# CHARACTERIZATION OF SUNFLOWER HUSKS FOULING IN A DROP TUBE FURNACE: COMPARISON OF DEPOSITS WITH $H_3PO_4$, $CaCO_3$ AND $Al_2Si_2O_5(OH)_4$ ADDITIVES

L. De Fusco*[,1] , J. Blondeau[2], H. Jeanmart[1] and F. Contino[3]

*[1]Université catholique de Louvain, iMMC, Place du Levant 2, 1348, Louvain-la-Neuve*
*[2]Laborelec ENGIE, Rodestraat 125, 1630, Linkebeek*
*[3]Vrije Universiteit Brussel, Department of Mechanical Engineering, Pleinlaan 2, 1050, Brussels*

## Introduction and objectives

Fouling of heat exchangers in combustion plants is an operational problem that can lead to a severe decrease of boilers efficiency and availability. This ash deposition phenomenon is encountered with solid biomass fuels with a high content of alkali metals, namely potassium (K) and sodium (Na). To counteract deposition, additives are used to bind the vaporized alkali in high melting temperature structures, such as solid phosphates or aluminum-silicates.

Aluminum (Al) present as silicates (e.g. in kaolin: $Al_2Si_2O_5(OH)_4(s)$) and organically bounded, can react with the released KCl(g) from the fuel, for example according to the gas – solid reaction (1) [1]:

$$2KCl(g) + Al_2Si_2O_5(OH)_4(s) \xrightarrow{\Delta G = -0.3\ MJ/mol} 2KAlSiO_4(s) + H_2O(g) + 2HCl(g) \quad (1)$$

where the Gibbs free energy (ΔG) is computed with the Reaction module of FactSage 7 (GTOX5) at 1000°C.

Phosphorus (P), released out as $P_2O_5$(g), can react with alkali to form alkali phosphates (see Eq. 2), which are rather volatile. They can further interact with alkaline earth metals to form solid ternary phosphates, belonging to the $K_2O$ – CaO – $P_2O_5$ system. These can have melting points above 1000°C [2] (see Eq. 3).

$$P_2O_{5(g)} + 2KOH_{(g)} \xrightarrow{\Delta G = -3.0\ MJ/mol} 2KPO_{3\,(l,g)} + \\ + H_2O_{(g)} \quad (2)$$

$$KPO_{3(l,g)} + CaO_{(s)} \xrightarrow{\Delta G = -0.2\ MJ/mol} KCaPO_{4(s)} \quad (3)$$

Recently, a few authors experimentally investigated the grate combustion of agricultural residues in presence of aluminum–silicates based additives. Obernberger in [3] measured the effect of kaolin for straw at 1250°C, evidencing a reduction on the K release to the gas phase from 30%w (per cent, in weight, with respect to fuel) to approximately 5 %w, with 4%w of addition. Konsomboon et al. [4], studying palm empty fruit bunch combustion, evidenced that at 800°C, 8%w kaolin addition, are sufficient to retain potassium in the solid phase.

In order to reproduce the thermal condition of industrial boilers and simulate ash deposition on heat exchangers, drop tube furnaces (DTF) are used. However, to our knowledge, the majority of the studies in DTFs are related to coal (co-firing), lignite, wood or torrified biomass (e.g. [5]), mostly without additives.

Fouling during the combustion of sunflower husks was studied in a recent test campaign [6, 7] in the UCL – Laborelec Drop Tube Furnace. In this study, the analysis is further expanded including the discussion of three fouling tests of sunflower husks in presence of additives. Two main mechanisms of fouling counteraction were compared, in the same experimental conditions: a combination of P and Ca–based additive ($H_3PO_4$ and $CaCO_3$, test: PA3c) and Al–silicates additives (kaolin or halloysite, respectively tests: KAO, HAL). Fouling tests with additives were compared with reference experiments with the raw fuel (tests: RAW1, RAW2). The experimental measurements are further discussed through thermodynamic equilibrium computations to identify the K partitioning among the different ash phases.

## Materials and methods

Details about the experimental set up are found elsewhere [6, 7]. The main component of the DTF is a 6 m–high vertical tube (17.8 cm ID)), heated by six electrical modules, which were regulated respectively to 900°C; 900°C; 800°C; 700°C; 600°C; 500°C, in order to mimic the conditions seen by a particle before depositing on the economizer convective section of a boiler. A deposition probe (25.4 mm ID) was inserted in the horizontal port of the penultimate module and cooled using air in order to maintain a temperature of 200 ± 30°C on its surface.

The fuel PA3c is sunflower hulls with a $4\%_w$ (% on weight with respect to fuel) concentration of phosphoric acid $H_3PO_4$ (PA) 85% aqueous solution as additive, in order to obtain a molar P/K ratio of about 2.0 in the fuel; and with limestone powder ($CaCO_3$) (> 98%, by Fisher Scientific) to reach P/Ca ratio > 1 (about 1.3) in the fuel composition. KAO and HAL are respectively milled fuel with $2\%_w$ of kaolin and halloysite minerals

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* *Corresponding author*: Lucio De Fusco
*Email address*: lucio.defusco@uclouvain.be

(by Imerys). Each fuel has been tested in the furnace. For the five tests (RAW1, RAW2, PA3c, HAL, KAO), the biomass flow rate was set to 1.5 kg/h and about 5 kg of each fuel were burned. Oxygen supplied through air with respect to theoretical oxygen demand for complete combustion was set up in order to get a $\boldsymbol{\lambda} = 1.7$. After the testing, the probe was removed and the deposits analyzed.

## Results

The fuels tested were characterized with XRF analysis (X–Ray Fluorescence spectroscopy; for RAW1, RAW2, PA3c) and ICP–AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy; for KAO, HAL). For specific samples, further analyses were performed, such as the chemical fractionation (CF) of the fuel. After the combustion testing, the five deposition probes were visually analyzed.

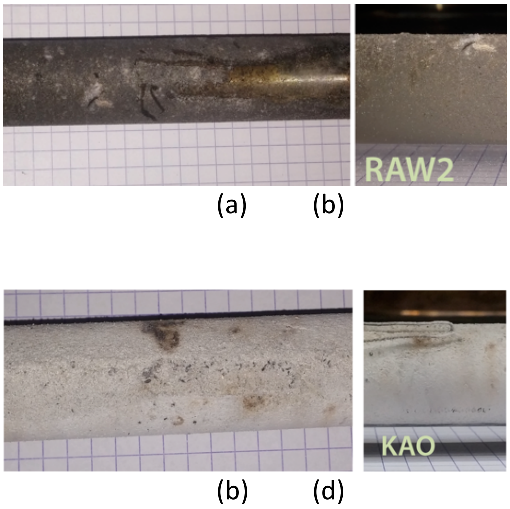

Figure 2: Photos of the deposition probes: RAW2 and KAO tests. Windward views (a, c); details (b, d).

The windward views and details of the deposition probes for the RAW2 and KAO tests are presented in Fig. 2 (a), (b). Mainly a smooth and uniform inner layer covering the probe is observed on the deposition probes. For the KAO deposit (see Fig. 2, (b)), the inner layer seemed more uniform and powdery than for the HAL case (not shown here).

In order to compare the five tests, the rate of build up on the probe (RBU, [g deposit/m$^2$h]), the mass of the deposits in [g deposits/g ash injected], the input ash flux [g injected ash/cm$^2$h] are computed. Furthermore, composition of the deposits was measured through SEM—EDX (Scanning Electron Microscopy – Energy Dispersive X-ray spectroscopy).

The experimental measurements are further discussed by computing the ternary diagrams K-Ca-P and K-Al-Si, and through thermodynamic equilibrium computations using different databases.

## Conclusions

Ash related issues, such as fouling of heat exchangers, are particularly troublesome for the industrial valorization of opportunity agro-fuels. In order to further increase their shares in the mixtures for combustion plants, additives are studied to reduce deposition issues.

In this study, three fouling tests of sunflower husks in presence of P and Ca- (test PA3c) and Al-based (tests HAL, KAO) additives are compared, on a quantitative basis, with reference deposition tests with the raw fuel (tests: RAW1, RAW2).

The use of additives, for all cases investigated, seemed to slightly decrease the sticky deposition behavior of the fuel, increasing the amount of loose deposit on the probe. Effectiveness of halloysite and kaolin was investigated: differently from other results [8], halloysite did not seem clearly more effective than kaolin. For the PA3c test, a decrease in K molar concentration in the deposits on the probe of 50% was found with respect to the RAW1 test.

Future research includes additional tests in the DTF of the same fuel, with Ca-only additives (e.g. with gypsum). Finally, it is of interest to further explore the sensitivity of the deposition reduction as a function of the of the kaolin composition.

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