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Complete List of Authors: Dumanli, Ahu; Sabanci University, Faculty of Engineering and Natural Sciences
Okyay, Firuze; Sabanci University, Faculty of Engineering and Natural Sciences
Çelik, Batuhan; Sabanci University, Faculty of Engineering and Natural Sciences
Kuru, Erkin; Sabanci University, Faculty of Engineering and Natural Sciences
Nergiz, Zeynep; Sabanci University, Faculty of Engineering and Natural Sciences
Ok, Ekin; Sabanci University, Faculty of Engineering and Natural Sciences
Saygi, Ceren; Sabanci University, Faculty of Engineering and Natural Sciences
Yurum, Yuda; Sabanci University, Faculty of Engineering and Natural Sciences

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Thermal Decarboxylation of Demineralized Turkish Beypazari Lignite by the Catalytic Effect of Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$

Ahu Gümrah Dumanli, Firuze Okyay, Batuhan Çelik, Erkin Kuru, Zeynep S. Nergiz, Ekin Ok, Ceren Saygi and Yuda Yürüm*

Faculty of Engineering and Natural Sciences, Sabanci University
Orhanli, Tuzla, Istanbul 34956, Turkey

Abstract

Demineralized Beypazari lignite were thermally decarboxylated using Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ as decarboxylation catalysts. Effective loadings of Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ were 2%, 5% and 3%, respectively. The calorific values of the demineralized lignite samples increased after the thermal decarboxylation experiments to values about 6%, 12% and 15% higher than that of the untreated demineralized sample, when Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$, respectively, were used as catalysts. The most effective catalyst with respect to the lowest activation energy attained was Cr$^{2+}$. Decarboxylation temperatures using Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ as catalysts were, 150°C, 100°C and 200°C, respectively.

Keywords  thermal decarboxylation, low rank coals, lignite, catalyst, calorific value

Introduction

Kerogens lose carboxylic acid groups during maturation and also when heated (Tissot and Welte, 1984). Analytical techniques exist that make it possible to follow closely the changes in oxygen functionality that occur during kerogen maturation and when kerogens are heated. These methods help to identify the reaction pathways that are responsible for the initial oxygen loss during kerogen maturation. The rapid formation of acid anhydrides from kerogen carboxylic acids by heating at low temperatures has been reported (Larsen et al. 2005). The primary route for low-temperature CO formation from kerogens and an important route for thermal decarboxylation of kerogens starts with anhydride formation. Thermal radical formation at temperatures as low as 300°C requires weak bonds. There are some data on the thermal decomposition of kerogens and shales to give CO$_2$ and CO. The evolution of CO$_2$ and CO from 15 oil shales heated at 10°C/min was studied by triple quadrupole mass...
spectrometry (Reynolds et al. 1991). It is apparent that there exist different reaction pathways for thermal kerogen deoxygenation. Shales indicated CO$_2$ evolution starting at about 200°C when heated at 2°C/min (Sato and Enomoto, 1997). Green River shale produced CO$_2$ and small amounts of CO on heating at 200 or 300°C (Tannenbaum and Kaplan, 1985). These data prove the presence of several pathways for thermal decarboxylation. Different shales produced both CO and CO$_2$ at very different temperatures and therefore were formed by different chemical mechanisms.

Attempts to decrease the decarboxylation temperature of low-rank coals using copper as catalyst were reported by Stournas et al. (1987), Ozvatan and Yürüm (2002) and Karabulut and Yürüm (2003). Thermal treatment of lignites and peats in the presence of Cu$^{2+}$ ions as a decarboxylating catalyst increases the calorific value of the coals. The magnitude of the increase of the calorific value depends both on the treatment temperature and concentration of the copper catalyst. Decarboxylation of low-rank Turkish Elbistan lignite at low temperatures by utilizing Cu$^{2+}$ (Ozvatan and Yürüm, 2002) and of Beypazarı lignite at low temperatures by utilizing Cu$^{2+}$, Zn$^{2+}$ and Ag$^+$ ions as catalyst was investigated in the initial parts of the present study (Karabulut and Yürüm, 2003). The calorific value of the Elbistan lignite treated with 4% Cu$^{2+}$ and decarboxylated at 200°C for 30 minutes increased about 40%. FTIR and solid state $^{13}$C NMR methods have been used to investigate the changes in the oxygen functional groups in Elbistan lignite that occurred during decarboxylation reactions. Activation energies of the decarboxylation reactions were calculated as 100.7 kJ/mol and 44.5 kJ/mol for the raw and treated Elbistan lignite samples, respectively. Addition of Cu$^{2+}$, Zn$^{2+}$ and Ag$^+$ ions as catalyst to the raw and demineralized Beypazarı lignite samples also decreased the activation energy of decarboxylation reactions. Cu$^{2+}$ seemed to be the most effective catalyst by reducing the activation energy to about 7–8 kJ/mol in the decarboxylation reactions of both raw and demineralized lignite samples. The sequence of the rate of loss of the oxygen functional groups in decarboxylation reactions for all of the metal charged sample was found as: carbonyl > carboxyl > carboxylate > hydroxyl. If the metal ions were compared in terms of effectiveness in decarboxylation reaction, the order was as follows: Cu$^{2+}$ > Ag$^+$ > Zn$^{2+}$ (for raw lignite samples) and Cu$^{2+}$ > Zn$^{2+}$ > Ag$^+$ (for demineralized lignite samples). With the presence of Cu$^{2+}$, Zn$^{2+}$, and Ag$^+$ ions, decarboxylation reactions progressed with higher rates by a dissociative mechanism to release CO or CO$_2$ simply by heating.

Akgül et al. (2005) found that 150°C was the optimum temperature to run the decarboxylation experiments, and 2% Cr$^{3+}$ or Fe$^{3+}$ metal loadings for the raw coal samples
and 1% Cr\textsuperscript{3+} or Fe\textsuperscript{3+} metal loadings for the demineralized coal samples were found to be the optimum values to obtain the highest calorific value coal after decarboxylation reactions. Addition of Cr\textsuperscript{3+} or Fe\textsuperscript{3+} to raw or demineralized coal samples decreased the activation energies of the decarboxylation reactions about 40% (raw coal samples) and 30% (demineralized coal samples). Activation energies calculated for experiments with Cr\textsuperscript{3+} loaded coal samples were lower than those for Fe\textsuperscript{3+} loaded coal samples, indicating higher activity of Cr\textsuperscript{3+} ions as catalysts.

The purpose of the present study was to investigate the catalytic effect of the transition metal ions Cr\textsuperscript{2+}, Fe\textsuperscript{2+} and Co\textsuperscript{2+} on the decarboxylation of Beypazarı lignite in terms of the change of calorific values of the decarboxylated lignite samples obtained after the decarboxylation process and activation energies for the decarboxylation processes.

**Experimental**

**Decarboxylation Experiments**

Turkish Beypazarı lignite (61.2% C) was used in this study. The lignite sample was ground to 65 mesh ASTM under a nitrogen atmosphere and dried to constant weight at 110°C under vacuum and stored under a nitrogen atmosphere. The elemental analysis of the lignite is given in Table 1. Beypazarı lignite was demineralized according to standard methods described previously (Yürüm et al., 1985) to investigate the catalytic effect of Cr\textsuperscript{2+}, Fe\textsuperscript{2+} and Co\textsuperscript{2+} ions that were doped to the structure of the demineralized lignite. About 10 g of demineralized lignite sample was stirred with solutions of chloride salts of Cr\textsuperscript{2+}, Fe\textsuperscript{2+} and Co\textsuperscript{2+} ions under a nitrogen atmosphere for 24 hours. The metal content charged to the coal was adjusted to about 1–5% of the coal sample (dmmf). Water in the mixture was evaporated using a rotary evaporator and the Cr\textsuperscript{2+}, Fe\textsuperscript{2+}, and Co\textsuperscript{2+} charged lignite samples were dried in a vacuum oven at 80°C under a nitrogen atmosphere. About 0.5 g of the metal-charged lignite sample was transferred to a porcelain crucible and placed in an oven under a dynamic nitrogen atmosphere (25 ml N\textsubscript{2}/min) and then decarboxylated at 100, 150 and 200°C for periods of 10-120 minutes in an oven under a nitrogen atmosphere. All of the experiments were repeated at least 3 times and all of the data reported in the present study was the average
of these repeated experiments. The effect of metal percentage, temperature and time on the calorific value were thus determined.

In the present work, to determine the proper metal ion percentage to be charged to the demineralized lignite and the lowest possible temperature for the highest conversion during decarboxylation reactions, and in order to obtain the highest calorific value, a set of experiments was carried out. Metal loadings changed between 1 and 5% and temperatures in the range of 100–200°C and for periods between 10 minutes and 120 minutes were employed throughout the experiments. The optimum values of the metal loadings and temperatures were determined according to the highest calorific values measured for a specific set of parameters in an experiment.

**Kinetic Analysis**

Conversion of decarboxylation experiments was calculated with the following equation:

\[
\text{\% Conversion} = \frac{W_0 - W_1}{W_0} \times 100
\]

where \(W_0\) is the weight of the demineralized coal (dry basis) at the beginning, \(W_1\) is the weight of the decarboxylated demineralized coal (dry basis).

For the kinetic analysis of the data the following general kinetic expression was used:

\[
\frac{dC}{dt} = kC^n
\]

where

- \(C\): concentration,
- \(k\): reaction rate constant, and
- \(n\): reaction order.

Conversion values were used to determine the order of reactions according to standard tests (Atkins and de Paula, 2006). Based primarily on statistical assessment of the data by linear regression, a zero-order model was postulated since linear relationship was observed between conversion values and time in all the experimental data (Figures 1-3). This was due to the integration of the differential equation which represented zero-order kinetics,

\[
\frac{dC}{dt} = kC^0
\]

that yielded
Therefore, it was assumed that the decarboxylation reactions followed zero-order reaction kinetics. Arrhenius plots constructed for the system to calculate the activation energies of the decarboxylation reactions were based on zero-order kinetics.

**Calorific Measurements**

Calorific values of the demineralized and decarboxylated lignite samples were measured with a Parr 6100 adiabatic calorimeter.

**Results and Discussion**

In the oxidation of pyritic sulfur, organic sulfur, and carbon for the Upper Freeport coal was investigated by Slagle et al. (1980) and it was found that the reactions demonstrated also zero-order kinetics. The data in the present report were found to strongly support a zero-order kinetic model. In all of the experiments, the order of the decarboxylation reactions was assumed to be of the zero-order, Figures 1-3. Decrease of the decarboxylation temperature and increase of the rate of decarboxylation reactions by the addition of metal ions to the structure of the lignites were reported previously by Ozvatan and Yürüm (2002), Karabulut and Yürüm (2003) and Akgül et al. (2005).

Higher concentrations of Cr\(^{2+}\) ions (3-5%) seemed to yield higher conversions at all temperatures. The highest conversion of 8-9% was observed at 150°C with 5% Cr\(^{2+}\) within the first 60 minute, Figure 1. Temperature was very effective in the decarboxylation reactions of the demineralized lignite doped with Fe\(^{2+}\). At 200°C very high conversions in the range of 50% was observed with 1% of Fe\(^{2+}\), Figure 2. At 100°C and 150°C, 3% Fe\(^{2+}\) was effective in producing 8-14% conversion. While lower charges of 1% of Fe\(^{2+}\) started to be catalytically effective at 200°C, higher percentage of 3% of Fe\(^{2+}\) seemed to be more effective at lower temperatures of 100°C and 150°C. Co\(^{2+}\) could only indicated low conversions of 5-7% with higher concentrations of 4-5% at all temperatures. Co\(^{2+}\) seemed to be the least effective one among the set of catalysts of Cr\(^{2+}\), Fe\(^{2+}\) and Co\(^{2+}\).

Activation energy of decarboxylation reactions of demineralized Beypazari lignite was found to be 60.7 kJ/mol by Akgül et al. (2005). Addition of Cr\(^{2+}\), Fe\(^{2+}\) and Co\(^{2+}\) ions to demineralized coal samples decreased the activation energies of the decarboxylation reactions to lower values of 2.6-34.1 kJ/mol, Table 2. The values of activation energies in the Table 2
indicated that higher percentages of the Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ were more effective in reducing the activation energy of the decarboxylation reactions and the order of catalytic effectiveness was the highest in the case of Cr$^{2+}$ and least in the case of Co$^{2+}$ as Cr$^{2+}$>Fe$^{2+}$> Co$^{2+}$. Electronic configurations of Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ are 3$d^4$, 3$d^6$ and 3$d^7$, respectively. Zang et al., 1993 claimed that metal ions with completely filled $d$-orbitals have very little catalytic activity. The results in the present work indicated that ions with the less populated $d$-orbitals were more effective catalytically in the decarboxylation reactions, as the $d$-orbitals got more crowded with electrons the catalytic activity of the ions began to decrease.

The calorific value of low rank coals increases with thermal decarboxylation, (Elliott, 1980; Stournas et al., 1987; Oztavat and Yürum, 2002, Karabulut and Yürum, 2003, Akgül et al. 2005). Akgül et al. 2005 observed that heating the raw and demineralized lignite samples to 100°C, 150°C, and 200°C for 30 minutes, increased their calorific values to only 2–5% higher than those of the unheated samples. This slight rise in the calorific values was claimed to occur due to the cleavage of a small number of carbonyl or carboxylic groups from the lignite structure. Higher increases in calorific values were observed in the present study. The calorific value of the demineralized Beypazarı lignite sample used in the present work was measured as 17119 J/g. Heating the Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ ions charged demineralized lignite samples to 100°C, 150°C, and 200°C for periods of 15-120 minutes, increased the calorific values of the lignite samples to values about 6%, 12% and 15% higher than that of the untreated demineralized sample, when Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$, respectively, were used as catalysts, Figures 4-6.

**Conclusion**

Optimum parameters in the decarboxylation experiments were summarized in Table 3. Effective loadings of Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ were 2%, 5% and 3%, respectively. These loadings were found to be the optimum values to obtain the highest calorific value in the demineralized lignite after decarboxylation reactions. The calorific values of the lignite samples increased after the thermal decarboxylation experiments to values about 6%, 12% and 15% higher than that of the untreated demineralized sample, when Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$, respectively, were used as catalysts. The most effective catalyst with respect to the lowest activation energy attained was Cr$^{2+}$. Decarboxylation temperatures using Cr$^{2+}$, Fe$^{2+}$ and Co$^{2+}$ as catalysts were, 150°C, 100°C and 200°C, respectively. These temperatures are even lower than those reported values...
in the literature previously, and these indicated that Cr\textsuperscript{2+}, Fe\textsuperscript{2+} and Co\textsuperscript{2+} were very effective in the decarboxylation reactions. Reproducible data were not obtained in certain experiments; 5\% Cr (200\textdegree C), 2\% Fe (150\textdegree C), 4\% Fe and 5\% Fe (200\textdegree C), 2\% Co and 5\% Co (200\textdegree C). Therefore the results related with these experiments were not reported. Lack of these results did not change the general conclusions reached with the data presented.
References


Table 1
Elemental analysis of Beypazarı lignite

<table>
<thead>
<tr>
<th>Element</th>
<th>%, dmmf</th>
</tr>
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<tbody>
<tr>
<td>Carbon</td>
<td>61.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.9</td>
</tr>
<tr>
<td>Sulfur, total</td>
<td>5.3</td>
</tr>
<tr>
<td>Oxygen, by difference</td>
<td>26.1</td>
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</table>

Table 2
Change of activation energy of decarboxylation reaction of Beypazarı lignite with different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%</th>
<th>Ea, kJ/mol</th>
</tr>
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<tbody>
<tr>
<td>Cr²⁺</td>
<td>1</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>1</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>12.1</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>1</td>
<td>34.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20.3</td>
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</table>

Table 3
Optimum parameters for the highest calorific values after decarboxylation experiments

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Loading, %</th>
<th>Calorific value, J/g</th>
<th>% Increase in calorific value</th>
<th>Decarboxylation temperature, °C</th>
<th>Time, min</th>
<th>Conversion, %</th>
<th>Activation energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr²⁺</td>
<td>2</td>
<td>18048</td>
<td>6</td>
<td>150</td>
<td>30</td>
<td>4.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>2</td>
<td>19515</td>
<td>12</td>
<td>100</td>
<td>30</td>
<td>2.1</td>
<td>13.2</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>3</td>
<td>19985</td>
<td>15</td>
<td>200</td>
<td>30</td>
<td>5.3</td>
<td>20.3</td>
</tr>
</tbody>
</table>
Figure 1. Change of conversion of Beypazari lignite after decarboxylation reaction with percentage of Cr\(^{2+}\) catalyst and temperature.

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Figure 2. Change of conversion of Beypazari lignite after decarboxylation reaction with percentage of Fe$_{2}^{+}$ catalyst and temperature
Figure 3. Change of conversion of Beypazari lignite after decarboxylation reaction with percentage of Co$^{2+}$ catalyst and temperature.
Figure 4. Change of calorific value of Beypazari lignite after decarboxylation reaction with percentage of Cr catalyst and temperature.
Figure 5. Change of calorific value of Beypazari lignite after decarboxylation reaction with percentage of Fe catalyst and temperature

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Figure 6. Change of calorific value of Beypazari lignite after decarboxylation reaction with percentage of Co catalyst and temperature