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**Abstract**—We successfully developed a new straw combustion technology that efficiently reduces problems with unmanageable deposits inside straw fueled boilers in Zluticka Heating Plant. The deposits are mainly created by glass-forming melts. We plotted straw ash compositions in  $K_2O$ -CaO-SiO<sub>2</sub> phase diagram and illustrated that they are in the area of low-melting eutectic points. To prevent the melting of ash and the formation of deposits, we modified ash compositions by injecting additives into biomass fuel.

Keywords-Biomass, straw, combustion, deposit, heat, additives

## I. INTRODUCTION

OR more than ten years, the central heating plant in FOR more than ten years, and T Zlutice has been burning wooden chips and packed straw. The plant is equipped with four horizontal boilers with piston stockers. Every year, they burn in average 4 000 tons of wooden chips and 1 000 tons of mainly wheat, rye, barley, or rape straw. For many years, the burning of straw had been causing slagging of the bottom parts of the boilers and fouling of their heat-exchanger compartments. These deposits had significantly decreased the efficiency of the boilers by hindering heat transfer and increasing the corrosion of the metallic and ceramic parts of the boilers. To maintain a high efficiency of heat generations, frequent shut-downs of the boilers had been necessary, usually every three months. For cleaning up the boilers, workers had to perform laborious and time-consuming removal of the deposits. We have successfully developed new technologies reducing problems with unmanageable deposits forming inside the straw fueled boilers in Zluticka Heating Plant. By applying these technologies, we significantly reduced the amount of the deposits in the boilers and prevented sticking of the deposits to the walls of refractory ceramics.

## II. GLASS DEPOSITS FORMATION

Figure 1 shows glassy and partially crystalline deposits that formed in a flame part of the boilers during the burning of different types of straw and wooden chips contaminated with soil.

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Fig. 1 Glass (upper) and partially crystalline (lower) deposits from a flamer part of the boilers that burned wheat straw (upper left), barley straw (upper right), rape straw (lower left), and brown wooden chips from pine loppings contaminated with soil

To find out what causes the formation of the deposits, we determined their chemical composition with x-ray fluorescence analysis (XRF). Table I lists examples of the chemical composition of the deposits formed when different types of biomass were fired. These results indicate a high concentration of oxides SiO<sub>2</sub>, CaO, and K<sub>2</sub>O. These main components can easily form glass. In this material, the glass forming oxide SiO<sub>2</sub> forms an amorphous network; and the other components CaO and K<sub>2</sub>O decrease glass melt viscosity. Other oxides of significant concentration are P<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO that also promote the formation of glass layers.

In the next step, we focused on analyzing ashes that formed during burning different types of biomass. To generate the ash, we developed a laboratory procedure for the controlled burning of biomass. We put a fuel of about 200g into a corundum crucible and burned it in a specially designed electric furnace with kanthal loops.

TABLE I Composition of Deposits for Different Fuels

Mass%	Wheat	Barley	Rape	Pine
Na <sub>2</sub> O	0.4	1.9	1.1	1.0
$K_2O$	19.7	24.9	11.4	5.0
MgO	3.4	1.8	4.4	3.4
CaO	16.2	15.1	30.7	15.6
MnO	0.1	0.0	0.1	1.2
$Al_2O_3$	2.6	1.5	3.7	12.7
Fe <sub>2</sub> O <sub>3</sub>	0.9	0.3	0.9	8.9
$P_2O_5$	2.2	3.1	3.3	1.4
TiO <sub>2</sub>	0.2	0.1	0.2	2.8
SiO <sub>2</sub>	54.1	49.4	43.9	47.4
Sum	99.8	98.1	99.7	99.4

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The temperature inside the combustion space was precisely monitored with PtRh thermocouple and the whole burning process was automatically controlled by a computer. The maximum firing temperature was 1100°C. The obtained ash was again analyzed with XRF. Table II shows examples of ash composition for selected types of straw; and in Figure 2 you can see solidified melts and ash residues after the burning of wheat and ray straw. Glossy surface of partially transparent solidified melts confirm their glass character.

TABLE II	
COMPOSITION OF ASH FROM DIFFERENT FUELS	
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Mass%	Wheat	Barley	Ray	Rape	Hay
Na <sub>2</sub> O	0.3	1.5	2.4	0.9	1.3
$K_2O$	10.3	25.4	42.1	32.4	27.7
MgO	2.3	3.3	3.0	2.8	4.2
CaO	5.9	16.4	9.5	53.7	7.6
$Al_2O_3$	0.7	0.7	4.5	0.3	2.7
$P_2O_5$	1.5	5.0	8.5	4.6	12.0
$SiO_2$	76.3	42.9	23.6	0.6	38.9
Sum	97.3	95.2	93.6	95.3	94.4

The ash composition that is close to low-melting eutectic points promotes the formation of glass melts that are very strongly bonded refractory materials. Therefore, to predict the effect of composition on the formation of a melt, we used a thermodynamic approach [1] based on K<sub>2</sub>O-CaO-SiO<sub>2</sub> phase diagram illustrated on Figure 3 [2]. For its application, we simplified the original ash multicomponent mixture. We added together components of similar chemical effects [3];  $K_2O=K_2O+Na_2O$ , CaO=CaO+MgO, and  $SiO_2=SiO_2+Al_2O_3$  $+P_2O_5$ . The remaining components of low concentrations were omitted. Using this simplification, we could plot the ash compositions in the phase diagram. The diagram illustrates, for example significant differences in the ash compositions for wheat straws from different suppliers. The ash from barley is richer in CaO and from ray or hay is richer in K<sub>2</sub>O. The ash from rape has very different composition; it contains only a small concentration of SiO<sub>2</sub>. Big differences are also in the compositions of ash from wood chips that generally contain a low concentration of K<sub>2</sub>O. The biomass ash contains usually more than 40 mass% of SiO<sub>2</sub> and up to 30 mass% of CaO.



Fig. 2 Solidified glass melts with ash residuals from burning wheat and ray straw



Fig. 3 Phase diagram K<sub>2</sub>O-CaO-SiO<sub>2</sub> with simplified ash compositions for different biomass fuels

The diagram indicates that this composition area contains low-melting eutectic points from 700 to 1000°C and the eutectic temperature increases with the increasing concentration of CaO. To suppress the formation of melts, the ash should contain a higher concentration of CaO and a lower concentration of K<sub>2</sub>O. The ash composition can be modified by blending biomass fuels of different composition or by injecting additives. In some cases, it is not possible to completely suppress the formation of a melt. For this situation, it is advantageous to modify the biomass ash composition that the ratio of melt to crystals in the mixture is as low as possible and the resulting solid phase contains a minimal fraction of the connecting glass phase. Mostly, the glass phase is probably responsible for the creation of very durable and compact deposit layers.



Fig. 4 Temperature dependence of absolute value of impedance for the ash from wheat straw and for a ash model mixture;  $T_{\rm E}$  represents the eutectic temperature



Fig. 5 Temperature dependence of absolute value of impedance for the ash model mixture with additive A1;  $T_E$  represents the eutectic temperature

The viscosity of a melt should be either very low or very high. The low viscosity promotes crystallization and thus the solid phase contains only a small fraction of the glass phase. On the other hand, the high viscosity prevents spreading and sticking of the melt to refractory ceramics. The viscosity is strongly increased by oxides  $SiO_2$  and  $Al_2O_3$  and decreased by CaO and K<sub>2</sub>O.

In our experiments, we modified ash composition by injecting additives to a fuel. We used two types of additives labeled A1 and A2. The additive A1 contains a high concentration of CaO and the additive A2 a high content of  $SiO_2$  and  $Al_2O_3$ . In our laboratory, we prepared model mixtures of oxides simulating the ash from wheat straw containing different concentrations of the additives.



Fig. 6 Temperature dependence of absolute value of impedance for the ash model mixture with additive A2;  $T_E$  represents the eutectic temperature



Fig. 7 Solidified glass melts with ash residuals from burning wheat and ray straw



Fig. 8 Solidified glass melts with ash residuals from burning wheat and ray straw

#### III. MEASUREMENT OF EUTECTIC TEMPERATURE

The eutectic temperature of a mixture is the lowest temperature at which the first melt appears. We determined the eutectic temperature of biomass ashes by measuring the temperature dependence of their electric impedance. The solid mixture of ash components was heated at 3°C/min and the impedance was measured with metallic electrodes introduced into the mixture. When a melt forms, it connects the electrodes and the impedance suddenly drops down. Figure 4 illustrates the temperature dependence of the absolute value of impedance for the wheat ash PSL10 and for the model mixture PSL10M. The resulting eutectic temperature for both mixtures was practically identical  $T_{\rm E}$ =627°C. It confirms that the model mixture was prepared correctly and behaves very similar to the real ash mixture. Then we added the additives A1 and A2 to this mixture. The additive A1 was injected in the amount of 2 mass% of the fuel and the additive A2 in the amount of 5 mass%. Figure 5 plots the temperature dependence of impedance for the mixture with the additive A1. The curve indicates that the eutectic temperature increased by 48°C. A similar plot for the mixture with the additive A2 is in Figure 6 where the eutectic temperature increased by 218°C. Our laboratory experiments revealed that 1 mass% of A1 increased  $T_{\rm E}$  by 24°C and 1 mass% of A2 by 44°C.

#### IV. TESTING OF ADDITIVES

We did the laboratory combustion tests of straw with the additives A1 and A2. The mixtures of wheat or barley straw with the additives were burned in a corundum crucible. Figures 7 and 8 show the obtained ashes. When we compare these ashes with the ash without an additive, we can conclude that the additives significantly suppressed the formation of glass-forming melts. The positive laboratory results with additives were verified in the biomass boiler of Zluticka Heating Plant.

# International Journal of Earth, Energy and Environmental Sciences ISSN: 2517-942X Vol:6, No:4, 2012

For five moths the additive A1 or A2 was injected into various types of straw. We observed very positive effects of the additives that strongly suppressed the formation of glass melts in a burner and a flamer. We also observed that the amount of deposits was significantly reduced as well.

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Martin Mika was born in Prague, Czech Republic, on October 30, 1964. He graduated at the Institute of Chemical Technology Prague (ICT) in "Chemistry and technology of glass" in 1988. In 1995, he obtained PhD in "Chemistry and technology of inorganic materials" at the same institute. He had been a visiting scientist at the Pacific Northwest National Laboratory, Richland, Washington from 1996 to 1997. Since 1998 he occupies a position of assistant professor at the Department of Glass and Ceramics, ICT. His research and teaching activities are glass materials - influence of chemical composition on their physical and chemical properties, biomass ash properties, ion migration, experimental design, calculation and modeling of their properties, formulation and preparation of special glasses (for example, optical glass for integrated optics, high level waste glass, or organic-inorganic hybrid glass). In 2004, he was awarded NATO Senior Fellowship and spent two months as a visiting scientist in the Institute of Applied Physics in Florence, Italy. Dr. Mika received Professor Vittorio Gottardi Memorial Prize granted by the International Commission on Glass for outstanding individual accomplishment in the field of glass in 2003. He is a member of the Czech Glass Society and the International Commission on Glass technical commission TC10 "Optical properties of glass".