THE EFFECT OF K₂CO₃ ON THERMAL OXIDATION OF COKES AND CARBONACEOUS MATERIALS

Silvie Vallová¹*, Eva Plevová*, Věra Valovičová*, Martin Hummel°

¹ Department of Chemistry, Technical University, 708 33 Ostrava-Poruba, Czech Republic,
º Institute of Geonics AS CR, 708 33 Ostrava-Poruba, Czech Republic

*e-mail: silvie.vallova@vsb.cz

The effect of K₂CO₃ on thermal oxidation of the blast furnace cokes and carbonaceous materials in the air was investigated by means of thermal analysis. The results obtained from the thermal analysis showed that coke contains two carbonaceous structures. The addition of K₂CO₃ affected mainly oxidation of a less ordered structure while the second stage oxidation went without changes. With increasing concentration of an additive, a decrease of both the characteristic temperatures and the values of activation energy occurred together with enhancement of reaction heat. The catalytic effect of potash on the oxidation of materials with variously ordered carbonaceous structure grows with no order of carbonaceous matter. In all cases (except graphite) the addition of potash caused a decrease of activation energies.

Keywords: coke, K₂CO₃, thermal oxidation, kinetics, carbonaceous materials, thermal analysis

Received 1. 8. 2013, accepted 18. 9. 2013

1. Introduction

Coke degradation in the blast furnace is a very complicated process. Even partial knowledge about its course has considerable technological and economic significance. The mechanical, chemical and thermal action on the blast furnace coke causes a decrease in its strength. Namely these are the surface reactions of carbon matter of coke with gaseous phase [1].

It was also found that the behavior of coke is considerably influenced by the reactions between the carbon matter and its ash under the highest temperatures [2-6]. At these temperatures the coke is graphitized, which is another mechanism of coke degradation.

The degree of coke degradation is mainly affected by the presence of alkalis [7] where the catalytic effect of alkali carbonates to the Boudouard reaction was unambiguously proved [8-9]. The enhanced alkali content distinctively increases coke reactivity under high temperatures and decreases its strength [10].

In the last ten years the action of alkalis on the blast furnace processes has been intensively investigated [11]. There are new findings about accumulation of alkali compounds in the lower part of blast furnace and their subsequent circulation.

Potash is one of the most effective catalysts in the coal gasification process [12]. In order to understand the mechanism of its action it is necessary to know the behavior of a separate compound depending on the atmosphere or temperature [13]. A lot of studies interested in these problems, however, observe properties of K₂CO₃ in the blend with other inorganic materials [14].

The results obtained in [15] which deals with coke thermal oxidation in the presence of ZnO, PbO, Fe₂O₃, CaCO₃ and K₂CO₃ proved that PbO and K₂CO₃ have the most distinct effect on coke oxidation in the air. But these two substances differ in the catalytic action mechanisms.

The aim of this paper was to look into the effect of K₂CO₃, which is effective catalyst in the gasification process, on the oxidation of cokes and carbonaceous materials using a method of thermal analysis. Unfortunately, only few papers deal with behavior of potash separately, most studies follow up properties of K₂CO₃ in the blend with other inorganic compounds. To explain the catalytic effect of potash, three factors were selected: different concentration of K₂CO₃, varied carbonaceous structure and cokes with variant reactivity. The activation energies of oxidation reactions of measured materials were determined by the method of direct non-linear regression [16].

2. Experimental

2.1. Materials

The original samples were blast furnace cokes: coke-IAC (Arcelor Mittal, a.s., Ostrava), coke IIIOKK, IIIIOKK, IVOKK (current OKK Koksovny, a.s., Ostrava; former coking plant Jan Šverma, Ostrava) and the materials with varied carbonaceous structure such as graphite (Fluka), soot (Vulcan 3, Cabot), charcoal (commercial grill wood coal). Potash (K₂CO₃, 95.5%, Fichema) was used as an additive.

The cokes were produced from coals (USA, Australia) with different content of volatile matter (VM⁴) and ash (A⁴), as showed in Table 1.

2.2. Techniques

The cokes were crushed, ground in the segmental mill Fritsch 02.102 and fractions below 0.1 mm were used. Coke-IAC was impregnated with 2, 4 and 10 wt. % solution of potash for 30 minutes, and after filtration it was dried at 60°C.
Table 1 Content of volatile matter and ash in studied coal samples

<table>
<thead>
<tr>
<th>Coal Sample</th>
<th>VM[^%]</th>
<th>A[^%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>*coalB (coke-IAC)</td>
<td>18.0</td>
<td>4.7</td>
</tr>
<tr>
<td>*coalGC (coke-IIOKK)</td>
<td>20.9</td>
<td>8.8</td>
</tr>
<tr>
<td>*coalC (coke-IIIOKK)</td>
<td>22.4</td>
<td>6.6</td>
</tr>
<tr>
<td>*coalBC4 (coke-IVOKK)</td>
<td>26.7</td>
<td>9.3</td>
</tr>
</tbody>
</table>

*coalB - Buchanan, Virginia (USA),
*coalGC - German Creek, Queensland (Australia),
*coalC - Curragh, Queensland (Australia),
*coalBC4 - Blue Creek No 4, Alabama (USA)

The effects obtained from the mechanical mixture in the segmental mill during 1 hour as blends of 5 wt. % K₂CO₃ and 95 wt. % carbonaceous materials.

Thermal analysis was carried out using simultaneous TG-DSC apparatus Netzsch STA 409 EP. All experiments were conducted under identical conditions: the samples (10-20 mg in weight) were heated up to 1000 °C in the crucibles (aluminum oxide) in a dynamic atmosphere of a dry air (with a flow rate of 100 cm³.min⁻¹) at a heating rate of 10 °C min⁻¹.

3. Results and discussion

The results obtained from the thermal analysis showed that the coke-IAC thermal oxidation is not a single process, but it proceeds in two partially overlapping stages. This corresponds to the authors’ findings [17]. It is highly probable that coke contains two carbonaceous structures, a less ordered structure oxidizes at lower temperature, and the more ordered one which is more oxidation-resistant. Fig. 1 (where dm/dt is rate of mass changes) represents the model DTG (derivative of thermogravimetry) curve of the coke-IAC thermal oxidation (curve 1+2) which is distributed into two separate curves corresponding with the oxidation of a less ordered structure of coke-IAC (curve 1) and the oxidation of a more ordered structure (curve 2). Curve marked orig indicates experimental curve.

![Fig. 1 Model DTG curves of oxidation of coke-IAC](image)

### 3.1. The effect of different concentration of K₂CO₃ on the coke oxidation

The catalytic effect of K₂CO₃ on the oxidation of coke-IAC was studied by means of a thermal analysis. It apparent, from the experimental DSC (differential thermal analysis) curves (Fig. 2, where dQ/dt is heat flux difference between sample and standard) of coke-IAC oxidation with potash, that addition of K₂CO₃ influenced the oxidation of the first stage (decrease of temperature of the maximum Tₘ) while the second stage oxidation went without any changes (comparable values of maximum temperature Tₘ).

The sample designation coke-IAC with 0 wt. % solution of K₂CO₃ means impregnation of coke-IAC with pure distilled water. Temperatures Tₘ (peak maximum on the temperature axis) were determined from DSC curves (Fig. 2, Tab. 2).

![Fig. 2 DSC curves of oxidation of coke-IAC with 0, 2, 4, 10 wt. % solution of K₂CO₃](image)

The effect of K₂CO₃ on the characteristic temperatures is negligible. The temperature of the second maximum Tₘ is about 700°C for all samples. On the other hand, the influence of potash on the maximum temperature Tₘ for the first stage oxidation is considerable. With an increasing concentration of additive the maximum temperature Tₘ shifts towards lower values (Fig. 2, Tab. 2).

The values of apparent kinetic parameters (Tab. 2) were calculated using the method of direct non-linear regression (DNR), which enables determination of apparent kinetic parameters of multistep reactions [16].

The calculation is based on the kinetic Eq. (1).

$$\frac{da}{dt} = A \exp \left( -\frac{E_a}{RT} \right) (1 - \alpha)^\varphi$$

where α is the degree of conversion, t - time (s), T - absolute temperature (K), R - molar gas constant (8.314 J K⁻¹mol⁻¹), A - frequency factor (s⁻¹), E_a - activation energy (J mol⁻¹) and n is the reaction order.

If the time step is set small enough, the derivatives in Eq. (1) may be replaced by differences [15]:

$$\frac{da}{dt} \approx \frac{a_{i+1} - a_i}{t_{i+1} - t_i}$$
\[ \Delta \alpha = A \exp\left( -\frac{E_a}{RT} \right) (1-\alpha)^n \Delta t \]  

(2)

Assuming the \( \alpha_0 \) and \( t_0 \) at the beginning of the \( \alpha \) vs. \( t \) curve, further points of the curve can be calculated from the recurrence relation

\[ \alpha_i = \alpha_{i-1} + A \exp\left( -\frac{E_a}{RT_{i-1}} \right) (1-\alpha_{i-1})^n (t_i - t_{i-1}) \]  

(3)

If the TG curve consists of \( p \) various processes with kinetic parameters \( A_j, E_{a_j} \) and \( n_j \) (\( j = 1 \) to \( p \)), Eq. (3) can be used for calculation of extent of conversion for individual reactions [15]. In this case, the equation describing the whole curve can express as a sum of particular equations:

\[ \alpha_i = \sum_j \alpha_{i,j-1} + \sum_j A \exp\left( -\frac{E_{a_j}}{RT_{i-1}} \right) (1-\alpha_{i,j-1})^{n_j} (t_i - t_{i-1}) \]  

(4)

This equation enables determination of apparent kinetic parameters of multistep reactions by non-linear optimization.

In our calculations we assumed, similarly to other authors, that the coke oxidation is the first-order reaction and that the effect of diffusion can be neglected under used experimental conditions.

Similarly like on characteristic temperatures, potash has an effect on activation energies (Tab. 2).

In the case of the first oxidation stage, an apparent decrease in values occurred. Activation energies \( E_{a_1} \) fall from 220 kJ mol\(^{-1}\) to 80 kJ mol\(^{-1}\) with increasing addition of K\(_2\)CO\(_3\) (except coke-IAC + 10 wt. % solution of K\(_2\)CO\(_3\)). The values of activation energy for the second stage \( E_{a_2} \) stay almost unchanged.

The influence of K\(_2\)CO\(_3\) also appeared in connection with reaction heat. The peak areas of DSC curves are proportional to the values of enthalpy changes. With increasing content of K\(_2\)CO\(_3\), the peak areas increase (Fig. 2).

3.2. The effect of K\(_2\)CO\(_3\) on the oxidation of varied carbonaceous structure

In order to assess the effect of K\(_2\)CO\(_3\) on the thermal oxidation of variously ordered carbonaceous structures, the following materials were chosen: a fully unorganized structure – soot and charcoal, a partially ordered turbostratic structure – blast furnace coke, and a highly ordered, free-dimensional periodic structure – graphite. The variously ordered carbonaceous structure can be assessed on the basis of maximum temperatures of oxidation \( T_m \) using DSC curves (peak maximum on the temperature axis). It can be said that the maximum temperature \( T_m \) increases with a more ordered structure (Fig. 3).

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>1. stage</th>
<th>2. stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>coke-IAC + 0 wt. % solution of K(_2)CO(_3)</td>
<td>( E_{a_1} = 220 ) [kJ mol(^{-1})]</td>
<td>( E_{a_2} = 150 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( A_1 = 3.259 \times 10^6 ) [s(^{-1})]</td>
<td>( A_2 = 1.228 \times 10^{11} ) [s(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( T_{m_1} = 616 ) [°C]</td>
<td>( T_{m_2} = 714 ) [°C]</td>
</tr>
<tr>
<td>coke-IAC + 2 wt. % solution of K(_2)CO(_3)</td>
<td>( E_{a_1} = 170 ) [kJ mol(^{-1})]</td>
<td>( E_{a_2} = 160 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( A_1 = 1.820 \times 10^9 ) [s(^{-1})]</td>
<td>( A_2 = 1.126 \times 10^{10} ) [s(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( T_{m_1} = 599 ) [°C]</td>
<td>( T_{m_2} = 712 ) [°C]</td>
</tr>
<tr>
<td>coke-IAC + 4 wt. % solution of K(_2)CO(_3)</td>
<td>( E_{a_1} = 80 ) [kJ mol(^{-1})]</td>
<td>( E_{a_2} = 160 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( A_1 = 3.628 \times 10^8 ) [s(^{-1})]</td>
<td>( A_2 = 1.134 \times 10^{10} ) [s(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( T_{m_1} = 565 ) [°C]</td>
<td>( T_{m_2} = 716 ) [°C]</td>
</tr>
<tr>
<td>coke-IAC + 10 wt. % solution of K(_2)CO(_3)</td>
<td>( E_{a_1} = 110 ) [kJ mol(^{-1})]</td>
<td>( E_{a_2} = 160 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( A_1 = 7.027 \times 10^9 ) [s(^{-1})]</td>
<td>( A_2 = 1.211 \times 10^{10} ) [s(^{-1})]</td>
</tr>
<tr>
<td></td>
<td>( T_{m_1} = 520 ) [°C]</td>
<td>( T_{m_2} = 701 ) [°C]</td>
</tr>
</tbody>
</table>
Next, a thermal analysis of mixtures of carbonaceous materials impregnated with potash (5 wt. %) was performed. Subsequently the values of activation energies ($E_{a1}$ - oxidation of original samples, $E_{a1*}$ - oxidation of carbonaceous materials with $K_2CO_3$) were determined using direct non-linear regression, Eq. 3 (Tab. 3).

In all cases (except graphite) the addition of potash caused a decrease in activation energies.

### Table 3 Activation energy $E_a$ of oxidation of carbonaceous materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{a1}$ [kJ mol$^{-1}$]</th>
<th>$E_{a1*}$ [kJ mol$^{-1}$]</th>
<th>$\Delta E_a$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphite</td>
<td>223</td>
<td>223*</td>
<td>0</td>
</tr>
<tr>
<td>coke-IAC</td>
<td>94</td>
<td>57*</td>
<td>37</td>
</tr>
<tr>
<td>soot</td>
<td>228</td>
<td>186*</td>
<td>42</td>
</tr>
<tr>
<td>charcoal</td>
<td>145</td>
<td>96*</td>
<td>49</td>
</tr>
</tbody>
</table>

### 3.3. The effect of $K_2CO_3$ on the oxidation of cokes with variant reactivity

In relation to previous experiments, the effect of $K_2CO_3$ on thermal oxidation of cokes with different reactivity was investigated. Reactivity of coke can be expressed in three ways: as rate constant $k$ of coke reaction with $CO_2$ or as activation energy $E_a$ at two different temperatures, or as spontaneous oxidation temperature $T_{so}$ (peak maximum on the temperature axis of DSC curve) in air atmosphere.

The reactivity of cokes, which is one of the most important criterion for assessing the quality of coke, is expressed here by the $CRI$ index and by the spontaneous oxidation temperature $T_{so}$, which corresponds with the maximum temperature and their value was determined from DSC curves (Fig. 4a, b). $CRI$ values were determined directly in coking plant. The most common method for determining the quality of coke is NSC method [18]: 200 g coke of granulation 19-21 mm reacts with $CO_2$ at temperature 1100°C for 2 hours. $CRI$ index indicates relative weight loss of coke mass after reaction:

$$CRI = \frac{A - B}{A} \times 100\%$$

A . . . weight of sample before reaction
B . . . weight of sample after reaction

The higher $CRI$ and the lower $T_{so}$, the higher reactivity of coke. Therefore, coke IVOKK is the most reactive, it has the highest $CRI$ and the lowest $T_{so}$ (Tab. 4)

### Table 4 Values of $CRI$ and $T_{so}$ for cokes II-IVOKK

<table>
<thead>
<tr>
<th>Type of coke</th>
<th>$CRI$ [%]</th>
<th>$T_{so}$ [°C]</th>
<th>$T_{so*}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>coke-IIOKK</td>
<td>31.6</td>
<td>640</td>
<td>501</td>
</tr>
<tr>
<td>coke-IIIOKK</td>
<td>47.0</td>
<td>629</td>
<td>495</td>
</tr>
<tr>
<td>coke-IVOKK</td>
<td>56.9</td>
<td>616</td>
<td>490</td>
</tr>
</tbody>
</table>

$T_{so*}$ - the maximum temperature after addition of $K_2CO_3$

The addition of $K_2CO_3$ caused that cokes oxidation occurs in two steps (two peak maximums on the temperature axis, Fig. 4a) unlike original cokes (Fig. 4b).

Fig. 4 DSC curves of oxidation of cokes II-IVOKK with 5 wt. % $K_2CO_3$ (a) and without $K_2CO_3$ (b)

### 4. Conclusions

The thermal oxidation of cokes and carbonaceous materials in the presence of $K_2CO_3$ was investigated by a thermal analysis. The aim of this paper was to give new findings on the effects of $K_2CO_3$, that could contribute to the understanding of the mechanism of its action and its behavior during coke degradation, what is of considerable technological and economic importance for the blast furnace process. The following results have been obtained:

- the coke thermal oxidation is not a single process, but it occurs in two partially overlapping stages; it is related to two differently ordered carbonaceous structures (Fig. 1)
- the addition of $K_2CO_3$ influenced mainly oxidation of the less ordered structure while the second stage oxidation occurred without changes (Fig. 2, Fig. 4a)
- the catalytic effect caused a distinct decrease in activation energy (from 220 kJ mol$^{-1}$ to 80 kJ mol$^{-1}$), in the temperature of maximum (Tab. 2)
- the effect of potash on the oxidation of carbonaceous materials increases with disorder of their structure: graphite < coke < soot < charcoal (Tab. 3)
The presence of $\text{K}_2\text{CO}_3$ in the mixtures with cokes with different reactivity, indicated by index CRI or $T_{\text{so}}$, shifts the spontaneous oxidation temperatures to lower values (Tab. 4, Fig. 4a).

References