

Thermal Decarboxylation of Turkish Beypazari Lignite by the Catalytic Effect of Cr²⁺, Fe²⁺ and Co²⁺

Journal:	<i>Energy Sources, Part A: Recovery, Utilization, and Environmental Effects</i>
Manuscript ID:	UESO-2009-0015.R1
Manuscript Type:	Original Article
Date Submitted by the Author:	
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
Keywords:	thermal decarboxylation, low rank coals, lignite, catalyst, calorific value

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



For Peer Review Only

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

1
2
3 spectrometry (Reynolds et al. 1991). It is apparent that there exist different reaction pathways
4 for thermal kerogen deoxygenation. Shales indicated CO₂ evolution starting at about 200°C
5 when heated at 2°C/min (Sato and Enomoto, 1997). Green River shale produced CO₂ and
6 small amounts of CO on heating at 200 or 300°C (Tannenbaum and Kaplan, 1985). These
7 data prove the presence of several pathways for thermal decarboxylation. Different shales
8 produced both CO and CO₂ at very different temperatures and therefore were formed by
9 different chemical mechanisms.

10
11 Attempts to decrease the decarboxylation temperature of low-rank coals using copper
12 as catalyst were reported by Stournas et al. (1987), Ozvatan and Yürüm (2002) and Karabulut
13 and Yürüm (2003). Thermal treatment of lignites and peats in the presence of Cu²⁺ ions as a
14 decarboxylating catalyst increases the calorific value of the coals. The magnitude of the
15 increase of the calorific value depends both on the treatment temperature and concentration of
16 the copper catalyst. Decarboxylation of low-rank Turkish Elbistan lignite at low temperatures
17 by utilizing Cu²⁺ (Ozvatan and Yürüm, 2002) and of Beypazarı lignite at low temperatures by
18 utilizing Cu²⁺, Zn²⁺ and Ag⁺ ions as catalyst was investigated in the initial parts of the present
19 study (Karabulut and Yürüm, 2003). The calorific value of the Elbistan lignite treated with
20 4% Cu²⁺ and decarboxylated at 200°C for 30 minutes increased about 40%. FTIR and solid
21 state ¹³C NMR methods have been used to investigate the changes in the oxygen functional
22 groups in Elbistan lignite that occurred during decarboxylation reactions. Activation energies
23 of the decarboxylation reactions were calculated as 100.7 kJ/mol and 44.5 kJ/mol for the raw
24 and treated Elbistan lignite samples, respectively. Addition of Cu²⁺, Zn²⁺ and Ag⁺ ions as
25 catalyst to the raw and demineralized Beypazarı lignite samples also decreased the activation
26 energy of decarboxylation reactions. Cu²⁺ seemed to be the most effective catalyst by
27 reducing the activation energy to about 7–8 kJ/mol in the decarboxylation reactions of both
28 raw and demineralized lignite samples. The sequence of the rate of loss of the oxygen
29 functional groups in decarboxylation reactions for all of the metal charged sample was found
30 as: carbonyl > carboxyl > carboxylate > hydroxyl. If the metal ions were compared in terms
31 of effectiveness in decarboxylation reaction, the order was as follows: Cu²⁺ > Ag⁺ > Zn²⁺ (for
32 raw lignite samples) and Cu²⁺ > Zn²⁺ > Ag⁺ (for demineralized lignite samples). With the
33 presence of Cu²⁺, Zn²⁺, and Ag⁺ ions, decarboxylation reactions progressed with higher rates
34 by a dissociative mechanism to release CO or CO₂ simply by heating.

35
36 Akgül et al. (2005) found that 150°C was the optimum temperature to run the
37 decarboxylation experiments, and 2% Cr³⁺ or Fe³⁺ metal loadings for the raw coal samples
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 and 1% Cr^{3+} or Fe^{3+} metal loadings for the demineralized coal samples were found to be the
4
5 optimum values to obtain the highest calorific value coal after decarboxylation reactions.
6
7 Addition of Cr^{3+} or Fe^{3+} to raw or demineralized coal samples decreased the activation
8
9 energies of the decarboxylation reactions about 40% (raw coal samples) and 30%
10
11 (demineralized coal samples). Activation energies calculated for experiments with Cr^{3+}
12
13 loaded coal samples were lower than those for Fe^{3+} loaded coal samples, indicating higher
14
15 activity of Cr^{3+} ions as catalysts.
16
17
18
19

20 The purpose of the present study was to investigate the catalytic effect of the transition
21
22 metal ions Cr^{2+} , Fe^{2+} and Co^{2+} on the decarboxylation of Beypazarı lignite in terms of the
23
24 change of calorific values of the decarboxylated lignite samples obtained after the
25
26 decarboxylation process and activation energies for the decarboxylation processes.
27
28

29 **Experimental**

30 *Decarboxylation Experiments*

31
32
33
34
35
36 Turkish Beypazarı lignite (61.2% C) was used in this study. The lignite sample was
37
38 ground to 65 mesh ASTM under a nitrogen atmosphere and dried to constant weight at 110°C
39
40 under vacuum and stored under a nitrogen atmosphere. The elemental analysis of the lignite is
41
42 given in Table 1. Beypazarı lignite was demineralized according to standard methods
43
44 described previously (Yürüm et al., 1985) to investigate the catalytic effect of Cr^{2+} , Fe^{2+} and
45
46 Co^{2+} ions that were doped to the structure of the demineralized lignite. About 10 g of
47
48 demineralized lignite sample was stirred with solutions of chloride salts of Cr^{2+} , Fe^{2+} and Co^{2+}
49
50 ions under a nitrogen atmosphere for 24 hours. The metal content charged to the coal was
51
52 adjusted to about 1–5% of the coal sample (dmmf). Water in the mixture was evaporated
53
54 using a rotary evaporator and the Cr^{2+} , Fe^{2+} , and Co^{2+} charged lignite samples were dried in a
55
56 vacuum oven at 80°C under a nitrogen atmosphere. About 0.5 g of the metal-charged lignite
57
58 sample was transferred to a porcelain crucible and placed in an oven under a dynamic
59
60 nitrogen atmosphere (25 ml N_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

$$C = k t$$

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

1
2
3 indicated that higher percentages of the Cr^{2+} , Fe^{2+} and Co^{2+} were more effective in reducing
4 the activation energy of the decarboxylation reactions and the order of catalytic effectiveness
5 was the highest in the case of Cr^{2+} and least in the case of Co^{2+} as $\text{Cr}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+}$. Electronic
6 configurations of Cr^{2+} , Fe^{2+} and Co^{2+} are $3d^4$, $3d^6$ and $3d^7$, respectively. Zang et al., 1993
7 claimed that metal ions with completely filled d -orbitals have very little catalytic activity. The
8 results in the present work indicated that ions with the less populated d -orbitals were more
9 effective catalytically in the decarboxylation reactions, as the d -orbitals got more crowded
10 with electrons the catalytic activity of the ions began to decrease.

11
12 The calorific value of low rank coals increases with thermal decarboxylation, (Elliott,
13 1980; Stournas et al., 1987; Ozvatan and Yürüm, 2002, Karabulut and Yürüm, 2003, Akgül et
14 al. 2005). Akgül et al. 2005 observed that heating the raw and demineralized lignite samples
15 to 100°C, 150°C, and 200°C for 30 minutes, increased their calorific values to only 2–5%
16 higher than those of the unheated samples. This slight rise in the calorific values was claimed
17 to occur due to the cleavage of a small number of carbonyl or carboxylic groups from the
18 lignite structure. Higher increases in calorific values were observed in the present study. The
19 calorific value of the demineralized Bepazari lignite sample used in the present work was
20 measured as 17119 J/g. Heating the Cr^{2+} , Fe^{2+} and Co^{2+} ions charged demineralized lignite
21 samples to 100°C, 150°C, and 200°C for periods of 15-120 minutes, increased the calorific
22 values of the lignite samples to values about 6%, 12% and 15% higher than that of the
23 untreated demineralized sample, when Cr^{2+} , Fe^{2+} and Co^{2+} , respectively, were used as
24 catalysts, Figures 4-6.

25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 **Conclusion**

45
46
47
48 Optimum parameters in the decarboxylation experiments were summarized in Table 3.
49 Effective loadings of Cr^{2+} , Fe^{2+} and Co^{2+} were 2%, 5% and 3%, respectively. These loadings
50 were found to be the optimum values to obtain the highest calorific value in the demineralized
51 lignite after decarboxylation reactions. The calorific values of the lignite samples increased
52 after the thermal decarboxylation experiments to values about 6%, 12% and 15% higher than
53 that of the untreated demineralized sample, when Cr^{2+} , Fe^{2+} and Co^{2+} , respectively, were used
54 as catalysts. The most effective catalyst with respect to the lowest activation energy attained
55 was Cr^{2+} . Decarboxylation temperatures using Cr^{2+} , Fe^{2+} and Co^{2+} as catalysts were, 150°C,
56 100°C and 200°C, respectively. These temperatures are even lower than those reported values
57
58
59
60

1
2
3 in the literature previously, and these indicated that Cr^{2+} , Fe^{2+} and Co^{2+} were very effective in
4 the decarboxylation reactions. Reproducible data were not obtained in certain experiments;
5 5% Cr (200°C), 2% Fe (150°C), 4% Fe and 5% Fe (200°C), 2% Co and 5% Co (200°C).
6
7 Therefore the results related with these experiments were not reported. Lack of these results
8
9 did not change the general conclusions reached with the data presented.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

- Akgül, M., Karabakan A., and Yürüm, Y. 2005. Decarboxylation of Beypazarı lignite by the catalytic effect of Cr^{3+} and Fe^{3+} ions, *Energy Sources*, 27:1193–1202.
- Elliott, D. C. 1980. Decarboxylation as a means of upgrading the heating value of low-rank coals. *Fuel* 59:805–806.
- Karabulut, S., and Yürüm, Y. 2003. Decarboxylation of Beypazarı lignite by the catalytic effect of Cu^{2+} , Zn^{2+} and Ag^+ ions. *Energy Sources* 25:969–982.
- Larsen, J.W., Islas-Flores, C., Aida, M.T., Opaprakasit, P., Painter P. 2005. Kerogen Chemistry 2. Low-Temperature Anhydride Formation in Kerogens. *Energy Fuels* 19:145-151.
- Ozvatan, S., and Yürüm, Y. 2002. Catalytic decarboxylation of Elbistan lignite. *Energy Sources* 24:581–589.
- Reynolds, J.G., Crawford, R.W., and Burnham, A.K. 1991. Analysis of oil shale and petroleum source rock pyrolysis by triple quadrupole mass spectrometry: comparisons of gas evolution at the heating rate of $10^\circ\text{C}/\text{min}$. *Energy Fuels* 5:507-523.
- Sato, S., and Enomoto, M. 1997. Development of new estimation method for CO_2 evolved from oil shale. *Fuel. Process. Techn.* 53:41-47.
- Slagle, D., Shah, Y.T., and Joshi, J.B. 1980. Kinetics of oxydesulfurization of upper Freeport coal, *Ind. Eng. Chem. Process Des. Dev.* 19:294-300.
- Stournas, S., Papachristos, M., and Kyriacopoulos, G. B. 1987. Upgrading of low-rank solid fuels with catalyzed decarboxylation under very mild conditions. *Fuel Processing Technology* 17:195–200.
- Tannenbaum, E., and Kaplan, I.R. 1985. Role of minerals in the thermal alteration of organic matter I: Generation of gases and condensates under dry condition. *Geochim. Cosmochim. Acta* 49:2589-2604.
- Tissot, B.P., Welte, D.H. 1984. *Petroleum Formation and Occurrence*; Springer-Verlag, New York.
- Yürüm, Y., Kramer, R., and Levy, M. 1985. Interaction of kerogen and mineral matrix of an oil shale in an oxidative atmosphere. *Thermochimica Acta* 94:285–293.
- Zang, Y., Kshirsagar, G., Ellison, J. E., and Cannon, J. C. 1993. Catalytic effects of metal oxides on the thermal decomposition of sodium chlorate. *Thermochimica Acta* 228:147–154.

Table 1
Elemental analysis of Beypazari lignite

Element	%, dmmf
Carbon	61.2
Hydrogen	5.5
Nitrogen	1.9
Sulfur, total	5.3
Oxygen, by difference	26.1

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

Catalyst	%	Ea, kJ/mol
Cr ²⁺	1	7.1
	2	2.3
	3	6.8
	4	2.6
Fe ²⁺	1	17.2
	2	13.2
	3	12.1
Co ²⁺	1	34.1
	2	27.0
	3	20.3

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

Metal ion	Loading, %	Calorific value, J/g	% Increase in calorific value	Decarboxylation temperature, °C	Time, min	Conversion, %	Activation energy, kJ/mol
Cr ²⁺	2	18048	6	150	30	4.9	2.3
Fe ²⁺	2	19515	12	100	30	2.1	13.2
Co ²⁺	3	19985	15	200	30	5.3	20.3

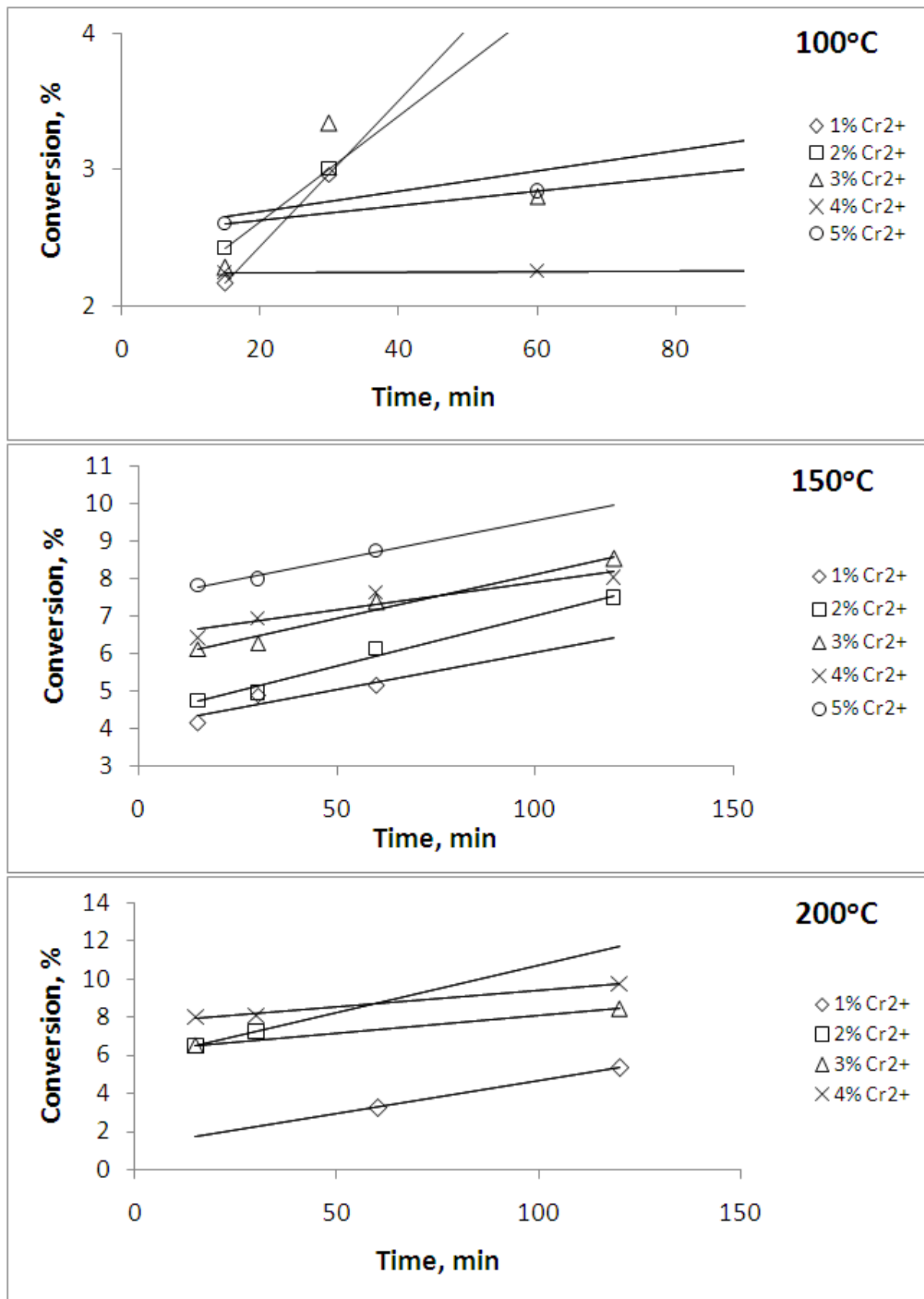


Figure 1. Change of conversion of Beypazari lignite after decarboxylation reaction with percentage of Cr²⁺ catalyst and temperature

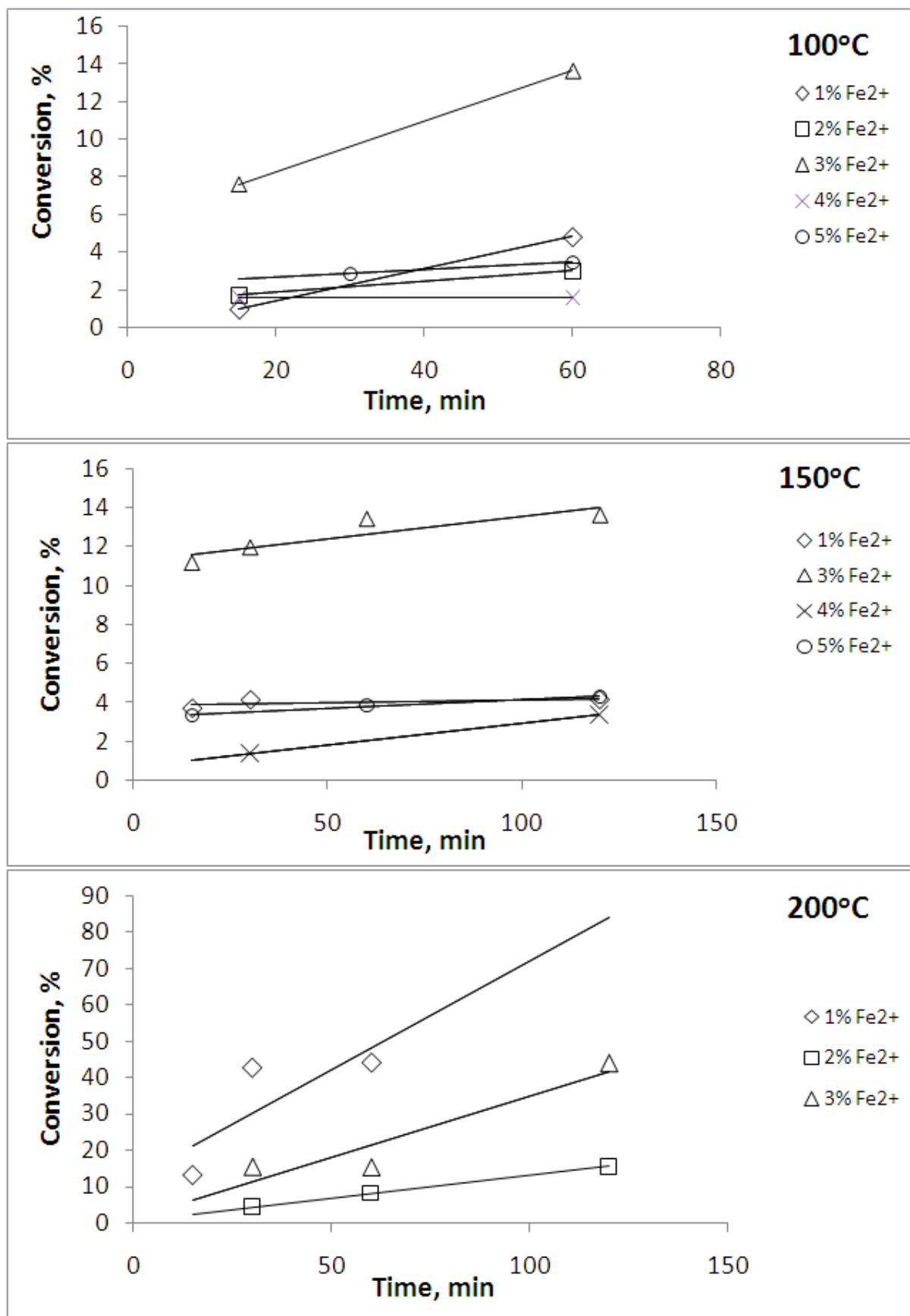


Figure 2. Change of conversion of Bey pazari lignite after decarboxylation reaction with percentage of Fe²⁺ catalyst and temperature

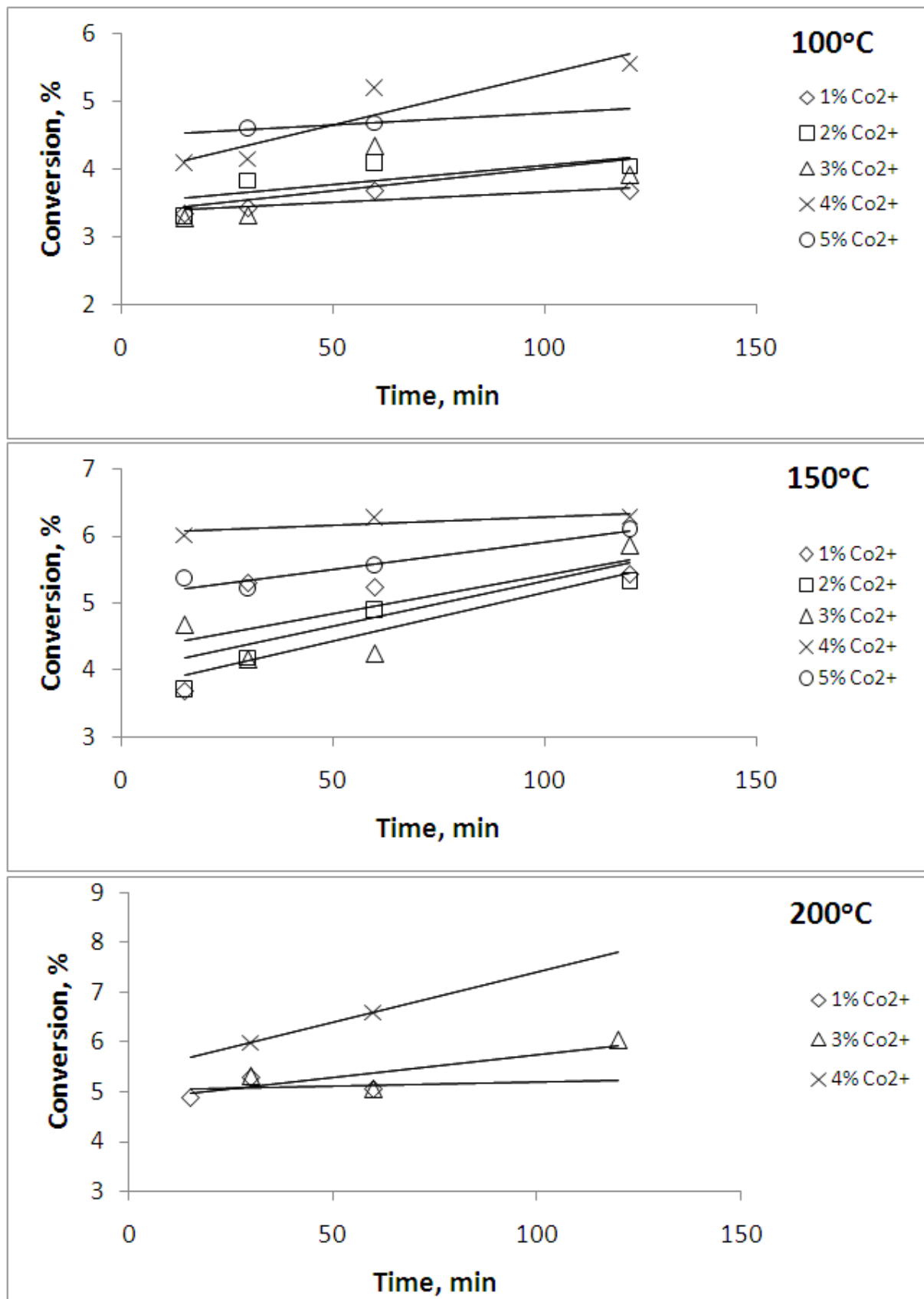


Figure 3. Change of conversion of Beypazari lignite after decarboxylation reaction with percentage of Co²⁺ catalyst and temperature

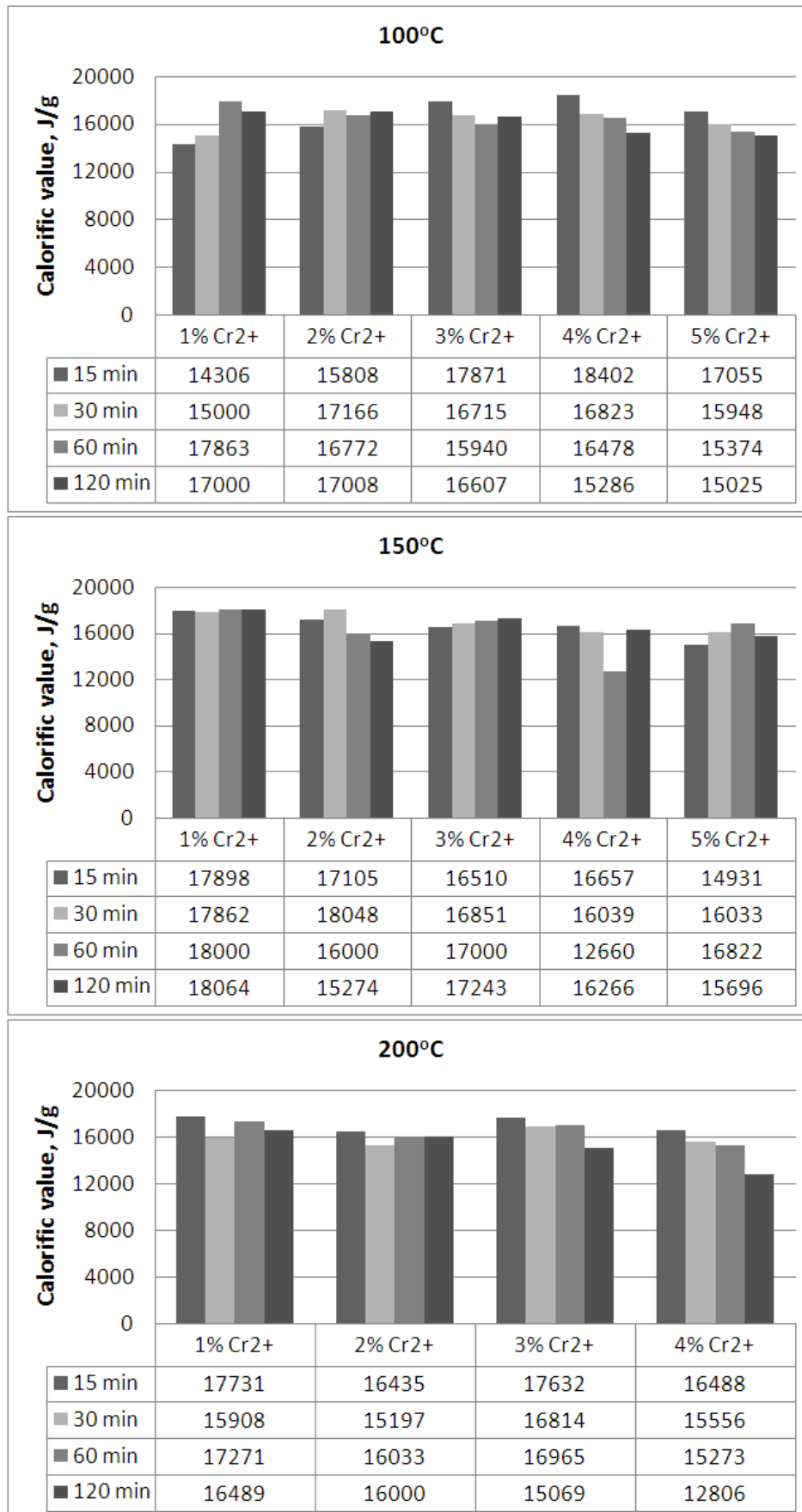


Figure 4. Change of calorific value of Bey pazari lignite after decarboxylation reaction with percentage of Cr catalyst and temperature

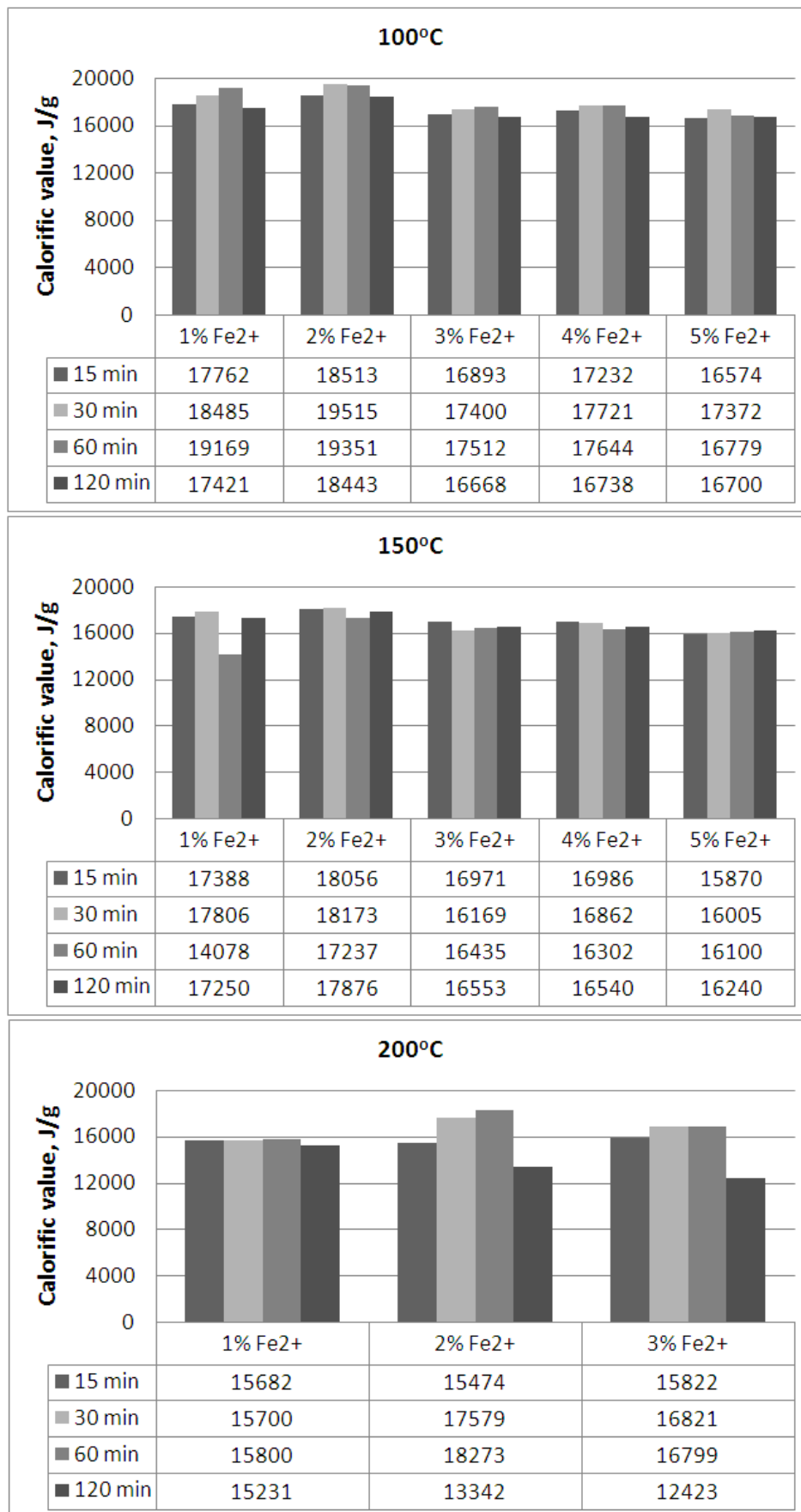


Figure 5. Change of calorific value of Bey pazari lignite after decarboxylation reaction with percentage of Fe catalyst and temperature

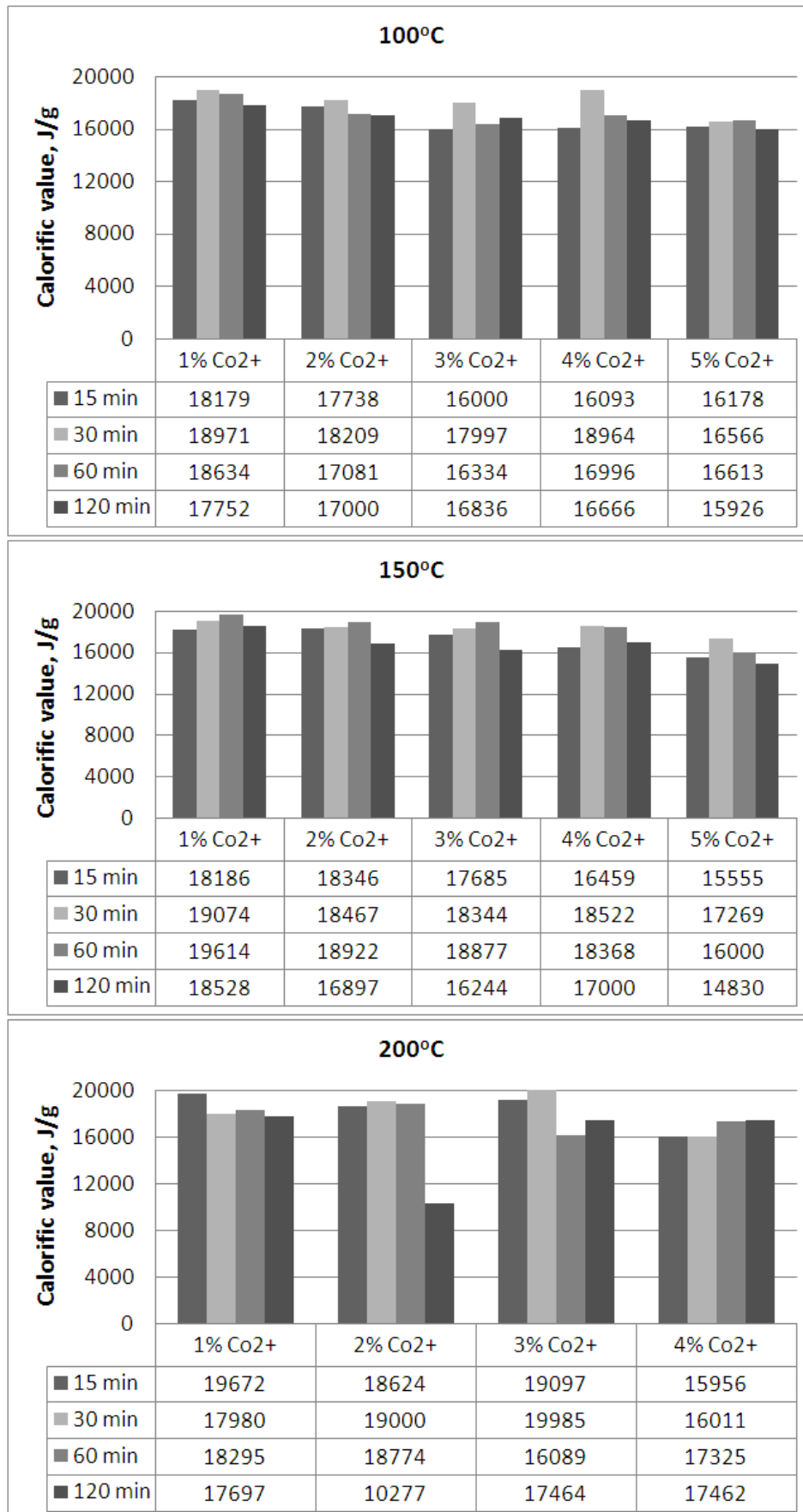


Figure 6. Change of calorific value of Beypazari lignite after decarboxylation reaction with percentage of Co catalyst and temperature