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HYDROGEN-RICH GAS PRODUCTION FROM PLASMATRON REFORMING OF BIOFUELS♣

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I. INTRODUCTION

Throughout the world it may be economically possible to cultivate crops that can be harvested for the manufacturing of biofuels that could potentially have a significant impact result in reducing emissions of greenhouse gases. Use of renewable fuels such as bio-fuels can also reduce the US dependence on foreign energy sources.

Plasma enhanced reforming is a promising approach for vehicular application involving onboard generation of hydrogen-rich gas (H_2, CO, light hydrocarbons) from renewable energy biofuels. The hydrogen-rich gas can be used in internal combustion engine vehicles to increase engine efficiency and reduce pollution[1]. The compact plasmatron fuel reformer technology presently under development at MIT uses special low current plasmas[2]. This type of plasma can be used to enhance partial oxidation reformation of a wide range of biofuels. Plasma enhanced reforming provides advantages of rapid response, capability to reform difficult to convert fuels (such as diesel and bio oils) and relaxation or elimination of catalyst requirements. The low current plasma has the advantage of low power consumption and long electrode life.

This paper reports further investigations of plasma enhanced partial oxidation reforming of biofuels that include corn, canola and soybean oils, and ethanol. Results were obtained for both homogeneous (non-catalytic) and catalytic reforming.

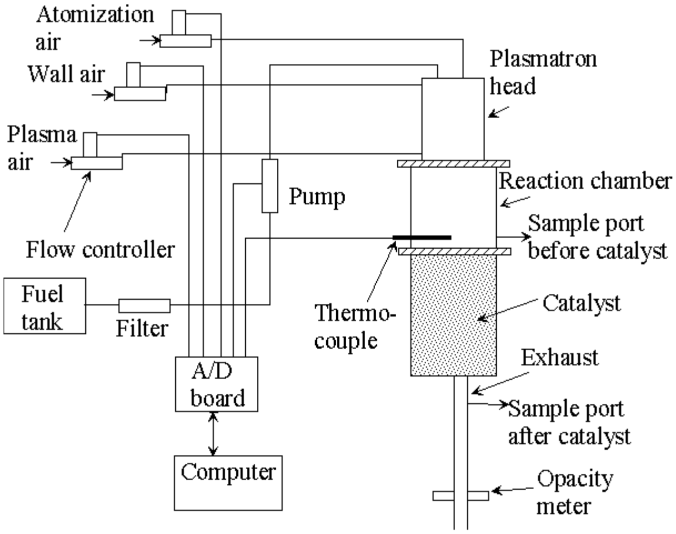
II. EXPERIMENTAL SETUP

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[2]. The unit was operated mainly at 700 W of electrical power. Limited tests were conducted at 200 W. The power supplies were operated as constant current sources operating between 200 kHz and 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 compressed air from building compressed air supply. The bio-oils used in the experiments were commercially available oils

Figure 1 depicts the experimental setup used to reform vegetable oils and ethanol. The plasmatron was mounted on a steel reaction chamber that allows the homogeneous partial oxidation reactions to take place with enough residence time. The dimensions of this chamber are 5 cm diameter by 12.5 cm long. The products of reaction from this chamber go into a 5 cm diameter by 17.5-cm 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.

Figure 1. Schematic layout of the reformer setup



Two sample ports are used for sampling the reformate gases. The first one is located on the reaction chamber immediately upstream from the catalyst and the second one is located at the exhaust, downstream from 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 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 continuously acquires and stores several parameters such as temperature, air and fuel flow rates during operation.

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. To prevent the fuel from striking the solid surfaces inside the plasmatron and produce soot by pyrolysis, wall air is introduced through an annular gap between the electrode and the atomization air plug. This wall air creates a sheath along the inner walls of the plasmatron and prevents the fuel from hitting the wall. A third air stream, the plasma air, is introduced with a large tangential component in the gap between the two cylindrical electrodes where the electric discharge takes place. The tangential motion of the plasma air prevents the plasma from attaching to one spot on the electrodes, by moving the discharge and its roots. The plasma air pushes the discharge into the main volume of the plasmatron, producing a discharge that in an average sense fills this region.

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, C_2H_2, C_2H_4, and C_2H_6, and other heavier hydrocarbons. A WAGNER opacity meter was used to monitor the production of soot. Water is not monitored.

The corn and soy bean catalytic experiments were done with a volume of 85 cm^3 of catalyst, whereas only 25 cm^3 of catalyst were used during the canola oil experiments.

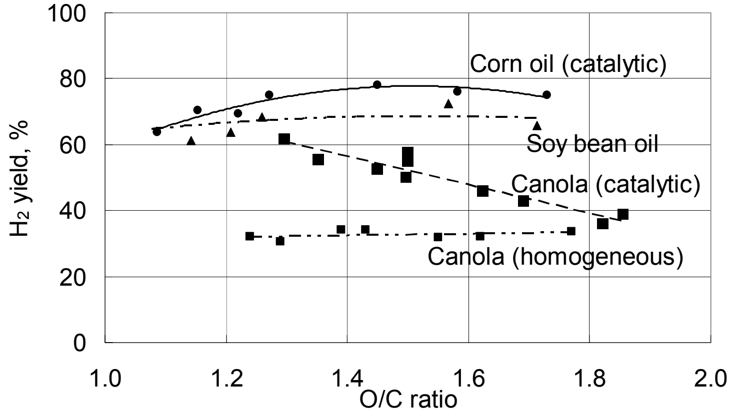
III. RESULTS AND DISCUSSION

A) BIO OILS

Figure 2 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. The bio-oil flow rate was 0.4 g/s, which corresponds to about 17 kW of chemical power.

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.

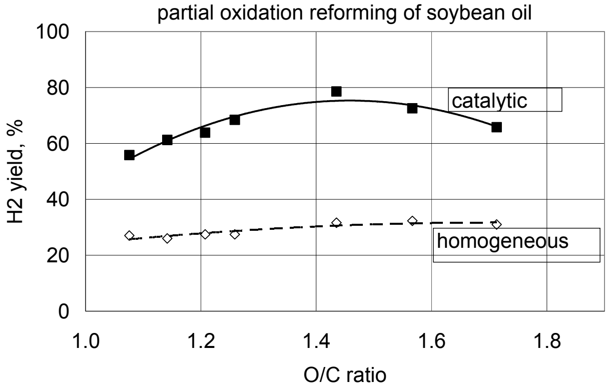
Figure 2. Hydrogen concentration for catalytic reformation of corn, canola, and soy bean oils



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 hit the walls). In the case of corn and soybean oils, the hydrogen yield 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 drive the partial oxidation reaction.

Comparison between homogeneous (non-catalytic) and catalytic reforming was carried out for the case of corn, canola and soybean oil. Figure 3 shows the effect of catalyst on the hydrogen yield, for a fixed soybean oil flow rate of 0.37 g/s. The hydrogen yield is the ratio of hydrogen in the form of H_2 to the hydrogen in the biofuel. For homogeneous reformation of soybean oil, the hydrogen yields are about 30%, while the yield increases to about 80% in the presence of a catalyst. The peak yield occurs at O/C ~ 1.5. The difference between the yield of 80% and the ideal yield of 100% is due primarily to loses of hydrogen resulting from full oxidation into water. For homogeneous reformation, the ratio of the heating value of the hydrogen, CO and light hydrocarbons byproducts to the heating value of the fuel was typically between 60 and 70%.

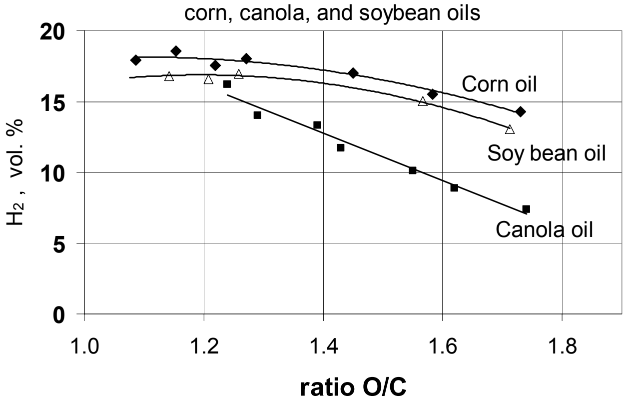
Figure 3. Hydrogen yield as a function of O/C ratio for partial oxidation reforming of soybean oil



Hydrogen concentration in the reformate as a function of O/C ratio for the processing of canola, corn, and soybean oils is given by Figure 4. 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.

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 to move toward combustion. Even though the hydrogen yield increases at the higher O/C ratios, the addition of combustion products decreases the actual hydrogen concentration.

Figure 4. H_2 concentration for catalytic reformation of corn, canola, and soybean oils



The composition of the gas reformation upstream and downstream the catalyst for soybean oil for an O/C ratio of 1.08 is shown in Table 1 bellow. The plasmatron converts homogeneously the high hydrocarbons into hydrogen, carbon monoxide and light hydrocarbons, with minimal soot production and eliminating all free oxygen. The catalyst then takes the oxygen-free plasmatron gas and basically doubles the hydrogen yield performing CO_2 and possibly steam reforming (notice that the CO_2 concentration is decreased downstream the catalyst; water, on the other hand, is not monitored).

	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_2H_4	5.7	3
C_2H_2	0.1	0.05
O_2	0.7	0.7

Table 1. Composition of the reformate gas

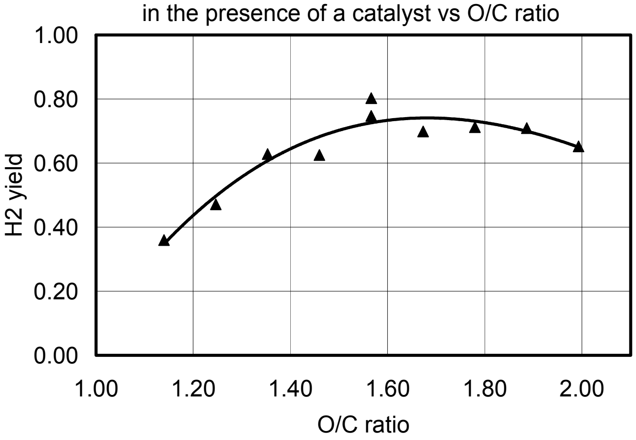
It should be stressed that the performance of the system was not optimized, and higher hydrogen yields could be possible by converting the substantial amounts of C2's present in the gas downstream from the catalyst.

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.

B) ETHANOL

The same experiments as for the veggie oils have been carried out for ethanol, but at lower power levels. Figure 5 gives the hydrogen yield for catalytic reformation of neat 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 5. Hydrogen yield for the reformation of ethanol in the presence of a catalyst vs O/C ratio



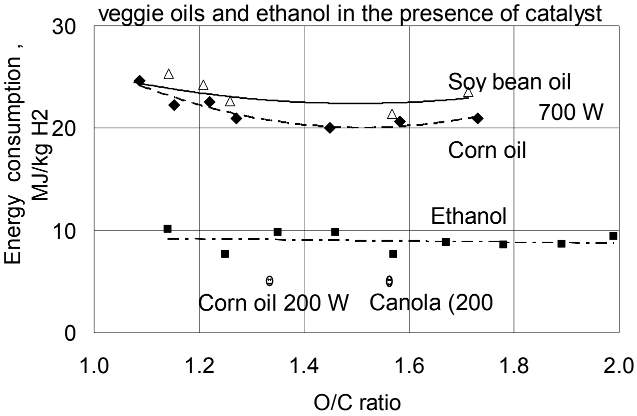
The hydrogen yield peaks at around O/C ~ 1.5 – 1.7, slightly higher than that for the bio oils. As mentioned previously, the O/C ratio includes the oxygen that is carried out by the fuel, which in the case of ethanol is very substantial.

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 as minimal as possible. Figure 6 gives the electrical energy consumption for corn, soybean oils, and ethanol versus O/C ratio at a power level of 700 W. For a maximum hydrogen yield at an O/C of 1.5, the electric energy consumption is 10 MJ per kg of hydrogen produced for corn and soybean oils. This is approximately 8 % of the energy in the hydrogen. The flow rate of fuel was limited by the size of the exhaust system being used, and it has not been established that the fuel flow rates at the 700 W level has been maximized. Instead of increasing the flow rate, a few experiments at lower power levels have been performed. As shown on Figure 6, the power consumption for canola and corn oils at respectively an O/C 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 6. Energy consumption for reformation of veggie oils and ethanol in the presence of catalyst



Energy consumption for the reformation of ethanol appears to be comparable to the energy consumption with veggie oils.

V. CONCLUSIONS

Low-current plasmatron fuel reformer technology has been used to convert both bio-oils and ethanol into a hydrogen-rich gas with high hydrogen yields (70 to 80%) where a catalyst is positioned after the homogeneous reforming zone. For homogeneous reforming alone hydrogen yields are typically about half those obtained with catalytic reforming. However, the conversion rate into H_2, CO and light hydrocarbons is still relatively high (close to 70%) for homogeneous reforming. More work is needed to further lower the energy consumption and increase the hydrogen yield by operating the plasmatron fuel reformer closer to an O/C ratio of 1.

References

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