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**Author(s)**
Sasaki, Mitsuru; Wahyudiono; Asli, Yuksel; Motonobu, Goto

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Applications of Hydrothermal Electrolysis for Conversion of 1-Butanol in Wastewater Treatment

Mitsuru Sasaki\textsuperscript{a,*}, Wahyudiono\textsuperscript{a}, Taku Kuroda\textsuperscript{a}, Asli Yuksel\textsuperscript{a}, Kazuya Fukuyama\textsuperscript{a} and Motonobu Goto\textsuperscript{b}

\textsuperscript{a} Graduate School of Science and Technology, Kumamoto University
\textsuperscript{b} Bioelectrics Research Center, Kumamoto University

2-39-1 Kurokami, Kumamoto 860-8555, Japan

*Corresponding author. E-mail: msasaki@kumamoto-u.ac.jp.
Tel: +81-96-342-3666; Fax: +81-96-342-3665.

Abstract

Hydrothermal electrolysis of organic compound in the presence of electrolyte was conducted for a woody biomass model compound. The reaction behavior of 1-butanol as a woody biomass model compound was studied in subcritical conditions at 200-250 °C and 8-12 MPa with a batch autoclave. The autoclave volume was 500 mL and equipped system with agitation stirrer, electric current control, electric heating and temperature control and a pressure gauge. The chemical species in aqueous products were identified by gas chromatography mass spectrometry (GC-MS) and quantified using gas chromatography flame ionization detector (GC-FID). The gaseous products were analyzed by gas chromatography with a thermal conductivity detector (GC-TCD). The effect of temperature and pressure on the conversion process of 1-butanol was presented. The main products from the conversion of 1-butanol were butanal, butyric acid, hydrogen, oxygen, and carbon dioxide. The value of global rate constant for 1-butanol conversion ($k$) is $1.2 \times 10^{-2}$– $1.5 \times 10^{-2}$ min$^{-1}$. 
Keywords: hydrothermal electrolysis; 1-butanol; wastewater; conversion; biomass

1 INTRODUCTION

In the recent years, the research on reactions in supercritical water ($T_c$: 647 K, $P_c$: 22.1 MPa) was focused mainly on the destruction of hazardous wastes by oxidation (supercritical water oxidation [1, 2]). Several degradation reactions like gasification [3-5] and thermal decompositions [6-11] were also examined. The application of water at supercritical conditions is considered a promising method for the degradation of hazardous waste into harmless compounds. Merely by varying its density (a strong function of pressure and temperature), it is possible to change other properties of water, such as the dielectric constant and ion product. The density of water is also an important property in determining reaction kinetics and mechanisms at supercritical water conditions. In the supercritical state, water acts like a dense gas, and organic compounds and gases become soluble, while inorganic compounds such as salt become insoluble [12, 13]. Therefore, supercritical water is a suitable medium for the degradation of hazardous compounds. In contrast, water in the subcritical state, i.e., below the critical point, is a good medium for electrical reactions, because subcritical water has a high ionic product and thus can dissolve electrolytes.

Generally, electrochemical oxidation process was operated at atmospheric condition [13-16]. It has attracted a great deal of attention and has been proposed for the treatment of certain industrial effluents because of their versatility, which makes the treatment of liquids, gases and solids possible and environmental compatibility. Electrochemical oxidation of wastewater containing poly-aromatic organic pollutants using special catalytic anodes, chloride ion catalysts or electrochemically generated Fenton's reagent was widely studied. However, there were some difficulties for achieving complete oxidation of the organic species [13]. Practically, electrochemical oxidation at ambient temperature and pressure is a slow reaction as a
consequence of its kinetic rather than thermodynamic limitations [14]. Therefore, the use of hydrothermal electrolysis system is expected to be rapid and efficient method.

Serikawa et al. [17] reported that generation of hydrogen and oxygen gases at an initial pressure of 3 MPa and at temperature of more than 250 °C was suppressed by the electrolysis of NaCl aqueous solution, and also that thermally stable materials such as phenolic compounds, polyols, and wastewater were easily decomposed into harmless components by this treatment. Nonaka et al. [18] and Sasaki et al. [19] also carried out the electrode oxidation reaction of glucose at 250 °C and investigated the fundamental reaction characteristics for the purpose of utilizing glucose solution. They focused on understanding the degradation behavior of glucose under hydrothermal conditions and to determine how to obtain gaseous compounds such as hydrogen and carbon dioxide. Nonaka et al. [18] clarified the mechanism of electrochemical degradation of glucose and some other materials under the above conditions, but they did not clarify what kind of intermediate compounds had been generated and had reacted to form the gaseous products. Another series of experiments using pressurized CO\textsubscript{2} [19] as an electrolyte was conducted in order to know whether CO\textsubscript{2} might be applicable as an alternative electrolyte to the conventional KCl electrolyte. It was found that pressurized CO\textsubscript{2} was useful as an environmentally friendly electrolyte, although there were still some problems concerning the reaction efficiency.

In this paper, electrochemical reaction experiments on 1-butanol which is generated as one of the intermediates during the decomposition process of woody biomass, under hydrothermal conditions has been conducted to produce fuel sources from biomass resources. In particular, the effects of operating factors such as temperature and reaction time on the pollutant removal were evaluated based on the experimental results. Also, the advantages of this hydrothermal electrolysis treatment and the effects of electrical loading on the molecular transformation of 1-butanol were presented through comparison of the product distribution
obtained by hydrothermal electrolysis and by hydrothermal degradation. On the other hand, aqueous solutions containing butanols which required to be processed to remove have been generated in industrial operations. Considered from this environmental concern, it is essential that any new efficient removal techniques like hydrothermal electrolysis proposed in this study should be investigated and developed [20].

2 EXPERIMENTAL SECTION

2.1 MATERIALS

1-Butanol (99.0%) obtained from Wako Pure Chemicals Industries Ltd. is used as a starting material and distilled water as a solvent. This compound was completely soluble in water and methanol at room temperature. Butanal, butyric acid and potassium chloride (KCl) were purchased from Wako Pure Chemicals Industries Ltd. and had purities more than 99.0%. The analytical reagents used were methanol (99.7%) and 1-pentanol (98.0%) from Wako Pure Chemicals Industries Ltd., Japan. All chemicals were used as received.

2.2 EXPERIMENTAL SETUP AND PROCEDURE

The experiments of hydrothermal electrolysis were carried out in batch autoclave at a controlled temperature. This autoclave made of stainless steel with volume of 500 mL. A cylindrical electrode made of iridium was used as an anode and the titanium beaker was used as a cathode to prevent the corrosion. Fig. 1 showed the hydrothermal electrolysis apparatus which is used in this study. At the beginning of the experiment, the aqueous solution (200 mL) was loaded in titanium beaker and placed in the autoclave. After its lid was closed tightly, the air in the autoclave was purged and pressurized with argon gas. This internal pressure of the autoclave was defined as the initial pressure of the experiment. The aqueous solution loaded in the autoclave expanded thermally as the temperature in the autoclave increased and subsequently the
internal pressure gradually increased. In detail, after repeated purging (basically three times) of the gas in the autoclave using argon gas with a pressure of about 0.5 MPa, it was pressurized to 3 MPa with argon gas and then heated up to the desired temperature with stirring at 180 rpm. A thermocouple was connected to the temperature pocket, which had been filled with silicone oil. The profile of them was plotted in Fig. 2. The same method was used for the experiments using 1-butanol solution and KCl as an electrolyte solution with concentrations of 0.266 mol L\(^{-1}\) and 20 g L\(^{-1}\), respectively. The electric current is applied in the autoclave when the whole system reached the desired condition. The reaction times were measured from the applying of the electric current on the autoclave. After the reaction time had elapsed, the electric current was cut off and the autoclave was cooled with stirring until the temperature became less than 40 °C. In this experiment, the time for heating to the reaction temperature and quenching to room temperature as much as possible was shortened. All the experiments were carried out at constant heating and quenching rates. For comparison, the hydrothermal degradation experiment without the applying of DC current was performed at the same conditions.

2.3 ANALYTICAL METHODS

The aqueous phase product was identified by GC-MS (HP model 6890 series GC system and 5973 mass selective detector) with a HP-5 MS capillary column (J&W Scientific, length 30 m, inside diameter 0.25 mm, film 0.25 μm) and quantified by GC-FID (Shimadzu Co. Ltd., model GC-14A) using the same column. The temperature program was 3.0 min at 40 °C, 6.0 °C min\(^{-1}\) to 300 °C, and 9 min at 300 °C. Helium carrier gas was used at a flow rate of 1.5 mL min\(^{-1}\). The NIST (National Institute of Standards and Technology) library of mass spectroscopy was used for identification of the compounds. Product concentrations were determined by GC-FID with 1-pentanol as an internal standard. The total organic carbon (TOC) in the aqueous product solution was determined by a TOC analyzer (TOC-5000, Shimadzu) so as to evaluate the level of
organic carbon before and after the experiment. The gaseous product was collected in a sampling plastic bag at the end of the experiment. It was analyzed by GC-TCD (Yanaco GC2800T).

3 RESULTS AND DISCUSSION

3.1 ANALYSIS OF PRODUCTS

Hydrothermal electrolysis treatment is one of the treatment methods used for the removal of organic impurities from wastewater. In this process, the pollutants are destroyed by oxidation and hydrolysis processes. The pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron-transfer reaction. The results of the 1-butanol product compositional analysis appear in Fig. 3, a GC-MS chromatogram of the compound produced from 0.266 mol L\(^{-1}\) of 1-butanol reaction at 250 °C and 8 MPa after 60 min of reaction time with and without DC current. The GC-MS traces exhibit a number of small features indicating the presence of lower and higher molecular weight products that varied as a function of temperature. The identities of compounds determined through a match of mass spectra in the GC-MS computer library are reliable. This figure shows that 2-butena and butyl ether were detected clearly as product decomposition of 1-butanol when the DC current was not applied during decomposition process. It showed that 1-butanol underwent the condensation reaction. Simply because of the high ionic product of water under this condition, this reactions usually catalyzed by protons or hydroxyl ions occur in near-critical water without the addition of acids or bases. Antal et al. [21] suggested that the dehydration of tertbutyl alcohol in hot compressed liquid water consisted of single reaction steps. This mechanism includes the ionic reaction steps forming alkene which is the free radical pyrolysis of the alcohol. Tables 1(a) and 1(b) show the list of 1-butanol derived products in the liquid fraction and their retention time, molecular weight and characteristic ions for 1-butanol conversion at 250 °C and pressure around 8 MPa after 60 min reaction time, respectively.
At hydrothermal electrolysis, the decomposition of 1-butanol produced butanal and butyric acid as main products. KCl in this concentration dissolves completely in water at the reaction temperature of 200 and 250 °C. This compound was considered the inert electrolyte that would enhance the ionic strength of the aqueous reaction medium and hence would influence the rate of ionic reaction, according the Bronsted–Bjerrum theorem for ionic reactions in solution [22]. However, the most important step is the protonation of 1-butanol. This means that the reaction rates of the ion reactions not only depend on the existence of KCl as an electrolyte solution but also depend on the self-dissociation of water. Solution of KCl in liquid water prevails as separate K⁺ and Cl⁻ ions. Due to charge interactions these distribution of charges generate dipole properties within the water molecule. On the other hand, the electron transfer from anode surface also promotes the oxidation of 1-butanol.

In this work, butanal and butyric acid were quantified, since these compounds were considered to be the main products in experiment of hydrothermal electrolysis. Butanal is produced by the catalytic dehydrogenation of 1-butanol. In further reaction, butanal was oxidized into butyric acid. Therefore the yield calculation of products was considered as follows: the amount of products except butanal and butyric acid formed and 1-butanol remained is negligible.

### 3.2 LIQUID PRODUCTS

The identified liquid phase products of 1-butanol decomposition are butanal and butyric acid. They were obtained by dehydration and oxidation. Fig. 4 shows the yield of product for 1-butanol decomposition in liquid phase at 250 °C at various electric currents. The yield and conversion of 1-butanol in weight fraction (wt%) were evaluated according to:

\[
Yield \ [\text{wt\%}] = \frac{\text{Amount of product or reactant} \ (\text{mol})}{\text{Amount of 1-butanol} \ (\text{mol})} \times 100
\]  

(1)

\[
Conversion \ of \ 1\text{-butanol} \ [\text{wt\%}] = 100 - \text{yield of 1-butanol}
\]  

(2)
The decomposition of 1-butanol led to the formation of butanal and butyric acid. They are the main product at nearly all conditions. According to the stoichiometry of 1-butanol conversion corresponded to butanal and butyric acid formed so that for 1 mol of 1-butanol can be converted to 1 mol of butanal and 1 mol of butyric acid. Butanal is formed by an ionic and a free radical pathway. It is formed by the primary protonated 1-butanol, followed by water abstraction. During electrolysis process, the oxidizers were formed from KCl solution such as hypochlorite, chloric acid and oxygen, oxidized butanal into butyric acid. From these figures it is clear that electrolysis process had a dramatic influence on the conversion rate of 1-butanol. For example, without the DC currents, the conversion of 1-butanol was 8.22 % at 60 min reaction time. By applying the DC currents, the conversion of 1-butanol could approach to 32.10 %, after 30 min of reaction, and gradually increased with longer reaction times to more than those in the absence of DC currents. The same phenomenon also occurred on the yields of butanal. In contrast, the yields of butyric acid were not obtained when the DC currents were not applied on the reaction. It indicated that the oxidizing agent which produced during electrolysis process was important factor for the oxidizing process.

3.3 GAS PRODUCTS

In general, 1-butanol can decompose into it derived compounds by bimolecular H-abstraction or by unimolecular dissociation, and dissociation can occur by multiple bonds break and form or by one bond breaks at hydrothermal conditions. In this work, the hydrothermal electrolysis of 1-butanol leads mainly to the formation of H₂ and CO₂ as gaseous products. Unfortunately, the GC-TCD could not identify the carbon monoxide product. Fig. 4 showed the yield of H₂ and CO₂ as a function of reaction time. They increased significantly with the presence of DC currents. When an oxidant is present, the route leading to the formation of
butyric acid predominates. This route begins with the hydrogen abstraction step followed by hydroxylation to form it. Further decomposition of butyric acid follows the producing hydrogen and carbon dioxide. This step requires relatively high activation energy. However, the results showed that the formation of H\textsubscript{2} seemed faster than the formation of CO\textsubscript{2}. The reason why more H\textsubscript{2} was generated than CO\textsubscript{2} is probably that H\textsubscript{2} was generated not only by dehydrogenation of butyric acid that was formed during the electrolysis, but also by the electrochemical degradation of water under hydrothermal conditions. It suggested by Serikawa et al. [17] that at hydrothermal electrolysis, hydrogen gas was produced from butyric acid and oxygen atoms of water could be converted into CO\textsubscript{2}. On the other hand, the remaining hydrogen atoms of water molecule seem to be converted to H\textsubscript{2} gas.

### 3.4 EFFECT OF TEMPERATURE

Subcritical water is a high-temperature water, but not higher than the critical temperature of water. It was well known that the ionic product of water increases slightly with temperature up to around 10\textsuperscript{-11} in the range between 200 and 300 °C [23]. At these conditions, the water can still dissolve the inorganic salts allowing the use of an electrolyte solution. Furthermore, the ionic product of water at subcritical condition is two orders of magnitude higher than at room temperature. The large quantity of dissociated water molecules at this condition can promote electrochemical reaction. Fig. 5 shows the electrolysis product of 1-butanol in KCl solution inside batch autoclave as a function of reaction time at 200 and 250 °C. It showed that the conversion of 1-butanol was almost similar at each condition. On the contrary, the yields of butanal and butyric acid are quite different with increasing electrolysis time. These indicated that thermal degradation of 1-butanol in hydrothermal electrolysis may occur simultaneously. As shown in Fig. 4, without the presence of DC currents, butanal was found to be a major intermediate product of 1-butanol degradation through hydrolysis. When the DC currents were
applied, the butyric acid was found as an oxidation product of butanal. Due to the large change of value of ion product for water with temperature, the character of the reaction may change from that of ionic reaction to that radical reaction. Therefore, the yields of butanal and butyric acid at 200 °C seemed higher than at 250 °C.

3.5 EFFECT OF INITIAL PRESSURE

Generally, hydrothermal oxidation involves the liquid phase oxidation of organics components at elevated temperatures and pressures using a gaseous source of oxygen (usually air). The solubility of oxygen in aqueous solutions enhanced at elevated temperatures and pressures. It provides a strong driving force for oxidation. The elevated pressures are required to keep water in the liquid state. Fig. 6 shows the conversion of 1-butanol versus electrolysis time at different initial pressures. In this batch autoclave system, the pressure inside the reaction vessel increased completely dependent on the temperature. After the temperature reached, the pressure inside increased from 3 and 7 to 8 and 12 MPa, respectively. At these conditions, there was small different in the values of the ion products of water, 7.6 $10^{-12}$ and 7.2 $10^{-12}$ at 8 and 12 MPa, respectively. Therefore, as shown in Fig. 6, the initial pressures did not appear to affect on the conversion of 1-butanol. Sasaki et al suggested that the rate constant of cellulose decomposition at subcritical water did not increase even if the reaction pressure increased. On the contrary, at supercritical water, the rate constant gradually increased with an increase of pressure. Akiya et al. [23] also reported the influences of pressure on decomposition organic compounds in supercritical water. They explained that water molecules may participate in elementary reaction steps as reactants. The properties of water, such as density, static dielectric constant and ion product, increase with pressure. As a result, the ion reaction rate increases and free-radical reaction is restrained with an increase of pressure. Secondly, water molecules can participate in elementary reaction steps as catalysts. Many organic compounds are hydrolyzed to various
degrees in supercritical water and hydrolysis reaction plays a significant role in organic compounds decomposition. It requires the presence of $H^+$ or $OH^-$. The ion concentration influences the hydrolysis rate. With increasing pressure, the ion product increases, and therefore the hydrolysis rate increases too.

3.6 REACTION KINETICS

Hydrothermal electrolysis is one of the treatment methods used for the removal of both organic and inorganic impurities from wastewater. The pollutants are destroyed by either hydrolysis or oxidation process. Since the reaction involved in this process is complex, hydrolysis might be occurred as a side reaction during hydrothermal electrolysis oxidation. The destruction process of pollutants in hydrothermal electrolysis took place on either a direct or indirect oxidation process. In a direct oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron-transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite, chloric acid and oxygen are electrochemically generated. The pollutants are then destroyed in the bulk solution by an oxidation reaction of the generated oxidant. The mechanism of its electrogeneration in basic solution containing chloride ions may be given by the following:

$$\text{Anode : } 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} + 2\text{e}^-$$

$$\text{Cathode : } 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$

In this study, the global kinetic analysis is applied to obtain global rates of 1-butanol conversion formed its derived compounds. The following reaction is: 1-butanol $\Rightarrow$ derived compounds. Since the derived compounds as products contain various components and the reaction involved in hydrothermal electrolysis is complex, development of a kinetic model is difficult and is not of much practical importance. During the conversion processes, 1-butanol is converted in the formation of butanal from abstraction of hydrogen by hydroxyl ion. Further
oxidation will convert butanal into butyric acid. The reaction proceeds from the various -CH₃, -CH₂, and -OH groups. The relative importance of OH attack at the various -CH₃, -CH₂, and -OH groups of 1-butanol were not estimated. More than one pathway to form butanal exists in the radical mechanism. Within the context of this study, a detailed mechanism has not been elucidated because, in principle, every compound could be obtained via different reaction pathways. Therefore, the reaction pathway would be simplified: “1-butanol ==> butanal + butyric acid” to obtain the global rates of conversion of 1-butanol in hydrothermal electrolysis, with considering that butanal and butyric acid are major products. The global reaction rate constant ($k$) is associated Arrhenius parameters. At this analysis, the dependence of the reaction rate on the initial reactant concentrations has to be established. The reaction rate constant is not truly a constant, and it is almost strongly dependent on temperature.

Kinetic experiments were carried out at different temperatures (200 and 250 °C) and for different reaction times (10, 30, 60, and 90 min). The kinetics was analyzed based on measurement of the amounts of reactant and products present after the experiments (1-butanol, butanal, and butyric acid)—unknown compounds and gas products were not included—and from these experimental results, a schematic of the reaction mechanism for 1-butanol conversion under hydrothermal electrolysis conditions was developed. We propose a simple conversion process, in which 1-butanol is oxidized to form butanal and butyric acid as the only products via series reactions. The formation of them via oxidation of 1-butanol followed first-order kinetics for all experimental temperatures. The reaction was assumed that batch operation and a completely homogeneous reaction mixture can be expressed in the following forms.

1-Butanol conversion:

$$\frac{dC_A}{dt} = -k C_A$$

$$\ln \frac{C_A}{C_A0} = k t$$

(1)

Butanal formation:
\[
\frac{dC_R}{dt} = k_1 C_A - k_2 C_R
\]  
(2)

Butyric acid formation:

\[
\frac{dC_S}{dt} = -k_2 C_R
\]  
(3)

Here, \( k_1 \) and \( k_2 \) are the kinetic constants for butanal, and butyric acid formation, respectively, and \( C_{A0}, C_A, C_R, \) and \( C_S \) are the concentrations of 1-butanol (initially), 1-butanol (at time \( t \)), butanal, and butyric acid, respectively. The fitting parameters were \( k_1 > k_2 \) at each temperature. Fig. 8 shows a typical result of the linear regression to experimental data. From the linear regression, \( k \) values were calculated for all temperature conditions studied. These two rate constants were obtained by optimally fitting the product concentrations to the experimental data using least-squares analysis. The global rate constant for 1-butanol conversion, \( k \), can be obtained from \( k_1 + k_2 \). Further, the activation energy was calculated using the Arrhenius equation:

\[
k = A \exp\left[-\frac{E}{RT}\right]
\]  
(4)

where \( A \) is the pre-exponential factor, \( E \) is the activation energy, \( R \) is the molar gas constant (8.3145 J mol\(^{-1}\)K\(^{-1}\)) and \( T \) is the absolute temperature (K). The kinetic parameters obtained are shown in Table 2. It can be seen that the rate constant for 1-butanol conversion at 200 °C seemed higher than at 250 °C. It might be due to an increase in temperature has resulted in a decrease at applied potential causing to decrease in energy consumption [17]. On the other hand, since the oxidative reactions are in series with each other, the electrode reactions might be occur by direct electron transfer at the anode surface by means of electrogenerated OH radicals. The value of \( E \) for butyric acid formation was higher than those for butanal formation. Therefore, the conversion of 1-butanol tends to produce butanal rather than butyric acid, as observed during the conversion process, especially at short reaction times.
In addition, TOC was also analyzed to investigate the conversion of 1-butanol into its derived compounds. The TOC content includes all organic substances solved in the water. This analysis is used to represent the carbon content of the aqueous reactor effluent which is needed to close the carbon balance. When no solids are formed, the sum of the carbon content in the gas phase with the carbon content in the liquid effluent has to be equal to the carbon content of the starting materials. The equipment used to determine the TOC content in the effluent was not adequate for the requirements of the process because with this equipment, only solved carbon can be determined. For this reason, the carbon balance cannot be closed. Fig. 9 shows the relationship between the yield of TOC in the aqueous products and the electrolysis time. The yield of TOC decreased rapidly with the increasing reaction time when hydrothermal electrolysis was carried out at 3 A. In contrast, 80 % of the TOC of the starting material remained in the product solution even after 120 min in the case of hydrothermal degradation (at 0 A). These results indicate that 1-butanol was converted into gaseous products (such as carbon dioxide and hydrogen) by the presence of an electric current. Sasaki et al. [19] suggested that the electrode oxidation reaction of glucose under hydrothermal electrolysis at 250 °C can produce gaseous compounds such as hydrogen and carbon dioxide. Also, the degradation rates of glucose and its degradation intermediates were greatly promoted.

4 CONCLUSIONS

The conversion of 1-butanol as a woody biomass model compound was studied in hydrothermal electrolysis at 200-250 °C, 8-12 MPa using batch autoclave. Under these conditions, 1-butanol was decomposed into its derived compounds. In this work, butanal and butyric acid are considered as main products of 1-butanol conversion in liquid products. The conversion of 1-butanol and the formation of butanal and butyric acid could approach to 70.00 %, 9.00 %, and 9.00 % in weight, respectively. They increased with an increase in electric current
proportionally. In gaseous phase products, hydrogen and carbon dioxide were obtained as main products. The first-order kinetics has been applied to describe the 1-butanol conversion in hydrothermal electrolysis. There are many aspects that affect the reaction mechanism and, consequently, the resulting rate law expression. With plot Arrhenius was found that the value of global rate constant for 1-butanol conversion ($k$) is $1.2 \times 10^{-2} - 1.5 \times 10^{-2}$ min$^{-1}$. Based on these results, it is proposed that hydrothermal electrolysis could be applied as a medium for 1-butanol conversion due to the presence of direct conversion pathway.
ACKNOWLEDGEMENTS

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REFERENCES


TABLE CAPTIONS

**Table 1.** 1-Butanol derived compounds in the aqueous fraction and their retention time, molecular weight and characteristic ions for 1-butano conversion at 250 °C, 8 MPa, 60 min, (a) without current; (b) with current.

**Table 2.** Kinetic parameters obtained for 1-butanol conversion in hydrothermal electrolysis at 200-250 °C; 8 MPa with 3 A of current.
FIGURE CAPTIONS

Figure 1. Hydrothermal electrolysis apparatus.

Figure 2. Typical temperature and pressure profile for hydrothermal electrolysis: at 250 °C with initial pressure 3 MPa, direct current 3 A, and electrolyte concentration 20 mg/L.

Figure 3. GC-MS chromatogram of the liquid phase recovered after treatment at 250 °C, 8 MPa, 60 min, (a) without current; (b) with current.

Figure 4. The main products of 1-butanol conversion in the aqueous phase after treatment at 250 °C, 8 MPa, at various electric currents.

Figure 5. The gaseous products of 1-butanol conversion after treatment at 250 °C, 8 MPa, at various electric currents.

Figure 6. Effect of temperatures on the conversion 1-butanol at 8 MPa with 3 A electric current.

Figure 7. Effect of initial pressures on the conversion 1-butanol at 250 °C with 3 A electric current.

Figure 8. First-order kinetic plot for 1-butanol conversion in hydrothermal electrolysis at 250 °C, 8 MPa with 3 A of current.

Figure 9. Total organic carbon in the product solutions at temperature of 250 °C and pressure of 8 MPa.
### Table 1

#### (a)

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## Table 2

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<th>( A \times 10^4 ) [min(^{-1})]</th>
<th>( E ) [kJ.mol(^{-1})]</th>
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Figure 1
Figure 3
Figure 5

(a) Hydrogen obtained [mol]

Electrolysis time [min]

(b) Carbon dioxide obtained [mol]

Electrolysis time [min]
Figure 6

(a) Conversion of 1-butanol [%]

(b) Yield of butanal [%]
Figure 7

The graph illustrates the conversion of 1-butanol as a function of electrolysis time. Two pressure levels, 7 MPa and 3 MPa, are compared. The solid line represents 7 MPa, and the dashed line represents 3 MPa. The conversion percentage increases with time, showing a clear trend for both pressures.
Figure 8

![Graph showing electrolysis time vs. \(-\ln(C_{Ag}/C_{AgO})\).](image)
Figure 9

Residual organic carbon in the solution [%]

Electrolysis time [min]

- 3 A
- 0 A