Potassium catalyzed hydrogasification of low-rank coal for synthetic natural gas production

1 Introduction

Natural gas (NG) is by far the most promising low-carbon alternative for energy generation in the near future. Its demand is rapidly growing globally as it is considered the cleanest and the most efficient fossil energy source [1,2]. Despite the introduction of shale gas, increasing natural gas demand and price volatility comprising significant burdens towards sustainable growth for the EU and Asia countries (e.g. China, India etc.). In addition, the security of energy supply in the EU currently became critical considering the turmoil in its neighbour (e.g. Arab spring, Ukraine crisis, Islamic State etc.). Last but not least, natural gas (shale gas included) will be exhausted far ahead of coal. The above revived the interest for alternative routes for synthetic natural gas production. Due to its obvious advantages [3-5], there is a renewed interest on coal hydrogasification (CHG) [6,7]. At the United States, the existence of huge domestic coal reserves, estimated to last for more than two centuries [7,8], boosted considerable interest in the coal to SNG process. This is also the case for China where more than thirty coal-based SNG plants are under construction or planned [9]. Although methane production via coal hydrogasification is a clean and an efficient way to produce synthetic natural gas, the required severe temperature and pressure conditions hindered its development and necessitate the use of catalysts [10]. Alkali and alkaline-earth compounds have been considered as attractive hydrogasification catalysts, increasing the reaction extended and its selectivity to CH₄ [11-14]. Potassium, a cheap and rather abundant alkali metal, is widely used as a quite reactive hydrogasification catalyst. Since the relative catalytic efficiency of the alkali cations corresponds to the increasing order in the ionization potentials of the metals (Cs > K > Na > Li) [15]. Aqueous solutions are used for the impregnation of potassium in the coal samples and the chemisorbed potassium on the coal matrix is considered to be catalytically active [15,16,19]. The alkali metals chemisorption is linked with the Cation Exchange Capability (CEC) of coal [16-19], which is attributed to the carboxylic acid and phenolic hydroxyl functional groups.
These dissociate in solution to form a negatively charged sites upon the coal surface, which is capable of complexing cationic species from solution to form a stabilized coal–metal structure. Thus, the chemisorption of alkali metals is linked with the cation exchange capability of coals, which subsequently, is related to the number of carboxylic acid functional groups [16-19].

The mainframe of the proposed mechanisms [12,20-30] for the catalytic activity of potassium in coal hydrogasification might be classified in four major groups. Thus, the first group of mechanisms considers that potassium might act as hydrogasification catalyst by hampering of coal agglomeration, while, the second states that potassium forms K–O–C complexes that enhance the reaction with H₂ at the inactive “zig-zag” <1120> graphitic plane. However, low rank coals such as lignite do not suffer from agglomeration problems as the first mechanism dictates and their structure is far from being similar to graphite as suggested by the second one. Furthermore, although oxygen is removed at early hydrogasification times, the catalytic action of potassium is identified at longer hydrogasification times also. Therefore, these mechanisms are not applicable to low rank coals such as lignite. The third group of mechanisms, originally proposed by Cypres [12], suggests that the increase of the coal specific surface area is responsible for the catalytic action of the potassium salts that dissociate at the gasification temperatures. However, this one is incapable to explain the catalytic activity of high boiling point potassium salts, such as KCl or K₂SO₄ (boiling point 1420°C and 1689°C, respectively). Furthermore, the low boiling point KHSO₄ (330°C) exhibited a very poor catalytic behaviour, while the high boiling point KOH (1327°C) was identified as an excellent hydrogasification catalyst. Finally, the fourth mechanism, of formation of multi-aromatic complexes of destabilised structure, vulnerable to H₂ attacks, also proposed needs further clarification about the ways and means of the formation of these complexes and the propagation of the catalytic hydrogasification reaction.

Thus, despite the importance of alkali metals chemisorption and the extensive research performed on catalytic hydrogasification [20-30] major uncertainties still exist, regarding the origin and the mechanism of the CEC, its correlation with the pH and the oxygen functional groups. In addition, important issues such as the conditions of the coal-catalyst system preparation, the nature and the role in the catalysis of the cation and/or the anion, and the mechanism of the catalysis etc. are still blurry and further research is required.

In this work the potassium catalyzed coal hydrogasification was investigated. The impacts of the impregnating solution pH on the fraction of the chemisorbed potassium and on the CEC of the coal samples were studied. Hydrogasification weight loss, elemental carbon and hydrogen conversions, gaseous products yields, and the specific gasification rates with respect to the impregnating solution pH were investigated also. Based on the experimental results, a three-stage reaction scheme was proposed to explain the mechanism of the catalytic activity of potassium and the relative specific gasification rate was linked with the CEC.

2 Experimental Procedure

Greek low rank coal (lignite) from Ptolemais reserve was used in this work, and its characteristics, obtained by the ASTM Standard Methods [ASTM D 5142-90, ASTM D 5373-93 and ASTM D 6349-98], are given in Table 1. This lignite is characterised by its high moisture, high ash and high volatile, high oxygen and low sulphur content, while its ash is characterised by the increased presence of calcium and silica and the quite small quantities of sodium and potassium.

In order to unravel the catalytic behavior of potassium compounds, several potassium compounds (KHSO₄, KCl, K₂SO₄, KH₂PO₄, KBr, KNO₃, C₂H₅KO, KF, CH₃COOK, K₂CrO₇, K₂CO₃, KOH, K₃PO₄) were used to prepare impregnating solution of various alkalinities. The impregnating solution’s pH was adjusted by using HCl, while, two samples acidified with H₂SO₄ and HNO₃ were prepared and tested to exclude any effect of the Cl⁻ on K⁺ chemisorption.

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.

| Parameter | Element | Compound |
|-----------|---------|----------|
| (a) Proximate | (b) Ultimate | (c) Ash analysis |
| Volatiles | 47.0 | C | SiO₂ | 33.64 |
| Fixed carbon | 30.8 | H | Al₂O₃ | 17.31 |
| Ash | 21.7 | N | Fe₂O₃ | 7.19 |
| CO₂ | 0.5 | S | CaO | 28.10 |
| HHV (kcal kg⁻¹) | 4193 | O⁺ | MgO | 0.83 |
| Ash | 21.7 | | SO₃ | 11.93 |
| | | | Na₂O | 0.58 |
| | | | K₂O | 0.60 |

* by subtraction
In all cases, the amount of each salt to be impregnated was calculated so that the atomic ratio K/C would be the same with 20% K$_2$CO$_3$, i.e. 0.092. In each case pre-weighted coal sample was mixed with the appropriate amount of the potassium salt (aqueous solution) and was mechanically stirred to form slurry. The coal-solution slurry then was placed under vacuum (250 mbar) to enhance catalyst impregnation by removing air from the coal pores. Samples were subsequently dried for 24 hrs. at 105°C in a N$_2$ atmosphere to prevent any oxidation and the desired granulometry (150–250 µm) was obtained by grinding and sieving. To distinguish the chemisorbed and the physically held K$^+$ ions each impregnated sample was extracted with water in a centrifuge, and 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. Acidification of the impregnating solution with HCl (and in some cases with HNO$_3$ or H$_2$SO$_4$) was used to study the potassium chemisorption at various pH and the corresponding CEC values of coal.

The cation exchange capability (CEC) of coal was measured by titration with aqueous solution of NaOH 0.1 N, analogously to the ISO 11260/2003 method. In order for the coal to be saturated with H$^+$ and to remove any extractable cations (i.e. Ca and/or Mg carbonates) that might increase the CEC, a pre-treatment procedure including extraction with HCl and CaCl$_2$ in successive steps and washing with methanol was applied. A more detailed description of the CEC measurement methodology is given elsewhere [16,18].

Hydrogasification tests were comprised at ambient pressure temperature 850°C and residence times up to 100 min in a tubular fixed bed reactor equipped with the proper gas and solids feeding controls and with product collection and analysis devices (GC equipped with FID and TCD detectors). A detailed description of the test unit is given elsewhere [31]. The U-shape reactor design permits rapid cooling (quenching) of the reactor and, thus, the hydrogasification reaction could be interrupted at any desirable time. In all cases the experimental results represent average values of at least three duplicate runs.

3 Results and Discussion

3.1 Potassium chemisorption in low rank coal and CEC

Potassium chemisorption: The effect of the solution pH on the fraction of the chemisorbed K$^+$ for the various potassium compounds is given in Figure 1(a). The solution pH plays the most important role on the cation chemisorption capacity of the coal [16,18], regardless the potassium compounds used. The fraction of the chemisorbed K$^+$ reached about 70 to 75% for the K$_2$CO$_3$ and KOH solutions (1 M), which have a pH of 13 to 14, while the acidification with HCl to pH 3 resulted to about half fraction of chemisorbed K. Similar behaviour was also observed for the other potassium compounds such as K$_2$SO$_4$ and KCl, Fig. 1a.

The observed differences among the various solutions might be attributed to the different isoelectric point of each solution. For the samples acidified with H$_2$SO$_4$ and HNO$_3$, the fractions of the chemisorbed K$^+$ were close to the ones
obtained when HCl was used for acidification and also found at the previously defined range, Fig. 1a, indicating that the Cl\(^-\) anions do not affect the chemisorption process.

Therefore, regardless of the potassium compounds used, the fractions of the chemisorbed K\(^+\) are found in a strip of 10 to 15 percentage points width, starting from about 70 to 80% (at pH 14) till 30 to 40% (at pH 3), which is marked by the dashed lines (Fig. 1a). In that range the K\(^+\) chemisorption curves of the K\(_2\)CO\(_3\) and KOH solutions followed sigmoid curves, due to the neutralisation phenomena taking place [16,18]. Thus, aqueous solutions of potassium compounds of high alkalinity are expected to result in increased K\(^+\) chemisorption, while a low fraction of chemisorbed K\(^+\) is anticipated when the solution pH is low.

A non-linear regression analysis was performed to validate and quantify the relationship between the fraction of the chemisorbed K\(^+\) and the solution pH, taking into account all the obtained experimental data, given in Fig. 1a. Several, commonly used, convex functions were tested using the best least squares estimates for the function parameters and the coefficient of determination R\(^2\) as a measure for the goodness of fit. The higher value of R\(^2\) (R\(^2\) = 0.8404) was obtained by the following quadratic function:

\[
\text{Fraction of } K^+ = 34.1776 + 0.21527 \times pH^2
\]  

The resulting quadratic function, along with the 95% confidence interval for the mean value of the fraction of the chemisorbed K\(^+\) as well as the 95% prediction interval for the fraction of the chemisorbed K\(^+\) for a given solution pH, are illustrated in Fig. 1b. For 95% probability, all experimental points lay within the confidence limits, thus justifying the direct correlation of the fraction of the chemisorbed K\(^+\) with the solution pH, regardless the anion of the potassium salts and of the acidification medium.

**Cation Exchange Capability:** The CEC of coals (measured by potentiometric titration) is closely related to the solution pH [16,18] and was found to increase continuously as the solution pH was increased, Fig. 2a, varying from a low – almost constant value at solution pH between 2 to 4 and continuously increased up to solution pH 12 to 14. The dependence of the CEC on the solution pH is reversible and declines when the solution pH decreases [16,18].

The amount of the chemisorbed K\(^+\), resulted for the various potassium compounds used (converted to meq per 100 g lignite), were included in Fig. 2a for direct comparison with the CEC of the lignite, measured by potentiometric titration [16]. In most cases the amount of the chemisorbed K\(^+\) (in meq/100 g lignite) closely followed the CEC of the lignite as obtained by titration with NaOH (Fig. 2a).

At solution pH 1 the CEC was minimum corresponding to the permanent ion exchange sites (mainly inorganic sites). The higher than the CEC amount of the chemisorbed K\(^+\) at pH 1 (impregnation with KHSO\(_4\)) might be attributed to the formation of intercalates that potassium, in contrast to Na\(^+\), tends to form with all coals [15]. The similarity of the CEC and the adsorbed K\(^+\) values indicates that adsorption varies due to changes in the sites available for ion exchange, caused by the solution pH variations.

A mathematical correlation between the CEC and the solution pH was developed based on Weibull distribution. Because of the nature of the cation exchange sites (Fig. 2a) the CEC is expected to reach very low – nearly constant – values at low pH values, to increase quite sharply at intermediate pH values 4 to 10) and to reach a plateau at high pH values. A similar behavior is found in most of the cumulative distribution function (cpf) and thus, some of the functions might be suitable. To achieve increased
accuracy and analogously to previous works [16,32,33], the combination of the cumulative distribution function (cdf) of two Weibull probability density functions (pdf) in a single function was used to correlate the CEC with the solution pH and the following function was elaborated:

$$C.E.C. = w_1 (1 - e^{-\frac{pH}{l_1}}) + w_2 (1 - e^{-\frac{pH}{l_2}}) + w_3$$

Where $k_i$ and $\lambda_i$ (i = 1 or 2) are the shape and scale parameters of the Weibull distribution and pH are the solution pH used in the potassium impregnation stage, and $w_1$ and $w_2$ are weight factors for the cdfs' of the two Weibull distributions and $w_3$ is a constant. The obtained best-fit parameters calculated for the Weibull parameters (shape and scale) were $k_1 = 9.164$ and $l_1 = 6.261$, $k_2 = 3.866$, $l_2 = 8.596$, while the least squares estimates for the weight factors and the constant were $w_1 = 124.957$, $w_2 = 166.813$ and $w_3 = 26.138$ and with $R^2$ value over 0.99936. Therefore, the function in Eq. 2 that comprised two cumulative distribution functions of the Weibull distribution successfully describes the variation of the CEC with the solution pH in the potassium impregnation stage. In Fig. 2a, the continuous curve represents the calculated results from Eq. 2.

Based on the defined relation between the CEC and the solution pH (Eq. 2), that seems to be of a deterministic form, the potential dependence of the chemisorbed $K^+$ (expressed in meq/100 g lignite) on the CEC (and consequently on the solution pH) was investigated. Towards that, the experimental values of the chemisorbed $K^+$ were compared with the ones obtained from the Eq. 2 (for the same solution pH), and the obtained scatter diagram is given in Fig. 2b. A linear correlation between the chemisorbed $K^+$ and the CEC is identified that is described by Eq. 3, estimated by linear regression analysis (in terms of the higher $R^2$ value) with $R^2 = 0.8229$.

$$K^+ = 60.465 + 0.7428 CEC$$

The resulting linear function, along with the 95% confidence interval for the mean value as well as the 95% prediction interval of the amount of the chemisorbed $K^+$ (for a given CEC value) are also illustrated in Fig. 2b. Therefore, it is clearly justified that the amount of the chemisorbed $K^+$ (in meq/100 g lignite) closely follows the CEC of the lignite as obtained by titration with NaOH, Fig. 2b. For all the potassium salts used the amount of the chemisorbed $K^+$ is found within the calculated confidence interval, Fig. 2b. Thus, given the solution pH, the expected CEC value can be almost perfectly predicted by the combined Weibull model (Eq. 1) and then, depending on the resulting CEC value, a prediction interval for the amount of the chemisorbed $K^+$ can be provided. Since the CEC of the coal is linked with the oxygen functional groups [16,18] and particularly the carboxyls found on its surface, the linear correlation between the CEC and the fraction of the chemisorbed $K^+$, Fig. 2b, justifies that potassium is adsorbed on O sites in the lignite structure.

### 3.2 Catalytic hydrogasification of low rank coal

To investigate the effect of solution pH on coal hydrogasification, coal samples impregnated with various potassium compounds (KOH, $K_2CO_3$, $K_2PO_4$, $CH_3COOK$, $KNO_3$, $KBr$, $KCl$, $KHSO_4$, $KH_2PO_4$ and KF) were gasified at 850°C under $H_2$ flow and the $CH_4$ formation rate was continuously monitored. Prior to hydrogasification, the fraction of the chemisorbed potassium was measured. The obtained results showed that the methane formation rates follow the trend of the fraction of the chemisorbed $K^+$ and two regions are found, adversarial the $CH_4$ formation rate of the un-catalysed coal sample, Fig. 3. These are (a) a region of high $CH_4$ yields, corresponding to samples impregnated with $K^+$ salts (KOH, $K_2CO_3$, $K_2PO_4$) of high alkalinity (pH > 11) and of increased fractions of chemisorbed $K^+$, and (b) a low $CH_4$ yield region, corresponding to samples impregnated with $K^+$ salts ($KCl$, KBr, $KHSO_4$) of low alkalinity and of decreased fractions of chemisorbed $K^+$. Between them the $CH_4$ formation rates of samples impregnated with $K^+$ aqueous solutions of intermediate pH (KF, $KNO_3$, $KH_2PO_4$, $CH_3COOK$) are found (Fig. 3).

Impregnation with high alkalinity solutions resulted in increased chemisorbed potassium and consequently high $CH_4$ yields were obtained (Fig. 3). Similar $CH_4$ yields were obtained for coal samples with similar amount of chemisorbed $K^+$, such as $K_2CO_3$ KOH and $K_2PO_4$ (pH 11). The catalyst regeneration possibility and easiness should be considered also. The observed increased $CH_4$ selectivity might be attributed to the stabilisation of the carboxylic groups by the substitution of the carboxylic $H$ by $K^+$ that hinders the early devolatilization of the carboxylic groups, which then decompose at the hydrogasification temperatures (700–750°C) with increased $H_2$ participation. In contrast, samples impregnated with aqueous solutions of low alkalinity yielded less methane compared even with the non-catalytic coal sample, Figure 3. This might be attributed to the early decomposition of carboxyls (below 700°C) and the subsequent continuous dissociation of the coal lattice resulting in lower $CH_4$ yields, or/and to pore plugging due to the formation of salt crystals that hamper the pore structure development and the gaseous reactants.
and products diffusion. It should be noted that in some cases the type of the anion, e.g. Cl⁻ and Br⁻, hindered the gasification phenomena. Thus, although that the KBr solution resulted to 50% higher amount of chemisorbed K⁺ than the KCl solution, similar CH₄ yields were obtained. This implies that Br⁻ probably inhibits methane formation, beyond the effect of low K⁺ chemisorption, which already suppresses this reaction. Since similar CH₄ yields were achieved when impregnation was performed with the high alkalinity solutions of K₂CO₃, KOH and K₃PO₄ (pH 11), the cheapest salt (K₂CO₃) might be used as hydrogasification catalyst in the following.

Catalytic hydrogasification experiments evidenced that coal conversions and product yields are closely linked with the impregnation conditions and/or cation chemisorption. Total weight loss, as well as, elemental carbon and hydrogen conversions during hydrogasification at 850°C of low rank coal impregnated with K₂CO₃, under various solution pH, are shown in Fig. 4a. Samples impregnated with high pH solutions (pH 11–13) presented the highest weight loss and elemental carbon conversion, while the ones prepared with low pH solutions (about 4) gave the lowest ones. The decrease in solution pH lowered the chemisorbed K⁺, and resulted in lower total weight loss and elemental carbon conversion. In contrast, for all solution pH values, elemental hydrogen conversion remained high, thus, not being affected by the alkalinity of the impregnating solution (Fig. 4a). When impregnating solutions of high alkalinity are used, the yields of light hydrocarbons (CH₄, C₂H₆, C₃H₈) were increased, as justified by the increased fractions of C converted to CH₄, C₂H₆, C₃H₈ (Fig. 4b). The total yield of light hydrocarbons increased more than 50% when the solution pH increased from 4 to 13, mainly due to the increase of CH₄ yield.

The effect of the solution pH on coal hydrogasification is clearly evident by the CH₄ formation rate, given in Fig. 5. In both hydrogasification stages the CH₄ formation rate is higher for samples prepared by solution with high pH (11 or 13). Low pH values appear to suppress the amount of metal ion chemisorption and hence, the hydrogasification rates and yields. Therefore, the reversibly (with pH) chemisorbed potassium, mainly on oxygen functional groups (carboxyls) plays the most important role in catalytic coal hydrogasification.
The negative impact of the low pH of the impregnating solution on the methane formation rates might be attributed to the decreased fraction of the chemisorbed potassium at low pH values, as defined previously. Furthermore, the physically mixed potassium remains inside the pores might form K$_2$CO$_3$ crystals that reduced the porosity [16,18,21], thus, hindering the diffusion rates. When K$_2$CO$_3$ solutions were acidified with HCl to reduce the solution pH, Cl$^- \text{anions were in excess in the coal – solution slurry. However, no direct relation between the addition of chlorides and the reduction of carbon conversion and product yields could be identified. Indeed, solution pH lowering from 13 to 11 required addition of 10 times more HCl than from pH 9 to 7, while in the same pH ranges K$^+$ chemisorption and CH$_4$ yields decline about 10% and 20% respectively. Thus, the presence of Cl$^- \text{anions seems not to affect the hydrogasification of coal.}$

### 3.3 Reaction scheme for the catalytic hydrogasification of low rank coal

Based on the above, the mechanism of the catalytic activity of potassium should be correlated with its ionic form and might be hypothesized reasonably that (a) it is chemisorbed on the carboxyls in the coal lattice and (b) during hydrogasification it forms poly-aromatic complexes with the remaining aromatic structure when oxygen groups are released. Based on these hypotheses, the mechanism would be applicable mainly to low rank coals with high oxygen content, where K$^+$ dispersion and chemisorption is more pronounced, and should be capable to explain the obtained experimental results.

According to the first hypothesis, the substitution of the carboxylic H$^+$ by K$^+$ stabilises the carboxyls minimizing its early devolatilization and, as a result, carboxylic groups decompose at the hydrogasification temperatures (above 700–750°C). Without catalyst the carboxyls decompose at lower temperatures (below 700°C); continuous dissociation of the coal lattice follows and the gaseous products are formed with limited contribution of H$_2$, resulting in lower CH$_4$ yields. The second hypothesis, leads to the formation of potassium – poly-aromatic complexes after the decomposition of the carboxylic groups, (between K$^+$ cations and the remaining aromatic structures).

Potassium cations act as stabilizers of the aromatic clusters, hampering its immediate pyrolysis and simultaneously hindering its stabilization reactions (re-polymerization etc.). At the same time, the presence of the K$^+$ cation destabilises the aromatic rings and activates them; being more vulnerable to H$_2$ attacks, resulting to its gradual dissociation to CH$_4$, via a scheme similar to the one proposed by Zielke and Gorin [34].

In this case the reaction starts from the activated carbon atoms of the poly-aromatic complexes, as proposed by Zahradnik and Glenn [35], and not from the carbon atoms of the aromatic rings exposed to H$_2$. The K$^+$ substituted rings were decomposed at the hydrogasification temperatures (> 700–750°C) with increased involvement of the gaseous H$_2$, resulting in increased CH$_4$ yields. The formation of an ionic poly-aromatic complex activated scission of the aromatic rings, followed by stepwise reaction of carbon atoms. Subsequently, K$^+$ moves to neighbouring complex with unsaturated bond and the hydrogasification reaction continues.

Therefore, the potassium catalysed coal-hydrogasification might comprise three steps, namely, potassium impregnation, ion exchange, and chemisorption in the carboxylic groups at high alkalinity impregnating solutions (Step 1), thermal dissociation
of the carboxyls at the hydrogasification temperature (T > 700°C) and formation of K⁺–poly-aromatic complexes (Step 2) and gradual dissociation of the K⁺–poly-aromatic complex to form CH₄ (Step 3), and is shown schematically in Scheme 1.

The experimental results of this work corroborated the above mechanism, since, the increased alkalinity (high pH) of the impregnating solution favoured K⁺ chemisorption, which in turn, increased CH₄ yields (Fig. 5a), without affecting significantly elemental carbon conversion (Fig. 4a). In the first step potassium cations were chemisorbed on the oxygen functional groups, found in the organic fraction of coal, that were dissociated extensively at increased solution pH (Fig. 2a), while the effect of the anion was limited (Fig. 3). Thus, high alkalinity impregnating solutions enhanced the dissociation of the oxygen functional groups (carboxyls) and increased the fractions of the chemisorbed potassium, which, in turn, hindered the early devolatilization of the aromatic rings, and simultaneously activated them, enhancing H₂ contribution in products formation. As a result, carboxylic groups were decomposed at the hydrogasification temperatures (above 700–750°C) and K⁺–poly-aromatic complexes were formed (Step 2).

The gradual decomposition of the potassium complexes increased the selectivity to CH₄ formation, while, the impact on the total weight loss was limited (Step 3). Subsequently, K⁺ mitigates to the next active aromatic group and promotes further the hydrogasification reaction. CH₄ formation rates tend to convergence at longer times due to the depletion of the activated aromatic rings and/or catalyst vaporization or deactivation.

**Kinetic analysis:** To quantify the above, the volume reaction model (VRM) and the Arrhenius equation were used to correlate the CEC with the specific hydrogasification rate. The volume reaction model assumes that the gasification reaction occurs on the active sites of the coal samples [36,37], uniformly throughout the particle volume in all possible places, both outside and inside the particle surface. The overall gasification rate is independent of particle size that remains constant while its density decreases. The reaction rate is given by the following equation [29]:

\[
\frac{dX_{CH_4}}{dt} = k_{VRM}(1 - X_{CH_4}) \Rightarrow X_{CH_4} = \exp(-k_{VRM}t) 
\]

By using Arrhenius plots and linear regression, the values of the specific hydrogasification rate at various solution pH were calculated, Table 2. Specific gasification rate increased with the solution pH, Fig. 5b, indicating that when potassium impregnation is performed by high alkalinity solutions, its catalytic activity was more pronounced.

At increase solution pH new active sites were formed for both the cation (K⁺) and the anion of the impregnating solution, due to the virtually complete dissociation of the acidic – mainly carboxylic – groups of the humic and
fulvic acids that form the organic matter of the lignite and to the solution pH effect on the aluminosilicate minerals \[16,18\].

A quite fair linear correlation \( R^2 = 0.9841 \) was identified between the relative specific hydrogasification rate and the impregnating solution pH, Fig. 6, of coal samples impregnated with \( \text{K}_2\text{CO}_3 \) solutions of various pH values. Deviations from linearity observed, might be attributed to the different isoelectric point of each solution or to neutralisation phenomena that might take place \[19\].

Therefore, the relative specific gasification rate might be described by the equation

\[
\frac{k_{VRM}}{k_{VRM}^0} = 5.410^{-3}[\text{CEC}]
\]

and, thus, (Eq. 4) is converted to the following (where \( k_{VRM}^0 \) is the specific hydrogasification rate of the non-catalytic coal samples):

\[
X_{CH} = 1 - \exp\left(-5.410^{-3} (\text{CEC}) k_{VRM}^0 t\right)
\] (5)

The above (Eq. 5) suggests that the oxygen functional groups, on which potassium is chemisorbed, act as “active sites” according to the definition of Radovic et al. \[36\] and are linked with the carbon’s reactivity as stated by Ehrburger et al. \[37\].

### 4 Conclusions

Production of coal-based synthetic natural gas might be a viable alternative to address energy security and carbon intensity in the energy generation. Towards that, potassium catalyzed hydrogasification of low rank coal was studied in a tubular fixed-bed reactor system. Potassium was found to be chemisorbed on the carboxylic groups of the lignite matrix and the fraction of the chemisorbed K’ was strongly affected by the solution pH and closely followed the CEC of the catalytic samples, which is also pH-dependent. A quadratic function described the relation between the solution pH and the fraction of the chemisorbed potassium, while the cumulative distribution function of two Weibull probability density functions successfully described the relation between the solution pH and the CEC, which in turn, was linearly correlated with the fraction of the chemisorbed potassium.

Hydrogasification tests shown that the increased alkalinity of the impregnating solution favoured K’ chemisorption, which, increased the methane yield, while, it slightly affected carbon conversion. When potassium impregnation was performed with high alkalinity solutions (pH > 11) the carboxylic groups were de-protonated appreciably, thus offering more active sites available for K’ chemisorption; resulting in increased fraction of chemisorbed K’. The substitution of the carboxylic H\(^+\) by K’ stabilised the carboxyls and hindered its early devolatilization. As a result, carboxylic groups were decomposed at the hydrogasification temperatures (> 700–750°C) and K’− polyaromatic complexes were formed. The K’ substituted rings were decomposed at the hydrogasification temperatures (> 700–750°C) with increased involvement of the gaseous \( \text{H}_2 \) resulting in increased \( \text{CH}_4 \) yields. The formation of an ionic poly-aromatic complex activated scission of the aromatic rings, followed by stepwise reaction of carbon atoms. Subsequently, K’ moves to neighbouring complex with unsaturated bond and the hydrogasification reaction continues.

**Table 2:** Specific hydrogasification rates of low rank coal samples impregnated by \( \text{K}_2\text{CO}_3 \) solutions of various pH.

| Solution pH | CEC [meq/100 g lignite] | Specific hydrogasification rate [min\(^{-1}\)] | Relative specific hydrogasification rate |
|-------------|--------------------------|---------------------------------------------|----------------------------------------|
| 0           | –                        | 0.44                                        | –                                      |
| 4           | 37                       | 0.53                                        | 1.21                                   |
| 7           | 198                      | 0.77                                        | 1.74                                   |
| 9           | 271                      | 1.01                                        | 2.29                                   |
| 11          | 302                      | 1.11                                        | 2.52                                   |
| 13          | 320                      | 1.24                                        | 2.82                                   |

**Figure 6:** Correlation between the CEC and the relative specific hydrogasification rate at 850°C (catalyst: potassium carbonate, 20% w/w).
The above were codified to a three stage reaction mechanism, consisting of (a) catalyst impregnation and potassium chemisorption on the carboxylic groups, (b) thermal dissociation of the carboxyls and formation of polyaromatic complexes and (c) gradual hydrogenation to methane. Based on the above, the relative specific hydrogasification rate; as calculated by the volume reaction model, was found to increase linearly with the CEC of the coal samples, suggesting that the oxygen functional groups, on which potassium is chemisorbed, act as “active sites” and are linked with the carbon’s reactivity.

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References

[1] Namkung H., Yuan X., Lee G., Kim D., Kang T-J., Kim H-T., Reaction characteristics through catalytic steam gasification with ultra clean coal char and coal, Journal of the Energy Institute, 2014, 87(3), 253-262
[2] Birol F., Golden rules for a golden age of gas, in World Energy Outlook – Special Report on Unconventional Gas. International Energy Agency, Paris, 2012 (www.worldenergyoutlook.org/media/weowebsite/2012/goldenrules /WE02012_GoldenRulesReport.pdf)
[3] Yan L., He B., Hao T., Pei X., Li X., Wang C., Duan Z., Thermogravimetric study on the pressurized hydropyrolysis kinetics of a lignite coal, Int J Hydrogen Energy, 2014, 39, 7826-7833
[4] Yan L.B., He B.S., Ma L.L., Pei X.H., Wang C.J., Li X.S., Integrated characteristics and performance of zero emission coal system, Int J Hydrogen Energy, 2012, 37, 9669-9676
[5] Yan L.B., He B.S., Pei X.P., Li X.S., Wang C.J., Energy and exergy analyses of a zero emission coal system, Energy, 2013, 55, 1094-1103
[6] Zhang J., Wang X., Wang F., Wang J., Investigation of hydrogasification of low-rank coals to produce methane and light aromatics in a fixed-bed reactor, Fuel Process Technol., 2014, 127, 124-132
[7] Kopyscinski J., Schildhauer T.J., Biollaz S.M.A., Production of synthetic natural gas (SNG) from coal and dry biomass—a technology review from 1950 to 2009, Fuel, 2010, 89, 1763-1783
[8] BP, Statistical Review of World Energy, June 2015, (https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf)
[9] Ding Y., Han W., Chai Q., Yang S., Shen W., Coal-based synthetic natural gas (SNG): A solution to China’s energy security and CO2 reduction?, Energy Policy, 2013, 55, 446-453
[10] Karcz A., Porada S., Formation of C1–C3 hydrocarbons during pressure pyrolysis and hydrogasification in relation to structural changes in coal, Fuel, 1995, 74, 806-809
[11] Takarada T., Sasaki J., Otsuka Y., Tamai Y., Tomita A., Direct production of high British thermal unit gas from the low-temperature steam gasification of brown coal, Ind. Eng. Chem. Res., 1987, 26, 627-629
[12] Cypres R., Ghodsi M., Feron D., Influence of added alkaline salts on hydrogenation kinetics of coal, Thermochim. Acta, 1984, 81, 105-112
[13] Xu W.C., Matsuoka K., Akiho H., Kumagai M., Tomita A., High pressure hydroprolysis of coals by using a continuous free-fall reactor, Fuel, 2003, 82, 677-685
[14] Karcz A., Porada S., The influence of coal rank on formation of gaseous hydrocarbons in hydrogasification of coal, Fuel, 1996, 75, 641-645
[15] Wood B.J. and Sancier K.M., The Mechanism of the Catalytic .Gasification of Coal Char: A Critical Review, Catal. Rev.–Sci. Eng., 1984, 26(2), 233-279
[16] Skodras G., Kokorotiskos P., Serafisidou M., Cation exchange capability and reactivity of low rank coal and chars, Central European Journal of Chemistry, 2014, 12(1), 33-43
[17] Lafferty C. and Hobday M., The use of low rank brown coal as an ion exchange material. I. Basic parameters and the ion exchange mechanism, Fuel, 1990, 69, 78-83
[18] Kokorotiskos P.S., Stavropoulos G.G. and Sakellaropoulos G.P., Effect of catalyst impregnation conditions on Greek lignite hydrogasification, Fuel, 1986, 65(10), 1462-1465
[19] Ansonle L., Klavmin M., Egilite L., Use of peat-based sorbents for removal of arsenic compounds, Central European Journal of Chemistry, 2013 11(6), 988-1000
[20] Tomita A., Takarada T. and Tamai Y., Gasification of coal impregnated with catalyst during pulverization: effect of catalyst type and reactant gas on the gasification of Shin-Yubari coal, Fuel, 1983, 62, 62-88
[21] Skodras G., Catalysis and compensation effect of K2CO3 in low rank coal – CO2 gasification, Central European Journal of Chemistry, 2013, 11(7), 1187-2000
[22] Porada S., A comparison of basket willow and coal hydrogasification and pyrolysis, Fuel Process Technol, 2009, 90, 717-721
[23] Yasuda H., Yamada O., Zhand A., Nakano K., Kailo M., Hydrogasification of coal and polyethylene mixture, Fuel, 2004, 83, 2251-2254
[24] Zhang A., Kailo M., YasudaH., Zabat M., Nakano K., Yamada O., Fundamental studies on hydrogasification of Taiheiyo coal, Energy, 2005, 30, 2243-2250
[25] Misirlioglu Z., Canel M., Sinag A., Hydrogasification of chars under high pressures, Energy Conversion and Management, 2007, 48, 52-58
[26] Lee S.H., Lee J.G., Kim J.H., Choi Y.C., Hydrogasification characteristics of bituminous coals in an entrained-flow hydrogasifier, Fuel, 2006, 85, 803-806
[27] Katalumba H., Takeda S., Hydrogasified coal char’s reactivity improvement technique through H2/coal feed ratio, coal loading, and slip velocity control, Energy & Fuels, 2002, 16, 428-435
[28] Cha W.S., Baek I.H., Jang H.T., Hydrogasification of various carbonaceous sources using pressure change properties, Korean Journal of Chemical Engineering, 2007, 24, 532-536
[29] Tomecek J., S. Gil S., The kinetics of coal chars hydrogasification, Fuel Process Technol, 2010, 91, 1564-1568
[30] Zhou Y., Zheng Y., Wang W., C. Zheng, An experimental investigation on hydrogasification of coal chars in a fixed bed
reactor under high pressure, Advanced Materials Research, 2012, 524-527, 863-870

[31] Skodras G. and Sakellaropoulos G.P., Mineral Mater Effects in Lignite Gasification, Fuel Processing Technology, 2002, 77-78, 151-158

[32] Cai J. and Liu R., Application of Weibull 2-Mixture Model To Describe Biomass Pyrolysis Kinetics, Energy & Fuels, 2008, 22, 675-678

[33] Skodras G., Nenes G. and Zafeirou N., Low rank coal – CO<sub>2</sub> gasification: Experimental study, analysis of the kinetic parameters by Weibull distribution and compensation effect, Applied Thermal Engineering, 2015, 74, 111-118

[34] Zielke C.W. and Gorin E., Kinetics of Carbon Gasification, Ind. Eng. Chem. Res., 1955, 47, 820-825

[35] Zahradnik R.I. and Glenn R.A., Direct methanation of coal, Fuel, 1971, 50, 77-90

[36] Radovic L.R., Walker Jr P.L. and Jenkins R.G., Importance of carbon active sites in the gasification of cla chars, Fuel, 1983, 62, 849-856

[37] Ehrburger P., Louys F. and Lahaye J., The concept of active sites applied to the study of carbon reactivity, Carbon, 1989, 27(3), 389-393