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Particulate and PCDD/F emissions from coal co-firing with solid biofuels in a bubbling fluidised bed reactor

H. Lopes [*], I. Gulyurtlu, P. Abelha, T. Crujeira, D. Salema, M. Freire, R. Pereira, I. Cabrita

INETI, DEECA, Edifício J, Estrada Paço do Lumiar 22, 1649-038 Lisbon, Portugal

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ABSTRACT

In the scope of the COPOWER project (SES6-CT-2004) that aimed at investigating potential synergies of co-combustion of different biofuels with coal, the study of emissions of particulate matter and PCDD/F was carried out. The biofuels tested were meat and bone meal (MBM), sewage sludge biopellets (BP), straw pellets (SP), olive bagasse (OB) and wood pellets (WP). The tests performed include co-firing of 5%, 15% and 25% by weight of biofuels with coals of different origin. Both monocombustion and co-firing were carried out to compare the results. Combustion tests were performed on a pilot fluidised bed, equipped with cyclones and air staging was used in order to achieve almost complete combustion of fuels with high volatile contents and to control gaseous emissions. Particulate matter emissions were isokinetically sampled in the stack and their particle size analysis was performed with a cascade impactor (Mark III). The results showed that most particles emitted were below 10 μm (PM_{10}) for all the tests, however, with the increasing share of biofuels and also during combustion of pure biofuels, especially for olive bagasse, straw and MBM, it was observed the presence of very fine particles, below about 1 μm. With the exception of sewage sludge, greater amounts of biofuels appeared to give rise to the decrease in particulate mean diameters and increase in PM percentages below 1 μm. One factor that influenced the total amount of PM emitted, as well as the amount of coarser PM, was the formation of less unburned matter with the increased share of biofuels. However, the most important factor that could lead to the formation of very fine particles could be related with the presence of aerosol forming elements such as K, Na (in the case of MBM) and Cl in biofuels, which even resulted in higher PM emissions when the ash content of fuels decreased, as was the case of straw and olive bagasse.

For some fuel mixtures with selected sulphur and chlorine contents, dioxin and furan emissions were also determined. It was verified a correlation between the increase of PCDD/F with the decrease of PM mean diameter. Among other factors, this correlation may be due to higher specific surface area and greater Cu concentration in the fly ashes.

1. Introduction

Following the European Union White Paper focused on encouraging renewable energy [1] and its ambitious target of doubling its share in the total European energy supply by 2010, from 6% to 12%, with some 85% of the renewables being bioenergy, several EU Directives were proposed and are being implemented. One of the most important is the Directive on the promotion of electricity from renewable sources that requires the commitment of each country to accomplish specific targets to fulfil the commission's goal of 22% of electricity by 2010 from renewable sources [2]. New targets are now being considered by the European Renewable Energy Council for the period from 2010 to 2020, proposing to increase the contribution of renewable energy to about 20% source in the total European energy supply and to about 33% of electricity production in 2020, in which biomass could represent a share of about 20–25%. For the first time, it was considered a target to the contribution of renewable energy also to heat production, being about 25% by 2020. For this reason, biomass use for energy in thermochemical conversion processes is expected to have a continuous increase and research efforts are essential to make sure that its use is in accordance with environmental good practices. Biomass co-combustion in coal thermal power stations is one way to contribute to meet those targets; however, one of the major concerns in biomass combustion is PM emissions.

The new European Directive on ambient air quality and cleaner air for Europe [3] focus on the importance of protection of human health and the environment, giving particularly importance to the combat of pollutants emissions at source and to the identification and implementation of the most effective emission reduction measures. This Directive establishes PM_{10} and fine particulate matter $PM_{2.5}$ assessment thresholds, endorsing member states to take all the necessary measures to reduce exposure to $PM_{2.5}$. Stationary

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[*] Corresponding author. Tel.: + 351 21 092 47 90; fax: + 351 21 716 65 69.
E-mail address: helena.lopes@ineti.pt (H. Lopes).

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installations using biomass combustion are one of the sources mentioned in the Directive for which particulate matter emissions requires a more strict control in order to achieve the national exposure reduction targets to be met by 2020.

During combustion of solid fuels, different types of particles are generated, depending on the fuel characteristics, such as composition, fuel particle dimension and morphology, and the combustion technology used. Particles with larger dimensions, arising essentially from the mineral litophilic matter contained in the fuels or additives used, usually above 100 μm, tend to remain in the combustion system. Smaller particles (fly ashes) may include a coarser fraction, typically between 10 and 1 μm, and a finer fraction (including aerosols) below 1 μm. Aerosols are mainly formed due to volatilization and homogeneous condensation of volatile compounds. Also heterogeneous condensation on the surface of other particles, particle coagulation and growth, and cenosphere explosion, as well aerodynamic transport of small mineral forms and unburned matter may occur, generating coarser fly ashes. Components that mostly contribute to the formation of small particles due to volatilization/condensation are heavy metals and alkali metals. The extension of volatilization is influenced by combustion technology and operational parameters, mainly temperature of combustion. The presence of chlorine is of major importance for aerosol formation as metals chlorides are more volatile than oxides or sulphates. The presence of sulphur usually decreases volatilization, due to the intermediate formation of sulphates that may remain in deposits.

Although ash contents vary significantly among solid biofuels, when compared to coal, vegetal biomass generally has less mineral matter, less sulphur but higher amounts of alkali metals and chlorine, especially those from agricultural origin. Even so, it is referred in the literature that biomass combustion can lead to higher PM emissions as it produces smaller particles with specific chemical composition. Available data on biomass combustion indicates that particle emission is dominated by submicron particles [4–6]. For this size range, main constituents are found to be compounds based on volatile elements such as K, Na, S and Cl [6–11]. Nevertheless, compounds containing Ca may also contribute to the submicron range due to thermal fragmentation of coarse particles [7,8]. On the other hand, studies on particle matter emissions from coal combustion indicate that fine particles main constituents are S, Si, K, P and Na, while coarse particles are dominated by Ca, Fe, and Al [12,13]. It should be noted that fixed carbon content of coal is usually much higher than that of biomass and that the prevalence of char oxidation over the reaction of volatile matter may change the transformation of mineral matter and the main pathways for PM formation in co-combustion process. Interactions between mineral matter of coals and biofuels in co-combustion process is gaining special attention, in order to develop synergies that may allow the safe use of problematic biofuels, such as straw or use of additives to prevent ash related problems [14]. Behaviour of K is by far the most important problem in agricultural biofuels and the same may apply to other materials containing Na. Its tendency to volatilization and hence formation of fine particles depends on the presence of Cl to form KCl (or NaCl), but co-combustion with coal containing enough quantities of S may lead to the formation of K_2SO_4, releasing HCl, although the reaction is kinetically limited by the availability of SO_3 formed [14]. However, in fluidised bed systems as the temperatures are relatively low, S tends to remain in the form of $CaSO_4$, when there is enough active Ca available, hence the presence of Cl may dictate the behaviour of alkali metals in these systems. Also, major ash forming elements present in coals in higher amounts than in biofuels, such as Al and Si, may contribute to capture alkali elements in solid forms, such as $KAlSi_2O_6$, decreasing availability of K for aerosol formation.

Environmental effects caused by particles released during combustion of solid fuels strongly depend on their chemical and physical properties. The worst problems occur with particles smaller than 2.5 μm in diameter since they may remain suspended in the atmosphere for days or even weeks. In terms of human health, particle size is directly linked to their potential for causing health problems. Small particles, less than 10 μm, pose the greatest problems, since they can get deep into the lungs, and some may even get into the bloodstream. In terms of ambient air, particulate matter may be classified as fine (0.1–2.5 μm) and ultra fine particles (<0.1 μm), the smaller ones being more toxic [15]. Enrichment of smaller particles in heavy metals has also been reported to be responsible for the increase of asthma [16].

Dioxins and furans are two of the Persistent Organic Pollutants (POP) defined both in the Stockholm Convention on Persistent Organic Pollutants [17] and in the 1998 Aarhus Protocol on Persistent Organic Pollutants (POP) [18]. PCDD is a family with 75 compounds and PCDF is a family of 135 compounds, from which only seven PCDD and ten PCDF listed are recognized as persistent, toxic and bio-accumulative. For evaluation of toxicological effects toxicity equivalent factors (TEF) were developed, being 2,3,7,8-TCDD (the most toxic known compound) the reference.

Combustion of fossil fuels is recognized to be one of the most important anthropogenic sources of dioxins and furans [19]. The two most important paths to PCDD/F formation [20] are the "de novo" mechanism and the PCDD/F formation through organic precursors. Both of these heterogeneous (solid-phase) reactions are catalysed by the metals present in the fly ash surfaces.

The particle size of the fly ash is one of the various factors influencing PCDD/F formation. The smallest particles often play the most important role in the PCDD/F formation mechanisms because they could offer much larger adsorption areas [20]. Several studies reported that PCDD/F concentrations are higher in particles from combustion with lower sizes and also in the smaller atmospheric particles [21–23].

Chlorine is directly involved in the formation of chlorinated dioxin compounds and interferes indirectly, because it promotes the volatility of heavy metals, thus enriching fly ash with Zn, Ni, Cu, Fe, Cr chlorides and their water-insoluble salts, all of which are well-known catalysts in organic reactions [20]. Of these, $CuCl_2$ is recognized to significantly contribute to the PCDD/F formation [24,25]. The presence of sulphur dioxide in combustion gases may reduce the level of PCDD/F formation during incineration processes [26,27]. One possibility of reducing the PCDD/F formation is to perform combustion of wastes or biofuels with coals containing significant levels of sulphur [28,29], which was confirmed earlier [30] for the present set of combustion tests reported in this work.

In this paper, PM emissions obtained during co-firing tests of coals with five different biofuels, and monocombustion of coals and biofuels in a pilot fluidised bed are characterized in terms of concentrations, presence of unburned matter, particle size diameter and the proportion of very fine particles and the relation with Cl and alkali contents of the different fuels is established. PM characteristics are also correlated with the PCDD/F emissions and with the presence of Cu and Cl in order to improve biomass utilization through co-combustion and provide better insight for efficient flue gas treatments.

2. Experimental

2.1. Fuels characterization

Five combustion campaigns were performed, in which coal and different types of biofuels were burned alone and blended with 5%, 15% and 25% (wt) of each biofuel.