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# Catalysis and compensation effect of $K_2CO_3$ in low-rank coal – $CO_2$ gasification

**Research Article**

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**Abstract:** The $CO_2$ gasification of a low rank coal catalysed by $K_2CO_3$ was studied, at 700 – 950°C and 1 atm. A two level full factorial design revealed that the gasification reaction was sensitive to the solid residence time, reaction temperature, $CO_2$ partial pressure and catalyst load. $K_2CO_3$ was an efficient catalyst at all temperatures studied, particularly during the second stage when the Boudouard reaction dominates. The gasification rate was increased continuously with increasing catalyst load up to a load of ~20% w/w $K_2CO_3$ concentration, following a sigmoid curve. Above this point, limited catalytic effect was observed, possibly due to the saturation of the lignite surface by $K^+$. A correlation was found to exist between the catalytic gasification rate and the Alkali Index, which increased with the impregnation of the inorganic $K_2CO_3$ salt. When $K_2CO_3$ load increased, the Arrhenius parameters, $E$ and $k_0$, increased simultaneously exhibiting a compensation effect. The isokinetic temperature was found about 600 to 650°C corresponding to the minimum temperature required for the formation of catalytic active intermediates. At temperatures studied, the catalytic active intermediates seemed to be always present and the catalysis progresses unhindered due to the redox cycle, resulting in high rates and conversion.

**Keywords:** *Low rank coal • Gasification • Catalysis • Compensation*



## 1. Introduction

Pulverised coal is a major energy source for electricity generation world-wide (*i.e.*, China, India, Germany, Greece etc), and the current EU energy policy recognizes the community coal as a strategic source enabling the security of the energy supply. In the Greek energy system low rank coal (Greek lignite) poses a special place, since it is the most important indigenous energy source and thus, the main fuel for electricity generation. However, the utilization of coal, especially of low rank, entails increased environmental risks due to air pollutant and $CO_2$ emissions and it implies the necessity to investigate the applicability of alternative, more efficient and environmentally sound, technologies. Gasification has emerged as a cleaner and more efficient way for the production of energy [1,2], since it provides the possibility of polygeneration and simultaneous $CO_2$ sequestration. In particular, $CO_2$ gasification offers the advantage of upgrading an environmentally detrimental gas, thus, a gas that is in compliance with the $CO_2$ mitigation policies. However, the application of such modern technologies (*i.e.,* Integrated Gasification Combined Cycle) is linked with the achievement of efficient coal gasification at reduced temperatures and pressures. Therefore, the study of catalytic coal gasification is an essential feature to allow understanding of the the reaction mechanism and kinetics. It is also important for sizing gasifiers.

The factors affecting the catalytic gasification of carbonaceous materials were extensively studied in recent years [3-6]. Gallagher and Harker [7], and Figueiredo *et al*. [8] found that Ni and Co are better catalysts than Fe in the $CO_2$ gasification of char. Ross and Fong [9] have reported that $K_2CO_3$ promotes the steam gasification of char, DeGroot and Richards [10] observed that chars containing ion-exchanged Co and Ca gasified in $CO_2$ much faster than corresponding Na-, K-, and Mg- exchanged samples. The most effective catalysts in coal gasification by $CO_2$ and steam are alkali metal salts such as alkali carbonates, oxides,

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hydroxides, chlorides [11-13] and potassium, the last showing the best catalytic activity, among alkali metals [14,15]. It is also well established [16-18] that certain highly dispersed metals composed of mineral matter in the coal affect the reactivity, especially for the lower-rank coals, by catalysing gasification reaction. It has been proposed that "alkali index" [16,18,19] could quantify the catalytic effect of the inherent inorganic constituents of coals. In addition, a correlation has been found between the alkali index and the $CO_2$ gasification rate.

An oxygen transfer mechanism, initially proposed by McKee *et al.* [11,20], is generally accepted to take place during the potassium-catalysed coal-$CO_2$ gasification, and, due to contradictory views and results several variations have been introduced [5,21-26], particularly regarding the type and the nature of the catalytic active sites. Several researchers [27-31] postulated the formation of active intermediates (intercalates) that were reactive surface complexes of K, O and C, such as $-CO_2K$, −COK and KO− with varying oxygen stoichiometry. It was postulated that they were present even in the absence of oxygen from the coal structure. In parallel, Chen and Yang [32] also noted the formation of micro-channels on the basal plane of graphite during alkali and alkaline earth catalysed gasification.

Based on the above results, previous researchers [33-36] reported the existence of a certain dependency between the Arrhenius parameters, that consist of the simultaneous change (increase or decrease) of the pre-exponential factor *($k_0$)* and the activation energy *(E)*. This, so called, "compensation effect" has been reported in several heterogeneous catalytic reactions [37,38], the pyrolysis of coal, biomass, wood or residues and carbonaceous material [33,39,40] and the degradation of polymer matrix composites [41,42]. The existence of the compensation phenomenon was not generally accepted, since it was often considered a statistical deviation (an experimental artifact) due to extrapolation necessary to calculate the $k_0$ values. However, previous studies [37,38,43,44] proved its significance and, based on that, solid theoretical explanations for the compensation phenomenon were proposed [35,36,45], considering a number of physico-chemical parameters, *i.e.*, structural or surface differences, change in the porosity, concentration and mobility of active species, partial pressure of gas, bond energy among different metals and ligands, defect concentration, chemical composition and impurities as responsible for that. Other views, such as the enthalpy-entropy relationships, were also proposed [36,41].

In coal gasification reactions, it is generally observed that the effect of catalyst load shows two trends, *i.e.*, simultaneous variations in ($k_0$) and ($E$) to the same direction (normal compensation behaviour) [46] or constant activation energy and increased pre-exponential factor, ($k_0$), (no compensation effect) [47]. The latter, observed in some cases, was attributed to the enormous increase of the active sites available for gasification. Feats *et al*. [48] studied the Fe-catalysed gasification of graphite by $O_2$ and of humic coke by $CO_2$ and developed a phenomenological correlation to interpret data of catalytic gasification of coal, while Cremer [49] investigated the general conditions that facilitate the compensation phenomenon. Feistel *et al.* [50] observed compensation effect in potassium-catalysed gasification of various coals with steam, while Marsh *et al*. [46] studied the catalytic $CO_2$ gasification of coals and observed simultaneous increase of $k_0$ and E. Heuchamps and Duval [51] observed compensation with a graphite-air system, which was attributed to structural and surface differences. The compensation phenomenon in the $CO_2$ gasification of chars with catalysts sodium lingo-sulphate and ferric nitrate was studied by Dhupe *et al*. [52].The $CO_2$ gasification of a gas-coal char catalysed by $Na_2CO_3$ and $K_2CO_3$ was studied by Li and Cheng [3] and in these catalytic gasification reactions a compensation effect appeared.

Although there was an extended work performed in the subject matter , there are still uncertainties regarding the principles and the mechanism of the catalysis. The inherent heterogeneity of the coals, the presence of various amounts of hydrogen and of oxygen functional groups, and the possible interaction between the catalyst and the coal ash accentuate the uncertainties. Furthermore, very limited work is available with respect to the correlation between the alkali index and the gasification rate and the compensation phenomena. In this work, the effect of $K_2CO_3$ loading on the rate of the char-$CO_2$ reaction and on the kinetic parameters was studied, aiming to determine the change in rate during gasification and it was interpreted in terms of the compensation effect. Alkali index was elaborated to quantify the combined catalytic effect of both, the inherent inorganic constituents of coal and the added inorganic catalyst ($K_2CO_3$).

## 2. Experimental procedure

In this work, a Greek lignite from Ptolemais reserve was used as a starting material. Coal samples were kept sealed with their moisture and in the absence of air to avoid any weathering. $K_2CO_3$ was used as catalyst for the gasification tests and its addition was performed according to the impregnation procedure previously developed [53]. Coal samples were impregnated with

**Table 1.** Conditions for the factorial design experiments to study the coal–$CO_2$ gasification.

| a/a | Parameter | Value | | |
|---|---|---|---|---|
| | | Lower limit (-) | Upper limit (+) | Intermediate* |
| 1 | Temperature, °C | 750 | 900 | 825 |
| 2 | Time, min | 5 | 20 | 12.5 |
| 3 | Catalyst load, % w/w | 10 | 25 | 17.5 |
| 4 | $CO_2$ partial pressure, atm | 0.1 | 1 | 0.55 |
| 5 | Particle size, $\mu$m | 150 – 250 | 355 – 500 | 250 – 355 |

** conditions of repeat tests*

**Table 2.** Experimental conditions for the catalytic coal – $CO_2$ gasification tests.

| a/a | Parameter | Value |
|---|---|---|
| 1 | Temperature, °C | 700 – 950 |
| 2 | Time, min | up to 50 |
| 3 | Catalyst load, % w/w | 0 – 25 |
| 4 | $CO_2$ partial pressure, atm | 1.0 |
| 5 | Particle size, $\mu$m | 150 – 250 |

1 M aqueous solution of $K_2CO_3$ and, by varying the amount of the impregnating solution, the catalyst load was altered, between 5 and 25% w/w $K_2CO_3$. The coal–solution slurry, thus created, was placed under vacuum (250 mbar) for one hour. Vacuum enhances catalyst impregnation by removing air from the coal pores, hence allowing easier solution entrance into the micropores. One hour was found to be sufficient for the adsorbed metal ($K^+$) ions to reach a constant value. Samples were subsequently dried for 24 hrs at 105°C in a $N_2$ atmosphere to prevent lignite oxidation.The desired granulometries were obtained by grinding and sieving.

Proximate, ultimate and ash analyses, of both, the raw and catalyst impregnated samples, were performed according to the appropriate ASTM Standard Methods. Since the amount of chemisorbed catalyst in the coal mass plays the most important role in the catalysis, by creating active sites in the coal matrix [53], it is important to distinguish between adsorbed and physically mixed catalyst. Aiming at the above, a pre-weighted amount of dried, impregnated sample was extracted with distilled water and centrifuged at 2500 rpm for 20 min. Thus, the mixed catalyst was removed in the extract and its $K^+$ concentration was determined by atomic absorption (Perkin Elmer 503AA). The difference between the total impregnated catalyst and the extracted amount gave the amount of adsorbed $K^+$ cations in the coal matrix. Samples of initial granulometry 150 – 250 μm were used for the bulk of the gasification tests. To account for the possible effects of the initial particle size on the amount of chemisorbed $K^+$, larger initial granulometries were also used to prepare impregnated coal samples.

Gasification tests were conducted in a fixed bed reactor, which was equipped with the proper gas and solids feeding controls and with product collection and analyses devices. A detailed description of the test unit is given elsewhere [16]. The main characteristic of this set-up is the U-shape reactor design, which permits rapid cooling (quenching) of the reactor. In that respect, the gasification reaction could be interrupted at any desirable time. Gaseous products were collected in samples bags and analysed by a GC equipped with FID and TCD detectors. The coal gasification is affected by the reaction temperature and solid residence time, the partial pressure of the reactive gasifying medium and the coal particle size. In catalysed gasification the catalyst load plays also an important role. Hence, a large number of experimental tests are necessary. A two-level full factorial design [54] was used to reduce the large number of experimental tests required to fully investigate the above five parameters affecting coal – $CO_2$ gasification.

In this work an ($2^5$) experimental design matrix was formed, according to the two level full factorial design methodology [54]. The experimental conditions for the initial screening of the affecting parameters are given in Table 1. The repeatability of the gasification tests was evaluated by performing four repeat tests at the intermediate conditions that correspond to the upper and the lower limits of the factorial design tests, Table 1. Following the initial screening of the affecting parameters with the factorial design tests, catalysed gasification tests were conducted isothermally in a $CO_2$ atmosphere, in the temperature range 700 – 950°C, at ambient pressure, 1 atm. Reaction time was extended up to 50 min and samples of about ~1 g and of 150 – 250 μm particle diameter were used to exclude any internal or external mass or heat transfer limitations, and the catalyst load varied up to 25% w/w $K_2CO_3$. The experimental conditions are summarised in Table 2.

**Table 3.** Proximate [ASTM D 5142-90] and ultimate [ASTM D 5373-93] analyses of raw and catalyst impregnated coal samples.

| (a) Proximate | | (b) Ultimate | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Parameter | (% w/w) | Element | Catalyst load (% w/w) | | | | | |
| | | | 0 | 5 | 10 | 15 | 20 | 25 |
| Volatiles | 47.17 | C | 47.16 | 44.80 | 42.44 | 40.09 | 37.73 | 35.37 |
| Fixed carbon | 36.23 | H | 4.68 | 4.45 | 4.21 | 3.98 | 3.74 | 3.51 |
| Ash | 16.6 | N | 1.27 | 1.21 | 1.14 | 1.08 | 1.02 | 0.95 |
| $CO_2$ | 0.87 | S | 0.99 | 0.94 | 0.89 | 0.84 | 0.79 | 0.74 |
| HHV (kcal/kg) | 4393 | O* | 29.3 | 27.83 | 26.37 | 24.90 | 23.44 | 21.98 |
| | | Catalyst | 0.00 | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
| | | Ash | 16.6 | 15.77 | 14.94 | 14.11 | 13.28 | 12.45 |
| | | $K^+$ / C | 0.001 | 0.019 | 0.041 | 0.065 | 0.092 | 0.123 |

** by subtraction*

**Table 4.** Elemental [ASTM D 6349-98] analyses of ashes and alkali index of raw and catalyst impregnated coal samples.

| Compound | Catalyst load (% w/w) | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 |
| **$SiO_2$** | 27.80 | 22.61 | 18.93 | 15.99 | 13.63 | 11.68 |
| **$Al_2O_3$** | 14.01 | 11.41 | 9.53 | 8.08 | 6.87 | 5.87 |
| **$Fe_2O_3$** | 7.99 | 6.51 | 5.43 | 4.61 | 3.92 | 3.36 |
| **CaO** | 33.10 | 26.95 | 22.57 | 19.06 | 16.24 | 13.90 |
| **MgO** | 1.26 | 1.03 | 0.86 | 0.73 | 0.62 | 0.54 |
| **$SO_3$** | 17.07 | 13.89 | 11.63 | 9.83 | 8.39 | 7.19 |
| **$Na_2O$** | 0.6 | 0.4 | 0.3 | 0.2 | 0.2 | 0.1 |
| **$K_2O$** | 0.6 | 17.61 | 31.06 | 41.7 | 50.33 | 57.47 |
| **Alkali index** | 0.19 | 28.85 | 41.96 | 58.48 | 79.04 | 104.51 |

# 3. Results and discussion

## 3.1. Raw materials characterisation

Proximate, ultimate and ash analyses of the coal used are given in Tables 3 and 4. Greek lignite from Ptolemais reserve is characterised by its high moisture, high ash and high volatile content, and also has a high oxygen and low sulphur content, Table 3.

Ptolemais lignite has increased inorganic phase, which is characterized by its high calcium and silica content, Table 4. Potassium was also found in small quantities in the ash of the raw coal samples, resulting in a very low (nearly zero) initial $K^+$ / C g-atoms ratio. The addition of $K_2CO_3$ increased the $K^+$ / C ratio of the catalytic samples by up to two orders of magnitude, Table 4.

## 3.2. Catalyst impregnation

By varying the amount of the impregnating solution, the catalyst load was altered between 5 and 25% w/w $K_2CO_3$.

The relative amount of chemisorbed $K^+$ varied between 63% and 70%, regardless of the catalyst load, Fig. 1, justifying the efficiency of the impregnation procedure, previously developed, to introduce in the coal matrix similar amounts of catalytically active $K^+$ cations. Therefore, the implemented impregnation conditions facilitated the entrance of the impregnating solution into the micropores. As a result, a uniform distribution of the catalytic active sites inside the coal particles was achieved. Previous studies [53] have shown that the fraction of chemisorbed $K^+$ was the key element in catalysed gasification, due to creating active sites in the coal matrix. As the catalyst load was increased, the fraction of chemisorbed $K^+$ seemed to decrease, Fig. 1, indicating possible saturation [13,54] of the coal surface particularly above 20% w/w $K_2CO_3$, which could be attributed to the fact that $K^+$ was chemisorbed on surface oxygen functional groups that were of limited number [53]. The impregnation of catalyst added on $K^+$ cations in the coal matrix; thus, modifying the K / C ratio. The K / C atomic ratio for all samples (raw and catalyst impregnated) is given in Table 3.

### 3.3. Alkali index

To account for the effect of the inherent inorganic matter, present in the parent coal, as well as, for the effect of the inorganic catalyst load, a generalised index, the alkali index (AI), was elaborated. Alkali index expresses the ratio of the sum of the mole fractions of the basic compounds (CaO, MgO, $Fe_2O_3$, $Na_2O$, $K_2O$) and of the sum of the mole fractions of the acid compounds ($SiO_2$, $Al_2O_3$) in the coal, multiplied by the total catalyst and ash content of the lignite. The alkali index (AI) was calculated for each coal-catalyst sample according to the following equation and are given in Table 4, in an effort to correlate it with the obtained gasification rate experimental results.

$$AI = X_{ash} \frac{\sum_{i=1}^{5} Y_i}{\sum_{j=1}^{2} Y_j} \quad (1)$$

Where AI = alkali index, $X_{ash}$ = ash content, $Y_i$ = mole fractions of the basic compounds (CaO, MgO, $Fe_2O_3$, $Na_2O$, $K_2O$), $Y_j$ = mole fractions of acidic compounds ($SiO_2$, $Al_2O_3$). The externally added K (in the form of $K_2CO_3$) in the impregnated samples was also included in the calculations, resulting in samples of significantly high alkali index values. The calculated alkali index (AI) values for the raw and the catalyst impregnated samples are given in Table 4.

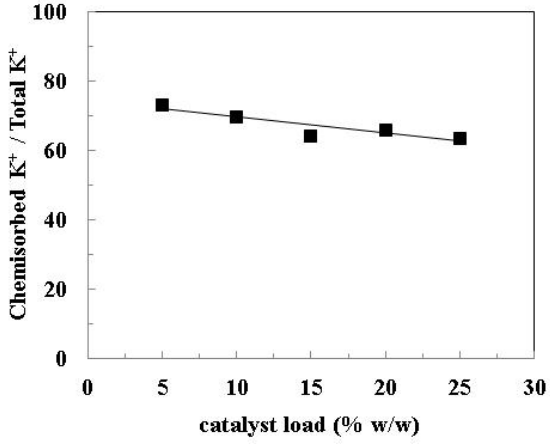
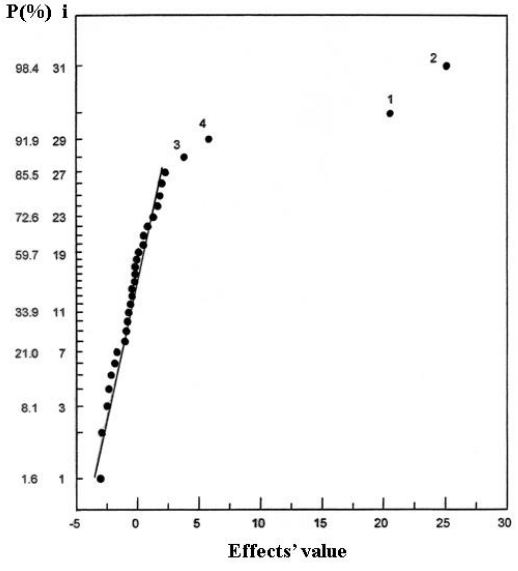



**Figure 1.** Evolution of chemisorbed $K^+$ with the catalyst load.

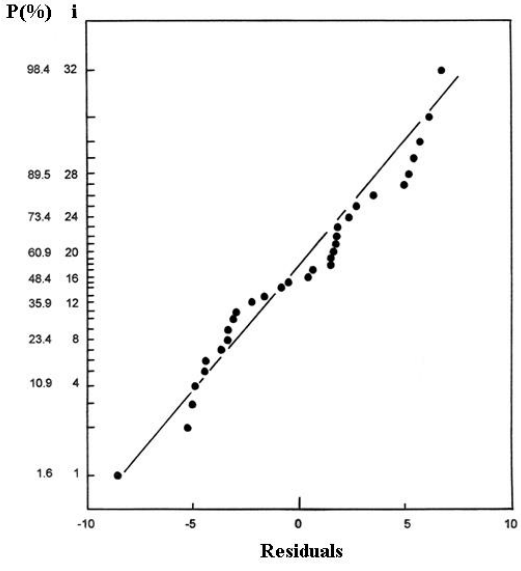
### 3.4. Initial parameters screening

The experimental weight loss (% dacf – dry, ash and catalyst free) values obtained during the isothermal catalytic gasification of coal – $CO_2$ for the initial parameters screening are given in Table 5 and the standard deviation of these results was calculated to be 1.695, indicating a good reproducibility of the gasification experiments. The Yates algorithm [54] was used to calculate the effect of each experimental parameter and of their combinations, and the obtained effect values were linearised by using the normal plot of the effects, Fig. 2. In that plot the effects of the single and of the combined parameters can be divided in two groups: (a) points lying on a straight line in the near zero area and (b) points deviating from the near zero area, Fig. 2.

Points in the first group represent either limited or rather random effects on the gasification weight loss, and could therefore be neglected. In this group belong




(a) normal plot of the effects




(b) normal plot of the residuals

**Figure 2.** Normal plots (a) of the effects and (b) of the residuals in isothermal $CO_2$ gasification of low rank coal (*Vertical axis: P(%): cumulative probability, i: the order number of the effects or the residuals).

**Table 5.** Factorial design matrix ($2^5$) of the affecting parameters and weight loss values (experimental and calculated) during isothermal $CO_2$ gasification of low rank coal.

| a/a | Parameters* | | | | | Weight loss (% w/w dacf) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | $X_{EXP}$ | $X_{CALC}$ | $X_{EXP}$-$X_{CALC}$ | % ($X_{EXP}$-$X_{CALC}$) |
| 1 | - | - | - | - | - | 54.4 | 48.8 | 5.6 | 10.3 |
| 2 | + | - | - | - | - | 72.2 | 69.5 | 2.7 | 3.7 |
| 3 | - | + | - | - | - | 70.6 | 73.9 | -3.3 | -4.7 |
| 4 | + | + | - | - | - | 100.0 | 94.6 | 5.4 | 5.4 |
| 5 | - | - | + | - | - | 51.8 | 52.6 | -0.8 | -1.5 |
| 6 | + | - | + | - | - | 75.2 | 73.3 | 1.9 | 2.5 |
| 7 | - | + | + | - | - | 74.1 | 77.8 | -3.6 | -5.0 |
| 8 | + | + | + | - | - | 100.0 | 98.5 | 1.5 | 1.5 |
| 9 | - | - | - | + | - | 51.6 | 54.6 | -3.0 | -5.8 |
| 10 | + | - | - | + | - | 76.0 | 75.3 | 0.7 | 0.9 |
| 11 | - | + | - | + | - | 78.2 | 79.82 | -1.62 | -2.1 |
| 12 | + | + | - | + | - | 100.0 | 100.52 | -0.52 | -0.5 |
| 13 | - | - | + | + | - | 64.6 | 58.5 | 6.1 | 9.4 |
| 14 | + | - | + | + | - | 84.2 | 79.2 | 5.0 | 5.9 |
| 15 | - | + | + | + | - | 90.4 | 83.7 | 6.7 | 7.4 |
| 16 | + | + | + | + | - | 100.0 | 104.4 | -4.4 | -4.4 |
| 17 | - | - | - | - | + | 46.6 | 48.8 | -2.2 | -4.7 |
| 18 | + | - | - | - | + | 60.9 | 69.5 | -8.6 | -14.1 |
| 19 | - | + | - | - | + | 79.1 | 73.9 | 5.2 | 6.6 |
| 20 | + | + | - | - | + | 98.1 | 94.6 | 3.5 | 3.6 |
| 21 | - | - | + | - | + | 47.4 | 52.6 | -5.2 | -11.0 |
| 22 | + | - | + | - | + | 68.5 | 73.3 | -4.8 | -7.0 |
| 23 | - | + | + | - | + | 79.5 | 77.8 | 1.7 | 2.1 |
| 24 | + | + | + | - | + | 100.0 | 98.5 | 1.5 | 1.5 |
| 25 | - | - | - | + | + | 57.0 | 54.6 | 2.4 | 4.2 |
| 26 | + | - | - | + | + | 77.1 | 75.3 | 1.8 | 2.3 |
| 27 | - | + | - | + | + | 74.9 | 79.8 | -4.9 | -6.5 |
| 28 | + | + | - | + | + | 97.6 | 100.5 | -2.9 | -3.0 |
| 29 | - | - | + | + | + | 55.2 | 58.5 | -3.3 | -6.0 |
| 30 | + | - | + | + | + | 80.9 | 79.2 | 1.7 | 2.1 |
| 31 | - | + | + | + | + | 84.1 | 83.7 | 0.4 | 0.5 |
| 32 | + | + | + | + | + | 100.0 | 104.4 | -4.4 | -4.4 |

** Parameters: (1) Temperature, (2) Solid residence time, (3) % catalyst load, (4) $CO_2$ partial pressure, (5) particle size*

the particle size and the combined effects of all the studied parameters (second or higher order effects).

Therefore, according to the effect values calculated by the Yates algorithm, the single parameters such as temperature (1), residence time (2) catalyst load (3) and $CO_2$ partial pressure (4) strongly affect the $K_2CO_3$ catalysed coal – $CO_2$ gasification reaction and should be investigated further. The relative effects of these parameters are given in Table 6 in a descending order.

Particle size does not affect the reaction, indicating that, in the studied region of granulometries, the coal – $CO_2$ gasification does not suffer from mass transfer limitations. The latter is in agreement with literature results [18] which showed that much larger particle (above 1000 μm) were required to hinder coal – $CO_2$ gasification.

**Table 6.** Enlistment of the effects (as calculated by the Yates algorithm) of the parameters in descending order.

| a/a | Parameter | Effect value |
|---|---|---|
| 1 | Time, min (2) | 25.188 |
| 2 | Temperature, °C, (1) | 20.696 |
| 3 | $CO_2$ partial pressure, atm (4) | 5.846 |
| 4 | Catalyst load, % w/w (3) | 3.848 |

Implicitly, all parameters and their combinations affect the coal – $CO_2$ gasification reaction. However, their effects, *i.e.*, time, temperature, $CO_2$ partial pressure and catalyst load, are one to three orders of magnitude lower and thus, they could be neglected. With respect to the $CO_2$ partial pressure previous studies [52] have shown that its effect became measurable when partial pressures lower than 0.25 atm were used. Therefore, in the following tests when $CO_2$ partial pressures near 1 atm are used, its effect can be neglected.

Based on the Yates algorithm results, the following linear empirical model, describing weight loss during $K_2CO_3$ catalysed coal – $CO_2$ gasification, could be formed, including the above main affecting parameters:

$$Y = 76.57 + 10.35X_1 + 12.59X_2 + 1.93X_3 + 2.94X_4 \quad (2)$$

Where Y = weight loss (% w/w $d_{acf}$), $X_1$ = gasification temperature, $X_2$ = solid residence time, $X_3$ = $K_2CO_3$ load and $X_4$ = $CO_2$ partial pressure. In this empirical model parameters vary linearly within the interval [-1. 1] that correspond to the lower and the upper limits of each parameter given in Table 1. The calculated values of weight loss, according to the above empirical equation (Eq. 2) along with the experimental ones and their residuals are given in Table 5. The normal plot of the residuals is given in Fig. 2b in order to validate the above empirical model. As shown in Fig. 2b the residuals lay on a sigmoid curve rather than on a straight line, indicating a non-linear dependence between the weight loss and the affecting parameters. It should be noted that the two-level full factorial design provides effective correlation when there is a linear dependence between the significant parameters and the measured value.

## 3.5. Catalytic gasification

### 3.5.1. Weight loss

The effect of $K_2CO_3$ addition and its load on organic matter weight loss during coal – $CO_2$ gasification is shown in Fig. 3. Reaction proceeds in two steps, *i.e.*, a devolatilisation (pyrolysis) reaction, and a gasification

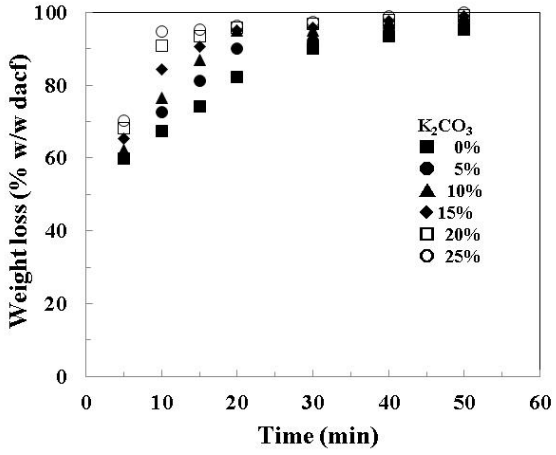



**Figure 3.** Weight loss values during isothermal catalytic coal – $CO_2$ gasification for various catalyst loads at 800°C.

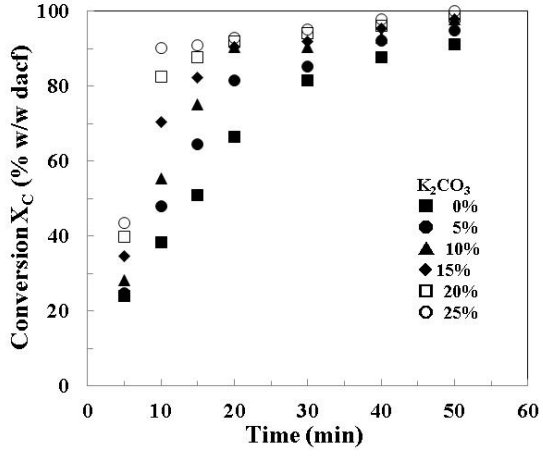



**Figure 4.** Fixed carbon conversion, $X_C$, during isothermal catalytic coal – $CO_2$ gasification for various catalyst loads at 800°C.

step between the reacting medium and the pyrolysed char [47]. In the case of $CO_2$, the heterogeneous reaction between carbon dioxide and the coal char is fast and the two regimes are not easily distinguishable, especially at high catalyst loads and gasification temperatures, Fig. 3.

Thus, at high catalyst loads (15 to 25% w/w) and temperatures (above 850°C) the gasification stage cannot be distinguished from the initial pyrolysis one. At short gasification times, when mainly pyrolysis takes place, the effect of $K_2CO_3$ presence is not clear. Thus, for 5 min residence time, weight loss increased only by about 5% when 10% w/w catalyst was added. Further increase of the catalyst load (up to 25% w/w) still results in a limited increase of weight loss (up to about 15%) for 5 min reaction time, Fig. 3. When the gasification is prolonged, the catalytic action is more distinguishable, since, at that stage the catalysed by the $K_2CO_3$

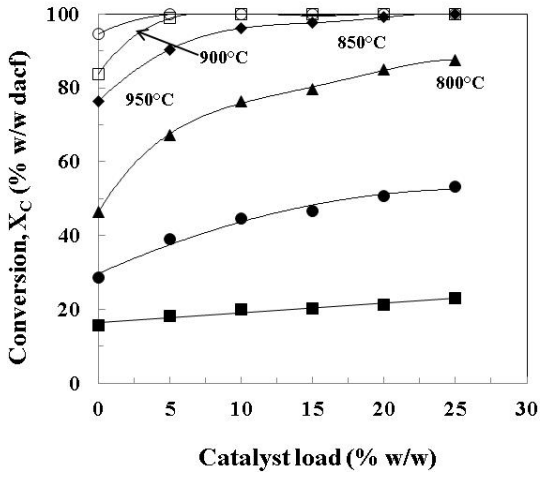



**Figure 5.** Effect of catalyst load on fixed carbon conversion at various temperature and reaction time 10 min.

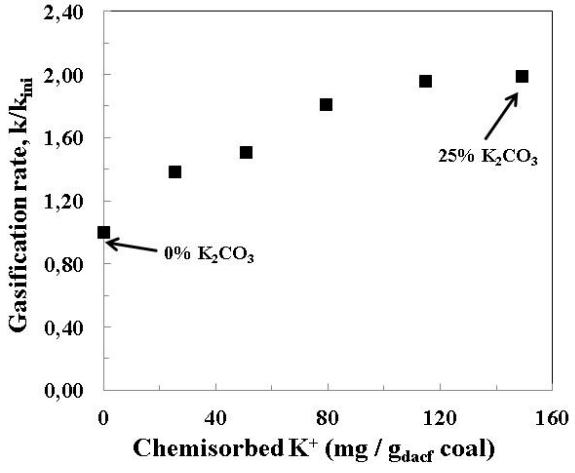



**Figure 6.** Relative specific gasification rate versus chemisorbed $K^+$ (mg/$g_{dacf}$ coal) at 800°C.

heterogeneous Boudouard reaction dominates, Fig. 3. Thus, for 20 min residence time weight loss above 90% w/w dacf was obtained, even for 5% w/w $K_2CO_3$ added, and almost complete conversion is achieved when more than 10% catalyst is added.

To account for the heterogeneous gas – solid reaction, the experimental weight-loss values were converted to fixed carbon conversions, $X_C$. The obtained results are shown in Fig. 4. The presence of $K_2CO_3$ significantly accelerates the gasification reaction, thus, resulting in about 80% fixed carbon conversion at 800°C and 20 min reaction time, even when the catalyst load is limited to 5% w/w, Fig. 4. Further increase of the catalyst load resulted in almost complete fixed carbon conversions in 15 – 20 min reaction time. In order to achieve analogous conversions without catalyst, much longer reaction times (about 30 to 40 min) and higher temperatures (above 900°C) are required [4,6,8]. Therefore, $K_2CO_3$ is an efficient catalyst for the coal – $CO_2$ gasification that reduces the required time and temperature for high conversions.

The strong catalytic action of $K_2CO_3$ is further elucidated in Fig. 5 where the effect of catalyst load on fixed carbon conversion is given,at various temperatures and at 10 min residence time. At low and medium gasification temperatures, fixed carbon conversion increased by about 50%, even for 5% w/w catalyst load, and it was almost doubled when 15% to 20% w/w $K_2CO_3$ was added. This is also true for the very low gasification temperature of 700°C, although the threshold of triggering the Boudouard reaction is about 650°C. At high gasification temperatures (850°C to 950°C) the impact of catalyst load was still visible, albeit masked by the stronger effect of the gasification temperature, Fig. 5.

The volume reaction model [55] was used to calculate the specific gasification rate (k [=] $min^{-1}$) and the relative gasification rate, based on the fixed carbon conversion values. Results show that the addition of $K_2CO_3$ strongly affects the specific gasification rate, Table 7, which is proportional to the amount of the chemisorbed $K^+$, Fig. 6. Even a low load such as 5% w/w resulted in about 40% increase of the gasification rate. Further increase of the catalyst load resulted in continuous increase of the gasification rate, which was almost doubled when 20% w/w $K_2CO_3$ was added, Fig. 6, following a sigmoid curve. Above this point, a limited catalytic effect has been observed and the specific gasification rate appears to reach a plateau, possibly due to the saturation of the lignite surface by $K^+$ cations, in agreement with results by previous researchers also [13,54]. If the chemisorption occurs on specific sites in the coal matrix, the addition of catalyst above a limit (*i.e.*, 20% w/w $K_2CO_3$) is meaningless. As mentioned above, the chemisorbed $K^+$ cations play the major role in catalysed gasification by forming active sites in the coal matrix. The addition of $K_2CO_3$ alters the K / C atomic ratio in the coal samples, Table 3. This ratio was calculated on a dry, ash and catalyst free basis to permit direct comparisons among samples. The relative specific gasification rate increases with the atomic ratio K / C, Table 7, in agreement with other coal studies [54,56].

The catalytic action of the added inorganic salt should not be examined separately from the effect of the inherent inorganic constituents of coal ash. This is particularly true for low rank coals which contain significant percentages of inorganic matter. Since, the addition of the alkaline $K_2CO_3$ alters the amount of the basic compounds of the inorganic phase, the combined effect of catalyst and of the inherent mineral matter in the gasification rate was examined by utilising alkali

**Table 7.** Specific and relative gasification rates at various catalyst loads at 800°C.

| Catalyst load (% w/w $K_2CO_3$) | Atomic ratio (g-atom K / g-atom C) | Chemisorbed $K^+$ (mg $g_{dacf}^{-1}$ coal) | Alkali index AI | Specific gasification rate, k ($min^{-1}$) | Relative gasification rate, $k/k_{ini}$ |
|---|---|---|---|---|---|
| **0** | 0 | 0.0 | 0.19 | $7.45\ 10^{-2}$ | 1.00 |
| **5** | 0.019 | 20.7 | 28.85 | $1.03\ 10^{-1}$ | 1.38 |
| **10** | 0.041 | 39.4 | 41.96 | $1.12\ 10^{-1}$ | 1.64 |
| **15** | 0.065 | 57.3 | 58.48 | $1.35\ 10^{-1}$ | 1.81 |
| **20** | 0.092 | 77.3 | 79.04 | $1.46\ 10^{-1}$ | 1.96 |
| **25** | 0.123 | 97.1 | 104.51 | $1.48\ 10^{-1}$ | 1.99 |

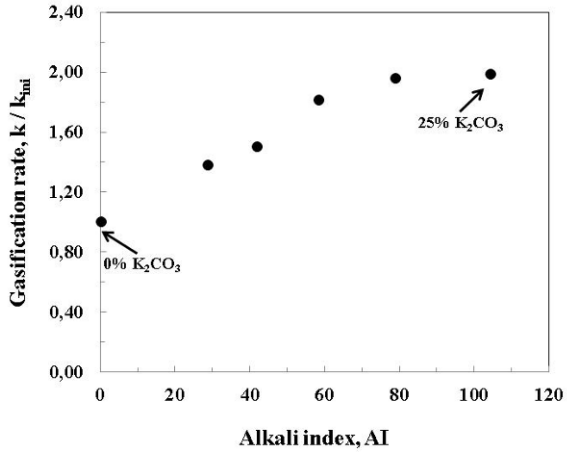



**Figure 7.** Relative specific gasification rate versus alkali index (AI), at 800°C.

index (AI). The calculated Alkali Index values are given in Table 7. Addition of only 5% w/w potassium carbonate results to an alkali index value of about 29, compared with 0.2 for raw lignite, and reaches about 105 for 25% w/w catalyst added.

Skodras *et al*. [16] studied the effect of the inherent inorganic matter during Greek lignite gasification by using samples of different ash qualities and found a reasonably good, almost linear, correlation between the specific $CO_2$ gasification rate and the alkali index, in the studied region of alkali indices. The experimental results of the present study show that the $CO_2$ specific gasification rate increases with the Alkali Index (AI), induced by the addition of $K_2CO_3$ (and the K / C atomic ratio there of), following also a sigmoid curve, Fig. 7.

The above results show that the low rank coal tested quite reactive with $CO_2$ and the addition of catalyst further increases its reactivity. This high reactivity is attributed to its highly disordered crystallographic structure [57]. The coal (lignite) tested is characterised by low carbon content and increased oxygen content, Table 3, and, thus, limited aromatic character. Consequently, higher numbers of oxygen functional groups which enhance the exchange of potassium salts, the formation of catalytic active sites and its propagation (by pitting and channelling) in the carbon matrix [57], are found in the Greek lignite tested. In addition, when catalyst is added, the limited aromatic character of the low rank coal is further relaxed, due to the addition of electrons in the coal matrix.

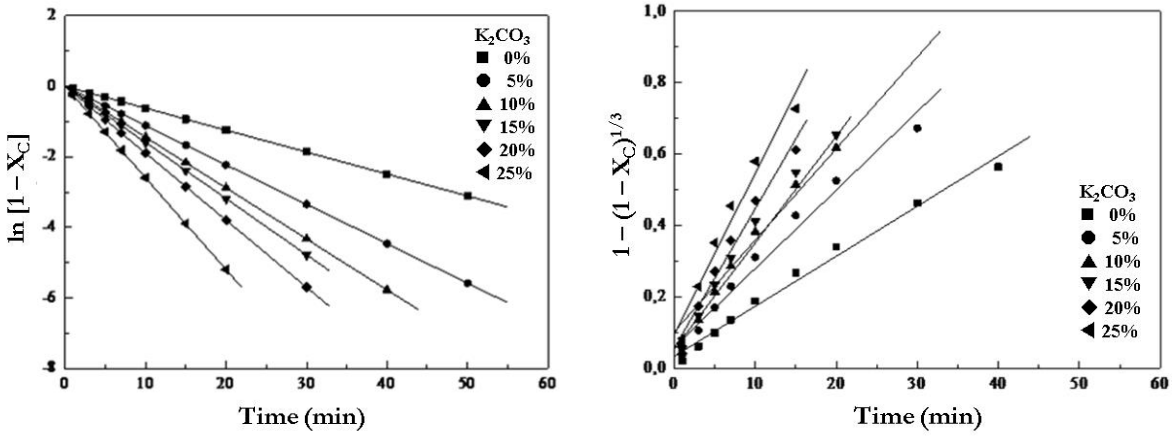
The active sites, where the reaction takes place, are considered to be concentrated at the edges of the basal planes of the coal [57], while the entire basal plane is considered to act as collector of the reacting molecules, subsequently diffusing them towards the edge (active sites) [58]. As discussed previously, catalytic gasification proceeds *via* a redox cycle mechanism, in which the potassium ion transfers oxygen to the carbon, resulting to the formation of two CO molecules and the disruption of the benzoic ring. The alkali is transferred to the next carbon atom and it continues to act as an oxygen carrier and further enhances the gasification reaction [24]. As a result, the gasification reaction is accelerated, the coal structure collapses and gasification reactivity increases.

### 3.5.2. Compensation effect

The volume reaction model (VRM) [55] and the unreacted (or shrinking) core model (UCM) [59], given in Eqs. 3 and 4, were used to estimate the kinetic parameters (pre-exponential factor $k_0$ and activation energy $E$) during catalytic $CO_2$ gasification reaction of Greek coal. Both models comprised relatively simple kinetic equations to describe the reaction rate, while, the Arrhenius equation (Eq. 5) was used for the calculation of the activation energy $E$ and the pre-exponential factor $k_0$.

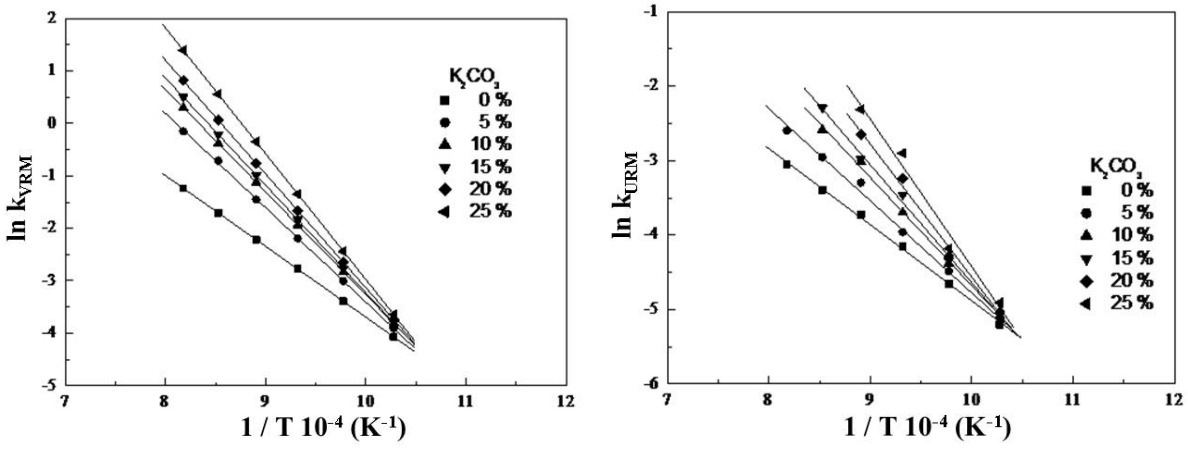
*Volume reaction model*

$$\frac{dX_C}{dt} = k_{VRM}\left(1-X_C\right) \Rightarrow X_C = 1-\exp\left(-k_{VRM}\,t\right) \Rightarrow \ln\left(1-X_C\right) = -k_{VRM}\,t \quad (3)$$




(a) Volume reaction model (b) Un-reacted core model

**Figure 8.** Specific gasification rates calculated for both kinetic models, at various catalyst loads and 800°C, (a) volume reaction model, (b) un-reacted core model.




(a) Volume reaction model (b) Un-reacted core model

**Figure 9.** Arrhenius plots for two kinetic models, at various temperatures (700°C – 950°C) and catalyst loads, (a) volume reaction model, (b) un-reacted core model.

*Un-reacted core model*

$$\frac{dX_C}{dt} = 3k_{UCM}(1-X_C)^{2/3} \Rightarrow X_C = \\ = 1-(1-k_{UCM})^3 \Rightarrow 1-(1-X_C)^{1/3} = k_{UCM}\,t \quad (4)$$

Arrhenius equation

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \Rightarrow \ln k = \ln k_0 - \frac{E}{R}\frac{1}{T} \quad (5)$$

Based on the experimentally obtained fixed carbon conversion values, the specific gasification rates were calculated for the two kinetic models, at various temperatures (700°C – 950°C) and at catalyst loads, Figs. 8a and 8b.

The activation energy ($E$) and the pre-exponential factor ($k_0$) were calculated from the corresponding Arrhenius plots, given in Figs. 9a and 9b. The calculated values indicate that by increasing of the catalyst load the activation energy ($E$) values increase accompanied by a simultaneous increase of the pre-exponential factor ($k_0$). This behaviour clearly suggests that the known as "compensation effect" was present in catalytic coal – $CO_2$ gasification reaction when the catalyst load increases.

Moreover, in the Arrhenius plots, Fig. 9, all lines merge at one point which corresponds to the so-called "isokinetic" temperature [35,43,44,52]. This was graphically found to be about 657°C for the volume reaction model and about 627°C for the unreacted core model, Fig. 9. Therefore, the observed variations in the kinetic parameters ($E$) and ($k_0$) could be attributed to the, so-called, "compensation effect", whereby a change in ($E$) was compensated by a nearly corresponding change in ($k_0$). A generalized interpretation between ($k_0$) and ($E$) is given in Eq. 6 [52] that is derived from Arrhenius equation (Eq. 5) and describes a linear

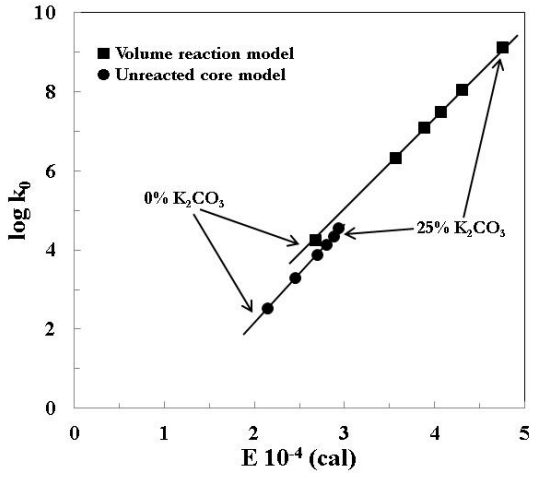



**Figure 10.** Compensation effect in $K_2CO_3$ catalysed lignite gasification.

correlation between the activation energy and the pre-exponential factor.

$$\log k_0 = \frac{1}{2.303RT_{is}}E + \log k \qquad (6)$$

The plot of (*log* $k_0$) *versus* (*E*), illustrating the compensation effect for this system, is shown in Fig. 10. For both models, any increase of the activation energy (*E*) is compensated by a simultaneous increase of the pre-exponential factor ($k_0$) and a linear interrelationship between them is found. By using Eq. 6 the isokinetic temperature was found to be 663°C for the volume reaction model and 591°C for the unreacted core model, values that are quite close to the ones calculated from the Arrhenius plots.

The validity of the compensation effect is not generally accepted and it is often considered as a statistical deviation (an artifact) due to the extrapolation necessary to calculate the ($k_0$) values. However, Bond [44] advocated for the compensation phenomenon and gave several correlations between ($k_0$) and (*E*). Wilson and Galwey [43] and Bond [44] proved the importance of the compensation phenomenon on the kinetic parameters, while, Galwey [35] gave several theoretic interpretations for that phenomenon.

It is widely accepted [52] that the $K_2CO_3$ catalysed coal gasification is mainly affected by (a) the chemical nature and the dispersion of the catalyst and (b) the individual mechanism of catalysis. As discussed previously, a redox cycle mechanism is considered to describe the $K_2CO_3$–catalysed coal gasification. This mechanism includes the formation of active intermediates (intercalates), suggesting that the active sites of catalytic activity are carbonylic, phenolic or completely reduced structures (*i.e.*, –C–O–K,–C–K, $K_2O$, K-H, metallic K *etc.*). The catalyst on the surface is considered as an oxygen carrier through the abovementioned oxidation-reduction cycle, in which potassium carbonate initially is reduced to the metal and is, subsequently, oxidized [12,27,28].

For any chemical reaction, such as coal – $CO_2$, to proceed, a spectrum of individual collisions must contribute to rate constants, ($k_0$) and (*E*), obtained from "bulk" experiments, involving molecules with many different reactant collision geometries and angles, different transitional and (possibly) vibrational energies. An oversimplified approach defines activation energy as the energy barrier that should be overcome in order for a chemical reaction to occur, indicating also the sensitivity of the reaction rate to temperature. In the catalytic coal –$CO_2$ gasification system the activation energy was found to increase as the catalyst load increases.

The reason for the increase in activation energy (*E*) on the addition of potassium is not clear. This could be attributed to the different nature of carbon atoms gasified, as the gasification reaction proceeds faster when higher amounts of catalyst are added. The pitting and channeling action of the catalyst is more intense at higher loads [57] and, thus, as the aromatic structure of coal is relaxed, potassium is transferred to more stable carbon atoms and gasification requires the cleaving of increasingly stronger bonds. Therefore, the reactants should overcome a higher energy barrier, resulting in increased activation energy for catalytic coal – $CO_2$ gasification.

With respect to the pre-exponential factor, the collision theory states that it expresses the number of reactive collisions, taking place during gasification. The catalytic coal – $CO_2$ gasification involves an oxidation/reduction cycle controlled by the reaction of carbon with unstable oxygen atoms, and the rate of gasification is proportional to the number of active sites for chemisorptions [57]. The presence of catalyst increased the number of active sites on the coal surface, thus, increasing the number of collisions of the reacting gaseous molecules with active sites. As the density of the active sites increased with the catalyst load, the number of reactive collisions also increases and much higher pre-exponential factor values are obtained.

It is well established [5] that the formation and propagation of active sites depends on the catalyst dispersion which is temperature sensitive, since pitting and channelling are strongly enhanced by temperature [13,52,57]. The nature of active sites also depends on temperature, since the formation of catalytically active intermediates (–C–O–K,–C–K, $K_2O$, K-H, metallic K *etc.*) and their activity to dissociate the adsorbed $CO_2$, strongly

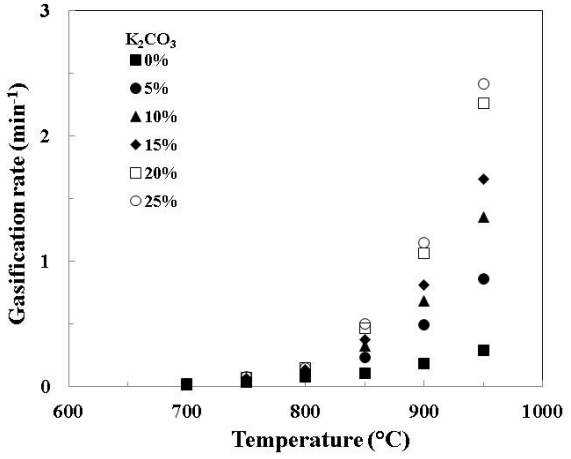



**Figure 11.** Specific gasification rates, based on volume reaction model, at various temperatures and catalyst loads.

depend on temperature [5,60]. The quite high catalyst dispersion, achieved by the impregnation procedure applied in this work, decreases the decomposition temperature of $K_2CO_3$, which also depends on its dispersion [60,61]. As a result, a temperature of about 720 to 740°C is considered as the minimum threshold for the formation of the above catalytically active intermediates [60,61]. The excess $CO_2$ in the gas phase blocks the dissociation of the potassium salt ($K_2CO_3$), inhibits the catalyst lost [61] and increases further the importance of temperature in catalytic gasification.

This behaviour is depicted in Fig. 11. Even at 950°C (the highest temperature studied) the catalytically active intermediates are continuously present and the catalytic reaction proceeds unhindered, thus resulting in very high gasification rates. The isokinetic temperature (600 – 650°C), previously calculated, suggests the abovementioned behaviour. At the isokinetic temperature the gasification rate is unaffected by the catalyst load, the $K_2CO_3$ is catalytically inactive and below that temperature the gasification rate is negligible. It should be noted that a temperature above 650°C is required (thermodynamically) to trigger the coal – $CO_2$ reaction. In contrast, at high temperatures, the catalyst is found in the form of active intermediates and increased conversions and rates were observed.

Therefore, by increasing the $K_2CO_3$ load, for the coal – $CO_2$ system, the Arrhenius parameters ($E$) and ($k_0$) showed an increasing trend and thus exhibiting the so-called compensation effect. The isokinetic temperature in the system coal – $K_2CO_3$ is the minimum temperature required for the formation of the catalytic active intermediates. It was found to be about 600 to 650°C. At the temperature region studied, the catalytic active intermediates were typically present and the catalysis, due to an oxidation – reduction cycle, progressed unhindered (until complete conversion) resulting in high gasification rates. *The above results support the idea that in coal gasification the "compensation effect" is an actual phenomenon and not an artifact, since the reactions of the various oxygenated species in coal have a broad range of reactivity with temperature, and, thus, their activation energy increases with temperature.*

The Arrhenius parameters, calculated in this work were found to increase simultaneously with the catalyst load. The corresponding isokinetic temperature was found to be much lower than the one calculated elsewhere [52,57,58], being rather a threshold than an upper limit as suggested by others [3,46]. In contrast to the present work, in high rank coal catalytic gasification a simultaneous decrease of ($k_0$) and ($E$) is often observed accompanied by a high isokinetic temperature [3,46,50]. These differences could be attributed to differences in experimental conditions, the chemical composition of the coals used, the catalyst addition procedure and the dominant reaction mechanism. For instance, Spiro *et al.* [33] found that the catalyst is less efficient when added in the pyrolysis chars. The presence of high concentrations of alumino-silicates in the ash of some coals could deactivate $K_2CO_3$ due to the formation of inactive complexes [13]. In addition, a highly efficient impregnation procedure was applied in this work and the catalyst was added in the parent coal prior to pyrolysis. The latter, along with its high oxygen content and oxygen functional groups reduces the temperature threshold for the start of the catalytic activity of the $K_2CO_3$ and enhances the formation and propagation of catalytic active sites. Simultaneously, the excess $CO_2$ present in the gas phase makes catalyst loss due to vaporisation at high temperatures quite unlikely.

## 4. Conclusions

This study of catalytic $CO_2$ gasification was focused on the catalytic activity of $K_2CO_3$, which was impregnated in the coal. $K_2CO_3$ was found to be an effective catalyst at temperatures studied from 700°C to 950°C and that it affected positively both, the pyrolysis-devolatilisation and the gasification stages. However its effect was stronger during the second stage when the Boudouard reaction was dominant. $K_2CO_3$ enhances the gasification reactions and reduces significantly the required time and temperature to achieve almost complete conversion. The gasification rate increases with increasing catalyst content, following a sigmoid curve up to ~20% w/w $K_2CO_3$ catalyst load. Above this point, a limited catalytic effect was observed, possibly due to saturation of the coal surface by $K^+$. A correlation

was found between the specific gasification rate and the alkali index, following a sigmoid curve. The estimated kinetic parameters ($E$, $k_0$) increased by increasing the $K_2CO_3$ load, exhibiting the so-called compensation effect that in coal gasification was an actual phenomenon and not an artifact. The isokinetic temperature, which is the minimum temperature required for the formation of the catalytic active intermediates, was found to be about 600 to 650°C for the system lignite – $K_2CO_3$. At the studied temperature, the catalytic active intermediates are present and the catalytic oxidation – reduction cycle, progresses unhindered at high gasification rates (until complete conversion).

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