

The Production of Hydrogen and Olefin Hydrocarbons by Electrical Discharge in Liquid Fuels

S. Mededovic Thagard, G. Prieto, K. Takashima, and A. Mizuno

Abstract—Biofuels such as bio-generated ethanol are an attractive renewable energy source. In addition to ethanol, liquid fuels such as diesel or gasoline could also serve as a source of hydrocarbons and hydrogen which are commonly used for flue gas treatment in selective catalytic reduction (SCR) reactors. The main goal of the present research is to study the production of hydrogen from liquid ethanol, iso-octane and hexadecane in an electrical discharge and to identify and quantify all the gaseous by-products. This hydrogen rich mixture could be used as a reductant in the process of exhaust gas treatments, as a fuel resource or as a reactant for fuel cells, among other potential uses.

Results have shown that electrical discharges in liquid hydrocarbons and ethanol give hydrogen, methane, acetylene, ethylene, and hydrogen cyanide as the main decomposition by-products. In the case of ethanol, carbon monoxide is also formed.

Index Terms—Electrical discharge, Ethanol, Hexadecane, Hydrogen, Iso-octane

I. INTRODUCTION

ENGINE emissions contain pollutants that adversely affect the atmosphere and contribute to an increase in the levels of carbon dioxide. In the search for solutions, biofuels such as bio-generated ethanol (or bio-ethanol) quickly emerged as a desirable alternative to petroleum products because growing crops for biofuel greatly reduces the carbon dioxide emitted into the atmosphere from fuel used to produce the biofuels and from burning the biofuels themselves.

Manuscript received April 17, 2009.

Selma Mededovic Thagard. Author was with the Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi, 441-8580, Japan. Corresponding author (tel. +81-532-44-6904, email: mededse@eng.fsu.edu)

Graciela Prieto. Author is with the Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi, 441-8580, Japan on leave from the Department of Chemical Engineering, National University of Tucuman, Argentine Republic Ave. Independencia 1800, (4000) San Miguel de Tucuman, Argentina (email: gprieto@herrera.unt.edu.ar).

Kazunori Takashima. Author is with the Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi, 441-8580, Japan. (email:takashima@eco.tut.ac.jp)

Akira Mizuno. Author is with the Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi, 441-8580, Japan. (email:mizuno@eco.tut.ac.jp).

Ethanol can be obtained in great quantities from biomass through a fermentation process from renewable resources like from sugar cane, wheat, corn, or even straw. The use of ethanol would also overcome both the storage and infrastructure challenge of hydrogen for fuel cell applications. In a fuel cell, the oxidation of any fuel requires the use of a catalyst in order to achieve the current densities required for commercially viable fuel cells, and platinum-based catalysts are some of the most efficient materials for the oxidation of small organic molecules.

Hydrogen is used by manufacturers in vegetable oil hydrogenation, pharmaceuticals, electronics, glass, chemical industries, refineries and fuel cells.

Because hydrogen is so flammable and must be stored under great pressure, it is a dangerous fuel to carry. An alternative to storing hydrogen gas is to carry a chemical that is a liquid at room temperature that contains a significant amount of hydrogen. The hydrogen atoms could be stripped from that molecule and then reformed into H₂ for use in the fuel cell. The classical method for producing H₂ from a hydrocarbon is known as steam reforming. Ethanol is heated to temperatures in excess of 600° C in the presence of steam and a catalyst, reacting to provide H₂ and carbon monoxide (CO). Ethanol steam reforming at 700° C with CaO as a CO₂ sorbent shows higher hydrogen production and lower CO content in the reformer gas exit [1]. Steam reforming of ethanol/water mixtures for the production of hydrogen, is using oxide-supported metal catalysts containing Rh, Pd, Ni, Pt [2]. High temperatures, low pressures and high water-to-ethanol ratios in the feed favor hydrogen production and overall, Ni, Co, Ni/Cu and noble metal (Pd, Pt, Rh)-supported catalysts are promising [3].

There are also few thermal and non-equilibrium plasma applications for hydrogen rich gas production from hydrocarbons [4]. Another way of producing hydrogen is via auto-thermal catalytic and non-equilibrium plasma partial oxidation of hydrocarbon fuels [5].

The main goal of the present research is to study the possibility of hydrogen production from liquid ethanol, hexadecane and iso-octane in an electrical discharge and to identify and quantify all other gaseous by-products. Possible uses of this hydrogen rich mixture could be as a reductant in the process of exhaust gas treatments, as a fuel resource, and as a

reactant for fuel cells. Also, the by-products of ethanol, hexadecane, and iso-octane decomposition such as low-molecular hydrocarbons could be used, in addition to hydrogen, to reduce car emissions inside the catalyst. For that purpose, it is very important to identify major by-products of these organic liquids since hexadecane is the main component of diesel fuel and iso-octane is the main component of the gasoline fuel.

II. EXPERIMENTAL SETUP

Fig. 1 shows the experimental setup. Nitrogen was used as a purge gas, flowing at 1.25 L/min through the glass tube immersed in the liquid solution inside the reactor. The high-voltage wire was placed in a glass tube (d=1 cm) through which nitrogen was flowing. The enlarged view of the glass tube is shown in Fig. 2. At the exit of the reactor, reaction by-products were identified and measured by an online FTIR (SESAM 3-N). This model of FTIR is intended to be used for the monitoring of the diesel gas and it requires a gas flow rate of minimum 4 L/min. Since the nitrogen gas flow through the reactor was maintained at 1.25 L/min, it was additionally mixed with 4.5L/min of nitrogen before the FTIR analysis so the concentrations of by-products shown later in the results section were actually 3.6 times (4.5L/min divided by 1.25 L/min) higher for the 1.25 L/min flow rate. A micro GC was used for the measurement of the hydrogen gas concentration.

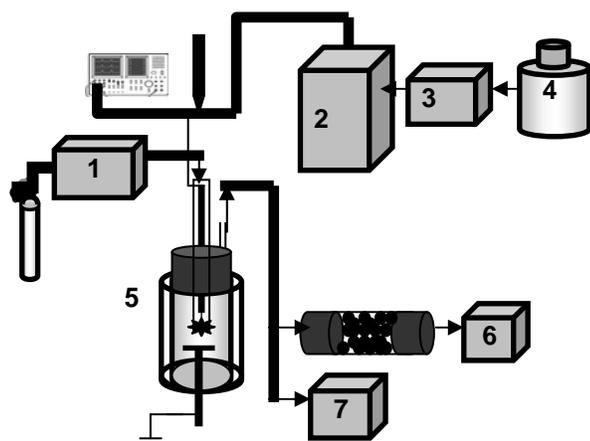


Fig.1. Experimental setup (1- Mass flow controller, 2-Rotating spark gap, 3-Power meter, 4 - 0-120V Variable AC transformer, 5- Reactor, 6-GC, and 7-FTIR).

A point-to-plane reactor configuration was used for these experiments. The high-voltage electrode was stainless steel (d=0.3mm) and the planar ground electrode was made from stainless steel. Both electrodes were immersed in an organic liquid and separated by a distance of 3-6mm. The point electrode was electrically connected to the output of the power

supply and the ground electrode was attached to the ground.

In the experiments a rotating spark gap, pulsed power supply was used to generate high-voltage pulses. The pulse-forming network consisted of a variable-voltage 0-120V AC source, 1000W transformer, four storage capacitors (each 9400pF) 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.

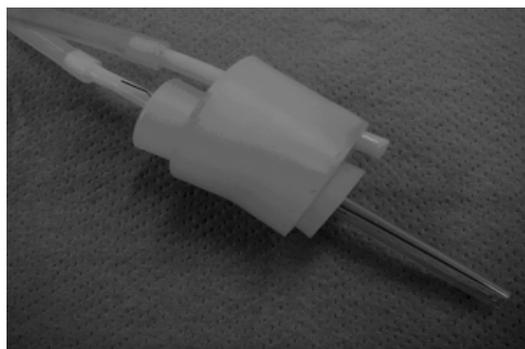


Fig.2. High-voltage needle inside a glass tube.

III. RESULTS AND DISCUSSION

Before the interpretation of the results, the authors would like to briefly discuss the difficulties associated with the discharge initiation in “relatively” polar liquids. Ethanol, hexadecane, and iso-octane, compared to water, are less polar, therefore, without any ions in the solution it is very difficult to initiate a discharge. Bubbling nitrogen through the glass tube (around the high-voltage wire) facilitated the discharge, although a decrease in solvent polarity required an increase in the input voltage regardless of the presence of nitrogen bubbles. Those experiments were characterized by an intense and uncontrollable discharge. The authors found that another way of facilitating the initiation of the discharge is to mix some NaCl in water and to add this solution to the organic liquid. The addition of salt solution to the ethanol formed an ethanol-water solution whereas an addition of water to either hexadecane or iso-octane formed an emulsion. Table 1 lists parameters for three experiments discussed in this manuscript. In any case, after the addition of water, the discharge was much less intense compared to the discharge that was initiated only by bubbling nitrogen (without adding salt solution). Also, it was noticed that with or without ions present in the solution there is a significant erosion of the high-voltage electrode. Table 1 also lists hydrogen concentrations for each experiment and the hydrogen production will be discussed later in the text. It should be mentioned that the discharge was the easiest in ethanol, whereas the discharge in hexadecane and iso-octane was more difficult even after adding salt solution. This is the reason why the authors were able to control the discharge in ethanol and as a result the by-product distribution is measured for three

different voltages (Table 1, experiment 1). This was not possible for the discharge in hexadecane or iso-octane where the experiments were much shorter due to the fast needle erosion. For those experiments with hexadecane and iso-octane, the by-product concentration was recorded for only one input voltage. The authors found that another way of facilitating the discharge in highly non-polar solvents is by wrapping the conductive carbon fibers around the high-voltage wire with. In that case, several loose carbon fibers were randomly touching the ground electrode which initiated the discharge in the form of a low-intensity spark. In the future experiments, this could surpass the need for adding conductive aqueous salt solution to the organic solvent and prevent fast high-voltage needle erosion.

TABLE I
COMPARISON OF THREE SEPARATE EXPERIMENTS

Experiment	Liquid composition	Added Salt (NaCl)	Applied (V) and (discharge) (kV) voltage	c(H ₂) vol %
1 (Fig. 3)	60 mL	0.2g	60 (1)	-
	Ethanol		70 (1.8)	-
	+10mL H ₂ O		80(2.5)	24
2 (Fig.4)	60mL	0.2g	70V (2)	22
	Hexadecane			
3 (Fig. 5)	+	0.2g	67 (1.5)	20
	10 mL H ₂ O			
	Iso-octane			
	+			
	10mL H ₂ O			

A. Ethanol

As it was mentioned in the introduction section, the purpose of the experiments was to identify the main degradation by-products of ethanol, iso-octane and hexadecane in the liquid-phase electrical discharge and to measure corresponding hydrogen concentration. Fig. 3 (a) and Fig. 3 (b) clearly indicate that the main decomposition by-products of ethanol in the liquid-phase electrical discharge are acetylene (C₂H₂), ethylene (C₂H₄), methane (CH₄), acetaldehyde (CH₃CHO), carbon monoxide (CO), carbon dioxide (CO₂) and hydrogen cyanide (HCN). Another interesting observation is the distribution of by-products in Fig. 3 (a); methane and ethylene are produced in approximately the same concentration that is

approximately half than that of acetylene. Also, the effect of the voltage increase on the production of methane, ethylene and acetylene follows a similar pattern in Fig. 3a; an increase in the input voltage leads to an increase in CH₄, C₂H₂ and C₂H₄ concentration, after which a steady-state concentration is reached.

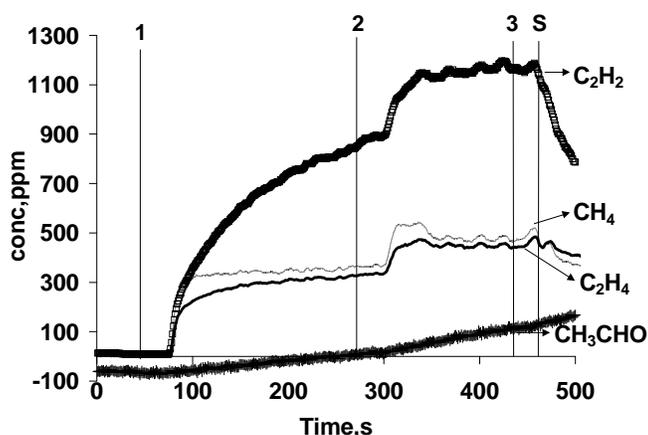
The plasma chemistry of ethanol is very complex and without chemical (kinetic) modeling it is almost impossible to say which reactions are responsible for the by-product distribution shown in Fig. 3. The authors are currently working on the detailed chemical model which will be used to describe electrical discharge in organic solvents. At this point the authors assume that methane and ethylene are produced via dehydration of the ethanol, and acetylene by the dehydrogenation of ethane. Further dehydrogenation of acetylene gives hydrogen and elementary carbon which was observed suspended in the ethanol solution and deposited on the reactor glass at the end of every experiment. Contrary to the production of methane, ethylene and acetylene, the acetaldehyde production is linear in Fig. 3 (a) and this can be explained by its boiling point. Acetaldehyde is a liquid with a very low boiling point of 20°C and even though the reactor is surrounded by a cooling jacket (T<15°C), the ethanol temperature around the streamers is probably much higher than 15°C which causes evaporation. In addition, flowing nitrogen through the ethanol solution further facilitates the evaporation of acetaldehyde. After exiting the reactor, there is probably a fast condensation inside the Teflon tubes connecting the reactor and FTIR. As the experiment proceeds, the gases passing through the tube get warmer and evaporate acetaldehyde in a linear fashion as seen in Fig. 3 (a).

A similar situation can be observed with HCN which is a liquid having a boiling point of 26°C. The production trend of HCN in Fig. 3 (b) is very similar to that of acetaldehyde, therefore it was also assumed that the condensation and evaporation of hydrogen cyanide takes place inside the Teflon tubes resulting in a linear production of hydrogen cyanide.

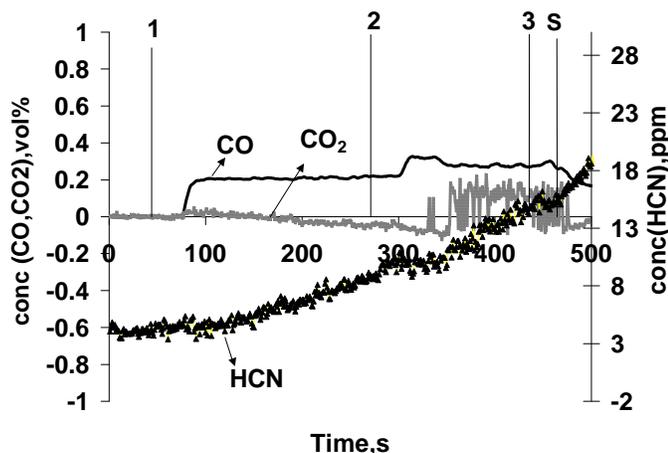
It is assumed that acetaldehyde is produced by the oxidation of ethanol and HCN by the reaction between nitrogen radicals and ethanol. HCN is a poisonous gas but it can be easily removed because it readily reacts with water. Results in Fig. 3 (b) reveal that carbon oxides consist of mainly CO and almost no oxidation to CO₂ takes place.

Hydrogen is produced in various ethanol dehydrogenation reactions where the final products are elementary carbon and hydrogen. Table 1 shows hydrogen concentration at input voltage of 80 V. It must be mentioned that an increase in voltage also led to an increased hydrogen concentration (data not shown) and at high input voltages (> 80 V) ethanol solution was rapidly turning black indicating carbon deposition. The carbon deposition, from the chemical point of view takes place via reduction of acetylene:





(a)



(b)

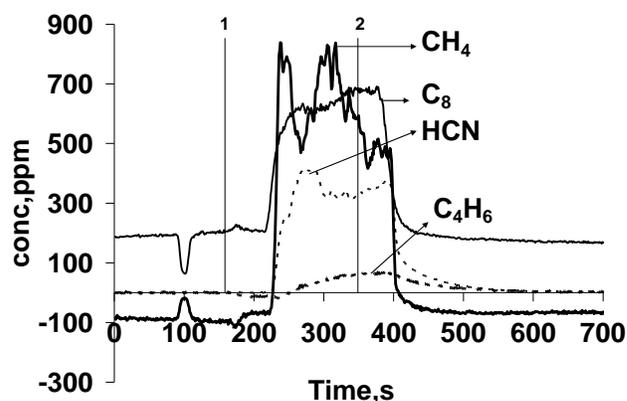
Fig. 3. (a) and (b): On-line FTIR measurement of the gas-phase ethanol decomposition byproducts (Table 1, experiment 1). Explanation: 1-Start (Input voltage 60V), 2-Voltage increases to 70V, 3-Voltage increases to 80V, S-Hydrogen sampling and finish.

B. Hexadecane

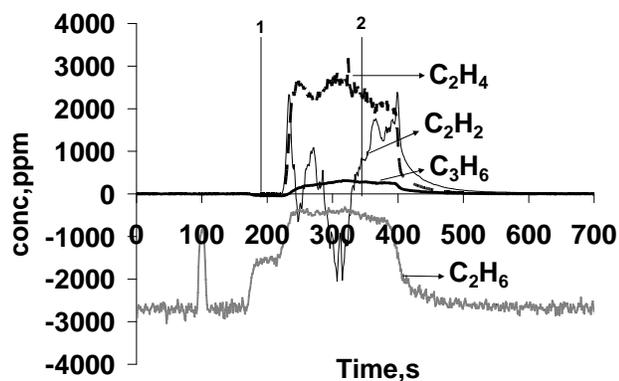
Hexadecane (or cetane) is an alkane hydrocarbon with the chemical formula $C_{16}H_{34}$. Fig. 4 (a) and 4 (b) show the by-products of the hexadecane decomposition in the liquid phase electrical discharge. As in the case of ethanol, hydrocarbons acetylene (C_2H_2), ethylene (C_2H_4), and methane (CH_4) and hydrogen cyanide (HCN) are also formed although here the concentration of ethylene is not twice that of methane and ethylene as it was the case with ethanol. This indicates a different mechanism of formation for these three compounds.

Fig. 4 also shows that hydrocarbons such as propene (C_3H_6), butadiene (C_4H_6), ethane (C_2H_6), and hydrocarbons C_8 , are also formed. Since hexadecane is a long chain alkane, the authors found, based on the kinetic model that is currently under development, that higher molecular by-products C_3 - C_8 are formed directly from hexadecane in the primary dissociation reactions. Hydrocarbons with less than three carbon atoms such as methane, acetylene and ethylene are formed in secondary reactions from hydrocarbons C_3 - C_8 . Similar by-products as in this study were identified in [6] where the reforming of heavy oils into light hydrocarbons has been experimentally studied by non-thermal plasma. The major products obtained in [6] were hydrogen and hydrocarbon compounds with one, two, three, and four atoms of carbon, such as CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , and C_4H_{10} , ethylene being the main compound.

Various dehydrogenation reactions in which alkenes are formed from alkanes and alkynes are formed from alkenes produce hydrogen. The hydrogen concentration of 22 vol. % (Table 1) is relatively high and indicates that hexadecane is a rich source of hydrogen.



(a)

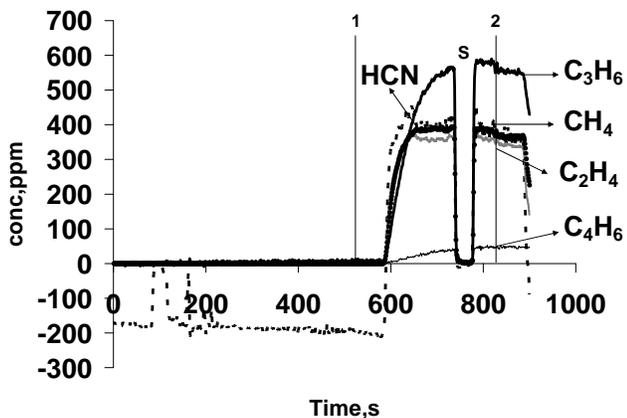


(b)

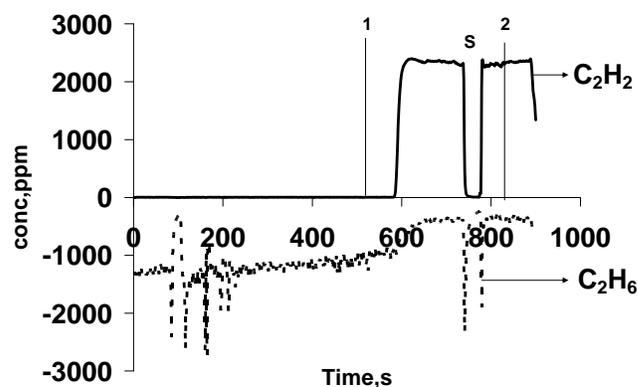
Fig. 4. (a) and (b): On-line FTIR measurement of the gas-phase hexadecane decomposition byproducts (Table 1, experiment 2). Explanation: 1-Start (Input voltage 65V), 2- Finish and hydrogen sampling.

C. Iso-octane

Iso-octane is also known as 2, 2, 4-trimethyl pentane (C_8H_{18}) and it is an octane isomer which defines the 100 point on the octane rating scale. It also represents an important component of gasoline. Fig. 5 (a) and 5 (b) show that electrical discharge in liquid iso-octane gives the same by-products (clearly except C_8) as electrical discharge in hexadecane (Fig.4 (a) and 4 (b)). This supports the hypothesis that low molecular hydrocarbons (C_1 - C_3) are formed from hydrocarbons which have less than eight carbon atoms. Furthermore, similar hydrogen concentrations between hexadecane and iso-octane lead to the conclusion that the dissociation chemistry of higher molecular weight hydrocarbons is relatively the same.



(a)



(b)

Fig. 5. (a) and (b): On-line FTIR measurement of the gas-phase iso-octane decomposition byproducts (Table 1, experiment 3). Explanation: 1-Start (Input voltage 65V), S-Hydrogen sampling, 2- Finish.

4. CONCLUSIONS

The initiation of the discharge in organic solvents is relatively difficult because these liquids are less polar than water and the miscibility with aqueous solutions is very low. Bubbling nitrogen through the discharge zone facilitates the discharge although relatively high input voltages are required for a strongly non-polar liquids such as hexadecane and iso-octane and at the same time, the liquid breakdown is relatively intense. As a final by-product, electrical discharge gives black carbon and hydrogen, in addition to various other hydrocarbons. For all three organic solvents, the authors postulated that hydrogen is produced by various dehydrogenation reactions in which alkenes are formed from alkanes and alkynes from alkenes produce. The hydrogen concentration is comparable for all three experiments.

Electrical discharge in ethanol gives hydrogen, methane, acetylene, ethylene, carbon monoxide, acetaldehyde, and hydrogen cyanide as the main decomposition by-products. Methane and ethylene are produced in roughly same concentrations and acetylene production is twice that of methane and ethylene. Bubbling nitrogen through the discharge zone gives HCN which is a poisonous gas but it could be easily removed by the hydrolysis reaction.

Electrical discharge in hexadecane and iso-octane gives almost identical by-products; acetylene, ethylene, methane, hydrogen cyanide, propene, butadiene, and ethane. In the case of hexadecane hydrocarbons C_8 are additionally formed.

The authors hypothesized that higher molecular by-products C_3 - C_8 are formed directly from hexadecane in the primary dissociation reactions. Hydrocarbons with less than three carbon atoms such as methane, acetylene and ethylene are formed in secondary reactions from C_3 - C_8 which is also the main mechanism in the dissociation of iso-octane.

Building on the results of this study, the next step will be to perform an electrical discharge in diesel fuel and gasoline fuel. The by-products will be compared with those presented in this

study and the low molecular hydrocarbons will be utilized in a catalytic dielectric barrier discharge for the reduction of NO_x.

REFERENCES

- [1] J. Comas, M. Laborde, and N. Amadeo, "Thermodynamic analysis of hydrogen production from ethanol using CaO as a CO₂ sorbent," *J Power Sources*, vol. 138, Nov. 2004, pp. 61–67.
- [2] J. P. Breen, R. Burch, and H. M. Coleman, "Metal catalyzed steam reforming of ethanol in the production of hydrogen for fuel cell applications," *Appl. Catal. B: Environmental*, vol. 39, 2002, pp. 65–74.
- [3] P.D. Vaidya, and A. E. Rodrigues, "Insight into steam reforming of ethanol to produce hydrogen for fuel cells," *Chem. Eng. J.*, vol. 117, 2006, pp. 39–49.
- [4] M. Deminsky, V. Jivotov, B. Potapkin, and V. Rusanov, "Plasma-assisted production of hydrogen from hydrocarbons," *Pure Appl. Chem.*, vol. 74, 2002, pp. 413–418.
- [5] M. G. Sobacchia, A. V. Savelieva, A. A. Fridman, L.A. Kennedy, S. Ahmedb, and T. Krause, "Experimental assessment of a combined plasma/catalytic system for hydrogen production via partial oxidation of hydrocarbon fuels," *Int. J. Hydrogen Energy*, vol. 27, 2002, pp. 635 – 642.
- [6] G. Prieto, M. Okumoto, K. Shimano, K. Takashima, S. Katsura, and A. Mizuno, "Reforming of heavy oil using nonthermal plasma," *IEEE Trans Ind. Appl.*, vol. 37, Sep/Oct 2001, pp.1464 – 1467.