

POX REFORMING OF BIO-METHANE INTO SYNTHESIS GAS

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Introduction

Methane from anaerobic fermentation of almost any biomass or organic waste starts to be available at relatively small scale but in numerous local sources. Its full combustion to generate heat has been successfully applied since ancient China. Its recent use as fuel for gas engines is controversial because of relatively high residual content of CH_4 in the exhaust contributing to greenhouse effect. So what about such bio-methane conversion into clean paraffin fuel for classical engines? And what about of a distributed small Biogas-to-Liquid (BTL) plants providing such fuel for local drivers?

Such BTL process asks however for an intermediate step of bio-methane reforming into so-called "synthesis gas" (SynGas, a mixture of CO and H_2) being an elementary brick for well-known Fischer-Tropsch (FT) synthesis of liquid fuels. There are two challenges to achieve such goal:

- small or medium scale methane reforming
- and small or medium scale FT plant

as the existing technologies are rather devoted to process huge flows of the natural gas. In two successive contributions we propose to solve these two problems (see our FT paper [1] describing the tests of our proprietary multiple-plate reactor and our Iron-based catalyst).

While a synthetic SynGas can be prepared by mixing pure CO with H_2 and ballasting N_2 from gas cylinders it would not reflect a real industrial-grade feed for testing and developing our FT technology. We generate therefore our real SynGas by Partial Oxidation (POX) of methane. The POX takes place in our proprietary "Gliding Arc" (GlidArc) reformers at up to 6 bar and can use an O_2 -enriched air so that the SynGas compression to higher pressure FT synthesis asks for only one-step operation. We describe the GlidArc reactor that electrically assists the reforming process, the Syngas quality, and its output flow rate as a function of various input parameters: flow rates of methane, enriched air and steam as well as the O_2 concentration in oxidant and the process pressure.

Principle of the Glidarc reactors as well as their use for the methane reforming were first described in papers [2] and [3]. The GlidArc plasma assists the POX at very low electric power (less than 1% of the output H_2 +CO power flow). Recycling such small portion of energy is therefore an acceptable compromise as our very active (and also very simple) GlidArc discharge plays a role of an igniter and homogeneous phase catalyst; it also activates and stabilizes a post-plasma zone of our reformer.

Experimental

Reformer and test procedure. Here-presented tests are performed in a small two-zone reformer presented on Fig. 1. The plasma zone (0.18 L) contains two flat electrodes that delimit a space filled with the gliding discharges. We mix separate flows of oxidant (air or O_2 -enriched air) and methane in a dual-flow injector. Steam can be added to one of the flows preheated in a double-wall. The reactants flow along the diverging electrodes where the discharges ionize them. Given the moderate temperature of the electrodes (not cooled) and a very short contact time of the discharge roots with the electrodes, we do not observe any deterioration that may prevent gliding of these current-limited discharges (50 mA). The plasma zone (0.57 L) communicates with

a post-plasma zone filled with small refractory granules. The flow of partially converted reactants containing long-living active radicals enters this second zone where the conversion is completed by deactivation of all excited species. The reformer is thermally insulated from outside to keep two zones hot.

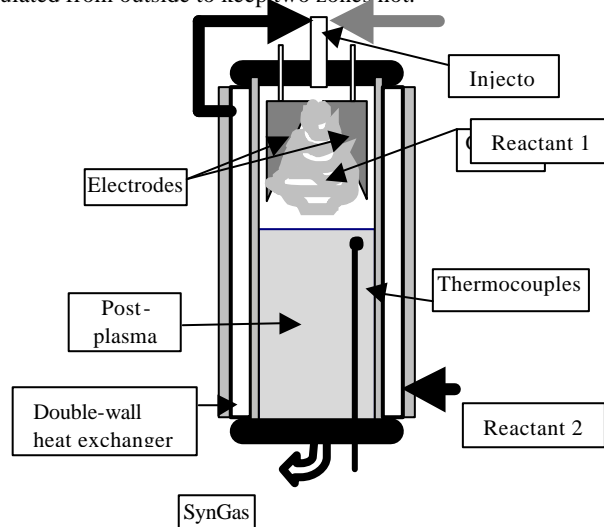


Figure 1. Principle of the double-zone GlidArc reactor.

Natural gas (NG) from the town pipe (instead of pure methane) is used as feed. Its composition is analyzed for each series of runs using 2channel μ -GC (Varian CP-2003). The gas contains typically >93 vol.% of CH_4 , 5% C_2H_6 , 0.5% C_3H_8 , 0.7% N_2 , and 0.5% CO_2 . No care is applied as concerns the Sulfur pollutants as the GlidArc-assisted reforming can accept even concentrated H_2S [4]. The NG, compressed air, and Oxygen flow rates are controlled by precise mass flow meters. During the tests we register the reformer's temperatures at several points.

When starting with a cold reactor it takes us less than 10 minutes to preheat it (*via* full combustion at a low NG flow) and then to collect a SynGas at a stronger NG flow. A fine regulation of oxidant/NG ratio is then applied during next few minutes after what the reforming reaches the suitable operating conditions. Any regulation can be then made anytime in order to obtain (at a quite short time) the required outflow and quality of the SynGas. To finish the run we simply cut the electric, air and NG supplies letting the reformer cool down in a natural manner. Such a hot reformer could be started again at a much shorter time.

The SynGas sample is analyzed for each run using the same μ -GC dedicated to H_2 , N_2 , O_2 , CH_4 , CO, CO_2 , C_2H_4 , C_2H_6 , C_2H_2 , and C_3H_8 + C_3H_6 . We also direct a small part of the SynGas into a burner indicating us the output gas quality. Almost invisible (blue) and stable flame indicates the best SynGas quality: no soot and a very low presence of C_2 and C_3 hydrocarbons. Otherwise, the flame presents a yellow top. Generated SynGas is flared or compressed to feed our FT process.

Some 130 runs at various operating conditions were performed in early 2006. At long accumulated runtimes we never changed any part of the reformer including the high-voltage electrodes and the post-plasma granules. The process is always very stable. When soot started to appear at an insufficient O_2 /NG ratio we just added more oxidant or reduced NG flow to reestablish totally non-sooting reforming conditions.

Results and Discussion

Three series of tests were performed: at atmospheric pressure with air as oxidant, at higher pressure using air, and at atmospheric or higher pressure using up to 44% O_2 -enriched air. The data (time,

temperatures, flow-rates, electric power, and other information) are used for further processing. The following ranges of parameters and conditions are explored (all data):

Air input flow-rate	4.4 - 116	L(n)/min
Oxygen input flow-rate	1.7 - 10.5	L(n)/min
O ₂ content in oxidant	21 - 44	vol.%
Steam flow rate	0 - 9.8	g/min
NG input flow-rate	2.7 - 28	L(n)/min
NG input power	1.5 - 21	kW

LHV

O ₂ /CH ₄ molar ratio	0.49 - 1.04	
Pressure	1.1 - 6.1	bar abs

As result we are generating the SynGas containing the following species (dry, in vol.%):

H ₂	17 - 49	C ₂ H ₄	0 - 0.02
CO	6.7 - 23	C ₂ H ₆	0 - 0.4
N ₂	21 - 65	C ₃	0 - 0.005
CO ₂	2.5 - 14	O ₂ , C ₂ H ₂	absent
CH ₄	0.2 - 7.3		

From the Input/Output data we obtain the mass balance based on the following assumptions:

- Conservation of N₂ as the non-reactive component,
- Total conversion of Oxygen from air into CO, CO₂ and H₂O,
- Total conversion of Carbon (no soot!) from initial NG into CO, CO₂, CH₄, C₂H₄, C₂H₆, C₂H₂, and C₃.

Such mass balance gives us an access to other output data, namely the following ones (all data):

Output SynGas (accounted as H ₂ + CO)	4 - 89
L(n)/min	
Output Syngas Power (LHV)	1 - 18 kW
Thermal efficiency (ratio of entry/exit LHV)	32 - 96 %
L(n) of H ₂ + CO per L(n) of Methane	0.8 - 3.3
Conversion rate of CH ₄	75 - 98 %
H ₂ /CO ratio in SynGas	1.7 - 4.1 mol/mol

Figure 2 shows some output data for POX of Natural Gas at atmospheric pressure as the function of Oxygen to Methane Input ratio. These data include the runs with CH₄ input flow rates varying from 5.5 to 15.5 L(n)/min. The optimal conversion is obtained for O₂/CH₄ molar ratio around 0.8 where the quantity of generated SynGas reaches the ideal maximum of 3 mol per mol of CH₄. (One should however remember that our feed contains 5% of C₂H₆ that contributes in the Syngas generation).

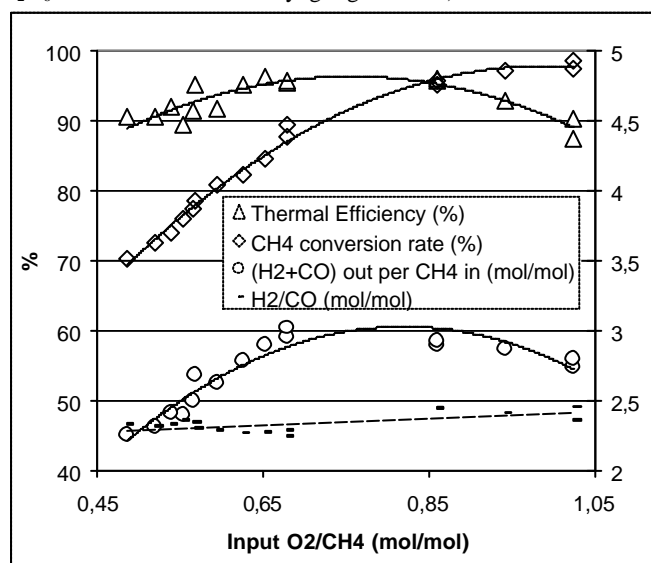


Figure 2. Selected output data for POX of Methane at atmospheric pressure as the function of Oxygen to Methane ratio.

When applying the air at 4 bar (see Fig. 3) we are finding a similar optimal reforming condition at O₂/CH₄ molar ratio around 0.8 but the quantity of generated SynGas reaches the maximum of only 2.8 mol per mol of CH₄. In these conditions the H₂/CO molar ratio is around 1.8 while at the atmospheric pressure this ratio is close to 2.3.

When applying the enriched air at atmospheric pressure and without additional steam injection we are finding the optimal reforming conditions at O₂/CH₄ molar ratio around 0.7, the quantity of generated SynGas reaches the maximum of 2.7 mol per mol of CH₄. In these conditions the H₂/CO molar ratio is around 2.0.

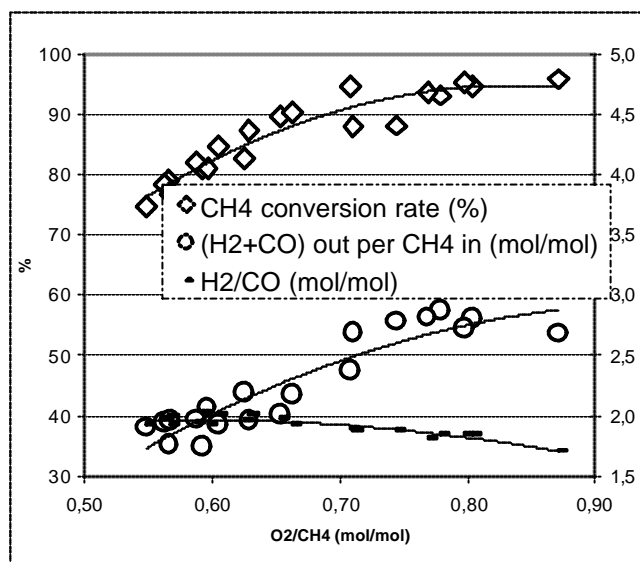


Figure 3. Selected output data for POX of Methane at 4 bar (abs.) as the function of Oxygen to Methane input ratio.

Conclusions

Natural gas is reformed at better than 90% energetic efficiency and without soot. Desired output flow of SynGas as well as its quality can be obtained by controlling the supply flow rates of the feed and oxidant. Here presented ¼ L reformer (inside volume) can produce up to 5 m³(n)/h of pure SynGas (N₂ and other components not accounted).

Electric power assisting our reforming is less than 1% of the LHV power of produced SynGas stream. Such a low power recycling (or an import) is, in our opinion, a worthy compromise. Instead of using delicate catalysts that ask for a very clean fuel we dedicate an almost negligible part of produced SynGas power to electrically support a non-catalytic reforming of almost any dirty fuel.

References

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