PSFC/JA-05-3

Plasmatron Reformation of Renewable Fuels

L. Bromberg, K. Hadidi, D.R. Cohn

September 30, 2005

MIT Plasma Science and Fusion Center

Work supported by the US Department of Energy, Office of FreedomCar and Vehicle Technologies

Abstract

The characteristics of plasmatron reformers for the generation of hydrogen rich gas using renewable fuels is discussed. Biodiesel and ethanol have been investigated. Operating as a function of the air/fuel ratio is evaluated, as well as the impact of the plasma.

I. Introduction

In a previous paper the homogeneous and catalytic reformation of refined and unrefined vegetable oils, as well as the catalytic plasma conversion of ethanol have been reported [1]. In this paper the results of plasmatron reformer operating on renewable fuels are discussed. The two most abundant renewable fuels, biodiesel and ethanol are investigated.

Biodiesel is one of a limited number of renewable fuels. It can be obtained from a variety of seeds. Its use in transportation is being investigated. Similarly, ethanol can be obtained from either cellulosic materials, corn, or sugar. Although there are discussions about the overall energy benefit of the use of renewable biofuels [2,3], it is generally accepted that they produce a net energy benefit.

We have previously reported in a series of papers [4-9] the performance of a plasmatron reformer using methane and propane. That work provides increased understanding of the behavior of the plasmatron reformer operating with heavier hydrocarbons.

Section II discusses the setup and the characteristics of the biodiesel and the ethanol. Section III describes the experimental results for biodiesel. Section IV presents results for ethanol. Section V discussed the results, and Section VI summarizes the work.

II. Experimental setup

The experimental setup has been described in [4] and will only be briefly described here. The plasmatron used is the same used in [4-9] and is shown in Figure 1. Figure 2 shows a picture of the plasmatron.

The experiments reported in [4-9] were carried out with gaseous fuels, and there was no need for an additional pump for the liquid fuel or for liquid fuel atomization. For liquid fuels, the approach used in the plasmatron fuel reformer work has been to form a fine spray from the liquid fuel, followed by air assit atomization. We expect to have droplet size on the order of < 20 μm. The liquid fuels in the present tests have been introduced into the plasmatron through a nozzle that forms a fine spray of droplets. The nozzle used in these experiments is a B-37 nozzle. The characteristics of this nozzle are given in Table 1.

Table 1. Characteristics of B37 nozzle

	40	60	80	100	200
Flow rate (gph)	0.37	0.45	0.52	0.59	0.83
Flow rate (cc/s)	0.38	0.46	0.53	0.61	0.85
Sauter Mean Diameter (μm)	54	39.4	34.5	32.1	26.5

Table 1 is shown for water, and thus it is only indicative of the performance for the case of ethanol and biodiesel, both of which are lighter and more viscous. The stream of droplets is further atomized by the fast flowing atomization air, which has a velocity on the order of 180 m/s at the exit of the air atomization nozzle (at 50 lpm STP flow rate, corresponding to ~ 1 g/s).

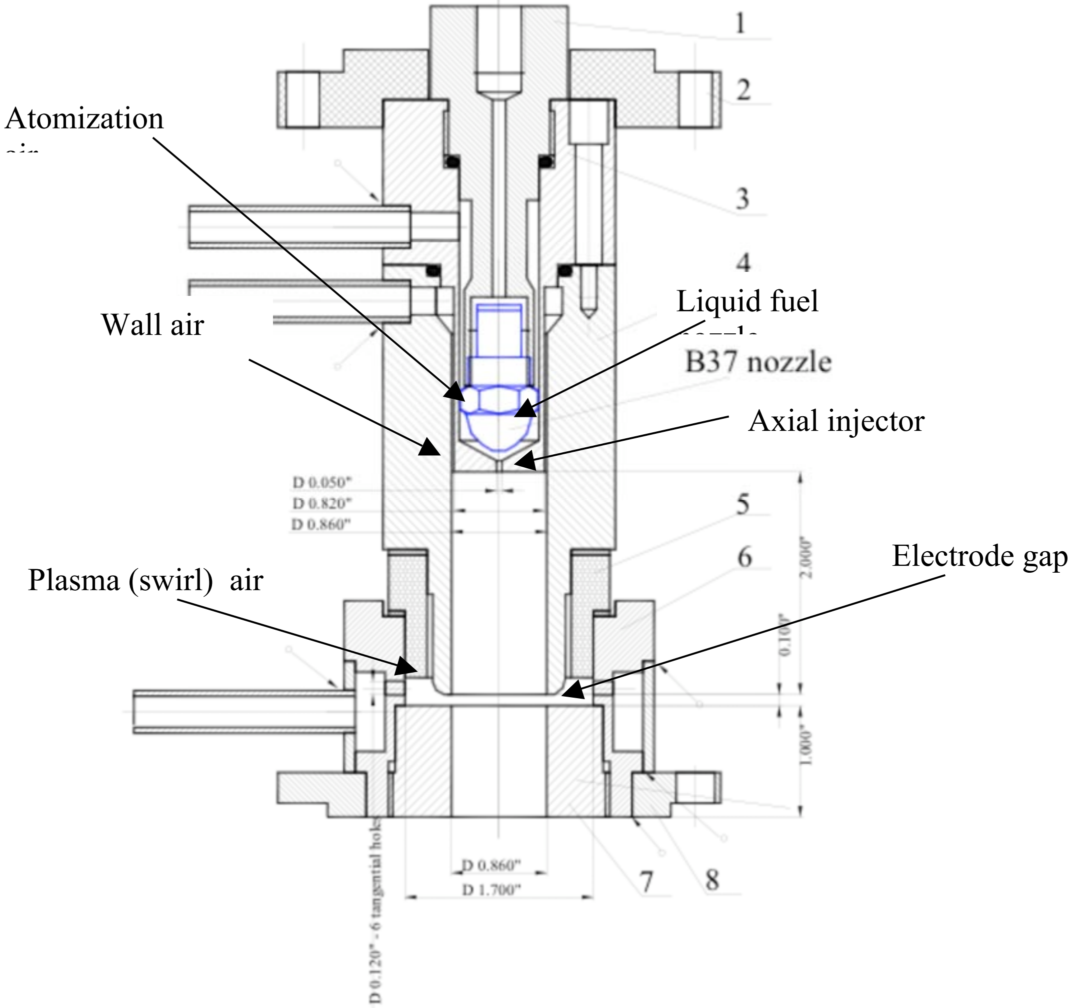

Figure 1. Plasmatron used in the experiments.

The pump used to pressurize and monitor the flow rate was a variable displacement pump attached to a variable speed drive from Fluid Metering. The pump was calibrated by capturing and then weighing the fluid for a given amount of time. The adjusted parameter was the speed of the drive. The pump provides constant flow rate for pressures lower than about 200 psi, and we have stayed below this limit, operating close to 50 psi.

Soot/raw fuel droplets were measured using a Wagner 2000 opacity meter.

The atomization air flow rate was monitored by a TSI air flow sensor. The TSI sensor was also used to confirm that the two other mass-flow controllers (for the wall air and for the plasma air) were within certification.

Figure 2. Photograph of the plasmatron used in these experiments, as well as those in reference [4-9].

The B-100 biodiesel was provided by Renewable Solutions, Oakland Park, Kansas. The average molecular weight of soybean oil methyl esters is 292.2, calculated using the average fatty acid distribution for soybean oil methyl ester shown in Table 2 [10]. Shown in Table 3 are the molecular weight and chemical formula for each of the component esters [10].

Table 2
Typical Soybean Oil Methyl Esters Profile

Fatty Acid	Wt. %	Mol. Weight	Formula
Palmitic	12.0	270.46	C15H31CO2CH3 $(C_{17}H_{34}O_2)$
Stearic	5.0	298.52	C17H35CO2CH3 $(C_{19}H_{38}O_2)$
Oleic	25.0	296.50	C17H33CO2CH3 $(C_{19}H_{36}O_2)$
Linoleic	52.0	294.48	CH3(CH2)4CH=CHCH2CH=CH(CH2)7CO2CH3 $(C_{19}H_{34}O_2)$
Linolenic	6.0	292.46	CH3(CH2CH=CH)3(CH2)7CO2CH3 $(C_{19}H_{32}O_2)$

Table 3
Carbon Chain Length Distribution and Percent Oxygen
Produced from Typical Soybean Oil.

Compound	CAS#	Bonding	Weight %	% O2
Methyl Palmitate	112-39-0	C-16	10.0	11.8
Methyl Stearate	112-61-8	C –18	4.0	10.7
		% Saturated	14.0	
Methyl Oleate	112-62-9	C-18=1	25.0	10.8
Methyl Linoleate	112-63-0	C-18=2	53.0	10.9
Methyl Linolenate	301-00-8	C-18=3	8.0	10.9
		% Unsaturated	86.0	
Total average O2				11.0

III. Biodiesel reformation

In this section, experiments of plasmatron biodiesel reformers are described. The flow rate of the biodiesel fuel is about 0.5 g/s, which match those of methane and propane carried out previously [4-9] with the same plasmatron setup.

In order to investigate performance with different stoichiometries, the O/C ratio of the plasmatron was changed by adjusting the wall air (see Figure 1). The plasma air and the atomization air were kept constant at 50 lpm (1 g/s). The plasma air has a narrow operating region, as too little air does not push the discharge into the volume of the plasmatron (the discharge remains in the inter-electrode region), and too high a flow results in an unstable discharge. Similarly, for atomization air flow rates less than about 50 lpm the fuel atomization decreases substantially, and much higher flow rates can not be obtained because of choke-flow limitations.

The wall air was varied from no flow all the way to 80 lpm.

The steady state composition of the reformate was measured using a calibrated gas chromatograph, described in [4]. It was assumed that steady state conditions were obtained when the temperature, measured by a thermocouple downstream from the plasmatron [4], reaches steady state conditions.

The composition of the reformate, as a function of the O/C ratio, is shown in Figure 3. The O/C ratio is defined as the ratio of the flows of all the oxygen atoms to the carbon atoms, and thus includes the oxygen atoms in the fuel.

Two sets of experiments were carried out, with the second set going to larger values of O/C, but also overlapping over the first set of experiments. The compositions in Figure 3 do not include C_2 compounds. Although the gas chromatograph indicates substantial levels of C_2

compounds, their calibration has been suspect. The carbon balance matches much better when in the analysis the concentrations of C_2H_6, C_2H_4 and C_2H_2 are ignored.

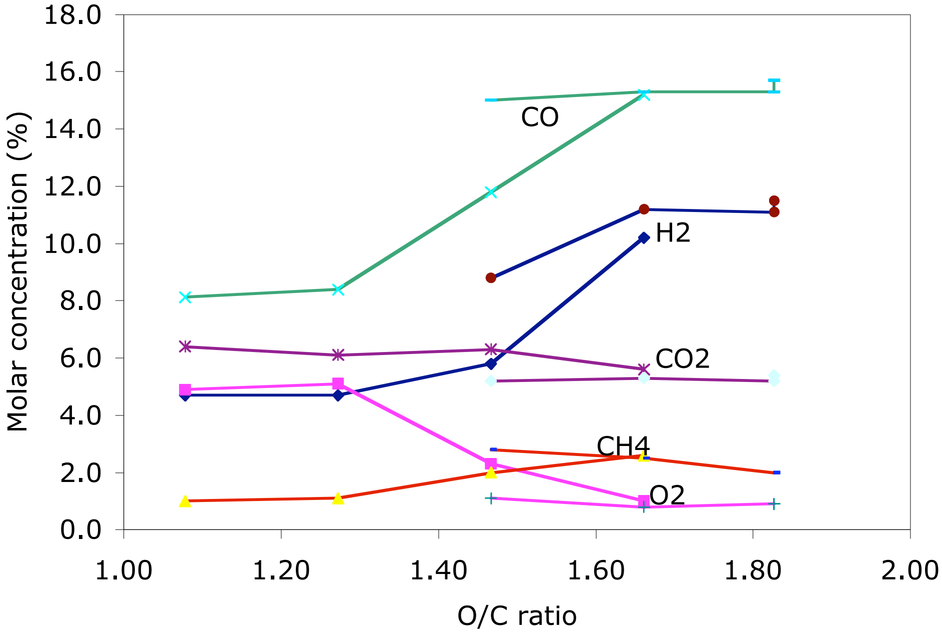

Figure 3. Composition of reformate from plasmatron biodiesel reformer as a function of the O/C ratio.

The hydrogen concentration is relatively low at the lower values of O/C, although there is still some present. Increased O/C results in large increase in hydrogen concentration, which approximately doubles when the O/C ratio increases from 1.3 to 1.7. Good conversion of the fuel is also indicated by the disappearance of oxygen, which drops substantially at O/C ~ 1.5 and even further at O/C ~ 1.7. The CO concentration follows the hydrogen concentration. Higher O/C were not investigated because of the limitations of the mass-flow controller, although the curves indicate that hydrogen concentration has peaked at O/C ~ 1.7.

The corresponding temperature measured downstream from the plasmatron and opacity are shown in Figure 4.

The energy efficiency of the process (defined as the heating value of the reformate divided by the heating value of the fuel) is poor (~ 20%) at low O/C values. At O/C ~ 1.5, with good carbon balance, the energy efficiency is about 60%. At O/C ~ 1.7, the energy efficiency is higher, about 66%.

The effect to the plasma power was investigated by turning the power off after steady state operation was achieved. The reaction became unstable without the plasma, as both the temperature decreased, the opacity increased and there was a low frequency (a few tenths of Hz) rumble coming from the plasmatron. The same phenomena was observed throughout the range of O/C ratios investigated with biodiesel. Thus it was concluded that the use of the plasma, for the range of conditions explored, was needed for stable, good reforming.

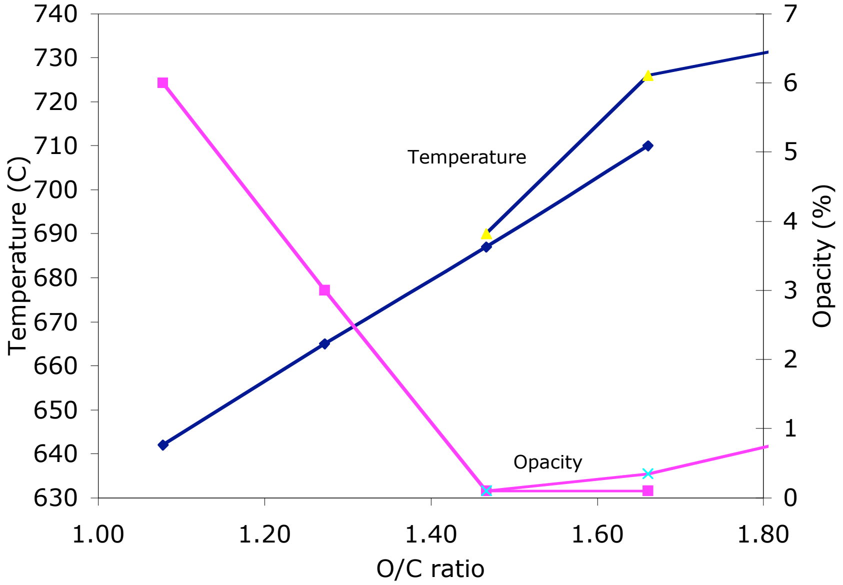

Figure 4. Temperature and opacity corresponding to tests in Figure 3.

IV Ethanol reforming

In this section, results for the reforming of neat ethanol are described. The setup was identical to that used for the B-100 experiments. Neat ethanol was introduced instead of the biodiesel through the B37 nozzle. The flow rate of ethanol in these experiments was 0.58 g/s. Only steady state characterization was investigated..

The composition of the reformate for various values of O/C are given in Figure 5. As in the previous section, the definition of O/C includes the oxygen in the fuel. Two sets of values are presented, with and without plasma. It is interesting to note, as discussed in the gaseous fuels as with B-100, that at high values of O/C there is a relatively small impact of the presence of the plasma. For the case of ethanol, at O/C > 2.1, the plasma plays a minor role, and the compositions with and without the plasma are comparable. The plasma has an impact at lower O/C, where the plasmatron is still operating, but with very poor performance.

Figure 6 shows the temperature and the opacity for the same cases in Figure 5. The temperature decreases monotonically with O/C, and is similar for both cases with and without plasma. The opacity, however, increases substantially. The opacity is not constant in the case on no plasma, and some averaging had to be made. Opacity in very transient, with a duration less than 1 s (can not be resolved with the present instrumentation).

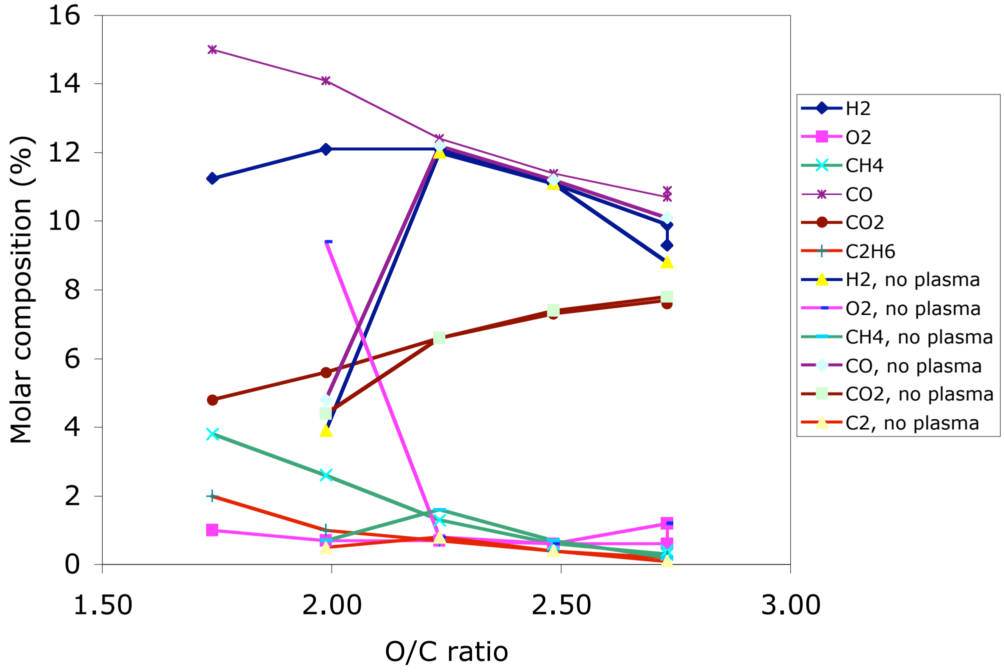

Figure 5. Composition of reformate from plasmatron ethanol converter as a function of O/C, with and without plasma on.

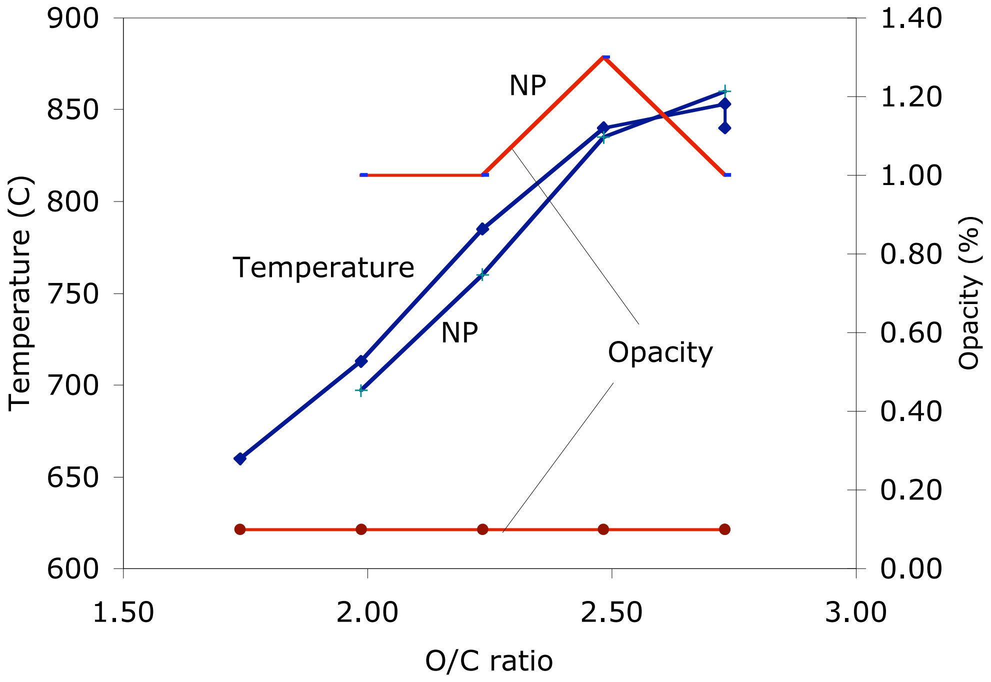

Figure 6 Temperature and opacity for the same cases as Figure 5. NP stands for No-Plasma.

The carbon balance for the experiments in Figures 5 and 6 is adequate, better than 10%, with the exception of the case with no plasma and lower O/C, where there is 50% carbon deficit. It is thought that this is due to the poor performance of the reformer, and with raw fuel coming through the device.

The reformer efficiency (ratio of heating value power of the reformate over heating value power of the fuel) in the presence of the plasma increases from about 50% at the highest values of O/C to a very respectable 75-80% at the lowest values considered. In comparison, for the case of no plasma the efficiency maximizes at ~70% at O/C ~ 2.1.

V. Discussion

The O/C ratio, as defined in this paper, includes the oxygen present in the fuel, rather than the free oxygen. The oxygen bound in the fuel does not contribute to the exothermicity of the reaction, as the oxygen is already bound either to carbon or to hydrogen. B-100 has a relatively small fraction of the oxygen (about 10% of the carbon atoms), while for ethanol, the fuel has 1 oxygen atom per 2 carbon atoms, a ratio of 50%. If the oxygen in the fuel is not included, the O_{free}/C ratio for the experiments in Figures 5 and 6 spans from ~ 1.24 to 2.2. The peak hydrogen concentration is at $O_{free}/C \sim 1.5$.

Similarly, for B-100 the optimal reforming occurs at about $O_{free}/C \sim 1.5$. However, ethanol performance remains high at lower values of O_{free}/C than biodiesel.

Hydrogen concentration in the reformate when using ethanol on the order of 12% can be obtained with or without a plasma, and the plasma is needed O/C ratios lower than about 2.1. For B-100, the comparable numbers are 11%, but a plasma is needed throughout the range that was explored. It is interesting to note that the heat of vaporization of ethanol is substantially higher than that of B-100. Under the assumption that the fuel needs to be vaporized prior to reforming, ethanol should be more difficult to reform. However, the experimental evidence points to the contrary, with better performance of ethanol reformers at lower O/C ratios and less sensitivity to the presence of the plasma..

The reformation at lower values of O/C degrades, with decreased conversion and increased opacity. It is possible that the increased opacity is due to raw fuel. However, for the fuel to be raw, the temperature must be lower (fuel would either pyrolyze or evaporate at 700 C). Thus, raw fuel must be accompanied with lower temperatures, from a reformer where the reformation has stopped. It has been determined that in the short residence time in the system, there is not enough surface heat transfer from the walls to the air/fuel mixture to increase the temperature of the air fuel mixture to more than 100 C. Thus, when there is a transient and the reforming stops, the air/fuel mixture remains relatively cold. This behavior may also be behind the “puffing” sounds that come from the exhaust under these conditions, with the reforming turning on and shutting down with a period of a few seconds..

Finally, it is not clear why the carbon balance is poor in the case of B-100. Carbon balance (including C_2H_4 and C_2H_6) is better than 10% for the case of ethanol, but about 30% for the case of B-100.

VI. Summary

A series of experiments reforming renewable fuels were carried out using a plasmatron fuel converter. Conditions of good non-catalytic performance were investigated, with hydrogen concentration in the dry reformate > 10% and energy efficiency > 70%. Operation at relatively high O-to-C ratio is required. The ratio of free-oxygen to carbon ratio, however, is $O_{free}/C \sim 1.5$ at the conditions of good performance.

The plasma is required for the start up for both fuels, until conditions near steady state are achieved. However, once steady state is achieved in ethanol, hydrogen concentration in the absence of plasma is maintained for all but the lowest value of O/C ratio, although with higher opacity that in the case with the plasma. For B-100, the plasma is needed throughout the O/C range explored.

Acknowledgement

We want to thank the continued support of Dr. Sidney Diamond. His encouragement, depth and width of knowledge, enthusiasm and *`Joye de Vivre'* will serve as standards for us to reach.

References

[1] K. Hadidi, L. Bromberg, D.R. Cohn, A. Rabinovich, N. Alexeev, A. Samokhin, *Hydrogen-Rich Gas Production From Plasmatron Reforming Of Biofuels*, presented at the World Renewable Energy Congress VIII and Expo, Denver CO (Aug 2004)

[2] Pimentel, D. and T.W. Patzek, *Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower, Natural Resources Research*, **14**, No. 1, March 2005 (2005)

[3] Shapouri, H., Duffield, J. A., and Wang, M., *The energy balance of corn ethanol: an update: USDA, Office of Energy Policy and New Uses, Agricultural Economics*. Rept. No. 813 (2002)

[4] L. Bromberg, K. Hadidi and D.R. Cohn, *Experimental Investigation of Plasma Assisted Reforming of Methane I: Steady State Operation,* Plasma Science and Fusion Center Report JA-05-10

[5] L. Bromberg, K. Hadidi and D.R. Cohn, *Experimental Investigation of Plasma Assisted Reforming of Methane II: Start-up,* Plasma Science and Fusion Center Report JA-05-11

[6] L. Bromberg and N. Alexeev, *Plasma Assisted Reforming of Methane: Two Stage Perfectly Stirred Reactor (PSR) Simulation*, Plasma Science and Fusion Center Report JA-05-12

[7] L. Bromberg, *Modeling of Plasma Assisted Reforming of Methane II: Partially Stirred Reactor (PASR) Simulation*, Plasma Science and Fusion Center Report JA-05-13

[8] L. Bromberg, *CFD modeling of Plasmatron Methane Reformers*, Plasma Science and Fusion Center Report JA-05-14

[9] L. Bromberg, K. Hadidi and D.R. Cohn, *Experimental Investigation of Plasma Assisted Reforming of Propane,* Plasma Science and Fusion Center Report JA-05-15

[10] Data of B-100 fuel used was provided by Bill Ayres, President, Renewable Solutions LLC (2005)