CO$_2$ strong chemisorption as an estimate of coal char gasification reactivity

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Abstract

In this article, coal char gasification reactivity was correlated with the strong chemisorption of CO$_2$ at 300°C. Chars of as-received, demineralized, K and Fe loaded coals were prepared at 800°C, under high purity nitrogen. The CO$_2$ chemisorption method described in this article allows differentiation between two types of chemisorption that takes place at low temperatures: strong CO$_2$ chemisorption (irreversible) which is related to the presence of the active inorganic components of the char, and weak CO$_2$ chemisorption (reversible) which is because of the organic matter of the char. The char doped with K showed the highest CO$_2$ strong chemisorption and at the same time the highest reactivity in the CO$_2$ gasification, while the char loaded with Fe had the highest amount of weak chemisorption. It was found that total chemisorption (weak + strong) at 300°C depends on the CO$_2$ pressure of the analysis. The reactivity of the CO$_2$ gasification of the char was normalized using the value of the amount of CO$_2$ strongly chemisorbed at 300°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Gasification; Reactivity; CO$_2$ chemisorption

1. Introduction

Reactivity of char gasification and its relationship to the structure of the char, particularly the active sites concentration has received considerable attention [1–4]. Char reactivity was considered in some cases to be proportional to the number of active sites in the char [5,6] and, as the slope of the Arrhenius plot does not differ much between catalyzed and non-catalyzed gasification [1,4] it was suggested that the catalyst increases the active site concentration without changing the main kinetic mechanism.

The nature of the active sites is still a matter of controversy. Different researchers have proposed different functionalities as the active sites, for example phenolates [7], C(O) superficial complexes [8], basic sites in the basal plane [9,10], benzylic bonding at the edge of hexagonal planes [11], etc.

The active sites concentration was associated with the active surface area (ASA) of char. However, there is no universal method for the measurement of ASA. The technique initially proposed by Walker and co-workers [12] and Laine [13] was one of the most common methods. This procedure uses O$_2$ as adsorbate. The sample is desorbed at 950°C in an inert atmosphere. Then the temperature is lowered to 300°C where the sample is exposed to O$_2$. The amount of O$_2$ chemisorbed is determined by temperature programmed desorption of CO and CO$_2$ up to 800°C. Other methods for determining the chemisorption of chars can be considered as variations of this method. These variations include: (i) different ways for estimating the amount of O$_2$ chemisorbed, for instance, gravimetric measurements of weight gain after exposure of the sample to O$_2$ at 200°C [14,15]. (ii) Modification of the adsorbate, for example CO$_2$ [16–18], hydrogen and C$_1$–C$_4$ hydrocarbons [19].

The value of the active surface area determined in this way is a good index of reactivity for the gasification of highly ordered graphite but for carbons which at molecular level are highly disordered, such as chars, it has found limited success [9,10]. One of the reasons for this behaviour is that oxygen adsorption at low temperatures (200°C–300°C) accounts for the total amount of active sites, and not only for the reactive ones. Transient kinetics methods have tried to overcome this weak point. Moulijn and Kapteijn [1] have used this technique for a better understanding of the gasification reaction mechanism. Jiang and Radovic [2] proposed the reactive surface area (RSA) based on the transient kinetics technique and successfully showed its proportionality to CO$_2$ gasification rate even at different stages of gasification. In these transient kinetics methods, the char sample is gasified up to a certain conversion, the

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Table 1
Ultimate and proximate analysis of amagá coal

Ultimate analysis (wt% daf)				Proximate analysis		
C	H	N	O (diff)	Moisture (%)	Ash (%db)	VM[a] (%daf)
74.9	5.5	1.5	18.1	7.6	3.4	49.3

[a] VM: volatile matter.

reactive gas is then changed either to an inert gas or to an isotope of the same reactive substance. The concentration of CO_2 and CO after the change is monitored, normally by a mass spectrometer and its value is considered as the amount of active sites in the instant when the reaction was stopped.

More recently, Miura and Nakagawa [20] proposed a square-input response (SIR) method as a modification of the transient kinetic. In SIR, the reactive isotope is changed to a different one of the same reactive substance but only for a predetermined time interval. This, as the authors suggested, enables a better understanding of the reaction mechanism.

Along with the method by which active sites are determined, it is important to keep in mind that CO_2 partial pressure is a factor strongly related to active sites. Traditionally [21–23], the CO_2 gasification reaction was considered as first order at low pressures up to atmospheric pressure, but it approaches zero order as the pressure rises. Different reaction orders, for instance 0.34 [24] and 0.60 [3], were found for this reaction at pressures near 1 atm or below. Zhang and Calo [3] state that this behaviour of CO_2 gasification reaction with partial pressure can be explained by a departure from desorption rate-control as the CO_2 partial pressure decreases from 1 atm.

In this work, the char active surface area is characterized using CO_2 chemisorption by an experimental method that can differentiate between strong and weak CO_2 chemisorption at 300°C. The strong chemisorption is proposed as a more reliable value of the active surface area, and is used to normalize char gasification reactivity in CO_2 at 800°C. The results show that strong chemisorption is because of the presence of inorganic components in the char and that the higher the amount of strong chemisorption, higher the gasification reactivity.

2. Experimental

Amagá coal less than 149 μm in particle size was used as the initial material to obtain the char used. The analytical data is shown in Table 1. The char was produced using fresh coal (as-received), demineralized coal and metal loaded coal samples. Demineralization was carried out with HCl and HF under nitrogen atmosphere, as described elsewhere [25]. Potassium addition was carried out by KOH ion exchange for 1 h, followed by washing with deionized water to a pH of 7, then the sample was dried under vacuum.

Fe was added by evaporation of an iron nitrate solution in ethanol, the impregnated coal was dried to constant weight under vacuum. Pyrolysis of the fresh, demineralized and metal loaded samples was carried out in a horizontal furnace in a quartz tube reactor under high purity N_2 flow. The samples were heated at 18°C/min up to 800°C and held at this temperature for 30 min. After pyrolysis the reactor was allowed to cool down to room temperature under nitrogen flow to prevent oxidation of the char.

Gasification reactions were carried out using a thermogravimetric balance. Approximately 20 mg of char was heated from room temperature to 800°C at 35°C/min under N_2 atmosphere. Then, the inlet gas was switched to CO_2 and the temperature held at 800°C for 60 min. The weight loss was recorded as function of time. Repeatability of the experiments was ± 3%.

The CO_2 chemisorption procedure that follows is oriented to determine the existence of more than one kind of chemisorbed species by evaluation of the reversible or irreversible nature of the CO_2 chemisorbed at 300°C. A conventional volumetric chemisorption unit was used. Before obtaining the weight of the sample, the char was outgassed for 24 h at 300°C at a residual pressure of 5×10^{-3} mmHg N_2. Then, heated up to 800°C at a pressure of 1.5×10^{-5} mmHg He for 30 min, in order to remove any oxygen that could have been adsorbed during handling of the sample after pyrolysis. It was then cooled down to 300°C and the CO_2 chemisorption experiment initiated. The CO_2 chemisorbed volume was recorded at the following equilibrium pressures: 100, 200, 400 and 600 mmHg. Equilibrium was considered to have been reached when the pressure change per equilibrium time interval (first derivative) was less than 0.01% of the average pressure during the interval. Each interval involved 11 pressure measurements with a lapse of 20 s between each measurement. After this first chemisorption experiment, the sample was outgassed again at 300°C for 120 min at 1.5×10^{-5} mmHg to remove any weakly chemisorbed CO_2 molecules. Then the CO_2 adsorption procedure was repeated.

In this way, two sets of chemisorption data were obtained for each sample, the first one gave the total chemisorbed CO_2 (strong and weak chemisorption) and the second one provided the weakly chemisorbed CO_2 at 300°C. The difference between the data is the amount of strongly chemisorbed CO_2 at that temperature. A new active surface area is defined as the area covered by this strongly chemisorbed CO_2 at 300°C. A value of 0.17 nm^2 was taken as the area of the CO_2 molecule, and it is assumed that chemisorption of
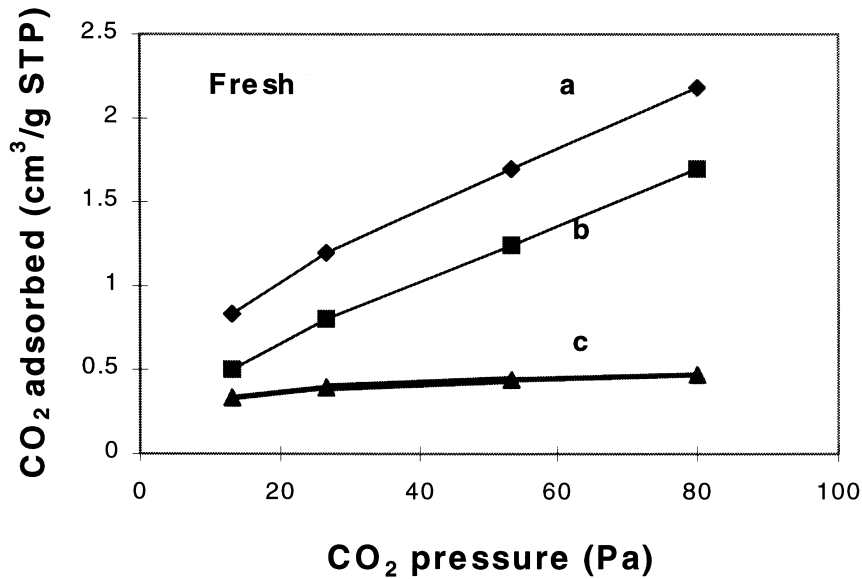
Fig. 1. CO_2 adsorption at 573 K by char obtained from fresh (as received) coal. (a) Total CO_2 chemisorbed; (b) weak chemisorption at 573 K; (c) strong chemisorption at 573 K.

CO_2 under this experimental condition is made by different surface complexes in the char structure without bond scission of the CO_2 molecule.

3. Results and discussion

The Amagá coal is a low rank coal with a mineral matter composed mainly of carbonates (calcite, siderite and dolomite) and sulphates (bassanite) [26]. During the char production some of the minerals could be transformed into the corresponding oxides, which depending on the metal could remain as the oxide, for example CaO, or could be reduced to the metallic form as is the case of potassium. Both species, CaO and K, are known to act as catalysts for the CO_2 gasification of char [17,27,28].

3.1. Char characterization

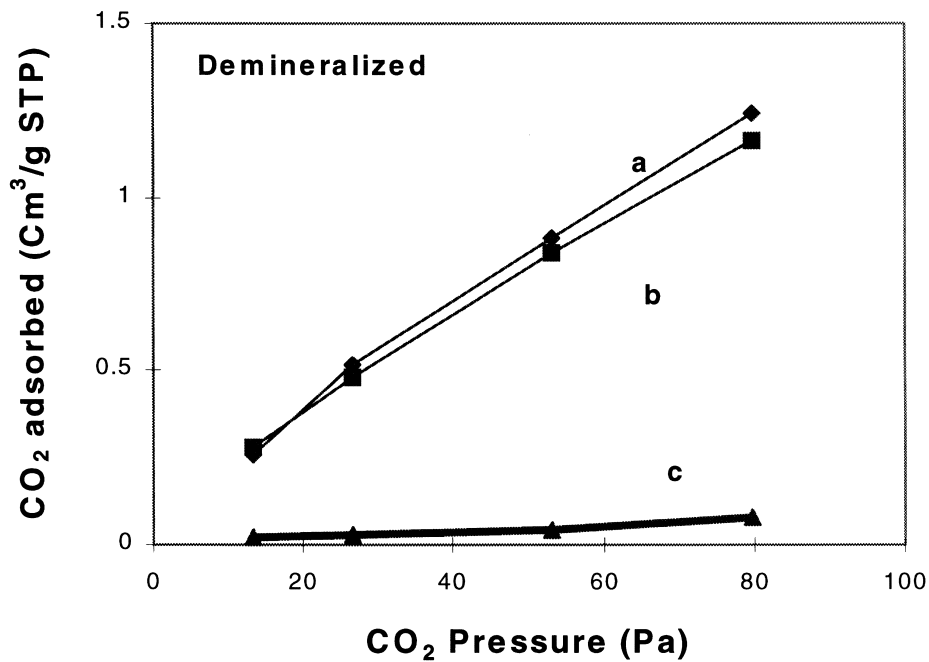Chemical adsorption of a gas on the surface of a

Fig. 2. CO_2 adsorption at 573 K by char obtained from demineralized coal. (a) Total CO_2 chemisorbed; (b) weak chemisorption at 573 K; (c) strong chemisorption at 573 K.
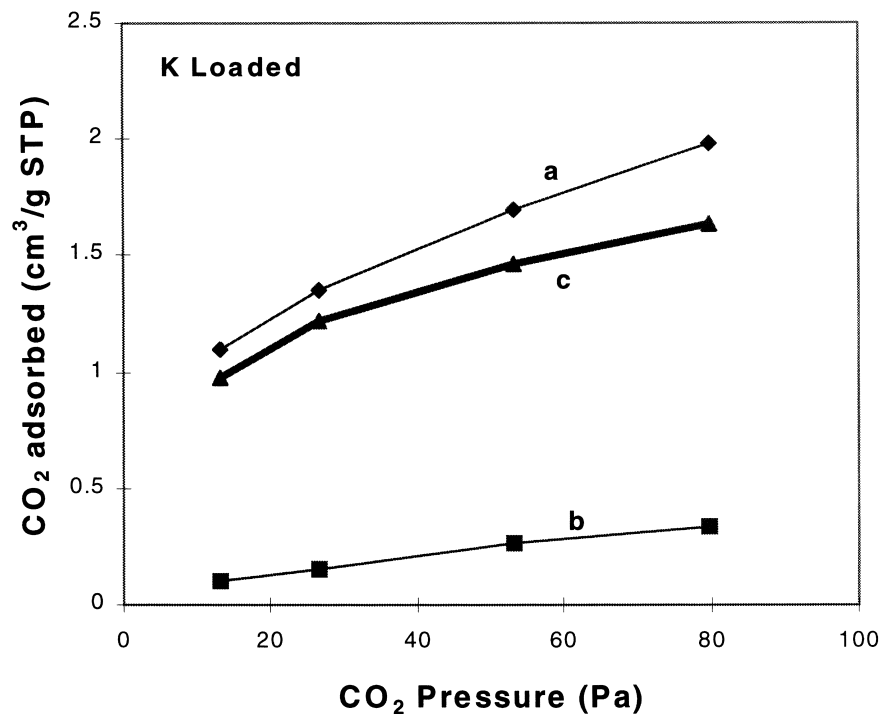
Fig. 3. CO_2 adsorption at 573 K by char obtained from coal loaded with K. (a) Total CO_2 chemisorbed; (b) weak chemisorption at 573 K; (c) strong chemisorption at 573 K.

solid is a process that takes place usually at temperatures higher than the critical temperature of the gas, therefore, chemisorption involves a much stronger solid-gas interaction than the physical adsorption, which is a 100% reversible process. The CO_2 adsorption experiments of the present research were carried out at 300°C, which is a temperature well above the critical temperature [29] of CO_2, 31°C, therefore all the
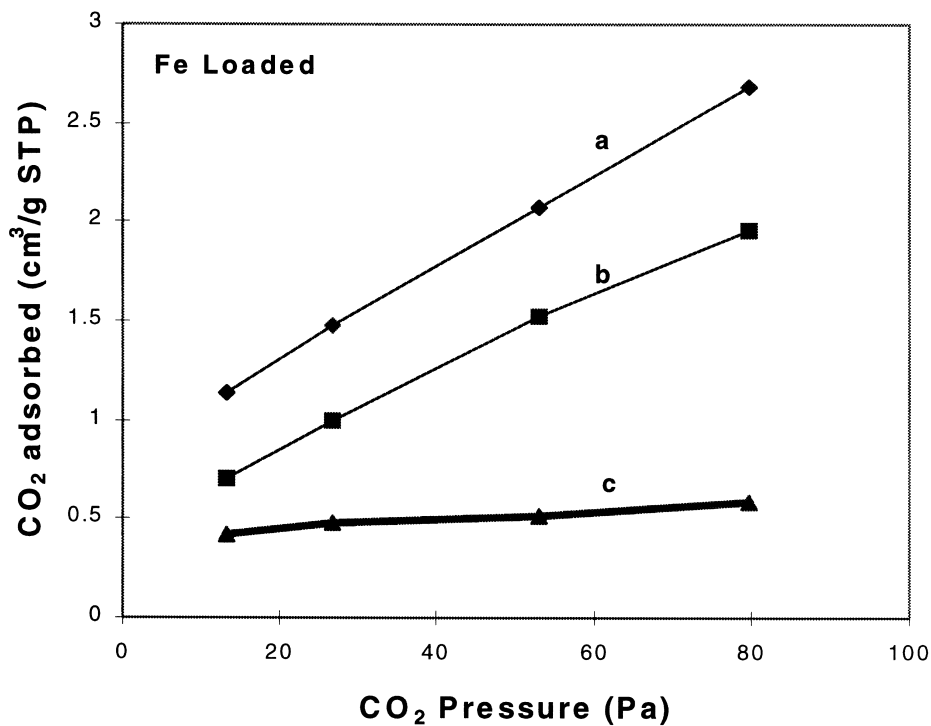

Fig. 4. CO_2 adsorption at 573 K by char obtained from coal loaded with Fe. (a) Total CO_2 chemisorbed; (b) weak chemisorption at 573 K; (c) strong chemisorption at 573 K.
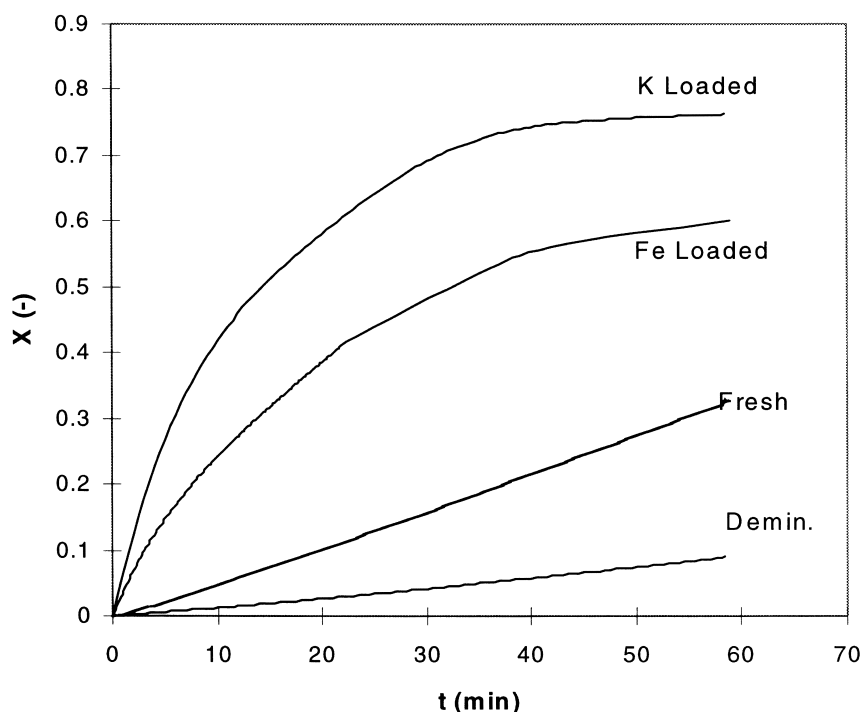
Fig. 5. Reaction profiles of CO_2 gasification of Amaga chars at 1073 K. Chars obtained by pyrolysis at 1073 K during 30 min under high purity nitrogen.

adsorption data are considered to be a result of chemisorption of CO_2.

Fig. 1 shows the results of the CO_2 chemisorption on the char prepared with the fresh coal sample. The data of curve (a) represent the CO_2 chemisorbed during the first adsorption experiment. The data of curve (b) represent the CO_2 chemisorbed during the second part of the experiment. And the data of curve (c) are the difference between the curves (a) and (b). The results show that there are two types of chemisorbed CO_2 on this char. As the (b) data represent the amount of CO_2 that is re-chemisorbed on the char, it represents the quantity of weakly chemisorbed CO_2 ("reversible chemisorbed" CO_2). The amount of CO_2 that is not removed during the outgassing of the sample at 300°C is assumed to be the strongly chemisorbed fraction of CO_2 ("irreversible chemisorbed" CO_2) and is shown in curve (c). The chemisorption data for the char prepared with the demineralized coal sample is shown in Fig. 2. The meaning of the curves is the same as that given for Fig. 1. It is noteworthy that the first (curve a) and the second chemisorption (curve b) are very similar, and therefore the difference between both curves (curve c) is almost a flat line along the x-axis. Comparision of the results in Figs. 1 and 2 shows that the mineral matter of this char is responsible for the strong chemisorption of CO_2 at 300°C and also that the organic part of the char is probably responsible for the weakly chemisorbed CO_2.

The data of the potassium loaded char (3.6% K) is presented in Fig. 3. Comparison of Fig. 3 with Figs.1 and 2, shows, that strong CO_2 chemisorption is very high while the weak chemisorption is very low. This effect is caused by the ability of potassium to strongly withhold the CO_2 molecule even at a temperature as low as 300°C. In the case of the Fe loaded char (20 wt% Fe), the amount of weakly chemisorbed CO_2 was the highest of all the samples used in the present research (Fig. 4). However, the amount of strongly chemisorbed CO_2 was relatively small. No further characterization of these samples was carried out, and so it is not possible to comment how the state of the metal (agglomeration, annealing, etc.) affected the results.

The char from the fresh coal sample (Fig. 1) and the potassium loaded char (Fig. 3) exhibit both strong, curve (c), and weak, curve (b), chemisorption of CO_2. Comparison of the data in the two figures show that the total chemisorption is very close in both chars, although the relation between the strong and weak chemisorption is inverted. In the char from fresh coal the irreversible adsorption is relatively small and is because of the mineral matter, while in the char loaded with K irreversible adsorption is predominant. These observations could be interpreted as if the sites where K is located after the pyrolysis at 800°C and the sites for reversible adsorption of CO_2 of the fresh coal char at 300°C are related to each other, perhaps associated to the oxygen functionalities in the char.

A clear dependence of the volume of CO_2 chemisorbed with pressure was observed for pressures below 1 atm, this being more significant in the metal loaded samples. This behaviour could be representative of the highly heterogeneous nature of the active sites in the char. High amounts of low temperature complexes produce a stronger effect of the pressure as the formation rate of surface complexes could be more comparable to the desorption rates. Limitations of the

Table 2
Reactivity for CO_2 char gasification at 800°C. Active surface area from CO_2 strong chemisorption at $P = 600$ mmHg CO_2

Sample	Reactivity $R \times 10^3$ (min^{-1})	ASA m^2/g $\pm$ 10%	Normalized reactivity[a] $\times 10^3$ (min^{-1}(m^2/g))
Demineralized	0.8	0.3	2.7
Fresh	4.7	2.2	2.1
Fe loaded	29.6	3.3	9.0
K loaded	69.7	7.5	9.3

[a] Normalized reactivity: R/ASA.

equipment prevented evaluation of the chemisorption at pressures higher that 700 mmHg. Therefore, the saturation pressure of the samples could not be determined.

3.2. Gasification in CO_2

Gasification profiles of the samples are shown in Fig. 5. As expected the sample loaded with potassium showed the highest reactivity and the demineralized char the lowest. It can be observed that the mineral matter of Amagá coal has some catalytic effect in the gasification reaction with CO_2. As the low conversion shown by the fresh and demineralized samples, char reactivity was calculated as the initial slope of the curve of conversion against time. Mechanistic aspects of the Fe and K catalysed CO_2 char gasification are discussed elsewhere [1,30].

Char reactivity, ASA determined from the amount of strongly chemisorbed CO_2 at 600 mmHg and normalized reactivity for the different samples are presented in Table 2. As shown, there is no strong CO_2 chemisorption in the char of the demineralized sample under the experimental conditions described before. This sample had low reactivity in gasification. The addition of potassium to the as-received sample gave a char whose reactivity increased by a factor of 15 (4.65–69.7 min^{-1}) compared to the char without any potassium. When char reactivity is normalized considering the active surface area, the ratio of the reactivity of char prepared from fresh coal to the catalyst loaded char is reduced from 15.0 to 4.5. This value is the ratio of the normalized reactivity between the char loaded with K and the fresh coal char. This factor is in the range of data previously reported [2,15].

It should also be considered that strong chemisorption of CO_2 as determined at 300°C by volumetric analysis accounts for the total amount of CO_2 irreversibly adsorbed, this being the CO_2 which is forming any kind of complex in the char. In contrast, temperature programmed desorption titrates stable carbon–oxygen complexes from 300°C up to 800°C and by registration of the CO and CO_2 evolved, considers the amount of carbon dioxide forming complexes which are more likely to be involved in the gasification reaction. The transient kinetics methods consider those active sites that are becoming part of the gasification reaction. Different results appear possible for each method.

4. Conclusions

The chemisorption method here described differentiates two types of CO_2 chemisorption sites at 300°C on a char. One is identified as strong chemisorption site which is related to the metals loaded on the char and the other a weak chemisorption site associated with the organic structure of the char. It was found that CO_2 chemisorption on the metal loaded char depends on the pressure of the analysis, there is no clear explanation for this finding, although it was suggested [3] that this tendency can be caused by an increase in low temperature complexes in the char.

The active surface area calculated from the quantity of CO_2 strongly chemisorbed allowed the normalization of the increased gasification rate for char loaded with K, to a factor of 4.5. This reduction as well as the fact that the less reactive char had the smallest amount of strong chemisorption imply that this method can be proposed for normalizing the gasification reactivity of different coals.

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