

Conversion of waste Glycerol into Synthesis Gas

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Abstract: Glycerol is successfully converted in long runs into H₂- and CO-rich syngas using air driven Partial Oxidation assisted by the GlidArc electric discharge. At up to 4.3kg/h Glycerol input flow rate we are obtaining soot-free and very clean syngas of up to 17kW LHV enthalpy power that should be good enough to generate a 5kW_e distributed green electric power. Additional 10kW_{th} of clean heat can be recovered for local uses.

Keywords: GlidArc, glycerol, glycerine, synthesis gas, CHP generation, biodiesel

1. Introduction

Glycerol (glycerine) C₃H₅(OH)₃ starts to be a waste co-product (~10%) of biodiesel production. Preliminary indicators show that Glycerol will be a very abundant, cheap, and petroleum free feedstock. This tri-alcohol burns with difficulties giving unpleasant acrolein. Fortunately, it still can be considered as matter for the synthesis gas (syngas) generation. Syngas (gas containing large quantities of H₂ and CO) can then fuel many types of internal combustion engines (ICE) or gas turbines. Moreover, it can directly feed the Solid Oxide Fuel Cells or be converted into clean synthetic oil (synfuel) [1] or, much better, into the Methanol.

Accordingly, we are testing the Glycerol conversion into syngas using our GlidArc-assisted reformer that ECP has already used for the natural- or bio-gas as well as for liquid fuels, wastes or bio-oils reforming [2], [3], [4], see also www.glidarc-tech.com. Our first vision is to use such syngas as very clean fuel-gas for a stand-alone Grid interconnected electric power generator. Only 3% of the electric power created will be required to perpetuate the process. The system will have a less-than 20-minute dwell time until it become energy self-sufficient. Taking into account the heat recycling for waste glycerol pre-processing and other use for the biodiesel production (Combined Heat and Power CHP generation) – our system will be 90% energy efficient.

2. Experimental

2.1. Feed and feeding

Two samples were tested: 91/9 Glycerol/water solution and 97%-grade Glycerol. The Lower Heating Value (LHV) of pure Glycerol is 4.4kWh/kg (means ~ 40% of Diesel Oil LHV value). Precise piston dosing pumps are used for feeding this viscous and dense liquid in the range of up to 4.3kg/h.

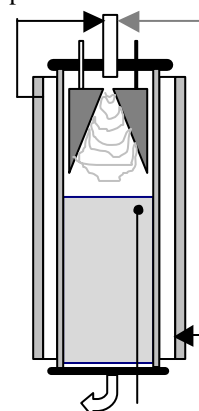
2.2. Reformers

Three successive reformers were used in ECP. The third one (the largest) was then installed on Florida Syngas LLC site (see www.floridasyngas.com) for further tests.

2.2.1. Reformer A

Small GlidArc-I reformer (**Fig. 1**) was used for initial trials. It has a 0.18L plasma space and a 0.57L post plasma zone filled with our high-temperature catalyst. This reformer can operate up to 22bars but the trials were performed at atmospheric pressure (see [6] for more details).

The plasma zone contains two flat High-Voltage electrodes that delimit a space filled with the gliding discharges. The feed and preheated O₂-enriched air is blown into that space where the mixture flows along the diverging electrodes. The discharges partially vaporize and ionize the feed. Given the moderate temperature of the electrodes (not cooled) and a very short contact time of the discharge roots with the electrodes, one does not observe any deterioration that may prevent the gliding of these current-limited discharges. A small flow [0.8 to 2.2L(n)/min] of an auxiliary Natural Gas (NG) is added to the Glycerol stream and the mixture is sent to a T-connector. An air/O₂ mixture enters the reformer's double-wall space where it is preheated.



At its exit such hot oxidant is sent to the same connector where it mixes with the NG/Glycerol bi-phase flow. Finally, whole mixture is injected by a 4-mm tube into the GlidArc-I discharge. Partially reformed reactants cross then the post-plasma zone where three thermocouples are installed for the temperature sensing. Hot syngas (SG) exits the reformer, cools down, and is then flared. A SG sample is analyzed online using a μ -GC.

Figure 1. Small GlidArc-I reformer A for initial tests

Initial trials are performed at various operating conditions:

Assisting GlidArc power	0.05kW
91% Glycerol input flow rate	6.1 – 16g/min
Auxiliary NG input flow rate	0.8 – 2.2L(n)/min

NG LHV input power	0.5 – 1.4kW
Air input flow rate	4.6 – 14L(n)/min
Oxygen input flow rate	0 – 4.8L(n)/min
O ₂ content in oxidizer	21 – 61vol.%

Based on precise mass balance (inert N₂+Ar conservation) we have obtained the following:

SG output flow rate (dry)	17 – 30L(n)/min
SG LHV output power	1.1 – 2.9kW
LHV released from Glycerol	1.2 – 2.6kWh/kg
LHV of the SG (dry)	1.0 – 2.0kWh/m ³ (n)

After the reformer dismantling neither harm nor soot/coke deposits inside the plasma zone as well as the post-plasma zone were found. The best results for this first series were obtained for 14.9g/min Glycerol, 0.8L(n)/min of NG, 4.6L(n)/min of air, and 1.7L(n)/min of O₂ input (such air/O₂ mixture contains therefore 40% O₂). We got some 28.5L(n)/min of syngas of LHV power of 2.8kW so 1.6kWh/m³(n) specific heating value. The SG contains 16.3% CO₂, 0.3% C₂H₄, 28.5% H₂, 38.3% N₂+Ar, 2.3% CH₄, and 14.2% CO. Taking into account 0.5kW of assisting NG input power we calculate the specific energy recovery as 2.6kWh per kg of reformed Glycerol corresponding to 64% chemical enthalpy conservation efficiency of the reforming process.

A 12-h continuous tests was then successfully performed at almost the same input conditions: 97% Glycerol @ 12.9g/min, auxiliary NG @ 0.5L(n)/min (0.3kW LHV), and only 28% O₂ in the oxidant. The LHV of produced syngas is now 1.5kWh/m³(n) as we work at lower O₂ concentration in the enriched air – so at higher N₂ ballast. Such gas would still be considered as a good fuel for an ICE or a gas turbine.

2.2.2. Reformer B

A larger 1.4-L reformer was then used. **Fig. 2** and **3** present respectively a schematic view of the GlidArc-III plasma head [5] and its assembling with the reformer.

We inject separately oxidant through (5) to a swirl zone (6) that protects a central GlidArc-III electrode (3), while preheated Glycerol is sent through (9) to the plasma zone (8) where the gliding and rotating high-voltage discharge strikes between the central high-voltage electrode (3) and a surrounding metallic nozzle (2) at the ground potential. Products of partial reforming of the feed are sent to the reformer's post-plasma zone through the exit (10).

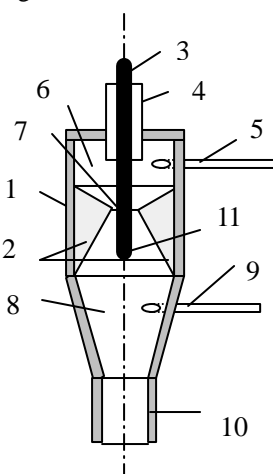


Figure 2. GlidArc-III head

The operating conditions were the following:

Constant GlidArc power	0.05kW
Glycerol input flow rate	13 – 52g/min
Auxiliary NG input flow rate	0.5L(n)/min
NG LHV power	0.3kW
Air input flow rate	25 – 54L(n)/min
Auxiliary Oxygen	none

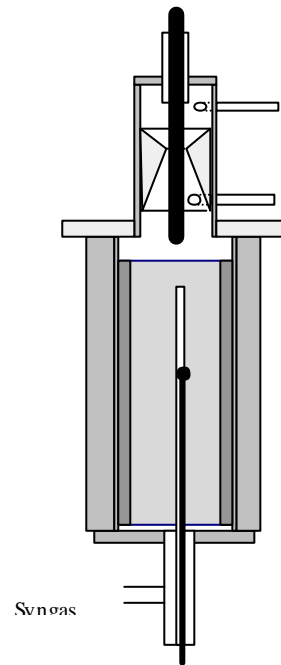


Figure 3. Larger reformer B

Based on precise mass balance we have obtained the following results:

SG output flow rate (dry)	26 – 127L(n)/min
SG LHV output power	1.9 – 14kW
LHV released from preheated feed	2.4 – 4.5kWh/kg
LHV of the SG (dry)	1.1 – 2.0kWh/m ³ (n)

Fig. 4 presents the most important reforming results. It appears that one can extract almost 90% of initial chemical enthalpy of Glycerol and that the LHV of obtained fuel gas is up to 2kWh/m³(n).

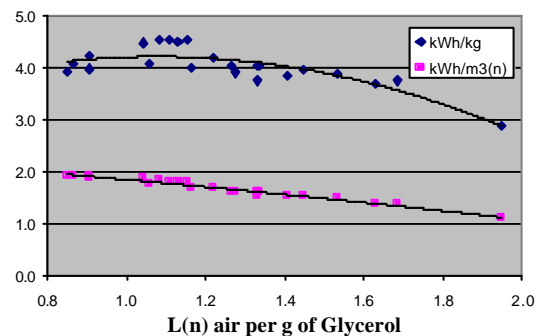


Figure 4. Chemical Enthalpy yield from the Glycerol reforming and the LHV of generated syngas as a function of air/fuel ratio

Using the Partial Oxidation we can therefore reform Glycerol into a fuel gas (SG) without any extra Oxygen. Such optimal reforming would ask some $1.1\text{m}^3(\text{n})$ of air per kg of Glycerol giving the fuel gas at around $1.8\text{kWh}/\text{m}^3(\text{n})$ LHV.

2.2.3. Reformer C

Based on acquired experience and know-how ECP has built a 3-L reformer for Florida Syngas as the first demo unit to be integrated with a 5kW_e electric generator. **Fig. 5** presents a picture of the reformer.



Figure 5. Demo 3-L Reformer C of Glycerol

A series of tests was successfully performed in ECP facility at up to 4.3kg of 97%-grade Glycerol input rate. At this scale no auxiliary natural gas is needed for the process. Higher thermal performances are expected using larger reformers and the process optimization. This work is still in progress. **Fig. 6** presents temperatures distribution inside this reformer during a typical run.

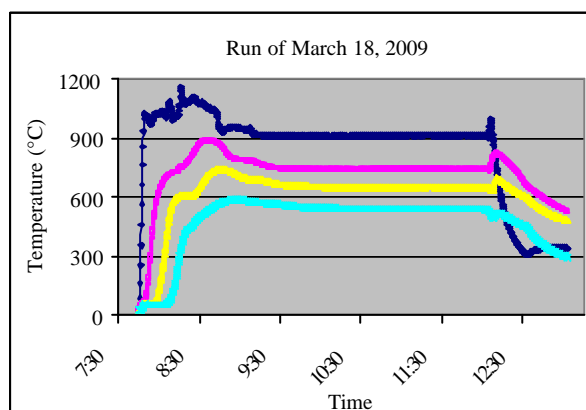


Fig. 6. Typical run of Glycerol into syngas reforming; four thermocouples are inserted in a thermal well put in the post-plasma zone of the reformer (like indicated on Fig. 3); the highest temperatures are near the plasma zone

It took only 3min from the cold-launch to get 1000°C at the top of the post-plasma zone and to begin producing first syngas - so to start using it for Combined Heat and Power (CHP) generation. The deeper parts of the catalyst

heat then progressively up and after 1hour one gets a perfect steady state. These stable conditions were observed during next 3hours after what the reforming was voluntarily shut down.

Produced syngas is really soot-free. When flared, it gives a very clean flame visible only in dark environment, see **Fig. 7**. Further results will be presented during this Symposium.



Fig. 7. Clean and soot-free syngas flare (diameter of 1.5inch)

3. Conclusion

Glycerol is successfully converted in long runs into H_2 - and CO -rich fuel gas / syngas using air driven Partial Oxidation assisted by the GlidArc electric discharge. At a $4.3\text{kg}/\text{h}$ Glycerol input flow rate we are obtaining a soot-free output gas of roughly 17kW LHV power that should be good enough to generate a 5kW_e distributed green electric power. Additional 10kW_{th} of clean heat will be recovered for local uses or for crude Glycerol processing.

References

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