Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: <www.elsevier.com/locate/fuproc>

Research article Formation of alkali salt deposits in biomass combustion

Hycointec-99 S.L., Danzas 2, 50003 Zaragoza, Spain Fluid Mechanics Group/LIFTEC-CSIC (Spanish Council for Scientific Research), University of Zaragoza, Maria de Luna 10, 50018 Zaragoza, Spain

ARTICLE INFO ABSTRACT

Article history: Received 24 March 2016 Received in revised form 20 July 2016 Accepted 25 July 2016 Available online 8 August 2016

Keywords: Combustion Biomass Alkali metals **KCl** Deposition prediction

In the present work, the alkali salts deposit formation on cooled surfaces in biomass-fired boilers has been studied. Different deposition tests with two real biomasses (orujillo and cardoon) as well as with several synthetic materials have been conducted in an entrained flow (pilot scale) reactor for a range of conditions representative of those prevailing at different locations inside industrial boilers. A number of parameters, such as gas temperature around the probe or surface temperature, have been changed in order to analyze their influence on the characteristics of the ash deposits (morphology, thickness, composition…). The deposits' morphologies observed in the experimental samples indicate that the dominant deposition path for alkali salts (in the conditions explored in this work) is thermophoresis of aerosols formed either in the thermal boundary layer next to the deposition surface or already in the external gas stream (in case gas conditions allow for their formation). The contribution of each possible deposition mechanism has also been studied by comparing the obtained experimental results with theoretical predictions from a deposition model developed by Castillo and Rosner. Experimental trends have usually been in good agreement with those calculated according to the mechanisms of arrival of small particles to the deposition surface. Furthermore, the agreement found between calculations and measurements has been good enough to support the applicability of the model due to Castillo and Rosner to the quantitative prediction of deposit formation rates.

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1. Introduction

The use of biomass as a fuel for heat and power generation has become more and more important in the last years for a number of reasons. First of all, the huge energy demand increase and the need of sustainable development have increased the interest on some renewable energy sources such as biomass. Furthermore, nowadays the use of biomass as a fuel is also promoted in order to reduce the discharge of the greenhouse gas $CO₂$. Biomass, produced at the rate it is consumed, is considered $CO₂$ -neutral because it accumulates during growth the same amount of $CO₂$ by photosynthesis as is released during combustion. Biomass use as a fuel can be also considered as a way to eliminate the large surplus of forest and agricultural waste that exists in many countries.

The biomass industry has developed rapidly within the last decades, but there are still some unresolved technical problems, with an unquestionable need of knowledge and research in order to further develop the biomass combustion technology. One of the most important problems comes from the deposition of inorganic species that are released during combustion of biomass fuels (mainly potassium and chlorine) and are subsequently transported to heat exchangers surfaces (see [Fig. 1](#page-1-0)), where they retard heat transfer and lead to decline in boiler efficiency and capacity, and possibly to corrosion [1–[3\].](#page--1-0) The corrosion processes are intimately related with chlorine-rich deposits. It has been observed that this kind of deposits tend to be highly corrosive at metal temperatures higher than 450 °C through several proposed mechanisms [\[4](#page--1-0)–7]. Chlorine in the deposits is usually joined to alkalis as chlorides. So, biomass fuels with high contents in alkalis and chlorine may affect negatively to the good performance of the plant.

Alkali salt deposit may be formed by three different routes [\[8,9\]](#page--1-0), depending on the physical state of the species that may be deposited (see [Fig. 2](#page-1-0)):

- 1- Direct vapor deposition (DVD): Vapors contained in the flue gases may traverse the boundary layer due to diffusion, heterogeneously condensing on the surface.
- 2- Direct deposition of aerosols from the flue gases (DAE): If the alkali salts are present in the gas stream as submicron particles, thermophoresis will be the main transport mechanism of the fine particles to the cooled surface. When existing a temperature gradient between gases and a cooled surface, transport by particle diffusion can be considered negligible compared with thermophoresis [\[10,11\]](#page--1-0).
- 3- Direct deposition of aerosols formed in the boundary layer (DABL): In this mechanism, not all vapor present in the gas stream diffuses towards the wall and condense there, but some condenses homogeneously or heterogeneously at some point inside the boundary layer, finally arriving at the cooled surface due to thermophoretic forces.

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E-mail address: joaquincapablo@gmail.com.

Fig. 1. Physico-chemical transformations followed by some specific compounds in a biomass boiler.

The various transport mechanisms may result in different deposit properties. In their deposition experiments burning straw, Nielsen et al. [\[1\]](#page--1-0) have mainly found the formation of two kinds of structures in the alkali salt deposits: dendritic and compact layers. To explain them, they propose the theory of "stick at first impact": an incoming particle will have a much higher tendency of first hitting the existing particle present at a surface than the surface in the vicinity of the particle. If the particle is sticky, it will most probably stay and not rebound from the surface it first impact on, resulting in columnar deposit structures, which will branch out from the surface possibly as dendritic structures. If the particle is non-sticky, it can rebound at impaction and work their way towards the surface filling out the gaps, resulting in a more dense structure (uniform particle layer). This theory is similar to the "active site sticking" theory developed by Tassopoulos et al. [\[12\],](#page--1-0) describing the formation of dendritic structures as a result of particle deposition. In order to explain the uniform particle layer they propose alternative sticking and post-arrival "restructuring" events [\[13\].](#page--1-0)

On the other hand, direct deposition of vapors is expected to result in a homogeneous layer, without particles (as opposed to the uniform particle layer). In fact, this morphology has been interpreted by some authors [\[11,14,15\]](#page--1-0) as an evidence of direct condensation of vapors on the exposed surface.

Nevertheless, the mechanisms involved in the formation of alkali salt deposits are usually declared as possibilities without further analysis of their relative importance, with few authors studying in detail the degree of participation of each mechanism in the transport to the surface of the alkali salts.

Some theoretical approximations [\[16](#page--1-0)–20] have modeled the transport and deposition of small particles and condensible vapors on cooled surfaces in the vicinity of stagnation points. They concluded that, depending on the circumstances, vapors can condense either directly on the cooled surface or inside the boundary layer, arriving at the deposition surface via small particle thermophoresis.

Deposit growth by thermophoresis would be expected to become less significant as deposits grow and surface temperature increases. Curiously, no such trend was observed in some experimental investigations from Sinquefield or Kaufmann [\[21,22\].](#page--1-0)

Pyykönen and Jokiniemi [\[23\]](#page--1-0) carried out a modeling study on the behavior of fume particle and condensible alkali chloride vapor in boundary layers around superheater tubes by applying two different approaches: numerical simulation using a computational fluid dynamics (CFD) code and an analytical model based on the boundary layer solution proposed by Rosner and Castillo [\[16\].](#page--1-0) NaCl deposition

Fig. 2. Deposition paths for fine aerosols and volatilized compounds.

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