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# Effect of catalysts in the quality of syngas and by-products obtained by co-gasification of coal and wastes. 2: Heavy metals, sulphur and halogen compounds abatement

Filomena Pinto *, Helena Lopes, Rui Neto André, I. Gulyurtlu, I. Cabrita

*INETI-DEECA, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal*

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## Abstract

This paper analyses the formation of sulphur and halogens compounds during co-gasification of low grade coals with different types of wastes that include: pine, petcoke and polyethylene (PE) with the aim of taking profit of waste energy value with the smallest possible impact on the environment. The influence of different types of catalysts or sorbents was studied: calcined dolomite, dolomite enriched with nickel, olivine, nickel and magnesium oxides, zinc oxide and cobalt and molybdenum oxides. The presence of dolomite led to the lowest HCl, HF and $H_2S$ concentrations in the syngas produced. ZnO also gave rise to significant decrease in $H_2S$ concentration, though higher concentrations were obtained than those with dolomite. It was found that when catalysts or sorbents were used, a significant fraction of sulphur, halogens and heavy metals were trapped in the solid residue left behind in the bed and cyclone. Higher temperatures increased the volatility of some metals and sulphur. Leachability assays of solids showed that small quantities of $SO_4^{2-}$ and $Cl^-$ could be released and most metals were not leachable, although the use of dolomite slightly increased metals leachability, because of the higher alkaline nature of residual solids produced.

*Keywords:* Co-gasification; Coal; Sulphur compounds abatement; Halogen compounds abatement; Heavy metals abatement

## 1. Introduction

Most EU countries, like Portugal, are very much dependent on imported petroleum for energy production, to decrease this dependency, EU directives encourage the use of renewable energies, alternative fuels and the development of new technologies to convert wastes to energy. These new technologies should be environmentally friendly. Most wastes usually contain nitrogen, sulphur, chlorine and metals contents higher than those present in biomass and coal, hence a large amount of these elements present in the feedstock might pass to the gas phase. Therefore, the environmental implications of the utilisation of wastes should be carefully evaluated, because, in many countries the clean air legislation imposes emission limits to minimise the impact on the environment. In addition, high concentrations of these elements in the fuel may cause the formation of compounds in the syngas that could give rise to corrosion and to deposition, hence increasing maintenance costs.

Gasification could be a technology suitable to process wastes, as it appears to be more environmentally friendly than combustion. Gasification technologies to produce electricity with high thermal efficiency can be combined satisfactory with a gas-steam turbine cycle (IGCC), or a fuel cell (MCFC). As co-gasification is performed under reducing conditions, the release of sulphur, nitrogen and chlorine into the gas phase occurs mostly as $H_2S$, $NH_3$ and HCl, all considered pollutants. The gas leaving the gasifier will require cleaning to remove particulate matter, metals and undesirable gaseous pollutants, such as sulphur, nitrogen

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* Corresponding author. Tel.: +351 21 092 4786; fax: +351 21 716 6569.
*E-mail address:* filomena.pinto@ineti.pt (F. Pinto).

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and chlorine compounds, before its final use for combustion or in a fuel cell. Generally, when high sulphur coals are gasified, the preliminary sulphur retention in the gasifier with the ash may be advantageous, as the gas produced is cleaner. The effect of adding Ca-based sorbents, like limestone, dolomite or olivine has been studied by several authors, who have shown that they have a positive effect on sulphur retention [1–3].

Drift et al. [4] used a circulating fluidized-bed gasification unit to study different biomass fuels: demolition wood (pure and mixed with sewage sludge and paper sludge), verge grass, railroad ties, cacao shells and different woody fuels. When the feedstocks contained low sulphur concentrations, these authors measured $H_2S$ contents of about 230 ppmv in the fuel gas obtained at 800 °C. When feedstocks presented measurable sulphur contents, the percentage of $H_2S$/S-fuel varied between 39% and 50% [4]. On the other hand, Kuramochi et al. [5] reported that due to the higher sulphur contents of sewage sludge, its gasification produced $H_2S$ contents of around 4000 ppmv. In another study, Khan et al. [6] showed that sulphur distribution between char, tars and the fuel gas depended on the form in which sulphur was present, as sulphur existed in both organic and inorganic forms in the fuel. The addition of CaO significantly reduced the release of $H_2S$ into the gaseous phase, whilst the presence of $CaCO_3$ had relatively low influence, because of significant calcination of $CaCO_3$ to CaO did not occur under the conditions used by Khan et al. [6]. The presence of MgO and $SiO_2$ did not affect $H_2S$ formation, but the addition of 10% of dolomite allowed great reductions of $H_2S$ in the gaseous phase, usually higher than 90%.

The release of sulphur compounds both in tars and gas phase could be diminished and controlled by the use of inorganic additives containing Ca, Fe, Mg and Si compounds [6]. Park et al. [7] also used additives based on metal oxides containing Fe with Zn, Ni and Co for hot gas desulphurization and stated that it was difficult to remove sulphur contents completely from the syngas, because of several secondary reactions. The metal sulphides (MS) produced could react either with CO, which is a major component of syngas, to produce COS or with $H_2O$ to produce $SO_2$. Xu et al. [8] also reported that higher retention of sulphur in the solid phase could be achieved in the presence of CaO, probably due to the formation of CaS. This was also proven by Sage and Welford [1], as during co-gasification of sludge with coal, the sulphur retention reached 96% in the presence of dolomite. Similar results were obtained by Paterson et al. [2], who achieved around 87% sulphur retention in the solid phase with the addition of dolomite.

Several authors have reported that HCl contents in the gas obtained during gasification depended on several factors, most important ones being the form of chlorine (in organic or inorganic compounds) and its content in the feedstock, gasification operating conditions: temperature, oxygen and steam contents and the presence of other elements or compounds that might react with chlorine, leading to its retention in the solid phase. Drift et al. [4] gasified different biomass fuels in a circulating fluidized-bed reactor and reported that for most tests, less than 15% of the fuel-bound chlorine was converted to HCl. Coal pyrolysis studies by Li et al. [9] showed that chlorine volatility in the presence of CaO was lower than that without CaO. The efficiency of slowing down chlorine volatility with the addition of CaO on chlorine volatility was greatly dependent on the pyrolysis temperature. Furthermore, these authors also stated that HCl formation was also dependent on the content of other elements such as: Si, Al, K and heavy metals. Wei et al. [10] also predicted that the HCl release was also affected by Na content and by its relative concentrations in relation to other elements. The information available so far has shown that the formation of chlorine compounds is a complicated issue that depends on so many factors, whose influence is not yet clear, therefore, further research work is still needed.

The presence of heavy metals in fuels may present problems [11–13]. Metals may remain in the solid phase, however, some of them may get volatilized at relatively low temperatures, especially under the typical reducing conditions of the gasification processes [14–16]. The presence of metals in the syngas produced by gasification is highly undesirable, because of corrosive effects of these metals on the final end-use equipment, such as turbines and fuel cells and also because of emissions of polluting gases. On the other hand, the retention of metals and other contaminants in the residual solid phase, being beneficial to decrease gas phase concentrations, may restrict its re-utilisation or may lead to increased landfill costs.

The aim of this work is to control the release of sulphur and halogen compounds to the syngas during co-gasification of coal blends with different types of wastes to improve the process viability and to take profit of energy value of wastes, whilst minimising emissions to atmosphere. Low-grade coals are usually difficult to gasify, but their negative properties, like high ash content and low volatile matter, could be counterbalanced by the presence of wastes, such as pine, PE and petcoke. This paper mostly focuses on understanding the behaviour of different fuel blends during co-gasification process, with the aim of decreasing sulphur and halogens compounds emissions, for which the effect of adding different catalysts or sorbents to the gasifier was also studied.

## 2. Experimental part

Fig. 1 shows a schematic representation of the installation used, which was previously described [17]. The gasifier is a bubbling fluidised bed electrically heated, circular in cross-section with an inside diameter of 80 mm and with a height of 1500 mm. The gasifying/fluidising agent was a mixture of steam and oxygen, introduced through a gas distributor located at the bottom end of the reactor.

The fuel gas first goes through a cyclone to remove particulates and then through a condensation system to retain