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ABSTRACT

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Keywords: Biochar Wire mesh reactor Electric arc furnace The thermochemical properties of two chars obtained from agricultural residues, grape seed and pumpkin seed chars, have been studied in order to address their suitability to be used in electric arc furnace (EAF) steelmaking. Four coals (a metallurgical coal and three different anthracites), currently employed in an EAF process, were used for comparison. Proximate analyses of the four coals and the two chars were determined and compared. Isothermal CO₂ reactivity and relative combustion reactivity of the carbonaceous samples were evaluated in a thermogravimetric analyser. Pyrolysis and gasification behaviour of these coal and char samples was studied in a wire mesh reactor in order to compare them at the high heating rate $(1000 \circ C s^{-1})$ typical of EAF and short residence times (5 and 10 s). The two biomass chars exhibited markedly different properties, which matched those of their coal counterparts. Pumpkin seed char and the metallurgical coal were found to present similar and thermochemical properties. Thermal behaviour of grape seed char was closer to that of the anthracite coals. Nevertheless, it was established that grape seed char was more volatile and presented higher combustion and gasification reactivities. The stages of the steelmaking process which are more appropriate to feed the chars were also proposed. © 2015 Published by Elsevier B.V.

1. Introduction

The iron and steel industry accounts for about 20% of industrial energy consumption, being the second-largest industrial consumer of energy after the chemical sector [1,2]. Moreover, the iron and steel production sector is the largest industrial emitter of CO_2 , with average emission of 1.8 tonnes of this greenhouse gas per tonne of steel produced according to data from World Steel Association (WSA) [1–3]. The worldwide production of steel has dramatically increased over the last decades and is expected to continue to grow due to economic and population growth. Therefore, steelmakers face the challenge of developing new technologies in order to reduce consumption of fossil fuels and, consequently, CO_2 emissions [4,5].

Nowadays, there are two well-established routes for steel production: (i) the blast furnace (BF) route, which uses up to 25% recycled ferrous scrap input; and (ii) the electric arc furnace (EAF) route, with feedstock of almost 100% scrap [1,4,6]. CO₂ emissions vary considerably depending on the production route, ranging from 1.8 tonne of CO₂ per tonne of steel for BF to 0.4 tonne of CO₂ per tonne of crude steel for EAF [7]. The use of EAF for producing steel has grown dramatically over the past two decades, partly due to these lower CO₂ emissions, along with its ability to run on a relatively small scale with low capital costs and flexibility in producing different alloyed steel grades [8]. The versatility of EAF lies in its capability to operate with several types of raw materials, mainly steel scrap, which saves consumption of virgin raw materials and energy. Scrap is melted using approximately 70% of electrical energy from the arcing process and 30% of chemical energy derived from oxy-fuel combustion, carbon oxidation and other chemical reactions [5,8]. Carbon sources are used as iron reducing reactants, fuels and alloying elements and, therefore, they are related to the chemical energy supply [9]. Carbon is used at different stages of the EAF steelmaking process [10]: (i) charge carbon, which consumes excess oxygen during melting period and supplies heat; (ii) injection carbon, which reacts with oxygen to produce a foamy slag that saves electricity consumption and protects the equipment covering the arcs; and (iii) recarburizer carbon, which is used to add carbon points to the steel. Metallurgical coke and anthracite coal, due to their high fixed carbon content, are usual sources of charge and injection carbon in EAF steelmaking,

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although the amount used varies with the melt shop practice and equipment [5]. Nevertheless, metallurgical coke and anthracite coal are not suitable as carbon for recarburizer due to their usually high ash and sulphur content, and calcined coke and synthetic graphite are preferred.

One of the available measures to decrease CO₂ emissions from EAF steelmaking involves switching from the use of fossil fuels to biofuels and reducing agents with lower CO₂ emission factors, for example feeding biogas instead of natural gas into the oxy-fuel burners, or using biomass chars and recycled carbonaceous waste as charge and/or injection materials [7]. The substitution of metallurgical coke by charcoal for BF steelmaking has been largely studied and predominantly used in the Brazilian iron and steel industry [11–15]. Moreover, the use of waste plastics and rubbers into blast furnaces as substitute for coke and coal has attracted significant attention from the steelmaking industry, based on the high content in carbon and hydrogen of these polymeric materials [4,16]. In fact, the injection of waste plastics and tyres has become normal practice in BF steelmaking industry since mid-1990s, when Arcelor Group and Nippon Kokan Co., (NKK) started to use this residue in their processes [16–19]. Based on the beneficial properties of the polymeric waste and the experience obtained from their use in blast furnaces, their application for EAF steelmaking has been recently investigated [5,8,16,20,21]. Laboratory-scale studies have mainly been focused on the interaction of blends of metallurgical coke and different polymeric materials (rubber tyres, HPDE, PET, PU or Bakelite) with slag and foam development. In addition, Michelin and Arcelor Group have jointly reported successful trials of partial substitution of coal by shredded tyres in two industrial electric arc furnaces [9]. Despite biomass chars presenting great potential in order to reduce greenhouse gas emissions of the process, research focused on the use of biomass char instead of coal in EAF steelmaking is more limited [2,10,22,23]. Moreover, given that charge and injection carbons are sacrificial materials, the substitution of metallurgical coke and anthracite coal by biomass chars may contribute to a reduction in process cost. Biomass from agricultural waste is considered one of the best candidates for large industrial applications based on its significant availability and its capacity to give rise to larger char yields compared to other biomass, such as wood [24].

The present work was developed to assess the suitability of biomass char for EAF steelmaking processes as part of the GreenEAF research project, funded by the European Research Fund for Coal and Steel (RFCS). The project studied the feasibility of replacing coal and natural gas in EAF with char and syngas produced by agricultural biomass pyrolysis. Thermal behaviour and reactivity are considered quality parameters of the carbon sources used in steelmaking processes and their evaluation is required as first step in order to address the appropriateness of biomass char for EAF processes [25,26]. Grape seed and pumpkin seed chars were selected as potential feedstock to replace coal in EAF steelmaking based on their importance in countries and regions involved in the project. Pumpkin is one of the three more important field fruit in the province of Styria (Austria), and production of pumpkin seed oil is of significant economic value for the region. Approximately 2.5 kg of pumpkin seeds are used in order to produce of 1 L of pumpkin oil [27]. The pumpkin seed cake left as residue after oil extraction is mainly used as feed for livestock. Char from this residue was used as carbon source in this work. Char from pumpkin seed press cake is named as pumpkin seed char for simplification purpose. On the other hand, grape seeds are a substantial agricultural residue from the wine industry in Italy. Approximately 245 thousand tonnes of grape seeds per annum are estimated to be available nationwide [28].

The aim of this work is to evaluate the suitability of chars produced from agricultural residues for their use in EAF steelmaking based on their chemical and thermal properties. Two different biomass chars, i.e., grape seed char and pumpkin seed char, were thermochemically characterised and their gasification and combustion reactivities compared to four different coals currently employed in EAF steelmaking. The stages of the process that are more appropriate to incorporate the biomass chars were identified.

2. Experimental

2.1. Samples

Four coals and two biomass chars were used in this work. The coals used as reference materials are currently employed at different stages of the EAF steelmaking process carried out at the facilities of Ferriere Nord (Osoppo, Italy), an industrial partner in the GreenEAF consortium: (i) Coal A, metallurgical coal used as charge carbon; (ii) Coal B, anthracite used as fine injection coal; (iii) Coal C, anthracite used as coarse injection coal; and, (iv) Coal D, anthracite used in the basket. The biomass chars studied were obtained from grape seeds and pumpkin seed press cake (named grape seed char and pumpkin seed char, respectively). Samples were produced in demonstrative rotatory kiln pyrolysers. Rotary kiln can be fed with up to 200 kg h^{-1} and the necessary heat energy for pyrolysis reactions is supplied by a gas burner of the maximum power of 500 kW. Pyrolysis temperature is monitored continuously by a pyrometer and it can be varied by means of burner thermal power variation. The pyrolyser rotation speed is variable. During pyrolysis tests, the gas produced can be sampled previous being burnt in a torch; the tar is separated from the gas in a treatment section and collected in a tank with cooling and washing water. The char is conveyed by a screw and discharged from the reactor at the pyrolysis temperature. Main operating conditions for pyrolysis experiments were: (i) O_2 content in the rotary kiln 2–3%; (ii) internal reactor depression -2/-3 mmH₂O; (iii) biomass feeding to the reactor 100 kg/h; (iv) pyrolysis temperatures 500-600 °C; and (v) residence time 30–50 min. Biomass chars were produced within the framework of the GreenEAF project, which targeted the production of both char and syngas. Consequently, operating conditions for optimization of char and syngas heating value were selected. Temperature of 500 °C and shorter residence times were selected in order to produce chars with high volatile matter content, required for injection and foaming materials. Pyrolysis at 600 °C and longer residence time were necessary to obtain chars with low values of volatile matter, similar to charge coals. Before being used in experiments described in this publication, all samples were crushed and sieved between 106 and 150 µm, dried overnight and stored under N_2 in a freezer.

2.2. Proximate analysis

Proximate analysis (moisture, volatile matter and ash content) of the carbonaceous samples was carried out in a PerkinElmer "Pyris 1" thermogravimetric analyser (TGA). Approximately 3–4 mg of sample were heated to 50 °C and held for 10 min under N₂ atmosphere (40 mL min⁻¹). Afterwards, the temperature was increased in two steps in order to record the moisture and volatile matter contents, respectively: (i) heated to 110 °C at 10 °C min⁻¹ and held for 30 min; (ii) heated to 900 °C at 10 °C min⁻¹ and held for 30 min. Temperature was then decreased to 800 °C at 10 °C min⁻¹ and held for 10 min under N₂. Next, the sweep gas was switched to air (40 mL min⁻¹) and held for 40 min in order to register the ash content. Fixed carbon content was calculated by difference.

2.3. Thermogravimetric analysis

Isothermal CO₂ reactivity and relative combustion reactivity of the carbonaceous samples were also evaluated in the PerkinElmer

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