Reactivity of biomass containing briquettes for metallurgical coke production

L. Florentino-Madiedo, E. Díaz-Faes, C. Barriocanal*

Instituto Nacional del Carbón, INCAR-CSIC, Francisco Pintado Fe, 26, 33011 Oviedo, Spain.

*Corresponding author: carmenbr@incar.csic.es

Abstract

The reactivity of cokes from 12 briquettes prepared from ternary blends of coal, three biomasses and four binders was evaluated. In order to determine the effect of the binder, 4 briquettes without biomass were also studied. The gasification tests were carried out by thermogravimetric analysis at 900 °C. Two gas-solid models i.e. the Volumetric model and the Grain model were applied to describe the behavior of the cokes. Chars and cokes from the briquette components were also tested to determine the degree of synergy. The two models were able to describe the gasification reaction and the predicted conversion fitted the experimental data very well. Reactivity was also determined by means of a greater scale method and a relationship between the two methods was obtained. The ash composition of the briquette components, the micropore surface area and quantitative optical microscopy were used to explain the gasification results obtained.

Keywords: Biomass; briquettes; reactivity; coke

1. Introduction

One possible solution for mitigating CO₂ emissions in the steel industry is to use biomass in coal blends [1]. This would result in the simultaneous reduction of material costs and neutral carbon emissions from the carbonization process [2–6]. In addition, it would widen the range of materials and technologies available to make this industry more environmentally friendly [7]. Moreover coal/biomass blends produce fewer polyaromatic hydrocarbon emissions than coal [8]. The addition of biomass to a coking blend also decreases the coking pressure during the carbonization process [9]. On the other hand, the direct addition of biomass has a deleterious effect on coke quality [9,10] and on the thermoplastic properties of coal [11]. In recent years however, it has been suggested that the use of briquettes would allow biomass to be added to coking blends without impairing the strength of the resulting bio-coke [12].

Coke is an essential material in the blast furnace because it supports the descending burden, providing a permeable matrix for the slag and metal to pass through on their way down and for hot gases to penetrate on their way up, while generating the gas needed for the reduction of the iron oxides (CO). What is more, coke reactivity is a very important parameter for determining coke quality because of its influence on an effective functioning of the blast furnace.

The inclusion of biomass is also advantageous not only because it is a neutral source of carbon, but also because its effect on coke reactivity may contribute to lowering the reserve zone temperature of the blast furnace, thereby reducing the amount of coke needed to produce a ton of hot metal [13,14].

Reactivity has been shown to be related to a large number of physical and chemical properties. The composition of mineral matter is an important parameter due to the catalytic effect of the active alkaline earth metals in the gasification reaction [6,15–18]. Microporosity also affects reactivity because it enables the access of CO₂ molecules to

the carbon surface [13,19]. In addition, the textural composition which reflects the degree of order of the carbonaceous structure influences reactivity, the highly ordered components, generally being less reactive than the more structurally disordered paracrystalline carbons [20].

Coal rank is an important parameter that controls most of these characteristics [21]. Previous studies have also demonstrated that the gasification reactivity of chars of lower rank coals ($C < 80\%$) is controlled by the catalytic activity of coal minerals. However, the gasification rates of chars from higher rank coals ($C > 80\%$) are controlled by the physicochemical properties of the char [22]. Other authors [23] have also reported that the gasification reactions of biomasses are influenced by the abundance of inherent alkali and alkaline earth metallic species, whereas, in the case of acid-treated biochars, which have a very low mineral matter content, the catalytic effect of alkali and alkaline earth metallic species is insignificant and, in consequence, the reactivity per unit of pore surface area is mainly controlled by the carbon structure.

Most previous studies on coke reactivity have been focused on the measurement of reactivity through weight loss, such as Coke Reactivity Index (CRI) and the United Nations Economic Commission for Europe test modified at the Spanish National Coal Institute (ECE-INCAR), or on the kinetic parameters of the gasification process. However very little attention has been paid to establishing a relationship between these techniques. In addition, most of the previously published results deal with either biomass, coal or biomass/coal blends, whereas in the present work, the reactivity of cokes from briquettes prepared from as many as twelve ternary blends (coal, biomass and binder) and four binary blends (coal and binder) have been evaluated.

The aim of the present study is to identify gasification parameters derived from kinetic studies that might help to define bio-coke reactivity. An exhaustive analysis of the properties of the resultant cokes (i.e. mineral matter, porosity and textural

components) has also been carried out in order to explain the reactivity results obtained.

2. Materials and methods

For the preparation of the briquettes an American low rank bituminous coking coal with a high volatile matter content (ca. 31.5 wt %) and high Gieseler maximum fluidity (ca. 26000 ddpm), four biomasses and four binders were used. The biomasses selected included: pine kraft lignin (Lg), pine sawdust torrefied at 300 °C for 30 minutes (SPT) and a commercial bio-coal derived from hydrothermally treated waste obtained from tree pruning (BIOC). The following binders were used to prepare the briquettes: molasses (Mol), paraffin (Par), coal tar (T) and a 1:1 blend of tar and coal tar sludge (T/CTS). The briquettes were cylindrical in shape with 40 mm in diameter and 35 mm in height. More detailed information about the materials used has been published elsewhere [8,11].

Ternary blends were employed to prepare 12 briquettes containing coal (70 wt%), biomass (15 wt%) and binder (15 wt%), except when molasses acted as binder, in which case the proportions of biomass and binder were 20 wt% and 10 wt% respectively. For comparison purposes four briquettes containing coal and the binders were prepared. The carbonizations were carried out in a horizontal oven, heated up to 1000 °C at a rate of 3 °C/min under a flow of 300 ml/min of N₂, applying a soaking time of 1 h. The nomenclature used included the biomass and type of binder. Thus Br(SPT-T) indicates a briquette prepared with coal, torrefied pine sawdust and tar as binder.

Proximate analyses were performed following the ISO 562 and ISO 1171 standard procedures for volatile matter and ash content, respectively. The elemental analysis was performed with the aid of a LECO CHN-2000 for C, H and N (ASTM D-5773), a LECO S-144 DR for sulfur (ASTM D-5016) and a LECO VTF-900 for the direct determination of oxygen.

2.1. Reactivity of cokes and bio-cokes.

2.1.1. Kinetic parameters of the gasification reaction with CO₂

The reaction rate constants (K) corresponding to the briquettes during CO₂ gasification were calculated using a TA Instruments SDT 2960 thermobalance. The cokes and bio-cokes (around 2 mg of sample with particle size < 63 µm was spread in the form of a thin layer) were placed inside a crucible to undergo isothermal gasification at 900 °C. The samples were heated at 20 °C/min under a N₂ atmosphere until they reached gasification temperature. Once the required temperature was reached the gas was switched over from N₂ to CO₂, and the CO₂ flow rate was set at 100 ml/min. These experimental conditions (i.e. flow of reactant gas and gasification temperature) were selected to ensure chemical regime and to nullify the external diffusion effect of the reactant gas upon the gasification [24].

Two models were employed to describe the reactivity of the chars and cokes: Volumetric Model (VM) and Grain Model (GM). These models have been used extensively in the literature both for coal [25] and for biomass [17,26].

The Volumetric Model assumes a homogeneous reaction throughout the particle and a linearly decreasing reaction surface area with conversion. The overall reaction rate is expressed by:

$$\frac{dX}{dt} = K_{VM}(1 - X) \quad (1)$$

Then, by a simple integration:

$$\int \frac{dX}{(1 - X)} = \int K_{VM} dt \quad \rightarrow \quad -\ln(1 - X) = K_{VM}t \quad (2)$$

The Grain Model assumes that a porous particle consists of an assembly of uniform non-porous grains and that the reaction takes place on the surface of these grains. The GM model applies under the regime of chemical kinetic control, and assuming the grains have a spherical shape, the overall reaction rate is expressed as:

$$\frac{dX}{dt} = K_{GM}(1 - X)^{\frac{2}{3}} \quad (3)$$

This model predicts a monotonically decreasing reaction rate and surface area because the surface area of each grain is receding during the reaction. Again, by simple integration:

$$\int \frac{dX}{(1-X)^{2/3}} = \int K_{GM} dt \quad \rightarrow \quad 3[1 - (1-X)^{1/3}] = K_{GM}t \quad (4)$$

The reaction rate constants K_{VM} and K_{GM} were obtained from the slope of the linearized models. Various stages were considered in the linearization so as to obtain a correlation coefficient higher than 0.9.

The deviation, $Dev(X)$, between the experimentally obtained conversion data and the values predicted by the models was percent-wise measured by means of Eq. (5) [27]

$$Dev X (\%) = \frac{\sqrt{\frac{\sum_{i=1}^n (X_{exp} - X_{calc})^2}{n}}}{X_{exp,max}} \cdot 100 \quad (5)$$

where n is the number of data points considered, X_{exp} and X_{mod} are the experimentally obtained and model-calculated values for conversion, respectively, and $X_{exp,max}$ is the maximum experimental conversion.

In order to evaluate the synergy during the CO_2 gasification of the coke and bio-coke briquettes a theoretical conversion (X_{Cal}) was calculated as follows [28,29]:

$$X_{Cal} = X_{Coal} \cdot F_{Coal} + X_{Biomass} \cdot F_{Biomass} + X_{Binder} \cdot F_{Binder} \quad (6)$$

where X_{Coal} , $X_{Biomass}$ and X_{Binder} are the conversions at time (t) for the coke/chars from the coal, biomass and binder, respectively, and F_{Coal} , $F_{Biomass}$ and F_{Binder} are the mass fractions of coal, biomass and binder in the coke from briquettes.

2.1.2. ECE-INCAR reactivity

The reactivities were measured following the United Nations Economic Commission for Europe test with some modifications incorporated by the Spanish National Coal Institute (ECE-INCAR method) [30]. The reactivity index derived from this test is related

to the parameter CSR which is used worldwide to assess coke reactivity at industrial scale [31]. In this test, 7 g of coke with particle sizes between 1-3 mm are subjected to a CO₂ flow of 120 ml/min at 1000 °C during 1 h. The reactivity is expressed as the mass loss after reaction.

2.2. Characterization of the cokes and bio-cokes

2.2.1. Inorganic matter and pore surface areas

The inorganic matter composition of each sample was analyzed by X-ray fluorescence (XRF) using a SRS 3000 Bruker spectrometer in accordance with the ASTM D4326-04 standard procedure. The presence of minerals in the samples is typically characterized by means of the Alkalinity Index (AI). The AI measures the ratio of basic to acidic oxides in the ashes:

$$\text{Alkalinity index (\%)} = \frac{[\text{Fe}_2\text{O}_3] + [\text{CaO}] + [\text{MgO}] + [\text{K}_2\text{O}] + [\text{Na}_2\text{O}]}{[\text{SiO}_2] + [\text{Al}_2\text{O}_3]} \times \text{Ash (\%)} \quad (7)$$

The basic oxides (CaO, K₂O, Na₂O, MgO and Fe₂O₃) generally act as a catalyst, while acidic oxides (SiO₂ and Al₂O₃) act as an inhibitor [6,17,32].

The pore surface areas were determined using a Micromeritics ASAP2420 instrument from CO₂ adsorption at 273 K and by means of the Dubinin–Radushkevich equation [33]. Coke particles (particle sizes in the range 0.6-1.18 mm) were degasified at 473 K for 18 h, before analysis. CO₂ adsorption is used to determine ultramicroporosity (i.e. pore size <0.7 nm)

2.2.2. Textural components as determined by optical microscopy

Samples with a particle size of 0.6–1.18 mm were mounted in resin for optical microscopy examination. The samples were then smoothed using silicon-carbide papers after which they were polished with fine alumina. To assess coke textural composition, the polished surfaces were examined using a polarising microscope fitted with crossed polars and a full-wave retarder plate. Their optical appearance at 250

points on the coke polished surfaces was evaluated using the classification developed by Patrick [34]. The coke textural components were divided into flow type, three sizes of mosaics and isotropic components. Two sizes of organic inerts were also differentiated. The effects of different additives on the type, as well as on the amount, of anisotropy were determined from the Optical Anisotropy Index (OAI) by means of equation (7) [34]:

$$OAI = 4 \cdot \text{Flow} + 3 \cdot \text{Coarse Mosaic} + 2 \cdot \text{Medium Mosaic} + \text{Fine Mosaic} \quad (8)$$

3. Results and Discussion

3.1. Main characteristics of the raw materials

Table 1 shows the main characteristics of the raw materials used. Lignin has the highest C content (64.7 wt.%db) of biomasses, whereas molasses has the least (26.5 wt.%db). The O/C atomic ratio of the tar, CTS and paraffin is lower than that of molasses. The coal has the highest ash content (7.3 wt.% db) followed by BIOC (6.1 wt.% db). Sawdust, tar and paraffin have ash contents lower than 1 wt% db. The volatile matter contents are all higher than 64 wt% db except in the case of coal.

Table 1. Proximate and ultimate analyses of the raw materials.

	Coal	BIOC	Lignin	SPT	Molasses	Tar	CTS	Paraffin
Ash (wt.% db) ^a	7.3	6.1	2.5	0.4	2.8	0.2	1.7	0.2
VM (wt.% db) ^{a,b}	31.5	68.0	64.0	78.5	94.4	65.5	71.1	99.6
C (wt.% db) ^a	81.2	59.8	64.7	56.0	26.5	90.3	85.9	85.1
H (wt.% db) ^a	5.0	6.0	5.7	5.8	8.1	4.7	4.9	14.5
N (wt.% db) ^a	1.6	1.2	0.9	0.4	1.7	0.8	1.4	0.2
S (wt.% db) ^a	1.03	0.15	1.52	0.03	0.18	0.38	0.54	0.04
O (wt.% db) ^a	4.8	25.5	26.3	37.4	55.9	3.0	6.6	0.3
H/C ^c	0.74	1.20	1.07	1.25	3.65	0.62	0.69	2.04
O/C ^c	0.04	0.32	0.31	0.50	1.58	0.02	0.06	0.00

^aDry basis; ^bVolatile matter; ^cAtomic ratio.

3.2. Reactivity of cokes and bio-cokes

3.2.1. Reactivity as described by K_{VM} , K_{GM} and an evaluation of the synergy between the briquette components during the gasification process

Figure 1 shows the application of the models VM (1a, 1b) and GM (1c, 1d) to the experimental results of the gasification of the chars obtained from the biomasses (lignin, BIOC, SPT), the binders (molasses, tar, CTS) and the coal. The reaction rate constants (K_{VM} and K_{GM}) calculated from the slope of the linearized models are shown in Table 2 together with the correlation coefficient (r^2) corresponding to the rate constant determination. BIOC and SPT have a rate constant in the range between 2 and $4 \times 10^{-3} \text{ s}^{-1}$, which are similar values to those obtained by Jeong [28]. In the case of the lignin and molasses the rate constants are almost one order of magnitude higher. In contrast, the binders T and T/CTS and the coal have considerably smaller rate constant values ($10^{-4} - 10^{-5}$).

The rate constant values (Table 2) were used to calculate the modelled conversion. The comparison between the experimental conversion values and those predicted by the VM and GM models for the biomases (BIOC, lignin and SPT) and binders (Molasses, Tar and T/CTS) (Figure 1e and 1f) confirm that the predicted values fit the experimental values very well over the entire conversion range. In order to quantify the errors associated with the calculated conversion using the two models the value of $\text{Dev}(X)$ was calculated using Eq (5) and displayed in Table 2 for briquette components. The deviation between the experimental and calculated conversion values is very small (i.e. $< 1.3 \%$) which validates the procedure used for the determination of the rate constants.

Figure 1. Plots of the VM (a-b) and GM (c-d) linearized models for CO₂ gasification and a comparison between the experimental conversions and those predicted by the VM and GM models versus time for the biomasses (lignin, BIOC, SPT) (e) and binders (molasses, tar, CTS) (f).

Table 2. Reaction rate constants for the CO₂ gasification of the coal, the three biomasses (Lignin, BIOC, SPT) and the three binders (Molasses, Tar, CTS), correlation coefficient of the linearization and Dev(X) calculated using the Volumetric Model (K_{VM}) and Grain Model (K_{GM}).

	K _{VM} (s ⁻¹)	r ² _{VM}	Dev _{VM} (X) (%)	K _{GM} (s ⁻¹)	r ² _{GM}	Dev _{GM} (X) (%)
Coal	6.80E-05	0.995	0.51	5.34E-05	0.996	0.74
Lignin	8.41E-03	0.996	0.81	1.27E-02	0.996	0.60
BIOC	4.21E-03	0.989	1.60	3.14E-03	0.997	1.29
SPT	3.05E-03	0.992	0.82	2.16E-03	0.995	0.56
Molasses	3.37E-02	0.991	0.81	2.39E-02	0.995	0.59
Tar	5.11E-04	0.993	1.11	3.80E-04	0.998	0.71
CTS	1.11E-04	0.996	0.83	8.74E-05	0.998	1.73

On the basis of the rate constant values the following order of reactivity for the biomasses can be established: lignin > BIOC > SPT, the times needed for them to achieve a conversion value of 0.8 being 3.15, 6.45 and 11.85 minutes respectively. Lignin has been described as highly reactive due to its mineral matter content [17]. The gasification time recorded in the present research work is in agreement with results found in the literature. Huo et al. reported gasification times below 5 min to achieve 50 % conversion at 900 °C for sawdust and straw [24].

The order of reactivity for the binders is as follows: Mol > T > CTS. The behaviour of the three binders used is completely different. Molasses needed only 1.1 min to attain a conversion value of 0.8, whereas, T and CTS, due to their aromatic nature are less reactive and they needed 56 and 235 min to reach a 0.8 conversion, respectively. These values are in agreement with the values of K_{VM} and K_{GM} shown in Table 2. It was impossible to test the char from paraffin because it does not leave any residue when pyrolyzed. The coke from the coal is the least reactive material considering the time needed to achieve a conversion of 0.8 (452 min) and the value of the rate constants.

Table 3 shows the K_{VM} and K_{GM} corresponding to the briquettes and the correlation coefficient corresponding to each linearization. The values are all in the range of $7 \times 10^{-5} - 4 \times 10^{-4} \text{ s}^{-1}$. The plots of the linearized models used to calculate these values are shown in Figure SM1. Figure 2 displays the gasification curves (i.e. X vs t) corresponding to all the briquettes grouped by binder. The conversion curves predicted by the models used are also included in each graph. The gasification of the briquettes with Par (Figure 2a), T (Figure 2b) and T/CTS (Figure 2c) occur within similar time ranges despite the differences observed in the gasification curves of the binders (Figure 1f). The least reactive are those prepared only with coal and the binder i.e. Br(Par), Br(T), Br(T/CTS) and Br(Mol). In the case of the briquettes prepared from ternary blends, reactivity depends on the type of binder used. In the case of paraffin and tar the order of reactivity is as follows $Lg > BIOC > SPT$ in agreement with the behaviour of the biomasses (Figure 1e). In the case of the binder T/CTS the order is $BIOC > SPT > Lg$. The briquettes prepared with molasses show a very high reactivity due to the effect of the binder that masks the effect of the biomasses (Figure 2d).

To quantify the errors associated with the conversion from the two models the value of $Dev(X)$ was calculated using Eq (5) and displayed in Table 3 for briquettes from ternary blends. The deviation between the experimental and calculated conversion values is very small (i.e. $< 3.2 \%$) which validates the procedure used for the determination of the rate constants. The error is greater than for binary blends (Table 2) but similar to values of $Dev(X)$ published by other authors [27].

In order to test for synergy between the three components of the cokes from the briquettes during their gasification, the additivity law as expressed by Eq. 6 was applied to the experimental data corresponding to the individual components. Figure 3 compares the variations of the experimental and calculated conversions with time, the curves being grouped in the graphs according to the binder. It is clear that the experimental curves differ from the calculated ones, which indicates that there is synergy between the coke components. Also, the calculated conversion is lower than

the experimental one for the same time. Which means that synergy between the briquette components leads to an increase in reactivity in all cases (Figure 3a, 3b, 3c y 3d) especially in the case of molasses.

Table 3. Reaction rate constant for the CO₂ gasification of briquettes calculated using the Volumetric Model (K_{VM}) and Grain Model (K_{GM}), Dev(X), ECE-INCAR reactivity (RECE-INCAR) and CO₂ surface area.

	K _{VM} (s ⁻¹)	r ² _{VM}	Dev _{VM} (X) (%)	K _{GM} (s ⁻¹)	r ² _{GM}	Dev _{GM} (X) (%)	RCEE (%)	S _{mi} (m ² /g)
Br(Lg-Par)	2.49E-04	0.992	0.73	1.67E-04	0.996	2.14	30.2	55
Br(BIOC-Par)	1.56E-04	1.000	0.78	1.24E-04	0.998	0.69	26.6	57
Br(SPT-Par)	7.90E-05	0.998	1.09	6.80E-05	0.995	2.92	20.6	14
Br(Par)	8.84E-05	0.996	1.35	6.83E-05	0.994	0.83	13.5	5
Br(Lg-T)	1.69E-04	0.988	2.95	1.34E-04	1.000	0.54	25.5	38
Br(BIOC-T)	1.47E-04	0.997	2.03	1.15E-04	0.994	1.88	27.3	34
Br(SPT-T)	1.19E-04	0.999	1.24	9.23E-05	0.983	3.16	25.3	32
Br(T)	8.44E-05	0.993	0.79	6.93E-05	1.000	0.53	13.3	17
Br(Lg-T/CTS)	1.00E-04	0.993	0.38	8.39E-05	0.987	1.03	25.3	56
Br(BIOC-T/CTS)	1.71E-04	0.993	2.47	1.35E-04	0.998	1.11	31.3	80
Br(SPT-T/CTS)	1.51E-04	0.997	1.15	1.22E-04	0.995	0.76	24.9	19
Br(T/CTS)	8.56E-05	0.993	0.37	7.24E-05	0.991	0.90	12.1	3
Br(Lg-Mol)	4.41E-04	0.997	1.72	3.47E-04	0.995	1.99	38.8	25
Br(BIOC-Mol)	3.57E-04	0.998	1.68	2.77E-04	0.992	2.26	39.3	95
Br(SPT-Mol)	4.03E-04	0.997	0.88	3.29E-04	0.995	0.85	40.8	77
Br(Mol)	2.34E-04	1.000	0.64	1.83E-04	0.987	3.10	32.2	36

308

310

311 Figure 2. Comparison between the experimental conversions and those predicted by
 312 the VM and GM models versus time for the: briquettes with paraffin (a), briquettes with
 313 molasses (b), briquettes with T/CTS (c) and briquettes with T (d).

314 The synergy was evaluated using a synergy index [29,35] defined as the ratio
 315 $t_{X,cal}/t_{X,exp}$ where $t_{X,cal}$ and $t_{X,exp}$ denote the experimental and calculated gasification time
 316 required to obtain a co-gasification conversion of X , respectively. A synergy index
 317 greater and smaller than 1 expresses the existence of synergistic effect on co-
 318 gasification at conversion value of X , and the greater or smaller the index value, the
 319 greater or smaller the synergistic effect. Figure 4 shows the variations in the synergy
 320 index at different conversions. The synergy during co-gasification between coal and the
 321 non-biomass binders (i.e. T, T/CTS and Par) is almost constant over the whole
 322 conversion range (Figure 4a). The synergy observed for the briquette prepared with
 323 paraffin i.e. Br (Par) is probably caused by the pyrolysis process since the paraffin does

not leave any char. On the other hand, the biomass binder (Mol) clearly shows that the synergy increases with the degree of conversion. Similar results were obtained in the case of the briquettes prepared from ternary blends. With the increase in conversion, the synergy index also increases. In the case of the briquettes prepared with BIOC and the four binders (Figure 4b) it is clear that synergy index is greater than that of the briquettes prepared from the binary blends (i.e. coal and binders) with the highest synergy when molasses is used as binder.

Figures 4c and 4d display the synergy index corresponding to briquettes prepared with the three biomasses and the same binder, Par and T/CTS respectively. Differences dependent on the type of binder used are apparent. It is also clear that the lowest degree of synergy corresponds to the briquettes prepared only with coal and a binder. When paraffin is used as binder the order in which synergy increases coincides with the degree of reactivity for $X > 0.3$, as shown in Figure 1. The higher the reactivity of the biomass present in the briquettes is, then the higher the synergy index is. On the other hand, when T/CTS is used as binder, BIOC and the torrefied sawdust (SPT) have similar synergy index values up to $X = 0.6$, after which the synergy index of Br(BIO-T/CTS) increases with conversion. However, it is the variation in the synergy index corresponding to the briquette Br(Lg-T/CTS) which is most surprising because it is lower than that of the other ternary briquettes prepared with T/CTS as binder. For low conversion values (i.e. $X < 0.15$) the effect of biomass on the reactivity of the briquettes is lower than expected and negative synergy is observed, which is in agreement with other authors [29].

Figure 3. Comparison between the experimental and calculated curves following the additive rule from those of the individual components. Briquettes with paraffin (a), briquettes with tar (b), briquettes with T/CTS (1:1) (c), briquettes with molasses (d).

355 Figure 4. Variation of synergy index with conversion. Briquettes from binary blends a);
356 briquettes from ternary blends containing BIOC and the four binders b); briquettes
357 prepared with paraffin as binder c) and briquettes prepared with T/CTS as binder.

3.2.2. ECE-INCAR reactivity

Table 3 displays the reactivity values as determined by means of the ECE-INCAR (RECE-INCAR) method. The data corresponding to the cokes from the briquettes prepared from binary blends (i.e. coal and binder) are similar (i.e. 12.2-13.5 %) when T, T/ CTS and Par are used. These values are in consonance with metallurgical coke reactivities measured by means of this technique [36]. The results obtained in the thermobalance also show similar values for these cokes. However, the coke from the blend with molasses exhibits a substantially higher reactivity value (32.2%). Similarly, the cokes from the ternary blends including molasses also show high reactivity values (i.e. 39.3-40.8 %), whereas the rest of the cokes from ternary blend briquettes display lower values in the 20.6-31.3 % range.

In general, the reactivity values obtained are similar regardless of the biomass used when T and T/CTS (i.e. 25-31 %) and molasses (i.e. 39-41 %) are used as binders. In the case of paraffin, the reactivity order coincides with the order established for biomasses (see **Figure 1**). Interestingly the cokes from blends of lignin and bituminous binders do not have higher reactivity values, which one would expect considering the high reactivity of lignin.

The reactivity of the bio-cokes from the briquettes studied in the thermobalance and using the ECE-INCAR method show the influence of both the biomass and the binder on the results obtained. The rate constants calculated by the Volumetric and Grain models show a logarithmic relationship with the reactivity ECE-INCAR (**Figure 5**), with the same correlation coefficient for the two models ($r^2 = 0.88$).

387

388

389 Figure 5. Relationship between ECE-INCAR reactivity and the constant rates (K_{GM} and
390 K_{VM}).

391 3.3. Characterization of cokes and bio-cokes

392 3.3.1. Quantitative analysis of mineral oxides in the coke ashes

393 Mineral composition is related with coke reactivity in many ways, e.g., minerals at
394 high temperatures can generate cracks and weak spots in the coke matrix [37], as well
395 as increase coke reactivity via the formation of an intermediate metal-carbon-oxygen
396 complex which leads to a faster conversion from CO_2 to CO [18]. In the present study
397 the inorganic matter composition of each sample and the resultant alkalinity indices are
398 shown in Table 4. Paraffin and coal tar are not included due to their low ash content.
399 Although coal has the highest ash content (Table 1) its alkalinity index is not high
400 compared to that of lignin and molasses. This is due to the presence of Al_2O_3 and SiO_2
401 in coal ashes [3,37,38]. SPT and CTS have the lowest alkalinity index value, 0.32 and

0.35, respectively, which is due to the low ash content in the case of SPT and to its composition in the case of CTS. It should be noted that SPT has the second highest K₂O content only after molasses. BIOC has an alkalinity index of ≈ 8 which is due to its ash content (i.e. 6.1 wt.% db) and its percentage of basic oxides in general is lower than in lignin and SPT except for CaO and Fe₂O₃. Lignin and molasses have the highest alkalinity index as a consequence of their high Na₂O and K₂O contents respectively. It is believed that the highest catalytic effect is produced by potassium followed by calcium, sodium and magnesium [18]. Moreover, lignin has the lowest Al₂O₃ and SiO₂ contents.

Table 4. Ash composition and alkalinity index of the raw materials.

	Coal	BIOC	Lignin	SPT	Molasses	CTS
Na ₂ O (wt%, db)	0.58	1.90	38.45	1.38	18.30	1.90
MgO (wt%, db)	0.68	2.10	1.04	10.71	0.67	1.00
Al ₂ O ₃ (wt%, db)	25.05	5.73	1.20	4.67	1.10	29.20
SiO ₂ (wt%, db)	59.90	28.55	2.98	27.51	7.98	49.20
P ₂ O ₅ (wt%, db)	0.00	15.10	0.00	2.52	0.24	0.97
K ₂ O (wt%, db)	2.08	2.74	4.72	14.00	50.73	1.72
CaO (wt%, db)	1.47	34.67	0.96	23.08	10.30	2.88
TiO ₂ (wt%, db)	2.09	0.37	0.21	0.11	< 0.01	1.67
Fe ₂ O ₃ (wt%, db)	6.79	3.99	0.28	1.33	0.25	6.85
SO ₃ (wt%, db)	1.31	4.43	50.00	4.29	6.72	2.13
MnO (wt%, db)	0.00	0.09	0.00	0.00	0.07	0.07
ZnO (wt%, db)	0.02	0.15	0.03	0.00	0.06	1.23
SrO (wt%, db)	0.13	0.11	0.02	0.00	0.03	0.13
V ₂ O ₅ (wt%, db)	0.00	0.08	< 0.01	0.00	0.10	0.00
Cr ₂ O ₃ (wt%, db)	0.00	0.00	< 0.02	0.00	0.04	0.00
NiO (wt%, db)	0.00	0.00	< 0.03	0.00	< 0.01	0.00
ZrO ₂ (wt%, db)	0.07	0.00	< 0.04	0.00	0.08	0.07
PbO (wt%, db)	0.00	0.00	< 0.05	0.00	0.45	0.00
As ₂ O ₃ (wt%, db)	0.00	0.00	< 0.06	0.00	0.08	0.00
Cl (wt%, db)	0.00	0.00	3.49	0.00	< 0.01	0.00
Alkalinity Index	0.99	8.02	26.96	0.35	24.57	0.32

The alkalinity index for biomasses in this study is as follows:
Lg > (26.96%) > BIOC (8.02%) > SPT (0.35%). The order is the same as that established for the rate constants K_{VM} and K_{GM} in section 3.2.1. In the case of the binders the alkalinity index is higher for molasses (24.57 %) than for T/CTS (0.32%), the high rate constant associated with the gasification of molasses being due to its alkalinity index.

In the case of the briquettes (Table 3), high reactivities are associated with high alkalinity indices. However, the correlation coefficients are low ($r^2 = 0.52, 0.55$ y 0.47 for K_{VM} , K_{GM} y RECE-INCAR respectively).

In view of the results shown in section 3.2.1 some kind of synergy could be expected between the inorganic compounds present in briquette components. Other authors have reported that the variations in synergy during the co-gasification of rice straw-bituminous coal blends are mainly due to the combined effects of active K and Ca transformation during co-gasification [29]. In our case the percentages of Ca and K were similar for BIOC and SPT whereas lignin contained smaller amounts of these two elements. Although the explanation for the low reactivity of the briquette Br(Lg-T/CTS) (see Figure 2c) might be probably the amount of Ca and K present in lignin, further research is needed to satisfactorily explain the interaction between the lignin and the binder T/CTS.

Gasification of coke is influenced by mineral matter composition but other structural factors associated to coal rank are also important [22]. The thermoplastic properties of coal have a strong influence on the structure of the resulting cokes [39]. Depending on the effect on coal plastic properties, the materials used for the preparation of the briquette in the present research work can be divided into two groups: on the one hand biomass (lg, BIOC, SPT and Mol) that has a deleterious effect on the thermoplastic properties and on the other T, T/CTS and Par that enhance these properties. T and

CTS have a high degree of aromaticity and increase the fluidity of the blends, thereby compensating for the effect of the biomass [8,11]. The influence of paraffin on coal thermoplastic properties is lower than that of bituminous binders [11]. This is in agreement with the fact that although Par and T can be considered to be ashless, in the first case, gasification is governed by the mineral matter of the biomass present in the briquettes, whereas in the case of the blends with T and T/CTS the mineral matter of the biomass is not as determinant.

3.3.2. Micropore surface areas

It is generally accepted that the greater the porosity of the coke, the greater its reactivity [13,40]. The micropore surface area values (S_{mi}) of the cokes prepared from the briquettes are presented in Table 3. The lowest values correspond to cokes from briquettes without biomass i.e. Br(T/CTS), Br(Par) and Br(T). The S_{mi} obtained in these cases are similar to the values presented in the literature for metallurgical cokes with a RECE-INCAR lower than 14 % [36]. In general, the S_{mi} of the cokes from the ternary blend briquettes is higher than that of the binary briquettes because biomass produces chars with a greater S_{mi} than coal [3,41].

The results of the present research work are in agreement with the generally accepted view that relates a high S_{mi} with high reactivity, but the correlations obtained in this study are poor $r^2 = 0.56$ for RECE-INCAR and $r^2 = 0.26-0.27$ in the case of the rate constants.

3.3.3. Textural composition of the cokes as measured by optical microscopy

The textural components present in cokes are considered to play a relevant role to explain coke reactivity [21]. It is recognized that carbons and graphites differ in their reactivity according to their degree of structural order, highly ordered graphite generally being less reactive than the more structurally disordered paracrystalline carbons. The degree of structural order is reflected in the optical anisotropy of the coke [20].

Table 5 shows the optical textural composition of the cokes obtained from binary briquettes (i.e. coal + binder) and from ternary briquettes prepared with BIOC as biomass and the four binders and the cokes obtained with the three biomasses and T/CTS as binder.

The cokes obtained from briquettes prepared with coal and the four binders have a similar textural composition except in the case of the coke from Br(Mol) whose percentage of isotropic components is greater than that of the rest (21 vol% vs 2-6 vol%). Molasses influences the plastic stage of the coal due to its high oxygen content which increases the reactivity of the system, giving rise to a shorter plastic range that impedes the complete development of anisotropy [42,43]. The distribution of textural components in the other three cokes is similar, the only difference being the low percentage of coarse mosaics in the coke from Br(Par) (i.e. 17 vol%) vs that of the cokes from Br(T) and Br(T/CTS) (i.e. 25 vol%). The larger amount of coarse mosaics is consistent with the fact that blends with T and T/CTS exhibit the highest Gieseler fluidity [11,44].

Table 5. Textural composition (vol.%) of the cokes.

Sample	F ^a	CM ^b	MM ^c	FM ^d	Iso ^e	InS ^f	InL ^g	OAI ^h
Br(T)	15	25	28	12	3	8	9	246
Br(T/CTS)	17	25	30	11	2	5	10	251
Br(Mol)	8	15	22	14	21	6	13	169
Br(Par)	19	17	30	14	6	6	9	234
Br(BIOC-T)	6	9	23	17	10	11	24	175
Br(BIOC-T/CTS)	8	10	18	18	13	10	24	171
Br(BIOC-Mol)	2	4	16	19	18	10	31	120
Br(BIOC-Par)	6	10	15	20	15	7	27	159
Br(Lg-T/CTS)	11	12	19	17	21	6	13	169
Br(SPT-T/CTS)	10	13	18	14	15	5	26	186

a: flow type anisotropy, b: coarse mosaic, c: medium mosaic, d: fine mosaic, e: isotropic, f: small inert, g: large inert, h: optical anisotropy index.

485

486 In the case of cokes obtained from ternary blends (i.e. coal, BIOC and the binders),
487 again the greatest difference corresponds to the briquette prepared with molasses
488 which has the greatest amount of isotropic material and large inerts. The inclusion of
489 biomass leads to a diminution of the amount of coarse and medium mosaics. There is
490 also a decrease in fine mosaics which is related to a modification of the coal plastic
491 stage [45]. As a consequence, the optical anisotropy index changes from values in the
492 range between 169-250 to 120-175 for the cokes from the briquettes with
493 coal/BIOC/binder. In addition, the isotropic material increases due to the deleterious
494 effect of the biomass upon the fluidity of the coals [5]. It should be noted that these
495 isotropic textures are more susceptible to attack by CO₂ than anisotropic areas.

496 In order to appreciate the influence of the biomass type on the texture of the bio-
497 cokes it is necessary to compare cokes from Br(SPT-T/CTS), Br(BIOC-T/CTS) and
498 Br(Lg-T/CTS). The effect of SPT and BIOC is similar and the effect is clearly seen in
499 the increase in isotropic material and organic inerts. The behaviour of lignin is,
500 however, different, there being a larger percentage of isotropic material but a lower
501 percentage of organic inerts. This is due to the ability of lignin to melt and form an
502 amorphous carbon phase that links coal grains [46]. The thermoplastic properties of
503 these biomasses have been evaluated in a previous research study where it was
504 shown that lignin passes through a plastic stage accompanied by a marked reduction
505 in complex viscosity, unlike SPT and BIOC [11].

506 The linear relationships between the RECE-INCAR and the percentages of
507 textural components show that the components that are related to a decrease in
508 reactivity are flow type ($r^2 = 0.89$) > coarse mosaics ($r^2 = 0.78$) > medium mosaics
509 ($r^2 = 0.69$). In contrast, fine mosaics, isotropic and inerts increase reactivity in the
510 following order: Iso ($r^2 = 0.69$) > InL ($r^2 = 0.58$) > FM ($r^2 = 0.54$) > InS ($r^2 = 0.31$). In
511 agreement with other authors small inerts do not appear to have a great influence on
512 reactivity [44,47]. **Figure 6** shows the relationship between the flow type components

and optical anisotropy index (OAI) with RECE-INCAR. OAI which gives an indication of the degree of order of the coke structure shows the best correlation with reactivity ($r^2=0.93$)

The relationship of the rate constants with OAI follow the same trend although the correlation coefficients obtained are poorer ($r^2 = 0.59-0.65$).

Figure 6. Relationship between ECE-INCAR reactivity with a) Flow type anisotropy and b) Optical Anisotropy Index (OAI).

4. Conclusions

- The order of reactivity can be established as follows: lignin > BIOC > SPT for biomasses and Mol > T > T/CTS for binders.
- The K_{VM} and K_{GM} obtained from gasification experiments show a logarithmic relationship with reactivity measured a greater scale (i.e. RECE-INCAR).
- The least reactive coke obtained from a ternary briquette corresponds to Br(SPT-Par) in agreement with the reactivity of the components. In the case of lignin, the lowest reactivities were obtained with bituminous binders probably due to its ability to soften during heating and the lower synergy index. On the other hand, molasses produces cokes with the greatest reactivity.
- Optical anisotropy index is the parameter which best explains the reactivity results.

Acknowledgements

The research leading to these results has received funding from the European Union's Research Fund for Coal and Steel (RFCS) research program under grant agreements No. [RFCR-CT-2014-00006].

References

- [1] R. Wei, L. Zhang, D. Cang, J. Li, X. Li, C.C. Xu, Current status and potential of biomass utilization in ferrous metallurgical industry, *Renew. Sustain. Energy Rev.* 68, Part 1 (2017) 511–524. doi:10.1016/j.rser.2016.10.013.
- [2] E. Beagle, Y. Wang, D. Bell, E. Belmont, Co-gasification of pine and oak biochar with sub-bituminous coal in carbon dioxide, *Bioresour. Technol.* 251 (2018) 31–39. doi:10.1016/j.biortech.2017.12.027.
- [3] M. Castro-Díaz, C.N. Uguna, L. Florentino, E. Díaz-Faes, L.A. Stevens, C. Barriocanal, C.E. Snape, Evaluation of hydrochars from lignin hydrous pyrolysis to produce biocokes after carbonization, *J. Anal. Appl. Pyrolysis.* 124 (2017) 742–751. doi:10.1016/j.jaap.2016.11.010.
- [4] C. Di Blasi, Combustion and gasification rates of lignocellulosic chars, *Prog. Energy Combust. Sci.* 35 (2009) 121–140. doi:10.1016/j.pecs.2008.08.001.
- [5] M.G. Montiano, E. Díaz-Faes, C. Barriocanal, R. Alvarez, Influence of biomass on metallurgical coke quality, *Fuel.* 116 (2014) 175–182. doi:10.1016/j.fuel.2013.07.070.
- [6] K.W. Ng, J.A. MacPhee, L. Giroux, T. Todoschuk, Reactivity of bio-coke with CO₂, *Fuel Process. Technol.* 92 (2011) 801–804. doi:10.1016/j.fuproc.2010.08.005.

- [7] E. Mousa, C. Wang, J. Riesbeck, M. Larsson, Biomass applications in iron and steel industry: An overview of challenges and opportunities, *Renew. Sustain. Energy Rev.* 65 (2016) 1247–1266. doi:10.1016/j.rser.2016.07.061.
- [8] L. Florentino-Madiedo, E. Díaz-Faes, R. García, C. Barriocanal, Influence of binder type on greenhouse gases and PAHs from the pyrolysis of biomass briquettes, *Fuel Process. Technol.* 171 (2018) 330–338. doi:10.1016/j.fuproc.2017.11.029.
- [9] L. Florentino-Madiedo, D. Casal, E. Díaz-Faes, C. Barriocanal, Effect of sawdust addition on coking pressure produced by two low vol bituminous coals, *J. Anal. Appl. Pyrolysis.* 127 (2017) 369–376. doi:10.1016/j.jaap.2017.07.013.
- [10] H. Suopajarvi, E. Dahl, A. Kemppainen, S. Gornostayev, A. Koskela, T. Fabritius, Effect of Charcoal and Kraft-Lignin Addition on Coke Compression Strength and Reactivity, *Energies.* 10 (2017) 1850. doi:10.3390/en10111850.
- [11] L. Florentino-Madiedo, E. Díaz-Faes, C. Barriocanal, M. Castro-Díaz, C.E. Snape, Importance of Biomass and Binder Selection for Coking Briquette Preparation. Their Effect on Coal Thermoplastic Properties, *Energy Fuels.* (2018). doi:10.1021/acs.energyfuels.8b02555.
- [12] M.G. Montiano, E. Díaz-Faes, C. Barriocanal, Partial briquetting vs direct addition of biomass in coking blends, *Fuel.* 137 (2014) 313–320. doi:10.1016/j.fuel.2014.08.012.
- [13] A. Babich, D. Senk, H.W. Gudenau, Effect of coke reactivity and nut coke on blast furnace operation, *Ironmak. Steelmak.* 36 (2009) 222–229. doi:10.1179/174328108X378242.
- [14] S. Nomura, H. Ayukawa, H. Kitaguchi, T. Tahara, S. Matsuzaki, M. Naito, S. Koizumi, Y. Ogata, T. Nakayama, T. Abe, Improvement in Blast Furnace Reaction Efficiency through the Use of Highly Reactive Calcium Rich Coke, *ISIJ Int.* 45 (2005) 316–324. doi:10.2355/isijinternational.45.316.
- [15] A.M. Fernández, C. Barriocanal, S. Gupta, D. French, Effect of blending carbon-bearing waste with coal on mineralogy and reactivity of cokes, *Energy Fuels.* 28 (2014) 291–298. doi:10.1021/ef401268f.
- [16] M. Grigore, R. Sakurovs, D. French, V. Sahajwalla, Influence of mineral matter on coke reactivity with carbon dioxide, *ISIJ Int.* 46 (2006) 503–512. doi:10.2355/isijinternational.46.503.
- [17] A. Gupta, S.K. Thengane, S. Mahajani, CO₂ gasification of char from lignocellulosic garden waste: Experimental and kinetic study, *Bioresour. Technol.* 263 (2018) 180–191. doi:10.1016/j.biortech.2018.04.097.
- [18] N. Sadhwani, S. Adhikari, M.R. Eden, Z. Wang, R. Baker, Southern pines char gasification with CO₂—Kinetics and effect of alkali and alkaline earth metals, *Fuel Process. Technol.* 150 (2016) 64–70. doi:10.1016/j.fuproc.2016.04.037.
- [19] M. Grigore, R. Sakurovs, D. French, V. Sahajwalla, Coke gasification: The influence and behavior of inherent catalytic mineral matter, *Energy Fuels.* 23 (2009) 2075–2085. doi:10.1021/ef8006728.
- [20] J.W. Patrick, H.C. Wilkinson, Coke reactivity, *Coke Oven Manag. Yearb.* (1981) 191–220.
- [21] M.A. Díez, R. Alvarez, C. Barriocanal, Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking, *Vol. 50.* 50 (2002) 389–412. doi:10.1016/S0166-5162(02)00123-4.
- [22] K. Miura, K. Hashimoto, P.L. Silveston, Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity, *Fuel.* 68 (1989) 1461–1475. doi:10.1016/0016-2361(89)90046-X.
- [23] H. Wu, K. Yip, F. Tian, Z. Xie, C.-Z. Li, Evolution of Char Structure during the Steam Gasification of Biochars Produced from the Pyrolysis of Various Mallee Biomass Components, *Ind. Eng. Chem. Res.* 48 (2009) 10431–10438. doi:10.1021/ie901025d.
- [24] W. Huo, Z. Zhou, X. Chen, Z. Dai, G. Yu, Study on CO₂ gasification reactivity and physical characteristics of biomass, petroleum coke and coal chars, *Bioresour. Technol.* 159 (2014) 143–149. doi:10.1016/j.biortech.2014.02.117.

- [25] M.F. Irfan, M.R. Usman, K. Kusakabe, Coal gasification in CO₂ atmosphere and its kinetics since 1948: A brief review, *Energy*. 36 (2011) 12–40. doi:10.1016/j.energy.2010.10.034.
- [26] K. Jayaraman, I. Gokalp, S. Petrus, V. Belandria, S. Bostyn, Energy recovery analysis from sugar cane bagasse pyrolysis and gasification using thermogravimetry, mass spectrometry and kinetic models, *J. Anal. Appl. Pyrolysis*. 132 (2018) 225–236. doi:10.1016/j.jaap.2018.02.003.
- [27] M.P. González-Vázquez, R. García, M.V. Gil, C. Pevida, F. Rubiera, Unconventional biomass fuels for steam gasification: Kinetic analysis and effect of ash composition on reactivity, *Energy*. 155 (2018) 426–437. doi:10.1016/j.energy.2018.04.188.
- [28] H.J. Jeong, S.S. Park, J. Hwang, Co-gasification of coal–biomass blended char with CO₂ at temperatures of 900–1100°C, *Fuel*. 116 (2014) 465–470. doi:10.1016/j.fuel.2013.08.015.
- [29] J. Wei, Y. Gong, Q. Guo, X. Chen, L. Ding, G. Yu, A mechanism investigation of synergy behaviour variations during blended char co-gasification of biomass and different rank coals, *Renew. Energy*. 131 (2019) 597–605. doi:10.1016/j.renene.2018.07.075.
- [30] J.A. Menéndez, R. Álvarez, J.J. Pis, Determination of metallurgical coke reactivity at INCAR: NSC and ECE-INCAR reactivity tests, *Ironmak. Steelmak.* 26 (1999) 117–121. doi:10.1179/030192399676997.
- [31] J.A. Menendez, R. Alvarez, Y.J.J. Pis, Relationship between different methods of determination of coke reactivity, *Rev. Metal. Madr.* 29 (1993) 214–222.
- [32] L. Zhang, J. Huang, Y. Fang, Y. Wang, Gasification Reactivity and Kinetics of Typical Chinese Anthracite Chars with Steam and CO₂, *Energy Fuels*. 20 (2006) 1201–1210. doi:10.1021/ef050343o.
- [33] M.M. Dubinin, Generalization of the theory of volume filling of micropores to nonhomogeneous microporous structures, *Carbon*. 23 (1985) 373–380. doi:10.1016/0008-6223(85)90029-6.
- [34] J.W. Patrick, P.D. Green, K.M. Thomas, A. Walker, The influence of pressure on the development of optical anisotropy during carbonization of coal, *Fuel*. 68 (1989) 149–154. doi:10.1016/0016-2361(89)90315-3.
- [35] L. Ding, Y. Gong, Y. Wang, F. Wang, G. Yu, Characterisation of the morphological changes and interactions in char, slag and ash during CO₂ gasification of rice straw and lignite, *Appl. Energy*. 195 (2017) 713–724. doi:10.1016/j.apenergy.2017.03.098.
- [36] J.J. Pis, J.A. Menéndez, C. Barriocanal, R. Alvarez, J.B. Parra, M.A. Díez, Relation between reactivity and textural properties in cokes from wet and preheated coals, *Solid State Ion.* 63–65 (1993) 772–776. doi:10.1016/0167-2738(93)90194-8.
- [37] H. Zhang, J. Bai, W. Li, F. Cheng, Comprehensive evaluation of inherent mineral composition and carbon structure parameters on CO₂ reactivity of metallurgical coke, *Fuel*. 235 (2019) 647–657. doi:10.1016/j.fuel.2018.07.131.
- [38] Goscinski, J.S., Gray, R.J., Robinson, J.W., A review of American coal quality and its effect on coke reactivity and after reaction strength of cokes, *J. Coal Qual.* 4 (1985) 21–29.
- [39] R. Loison, P. Foch, A. Boyer, *Coke: Quality and Production*, Elsevier, London, 1989.
- [40] P. Lahijani, Z.A. Zainal, M. Mohammadi, A.R. Mohamed, Conversion of the greenhouse gas CO₂ to the fuel gas CO via the Boudouard reaction: A review, *Renew. Sustain. Energy Rev.* 41 (2015) 615–632. doi:10.1016/j.rser.2014.08.034.
- [41] M. Guerrero, M.P. Ruiz, M.U. Alzueta, R. Bilbao, A. Millera, Pyrolysis of eucalyptus at different heating rates: studies of char characterization and oxidative reactivity, *Pyrolysis* 2004. 74 (2005) 307–314. doi:10.1016/j.jaap.2004.12.008.
- [42] M.A. Díez, A. Domínguez, C. Barriocanal, R. Alvarez, C.G. Blanco, C.S. Canga, Hydrogen donor and acceptor abilities of pitches from coal and petroleum evaluated by gas chromatography, *J. Chromatogr. A*. 830 (1999) 155–164. doi:10.1016/S0021-9673(98)00900-5.

- [43] H. Marsh, R.C. Neavel, Carbonization and liquid-crystal (mesophase) development. 15. A common stage in mechanisms of coal liquefaction and of coal blends for coke making, *Fuel*. 59 (1980) 511–513. doi:10.1016/0016-2361(80)90179-9.
- [44] C. Barriocanal, S. Hanson, J.W. Patrick, A. Walker, Reactive-inert interfaces in metallurgical cokes: effect of added inerts, *Fuel*. 75 (1996) 243–245. doi:10.1016/0016-2361(95)00233-2.
- [45] Q. Lin, H. Tang, C. Li, L. Wu, Carbonization behavior of coal-tar pitch modified with lignin/silica hybrid and optical texture of resultant semi-cokes, *J. Anal. Appl. Pyrolysis*. 90 (2011) 1–6. doi:10.1016/j.jaap.2010.09.012.
- [46] L. Peña, G. Mitchell, F.S. Cannon, S. Komarneni, N.R. Brown, The pyrolytic evolution of morphology in biobased coke replacement briquettes: Links between morphology, nanowire characteristics, and performance in cupolas, *Carbon*. 140 (2018) 458–464. doi:10.1016/j.carbon.2018.08.046.
- [47] C. Barriocanal, S. Hanson, J.W. Patrick, A. Walker, The characterization of interfaces between textural components in metallurgical cokes, *Fuel*. 73 (1994) 1842–1847. doi:10.1016/0016-2361(94)90209-7.