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Cation exchange capability and reactivity of low-rank coal and chars

Research Article

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Abstract: In this work the C.E.C. and its effect on the reactivity of low rank coal and chars were investigated. The C.E.C. was measured by potentiometric titration and was correlated with the solution pH, the carbonization extent and the oxygen content. Coal and chars presented permanent C.E.C. primarily derived from inorganic sites and was independent of solution pH, and variable C.E.C. derived from organic matter and was increased continuously, and reversibly, as the solution pH increased. The latter is due to the complete dissociation of the carboxylic groups of the organic matter of the coal and, thus, the C.E.C. is directly related with the oxygen content. The C.E.C. of chars decreased with the carbonization extents and its variation was described by a modified cumulative distribution function of the Weibull probability density function. A linear correlation was identified between the C.E.C. and the elemental oxygen conversion, justifying further the direct relation between the C.E.C. and the oxygen functional groups. Following the decrease of the C.E.C., the potassium chemisorption capacity of the chars also decreased. Chars of decreased C.E.C. were less reactive during CO_2 gasification and reduced maximum weight loss and CO formation rates were obtained, also shifted at higher temperatures.

Keywords: *Low rank coal • Chars • Cation exchange capability • Gasification • Reactivity*

1. Introduction

Low-rank coals are well known for their high concentration of oxygen-containing functional groups, the high proportion of transitional and macropores and the high dispersion of catalytic inorganic constituents, that affect their gasification behavior. The high oxygen content imparted to these materials allows the ability to remove cations from solutions *via* ion exchange. Since the 1930s low rank coals were used as an ion exchange medium [1-3] and various chemical modifications were elaborated (*e.g.* sulphonation *etc.*) to increase the ion exchange capacity of bituminous coals [3-5]. Recently, peat-based sorbents, modified with iron compounds, were tested successfully for the removal of arsenic from water and it was found that sorption of different arsenic speciation forms was strongly dependent on solution pH, reaction time and temperature [6]. As a result of this ion exchange ability and of their high content in humic substances, low rank coals have been considered to be suitable for production of soil amendments [7-9] and for the removal of metal ions from aqueous solutions [6,10]. Janos *et al.* [11] investigated the ion exchange capacity and the sorption properties of selected Central European young brown coals.

The cation exchange capability of a soil is the measure of the total capacity of the soil (organic and inorganic) to hold exchangeable cations and indicates the negative charge per unit mass of soil [12]. Soils might have permanent charge ($C.E.C._p$) that is derived from certain clay minerals when Mg is replaced by Al or Si is replaced by Al and the pH-dependent variable charge ($C.E.C._v$) that illustrates the contribution of soil organic matter and minerals to soil C.E.C. and is therefore influenced by the chemical environment. Most soils have both types of charges and the soil C.E.C. tends to increase with increasing pH. $C.E.C._p$ is considered to be derived from the clay fraction and other mineralogical

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components while C.E.C.$_v$ is regarded to be derived from soil humus and accordingly, the presence of organic matter generally causes the C.E.C. in variable-charge clay soils to be higher. Functional groups of soil organic matter have been associated with an increase in C.E.C.$_v$ [12] and a decline in soil organic matter, but unchanged clay content and composition, resulted in decreased C.E.C.

The cation exchange capability (C.E.C.) of low rank coals is attributed to the carboxylic acid and phenolic hydroxyl functional groups that dissociate in solution to form a negatively charged site upon the coal surface which is subsequently capable of complexing cationic species from solution to form a stabilized coal-metal structure. The carboxylic acid functional groups are the most important sites involved in the ion exchange process [13], since these weak acid sites are virtually completely dissociated at solution pH's greater than 4. Metal ions complexed by coals are incorporated into the coal matrix as metal carboxylates, and increase the thermal stability of the coal [13], since the pyrolysis of them occurs at higher temperatures [5,13]. Therefore, the cation exchange capability of coals is related to the number of carboxylic acid functional groups. Particularly the chemisorption of K^+ is quite important, since its salts are common catalysts for coal gasification.

There are several different methods to measure the C.E.C. [12,14] and the factors influencing C.E.C. (*e.g.* pH and ionic strength) and the degree of variable and permanent charge should be accounted in order to select the most appropriate one. The techniques used to measure the C.E.C. of soils could be used for low rank coals and chars, since humic substances are major components of both the natural organic matter in soil and of the geological organic deposits such as peats and coals. It is generally accepted that oxygen-containing functional groups found in coals act as active sites [15-19] and their contribution in ion exchange and in the gasification reactions is fully justified [20,21]. Thus, the reactivity of coals and chars is controlled by the concentration of active sites that is influenced by the coal rank and the char preparation conditions [22,23]. Increased temperatures and longer times resulted in decreased number of active sites and thus chars of lower reactivity were produced [20,21].

Despite the importance of the ion exchange properties of low rank coals only limited work has been performed and, thus, there are major uncertainties regarding the origin and the mechanism of the C.E.C. The correlation of C.E.C. with the pH and the oxygen functional groups and, subsequently, its effect on the reactivity of coal and chars also needs clarification. The inherent heterogeneity of the coals, the presence of various amounts of hydrogen and of oxygen, and the possible contribution of the coal ash accentuate the above uncertainties. In this work the cation exchange capability (C.E.C.) and its effect on the reactivity of low rank coal and chars was investigated. The C.E.C. of coal and chars was measured by potentiometric titration and was correlated with the solution pH, the carbonization extent and the oxygen functional groups. To account for the C.E.C. of the inherent mineral matter, the ash contained in the coal was isolated by a low temperature procedure and its C.E.C. was also measured. The reactivity of coal and chars was studied by means of non-isothermal CO_2 gasification.

2. Experimental procedure

Low rank Greek coal (lignite) from the Ptolemais reserve was used as a starting material and coal samples were kept sealed with their moisture and in the absence of air to avoid any weathering. When required, samples were dried for 24 hours at 105°C in a N_2 atmosphere to prevent oxidation and the desired granulometries were obtained by grinding and sieving. The appropriate ASTM Standard Methods were used for the proximate (ASTM D 7582-12), ultimate (ASTM D 5373-08) and ash analyses (ASTM D 6349-09) of the raw samples and of the pyrolysis chars. The obtained results for the raw coal are given in Table 1, while the corresponding ones for the carbonization chars are given in Table 2. Greek lignite from the Ptolemais reserve is characterized by its high moisture, high ash and high volatile content, as well as its high oxygen and low sulphur content. Its inorganic phase is characterized by high calcium and silica content. Sodium and potassium are also found but in quite small quantities.

Using the method outlined in ISO 11260/2003, the cation exchange capability (C.E.C.) of coal, chars and ash samples was measured by titration with aqueous solutions of NaOH, 0.01 N to 0.1 N. Prior to C.E.C. measurements, samples were pre-treated in order to be fully protonated (saturated with H^+) and to remove any extractable cations (*i.e.*, Ca and/ or Mg carbonates) which are likely to exceed the C.E.C. value [12,18]. Briefly, the procedure (pre-treatment and C.E.C. measurement) includes the following stages:

- The pre-treatment included five successive steps of extraction in a centrifuge with 0.05 N HCl, heating up to 60-70°C, extraction in a centrifuge with 0.1 N $CaCl_2$, and washing with distilled water.
- During the pre-treatment steps the pH was maintained at 3, by adding small amounts of 1.0 N HCl when it was required.

Table 1. Proximate [ASTM D 7582-12], ultimate [ASTM D 5373-08] and elemental ash [ASTM D 6349-09] analyses of low rank Greek coal samples.

(a) Proximate Parameter		(b) Ultimate Element		(c) Ash analysis Compound	
Volatiles	47.0	C	48.2	SiO_2	36.64
Fixed carbon	30.8	H	3.0	Al_2O_3	17.31
Ash	21.7	N	1.5	Fe_2O_3	7.19
CO_2	0.5	S	1.0	CaO	28.10
HHV (kcal kg^{-1})	4193	O*	24.6	MgO	0.83
		Ash	21.7	SO_3	11.93
				Na_2O	0.6
				K_2O	0.6

* *by subtraction*

- Finally, the obtained solid was washed out with methanol till the Cl^- ions were completely removed.
- Titration with the appropriate NaOH solution (0.01 N to 0.1 N) while the pH was continuously monitored.
- Prior to titration, a 0.2 N NaCl solution was added as catalyst to initiate the titration process (solution pH decreased from about pH6 to about pH3-4).

The C.E.C. was calculated by the amount of NaOH (in cm^3) used to reach pH10 in the solution. Above that pH value the cation exchange was completed and the solution tends to become a (asymptotically) buffer. The C.E.C. was calculated from the following Eq. 1:

$$C.E.C. = \frac{V_{NaOH}\, N_{NaOH}}{m_{solid}} 100 \qquad (1)$$

Where *C.E.C.* [meq/100 g solid] is the cation exchange capability, V_{NaOH} [cm^3] is the volume of NaOH used till pH = 10, N_{NaOH} is the normality of the NaOH solution and m_{solid} [g] is the mass of solid used (coal or char or ash). The above described procedure for measuring the C.E.C. was applied in all samples tested (*e.g.* coal, chars, mineral matter).

Standard methods for the determination of ash in coal (*e.g.* ASTM D3174-12 Standard Test Method) elaborate severe oxidation conditions (750 – 815°C and 1 hour residence time) that transform the inherent minerals to oxides and alter their ion exchange behavior. To avoid this, the contained ash in the coal was isolated by low temperature oxidation comprising the destruction of the organic compounds by H_2O_2 solution (30% w/w) at 60°C to 70°C, in successive steps. Sodium acetate (CH_3COONa) was used as a buffer solution to maintain the pH at 5 during the oxidation. Treatment with H_2O_2 was continued till complete oxidation of the organic matter was achieved (defined by ultimate analysis).

Coal-chars were prepared in a fixed bed reactor equipped with the proper gas and solids feeding controls and with product collection and analyses devices. The U-shape reactor design permits rapid cooling (quenching) and thus the charring reactions could be interrupted when required. A detailed description of the test unit is given elsewhere [24]. Chars were prepared under nitrogen flow (100 cm^3 min^{-1}) and the corresponding experimental conditions (temperature and time) are given in Table 2. A LECO CHNS-932 elemental analyzer was used to perform ultimate analysis of the obtained chars in order to calculate the elemental conversions of C, H, N and O.

The chemisorption of K^+ in coals is quite important, since its salts are low cost and efficient catalysts for coal gasification. Coal-char samples were impregnated with 1 M aqueous solution of potassium carbonate (K_2CO_3) according to the impregnation procedure previously developed [18,25]. The physically held K^+ ions were extracted with water in a centrifuge and the K^+ cations in the extract were measured by atomic absorption. The difference between the total and the extracted amount of cations represents the chemisorbed K^+ ions on the lignite. Previous studies [18,25] have shown that the fraction of chemisorbed K^+ is the key element in the ion exchange process since it is bounded on oxygen-containing functional groups (active sites) on the coal surface.

Non-isothermal gasification tests were performed on a TA Instruments Q600 simultaneous TGA/DSC apparatus, coupled with an on-line IR CO analyser (Beckman 864 ND-IR). This offered the advantage of simultaneous monitoring of coal-char weight loss and

CO evolution during non-isothermal CO_2 gasification. In all tests a sample of 20 mg mass, 20°C min^{-1} heating rate and a 100 $cm^3\,min^{-1}$ CO_2 flow were used. In order to have fully comparable results the conversion values and the CO production rates were converted per gram of the parent coal (on dry, ash free basis).

3. Results and discussion

3.1. Cation exchange capability of low rank coal

The total C.E.C. of lignite (in meq / 100 g lignite) measured by potentiometric titration was found to increase continuously as the solution pH was increased, Fig. 1. Thus, the total C.E.C. of the lignite started from a low, almost constant, value at solution pH between 2 to 4 and continuously increased up to solution pH 12 to 14. Above solution pH 10 the C.E.C. tends to reach a plateau (asymptotically), Fig. 1. The cation adsorption phenomena in low rank coals (such as lignite) are quite complex since these materials consist of organic and inorganic compounds exhibiting acidic or basic behaviour [26]. Ion exchange studies of soils have shown that alkalis such as Na and K could be held up in both the organic and inorganic phases and two types of cation exchange capability exist, a permanent one that is unaffected by the solution pH variations and a pH-dependent one [27]. In the case of lignite the inorganic matter mainly consists of clay minerals and the chemisorption of cations on the surface of a lattice at sites with broken and free bonds and at sites having excess electrons is responsible for the permanent C.E.C. [18]. Furthermore, the phenolic hydrogen atoms at highly aromatic stable structures between the carbon layers might also act as permanent ion exchange sites [18] accounting for the permanent C.E.C. at the usual pH values of the lignite (5 to 8). In contrast, the pH-dependent variable C.E.C., that illustrates the contribution of the organic matter, was strongly influenced by the solution pH, Fig. 1. Increase of the solution pH resulted in the replacement of H^+ by Na^+ (or K^+) ions on the solid and the formation of water with the OH^- of the solution, therefore, new ion exchange sites were formed and the C.E.C. increased.

As the pH increased during the titration new active sites were formed for both the cation (Na^+) and anion (OH^-) of the titrating solution, and, therefore, the C.E.C. was increased. This could be attributed to the solution pH effect on the aluminosilicate minerals and to the virtually complete dissociation, at increased pH values, of the acidic –mainly carboxylic– groups of the humic and fulvic acids that form the organic matter of the lignite [13,18]. The dependence of the C.E.C. on the solution pH is reversible and declines when the solution pH decreases, as described by the following reaction scheme [13,18].

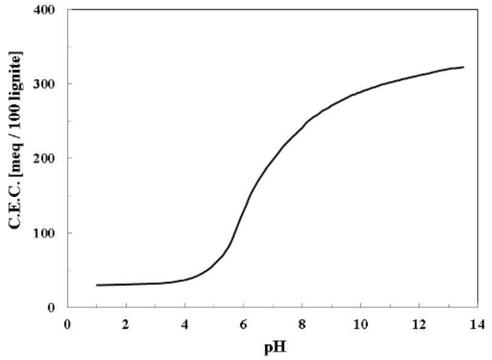

Figure 1. Variation of the C.E.C of lignite with the solution pH, obtained by titration with NaOH 0.1 M.

$$Coal-COOH \xleftrightarrow{OH^-} COO^- + H^+(aq) \tag{2}$$

$$M^{n+} + n\,Coal-COO^- \longleftrightarrow (Coal-COO)_n M \tag{3}$$

$$H^+ + OH^- \longleftrightarrow H_2O \tag{4}$$

In such a system the equilibrium shifts with pH. The high concentration of H^+ at low (below 4) solution pH shifts the equilibrium of Eq. 2 to the left, resulting in very limited or no dissociation of the weak acidic – mainly carboxylic– groups. Thus, at low pH values, the temporary ion exchange sites of the organic matter were less or not available for ion exchange and the C.E.C. declines. At higher solution pH (above 4) the carboxylic groups started to be deprotonated appreciably. The progressive dissociation of the carboxylic groups as the pH increased shifted the equilibrium of Eqs. 2 and 3 to the right and the C.E.C. continuously increased, Fig. 1. At high solution pH the acidic groups were almost fully dissociated and the C.E.C. increased rapidly, while at solution pH above 10 to 11 reached a plateau (asymptotically), Fig. 1, possibly due to the saturation of the lignite surface, since virtually all the available ion adsorption sites might be occupied by cations. The minimum (permanent) C.E.C. measured at pH 1 is attributed to the inorganic matter and to compounds of C–O–Na type formed with the phenolic groups found in the coal. Therefore, coal presents C.E.C. derived primarily from inorganic sites (permanent) that is almost independent on solution pH; and C.E.C. derived from organic matter (variable) that strongly depends on the solution pH. The latter continuously increased as the solution pH increased and is considered responsible for the catalytic activity of the chemisorbed metals [13].

Table 2. Carbonization conditions and weight loss, C.E.C. and elemental composition of the obtained chars.

Sample	Temp/Time (°C)/(min)	Weight loss (% w/w)	C.E.C. (meq/100 g)	Pyrolysis char composition (% w/w)					
				C	H	N	Ash	O*	g-atom C / g-atom O
Coal	-	0	330.0	48.20	3.00	1.50	21.7	24.6	2.6
CH-1	340/1	0.80	317.5	48.47	2.98	1.52	21.9	24.6	2.6
CH-2	380/2	4.08	325.0	47.41	3.10	1.54	22.6	24.7	2.6
CH-3	550/1	8.10	315.0	49.57	3.08	1.62	23.6	21.5	3.1
CH-4	400/3	11.81	290.0	49.48	2.99	1.49	24.6	20.8	3.2
CH-5	400/5	16.99	220.0	49.79	2.76	1.66	26.2	19.1	3.5
CH-6	400/10	19.88	190.0	51.52	2.47	1.73	27.1	16.6	4.2
CH-7	400/10	20.89	214.0	51.73	2.50	1.64	27.2	16.4	4.2
CH-8	700/1	22.88	186.4	52.47	2.88	1.58	27.4	15.0	4.7
CH-9	600/2	28.92	124.0	49.33	1.85	1.71	30.5	16.0	4.1
CH-10	600/15	35.61	82.0	51.72	0.89	1.61	33.7	11.5	6.0
CH-11	600/15	35.62	76.0	52.43	0.80	1.62	33.7	10.8	6.5
CH-12	700/2	38.56	30.	55.10	0.96	1.55	35.3	6.5	11.4
CH-13	800/2	45.30	27.2	52.77	0.68	1.57	39.7	4.7	14.9
CH-14	900/2	52.94	22.8	55.12	0.23	1.16	42.7	0.5	147.0

** by subtraction*

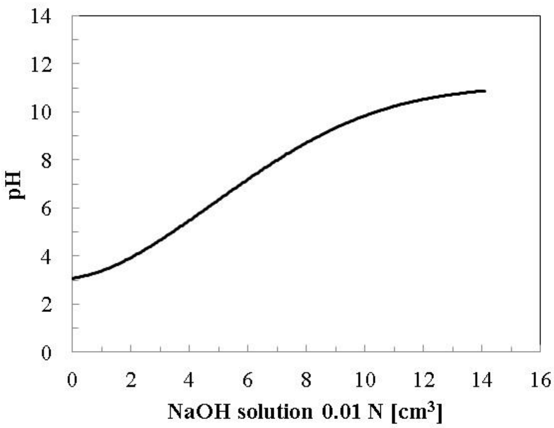

Figure 2. Potentiometric titration curve of Greek lignite low temperature ash (C.E.C. = 7.1 meq / 100 g solid).

3.2. Cation exchange capability of inorganic matter

Low temperature lignite ash was prepared according to the previously described low temperature oxidation procedure and its potentiometric titration curve is given in Fig. 2. The C.E.C. of the inherent mineral matter (ash) of the coal was measured to about 7 to 8 meq/100 g, that is two orders of magnitude lower than that of the parent coal (300 to 350 meq/100 g). Therefore, it can be suggested that the C.E.C. of the coal is mainly attributed to the organic sites which are found in much higher numbers than the inorganic ones due to the increased content of acidic –mainly carboxylic– oxygen functional groups [13,18]. The inorganic matter of the lignite mainly consists of clay minerals (c.f. Table 1) and, consequently, the C.E.C. of its (low temperature) ash was, plausibly, similar to the one of kaolinite (3 – 7 meq/100 g) that is the most abundant mineral found in lignite [28].

3.3. Cation exchange capability of chars

The effect of carbonization (pyrolysis) conditions on the C.E.C. was studied by preparing chars at various temperatures (350 – 900°C) and residence times (1 – 30 min), in an inert atmosphere. The carbonization conditions used, the corresponding weight loss, the elemental analyses and the cation exchange capability (C.E.C.) of the obtained chars (measured by potentiometric titration with NaOH solution) are given in Table 2.

It is well established, that weight loss (% w/w) increases at higher carbonization temperature and prolonged residence time. Thus, by altering the charring conditions chars with weight loss values varying between about 0.8% to about 52% w/w were achieved, Table 2. Based on the ultimate analyses of the chars the elemental conversions (that depend on both the devolatilisation temperature and residence time) of C, H and O were calculated, and the obtained results are given in Fig. 3.

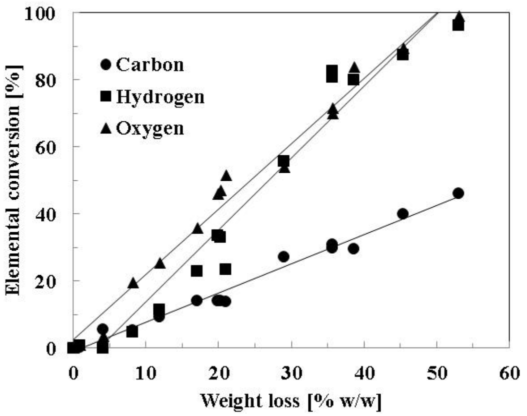

Figure 3. Elemental conversions of carbon, hydrogen and oxygen with carbonization weight loss.

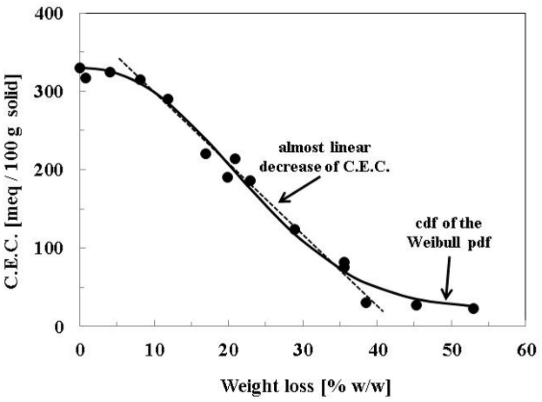

Figure 4. Variation of cation exchange capability (C.E.C.) with pyrolysis weight loss.

Elemental carbon conversion closely followed the sample weight loss and an almost linear relation was observed between elemental carbon conversion and weight loss, Fig. 3. Thus, at mild devolatilisation conditions (low temperature and residence time) the elemental carbon conversion is limited, analogously to the low weight loss observed. At increased temperatures and residence times elemental carbon conversion reached about 45% corresponding to weight loss about 52% w/w, Fig. 3. Elemental hydrogen and oxygen conversions were higher even at low weight loss values and increased sharply, above 80%, when weight loss reached about 35%, Fig. 3. At weight loss above 40% w/w elemental hydrogen and oxygen conversions were almost complete (above 90%).

A direct relation between the C.E.C. and the carbonization (pyrolysis) weight loss (that corresponds to the removed volatiles) was observed, Fig. 4. More specifically, at low weight loss values, below 10%, the C.E.C. decreased slowly, corresponding to the limited removal oxygen functional groups at these carbonization conditions, Fig. 4. During pyrolysis, the carboxylic groups are removed in the form of CO_2 that is detected at temperatures above 250°C [13]. Up to that temperature the observed weight loss is mainly attributed to the removal of water that is chemically bounded in the coal matrix, and does not contribute to the C.E.C. of the chars [29]. As the carbonization weight loss increased above 10 and up to 40% w/w, the C.E.C. decreased rapidly, declining almost linearly as indicated by the dotted line in Fig. 4. The C.E.C. strongly depends on the number of oxygen functional groups and particularly on the carboxylic ones. The evolution of volatiles during carbonization resulted in extensive elemental oxygen removal and its elemental conversion varied almost linearly with weight loss, Fig. 3, thus justifying the simultaneous linear decrease of the C.E.C. Therefore, the thermal decomposition of the oxygen functional groups taking place during carbonization decreased the number of the available sites for cation adsorption and is responsible for the reduced C.E.C. of the chars.

Above 45% w/w weight loss the C.E.C. was stabilised and reached a plateau of 20 – 30 meq/100 g. This residual C.E.C. should be attributed partly to the inherent mineral matter of the coal (about 7 to 8 meq/100 g) and partly to the formation of organo-metallic complexes with the remaining aromatic structure of the coal [18,30,31]. Therefore, for weight loss values above 45%, almost complete elemental oxygen removal, Fig. 3, resulted in quite low C.E.C. of the corresponding chars, Fig. 1. A modified cumulative distribution function (cdf) of the Weibull probability density function (pdf) was used to correlate the C.E.C. with the weight loss during the carbonization stage. The following function was used:

$$C.E.C. = a + b e^{-\left(\frac{x}{\lambda}\right)^{\kappa}} \tag{5}$$

Where *k* and *l* are the shape and scale parameters of the Weibull distribution and *x* is the weight loss (% w/w) during the char preparation stage. To reproduce the initial C.E.C. of the parent coal and the asymptotic value at the end of the C.E.C. curve the cdf of the Weibull pdf was modified (Eq. 5) and two constants (a, b) were added. The constant a represents the C.E.C. of the char at complete devolatilisation and the sum of *a* and *b* constants equals the C.E.C. of the parent coal. For the Ptolemais lignite used, the constant (a) was measured to be 22 meq/100 g_{solid} while the C.E.C. of the parent coal was measured to be 330 meq/100 g_{solid} (a + b = 330). A non-linear optimization model was used for the derivation of the optimum distribution parameters, namely, the model/distribution parameters that lead to the maximization of R^2, *i.e.*, the best fit. The obtained

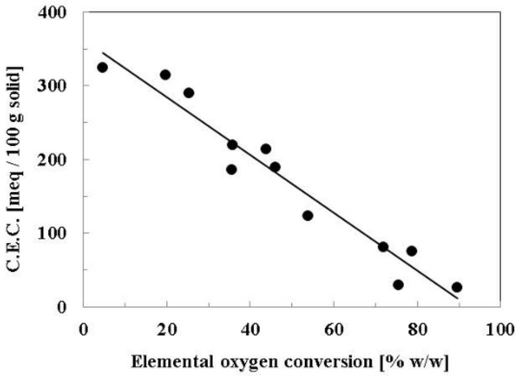

Figure 5. Variation of cation exchange capability (C.E.C.) with elemental oxygen conversion.

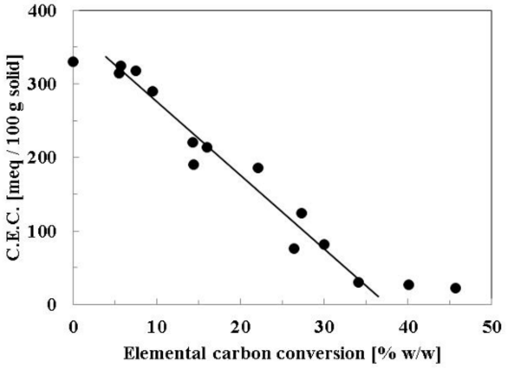

Figure 6. Variation of cation exchange capability (C.E.C.) with elemental carbon conversion.

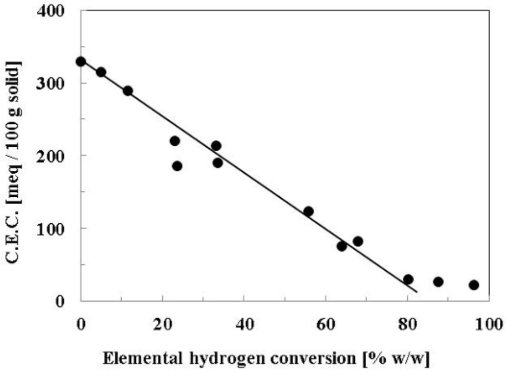

Figure 7. Variation of cation exchange capability (C.E.C.) with elemental hydrogen conversion.

best-fit parameters found for the C.E.C. were $\kappa = 2.256$ and $\lambda = 26.922$ with R^2 value over 0.998. Therefore, the modified cumulative distribution function of the Weibull distribution successfully describes the variation of the C.E.C. with weight loss during the carbonization stage. In Fig. 4 the continuous curve represents the calculated results from Eq. 5.

To clarify further the above-described phenomena, efforts focused on correlating the C.E.C. of the chars with the elemental conversions of oxygen, carbon and hydrogen, Figs. 5 to 7. A continuous, almost linear, decrease of the C.E.C. with elemental oxygen conversion was observed, Fig. 5, justifying a direct (linear) dependence between the oxygen functional groups (mainly carboxyls) and the C.E.C. The following semi-empirical equation correlates the C.E.C. and the elemental oxygen conversion (X_O in % w/w).

$$C.E.C. = -a\,X_O + b \qquad (6)$$

Where, the constant a stands for the rate of C.E.C. decrease with the elemental oxygen conversion, and b is the C.E.C. of the parent coal. For the Ptolemais lignite constants *a* and *b* where calculated *a = 3.9333* and *b = 363.39* with fair accuracy ($R^2 = 0.96$).

The C.E.C. of the chars also decreased as the elemental carbon and hydrogen conversions increased, Figs. 6 and 7. However, the C.E.C. decreased almost linearly with elemental carbon conversion only up to about 35%, Fig. 6. Above that it tends to reach a plateau, thus being almost constant at higher elemental carbon conversions. Therefore, no direct relation between the elemental carbon conversion and the C.E.C. is justified. A similar behaviour was also observed for elemental hydrogen, as the C.E.C. decreased almost linearly for elemental conversions up to about 80% and stabilised above that value, Fig. 7. Above specific levels the elemental carbon and hydrogen conversions mainly came from the dissociation of aliphatic groups or even destabilised aromatic rings and not from carboxyls, thus leaving unaffected the C.E.C. of the chars. Hence, the C.E.C. is not linked directly with the elemental carbon and hydrogen conversions and any correlation between them is mechanistic and thus meaningless; coming from the parallel devolatilisation of the oxygen functional groups.

Thus, the C.E.C. continuously decreased with the elemental oxygen conversion indicating a direct (almost linear) relationship between the C.E.C. and the oxygen containing functional groups (such as carboxyls). Such relation between the C.E.C. and elemental carbon and/or hydrogen conversions was identified only up to specific elemental conversion levels and a correlation between the C.E.C. and elemental carbon and/or hydrogen conversions is not plausible.

3.4. Potassium chemisorption capacity of pyrolysis chars

Due to its importance in catalytic gasification, the K^+ chemisorption capacity of the pyrolysis chars was investigated and correlated with their C.E.C. The amount of potassium added was kept constant

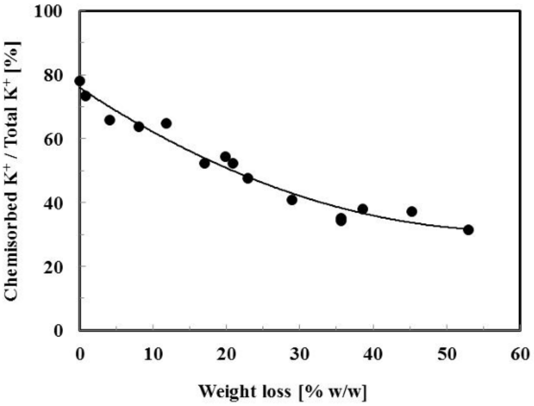

Figure 8. Variation of the % of chemisorbed K$^+$ with the weight loss of the pyrolysis chars.

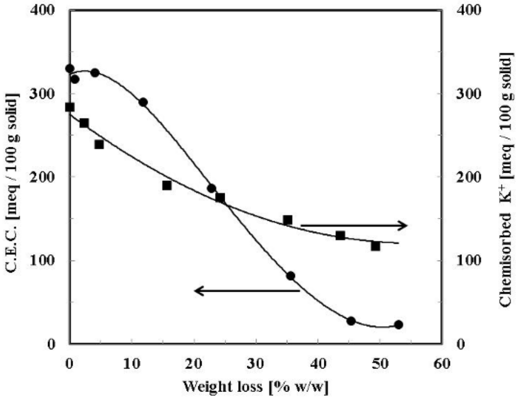

Figure 9. Variation of the C.E.C. and of the chemisorbed K$^+$ with weight loss in the carbonization stage.

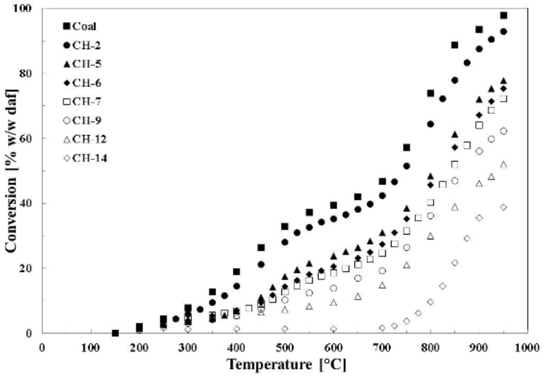

Figure 10. Effect of the carbonization conditions on conversion during non-isothermal CO_2 gasification of coal and chars.

(11.32 g K$^+$ per 100 g of lignite and potassium carbonate), corresponding at 20% K_2CO_3 in the mixture of lignite and potassium carbonate. The fraction of the chemisorbed K$^+$ decreased as the weight loss of the carbonization stage increased, Fig. 8. As discussed previously, severe pyrolysis conditions, which resulted in increased weight loss values, removed from the coal surface the majority of the oxygen functional groups (particularly carboxyls) and the ion exchange sites were diminished, resulting in decreased fraction of the chemisorbed K$^+$.

The potassium chemisorption capacity was converted to meq / 100 g solid for direct comparison with the C.E.C. of the chars. The amount of the chemisorbed K$^+$ closely followed the decrease of the C.E.C. with the carbonization weight loss; however its decrease was less steep, Fig. 9. Up to about 25% w/w weight loss in the carbonization stage, the C.E.C. of the chars is higher than their K$^+$ chemisorption capacity, Fig. 9. It should be noted that before the C.E.C. measurements the samples were pre-treated (*i.e.*, fully protonated) to remove all the chemisorbed cations (*e.g.* Ca^{+2}, K$^+$, Mg^{+2}) and thus the maximum C.E.C. was measured. In contrast, such pre-treatment was not applied in K$^+$ chemisorption and, reasonably, the number of the available sites for K$^+$ chemisorption was lower.

Above 25% w/w weight loss the C.E.C. declined rapidly and reached asymptotically a minimum (about 20 to 30 meq/100 g solid) that corresponds to the permanent C.E.C. of the char. The K$^+$ chemisorption capacity decreased also, however in a less steep way and remained constantly much higher than the corresponding C.E.C., Fig. 9. At these carbonization levels a fully developed microporous structure has been created in the lignite chars. Potassium cations penetrate deeply inside the pores, forming rather stable intercalate compounds with the coal char [28]. Therefore, the higher than the C.E.C. amount of the chemisorbed K$^+$ might be attributed to the formation of intercalates that potassium, in contrast to Na$^+$, tends to form with all coals and chars [30,31]. Complementary, the increased K$^+$ chemisorption might also be attributed to the formation of compounds such as C – O – K formed by the reaction between the char and the K_2CO_3.

3.5. Reactivity of pyrolysis chars under CO_2 gasification

Raw coal and selected chars were gasified non-isothermally (20°C min^{-1}) under CO_2 flow (100 cm^3 min^{-1}), to study their reactivity. In order to have fully comparable results the conversion values and the CO production rates were converted per gram of the parent coal (on dry, ash free basis). The simultaneous determination of weight loss and CO_2 evolution during the TGA reactivity tests provided a rational and detailed examination of the phenomena involved and permitted to illuminate the relation between the C.E.C. and the reactivity of the raw coal and of the chars.

Raw coal (lignite) was found quite reactive with CO_2 and, thus, almost complete conversion is achieved by the end of the non-isothermal test. Its behaviour during non-isothermal CO_2 gasification is characterised by the existence of two temperature regions that control conversions and yields, Fig. 10. In the first stage (below 650°C) pyrolysis takes place, characterised by evolution of volatiles, fast weight decrease and formation of carbon oxides as well as light and heavy (mainly tars) hydrocarbons. In that stage the weight loss rate presented a wide maximum at the temperature region 400°C to 500°C, Fig. 11. During the second stage of the non-isothermal CO_2 gasification (above 650°C), the heterogeneous Boudouard reaction dominates, accompanied by fast weight decrease and CO production, Fig. 10. Traces of hydrocarbons are also produced in this stage coming from the remaining volatiles strongly bounded in the lignite structure.

Following the behaviour of the raw coal, two stages of weight loss were observed during the CO_2 gasification of the chars and the temperature limit between them lies also at about 650°C, Figs. 10 and 11. The thermal pre-treatment of coal affected both regions of the non-isothermal CO_2 gasification and resulted in reduced weight loss and CO_2 gasification rates. Below 650°C where pyrolysis occurs, increased weight loss was observed for chars of low carbonization, Fig. 10. During the char preparation stage (carbonization) devolatilisation and pyrolysis reactions are taking place and, thus, increased carbonization resulted in reduced weight loss during the first stage of the non-isothermal CO_2 gasification. As the carbonization extent increased the first stage of the non-isothermal CO_2 gasification was gradually diminished and the wide maxima observed practically, vanished, Fig. 11. This was anticipated, since at high carbonization extent almost complete devolatilisation was achieved in the char preparation stage.

In the second stage, above 650°C, where the heterogeneous Boudouard reaction dominates, relatively high weight loss values were obtained for all samples, Fig. 10. Chars of low carbonization extent presented higher total weight loss and gasification rates, thus being more reactive with CO_2, Figs. 10 and 11. The increased reactivity of the chars with CO_2 resulted in high (almost complete) weight loss for these samples, Fig. 10. In contrast, chars of increased carbonization extent were less reactive and lower total weight loss and CO_2 gasification rates were observed, Fig. 11. Simultaneously, for these chars the temperature at which the maximum weight loss rate occurs in the second stage of the non-isothermal CO_2 gasification was shifted at higher values. As discussed previously, increased carbonization resulted in samples of decreased C.E.C. which were proven less reactive due to the extensive removal of oxygen functional groups during the char preparation stage and the consequent reduction of the available active sites for gasification.

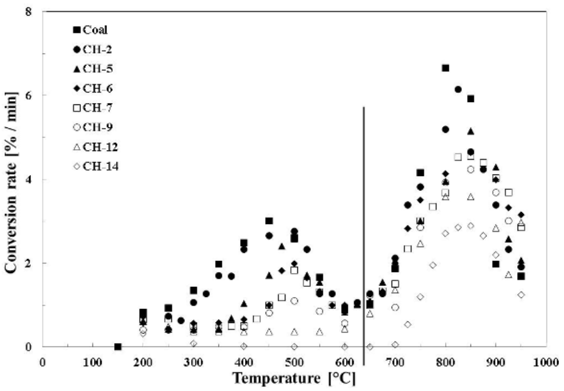

Figure 11. Conversion rates during non-isothermal CO_2 gasification of coal and chars.

As the C.E.C. of the chars decreased, the maximum CO formation rate also decreased, while it was shifted at higher temperatures, Fig. 12. It is well established that oxygen-containing functional groups found in coals act as active sites in gasification reactions [15-19] and their concentration is one of the major factors controlling the reactivity of coals and chars [22,23]. The evolution of volatiles during the carbonization stage resulted in extensive elemental oxygen removal and, thus, in decreased C.E.C. of the obtained chars. Thus, the thermal decomposition of the oxygen functional groups, taking place during carbonization, decreased the number of the available active sites for gasification and less reactive chars of reduced C.E.C. were obtained. The removal of oxygen atoms during carbonization increased the g-atom C / g-atom O ratio by one or two orders of magnitude, Table 2, leading to more stable (similar to graphite) and less reactive char structure. These results are in agreement with previous researchers [20-23] who found that preparation of chars at increased temperatures and longer times resulted to decreased number of active sites and thus to less reactive chars. Therefore, chars of reduced C.E.C. are less reactive, since oxygen functional groups were removed during the carbonization stage and chars of more stable structure were obtained.

4. Conclusions

Coal presented C.E.C. derived from inorganic sites (permanent) was almost independent on solution pH; and C.E.C. derived from organic matter (variable) continuously increased as the solution pH increased. The chemisorption of cations on the surface of a lattice at sites with broken and free bonds, at sites having excess

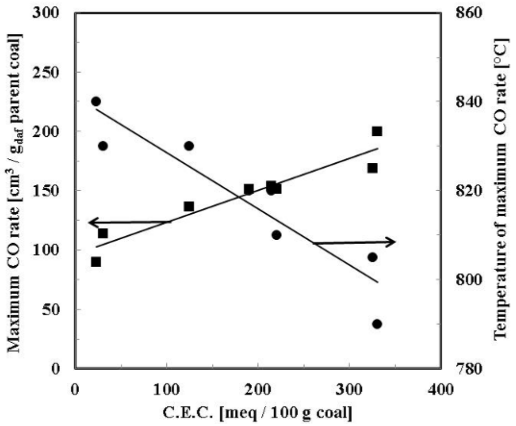

Figure 12. Effect of C.E.C. on the maximum CO formation rate and on the temperature of maximum rate during non-isothermal CO_2 gasification of coal and chars.

electrons and the substitution of phenolic hydrogen in groups between the carbon layers was responsible for the permanent C.E.C. The pH-dependent variable C.E.C. illustrated the contribution of the organic matter and was strongly influenced by the solution pH. As the solution pH increased new active sites were formed for both the cation (Na^+) and anion (OH^-) of the titrating solution and the C.E.C. was increased. This could be attributed to the solution pH effect on the aluminosilicate minerals and to the virtually complete dissociation at increased pH values of the carboxylic groups of the humic and fulvic acids that form the organic matter of the low rank coal. Therefore, the C.E.C. of coal is directly related with its organic oxygen content. The dependence of the C.E.C. on the solution pH is reversible and declines when the solution pH decreases. The mineral matter of the coal accounts for less than 3% of the total C.E.C.

A direct relation between the C.E.C. and the char preparation conditions was identified. The evolution of volatiles during the carbonization stage resulted in extensive elemental oxygen removal and, thus, in decreased C.E.C. of the obtained chars. The C.E.C. of coal and chars decreased linearly with the elemental oxygen conversion while for elemental carbon and/or hydrogen such relation was identified only up to specific elemental conversion levels. A modified cumulative distribution function of the Weibull distribution successfully described the variation of the C.E.C. with weight loss during the carbonization stage. Since the cations are chemisorbed on oxygen functional groups, the fraction of the chemisorbed K^+ decreased following the decrease of the C.E.C. at increased carbonization extend levels, which reduced the number of the available ion exchange sites. Chars of decreased C.E.C. were proven less reactive due to the extensive removal of oxygen groups during the char preparation stage and the consequent reduction of the available active sites for gasification. Thus, both the maximum weight loss and CO formation rates were decreased and shifted at higher temperatures also.

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