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Electrolysis of coal slurries to produce hydrogen gas: Relationship between CO₂ and H₂ formation

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ABSTRACT

The purpose of this study was to produce hydrogen gas by electrolysis of coal slurries and to investigate the relation between hydrogen (H₂) and carbon dioxide (CO₂) formation. Electrolysis of coal slurries was evaluated at 40 °C and 1.0 V cell potential to examine H₂ and CO₂ relationship. When electrolysis was performed after the coal slurry was mixed with Fe(II)/Fe(III) ions and stirred overnight (>12 h), no CO₂ gas was observed at the anode compartment. The results of total organic carbon (TOC) indicated that after electrolysis, few organic compounds were transformed into the solution and these organic compounds did not convert into CO₂. GC analysis, on the other hand, revealed that the H₂ collected at the cathode was pure and did not require any further purification process. Hydrogen generation or electrolysis efficiency of coal slurries cannot be calculated or estimated by examining CO₂ generation as reported in the literature. Low temperature and low cell potential were not sufficient to oxidize coal quantitatively.

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1. Introduction

Coal is expected to play an important role in the energy production in the future because of its largest share in the available fossil fuel reserves in the world [1]. Most of the world's energy utilization comes from the combustion of fossil fuels. Direct burning of these fossil fuels brings about major environmental pollution. The use of high ash and sulfur containing coals for domestic purposes and in power generation causes serious environmental problems [2,3]. Statistics on the global warming shows that CO₂ produced from combustion of coal is the main reason for greenhouse effect. Therefore, the present research on the sequestration of carbon dioxide has the priority over many other research issues. In addition, the quantity of world reserves, production

cost and utilization of fuels other than coal shows that fossil fuel will lead as a main energy resource in the twenty first century. Therefore, it is essential that there be more research on coals to solve pollution problem during production and utilization of coal and coal-derived fuels.

Electrolysis of coals in an acidic media is an alternative way to produce clean hydrogen gas and reduce ash and sulfur content in coal. Electrolysis of coal was first proposed by Coughlin and Farooque [4–8]. According to the authors [4], coal is oxidized at the anode of the electrochemical cell as shown in the following reaction:



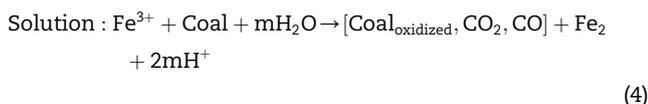
while protons are reduced to produce hydrogen at the cathode:

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The theoretical standard potential for this process is 0.21 V, which is significantly lower than the standard potential of water electrolysis (1.23 V). The production cost of hydrogen gas including the isolation cost of carbon dioxide from coal is much cheaper than if obtained from water electrolysis [9]. In the previous studies the efficiency of CO₂ generation was examined and the efficiency of hydrogen generation from the electrolysis of coal slurries was assumed to be 100% [4,5,10]. The values previously reported for the efficiency of CO₂ production from coal oxidation have widely varied [5,10]. Some authors in their studies have calculated the efficiency of coal electro-oxidation by comparing the ratio of between CO₂ gas generated at the anode to the CO₂ gas calculated by the Faraday's law [11–13]. In another study, the reduction in carbon, hydrogen, sulfur, and ash contents of coal before and after electrolysis was determined, and the electro-oxidation process of coal was reported to be the reason of decreased values after electrolysis [8]. However, no research has been conducted to find out whether this decrease was resulted from the reactions between acids and some minerals in the coal structure. Several researchers [10,11,14–19] have evaluated the effect of iron on the electro-oxidation of coal. The depletion of ferrous ion is low, because it is regenerated by the coal in the solution, as indicated below.



The relationship between carbon dioxide and hydrogen gas evolutions, generated during electrolysis, has not been reported to date. Therefore, in the current research, we also aimed to determine the effect of acid treatment (acid leaching) of coal and its duration on hydrogen production and the carbon dioxide evolutions. Before and after electrolysis, total organic carbon (TOC) contents of the anode slurries were analyzed and carbon consumption was examined. In addition, two different types of electrochemical cells were used in electrolysis of coal slurry and the effect of cell configuration on hydrogen evolution was evaluated.

2. Experimental

2.1. Coal samples

Tuncbilek coal used in the study was characterized by high levels of ash and sulfur contents. The relevant analytical data of Tuncbilek coal is given in Table 1. The coal samples were ground to pass a, 80 mesh screen (180 μm), sealed in glass ampoules under nitrogen, and kept at –20 °C until they were used in the electrochemical oxidation experiment. All

Table 1 – Analytical data of Tuncbilek coal.

Coal components	Composition, wt %
Moisture	14.06
Ash, (dry)	24.09
C, (daf) ^a	76.56
H, (daf)	5.44
N, (daf)	2.76
O, (daf) ^b	13.03
S _{Total} (dry)	2.21

a Daf: dry, ash-free.

b Calculated from difference.

solvents and chemicals were bought from Merck and used as received.

2.2. Electro-oxidation of coal

Electrochemical experiments were performed under potentiostatic conditions, using an IviumStat electrochemical analyzer. Two different types of divided glass electrochemical cells were used for the electrolysis. One of them, with 200 ml capacity, was designed according to the cell model that was used by Lalvaniet. al. (Fig. 1) [20]. The second electrochemical cell was H-shaped, with 500 ml capacity, and was also designed as described in the literature (Fig. 2) [21]. Both systems were completely sealed in order to measure the amount of gas generated. Within the electrolytic cell, the anode and cathode were separated using a Nafion 117 membrane. The circular geometric areas of the membrane the capacity of which was

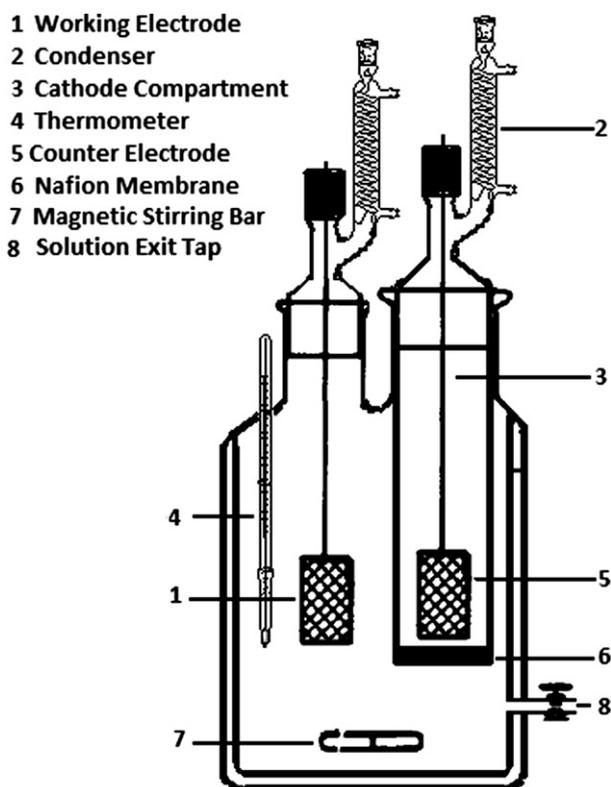


Fig. 1 – Electrochemical cell for the electrolysis of coal slurry (200 ml capacity).

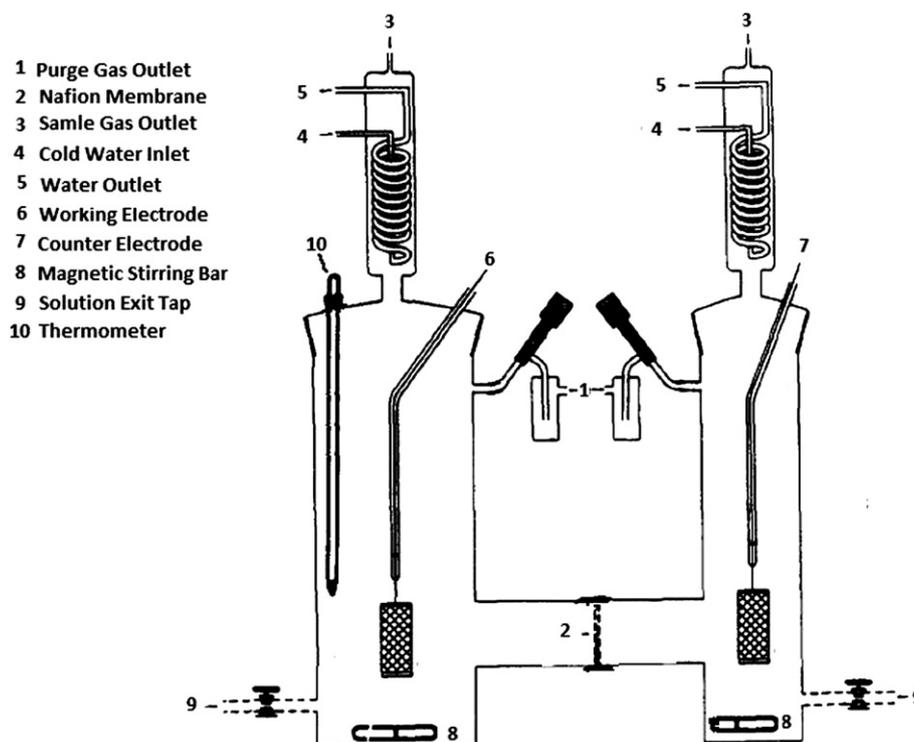


Fig. 2 – H-shaped electrochemical cell for the electrolysis of coal slurry (500 ml capacity).

200 ml and 500 ml were 2.6 cm² and 12.3 cm², respectively. Before initiating the test, the anode and cathode solutions were heated until they reached the test temperature. Experiments were performed at 40 °C, applying constant cell potential of 1.0 V with a constant mixing of the slurry in a two-compartment cell. In both systems, the Pt electrodes were used as anode and cathode. In the electrolysis cell of 500 ml capacity, the geometric area of each electrode was 6 cm² and the coal slurry concentration in the anode compartment was 0.12 g/ml

with a total volume of 400 ml of the slurry. In the electrolysis cell of 200 ml capacity, the geometric area of the electrodes was 1 cm² and the coal slurry concentration in the anode compartment was 0.12 g/ml with a total volume of 100 ml of the slurry. Sulfuric acid was used as the electrolyte in 1.0 M concentration. In all of the experiments, the iron ions used were combination of 100 mM Fe(II) and 100 mM Fe(III) solutions. Electrolysis was initiated after the coal slurry was mixed with Fe(II)/Fe(III) ions and stirred for 30 min or overnight (>12 h). All

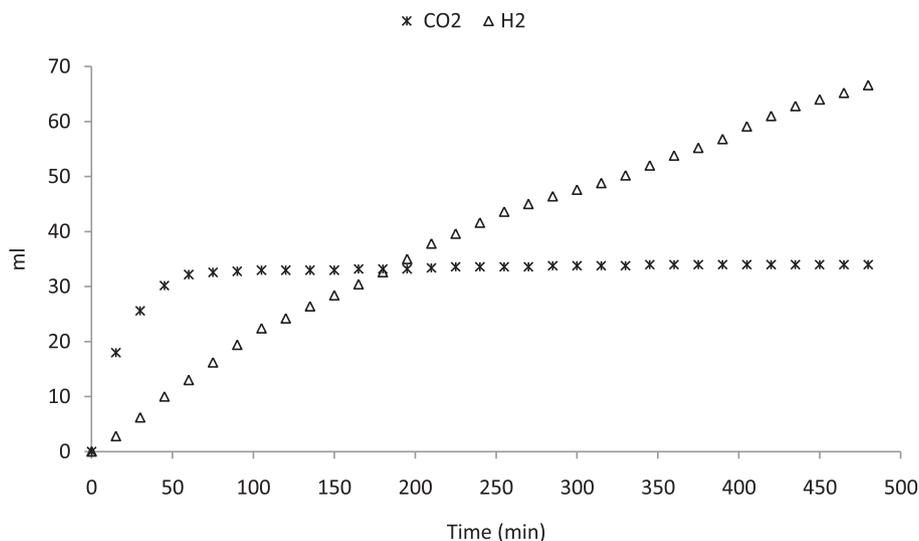


Fig. 3 – Carbon dioxide and hydrogen evolution at the anode and at the cathode under potentiostatic conditions for Tuncbilek coal/Fe(II)/Fe(III) slurries in 1.0 M H₂SO₄ at 40 °C. Electrolysis was initiated after coal slurry was mixed with Fe(II)/Fe(III) ions and stirred for 30 min (Coal concentration: 0.12 g ml⁻¹).

of the experimental runs were performed simultaneously, at a constant time of 480 min.

2.3. Product analysis

2.3.1. Gas analysis

The product gases formed at anode and cathode were collected in measuring cylinders using the method of displacement of water and analyzed with the Thermo Finnigan Trace Gas Chromatograph (TFTGC).

The Thermo Finnigan Trace Gas Chromatograph (GC) was equipped with TCD detector, and a Supelco Carboxen 1010 plot fused silica capillary column (30 m × 0.32 mm i.d.). GC oven temperature was programmed from 35 °C (5 min hold) to 230 °C (10 min hold) with 10 °C/min heating ramp. The injection port and detector temperatures were set up to 150 °C and 230 °C, respectively, and a 10 μ L gas sample was injected. The flow rate of the carrier gas (Ar) was 15 ml/min.

2.3.2. Total organic carbon analysis

Before and after electrolysis, the total organic carbon (TOC) contents of the anode slurries were analyzed using Tekmar Dohrmann Apollo 9000 instrument. A solution of 10.0 ml from the anode compartment was filtered through a 0.2 μ m nylon filter, and clear solution was analyzed for total organic content. In the TOC analysis, samples were ignited at 700 °C on a platinum-based catalyst, and the carbon dioxide formed was swept by pure oxygen as the carrier gas through a non-dispersive infrared (NDIR) detector.

2.3.3. The CHN analysis

The C, H and N analyses of coal before and after electrolysis were performed using a LECO CHNS-932 instrument. The solid residue left after electrolysis was filtered from the slurry, washed with deionized water and dried overnight in vacuum at 105 °C, before CHN analysis.

3. Results and discussion

3.1. Evaluation of carbon dioxide and hydrogen formation obtained from coal slurries

Electro-oxidation of coal and coal-iron slurry solution carried out at 40 °C using experimental setup was shown in Fig. 1. Electrolysis was initiated after the coal slurry was mixed with Fe(II)/Fe(III) ions and stirred for 30 min. The result of the evolution of CO₂ at the anode is shown in Fig. 3. At the beginning of the electrolysis, remarkable increases in CO₂ formation were observed. After 30 min, CO₂ was stable and hydrogen evolution kept going at the cathode compartment.

These results are not congruent with those reported in the related literature. The striking difference is that 1 mol CO₂ was not obtained during 2 mol of H₂ formation as given in the (1) and (2) reactions [4–8]. Given these results, we assume that the efficiency of hydrogen generation or the electrolysis efficiency of coal slurries cannot be calculated or estimated only by examining CO₂ generation as reported before [4,5,10–13].

Furthermore, a set of experiments were performed with and without electrolysis so as to find out whether or not carbon dioxide form only from electrolysis (as indicated by Eq. (1)) or from interactions between acid and mineral matter in the coal structure or from both of them. In the experiment set without electrolysis, 1.0 M H₂SO₄ aqueous solution was added into the coal samples in the presence and absence of iron ions (100 mM Fe(II)/100 mM Fe(III)). The amount of gas subsequently formed was determined in the course of time (Fig. 4). The GC analysis of the gas formed during the experiment which was performed either with or without iron ions confirmed that the gas was carbon dioxide. When iron ions were added into the coal slurry mixture (40 °C), without electrolysis, an increase in the amount of CO₂ produced was observed. This result showed that iron ions catalyzed the reactions between acid and some groups of coal structures and enhanced the evolution of CO₂. The related

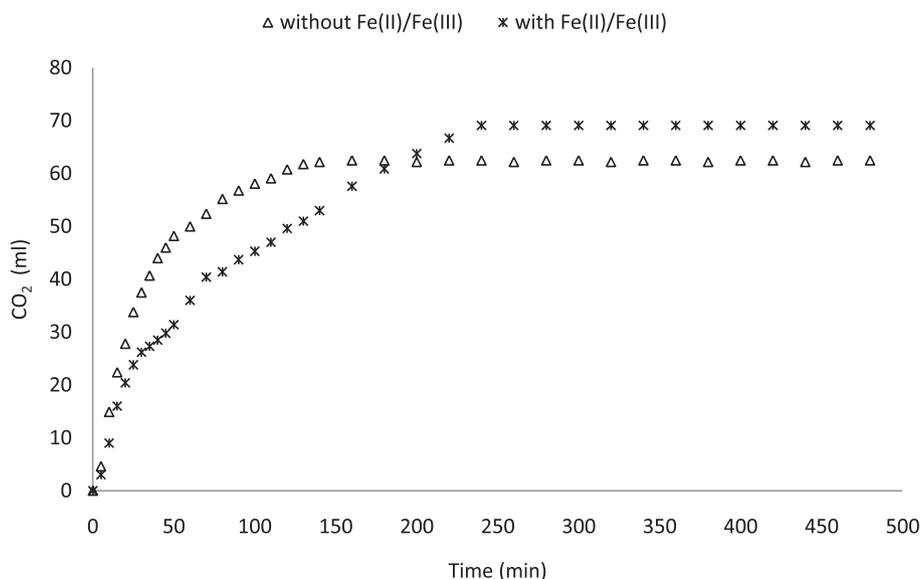


Fig. 4 – Without electrolysis carbon dioxide evolution in the presence and absence of Fe(II)/Fe(III) in 1.0 M H₂SO₄ solution at 40 °C (Coal concentration: 0.12 g ml⁻¹).

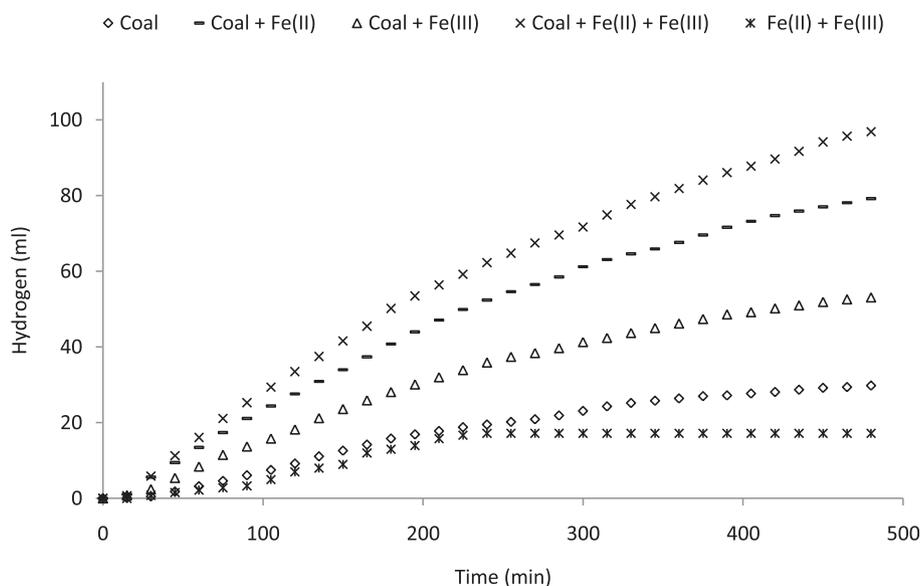


Fig. 5 – Hydrogen evolution under potentiostatic conditions with and without coal in the presence and absence of Fe(II) and Fe(III) in 1.0 M H₂SO₄ at 40 °C. (Coal slurries concentration: 0.12 g ml⁻¹; electrolysis was initiated after coal slurry was mixed with Fe(II)/Fe(III) ions and stirred overnight (> 12 h)).

literature have revealed that some organic compounds such as p-benzoquinone form CO₂ in an acidic medium in the presence of Fe(III) ions [22]. Thus, it is evident that the iron ions interacted with p-benzoquinone and similar compounds in the coal structure, and this interaction resulted in enhancing CO₂ evolution. Our results, on the other hand, indicated that carbon dioxide was not generated by electrolysis, but by the interaction between coal and acids. For further information to obtain, the coal samples and Fe(II)/Fe(III) mixture was stirred

throughout overnight (>12 h) in 1.0 M H₂SO₄ solution before electrolysis. When this slurry was electrolyzed, 96.9 ml of H₂ gas was obtained at the cathode compartment. On the other hand, there was no gas evolution in the anode compartment. As a result, we concluded that CO₂ was not generated through electrolysis but by chemical reactions. The amount of hydrogen evolution during the electrolysis, which was initiated after the coal slurry, was mixed with Fe(II)/Fe(III) ions and stirred for either 30 min or overnight (>12 h) were differed. H₂ volume

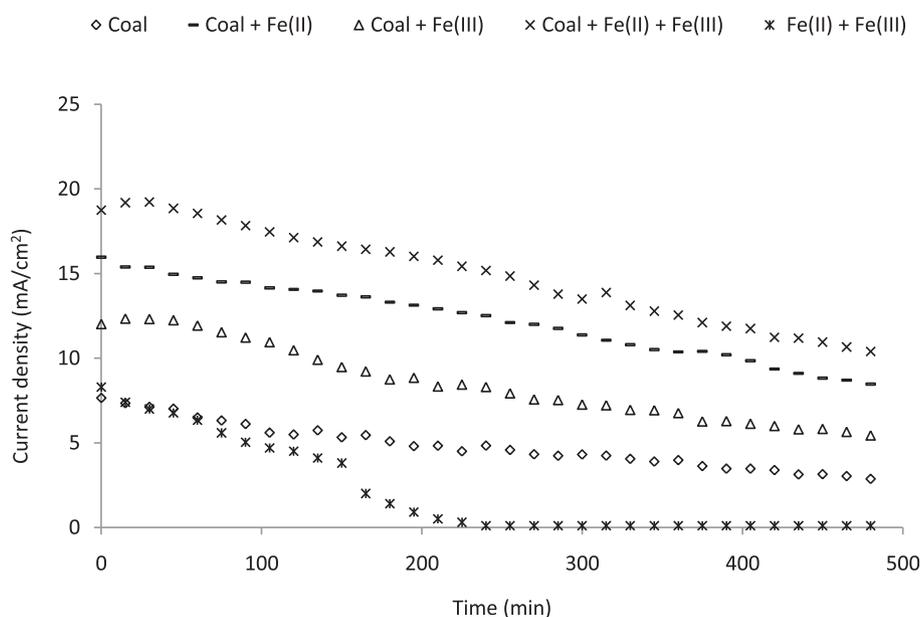


Fig. 6 – Average current densities under potentiostatic conditions with and without coal in the presence and absence of Fe(II) and Fe(III) in 1.0 M H₂SO₄ at 40 °C. (Coal slurries concentration: 0.12 g ml⁻¹; electrolysis was initiated after coal slurry was mixed with Fe(II)/Fe(III) ions and stirred overnight (> 12 h)).

Table 2 – Hydrogen evolution under potentiostatic conditions with coal/Fe(II)/Fe(III) in 1.0 M H₂SO₄ at 40 °C in different configuration electrochemical cells. (Coal slurries concentration: 0.12 g ml⁻¹; electrolysis was initiated after coal slurry was mixed with Fe(II)/Fe(III) ions and stirred overnight).

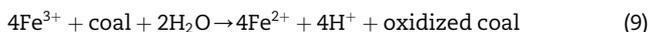
Geometric area of the electrodes	Geometric area of the membrane (cm ²)	Electrochemical cell	Coal slurry (ml)	H ₂ volume after 480 min (ml)
Pt (6 cm ²)	12.3	500 ml capacity	400	48 ± 4
Pt (1 cm ²)	2.6	200 ml capacity	100	97 ± 6

obtained from the electrolysis of the coal slurry stirred overnight (96.9 ± 4.2 ml) was more than the one stirred for 30 min (66.6 ± 3.1 ml).

The following assumptions can explain the positive effect of stirring coal slurries throughout overnight. When the coal slurry was stirred throughout overnight in the presence of Fe(II)/Fe(III) ions, the sulfate and carbonate forms of iron could be leached out from the coal particles into acidified solution and Fe(III) ions oxidized pyrite (FeS₂) in the coal particles and produced sulfate ions and elemental sulfur [23–25].



The coal matrix was also oxidized by Fe(III) ions and those iron ions converted into Fe(II) ions. Oxidation occurred simultaneously at specific reaction sites distributed through the coal, and those sites disappeared by the transformation of one type of carbon bond into another during the reaction [14].



Fe(II) ions depolarize the anode for hydrogen production at the cathode. The electrochemical reactions are expressed by:



The oxidation of pyrite and the anodic depolarization reaction proceed through a common redox couple of iron, Fe(II)/Fe(III).

The subsequent electrolysis experiment, was performed after coal slurry was mixed with Fe(II)/Fe(III) ions and stirred overnight (>12 h). The hydrogen gas evolution was limited to a 240-min electrolysis time in the blank solution consisting of 100 mM Fe(II) and 100 mM Fe(III) in 1.0 M H₂SO₄ (Fig. 5). In this electrolysis, due to the complete oxidization of Fe(II) to Fe(III), hydrogen gas was not generated at the cathode, and the current values were down to zero (Fig. 6). Electrolysis of coal slurries in the presence of 100 mM Fe(III), a significant increase was observed in the hydrogen evolution. When only coal was used in electrolysis experiments, the hydrogen yield reached to 29.8 ml after 480 min electrolysis time, whereas, the hydrogen amount was enhanced to 53.1 ml by the addition of Fe(III) into coal slurry. As a result, we assume that, Fe(III) acted as a catalyst, which improved the efficiency of coal electrolysis [11,21] and hydrogen evolution. As seen from in Fig. 5, Fe(II) also acted as an indirect catalyst, since the amount of hydrogen (79.2 ml) generated from the coal/Fe(II) system was higher than the total amount of hydrogen obtained by electrolysis of blank

solution and electrolysis of coal in the absence of iron ions, which was 17.2 ml and 29.8 ml, respectively. Thus, it is obvious that Fe(III) was continuously generated at the anode by oxidizing Fe(II), and then Fe(III) turned into the Fe(II) form and triggered the evolution of hydrogen gas via the reaction with the coal structures. GC analysis, on the other hand, showed that the H₂ gas produced at the cathode was pure.

In the absence of iron ions the current density at the beginning of electrolysis was 8.3 mA/cm² (Fig. 6). In the presence of iron ions, an increase in the current density as reported in previous studies was determined [10,11,14,16].

3.2. Effect of cell configuration on hydrogen evolution

Table 2 shows the effect of electrochemical cells configuration on hydrogen evolution. Hydrogen volume after 480 min of electrolysis in a H-shaped 500 ml capacity cell was less than the one with 200 ml capacity in spite of the large geometric area of the electrodes and membrane, and large coal slurry being used. In the H-shaped cell, lesser hydrogen yields were obtained because coal particles had collected on the nafion surface (Fig. 2, area 2), which hindered the transition of protons between the anode and cathode solutions. Although the magnetic stirrer fluently stirred the bulk solution in the cell (Fig. 2, area 8), the interface of the compartments, where nafion was placed, was not stirred well due to the unsuitable shape of the cell.

3.3. Total organic carbon results

Before and after electrolysis, the total organic carbon (TOC) contents of the anode slurry were analyzed. Before electrolysis, the total organic carbon content of the anodic solution after acid leaching of coal (mixed with iron solutions and stirred overnight) was determined to be 43 ppm. After electrolysis, TOC content of the anodic solution increased up to 65 ppm. This result indicated that after electrolysis few organic compounds transformed into the solution and these

Table 3 – The analytical data of Tuncbilek coal before and after acid (1.0 M H₂SO₄) treatment and after electrolysis^a (1.0 V).

	C	H	N	Ash
Before acid treatment	54.5 ± 1.3	4.1 ± 0.7	1.8 ± 0.7	24.1 ± 1.2
After acid treatment	54.1 ± 1.8	4.1 ± 1.0	1.7 ± 0.8	20.9 ± 1.1
After electrolysis	53.6 ± 1.1	4.1 ± 0.6	1.5 ± 0.6	19.7 ± 0.8

^a Weight percent based on dry material.

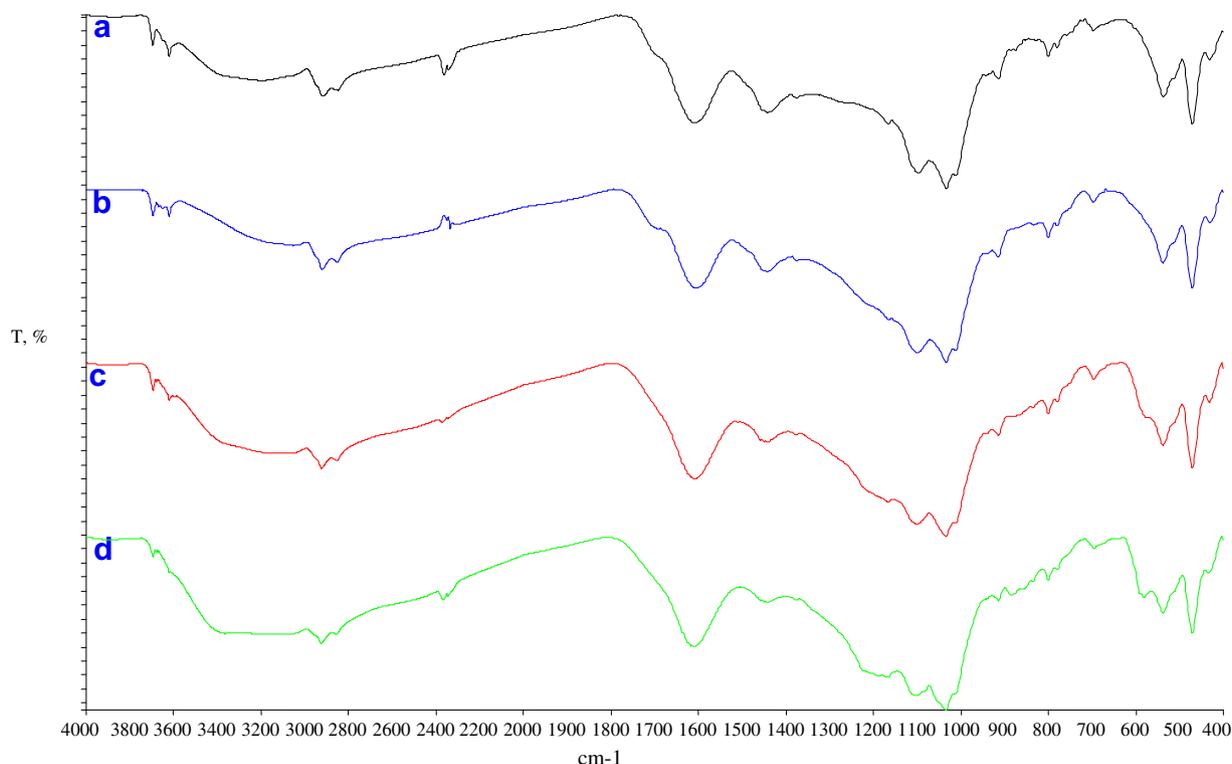


Fig. 7 – The FTIR spectra of the coal samples a) original coal, b) after 1.0 M acid treatment, c) after 3.0 M acid treatment and d) after 5.0 M acid treatment.

organic compounds did not convert into CO_2 (during electrolysis there was no CO_2 evolution).

Table 3 shows the analytical data of Tuncbilek coal before and after acid treatment (1.0 M H_2SO_4) and after electrolysis. The original carbon content of Tuncbilek coal was 54.5% (wt % based on dry basis). After the acid treatment, change in the carbon content in coal was meaningful in spite of the reaction between carbonates and acid. After the electrolysis, the change in carbon content was also very little. We assume that After 8 h of electrolysis of the coal slurry at 40°C , the change of carbon content in the coal and the consumption of coal was also very little. In addition, no significant change was observed in the hydrogen and nitrogen content of the coal. The ash content in the coal reduced after acid treatment and electrolysis (Table 3).

The spectra of coal before and after acid treatment is displayed in Fig. 7. Some spectral changes were observed in coal structure after acid treatment. It was also observed that the intensity of signals at $3560\text{--}3900\text{ cm}^{-1}$ associated with the mineral content of coal decreased after acid treatment. It is seen from the spectra of 5.0 M acid treatment that a large amount of mineral matter of coal dissolved. The broad absorption band between 3200 and 3400 cm^{-1} are assigned to N–H and surface O–H groups from all possible structures (e.g., alcohols, phenols, or even those from clay structures). The absorbance intensity and appearances of those bands depends on the cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) present in the clay structure [26]. In acidic media, protons may enter inside the clay and other minerals therefore, interaction with –OH groups which resulted

in dehydroxylation. The clay structure turns into amorphous after that interaction [27,28], which is assumed to have resulted from the change in absorption intensity of 3400 cm^{-1} . The decrease in intensity of 1600 cm^{-1} indicates the release of some materials (e.g. humic substances) from coal structure. At $1000\text{--}1100\text{ cm}^{-1}$ a Si–O–Si band was observed which is specific to clay mineral. The bands seen at 1430 , $880\text{--}860$ and $720\text{--}760\text{ cm}^{-1}$ belong to the carbonates/bicarbonates in the coal structures [29]. Because of reaction between carbonates and acid, the intensity of the bands decreased after acid treatment. The 420 cm^{-1} absorption band belongs to pyrite in the coal was also lowered in its intensity after acid treatment.

4. Conclusions

The purpose of this study was to produce hydrogen gas by electrolysis of coal slurries and to investigate the relation between H_2 and CO_2 . The data revealed that H-shaped cell was not suitable for the electrolysis of coal slurries. It was also determined that after electrolysis of Tuncbilek coal, the H_2 gas collected at the cathode was pure and ready to use without any further purification needed. After electrolysis there was no CO_2 production at the anode. In addition, analysis of generated gases in course of time during the electrolysis showed that mole ratio of H_2 produced in cathode as compared to CO_2 produced in anode was not 2:1. Indeed, during electrolysis, the undesirable CO_2 as a byproduct did not occur, as indicated by Eqs. (1), (4), and (6). Ferrous ions used with coal in electrolysis,

on the other hand, played a role to shuttle electrons between anode and coal structures. Carbon dioxide gas evolution produced by reactions between the acids and minerals (carbonates and bicarbonates) in the coal structures.

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