Production of Hydrogen from Sugar by a Liquid Phase Electrical Discharge

S. Mededovic Thagard[1], E. R. Fisher[2], G. Prieto[3], K. Takashima[4], and A. Mizuno[4]

[1]Department of Chemical and Biomolecular Engineering, Clarkson University, USA
[2]Department of Chemistry, Colorado State University, USA
[3]Department of Chemical Engineering, National University of Tucuman, Argentina
[4]Department of Environmental and Life Sciences, Toyohashi University of Technology, Japan

Abstract—In this study, the production of hydrogen by electrical discharge in a sugar (sucrose) solution was explored. The results demonstrated that after fifteen minutes, the hydrogen concentration measured from the electrical discharge in sugar solution using gas chromatography is four times higher than that measured from the electrical discharge in tap water. Moreover, when the initial solution conductivity of the tap water and sugar solution was raised by a factor of twenty, the hydrogen concentration from the sugar solution was increased five times compared to the hydrogen concentration measured from tap water of the same conductivity. We hypothesize that the mechanism of hydrogen production is that the electrical discharge in water converts sugar to an organic acid, which then further decomposes to give hydrogen. Hydrogen production from the sugar solution was also compared to that from an ethanol-water solution. Overall, these results demonstrate that the electrical discharge in a sugar solution converts sugar into carbon dioxide and hydrogen within minutes, whereas the timescale required for the same reaction under the action of yeast is measured in days. This makes electrical discharge a competitive new technology for the hydrogen production from renewable sources.

Keywords—Electrical discharge, hydrogen, plasma, sugar solution

I. INTRODUCTION

As an environmentally friendly molecule, hydrogen has gained significant attention as fuel in the fuel cells applications, combustion engines and gas turbines. Commercially, hydrogen is produced by the steam reforming of methane or natural gas, partial oxidation of coal and electrolysis [1-3]. Indeed, a recent review of methods for decomposing methane to produce H_2 suggests this will likely be the greatest source of H_2 for the foreseeable future [4]. Nevertheless, there have been additional investigations into the processes of hydrogen generation from other sources, such as photo-catalytic decomposition of biomass and water as well as the enzyme-catalyzed decomposition of sugar [5, 6]. In these bio-technologies, however, the hydrogen production rate is low and, therefore, not applicable to commercial use. Moreover, a recent review of various methods for hydrogen production indicates that these alternative sources of H_2 are not yet cost effective enough to be competitive in the marketplace [7]. Nonetheless, there is significant potential in methodologies that rely on ubiquitous feed stocks.

Decomposition of methanol is another interesting and promising option for the hydrogen production. For example, it has been shown that hydrogen can be efficiently produced from methanol in a liquid phase electrical discharge, a powerful technology that is based on plasma formation between two electrodes submersed under a liquid surface using very short electrical pulses in the microsecond range [8, 9].

Plasma comprises electrons, neutral molecules and radicals with an average electron temperature of 3-5 eV, whereas the temperature of the neutral gas molecules is usually near room temperature. The advantage of using plasmas (electrical discharges) over other technologies to either synthesize or decompose molecules is that the energy required for the dissociation of molecules can be supplied at very low cost and often no catalyst is required. In recent years, various types of plasmas have been used to decompose a range of hydrocarbon molecules with the intent of both H_2 production and reduction of CO_2 emission [10-13]. In most of these studies, the plasma has been produced in the gas-phase either with or without the presence of a catalytic surface. In some instances, the plasma is used in the catalytic role, serving to produce high energy gas-phase radicals that can further react to decompose the feed gas molecules [12]. Both dielectric barrier discharges (DBDs) and microwave-based plasmas have been shown to convert large hydrocarbons (e.g. hexane, or octane) to smaller C_1-C_4 species and H_2 with greater than 80% conversion efficiency [11]. Although many of these studies have examined gas-phase discharges formed from liquid precursors [14-19], few of them have focused on the formation of plasmas directly in liquids [17, 20].

For example, Nishioka and co-authors have explored the use of a plasma torch to decompose organic molecules such as ethanol and methanol [14, 15]. The primary decomposition products in these studies were H_2, CO, and CO_2, although emission from CN, CH, and other atomic and ionic products were observed using gas chromatography mass spectrometry (GC-MS) and optical emission spectroscopy.

Here, we investigated the possibility of producing hydrogen from sugar solution using liquid phase electrical discharge. Although the results presented in this study are somewhat limited in scope, we discuss the possible mechanisms of sucrose decomposition into

Corresponding author: Selma Mededovic Thagard
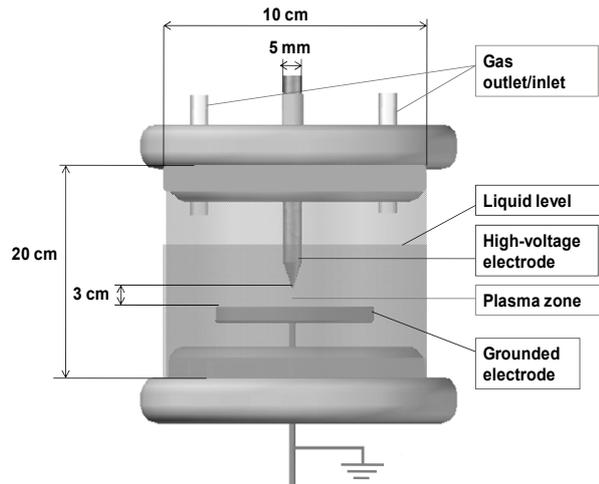e-mail address: smededov@clarkson.edu

Fig. 1. Reactor configuration.

TABLE I
EXPERIMENTAL CONDITIONS

Experiment no.	Solution composition	Initial (final) conductivity, μScm^{-1}	Initial (final) pH	Discharge voltage, kV
1	Tap water	70 (90)	6 (3)	9.5
2	Sugar[a] in tap water	11 (50)	6.5 (3)	10
3	Ethanol	60 (75)	6.5 (6)	10
4	Tap water and 3 drops of H_2SO_4	1000 (600)	3 (3)	9.5
5	Sugar[a] in tap water and 3 drops of H_2SO_4	1000 (500)	2 (2.5)	9.5
6	Tap water and oxalic[b] acid	1000 (600)	3 (3.5)	10

[a] Sugar concentration = 4.87 M.
[b] Oxalic acid concentration = 0.253 M.

hydrogen and report the main degradation byproducts that were identified using FTIR spectroscopy. In addition, we measured the hydrogen production from ethanol and studied the effects of sucrose solution conductivity on hydrogen production.

II. METHODOLOGY

The reactor configuration used in the experiments is shown in Fig. 1. The high-voltage (HV) electrode ($d = 0.05$ cm) and the grounded plate ($2 \times 1.5 \times 0.5$ cm) were immersed in the liquid. Both electrodes were made of stainless steel and the total distance between them was 3 cm. The HV needle was insulated with a glass tube and connected to the positive output of the rotating spark gap power supply.

The pulse-forming network consisted of a variable-voltage 0-120 V AC source, 1000 VA transformer, four storage capacitors (each 9400 pF) and a rotating spark gap with a pulse repetition frequency of 250 Hz. Voltage waveforms were recorded with a Tektronix TDS 1012B fast digital storage oscilloscope. Nitrogen was used as a purge gas and introduced at the top of the reactor at 1.25 L/min. Hydrogen was measured using a micro gas
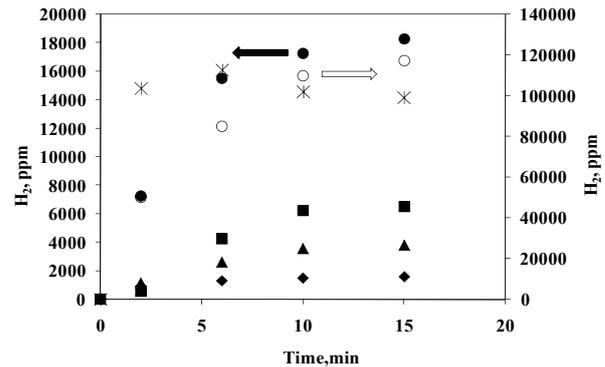

Fig. 2. Hydrogen production from tap water (♦ Exp.1), sugar solution (■ Exp.2), ethanol (○ Exp. 3), tap water and sulfuric acid (▲ Exp.4), sugar solution and sulfuric acid (● Exp. 5) and oxalic acid (✴ Exp. 6). Estimated error is approximately 5%.

chromatograph (Varian micro GC-4900). The FTIR measurements were performed using either SESAM-3N instrument (in-situ, continuous analysis) or the BIO-RAD FTS 3000 (batch analysis). The liquid volume in the reactor was 30 mL and the chemicals were used as received from the manufacturer. Conductivity and pH were measured using a conductivity-pH meter (Cole-Palmer). Table 1 lists the conditions under which all the experiments were performed. Each experiment was repeated at least four times with a variability of less than 5%.

III. RESULTS

Fig. 2 shows the measured hydrogen concentration for Experiments 1- 6 listed in Table 1. In Experiment 1, we measured hydrogen production from tap water and found that the steady-state hydrogen concentration is achieved after approximately 15 minutes. Electrical discharges in pure water yield hydrogen, oxygen and hydrogen peroxide and their production rate depends on the discharge power, solution conductivity, and the high voltage electrode material. Regardless of the discharge power or solution conductivity, hydrogen gas, hydrogen peroxide and oxygen ratio is always 4:2:1, respectively. The global reaction describing water dissociation inside the plasma is shown by (1) [21].

$$6H_2O \rightarrow 4H_2 + 2H_2O_2 + O_2 \qquad (1)$$

Plasma reactions that lead to molecular hydrogen production are electron impact water dissociation [22]:

$$H_2O + e \rightarrow H^\bullet + OH^\bullet + e \qquad (2)$$

and hydrogen radical recombination

$$2H^\bullet + M \rightarrow H_2 + M \qquad (3)$$

where M (=H_2O) is a third body.

In Experiment 1, hydrogen production is described by (2) and (3). In Experiment 2, we measured hydrogen production from the sugar solution. Fig. 2 shows the corresponding hydrogen concentration for this experiment and it is clear that after 15 minutes, the measured hydrogen concentration is four times the hydrogen concentration without added sugar. We hypothesized that the production of hydrogen proceeds via an intermediate state where alcohol and/or organic acid are formed by the direct decomposition of sucrose after which they further decompose to give hydrogen. The conversion of sugar into ethanol under the action of the yeast is a well-known process for the production of bio-ethanol [23]:

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH \qquad (4)$$

In addition, it has been shown experimentally that electrical discharge in water-methanol solutions produces high concentrations of hydrogen [8, 9, 24].

By connecting the results where electrical discharge in ethanol gives high hydrogen concentrations with the possibility of conversion sugar into ethanol, (4), we assumed the hypothesis wherein electrical discharge in sugar solution gives ethanol (and hydrogen) is reasonably valid. We conducted the electrical discharge in ethanol solution (Table 1, Experiment 3) and measured the corresponding hydrogen concentration, Fig. 2. The results in Fig. 2 show that the concentration of hydrogen formed from ethanol is more than five times higher than the same concentration from sugar for any other experiment. This is consistent with the work of Nishioka and co-authors who found that the effluent following decomposition of ethanol or methanol in a DC generated water plasma contained more than 60% H_2 (by mole fraction), regardless of the initial alcohol concentration [14, 15].

The plasma initiation, propagation and termination reactions that take place in water-ethanol solution comprise a complex set of reactions and the overall reaction describing ethanol decomposition into hydrogen is shown in (5) [24]:

$$C_2H_5OH \rightarrow H_2 + CO + CH_4 \qquad (5)$$
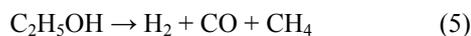
We also sought to identify the ethanol decomposition byproducts, utilizing two possible approaches to acquisition and analysis of gas phase FTIR spectra. First, we could collect a certain volume of the gas into a gas sampling cell and analyze it separately using one type of FTIR instrument ("batch" measurement). Second, we could identify and measure the gas-phase by-products continuously (in-situ) using a different type of FTIR instrument. Fig. 3 shows the FTIR spectrum recorded using the batch-type measurement. Clearly, the spectrum in Fig. 3 does not reveal the exact identification of byproducts formed. Moreover, many of the functional groups observed have very broad peaks, such as the C-H stretching band, which can be assigned to a number of molecules. Consequently, it was necessary to use a
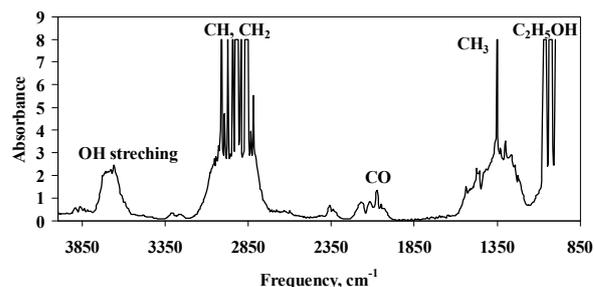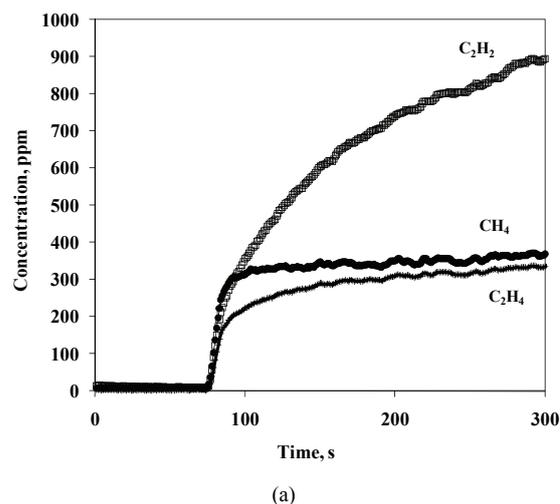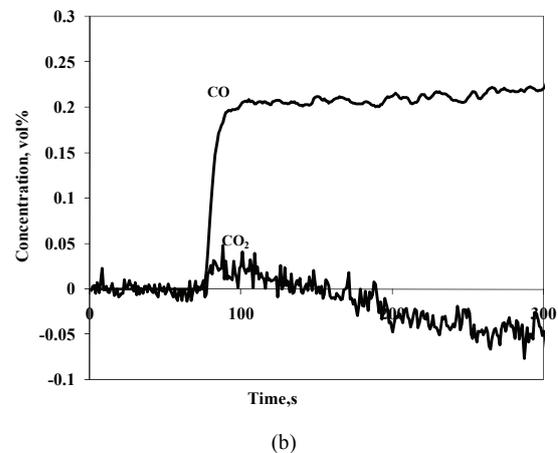
Fig. 3. FTIR spectrum of the ethanol gas phase byproducts.

(a)

(b)

Fig. 4. (a) Organic and (b) COx gas phase byproducts of electrical discharge in ethanol measured in situ (continuously) using FTIR spectroscopy.

continuous FTIR measurement, Fig. 4. The FTIR instrument used for these experiments was already calibrated to analyze somewhere between 30-40 compounds and the results showed that the main byproducts from ethanol decomposition in electrical discharge are acetylene (C_2H_2), ethylene (C_2H_4), methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2). Thus, for ethanol to be formed in (4), sugar (sucrose, $C_{12}H_{22}O_{11}$), needs to be converted into glucose ($C_6H_{12}O_6$) and the conversion is known to be acid-catalyzed (e.g. sulfuric acid) [25]:
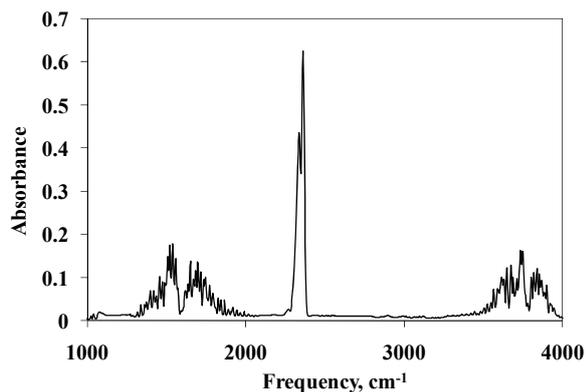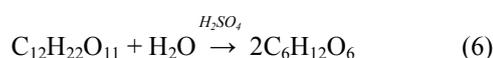
Fig. 5. Gas phase FTIR spectra of Experiment 2.

$$\overset{H_2SO_4}{C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6} \quad (6)$$

In Experiment 2, the initial pH is mildly acidic and probably not low enough to catalyze sugar decomposition into glucose but because of the increase in the measured hydrogen concentration in the first fifteen minutes, it is possible that H^+ ions produced simultaneously towards the end of the experiment (final solution pH = 3) catalyze sugar decomposition. The gas-phase FTIR spectrum (batch-type) from Experiment 2 is shown in Fig. 5, revealing that the only gaseous product formed is CO_2 (2200-2400 cm^{-1}). This result is not completely consistent with our initial hypothesis that glucose decomposes to ethanol which further decomposes to give hydrogen. If this initial hypothesis were true, we would expect to see both CO as well as CO_2 because the primary decomposition product of ethanol is CO, although both CO_2 and other products are formed. Glucose decomposition studies conducted under supercritical pressures identified aldehydes as well as short-chain acids as the main glucose decomposition byproducts [26]. Taking into account the discrepancy between the gas-phase FTIR spectra of the sugar solution and that of ethanol we hypothesized that hydrogen is formed in a sugar-organic acid mechanism.

It is well-known that the catalytic oxidation of sugar by the nitric acid leads to the formation of oxalic acid in a two-step process: (1) conversion of sucrose to glucose ((6)) and (2) oxidation of glucose to oxalic acid ((7)) [25]:

$$\overset{V_2O_5}{C_6H_{12}O_6 + 6HNO_3 \rightarrow 3(COOH)_2 + 6NO + 6H_2O} \quad (7)$$

Thus, there is a theoretical possibility that electrical discharge in sugar solution oxidizes sugar with, for example OH radicals, to oxalic acid and then oxalic acid further decomposes to give hydrogen. Before we test this hypothesis, we first present the experiments wherein we explored the effect of conductivity (pH) on the hydrogen yield because the oxidation of sugar to acid takes place in the acidic medium.

In Experiment 4, Table 1, we studied the effect of concentrated sulfuric acid on hydrogen production from the tap water. Note that the operation of underwater electrical discharges is highly dependent on the solution conductivity; we were, therefore, able to add only a limited amount of sulfuric acid to the solution. Indeed, three drops of concentrated sulfuric acid raised the conductivity value to 1000 µS/cm, which thus became the conductivity we used for our experiments. The Fig. 2 results illustrate that, compared to results without sulfuric acid (Experiment 1), the hydrogen more than doubles when sulfuric acid is added to the solution. This is probably not caused by the nature of sulfuric acid itself (any other inorganic acid would probably have the same effect), but rather to the increase in conductivity as hydrogen production increases with an increase in solution conductivity [24]. This dependence of hydrogen production on solution conductivity is understood by considering the relationship in (8), wherein the increase in solution conductivity leads to an increase in the power deposition into the plasma and concomitantly, higher dissociation of water molecules [24, 27]:

$$P = \sigma \cdot E \cdot A \cdot U \quad (8)$$

Here, P is the discharge power, σ is the solution conductivity, E is the electric field, A is cross section area and U is the voltage.

When Experiment 4 was repeated with adding sugar (Experiment 5), sulfuric acid catalyzed the decomposition of sugar to hydrogen. In Experiment 5, the addition of H_2SO_4 increases conductivity and thereby hydrogen production, Fig. 2, with the overall hydrogen production in Experiment 5 being higher than the sum of individual Experiments 2 and 4. Thus, the increased hydrogen production in Experiment 5 cannot be explained solely on the basis of increased solution conductivity. Most probably, when H_2SO_4 is present, high initial concentrations of H^+ immediately decompose sucrose to glucose which increases the rate of formation of organic acid and thereby hydrogen production. The observation that sugar decomposes faster in an acidic solution is in agreement with the hypothesis that hydrogen is produced by first converting sucrose into glucose and then glucose into hydrogen. Notably, apart from the catalytic oxidation shown in (7), glucose (sucrose) can be electrochemically converted (electro-oxidized) into formic and oxalic acid on iron and copper electrodes [28]. The oxidation of glucose into oxalic acid is shown in (9):

$$C_6H_{12}O_6 + 5O_2 \rightarrow 2(COOH)_2 + 2CO_2 + 4H_2O \quad (9)$$

When an electrical discharge occurs in pure water, the steady-state oxygen concentration is achieved after approximately ten minutes [21]. If we, therefore, assume that hydrogen is produced from oxalic acid, its production is limited not only by the conversion of sucrose into glucose, but also by the oxidation of glucose to (oxalic) acid. This may be the reason the production of

hydrogen from sugar initially increases before reaching a steady-state; oxygen production follows the same trend. In addition to oxygen, OH radicals are also responsible for the degradation of many organic species and it is highly probable that glucose is decomposed by OH radical attack (initiation reaction-the formation of a free radical) and the subsequent oxygenation of a free radical (termination reaction). Indeed, radiation chemistry studies of polysaccharides propose a detailed radical mechanism for sucrose decomposition into organic acid [29].

In the remaining experiment, Experiment 6, we examined the possibility of oxalic acid conversion to hydrogen, Fig. 2. Although we assumed that the oxalic acid is a source of hydrogen, it is possible that some other acids such as formic acid are formed instead and the production of hydrogen is achieved by the degradation of those acids. The comparison of Experiment 6 with Experiment 4 in Fig. 2 indicates more hydrogen is produced from oxalic acid in the first six minutes than from the sugar solution. After six minutes, the production of hydrogen from oxalic acid slowly starts to decrease. Initially, in Experiment 4, the fraction of an organic acid (oxalic acid) that is formed by the sugar decomposition and that yields hydrogen is low compared to that observed when large concentrations of oxalic acid are initially present and directly decomposed into H_2. This clearly explains why the first 6 minutes yields more H_2 from oxalic acid than from sugar solution. In time, the concentration of oxalic acid must decrease, leading to a decrease in hydrogen. In the case of hydrogen production from sucrose, the H_2 concentration after 6 min continues to increase because the initial sugar concentration is nineteen times greater than that of oxalic acid.
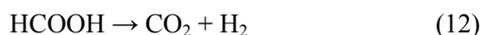
The literature on the radiation chemistry of oxalic acid solutions suggests the following overall equation as a source of hydrogen [30],

$$(COOH)_2 \rightarrow 2CO_2 + H_2 \qquad (10)$$

which proceeds via two steps wherein oxalic acid is decomposed to formic acid,

$$(COOH)_2 \rightarrow HCOOH + CO_2 \qquad (11)$$
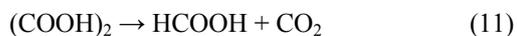
and formic acid could subsequently decompose to yield hydrogen :

$$HCOOH \rightarrow CO_2 + H_2 \qquad (12)$$

The gas phase FTIR spectrum collected during Experiment 6 is virtually identical to the spectra shown in Fig. 2, supporting our hypothesis that sugar decomposition proceeds via organic acid formation.

IV. CONCLUSION

Here, we demonstrated that hydrogen gas can be produced by electrical discharge in sugar solution. Two hypotheses were proposed to explain the formation of H_2 in these systems using FTIR spectroscopy. The first hypothesis assumed that sucrose decomposes to ethanol which then produces hydrogen. It was confirmed experimentally that electrical discharge in ethanol yields large concentrations of hydrogen; however, the FTIR spectra revealed that the main ethanol decomposition byproducts are acetylene, ethylene, methane, carbon monoxide and carbon dioxide. These results clearly suggest our first hypothesis has limited utility. In the second hypothesis, we assumed that sucrose decomposes occurs in two steps, forming first an organic acid such as oxalic and/or formic acid which can then further decompose to produce hydrogen. It was experimentally confirmed that the electrical discharge in an oxalic acid solution produces large concentrations of H_2. Additionally, the FTIR spectra of the oxalic acid decomposition byproducts revealed the presence of only carbon dioxide which is also the main sugar decomposition byproduct. The advantage of generating hydrogen by an electrical discharge in sugar solution has several advantages over other methods: (1) simplicity of the experimental setup and (2) no CO is produced along with H_2, thus high-purity hydrogen is obtained as an ideal fuel for fuel cells. In addition, an in-situ hydrogen production from sugar in hydrogen cars could overcome current issues associated with hydrogen production, storage and transport.

REFERENCES

[1] J. P. Breen, R. Burch, and H. M. Coleman, "Metal catalyzed steam reforming of ethanol in the production of hydrogen for fuel cell applications," *Applied Catalysis B*, vol. 39, pp. 65-74, 2002.

[2] M. Deminsky, V. Jivotov, B. Potapkin, and V. Rusanov, "Plasma-assisted production of hydrogen from hydrocarbons," *Pure and Applied Chemistry*, vol. 74, pp. 413-418, 2002.

[3] P. D. Vaidya and A. E. Rodrigues, "Insight into steam reforming of ethanol to produce hydrogen for fuel cell," *Chemical Engineering Journal*, vol. 117, pp. 39-49, 2006.

[4] H. F. Abbas and W. M. A. Wan Daud, "Hydrogen Production by Methane Decomposition: A Review," *International Journal of Hydrogen Energy*, vol. 35, pp. 1160-1190, 2010.

[5] M. Watanabe, H. Inomata, and K. Arai, "Catalytic hydrogen generation from biomass (glucose and cellulose) with ZrO_2 in supercritical water," *Biomass & Bioenergy*, vol. 22, pp. 405-410, 2002.

[6] J. Woodward, K. A. Cordray, R. J. Edmonston, M. Blanco-Rivera, S. M. Mattingly, and B. R. Evans, "Enzymatic hydrogen production: Conversion of renewable resources for energy production," *Energy & Fuels*, vol. 14, pp. 197-201, 2000.

[7] J. D. Holladay, J. Hu, D. L. King, and Y. Wang, "An overview of hydrogen production technologies," *Catalysis Today*, vol. 139, pp. 244-260, 2009.

[8] S. Mededovic Thagard, K. Takashima, and A. Mizuno, "Electrical discharges in polar organic liquids," *Plasma Process and Polymers*, vol. 6, pp. 741-750, 2009.

[9] Z. C. Yan, C. Li, and W. H. Lin, "Hydrogen generation by glow discharge plasma electrolysis of methanol solutions," *International Journal of Hydrogen Energy*, vol. 34, pp. 48-55, 2009.

[10] D. H. Lee, K.-T. Kim, M.-S. Cha, and Y.-H. Song, "Effect of excess oxygen in plasma reforming of diesel fuel," *International Journal of Hydrogen Energy*, in press, 2010.

[11] M. Mora, M. del Carmen Garcia, C. Jimenez-Sanchidrian, and F. J. Romero-Salguero, "Transformation of light paraffins ina microwave-indcued plasma-based reactor at reduced pressure," *International Journal of Hydrogen Energy*, vol. 35, pp. 4111-4122, 2010.

[12] T. Paulmier and L. Fulcheri, "Use of non-thermal plasma for hydrocarbon reforming," *Chemical Engineering Journal*, vol. 106, pp. 59-71, 2005.

[13] G. Petitpas, J. D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, and L. Fulcheri, "A comparative study of non-thermal plasma assisted reforming technologies," *International Journal of Hydrogen Energy*, vol. 32, pp. 2848-2867, Sep 2007.

[14] H. Nishioka, H. Saito, and T. Watanabe, "Liquid Waste Decomposition by DC Water Plasmas at Atmospheric Pressure," in *Transactions of the Materials Research Society of Japan, vol 33, no 3*. vol. 33, S. Somiya and M. Doyama, Eds., ed, 2008, pp. 691-694.

[15] H. Nishioka, H. Saito, and T. Watanabe, "Decomposition mechanism of organic compounds by DC water plasmas at atmospheric pressure," *Thin Solid Films*, vol. 518, pp. 924-928, 2009.

[16] P. Bruggeman, D. Schram, M. A. Gonzalez, R. Rego, M. G. Kong, and C. Leys, "Characterization of a direct dc-excited discharge in water by optical emission spectroscopy," *Plasma Sources Science and Technology*, vol. 18, 2009.

[17] M. A. Malik, "Water Purification by Plasmas: Which Reactors are Most Energy Efficient?," *Plasma Chemistry and Plasma Processing*, vol. 30, pp. 21-31, 2010.

[18] H. Yang, X. S. Zhang, S. Wen, and W. K. Yuan, "Decomposition of Organic Compounds in Water by Direct High Voltage Discharge," *Chemical Engineering & Technology*, vol. 32, pp. 887-890, 2009.

[19] Y. Wu, J. Li, G. F. Li, N. Li, G. Z. Qu, C. H. Sun, and M. Sato, "Decomposition of Phenol in Water by Gas Phase Pulse Discharge Plasma," in *Industry Applications Society Annual Meeting, 2009. IAS 2009. IEEE*, 2009, pp. 521-524.

[20] O. Sakai, M. Kimura, T. Shirafuji, and K. Tachibana, "Underwater microdischarge in arranged microbubbles produced by electrolysis in electrolyte solution using fabric-type electrode," *Applied Physics Letters*, vol. 93, p. 231501, 2008.

[21] M. J. Kirkpatrick and B. R. Locke, "Hydrogen, oxygen, and hydrogen peroxide formation in aqueous phase pulsed corona electrical discharge," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 4243-4248, 2005.

[22] S. Mededovic and B. R. Locke, "Primary chemical reactions in pulsed electrical discharge channels in water," *Journal of Physics D: Applied Physics*, vol. 40, pp. 7734-7746, 2007.

[23] G. Amin and A. M. Khalaf Allah, "By-products formed during direct conversion of sugar beets to ethanol by Zymomonasmobilis in conventional submerged and solid-state fermentations," *Biotechnology Letters*, vol. 14, pp. 1187-1192, 1992.

[24] M. J. Kirkpatrick, "Plasma-catalyst interactions in treatment of gas phase contaminants and in electrical discharge in water," Ph.D., Chemical Engineering, Florida State University, 2004.

[25] S. D. Deshpande and S. N. Vyas, "Oxidation of sugar to oxalic acid and absorption of oxides of nitrogen to sodium nitrite," *Industrial & Engineering Chemistry Product Research and Development*, vol. 18, pp. 69-71, 1979.

[26] V. A. Sharpatyi, "Radiation chemistry of polysaccharides: 1. Mechanisms of carbon monoxide and formic acid formation," *High Energy Chemistry*, vol. 37, pp. 369-372, 2003.

[27] I. V. Lisitsyn, H. Nomiyama, S. Katsuki, and H. Akiyama, "Thermal processes in a streamer discharge in water," *IEEE Transactions on Dielectrics and Electrical Insulation*, vol. 6, pp. 351-356, 1999.

[28] G. Güven, A. Perendeci, and A. Tanyolac, "Electrochemical treatment of simulated beet sugar factory wastewater," *Chemical Engineering Journal*, vol. 151, pp. 149-159, 2009.

[29] G. N. Pirogova, T. P. Zhestkova, Y. V. Voronin, N. M. Panich, R. I. Korosteleva, N. N. Popova, I. I. Byvsheva, and A. K. Pikaev, "Radiolytic gas formation in dilute oxalic acid aqueous solutions," *High Energy Chemistry*, vol. 36, pp. 287-289, 2002.

[30] E. J. Hart, J. K. Thomas, and S. Gordon, "A review of the radiation chemistry of single-carbon compounds and some reactions of the hydrated electron in aqueous solution," *Radiation Research*, vol. 4, pp. 74-90, 1964.