

# Miniaturized GlidArc® reformer for conversion of methane and propane to synthesis gas

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**Abstract:** The current paper focuses on the utilization and miniaturization of the GlidArc® principle for the reforming of fuel gases (such as methane and propane) to synthesis gas (H<sub>2</sub>+CO). The reforming characteristics and optimal operating conditions to achieve maximum synthesis gas yield were determined. Parametric screening studies were performed with different (i) atomic ratios of oxygen to carbon (*O/C*) in the range from 1 to 2, (ii) and feed flow rates from 2 to 10 L/min using alternating current voltage to produce the plasma in the reactor, which was varied from 2.8 to 4.6 kV. Higher synthesis gas H<sub>2</sub>/CO  $\approx$  2.35 ratio was achieved when methane was processed at *O/C* = 1 in comparison with propane (H<sub>2</sub>/CO  $\approx$  1.52) and similar thermal efficiency was achieved for both gases, namely  $\eta$ (CH<sub>4-vaveraged</sub>) = 38.86% for methane and  $\eta$ (C<sub>3</sub>H<sub>8-vaveraged</sub>) = 38.35% for propane respectively.

Keywords: Miniaturization, gliding arc discharge, GlidArc® reformer, synthesis gas.

### 1. Introduction

The increasing concern in environmental control, pollution problems as well as cost competitiveness have resulted in a large efforts to develop alternative and efficient technologies for energy and electricity production. Plasma technology appears to be very promising in this respect, especially in the diverse fields of chemistry, and environmental protection A new way of plasma generation, called GlidArc® has been developed to generate high energy efficiency and selectivity for chemical applications [1, 2, 3].

The current research work focuses on the utilization and miniaturization of the GlidArc® (gliding arc discharge) functional principle for the reforming of fuel gases to synthesis gas (H<sub>2</sub>+CO) and the development of a new system applying combined plasma and micro-reactor technology along with perovskite catalysts for conversion of fuel gases (such as methane, propane and higher hydrocarbons. The initial plasma reaction is to break the molecules and after that has to be supported by subsequent catalytic processing with perovskite catalysts to maximize the hydrogen yield (see **Fig.1**).



Fig.1 Plasma reforming with coupled catalytic reforming.

### 2. Experimental procedure

The reforming characteristics and optimal operating conditions were determined for the miniaturized gliding arc reactor applying methane and propane as fuel gases under conditions of partial oxidation.

**Fig. 2** shows a schematic of the experimental setup, used in this research work, which consists of the miniaturized plasma reformer, input power supply, gas feeding lines, product gas analysis (*FT-IR* and Micro-*GC*).



Fig.2 Schematic representation of the experimental setup.

The gases were dosed by thermal mass flow controllers into the reactor. The body of the plasma reformer was made of Macor® with a glass cover on the top, which allowed the observation of plasma behavior during operation. The plasma reformer mainly consists of two Wolfram electrodes (8 cm long and 2.5 mm thick) which were



knife-shaped and had a short distance of 1 mm between the electrodes.

The miniaturized plasma reformer was supplied with a 50 Hz high voltage transformator with lower current (max. 5 kV, 80/124 mA) and leakage fluxes. The effect of leakage fluxes is to produces a constant root mean square (RMS) value of current in the secondary coil of the transformator. The alternating current voltage was applied to produce a stable gliding arc plasma discharge in the reformer, which was varied by the screening tests from 2.8 to 4.6 kV as power supply.

The power input applied was measured as function of the arc current and the applied voltage between the electrodes, the values were acquired by a special Labview software.

The gas mixture (fuel gases and air) was preheated in the gasheater to 195 °C before the gas was fed into the plasma reactor. The reactor itself was not heated and experiments were realized at room temperature. The feed gases (methane, propane and air) were dosed by thermal mass flow controllers (*MFC* from Bronkhorst).

The product mixture was analyzed by a *FT-IR* spectrometer (Multi Gas 2030 on-line gas analyzer from MKS-technology), which was equipped with a LN<sub>2</sub>-cooled MCT detector and CaF<sub>2</sub> windows. Based on the device specification the spectral resolution is in the range from 0.5 to 128 cm<sup>-1</sup>, which was used to quantify the product gases in the current case C<sub>2</sub>H<sub>2</sub>, CH<sub>2</sub>O, NO<sub>x</sub> (NO, N<sub>2</sub>O, NO<sub>2</sub>), and HNCO. For the determination of the main product gas components (H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and higher hydrocarbons such as C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>) an micro gas chromatograph (µ-GC) was applied.

The performance tests for methane and propane were carried out with different (i) atomic ratios of oxygen to carbon (O/C-ratio) in the range from 1 to 2, (ii) at different total feed flow rates from 2 to 10 L/min, (iii) the alternating current voltage was varied from 2.8 to 4.6 kV.

# 3. Results and discussion

### Effect of the applied voltage

**Fig. 3** shows the experimental result for methane, when the applied voltage is changed from 2.8 to 4.6 kV in the case of O/C = 2 at a flow rate of 2 L/min. When the input electric supplied power increases, the methane conversion  $X(CH_4)$  increases and the methane is converted into synthesis gas. The main products of the reaction were H<sub>2</sub> and CO, but hydrocarbons such as C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> were also formed. The products were determined at the max. supply power  $U_g = 4.6$  kV: H<sub>2</sub> = 0.79 Vol.%, CO = 0.61 Vol.%, CO<sub>2</sub> = 0.14 Vol.%, C<sub>2</sub>H<sub>2</sub> = 0.03 Vol.%, C<sub>2</sub>H<sub>4</sub> = 0.02 Vol.%, C<sub>2</sub>H<sub>6</sub> = 0.02 Vol.% and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> = 0.01 Vol.%, CH<sub>2</sub>O = 0.01 Vol.% and



Fig.3 Effect of the applied voltage on the methane conversion.

**Fig.4** shows the product selectivity *S* [%] for methane at different electrical power input. H<sub>2</sub>, H<sub>2</sub>O and CO were the predominant compounds at O/C = 2 and flow rate = 2 L/min. Radicals or ions are generated from O<sub>2</sub>, which oxidize the CH<sub>4</sub> molecule followed by the formation of C<sub>2</sub>-compounds. For example the work of Tsai et al. [4] shows that a large number of free radicals are produced via electron impact through the dissociation of CH<sub>4</sub> [5, 6], according to the reaction:

$$CH_4 \rightarrow CH_3 + H \text{ or } CH_2 + H_2 \text{ or } CH \text{ and } H_2 + H$$
 (1)



Fig.4 Product selectivity as determined for methane at different input electrical power.

Under any of the conditions studied, the main products of the plasma treatment for methane and propane were hydrogen and CO (see **Table 1**). The conversion of propane is higher as for methane, because in order to produce hydrogen, hydrocarbon molecules have to be "cracked", to break the *C*-*C* and *C*-*H* links [7]. The common bond energies D (kJ/mol) are 348 and 413 respectively [8], according to this the power input for propane is approx. 44 W and for methane approx. 126 W.

Table 1. Plasma reforming results for methane and propane (O/C = 2 and Flow rate = 2 L/min)

Methan			Propan		
Conversion of CH₄	Selectivity of H <sub>2</sub>	Selectivity of CO	Conversion of C <sub>3</sub> H <sub>6</sub>	Selectivity of H <sub>2</sub>	Selectivity of CO
6	42	68	14	44	67



**Fig.5** shows the effect of the total flow rates on methane conversion when changed from 2 to 10 L/min (O/C = 1.6). The methane conversion decreases, when the feed flow rate increases, which is in a good agreement with the work of Pietruszka et al. [9]. In this case the residence time in the reactor is not sufficient.



Fig.5 Methane conversion at different total feed flow rates (2-10 L/min)

The product selectivities of methane in the case by the change of the total flow rates from 2 to 10 L/min (O/C = 1.6) are show in **Fig. 6** as influence of feed flow rate. In this case the CO selectivity decreases with the flow rate and CH<sub>2</sub>O increases with increasing the flow rate.



Fig.6 Product selectivity of methane at different total feed flow rates (2-10 L/min)

The product selectivities for propane are show in **Fig. 7**. In comparison with methane, propane is more selective towards  $C_2H_4$ ,  $C_2H_2$  but also formation of  $CH_4$  was observed, according to the reaction route from Barsan and Thyrion [10].

$$C_3H_8 \rightarrow CH_4 + C_2H_2 + H_2 \tag{2}$$



Fig.7 Product selectivity of propane at different total feed flow rates (2-10 L/min)

## Effect by the variation of the oxygen to carbon ratio

The O/C = ratio has a more strong effect on conversions and products distribution. A higher synthesis gas H<sub>2</sub>/CO  $\approx 2.35$  ratio was achieved from methane at O/C = 1 in comparison with propane (H<sub>2</sub>/CO  $\approx 1.52$ ) (see **Fig. 8**).



Fig.8 Effect of the oxygen to carbon ratio for methane

#### Thermal efficiency

The thermal efficiency for the fuel processor is calculated as follows with lower heating value (*LHV*) of hydrogen and carbon monoxide produced divided by the LHV/(kJ/mol) of the fuel injected:

$$\eta = \frac{n(H_2, out) \cdot LHV(H_2) + (n(CO, out) \cdot LHV(CO))}{LHV(fuel) \cdot fuel(injected)} 100$$

The fuel reacts with oxygen at different (O/C = ratio) to produce synthesis gas (H<sub>2</sub>+CO)/(mol/min). Similar thermal efficiency was achieved for both gases, namely  $\eta(CH_{4,averaged}) = 38.86\%$  for methane and  $\eta(C_3H_{8,averaged})$ = 38.35% for propane respectively (see **Fig. 9**).



Fig.9 Conversion and thermal efficiency  $\eta[\%]$  for methane and propane at a flow rate of 10 L/min.

#### 4. Conclusion

This study was successfully conducted to production synthesis gas from non-catalytic direct conversion of methane and propane using a miniaturized gliding arc reactor.

The major results obtained in this work by the parametric screening tests so far are as follows:

> Methane conversion increases with the applied voltage from 2.8 to 4.6 kV, the methane is converted into synthesis gas with high selectivity.



- The products from the partial oxidation of methane were synthesis gas and hydrocarbons such as C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>. Other gases such as CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>2</sub>O, HNCO and NO<sub>x</sub> (NO, N<sub>2</sub>O, and NO<sub>2</sub>) were also observed mostly in trace amounts
- A higher H<sub>2</sub>/CO ≈ 2.35 ratio was achieved from methane at O/C = 1 in comparison with propane (H<sub>2</sub>/CO ≈ 1.52).
- For both methane and propane the selectivities towards H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O were higher at O/C = 2 at all residence times under investigation compared to a lower O/C ratio of 1, which revealed an increasing selectivity towards acetylene. Similar thermal efficiency was achieved for both gases, namely  $\eta(CH_{4,averaged}) = 38.86\%$  for methane and  $\eta(C_3H_{8,averaged}) = 38.35\%$  for propane respectively (see Fig. 9).
- As the feed flow rate increases, the methane conversion decreases, due to short residence time in the reactor.

## 5. Acknowledgment

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## 6. References

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