

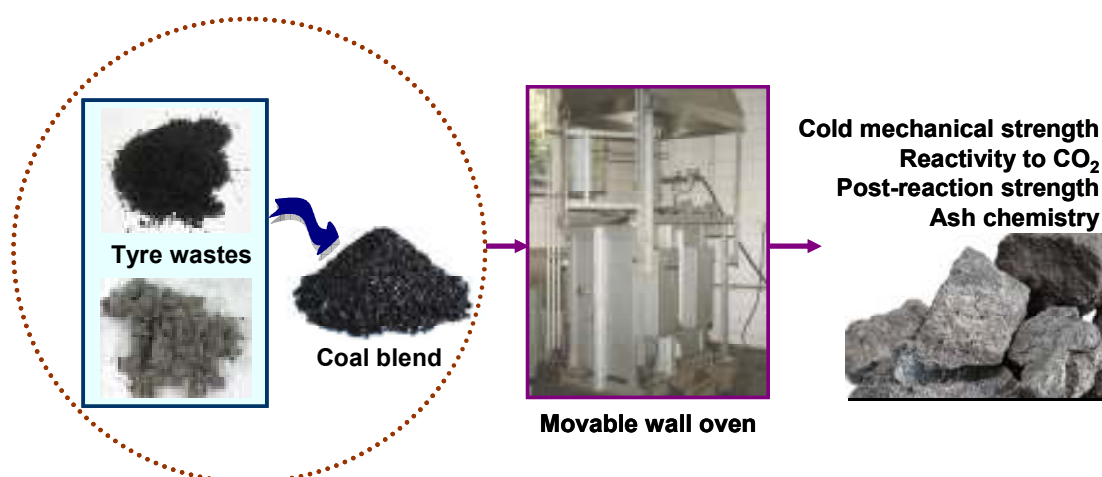
## Recycling tyre wastes as additives in industrial coal blends for cokemaking.

A.M. Fernández,\* C. Barriocanal, E. Díaz-Faes.

*Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain*

### ABSTRACT

Two industrial coal blends (B1 and B2) used in cokemaking were selected for this study. Two wastes from scrap tyres (TC, F) were added to these coal blends at different ratios (98:2 and 95:5). The investigation was focused on assessing the influence of the additives on thermoplastic properties of coal by means of the Gieseler fluidity test and thermogravimetric. In addition, the blends were carbonized in a 17 kg electrically heated movable wall oven in order to examine the quality of the resultant cokes. Quality of the cokes produced was evaluated by measuring their cold mechanical strength, reactivity and post-reaction strength. It was found that ash composition of the additives contribute to a deterioration in coke quality. Moreover, F causes a greater decrease in coke strength after reaction with CO<sub>2</sub> due to the diminution of bulk density in the coking process and to the higher basicity index. Trace elements were also studied in relation to waste addition.



**Keywords:** scrap tyres; coal blends; fluidity; ash composition; coke quality.

## 1. Introduction

The International coal market has changed considerably in recent years, giving rise to a notable variability in prices. Because of the short supply of high-quality coking coals, industrial coal blends are normally used in cokemaking. The quality of the blend depends on the quality of individual coals and their interaction within the blend. The coal blends are usually made up of coals with different characteristics and from different origin. The co-carbonization of coal blends with additives has been observed to modify the coking properties of coals and the quality of the resulting cokes significantly [1, 2]. In the present work, effects of adding carbon-rich materials from the recycling tyre industry to industrial coal blends were studied. Only small proportion of additives was used because of their high sulphur content that could negatively affect coke quality. Carbonization was studied as a possible route for recycling waste tyres to avoid the need for dumping, thereby contributing to the protection of the environment, and reducing the costs related to waste disposal. Previous investigations studied that tyres and their char could be used as additives to coke-oven blends without causing any apparent deterioration in coke quality, although the particle size of the waste tyre added had an impact on the quality of the coke produced [3, 4]. Moreover, the heaviest fraction of tyre-derived liquid can be used as a raw material for producing coke of good quality with low sulphur, ash and metal contents [5]. There are other ways to recycle these kinds of wastes. Waste tyres can be co-injected with metallurgical coke in the electric arc furnace steelmaking process to provide additional energy for combustion [6]. Previous works study the combustion of different rank coals mixed with end-of-life tyres in an atmospheric fluidized bed combustion (AFBC) pilot plant [7]. This combustion system shows several advantages over conventional systems, such as fuel flexibility and better emissions control. It offers the advantages of making tyres a proper fuel to generate energy when mixed with high ash coals. Addition of tyre to coal hydrogenation processes improves conversions due to a cheap hydrogen donation or

to a simple reduction of heat and mass transport phenomena, and thus to lower costs [8].

The resultant coke will be used in a blast furnace for pig iron production, a route that will remain the basis of steel production in the foreseeable future. Coke cannot be fully replaced as a raw material in the blast furnace for physical reasons [9, 10]. Its quality plays a significant role in controlling the performance of the furnace. Coke quality mainly depends on the characteristics of the coal or blend, although coking parameters and precarbonization techniques, such as compaction of the blend, also have an influence on its bulk density [11]. A high-quality coke should be able to withstand the gradual descent of the charge in the blast furnace with as little degradation as possible while providing the lowest possible amount of impurities, a high level of thermal energy, a high degree of metal reduction, and optimum permeability for the flow of gaseous and molten products. The use of high-quality coke in the blast furnace will result in a lower coke rate, greater productivity and a lower pig iron cost.

Fluidity is another factor that has a significant influence on coke quality. When a bituminous coal is heated, the individual coal particles fuse and form a porous coherent mass that expands and finally solidifies to form a semicoke that with further heating is converted into coke [1, 2, 12].

Ash is undesirable firstly because it reduces the carbon content, and also because it has to be melted which will require the addition of more limestone in the ironmaking process. This in turn will result in extra slag, leading to higher coke consumption and the restriction of output [13]. In simple terms the coke ash content should not exceed 8-12 wt.% on a dry basis [14].

The sulphur content of the coke directly affects the quality of the iron and the steel produced becomes brittle because of its presence. According to blast-furnace coke specifications, sulphur content should not exceed 0.6 % [15]. Ash sulphur is also regarded as an undesirable component in coke, as it impairs its quality and increases

its consumption in pig iron production. Furthermore a large amount of thermostable sulphur compounds in the coal increases the thermostability of the sulphur compounds in the coke, the sulphur concentration in the gas phase within the tuyere zone of the blast furnace, and hence the sulphur content of the pig iron [16].

In a previous paper [17], variations in the mineralogy of a coke obtained from blends of a medium rank coal and additives and their effect on coke reactivity was studied. The presence of new Zn-bearing phases in the tyre wastes was found to be the main cause of the increase in coke reactivity along with magnetite levels and pore size. The amount of Zn that remains in the coke depends on the coal, and it has been observed that the higher the rank of the coal, the lower the amount of zinc that remains in the coke [18]. The tyre wastes produced the most reactive chars and consequently only small amounts of tyre wastes should be added to industrial coal blends to avoid any severe impact on the CSR index. In light of these problems, the aim of the present research work was to investigate the possibility of recycling tyre wastes by means of co-carbonization with industrial coal blends and assess the impact of these wastes on coke quality. Two kinds of tyre waste were added to two industrial coal blends. An exhaustive analysis of the properties of the raw materials as well as of the resultant blends was carried out at laboratory scale in order to evaluate the effect of the amount of wastes to be added. The coking of coal blends and their blends with tyre wastes was conducted at semi-pilot scale.

## **2. Experimental**

### *2.1. Materials*

To avoid weathering, two industrial coal blends prepared in the same coking plant and composed of 10 coals of different origin were chosen for the study (B1, B2). Two wastes from the tyre recycling industry were selected as additives: the tyre crumbs (TC) and fluff/fibres obtained as a waste from the grinding and shredding of scrap tyres (F) during the processing of car and truck tyres. The fluff, a mixture of thermoplastic

polymers (e.g., polyester and nylon) and tyre crumbs, contains around 60 wt.% of rubber.

## *2.2. Proximate and elemental analyses*

Proximate analyses were performed following the ISO562 and ISO1171 standard procedures for volatile matter and ash contents, respectively. The elemental analysis was carried out on a LECO CHN-2000 for C, H and N (ASTM D-5773), and a LECO S-144 DR (ASTM-ASTM D-5016) for sulphur.

## *2.3. Gieseler plastometry*

Thermoplastic properties of the industrial coal blends and the laboratory-prepared blends formed by adding 2, 5 and 10 wt.% of each additive were assessed by means of the Gieseler method in a R.B. Automazione Gieseler plastometer PL2000, following the ASTM D2639-08 standard procedure which has been explained in detail in a previous paper. The optimum Gieseler maximum fluidity as established by the MOF diagram, ranges from 200 to 1000 ddpm [19].

## *2.4. Thermogravimetric analysis (TG/DTG)*

The TG/DTG analysis of the coal blends was carried out using a TA Instruments SDT 2960 thermoanalyser. 10-15 mg samples with a particle size of < 0.212 mm were heated to 1000°C at a rate of 10°C/min under a nitrogen flow of 100 ml/min. From the data obtained by thermogravimetric analysis the volatile matter evolved up to a specific temperature ( $VM_T$ ) and the derivative of the weight loss curve (DTG curve) were calculated. The volatile matter evolved over a specific temperature range was calculated as the difference between the volatile matter evolved up to two specified temperatures ( $VM_{T_1-T_2}$ ). In addition,  $T_{max}$ , the temperature of maximum volatile matter evolution was derived from the TG/DTG curves [20, 21].

## *2.5. Carbonization test*

Carbonization tests were carried out in a movable wall oven of approximately 17 kg capacity (MWO17). The dimensions of the oven are 270 mm L X 165 mm W X 790 mm H. A load cell was mounted on the movable wall to measure the force exerted on

the wall during carbonization. A programmable controller was used to control the oven temperature. The temperature at the centre of the coal charge was monitored by means of a thermocouple connected to a computer. The coal was charged when the oven reached 1100°C. The temperature of the wall was kept constant throughout the test. The coke was pushed out of the oven 15 minutes after the centre of the charge had reached 950 °C. The coking time was around 3.5 h. The moisture of the charge was fixed at 5 wt.%. The bulk density expressed on a dry basis was 771 and 778 kg/m<sup>3</sup> for B1 and B2, respectively. More than 80 wt.% of the grain size of the coal blends was smaller than 3 mm. 43 wt.% of the tyre crumbs had a particle size in the 2-3 mm range, while in the case of the fluff/fibres, 57 wt.% it was smaller than 2 mm.

## *2.6. Ash analysis*

The total ash content of the coke samples was obtained by combustion of the organic matter at 815 °C until constant mass, following the ISO 1171 (2010) standard. The concentrations of oxides (Al, Ca, Fe, K, Mg, Na, Si, P and Ti) were determined using X-ray fluorescence spectroscopy (XRF). The XRF apparatus was a sequential wavelength-dispersive Siemens SRS 3000 X-ray spectrometer equipped with a Rh X-ray tube, a 58 position sample turntable, and a flow counter detector. Prior to the XRF analysis the ashes obtained from the coke samples were subjected to a fusion step using lithium tetraborate in order to obtain sample beads for analysis. The device used to prepare the sample was a Philips Perl' X3 automatic fused bead machine.

In order to determine trace elements (Zn, Mn, V, Ni, Pb, Co, Cu and Sb), analyses were carried out using Inductively coupled plasma spectrometry (ICP-MS) in a ICP-MS 7700x Agilent device. The ashes were digested with HNO<sub>3</sub>:HCl at a ratio of 3:1 in a microwave oven.

## *2.7. Textural characterization*

The coke densities were measured using the displacement method in gas and liquid media (helium, water and mercury). The true density ( $\rho_{\text{He}}$ ) of the cokes was measured by means of helium picnometry in a Micromeritics Accupyc 1330

Pycnometer. The apparent mercury density ( $\rho_{Hg}$ ) was determined with mercury at a pressure of 0.1 MPa in a Micromeritics autopore IV 9500 mercury porosimeter. The particle size used for both methods was between 1-3 mm. The apparent water density ( $\rho_{H_2O}$ ) was determined by water displacement using 300 g of coke sample with particle sizes between 19–22.4 mm.

Total coke porosity was calculated from the apparent water and true helium densities, while the true helium and apparent mercury densities were used to determine the open porosity corresponding to pore sizes of less than 12  $\mu\text{m}$  as follows:

$$\varepsilon(\%) = 1 - \frac{\rho_a \text{ (g/cm}^3\text{)}}{\rho_t \text{ (g/cm}^3\text{)}} \times 100 \quad (1)$$

The total pore volume ( $V_T$ ) was obtained from the equation:

$$V_T \text{ (cm}^3\text{/g)} = \frac{1}{\rho_a \text{ (g/cm}^3\text{)}} - \frac{1}{\rho_t \text{ (g/cm}^3\text{)}} \quad (2)$$

where  $\rho_a$  represents the apparent density and  $\rho_t$ , the true density.

The pore size distribution was calculated by applying increasing pressure to the sample from 0.1 to 227 MPa. This resulted in pore sizes ranging from 12  $\mu\text{m}$  to 5.5 nm according to the Washburn equation:

$$d_p \text{ (nm)} = \frac{1244}{P \text{ (MPa)}} \quad (3)$$

Pore size distribution was classified into two categories: macropores (12  $\mu\text{m}$  >  $d_p$  > 50 nm) and mesopores (50 nm >  $d_p$  > 5.5 nm).

## 2.8. Coke quality

The cold mechanical strength of the cokes produced was assessed by the JIS test (JIS k2151 standard procedure). Coke reactivity and mechanical strength after reaction were assessed by means of the NSC test (ASTM D5341 standard procedure). A coke destined for use in blast furnaces should have a CRI index in the 20-30% range and a CSR index of above 60-65% [9]. The repeatability limit of this method is 2.8

points in the case of CRI and 5.4 for CSR. It is well known that the lower the CRI and the higher the CSR, the better the coke quality.

### **3. Results and discussion**

#### *3.1. Material properties*

Table 1 shows the results of the elemental and proximate analyses of the raw materials. Coal blend B1 has a volatile matter of 23.8 wt.% db, whereas volatile matter of B2 is 26.4 wt.% db. The industrial coal blends contain more than 13 coals of different geographical origin with volatile matter contents ranging from 14 to 33 wt.% db. High sulphur and oxygen contents and a high volatile matter content are found in the two tyre wastes. Sulphur is introduced into tyres as a catalyst for the vulcanisation of rubber in order to achieve greater stability, toughness, and heat resistance for industrial purposes.

#### *3.2. Influence of the additives on the fluidity of the coal blends*

The thermoplastic behaviour of a coal is considered to be very important in the formation of semicoke and consequently in determining the quality of the resulting coke. The effect of the additives TC and F on the thermoplastic properties of single coals has been studied previously [22, 23] where it was demonstrated that these wastes cause coal fluidity to deteriorate. The deterioration is attributed to chemical and physical interactions. The chemical interactions are due to the greater heteroatom content (O, S) which produces an increase in the reactivity of the blend. The physical interactions are explained by the removal of the plasticising components of the coal [23, 24, 25]. A similar behaviour can be expected in industrial coal blends. In the present work the blend with a fluidity value of 1762 ddpm (B2) was selected to study the effect of tyre waste addition. In order to assess influence of the two wastes on coal blend fluidity, the mixtures containing 2 and 5 wt.% of TC and F were carefully prepared and the variation in fluidity with temperature was recorded and listed in Table 2. B2 has the highest fluidity (1762 ddpm) while addition of tyre wastes results in lower maximum Gieseler fluidity. The effects of TC and F on coal blend fluidity are similar.



Additions of 2wt.% reduced maximum fluidity by an average of 22 % whereas 5wt.% addition reduced maximum fluidity by an average of 25%. The additions of 2 and 5 wt.% of TC and F did not lead to a proportional reduction in maximum fluidity. The non-additive character of Gieseler fluidity and the large number of coals of different rank that made up the blend may have affected the addition in different ways. In a previous work by Montiano et al. [26] the addition of sawdust to an industrial coal blend also produced a non-proportional reduction in fluidity. The decrease in fluidity caused by the addition of tyre wastes will not affect the ability of coal blends to produce good quality coke since the MF values remain within the optimum range, 200-1000 ddpm [19].

### *3.3. Thermogravimetric analyses of the blends*

Table 3 shows the most relevant parameters derived from thermogravimetric analysis of the industrial coal blends, the tyre wastes and their blends. In coal blend B2 the volatiles evolve at lower temperatures than in B1 (i.e., lower T<sub>max</sub>) and there is a higher maximum rate of volatile matter evolution (DTG<sub>max</sub>) than in B1.

In blend preparation for cokemaking it is important to know the degree of interaction between the materials that make up the blend [21, 27]. The two industrial coal blends present one devolatilization step while TC and F devolatilize in two and three stages, respectively [22, 28]. Figure 2 shows the DTG curves corresponding to the industrial coal blends, tyre wastes and their mixtures. Their influence on the thermogravimetric behaviour of the coal blends is clear since two thermal events were identified during the co-pyrolysis of the industrial coal blends with TC; and three in the case of F addition. The two first peaks are associated to the tyre waste pyrolysis, while the last one is linked mainly to the coal pyrolysis, which occurred at higher temperatures (Table 3). This trend is due to the high volatile content and the difference in the strength of the molecular structure of the additives [29, 30], compared to coal blends. For this reason, the volatile matter that evolved in the plastic and post-plastic stages decreases. Previous research works [31, 32, 33] showed that the ability of a plasticizing additive to modify a coal can be explained in terms of the amount of volatile

matter evolved during the plastic stage of the system. The additives added to the coal blends increase the evolution of volatile matter content by 5-14% before the softening stage of the coal blend begins. The results obtained from thermogravimetry indicate that the carbonizations of the coals and the tyre wastes occur independently of each other. At around 425 °C a porous char forms from the wastes, whereas the coals are just starting to decompose. This porous char that appears in the reaction system adsorbs the plastizing components from the decomposition of coal and as a result these wastes have a deleterious effect on the coal's properties [23].

On the other hand, coke yield decreases by 0.8 to 2.4% as waste addition increases (Table 3). A comparison of the experimental and calculated coke yield values reveals that there is no synergistic effect between the components of the blends. Similarly, in a previous research work in which these wastes were used [34] no interaction was observed with the coal.

#### *3.4. Carbonization and coke quality*

Industrial coal blends and mixtures containing 2 and 5 wt.% tyre wastes were carbonized in a movable wall oven of approximately 17 kg capacity (MWO17). The proximate and ultimate analyses of the resulting cokes are presented in Table 4. In the present study, it can be seen that the addition of relatively high sulphur containing tyre wastes causes no serious increase in the sulphur content of the coke for 2 and 5 wt.% additions. According to the law of additivity, the sulphur contents that can be expected of the coal blends and additives are 0.61 for B1+2TC, 0.65 for B1+5TC, 0.75 for B2+2F and 0.78 wt.% for B2+5F. There is an increase in the sulphur content with the amount of additives. In general the S content of the cokes is lower than that of the coal used in their preparation. However, it is necessary to take into account that the chars prepared from TC have a higher S content than the initial raw material [23]. The S that is added during the vulcanization of the rubber produces very stable chemically bound sulphur complexes [18]. In the present case, S content of the cokes prepared with TC was larger than that of the initial blends. When F is used as additive, the S content of the

cokes is lower than in the initial blends as occurs in the coal blends. Because of its lower rubber content, the influence of coal is predominant.

The bulk density of the charge (mass charged per unit volume) is an important operational factor in cokemaking which influences throughput and coke quality [2]. It is influenced by the particle size distribution and the moisture content of the coal. As the moisture of the charge is fixed and the particle size of the raw materials is maintained, the variations in bulk density must be due to the effect of the additive. The reference industrial coal blends B1 and B2, were charged into the movable wall oven, with bulk densities of 771 and 778 kg/m<sup>3</sup> on a dry basis (db), respectively. The behaviour of the two types of wastes differs considerably. TC produces a slight increase in bulk density to 784 and 787 kg/m<sup>3</sup> db for the 2 and 5 wt.% additions, respectively. However, F causes a decrease in bulk density yielding values of 760 and 751 kg/m<sup>3</sup> for 2 and 5 wt.% additions, respectively. Differences in the bulk density of the mixtures with the two additives are due to the low bulk density of the fibre (i.e. 94 kg/m<sup>3</sup>).

The most important function of coke in a blast furnace is to act as a support for the ferrous burden and to offer a permeable matrix for reducing gases in the lower region of blast furnace, a function which is related to its size and its resistance to breakage and abrasion. The cold mechanical strength of the cokes produced in the MWO was assessed by means of the JIS test. Figure 3a shows the variation of the  $DI_{15}^{150}$  index for the blends B1 and B2 containing 2 and 5 wt.% of tyre wastes respectively (TC, F). In both blends, 2 wt.% tyre waste addition appears to be acceptable, since the greatest reduction for this level of addition is 3.7 units. For 5 wt.% TC or F addition, the JIS index decreases 10.9-12.7 units, respectively, F being the worst additive at this percentage of addition. Although coke mechanical strength indices provide blast furnace operators with a useful assessment of coke performance, they are taken at ambient temperature and hence fail to take into account the conditions to which the coke is subjected in the blast furnace.

An exhaustive analysis of coke behaviour in the blast furnace was carried out, so coke reactivity to CO<sub>2</sub> (CRI) and mechanical strength post-reaction (CSR) was studied bearing in mind that the latter is considered to be the most important parameter as a metallurgical coke quality indicator. Figure 3b shows the variation in the CRI index. No substantial changes are found in the CRI index in the case of the B1 coal blend with a 2 or 5 wt.% addition of TC. The 2 wt.% addition does not modify the CRI index at all (cf. B1 and B1+2TC) while the 5 wt.% addition causes an increase of 3 units (cf. B1 and B1+5TC). On the other hand, in the case of the 2 and 5 wt.% F additions to B2, the CRI index increases by 3 or 5 units, respectively. The CSR of B1 (Figure 3c) is higher than that of B2 (59 vs 55) and the addition of the TC diminishes the mechanical post-reaction strength index by 1-5 units, i.e., to 58 and 54% for B1+2TC and B1+5TC, respectively. However, F has a greater deleterious effect on the CSR which decreases 5 and 8 units for B2+2F and B2+5F, respectively. It is apparent that tyre crumbs from the tyre recycling industry (TC) do not significantly affect the cold mechanical strength of the resultant coke, especially at the 2 wt.% addition level. However, addition of F produces cokes of a lower quality than addition of TC. It is well known that CRI is inversely related to CSR, and therefore the deleterious effect of F upon CRI is reflected in a lower CSR.

As aids to coke quality prediction, several mathematical models are available. Although no prediction model has acquired universal application, almost all coking plants have some form of a model based on coal rank, rheological properties, petrology and ash chemistry. Due to its influence on the CRI and CSR indices, the role of the ash composition has been given more consideration because certain minerals in coke have an accelerating or inhibiting effect on coke gasification as a result of catalytic reactions [7]. Alkalis are also responsible for the deterioration of coke quality, since they attack and degrade the carbon fraction of coke in a blast furnace [35]. The basicity index of the ash was calculated from an analysis of its chemical composition using the ratio of the total content of the basic oxides (Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O) to the total

content of acidic oxides ( $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) according to XRF analysis (Table 5). This index increases with tyre waste addition, especially in the case of 5 wt.% F addition, which produces the highest CRI index value. CRI (Table 4) and basicity indices (Table 5) in the present research point to a linear relationship between the two with sets of indices with a correlation coefficient of  $r = 0.906$ . To explain the different effects on coke quality of TC and F additions, two factors need to be taken into account: (1) the different effect of both additives on bulk density which will affect the CSR, and, (2) the chemical composition of the ash. F causes greater deterioration in CSR than TC, because of the decrease in the bulk density of the charge and the higher basicity index.

The incorporation of waste materials into coal blends without any deterioration in coke quality is essential for ironmaking via the blast furnace route [2, 36, 37]. Moreover, the steel process itself produces a significant amount of waste materials or by-products, some of which are considered to be highly problematic. Zinc in particular poses a problem during the metallurgical process. This element gets into the blast furnace, not only as a component of ore but also through coke in the form of oxides and sulphides. As a result a large amount of dust is generated, which may even damage the furnace [38, 39]. Trace elements of coke ash were assessed by means of ICP-MS, the results of which are shown in Table 6. It can be seen that the inclusion of 5 wt.% of the two wastes increases the amount of Zn in the cokes to 70.65 and 29.84 ppm in the B1+5TC and B2+5F blends, respectively. The B2+5F blend shows a similar Zn content to that found in a coke product reported in the literature [40]. However, it is present in greater quantity in the case of 5 wt.% TC addition which could cause a deterioration in the quality of the coke to be used in the blast furnace. Although the presence of zinc might affect the process, recycling of these wastes could help to alleviate a serious environmental problem. To a smaller extent an increase in Co content is also observed with the addition of both these additives but only the addition of F increases the V, Pb, Mn, Cu and Sb contents of the coke.

Shattering and abrasion, the principal forms of degradation in the upper parts of the blast furnace, are related to the cold coke strength which in turn is influenced by the physical properties of the coke, such as porosity and the nature of the pores. A higher porosity and a greater specific surface area enhance the diffusion of CO<sub>2</sub> into the inner part of coke and intensifies the gasification process [41]. A slight increase in mesopore volume (2%) was observed in the mixtures of industrial coal blends with tyre wastes (Table 7) owing to the nature of the additives themselves. In a previous work [22] it was found that the chars from tyre wastes presented a high proportion of mesopores and a low char yield [42]. The effect of coke blends textural properties at the level of addition in the present research work was insignificant, although TC tended to reduce porosity (values from 55.1 to 53.7 vol.% for total porosity) while F caused a slight increase (values from 53.6 to 55.6 vol.% for total porosity).

A comparison of the effect of the two additives on industrial coal shows that tyre crumbs (TC) are preferable for adding to industrial coal blends and that a maximum of 2 wt.% addition is the best option in order not to cause any deterioration in coke quality or blast furnace operation.

#### **4. Conclusions**

The addition of tyre wastes reduces the plastic properties of industrial coal blends. Fibres from the tyre recycling industry (F) decrease the bulk density of the charge and produce a higher ash basicity index, resulting in cokes of poorer quality (lower CSR). Tyre crumbs (TC) cause a slight increase in the sulphur content of the cokes in comparison to the initial blends. Moreover, TC produces a slight increase in bulk density (16 kg/m<sup>3</sup> for a 5wt.% addition) and a less noticeable increase in the basicity index than F. The zinc content of the coke with 5 w% of tyre crumbs might damage the blast furnace wall. No significant changes on coke quality based on textural properties of the cokes were observed. The amount that can be added is limited due to the deleterious effect that tyre wastes have on coke characteristics. To sum up, the incorporation of tyre crumbs into industrial coal blends in a proportion of 2

wt.% is the best option for ensuring acceptable coke quality and a good blast furnace performance.

## References

- [1] H. H. Lowry, in: M.A. Elliot (Ed), Chemistry of coal utilization 2<sup>nd</sup> Ed, Wiley Interscience Publishers: New York, 1981.
- [2] R. Loison, in: Coke. Quality and production, Butterworths: London, 1989.
- [3] W.R. Leeder, Additions of discarded automobile tyres to coke-oven blends, Fuel 53 (4) (1974) 283-284.
- [4] X. Liu, H.Q. Liao, Z.G. Zhang, D.M. Deng, Study on Improving Quality of Coke Co-coked With Addition of Waste Tire, Iron and Steel 41 (6) (2006) 17-21.
- [5] A. Chaala, C. Roy, Production of coke from scrap tire vacuum pyrolysis oil, Fuel Processing Technology 46 (1996) 227-239.
- [6] M. Zaharia, V. Sahajwalla, B.C. Kim, R. Khanna, N. Saha-Chaudhury, P. O'Kane, J. Dicker, C. Skidmore, D. Knights, Recycling of Rubber Tires in Electric Arc Furnace Steelmaking: Simultaneous Combustion of Metallurgical Coke and Rubber Tyres Blends. Energy & Fuels 23 (2009) 2467–2474.
- [7] M.A. Díaz-Bautista, R. Alvarez-Rodríguez, C. Clemente-Jul, A.M. Mastral, AFBC of coal with tyre rubber. Influence of the co-combustion variables on the mineral matter of solid by-products and on Zn lixiviation, Fuel 106 (2013) 10–20.
- [8] A.M. Mastral, R. Murillo, M.S. Callén, T. García, Evidence of coal and tire interactions in coal–tire coprocessing for short residence times, Fuel Processing Technology 69 (2001) 127–140.
- [9] M.A. Díez, R. Álvarez, C. Barriocanal, Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking, International Journal of Coal Geology 50 (2002) 389-412.
- [10] J.A. Pajares, M.A. Díez, Coal and Coke, in: W. Paulworsfold, A. Townshend, C. Poole (Eds.), Encyclopedia of Analytical Science, Elsevier: Oxford 2005, pp 182-197.

[11] P.K. Prachethan, S. Barman, M. Ranjan, S. Ghosh, S., V.V.S. Raju, Maximisation of non-coking coals in coke production from non-recovery coke ovens, *Ironmaking and Steelmaking* 35 (2008), 33-37.

[12] D. Hays, J.W. Patrick, A. Walker, Pore structure development during coal carbonization. 1. Behaviour of single coals, *Fuel* 55 (1976) 297-302.

[13] A. Konstanciak, The effect of blast furnace coke quality on the possibility of its use, *Metalurgija* 52 (2013) 193-196.

[14] D.C. Leonard, L. Bonte, A. Dufour, A. Ferstl, K. Raipala, P. Schmole, P. Schoone, J.L. Verduras, R.R. Wilmers, Coke quality requirements of European blast furnace engineers (Joint EBFC-Paper), Proceedings 3rd European Cokemaking Congress, CRMVDEh, Gent, Belgium 1-10, 1996.

[15] J.P. Graham, Specification of the Properties of Coke for Ironmaking: UK Blast-Furnace Coke Specifications. Conference on Coke in Ironmaking, The Iron and Steel Institute and the Institute of Fuel, London, 1969.

[16] M.L. Ulanovskii, D.V. Miroshnichenko, Sulfur in Coal and Its Influence on the Quality and Consumption of Coke in the Blast Furnace, *Coke and Chemistry* 51 (2008) 51-56.

[17] A.M. Fernández, C. Barriocanal, S. Gupta, D. French, Effect of Blending Carbon-Bearing Waste with Coal on Mineralogy and Reactivity of Cokes, *Energy and Fuels* 24 (2014) 291-298.

[18] A. Koszorek, A. Mianowski, T. Radko, E. Zajusz-Zubek. Behaviour of zinc in cokemaking process of coal blends with scrap tires granulates, W: Twenty-fourth Annual International Pittsburgh Coal Conference. Coal energy, environment and sustainable development, Johannesburg, South Africa, September 10-14, 2007, Pittsburgh: Pittsburgh Coal Conference.

[19] T. Miyazu, The evaluation and design of blends using many kinds of coals for cokemaking. *Int. Iron Steel Cong.*, Dusseldorf 1974, Pap. 1.2.2.1.



- [20] C. Barriocanal, M.A. Díez, R. Álvarez, M.D. Casal, C.S. Canga, On the relationship between coal plasticity and thermogravimetric analysis, *Journal of Analytical Applied Pyrolysis* 67 (2003) 23-40.
- [21] E. Díaz-Faes, C. Barriocanal, M.A. Díez, R. Álvarez, Characterization of different origin coking coals and their blends by Gieseler plasticity and TGA, *Journal of Analytical Applied Pyrolysis* 80 (2007) 203-208.
- [22] A.M. Fernández, C. Barriocanal, M.A. Díez, R. Álvarez, Influence of the additives of various origins on thermoplastic properties of coal, *Fuel* 88 (2009) 2365-2372.
- [23] A.M. Fernández, C. Barriocanal, M.A. Díez, R. Álvarez, Importance of the textural characteristics of inert additives in the reduction of coal thermoplastic properties, *Fuel* 89 (2010) 3388-3392.
- [24] R. Sakurovs, Interactions between coking coals and plastics during co-pyrolysis, *Fuel* 82 (2003) 1911-1916.
- [25] A. Domínguez, C.G. Blanco, C. Barriocanal, R. Álvarez, M.A. Díez, Gas chromatographic study of the volatile products from co-pyrolysis of coal and polyethylene wastes, *Journal of Chromatography A* 918 (2001) 135-144.
- [26] M.G. Montiano, E. Díaz-Faes, C. Barriocanal, R. Alvarez, Influence of biomass on metallurgical coke quality, *Fuel* 116 (2014) 175–182.
- [27] C. Barriocanal, M.A. Díez, R. Álvarez, M.D. Casal, C.S. Canga, On the relationship between coal plasticity and thermogravimetric analysis, *Journal of Analytical Applied Pyrolysis* 67 (2003) 23-40.
- [28] B. Acevedo, C. Barriocanal, R. Álvarez, Pyrolysis of wastes from tyre grinding, *Proceedings of the 9th ICCS&T conference*, P1.29, Oviedo, 2011.
- [29] F. Parres, J.E. Crespo-Amorós, A. Nadal-Gisbert, Characterization of fibers obtained from shredded tires, *Journal of Applied Polymer Science* 113 (2009) 2139-2142.

- [30] S. Seidelt, M. Müller-Hagedorn, H. Bockhorn, Description of tire pyrolysis by thermal degradation behaviour of main components, *Journal of Analytical and Applied Pyrolysis* 75 (2006) 11-18.
- [31] M.A. Díez, C. Barriocanal, R. Álvarez, Plastic wastes as modifiers of the thermoplasticity of coal, *Energy & Fuels* 19 (2005) 2304-2316.
- [32] C. Barriocanal, R. Álvarez, C.S. Canga, M.A. Díez, On the Possibility of Using Coking Plant Waste Materials as Additives for Coke Production, *Energy & Fuels* 122 (1998) 981-989.
- [33] J.A. Menéndez, J.J. Pis, R. Álvarez, C. Barriocanal, C.S. Canga, E. Fuente, M.A. Díez, Characterization of petroleum coke as additive in metallurgical cokemaking. Influence on metallurgical coke quality, *Energy & Fuels* 11 (1997) 379-384.
- [34] B. Acevedo, C. Barriocanal, Pyrolysis of blends of coal and tyre wastes in a fixed bed reactor and a rotary oven, *Fuel* 113 (2013) 817-825.
- [35] J. Kaczorowski, T. Lindstad, M. Syvertsen, The influence of Potassium on the Boudouard Reaction in Manganese Production, *ISIJ International* 47 (2007) 1599-1604.
- [36] S. Gupta, D. French, R. Sakurovs, M. Grigore, H. Sun, T. Cham, T. Hilding, M. Hallin, B. Lindblom, V. Sahajwalla, Minerals and iron-making reactions in blast furnace, *Progress in Energy and combustion Science* 34 (2008) 155-197.
- [37] R. Álvarez, C. Barriocanal, M.A. Díez, J.L.G. Cimadevilla, M.D. Casal, C.S. Canga, Recycling of Hazardous Waste Materials in the Coking Process, *Environmental Science & Technology* 38 (2004) 1611-1615.
- [38] J. Veres, M. Lovás, S. Jakabsky, V. Sepelak, S. Hredzak, Characterization of blast furnace sludge and removal of zinc by microwave assisted extraction, *Hydrometallurgy* 129-130 (2012) 67-73.

[39] P. Besta, A. Samolejová, K. Janovská, R. Lenort, J. Haverland, The effect of harmful elements in production of iron in relation to input and output material balance, *Melalurgija* 51 (2012) 325-328.

[40] L. Mu, L. Peng, X. Liu, H. Bai, C. Song, Y. Wang, Z. Li, Emission Characteristics of Heavy Metals and Their Behaviour During Coking Process, *Environmental Science & Technology* 46 (2012) 6425-6430.

[41] S. Pusz, M. Krzesińska, L. Smędowski, J. Majewska, B. Pilawa, B. Kwiecińska, Changes in a coke structure due to reaction with carbon dioxide, *International Journal of Coal Geology* 81 (2010) 287-292.

[42] A.M. Fernández, C. Barriocanal, R. Álvarez, Pyrolysis of a waste from the grinding of scrap tyres, *Journal of Hazardous Materials* 203-204 (2012) 236-243.

### **Author information**

Corresponding Author

\*Phone: +34 985 11 90 90; fax: +34 985 29 76 62

E-mail address: [anamf@incarcsic.es](mailto:anamf@incarcsic.es)

### **Acknowledgements**

The research leading to these results has received funding from the European Union's Research Fund for Coal and Steel (RFCS) research programme under grant agreement No. RFCR-CT-2010-00007 and contract No. RFCR-CT-2006-00002.

Table 1. Proximate and ultimate analyses of the two industrial coal blends (B1, B2), tyre crumbs (TC) and fibres (F) studied.

Raw material	B1	B2	TC	F
Ash (wt.% db <sup>a</sup> )	8.5	7.9	9.3	8.4
VM <sup>b</sup> (wt.% db <sup>a</sup> )	23.8	26.4	63.0	65.7
C (wt.% daf <sup>c</sup> )	90.1	90.6	87.6	83.6
H (wt.% daf <sup>c</sup> )	5.1	5.0	7.6	7.2
N (wt.% daf <sup>c</sup> )	1.9	1.8	0.3	0.3
S (wt.% daf <sup>c</sup> )	0.58	0.73	2.01	1.75
O <sup>d</sup> (wt.% daf <sup>c</sup> )	2.3	1.9	2.5	7.2
C/H <sup>e</sup>	1.47	1.51	0.96	0.97

<sup>a</sup>Dry basis.

<sup>b</sup>Volatile matter.

<sup>c</sup>Dry ash-free basis.

<sup>d</sup>Oxygen content calculated by difference.

<sup>e</sup>Atomic ratio.

Table 2. Thermoplastic properties of B2 and blends with 2 and 5 wt.% of the two wastes.

	$T_s^a$ (°C)	$T_f^b$ (°C)	$T_r^c$ (°C)	$T_r-T_s^d$ (°C)	MF <sup>e</sup> (ddpm)
B2	400	448	490	90	1762
B2+2TC	401	449	488	87	1373
B2+5TC	403	448	487	84	1286
B2+2F	395	449	488	93	1395
B2+5F	395	448	487	92	1366

<sup>a</sup>Softening temperature, defined as the temperature at which the stirrer starts to rotate.

<sup>b</sup>Maximum fluidity temperature.

<sup>c</sup>Resolidification temperature, defined as the temperature at which the stirrer stops.

<sup>d</sup>Plastic range.

<sup>e</sup>Maximum fluidity, expressed as dial division per minute.

Table 3. Parameters derived from thermogravimetric analysis (at 10°C/min) of the industrial coal blends and mixtures with 2 and 5 wt.% additions of tyre crumbs and fibres.

	B1	TC	B1+2TC	B1+5TC	B2	F	B2+2F	B2+5F
VM375 <sup>a</sup> (%)	5.0	34.2	6.8	9.1	5.0	39.5	7.7	10.8
VM400 <sup>a</sup> (%)	7.6	51.9	10.4	13.7	7.8	56.9	11.2	15.7
VM400-500 <sup>a</sup> (%)	43.4	42.3	42.6	42.4	47.2	36.9	46.5	46.0
VM500-750 <sup>a</sup> (%)	41.1	2.4	39.4	36.3	37.0	2.6	35.1	31.7
DTGmax <sub>1</sub> <sup>b</sup> (%/min)			0.315 <sup>e</sup>			4.436 <sup>e</sup>		0.379 <sup>e</sup>
DTGmax <sub>2</sub> <sup>b</sup> (%/min)		4.893 <sup>e</sup>		0.464 <sup>e</sup>		5.236 <sup>e</sup>	0.334 <sup>e</sup>	0.538 <sup>e</sup>
DTGmax <sub>3</sub> <sup>b</sup> (%/min)		4.430 <sup>e</sup>				3.975 <sup>e</sup>		
DTGmax <sub>4</sub> <sup>b</sup> (%/min)	1.718 <sup>e</sup>		1.672 <sup>e</sup>	1.637 <sup>e</sup>	1.931 <sup>e</sup>		1.870 <sup>e</sup>	1.844 <sup>e</sup>
Tmax <sub>1</sub> <sup>c</sup> (°C)			375 <sup>e</sup>			359 <sup>e</sup>		350 <sup>e</sup>
Tmax <sub>2</sub> <sup>c</sup> (°C)		380 <sup>e</sup>		379 <sup>e</sup>		389 <sup>e</sup>	373 <sup>e</sup>	381 <sup>e</sup>
Tmax <sub>3</sub> <sup>c</sup> (°C)		432 <sup>e</sup>				434 <sup>e</sup>		
Tmax <sub>4</sub> <sup>c</sup> (°C)	484 <sup>e</sup>		488 <sup>e</sup>	485 <sup>e</sup>	476 <sup>e</sup>		477 <sup>e</sup>	474 <sup>e</sup>
CY <sup>d</sup> (%)	76.5	34.8	75.7 (75.6 <sup>f</sup> )	74.2 (74.4 <sup>f</sup> )	75.2	28.9	74.3 (74.2 <sup>f</sup> )	72.6 (72.9 <sup>f</sup> )

<sup>a</sup>Volatile matter evolved up to a specific temperature (T) or in a specific temperature range and normalized to 100%.

<sup>b</sup>Rate of maximum volatile matter evolution.

<sup>c</sup>Temperature of maximum volatile matter evolution.

<sup>d</sup>Coke yield at 1000 °C.

<sup>e</sup>Different values of TGA<sub>max</sub> and T<sub>max</sub> for each devolatilization step.

<sup>f</sup>The values in parenthesis were calculated by applying the additivity law.

Table 4. Proximate and ultimate analyses, JIS, CRI and CSR values of cokes studied from the two industrial coal blends and their blends with tyre crumbs (TC) and fibres (F).

Coke	B1	B1+2TC	B1+5TC	B2	B2+2F	B2+5F
Ash (wt.% db <sup>a</sup> )	11.1	12.1	11.7	10.5	10.4	10.5
VM <sup>b</sup> (wt.% db <sup>a</sup> )	1.5	1.6	1.5	1.1	1.3	1.1
C (wt.% daf <sup>c</sup> )	95.3	96.6	95.9	96.8	95.4	96.9
H (wt.% daf <sup>c</sup> )	0.8	0.8	0.7	0.6	0.7	0.6
N (wt.% daf <sup>c</sup> )	2.0	2.0	1.9	1.8	1.9	1.9
S (wt.% daf <sup>c</sup> )	0.58	0.63	0.69	0.65	0.70	0.68
O <sup>d</sup> (wt.% daf <sup>c</sup> )	1.3	0.0	0.8	0.2	1.3	0.0
C/H <sup>e</sup>	9.9	10.1	11.4	13.4	11.4	13.5
JIS	78.8	75.1	67.9	86.3	86.8	73.6
CRI	27	27	30	30	33	35
CSR	59	58	54	55	50	47

<sup>a</sup>Dry basis.

<sup>b</sup>Volatile matter.

<sup>c</sup>dry ash-free basis.

<sup>d</sup>Oxygen content calculated by difference.

<sup>e</sup>Atomic ratio.

Table 5. Ash chemical composition (wt.%) of the cokes as determined by XRF.

Sample	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	I <sub>B</sub> <sup>a</sup> *Ash (%)
B1	0.09	0.08	3.47	6.24	0.10	0.15	0.26	0.19	0.75	1.51
B1+2TC	0.08	0.09	3.52	6.57	0.11	0.16	0.37	0.18	0.70	1.67
B1+5TC	0.10	0.08	3.31	6.11	0.09	0.16	0.28	0.18	0.69	1.63
B2	0.06	0.09	3.10	5.38	0.07	0.18	0.29	0.18	0.87	1.85
B2+2F	0.06	0.09	3.03	5.11	0.07	0.18	0.28	0.16	0.89	1.91
B2+5F	0.07	0.09	3.07	5.34	0.08	0.19	0.27	0.17	1.01	2.05

<sup>a</sup>Basicity index



Table 6. Chemical composition of the cokes (ppm) from coal blends and their blends with 5 wt.% addition of the two tyre wastes as determined by ICP-MS analysis.

Sample	Zn	Mn	V	Ni	Pb	Co	Cu	Sb
B1	2.29	3.93	3.65	1.14	0.69	0.60	1.81	-
B1+5TC	70.65	2.84	2.65	1.71	0.54	1.15	1.56	-
B2	1.62	2.91	2.82	1.63	0.47	0.56	1.56	-
B2+5F	29.84	8.25	3.22	2.21	0.62	1.15	4.29	0.08

Table 7. Textural parameter results of the cokes from coal blends and their blends with 5 wt.% addition of the two tyre wastes.

Sample	B1	B1+5TC	B2	B2+5F
$\rho_{\text{H}_2\text{O}}^{\text{a}}$ (g/cm <sup>3</sup> )	0.796	0.814	0.836	0.793
$\rho_{\text{Hg}}^{\text{b}}$ (g/cm <sup>3</sup> )	1.415	1.415	1.452	1.441
$\rho_{\text{He}}^{\text{c}}$ (g/cm <sup>3</sup> )	1.771	1.759	1.800	1.788
$V_{\text{T}}^{\text{d}}$ (g/cm <sup>3</sup> )	0.550	0.522	0.508	0.566
$V_{<12}^{\text{e}}$ (g/cm <sup>3</sup> )	0.142	0.138	0.133	0.135
$V_{\text{macro}}^{\text{f}}$ (cm <sup>3</sup> /g)	0.086 (61%)	0.088 (63%)	0.082 (62%)	0.084 (62%)
$V_{\text{meso}}^{\text{g}}$ (cm <sup>3</sup> /g)	0.011 (8%)	0.014 (10%)	0.010 (8%)	0.012 (9%)
$\epsilon_{12}^{\text{h}}$ (vol.%)	20.1	19.5	19.3	19.5
$\epsilon_{\text{T}}^{\text{i}}$ (vol.%)	55.1	53.7	53.6	55.6

Values in parenthesis correspond to macro- and mesopores expressed in percentage.

<sup>a</sup>Water apparent density.

<sup>b</sup>Mercury apparent density.

<sup>c</sup>Helium true density.

<sup>d</sup>Total pore volume obtained from  $\rho_{\text{He}}$  to  $\rho_{\text{H}_2\text{O}}$ .

<sup>e</sup>Total pore volume obtained from  $\rho_{\text{He}}$  to  $\rho_{\text{Hg}}$ , corresponding to pores lower than 12  $\mu\text{m}$ .

<sup>f</sup>Macropore volume.

<sup>g</sup>Mesopore volume

<sup>h</sup>Porosity < 12  $\mu\text{m}$ .

<sup>i</sup>Total porosity.

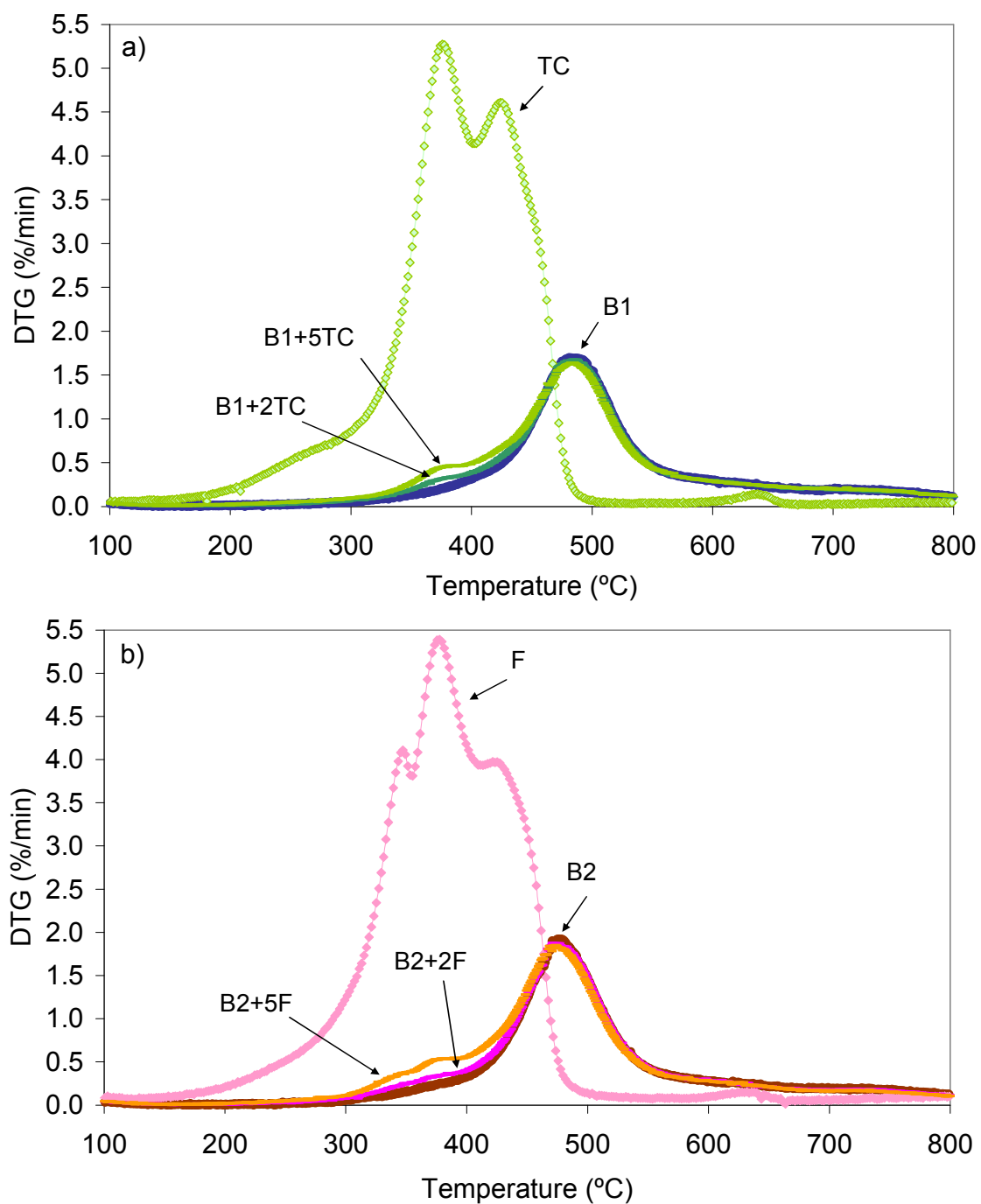


Figure 1. DTG curves corresponding to the industrial coal blends, tyre wastes and their mixtures with 2 and 5 wt.% of the additives (a) B1, tyre crumbs and their mixtures (b) B2, fibres and their mixtures.

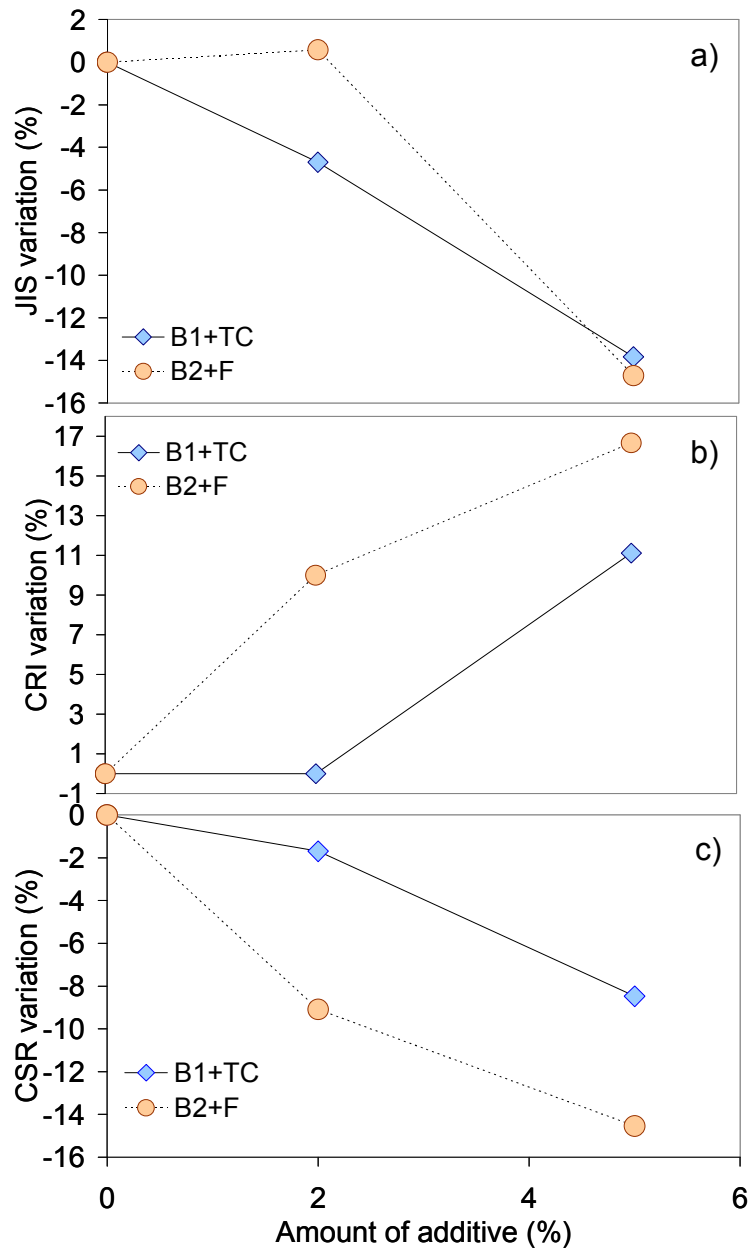


Figure 2. Percent variation of (a) the cold mechanical strength (JIS index), (b) the coke reactivity (CRI index) and (c) the mechanical coke strength post-reaction (CSR index) of the industrial coal blends B1 and B2 due to 2 and 5 wt.% tyre crumb and fibre (TC, F) addition.