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PLASMA CATALYTIC REFORMING OF
BIOFUELS

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ABSTRACT

Vegetable oils and ethanol have been used in a plasmatron reformer to generate synthesis gas. Corn, canola, and soybean oils and ethanol have been reformed at different oxygen to carbon ratios and different power levels. Both homogeneous plasma reforming (uncatalyzed) and catalytic plasma reformer have been evaluated.

I. INTRODUCTION

Throughout the world large quantities of agricultural and forestry residual wastes are generated. These renewable resources can potentially be converted into economically attractive fuels for transportation uses. In addition, it may be economically possible to cultivate crops that can be harvested for the manufacturing of fuels. Use of these resources could potentially have a significant impact result in reducing emissions of greenhouse gases. Use of these alternative and renewable fuels such as bio-fuels can also reduce the US dependence on foreign energy sources.

This biomass can be converted to a liquid product (called bio-oil or biofuel) using several methods, including fast pyrolysis. This technique has now reached the small scale commercial Stage [1]. For example, two commercial plants using this technique (ENSYN Technologies Inc., Ottawa, ON, Canada) are being operated by Red Arrow Products Co., of Wisconsin (50 tonnes/day). Also, a pilot demonstration unit (3 tonnes/day) is being operated in Galicia, Spain, using a bubbling fluidized bed [2] (using the technology developed at the University of Waterloo, Canada). In addition, progress is being made in developing economically attractive high yield production of ethanol from dedicated crops. These biofuels can be used for blending with diesel or gasoline. However, they are not suitable for direct use in transportation.

Unrefined or lightly refined bio-oils are difficult to use directly in the transportation sector, because of their heavy molecular weights and high viscosity. Using directly bio-fuels such as veggie oils as fuel for transportation would be very difficult because of the combustion properties of the fuels.

Several processes have been considered for the reformation of biomass into hydrogen. They include fast pyrolysis [3], catalytic steam reforming [4,5], catalytic pyrolysis [6, 7] and supercritical water reforming. However, these technologies can not be used for onboard applications.

An alternative approach is to use on-board generation of hydrogen from renewable energy biofuels. The plasmatron technology being developed at MIT for reformation of a wide range of fuels into synthesis gas (hydrogen and carbon monoxide) uses special low current plasmas. This type of plasma can be used to enhance the reformation process and has the advantage of low power consumption and long electrode life. Because of the heavy nature of the bio-oils, successful operation of the plasma process has been found to be relatively sensitive to plasmatron design and operation. Because of poor atomization or volatilization of biofuels, care must be taken to prevent formation of soot. On the other hand, since partial oxidation of ethanol is only mildly exothermic care must be taken to ensure good conversion.

In this report, fuel reforming results from partial oxidation of biofuels is described. In the partial oxidation reaction enough oxygen is present in the reactor in order to capture each carbon atom in the fuel as carbon monoxide, with the hydrogen released as hydrogen molecules. The oxygen comes from both the fuel (fuel-borne oxygen) and from air. The

nitrogen from this air is inert at the temperatures and pressures of operation, and thus goes unaffected through the reactor. The use of the plasma allows for a robust and large volume reaction initiation of the air/fuel mixture.

This report summarizes plasmatron reforming technology work for a wide range of bio-fuels. These fuels include corn, canola and soybean oils (both refined and unrefined), and ethanol. The work presented in this report will describe the procedure, the results and analysis of bio-fuels reformation using low-current plasma discharges.

II. EXPERIMENTAL SETUP

The plasmatron reformer used in the biofuel conversion experiments is a modification of a plasmatron fuel reformer that had been optimized for diesel fuel operation. [10]

Because of power supply limitations, the unit was operated mainly at 700 W of electrical power. However, limited tests were conducted at lower electrical powers using a modified power supply. These units were operated as constant current sources. The frequencies of the two different power supplies were 200 kHz to 260 kHz.

Reforming experiments at different oxygen-to-carbon (O/C) ratios were carried out. In the case of ethanol, some of the oxygen required for the reformation is provided by the fuel itself. In this case, the O/C ratio includes this oxygen. The free oxygen was provided by supplying air. Air required for the partial oxidation reaction was provided from building compressed air supply. This air was conditioned by drying.

The bio-oils used in the experiments were commercially available oils. The corn and canola oils were fit for human consumption, while the refined and unrefined soybean oils were purchased from a soybean grower from Illinois. The unrefined soybean oil was obtained as “crushed,” while the refined oil was the output after de-glyceration process. Neat ethanol was used in the experiments.

Figure 1 depicts the experimental setup used to reform vegetable oils and ethanol.

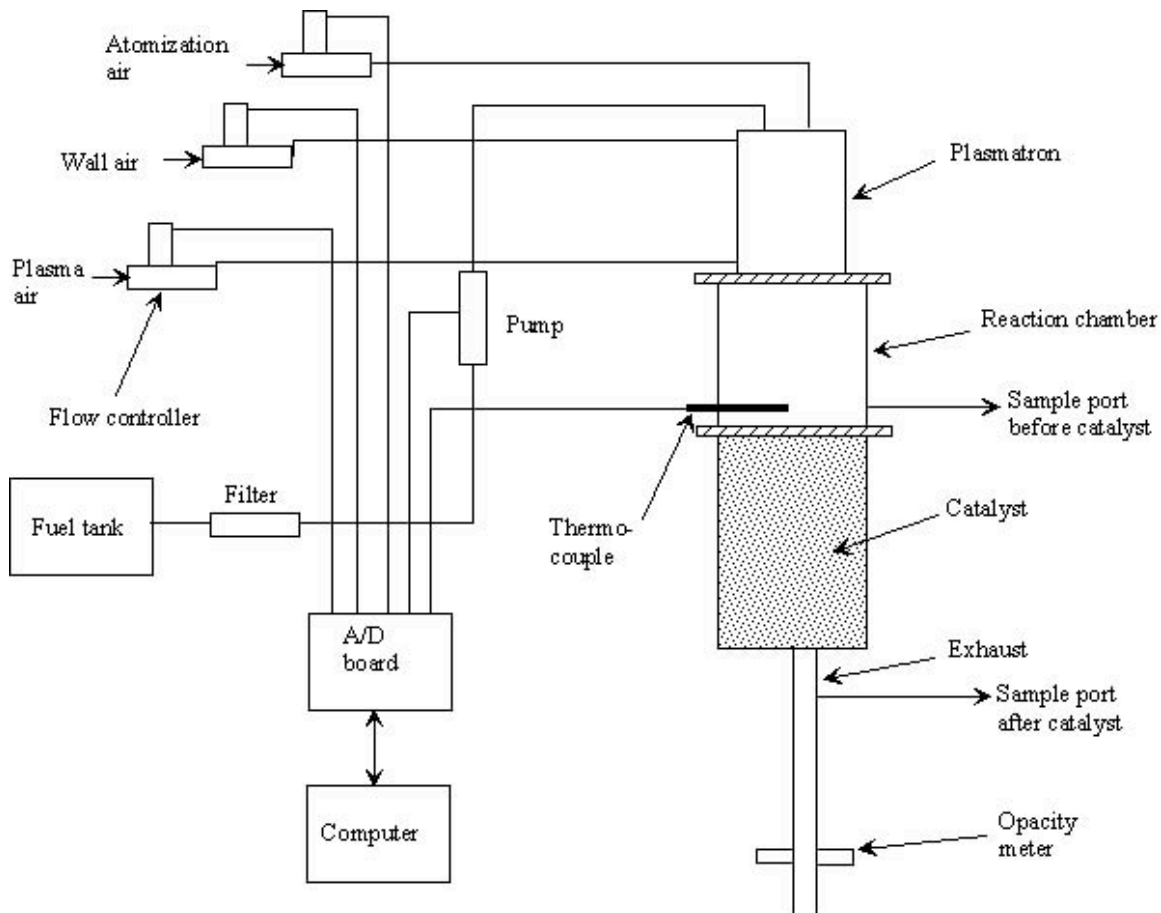


Figure 1. Schematic layout of the plasmatron reformer setup

The plasmatron is mounted on a steel reaction chamber that allows the partial oxidation reactions to take place with enough residence time. The dimensions of this chamber are 2 inches diameter by 5 inches long. The products of reaction from this chamber go into a 2-inch diameter by 7-inch long chamber packed with nickel-based catalyst on an alumina substrate. The chamber is thermally insulated by a half-inch thermal insulation made of porous alumina ceramic from Zircar.

Two sample ports are used for sampling the reformat gases. The first one is located on the reaction chamber right before the catalyst and the second one is located at the exhaust, after the catalyst chamber. Both sampling lines are water cooled.

The temperature inside the reactor is measured by a thermocouple located inside the catalyst.

Calibrated mass flow controllers from Omega Engineering Corporation are used to control the multiple air inputs into the plasmatron.

The system is controlled by a LabView software developed in our laboratory. The software allows real-time control of the different components of the system and

continuously acquires and stores several parameters such as temperature and air and fuel flow rates during operation.

A schematic of the plasmatron used in the experiments is depicted in Figure 2. In this configuration, the fuel is injected from the top of the plasmatron through a commercially-available nozzle. Directly downstream from the fuel nozzle there is an orifice. The high velocity of the air downstream from this orifice further atomizes the fuel into a fine mist.

The spray angle of the combine nozzle/orifice atomizer is about 30 degrees. To prevent the fuel from striking the solid surfaces inside the plasmatron, wall air is used. This wall air is introduced through an annular gap between the electrode and the atomization air plug. The wall air is introduced without any swirl.

A third air, the plasma air, is introduced with a large swirl component in the gap between the two electrodes. The electrical discharge takes place between these two electrodes. The swirl motion of the plasma air prevents the plasma from attaching to one spot on the electrodes, by hydrodynamically moving the discharge and its roots. The radial motion associated with the plasma air also pushes the discharge into the main volume of the plasmatron, producing a discharge that in an average sense fills this region.

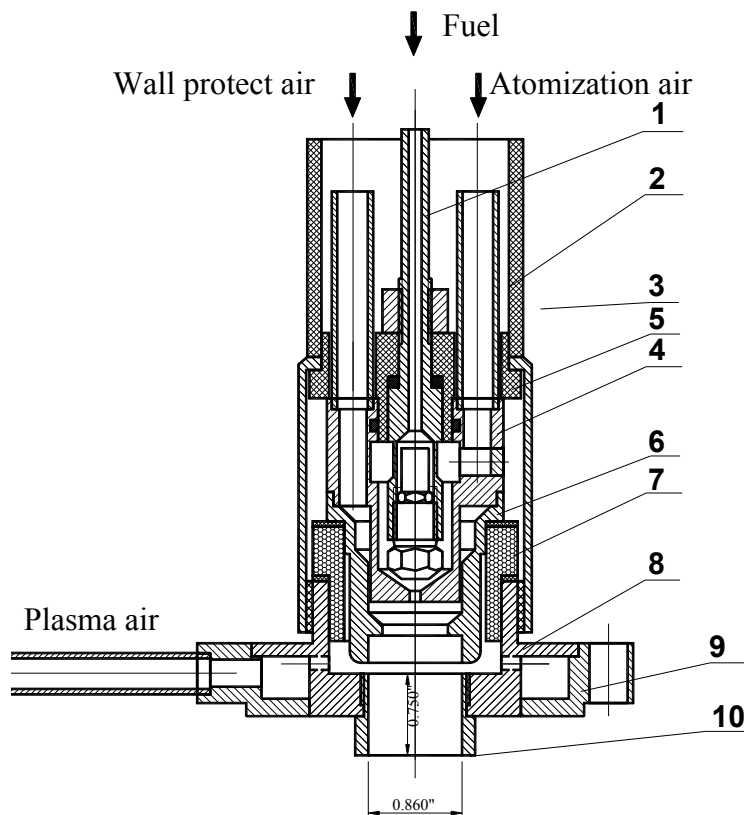


Figure 2. Details of the plasmatron used for bio-fuels reforming

Samples from the reformat gases are drawn into syringes and analyzed using an MTI-2000 gas chromatograph (GC). The unit has a molecular sieve column for analyzing hydrogen, oxygen, nitrogen, methane, and carbon monoxide, and a second column that can analyze carbon dioxide, C₂H₂, C₂H₄, and C₂H₆, and other heavier hydrocarbons. A WAGNER opacity meter was used to monitor the production of soot.

III. RESULTS AND DISCUSSION

A) BIO OILS

Figure 3 shows results for hydrogen yields from the reformation of canola, corn, and soybean oils as a function of O/C ratio for catalytic and homogeneous (non-catalytic) reforming. The hydrogen yield is defined as the ratio of the mass flow rate of hydrogen in the reformat gases to the mass flow rate of hydrogen in the fuel. A hydrogen yield of 100% thus means that all the hydrogen in the fuel has been released as hydrogen in the reformat gases. The bio-oil flow rate was 0.4 g/s. 0.4 g/s corresponds to about 16 kW of chemical power.

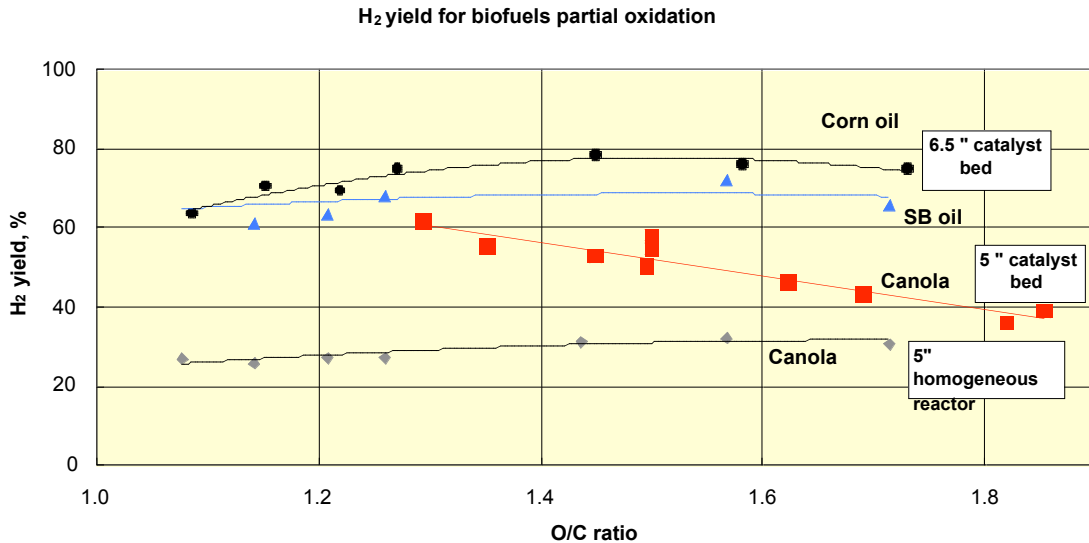


Figure 3. Hydrogen yield for the reformation of canola, corn, and soybean oils vs O/C ratio

It appears from Figure 3 that the hydrogen yield for the reformation of corn and soybean oils are very similar in the presence of a catalyst. The difference between the two falls within the error bar due to sampling and GC analysis uncertainties. On the other hand, the hydrogen yield for canola oil in the presence of a catalyst appears to be lower than for corn and soybean oils, especially at the higher values of O/C. This may be due to the use of less catalyst in the case of canola, or to issues with the air-fuel injection (for example, misalignments of the injector where the oil spray hits the walls). In the case of corn and soybean oils, the hydrogen yields peaks at an O/C ratio close to 1.5; this is due to the fact that some of the fuel needs to be combusted in order to provide the heat necessary to result in efficient partial oxidation reaction. It is not clear whether the O/C ratio higher

than stoichiometry for partial oxidation is a result of increased temperature to drive the reactions, or by appropriate vaporization and mixing that may result at $O/C \sim 1.5$.

Comparison between homogeneous and catalytic reforming was carried out for the case of corn, canola and soybean oil. Figure 4 shows the effect of the use of catalyst on the hydrogen yield, for a fixed soybean oil flow rate of 0.37 g/s. In homogeneous reformation of soybean oil, i.e. in the absence of a catalyst, the hydrogen yields are about 30%, while the yield increases to about 80% in the presence of a catalyst downstream from the plasmatron. The peak yield occurs at $O/C \sim 1.5$.

The hydrogen concentration in the reformat as a function of O/C ratio for the processing of canola, corn, and soybean oils is given by Figure 5. Here again, the hydrogen concentration during the reformation of corn and soybean oils are identical and larger than the results with canola oil. It is likely that the difference between the canola and the soybean/corn results are due to the difference in catalyst volume.

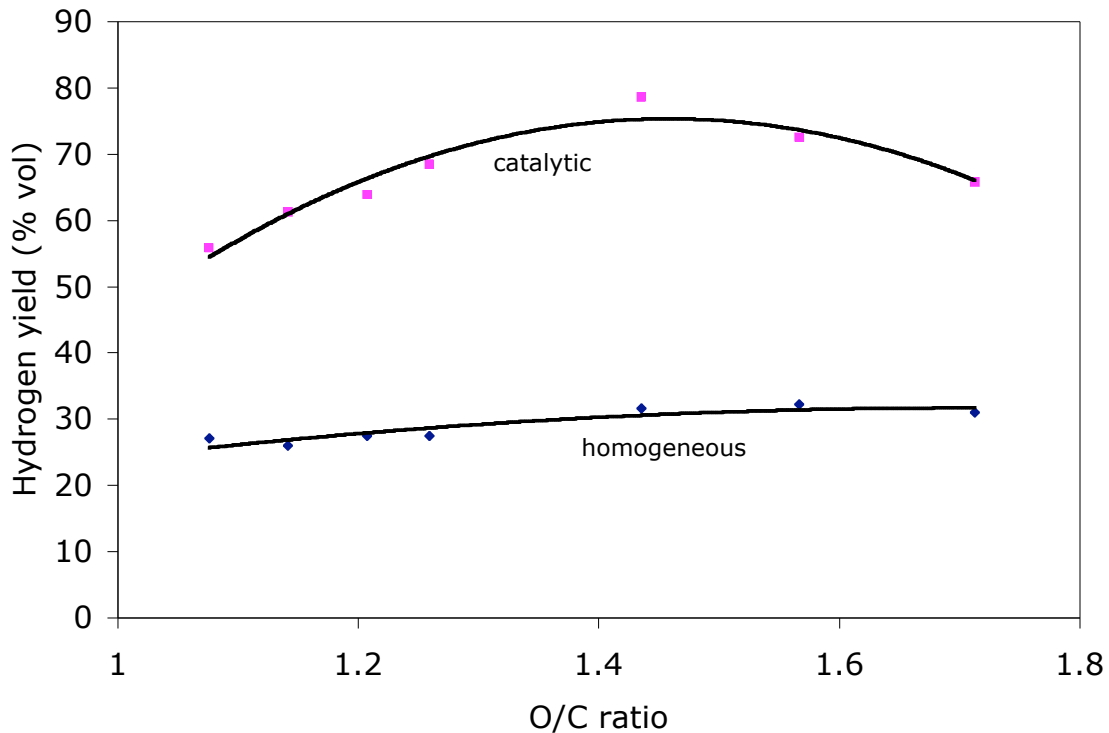


Figure 4. Hydrogen yield as a function of O/C ratio for partial oxidation reforming of soybean oil.

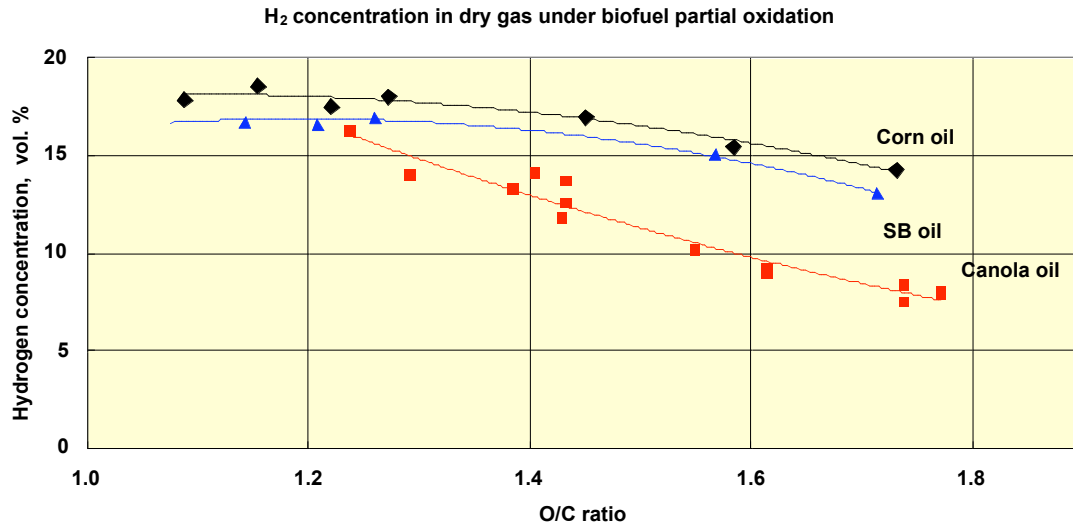


Figure 5. Hydrogen concentration for catalytic reformation of corn, canola, and soybean oils

The hydrogen concentration for the three oils is higher at lower O/C ratios and decreases when O/C ratio increases. This is because as O/C ratio increases, some of the oxygen reacts with the hydrogen to form water and the reaction tends more toward combustion. Even though the hydrogen yield increases at the higher O/C ratios (as shown in Figure 3), the addition of combustion products decreases the actual hydrogen concentration.

The composition of the gas reformation before and after the catalyst for soybean oil for a O/C ratio of 1.08 is shown in Table 1. The plasmatron converts the high hydrocarbons into hydrogen, carbon monoxide and light hydrocarbons, with minimal soot producton. The catalyst then takes the plasmatron gas and basically doubles the hydrogen yield. It should be stressed that the performance of the system was not optimized, and higher hydrogen yields should be possible by converting the substantial amounts of C₂'s present in the gas downstream from the catalyst. Note that the oxygen concentration is very small, even in the gas from the homogeneous zone. Experiments were carried out with a flow rate of soybean oil of 0.37 g/s.

Table 1. Reformate composition for soybean oil reforming at an O/C = 1.08, 0.37 g/s

	Homogeneous	Catalytic
	% vol	% vol
H ₂	9	16
CO	12	17
CO ₂	7.4	5.2
N ₂	63	56
CH ₄	1.4	1
C ₂ H ₄	5.7	3
C ₂ H ₂	0.1	0.05
O ₂	0.7	0.7

For all the experiments performed with veggie oils, the opacity was 0.1, which is the sensitivity limit of the instrument and which indicates that at most very small amounts of soot were produced.

The temperatures were measured in the middle of the catalyst. Figure 6 shows the dependence on O/C ratio of the temperature. As expected, as the O/C ratio increases, the temperature increases. At the lowest value of O/C ratio, the temperature is about 800 C. It would be interesting to explore the implications of even lower O/C ratios, both on the temperature, hydrogen yield and soot production. This will be done in the future.

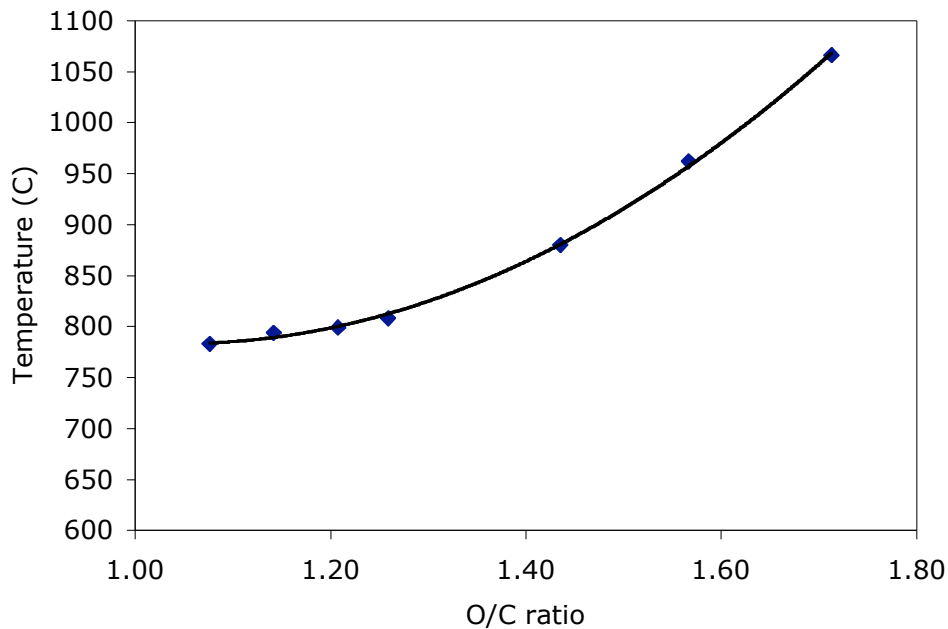


Figure 6. Dependence of mid-catalyst temperature on O/C ratio for 700 W and 0.37 g/s operation.

B) ETHANOL

The same experiments as for the veggie oils have been carried out for ethanol, but at lower power levels. Figure 7 gives the hydrogen yield for catalytic reformation of ethanol at 200 W as a function of the oxygen to carbon (O/C) ratio. Homogeneous reformation of ethanol is difficult to achieve because of the presence of oxygen in the molecule, leading to a very mildly exothermic reaction. It appears however that the results of the plasma catalytic reformation of ethanol are comparable to those obtained for veggie oils and at the same O/C ratios.

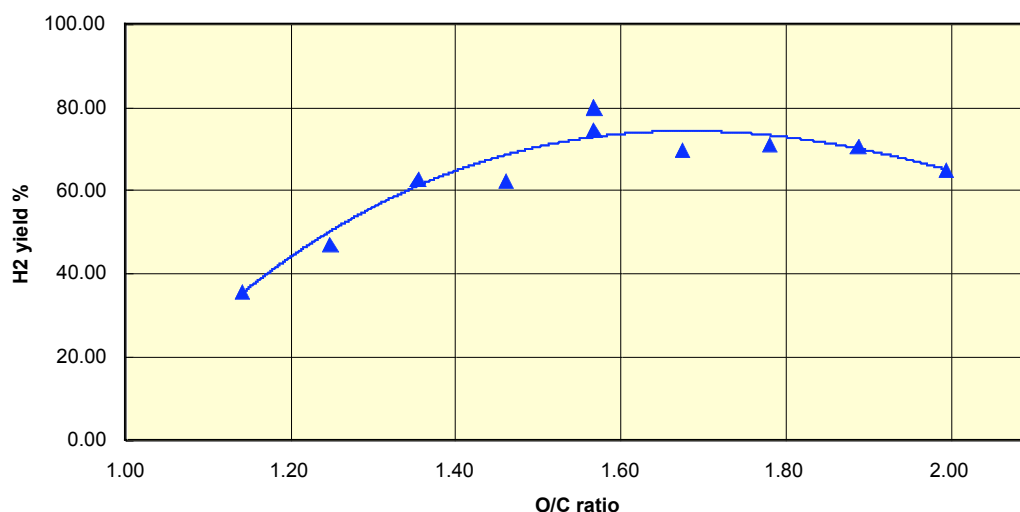


Figure 7. Hydrogen yield for the reformation of ethanol in the presence of a catalyst vs O/C ratio for 200 W electrical power input into plasma

The hydrogen yield peaks at around $O/C \sim 1.5 - 1.7$, slightly higher than that for the bio oils. It should be stressed that the O/C ratio includes the oxygen that is carried out by the fuel, which in the case of ethanol is very substantial ($O/C \sim 0.5$ even in the absence of additional oxygen from air).

As for the veggie oils, the opacity measured during ethanol reforming was 0.1, which indicates that no soot was produced.

C) ENERGY CONSUMPTION

In order to make plasma reformation of fuels into syngas attractive, the energy consumption of the process has to be minimal as possible.

Figure 8 gives the energy consumption for corn and soybean oils versus O/C ratio at a power level of 700 W. For a maximum hydrogen yield at an O/C ratio of 1.5, the energy consumption is about 10 MJ per kilogram of hydrogen produced for corn and soybean oils.

A few experiments at lower power levels have been performed. As shown on Figure 8, the power consumption for canola and corn oils at respectively an O/C ratio of 1.2 and 1.5 is about 2.5 MJ per kg of hydrogen. This is an important result since it shows that high fuel conversion factors can be achieved with low electrical energy consumption.

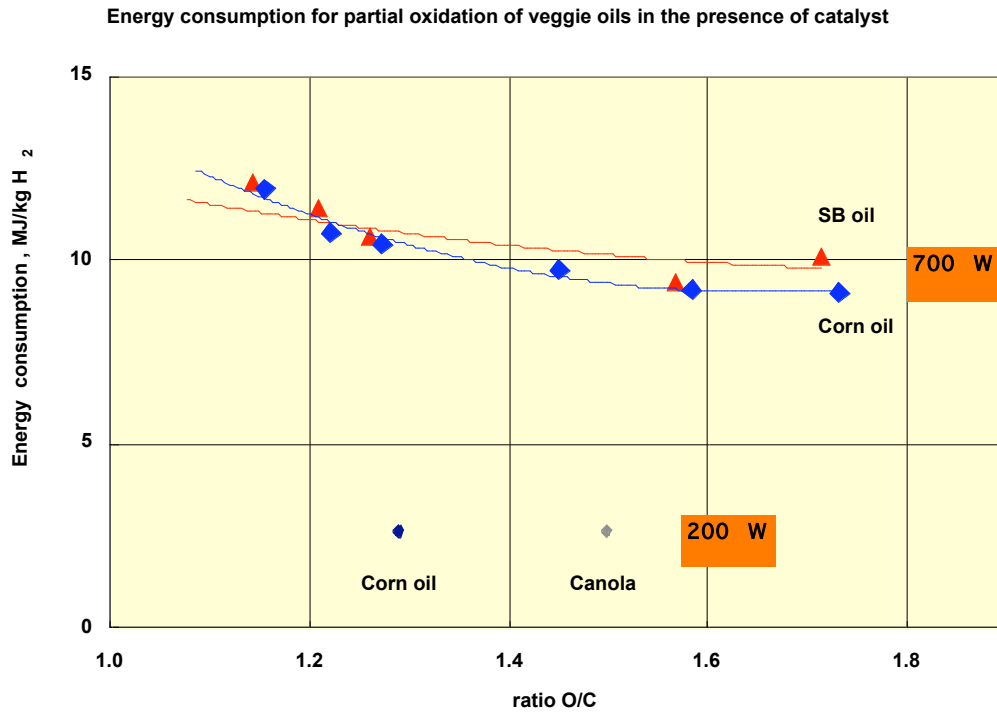


Figure 8. Energy consumption for reformation of veggie oils in the presence of catalyst

Energy consumption for the reformation of ethanol appears to be comparable to the energy consumption with veggie oils as shown in Figure 9.

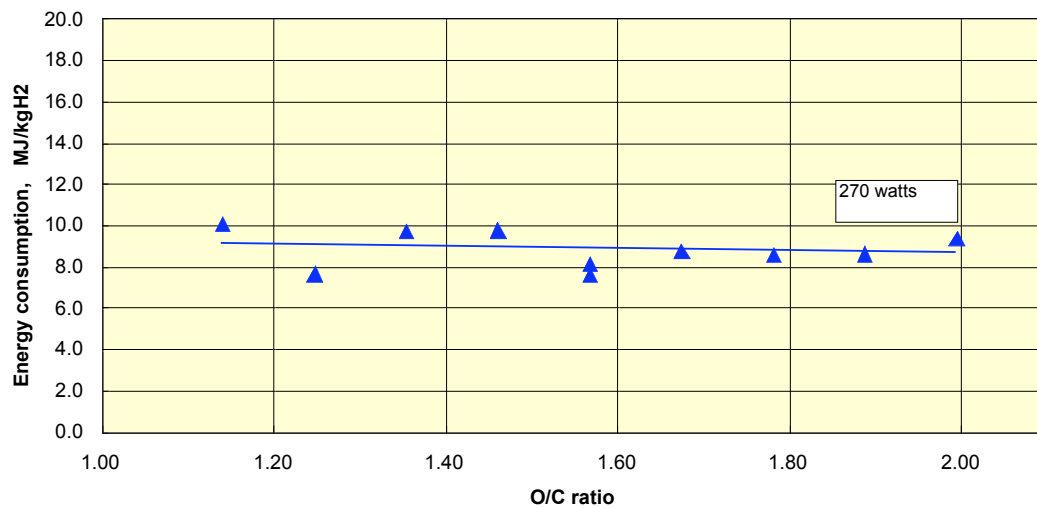


Figure 9. Energy consumption for reformation of ethanol

IV. MODELING

The plasmatron flows have been modeled in order to understand the behavior. The model has yet to incorporate chemistry, and only includes flow dynamics of uncombusted air/fuel mixtures. Computational Fluid Dynamic (CFD) models of the steady state, axisymmetric plasmatron have been developed. The plasmatron geometry is shown in Figure 10. Because of symmetry, only the upper portion of the results will be shown.

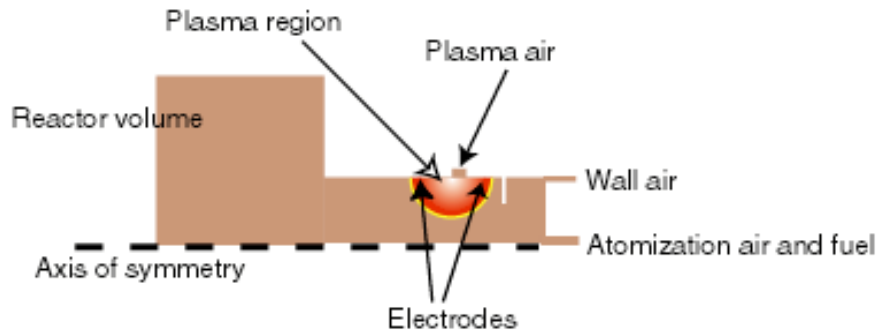


Figure 10. Plasmatron geometry analyzed.

Calculations for the plasmatron design were performed using parameters close to those of the experiments with biofuels. The case illustrated in this section has a total flow rate of air of 3.9 g/s with a corresponding flow of fuel of about 0.7 g/s.

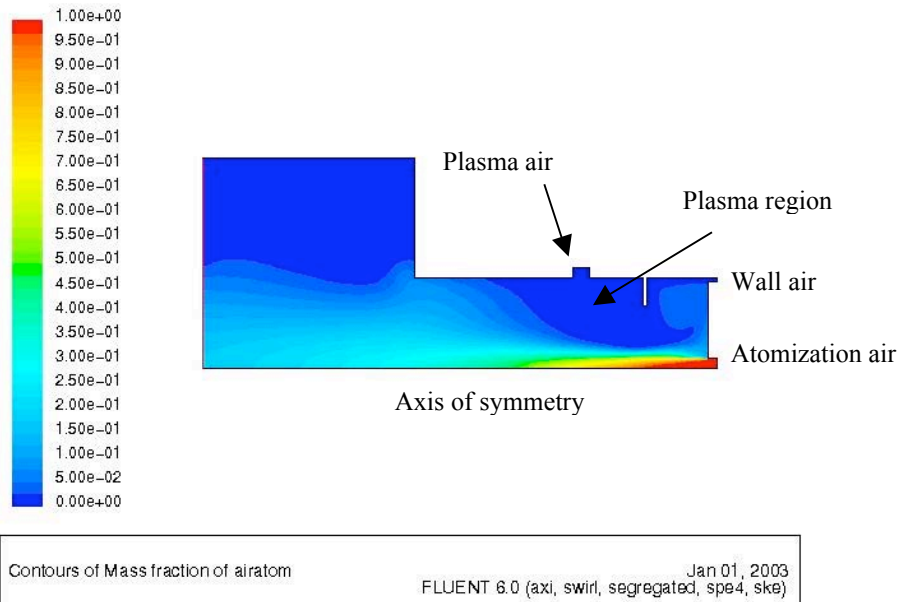


Figure 11. Contours of mass fraction of atomization air

To understand the mixing of the different air flows, the different air sources have been labeled. The atomization air corresponds to the air that is introduced axially with the fuel (for proper atomization). contours of constant mass fraction of atomization air is shown

in Figure 11. Adequate mixing occurs downstream from the plasma region (shown by arrow in Figure 11).

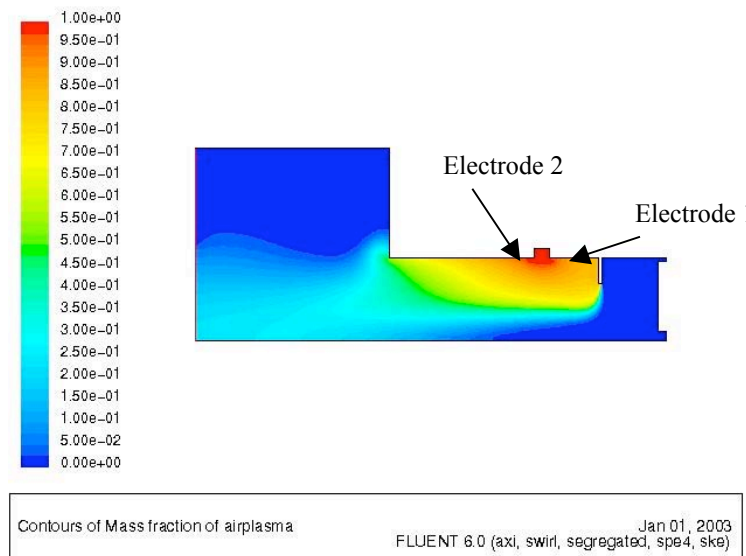


Figure 12. Contours of constant plasma-air mass fraction.

The plasma air is the air introduced in the electrode gap. The plasma air is introduced tangentially, so as to introduce swirl in the system. Figure 12 shows contours of constant mass fraction for the plasma air, confirming poor mixing in the region of the plasma, but good mixing downstream. The plasma is generated on opposite sides of the region of the plasma air injection (shown schematically in Figure 11). The plasma air drives the plasma into the main volume of the plasmatron, and swirls it to minimize electrode erosion and to maximize the volume of the flow that gets into contact with the plasma.

Substantial recirculation occurs in the reactor region downstream from the plasmatron. This recirculation reintroduces hot reformate to the region just downstream from the plasmatron.

It has been experimentally determined that this stratification is very important for proper operation of the plasmatron. The plasmatron reforming appears to be poor or does not occur at all for well mixed air and fuel, as determined with the use of methane as the fuel (easy to premix). The parameters shown in Figure 11-12 correspond to those in the experiments where good reforming was obtained. The evidence points to a model with a stratified air/fuel mixture, with some regions igniting (probably those with air/fuel mixtures best for combustion). The heat release from those ignited regions heats the rest of the system and drives reactions in the rest of the volume. The reforming process in the overall axi-fuel mixture is aided by good mixing downstream from the plasma region.

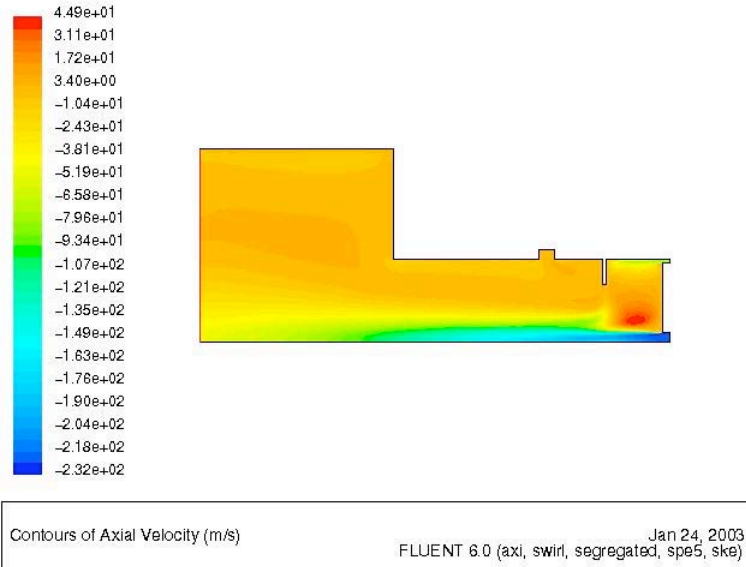


Figure 13. Axial velocity with fuel injection (0.5 g/s)

The axial velocity of the air is shown in Figure 13. The axial velocity is inversely proportional to the residence time in the reactor. In the area of interest, where there is both air and fuel mixture, the axial velocity is about 100 m/s. Since the axial extent of the plasma region is about 3 cm, a residence time in the plasma zone is about 0.3 ms. Reaction initiation must to take place during this time. On the other hand, in the plasma regions corresponding to larger radii, the axial velocity is more on the order of 20 m/s, with residence times on the order of 1.5 ms. Chemical models are being developed to include kinetics and relate the results to the calculated values of residence and mixing developed in the CFD calculations. Unfortunately, the chemical mechanisms are best developed for methane, and need to be developed and benchmarked for modeling partial oxidation reactions of heavy hydrocarbons.

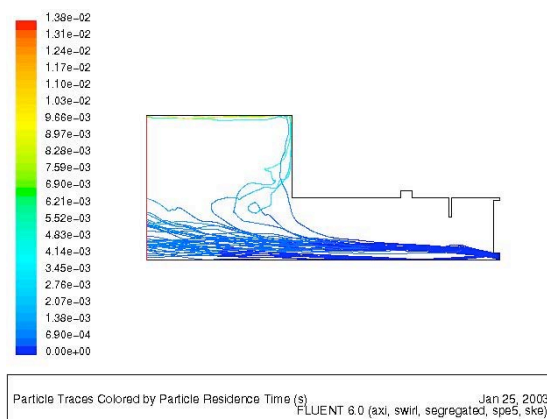


Figure 14. Stochastic paths of fuel droplets

Stochastic paths of fuel droplets are shown in Figure 14, for the same conditions. The code launches a large number of droplets from the region of the nozzle, with axial velocity and angle that match the experimentally determined distribution. The motion of

the droplets is then followed, using stochastic modification to the droplet path and velocity. The stochastic forces on the droplet match the calculated turbulence in the system. Thus shown in the Figure 14 are a few random droplet paths, not the average path. It can be seen that a substantial region where the plasma exists is void of fuel. On the other hand, there is stratification of the air fuel mixture. The design is good at keeping the droplets away from the walls and preventing agglomeration of the fuel.

It should be stressed again that the present calculations do not include chemical reactions. Once chemical reactions begin, the flows are substantially modified. The present model is used to try to understand the flows upstream from the plasma region, including the plasma region, since it is expected (and experimentally verified) that the reactions take substantial time to develop and come to completion compared with the residence time in the plasma region.

V. CONCLUSIONS

Production of hydrogen from renewable feedstocks such as biofuels through plasma reformation can be an attractive and viable solution as a source of energy. The results shown above demonstrate clearly that high hydrogen yields at low energy consumption can be achieved in the presence of a catalyst. However, more work needs to be done to further lower the energy consumption and approach a hydrogen yield of 100% by operating the plasmatron fuel reformer closer to an O/C ratio of 1.

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