8	33	3 10	8 23	∞	-	33	35		13	37	35	* *		9 30	9 55

^a The values in the table give the contents of crystalline phases (wt %) in the different samples as the result of semi-quantitative refinement of the XRD data with Rietveld technique of slag (SL), burner ash (BuA), boiler ash (BoA), ash from the rear boiler wall (BW), deposits in the burner (DB), deposits from the air-cooled sample rings (SR), submicrometer mode from impactor sample (stages 3–5). K, pC, and gC are kaolin and precipitated and ground calcite, respectively. ^b Quantification was not possible due to the scarce amount of sample. ^c The number of asterisks indicates the rough estimation of relative amounts.

Oat Oat Oat Oat Oat SR Table 5. Results from SEM/EDS Elemental Analysis in Terms of Atomic %, Normalized for the Given Elements^a Oat Oat

presumably also a fraction of glass. The latter cannot be directly identified by XRD, though. Thus only indirect evidence for its existence is at hand. It should be pointed out that the relation between the glassy and crystalline fractions of the slag is highly dependent on the cooling history of the slag. Furthermore, in the analysis of the results the "dilution factor", as the result of the use of additives, has to be considered. It is for kaolin and precipitated and ground calcite, 1.4, 1.7, and 2.1, respectively, assuming a proportional increase of the amount of ash.

4.2. Ash and Slag Formation without Additives. Thermodynamic calculations and earlier experimental experiences have shown that P dominates over Si in the competition for the base cations: K⁺, Mg²⁺, and Ca²⁺. Thus, K-Mg-Ca phosphates form prior to the corresponding silicates. Initially, the latter involves formation of relatively low melting K-silicates. The eventual rest of Si will form cristobalite or tridymite depending on the temperature of combustion, i.e. the thermodynamical stable modification of silica (SiO₂). Considering the amounts and the speciation of K-containing crystalline phases in the slag that were identified by XRD analysis (see Table 4), in a comparison with the amounts of K in slag as obtained from the SEM/EDS analysis (Table 5), it is obvious that there is a deficiency of K in the former. For instance, this condition becomes apparent by comparing the K/Ca ratios. The difference may be explained by the presence of a K-containing glass that is "invisible" for XRD. The assumption presupposes formation of a glass from the low melting K-rich silicate remnants after the crystalline precipitation of the slag

4.3. Ash and Slag Formation with Calcite Additives. Upon the addition of calcite, increased amounts of Si are bound in the slag, whereas the tendency in the boiler (bottom) ash appears to be the opposite. Thus, a redistribution of Si from ash to slag has taken place. Since the amounts of crystalline silicates in the slag, here solely åkermanite (Ca₂MgSi₂O₇), is considerably less (see Table 4), it is concluded that the glass forming low melting silicate phase has incorporated an increased amount of Ca. Hereby, the addition of calcite provides a basic oxide for reaction with silica and accordingly no formation of cristobalite (SiO₂) is observed in the slag (see Table 4). The glass will most probably also contain significant amounts of K. This conclusion is also supported by the observation of increased amounts of slag in presence of calcite additives (see Table 3).

Concerning the P content in the slag, the total amount does not appear to have been changed, taking into account the dilution effect of the additives. On the other hand, the composition of the crystalline phosphates has changed becoming more Ca-rich. These phosphates melt at higher temperatures which is positive from a slagging point of view. In the burner and bottom ashes, however, a certain enrichment of P was observed. Altogether, this implies that less P is volatilized upon addition of calcite to the oat fuel. Concerning the K content in both ash and slag, it appears to be only marginally affected taking into account the dilution effect of the additives. It was also noted that lesser amounts of the calcite additive did not react since CaO, Ca(OH)2, and CaCO₃ were found in burner and boiler ashes (see Tables 4 and 5). Finally, judging from the amounts of slag, the precipitated calcite appears to be more reactive, presumable due to the finer grain size.

4.4. Ash and Slag Formation with Kaolin Additive. The kaolin additive was intended to act as a K capturer. That is,

the following reactions were anticipated in according to suggestions from earlier studies:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \tag{1}$$

$$Al_2O_3 \cdot 2SiO_2 + 2KCl + H_2O \rightarrow 2KAlSiO_4 + 2HCl$$
 (2)

$$Al_2O_3 \cdot 2SiO_2 + 2SiO_2 + 2KCl + H_2O \rightarrow 2KAlSi_2O_6 + 2HCl$$

Al₂Si₂O₅(OH)₄ (kaolinite) is the dominating mineral in kaolin clay, and Al₂O₃·2SiO₂ (meta-kaolinite) is an amorphous mixture of alumina and silica that forms when kaolinite losses water at high temperatures. KAlSiO₄ (kalsilite) and KAlSi₂O₆ (leucite) are typical high-temperature K-Al silicate minerals formed. Note that in reaction 3, in the formation of leucite, kaoline reacts besides with KCl also with two SiO₂ molecules. These reactions, that are written with KCl as K-containing species, can in principle also be written with K-species such as as K₂O and KOH. The potassium—aluminum silicates in reactions 2 and 3 are very stabile phases implying that meta-kaolinite readily reacts with available gaseous K-species. This will reduce the amount of K available for reaction with silica to more low melting K-silicates. The absence of slag in the experiments with kaolin additive confirms this. A minor decrease of P, (with dilution effect accounted for) was also observed. It is therefore plausible that the entrapment of reactive K with kaolin addition in turn will increase the volatilization of P. Thus, it is apparent that the effect of kaolin and calcite additives on the capture of P in ash and slag differs. The observed effects of the used additives in ashes and slags concerning the behavior of K and P were in most cases rather small, but most probably responsible for the much more tangible effects related to the formation of acidic gases and particles.

4.5. Volatilization of Inorganic Matter. In general, condensed phases in flue gases from biomass combustion are formed via condensation of alkali metal species or reactions between such alkali components and other gases to form sulfates, chlorides, carbonates, phosphates, and hydroxides. The thermodynamical stability for this category of substances is increasing in the following order; hydroxides, carbonates, chlorides, sulfates, and phosphates. Thus, if equilibrium is attained, K-phosphates will be the first species to form, followed by K-sulfate, K-chloride, K-carbonate, and K-hydroxid. A consequence of P-containing flue gases may therefore be higher levels of HCl and SO₂ (and SO₃) gases, which at lower temperatures together with water vapor will condense to acids.

Clear effects of all three additives were observed in the present work. The kaolin affected the composition of the deposits and the fine particle forming matter to a lesser extent than the calcite additives.

K-phosphates dominated the deposits formed on the rear boiler wall and the heat exchanger, as well as in the fine particle emissions in combustion of pure oat fuel. (See Tables 4 and 5.) Lesser amounts of sulfates were also found in deposits at the various sampling positions along the route of the flue gas.

The K-capturing effect of the kaolin additive in the flue gases resulted in generally lower concentration of K in deposits and fine particles formed. The reduced volatilization of K resulted in an increased fraction of phosphate in the condensed flue gas matter, since there was not enough K to form the other salts.

The P-capturing effect of the calcite additives (in bottom ash and slag) was evident as considerably lower concentrations of phosphates were found in the fine particles emissions. These were instead dominated by sulfates and chlorides.

The observations and conclusions from the analysis of the flue gas particles were confirmed by the variations in the concentrations of HCl and SO₂ in the flue gases (see Table 2). In general, the levels of HCl and SO₂ in the flue gases from the pure oat fuel and from the fuel with kaolin additive were substantially higher than for the fuels with calcite additives. That is, a high level of volatilized P in the flue gases in combinations with a low level of volatilized K, resulted in higher concentration of acidic gases in the emissions.

Both types of additives resulted in substantial reductions of the amounts of fine particles in the flue gases (see Figure 2). The mechanism of their action differs though. As mentioned the calcite additive appears to increase the capture of P into ash and slag, whereas kaolin is capturing more K in ash and slag. In general, K has a key role in the formation of fine particles in flue gases from biomass combustion, since it constitute the dominating cation. Measures decreasing the concentration of K in the flue gas will therefore reduce the amount of condensed flue gas matter, which was observed in the case of kaolin addition. For the calcite additive, on the other hand, no such K capture to bottom ash and slag could be discerned. This implies that the amount of fine particles should not decrease compared to the experiment without additive. However, with the calcite additives, significantly higher levels of K-sulfate were observed on the walls of the boiler and on the deposition probe rings (see Tables 4 and 5). Thus, a significant share of the fine particle forming matter in the flue gas condensed on heat exchanging surfaces in the boiler before reaching the impactor sampling.

5. Conclusions

The previously reported K and Si capturing effect of kaolin additive were observed also in the present study using P-rich biomass fuels.^{7–11} That is, the prerequisites for the formation of low melting K-rich silicates were reduced. The result of the use of kaolin additive on the bottom ash was that no slag was formed.

The effect of the kaolin additive on the formation of fine flue gas particles was an increased share of condensed K-phosphates at the expense of K-sulfate and KCl. The latter phase was almost completely absent in the particulate matter. Consequently, the levels of HCl and SO₂ in the flue gases increased somewhat.

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The addition of both calcite assortments increased the slag formation, although to a much higher extent for the precipitated calcite. P was captured to a higher degree in the bottom ash, compared to the combustion of pure oat.

The effect of the calcite additives on the fine particle emissions in the flue gases was that the share of K-phosphate decreased considerably, while the content of K-sulfate and KCl increased. Consequently, also the flue-gas levels of acidic HCl and SO₂ decreased. This implies that the low-temperature corrosion observed in small scale combus-

tion of oat possibly can be abated by employing calcite

Alternatively, if problems with slagging and deposition of corrosive matter at heat convection surfaces are to be avoided, kaolin additive can be utilized, on the condition that higher concentrations of acidic gases can be tolerated.

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