



A NON-THERMAL GLIDING ARC PLASMA REFORMER FOR SYNGAS PRODUCTION

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ABSTRACT

The use of a non-thermal (gliding arc) plasma fuel reformer for producing syngas by partial oxidation of methane is addressed. Experimental results from laboratory experiments are reported with attention to the hydrogen and carbon monoxide yields and their selectivities as a function of the inlet reactant composition, the flowrate, and the applied electrical power used to generate the electrical discharge. The specific energy density (defined as the ratio of the electrical energy applied per unit mass of hydrogen or syngas produced) is also reported along with the efficiency of the plasma fuel reformer. Baseline results with and without reactant preheating are reported.

KEY WORDS: Non-equilibrium plasma, ‘Warm’ plasma, Gliding arc, Partial oxidation of methane, Syngas

1. INTRODUCTION

Markets exist for low volume, distributed production of hydrogen-rich syngas from natural gas and other hydrocarbon feedstocks, yet higher costs associated with scaled-down variants of conventional technologies (electrolysis, steam methane reforming) limit broader implementation. With that said, costs are clearly dependent on production volume noting that most of the distributed hydrogen prototype units developed to date (by companies that include Air Products, Chevron Technology Ventures, Praxair, GE Global Research, and others) have been on the scale of 100 kg/H₂ per day or smaller with a higher volume DOE target for distributed hydrogen production (defined even 10 years ago) of 1,500 kg/H₂ per day [1]. By comparison, centralized hydrogen production facilities are much larger and can produce > 50,000 kg H₂/day. As such, it is understandable that small-scale versus centralized production costs are a factor of three times higher [2].

In this study, we consider the use a non-traditional, laboratory-scale plasma system to produce hydrogen-rich syngas. Specifically, our focus is on a gliding arc plasma system, which has received notable interest from the research community in the past 10-15 years [3,4]. These non-thermal plasmas have high electron temperatures (~1-3 eV) with modest gas temperatures ~1,000K. More to the point, these plasmas have characteristics that are intermediate between cold plasmas and high temperature thermal plasmas that accelerate kinetics of reforming reactions by achieving temperatures ~3,000-10,000°C. Having intermediate properties, gliding arc plasmas are considered “warm” plasmas and offer an attractive, non-catalytic, fuel flexible approach for on-site hydrogen-rich syngas production. For the technology to be commercialized, however, the specific energy density (SED) - defined as the electrical energy needed to sustain the discharge per kilogram of hydrogen or syngas produced – must be sufficiently low and competitive with alternative methods (e.g., steam reforming).

In terms of the operation of our gliding arc plasma reformer, an arc discharge is generated between two cylindrical electrodes as the reactants are introduced with tangential swirl, interact and cause the discharge

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to translate in a circular path in the gap between the opposed electrodes. This discharge is akin to a “Jacob’s ladder” or high voltage traveling arc albeit in three-dimensions. Moreover, the internal geometry and gas entry is such that a reverse vortex flow is generated internal to the reformer. Specifically, the reacting gases enter with a tangential swirl, flow helically upwards into a hollowed out core in the high voltage electrode and the flow then reverses direction and flows back through the core of the helically rotating outer flow. The plasma then exits into a thermally-insulated cylindrical “adiabatic section” where the reformat is sampled and then analyzed.

In the present study, our focus is solely experimental with the intent is to characterize the performance of a gliding arc plasma reformer as a function of the bulk reactor parameters. These parameters include: the plasma power, the fuel-air composition, and the gas flowrate. Efforts to understand parametric dependencies are made with the end-goal to identify and demonstrate effective approaches that enable the specific energy density to be reduced such that this non-thermal plasma technologies can be cost competitive. With that said, however, it is noted that the plasma chemistry is undoubtedly complex as interactions between electrons, excited atoms and molecules, ions, and radicals are involved. The rates of these reactions clearly depend on parameters that include: the electron energy, the electron density, the gas temperature, the gas pressure, and other gas properties.

2. EFFECT OF INLET REACTANT TEMPERATURE ON NON-THERMAL PLASMA REFORMER FUEL CONVERSION

One approach to lower the specific energy density is to preheat the inlet reactants, which can be achieved through efficient heat recuperation from the hot reformat [4,5,6]. Two studies in the literature have addressed the effect of inlet reactant temperature on non-thermal plasma-assisted partial oxidation of methane for syngas production. The first study by Kalra et al. in 2005 [5,6] developed a “gliding arc plasma tornado (GAT)” and coupled it to an external, albeit large, commercial flat plate heat exchanger to evaluate the effect of heat recovery on reformer performance. Their experiments showed percent methane conversion and syngas yield (both hydrogen and carbon monoxide) increase with an increase in reactant inlet temperature for inlet temperatures between 600K to 700K for premixtures having an [O]/[C] ratio = 1.08 (equivalent to mixture having a fuel-air equivalence ratio of 3.7). Moreover, they were able to achieve high syngas yields and a specific energy density for the syngas produced of 0.1 kW-h/m³ syngas, defined here as the electrical power applied to sustain the plasma relative to the volumetric flowrate of syngas produced. This specific energy density is low compared to values from other studies which report values roughly 10 times higher [4,7,8]. The difference is arguably due to the high temperatures generated primarily by the exothermicity of the partial oxidation reforming reactions made possible in Kalra’s work by preheating the reactants.

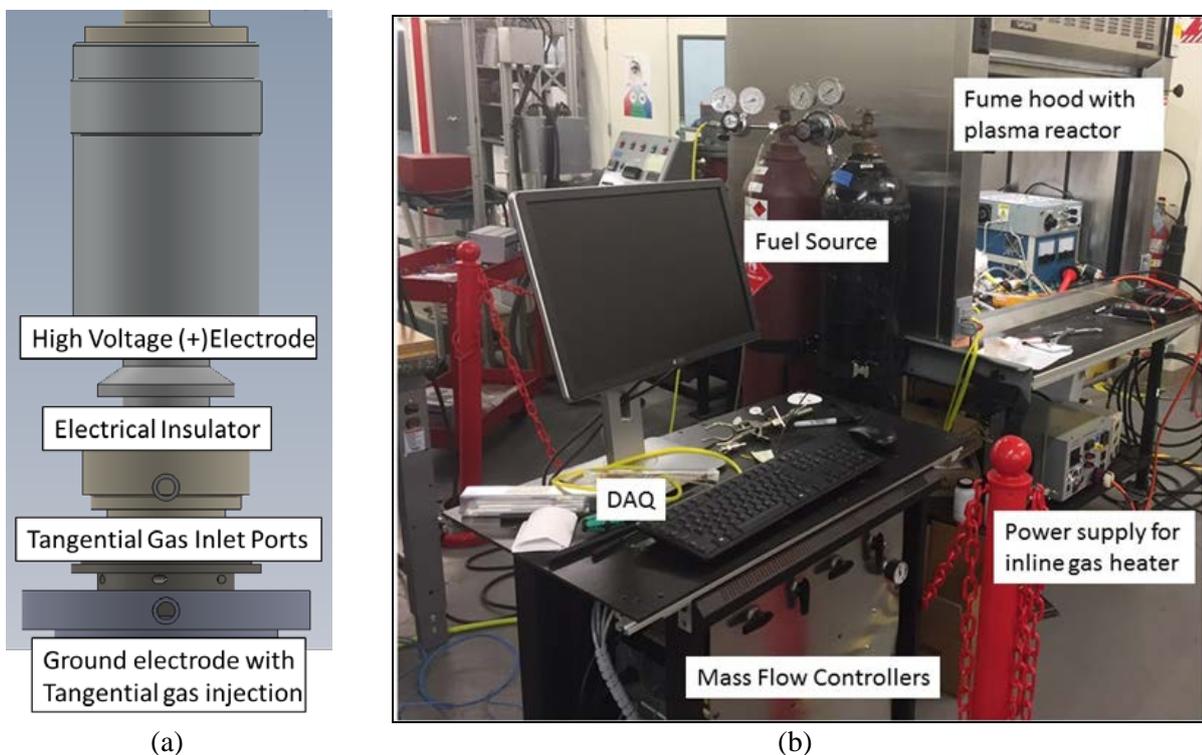
In a separate study, Jo et al. [9] also evaluated the effect of reactant temperature on methane partial oxidation albeit in a rotating arc plasma reformer with lower preheat temperatures. In their reactor, one electrode (high voltage) was conical in shape and the ground electrode was a cylindrical element that jacketed the high voltage electrode. In their work, the methane conversion rate is reported to increase with an increase in reactant temperature for temperatures as low as 300-400K, contingent however that the ratio of the electrical energy applied divided by the volumetric flowrate of the reactants was greater than a certain value (0.9 kJ/liter). For ratios less than 0.9 kJ/liter, the methane conversion rate was found to be insensitive to the inlet temperature (for the low inlet temperatures considered in this work). Based on their results, it was argued that the plasma chemistry controls the reaction kinetics at low gas temperatures and thermal effects play an increasingly important role as the applied electrical power increases. At high ratios of applied power to inlet flowrate, the authors further suggest that the arc properties, i.e., length of the arc discharge and associated plasma volume also increase which in turn improves performance. Also, for cases having higher gas inlet temperatures (with preheating), the heat loss in the vicinity of the arc arguably decreases and thus the available plasma energy needed for reforming can be reduced. This is possible because a large portion of the energy of the discharge may otherwise be needed to compensate for heat

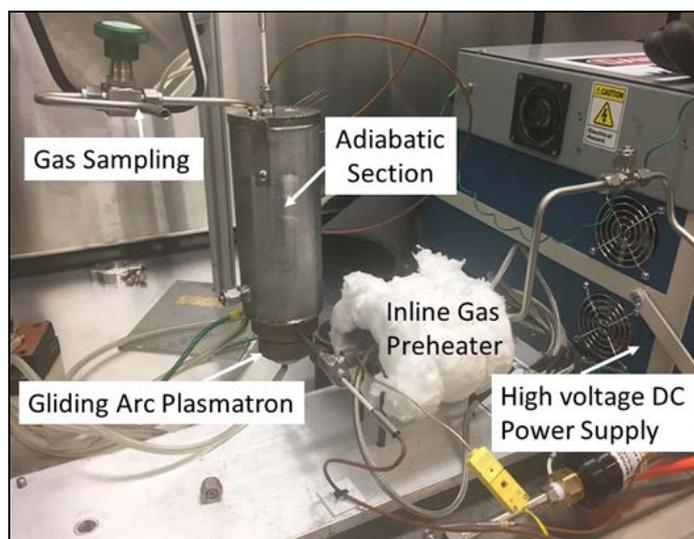
losses from the arc to the surroundings. Also, in this work, the authors suggested that a decrease in the gas density associated with an increase in the reactant gas temperature together with the local production of hydrogen produced by the plasma discharge (change in local gas composition) can also affect performance that may even help sustain the arc discharge.

3. EXPERIMENTS USING A GLIDING ARC PLASMA REACTOR

3.1 Apparatus

A gliding plasma reactor that accepts an ambient temperature or preheated reactant flow was designed, fabricated and tested (Fig.1a). The reactor was outfitted with multiple tangential injection ports such that an internal reverse vortex flow was generated within the reactor. Regarding the electrode design, the housing itself served as the ground electrode and an opposed cylindrical high voltage electrode with internal cylindrical cavity (in which the reverse vortex was generated) was used. The discharge was initiated at high voltage between the electrodes using a high voltage DC power supply. Once ignited, the arc discharge was sustained at lower voltage (fixed power) and continuously rotated in the gap between the electrodes (fixed at 1-3mm). The voltage applied to sustain the discharge was typically 1-2kV and the current ranged from 200-500 mA such that the average output power was controlled between 100-800W. Support hardware for gas control/ metering, mixing, preheating, sampling and temperature measurements is shown in Figs.1b and 1c. An SRI gas chromatograph was also used to sample the inlet reactants and reformat exiting the plasma fuel reformer. Particular attention was given to quantify the hydrogen, carbon monoxide, methane, oxygen, nitrogen, and carbon dioxide species concentrations as a function of equivalence ratio, flowrate, and applied plasma power. Experiments are also now being performed with steam addition.





(c)

Fig. 1 (a) Gliding arc plasma reactor, (b) Test apparatus showing mass flow control system and data acquisition system, (c) Reactor assembly outfitted with post adiabatic section.

3.2 Representative Experimental Results

No Preheating of Reactants (Baseline Case). Initial experiments were performed for flowrates (15-50 SLPM), equivalence ratios ($\Phi=2-4$ corresponding to O/C ratios from 2 to 1), at different electrical discharge power levels and preheats up to 400°C. Figure 2 shows results without reactant preheating at two relatively low power levels (142W and 235W) for a fixed flowrate (15 SLPM). The measured hydrogen concentration (Fig.2a) and the carbon monoxide concentration (Fig.2b) are plotted where red and blue lines correspond to the 142W and 235W cases, respectively, and the green line corresponds to the thermodynamic equilibrium concentrations computed using GASEQ [10]. As shown, the measured hydrogen and carbon monoxide concentrations are roughly 50% and upwards of 70-80%, respectively, of the thermodynamic equilibrium values. Higher conversion percentages have also been achieved with near-equilibrium hydrogen and carbon monoxide concentrations, albeit at substantially higher power (i.e., 820W for a methane-air premixture having $\Phi=4$ at 35 SLPM total flowrate yielded 28.6% hydrogen and 14.5% carbon monoxide). These high power results will be presented at the conference.

Based on the measured values reported in Figure 2 (for these low power cases), the H_2/CO ratio was also computed (Fig.2c). This ratio is important depending on the end-application, e.g., for Fischer-Tropsch synthesis, the desired H_2/CO ratio is 2. Based on the measured methane concentration into the plasma reactor and that remaining unreacted in the reformat, the percent methane conversion was also computed (Fig.2d) in addition to the hydrogen selectivity and carbon monoxide selectivity (Fig. 2e and Fig.2f). Interestingly, the methane conversion percent was 100% at $\Phi=2$ although only a fraction of that converted was hydrogen and carbon monoxide while the balance was water and carbon dioxide (combustion products at this lower equivalence ratio). As the equivalence ratio increased, the percent methane converted decreased (likely because of the lower temperatures at higher equivalence ratios) while selectivity for hydrogen and carbon monoxide increased. At the highest equivalence ratio considered ($\Phi=4$), the methane conversion percent was ~20% and the hydrogen and carbon monoxide mole fractions also decreased. Perhaps this decrease is due to decreasing reaction temperature with increase in equivalence ratio. Further attention to the reaction temperature as a function of flowrate, equivalence ratio and applied plasma power is needed.

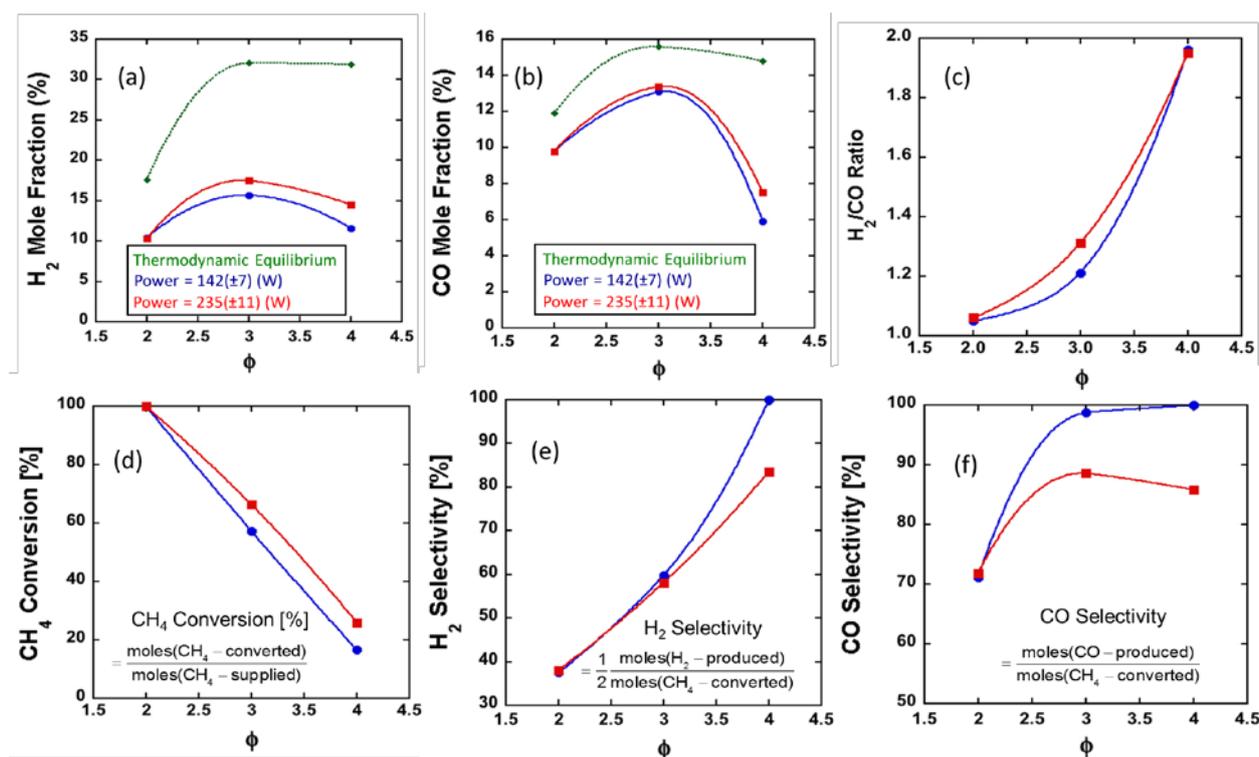


Fig. 2 (a) Hydrogen Concentration (based on GC measurement), (b) Carbon Monoxide Concentration (based on GC measurement), (c) Hydrogen to Carbon Monoxide Ratio, (d) Methane Percent Conversion (based on GC measurements of the reactor inlet/exit compositions), (e) H_2 Selectivity and (f) Carbon Monoxide Selectivity: (blue line) 142W, (red line) 235W, Total flowrate in all cases is 15 SLPM.

Effect of Preheating the Inlet Reactants. To further demonstrate and quantify the benefit of heat recuperation on the hydrogen and carbon monoxide concentrations, bench-scale experiments were also performed by preheating the inlet reactant gases (CH_4 -air) to temperatures up to $400^\circ C$ in roughly $100^\circ C$ increments. In these experiments, a resistively heated metal block was machined and placed around the inlet reactant gas line (directly upstream of the plasma reactor inlet) and all transfer lines (and the plasma reactor itself) were thermally insulated to minimize heat loss from the preheated stream to the ambient. Each test performed was also performed over the course of 1.5-2 hours to ensure the reactor was being operated at steady-state.

For fixed flowrate (30 SLPM), equivalence ratio (2.0), and applied electrical power (60-66W), results from GC measurements on the hydrogen and carbon monoxide concentrations as a function of inlet reactant temperature are plotted in Fig.3a. For these conditions, increasing inlet reactant temperature increased hydrogen and carbon monoxide concentrations more so than can arguably be attributed to an increase in the gas temperature owed simply to sensible heating of the gas. For example, if all of the electrical power was used to sensibly heat the reactant stream (having a mixture density = 1.08 kg/m^3 , specific heat = 1.13 J/g-K , and average molecular weight = 26.63 g/mol , computed using GASEQ), the temperature rise of the reactant stream would be a modest 108K. In this case, it is also worth noting that the applied electrical power is quite low. Higher electrical powers would result in higher gas temperatures and thermal effects are expected to become increasingly important (consisted with discussions of Jo et al. [9]).

In Fig.3b, the hydrogen and carbon monoxide selectivities and CH_4 percent conversion are also plotted. As shown, the CH_4 percent conversion remained at 90-100% (decreased slightly with increasing inlet temperature) while the hydrogen and carbon monoxide selectivities increase with increasing inlet reactant temperature. In Fig.3b, the specific energy density (SED) is also computed, defined again as the ratio of the electrical energy

input to the reactor divided by the mass flowrate of hydrogen produced ($SED(H_2)$) and mass flowrate of syngas produced ($SED(H_2+CO)$). The units are kW-h of electricity per kg of hydrogen or kg of syngas produced. Note that 0.5 kW-h/kg syngas corresponds to ~ 0.3 kW-h/m³ syngas on a volumetric basis (taking the syngas molecular weight=10.5 g/mol, which is that for a syngas composition with H₂/CO ratio of 2); this is a higher value than the 0.1 kW-h/m³ syngas value reported by Kalra et al. [5,6] but less than values ~ 1 kW-h/m³ syngas reported by others.

With that said, the hydrogen and carbon dioxide selectivities for these tests are lower than desired and efforts are being made to achieve a low specific energy density, while maximizing the percent methane converted and hydrogen and carbon monoxide selectivities.

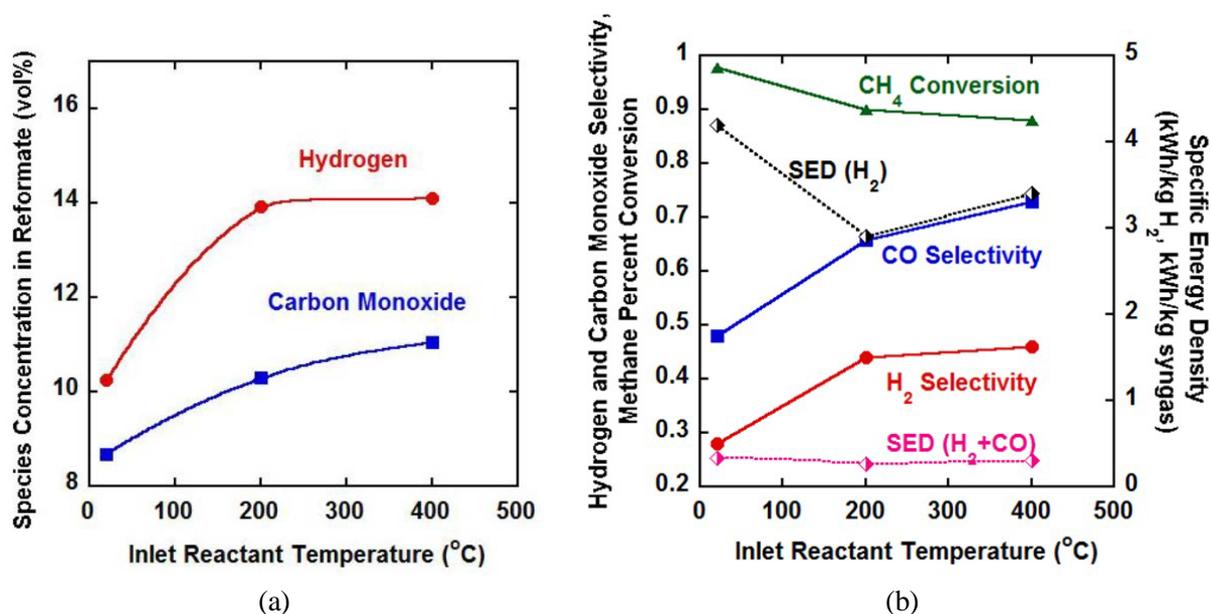


Fig.3 Increasing reactant inlet temperature (a) increases hydrogen and carbon monoxide concentrations in the reformat and (b) increases hydrogen and carbon monoxide selectivities. Experimental parameters: electrical power applied = 60-66W, 30 SLPM total flowrate, $\Phi = 2$, CH₄-air, Measurements taken midway in adiabatic section (insulated section appended to the plasma reformer exit).

Lastly, in Fig.4, the overall efficiency of the plasma fuel conversion process corresponding to the same case as in Fig.3 is plotted as a function of the inlet reactant gas temperature. The efficiency is defined as the total chemical enthalpy associated with the hydrogen, carbon monoxide, and unreacted methane in the reformat, divided by the chemical enthalpy of the parent fuel (methane) input to the reformer. As shown, preheating the inlet stream increases the efficiency of the process and efficiencies upwards of 60% are achieved for the test parameters considered here. Further note that higher efficiencies have also been obtained at higher electrical discharge powers.

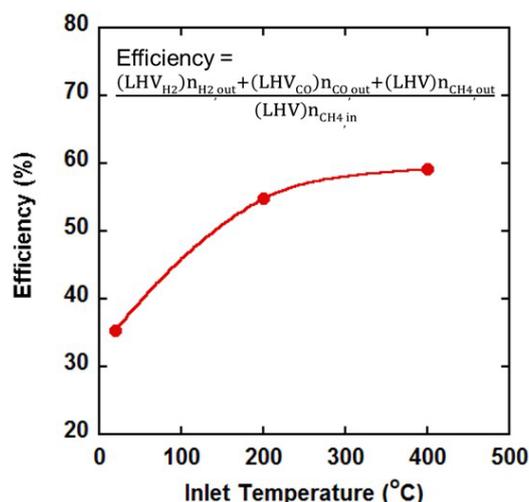


Fig.4 Increasing reactant inlet temperature increases the reformer efficiency. Same experimental parameters as in Fig.3: Electrical power applied = 60-66W, 30 SLPM total flowrate, $\Phi = 2$, CH₄-air, measurements taken midway in adiabatic section.

4. CONCLUSIONS

A non-thermal gliding arc plasma reformer for methane partial oxidation was tested with and without reactant gas preheating. The hydrogen concentration in the reformat was roughly 50% of the thermodynamic equilibrium concentration and the carbon monoxide concentration was 70-80% of the thermodynamic equilibrium value. Additional tests with reactant preheating were performed showing hydrogen and carbon monoxide concentrations increase with reactant preheating while the methane conversion percent remained high. These tests were however done for cases have low electrical powers and additional work is needed to screen a broader range of parameters (flowrates, fuel-air ratios, plasma powers) and quantify their effect on the syngas composition. Here it is noted that higher near-equilibrium concentrations of hydrogen and carbon monoxide with an associated efficiency in excess of 90% have also been obtained in laboratory studies albeit with notably higher electrical power.

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