

PLASMA-ASSISTED SELECTIVE PARTIAL OXIDATION OF TARS AND OTHER POLLUTANTS IN PRODUCER GASES

Albin Czernichowski and Piotr Czernichowski*

ECP – GlidArc Technologies, 45240 La Ferté St Aubin, France
*Ceramatec Inc., Salt Lake City, UT 84119, USA

Introduction

As geopolitical problems related to foreign natural gas supply appear - old gasification technology emerges as one of the solutions. Any biomass and almost any rubbish can be processed this way. It is however commonly thought that all types of gasification are problematic and any resulting "producer gas" is always not clean enough for modern applications. Its main drawback is the presence of residual tars. Various filtering, catalytic, and other methods have been tested giving "too complicated and expensive" and/or "not yet sufficient" results. Almost the same strategies of "clean" gasification are applied universally:

- Gasification of a solid feed into as-clean-as-possible producer gas using "modern" high-temperature and/or fluidized bed and/or other high-tech gasifiers,
- Removal of still-present residual tars and other pollutants using various physical and/or chemical "filters".

New Concept

ECP proposes totally different and just opposite strategy assisted by our GlidArc¹ low-tech plasma devices:

- Gasification of any solid feed into as-dirty-as-possible producer gas (using rather a simple low-temperature gasifier),
- Second-step total conversion of highly abundant tars, vapors, hydrocarbons, and other volatile carbonaceous molecules into a supplementary amount of very clean synthesis gas (H₂ + CO) using our GlidArc-assisted selective partial oxidation.

Since years ECP is elaborating various GlidArc-assisted reformers to convert a range of gaseous and liquid feeds into clean syngas. These very simple reformers attain already a significant scale and have been used for very efficient conversions of natural gas, LPG, heptane, toluene², xylene, road gasoline, road Diesel oil, aviation kerosenes, dirty bunker oil, ethanol, sugar/water mix, rapeseed and soybean oils, glycerol (by-product from biodiesel production), waste bone oil or animal fat, bio-oil issued from fast wood pyrolysis, etc. The feeds can also contain soot and poly-aromatic hydrocarbons³, hydrogen sulphide⁴, chlorinated

compounds⁵, nitrous oxide N₂O⁶ and many other pollutants - except ashes.

Therefore the main and sufficient target of proposed step A is only a separation of ashes, minerals, and metals from all other volatile elements and compounds that gives "dirty" producer gas. The step B then deals separately with all complex molecules in order to convert them totally into Hydrogen H₂ and Carbon Monoxide CO. A particular property of our step B is its selectivity: any initial H₂ and/or CO present in initial dirty producer gas are not attacked in the process so that more syngas exits our selective Oxidizer. At least 3 vol.% level of cumulated organic Carbon (any form) is necessary in the "dirty" producer gas.

Experimental

Go/no-go trials

To check such strategy ECP has first performed some trials in March 2007 using our 1.4-L GlidArc-reformer⁷. By controlled mixing of a clean syngas (accumulated in pressurized gas cylinders) with natural gas (sucked from the local pipe) we have obtained a stream of a methane-enriched syngas. The composition of the feed (vol.%, dry basis) is given in Tab. 1. The feed was completely dry (instead of 100 – 200 g H₂O per m³(n) in the real producer gas). Trials were performed at the gas flow rate around 23 L(n)/min. An enriched air containing 28 vol.% of O₂ was used as oxidizer at the constant flow rate of 8.0 L(n)/min. Our best test gave the following output syngas composition (vol.%, dry basis, showed as "Out"):

Table 1. Input/output dry syngas composition

	CO ₂	C ₂ H ₆	C ₃ H ₈	H ₂	N ₂ +Ar	CH ₄	CO
In	5.33	0.30	0.07	46.28	14.15	8.66	25.20
Out	7.43	0.00	0.00	40.68	27.40	0.14	24.06

Based on precise mass balance we have obtained 15% more of syngas at the reformer exit. The conversion rate of CH₄ was 98% while the conversions of C₂H₆ and C₃H₈ were total. Such results have encouraged ECP to prepare the next trials.

Preliminary trials including steam and the feed preheat

Following actions were performed:

- Addition of steam and the feed preheat to simulate hot producer gas (water pump, rotameter, electric oven, 200°C)
- Use of 60% O₂ enriched air.

Our results are presented in Tab. 2 for two tests.

Table 2. Input/output wet syngas composition

	H ₂ O	vol.% dry						
Test	g/m ³	CO ₂	C ₂ H ₆	C ₃ H ₈	H ₂	N ₂ +Ar	CH ₄	CO
8 In	222	1.77	2.65	0.53	12.17	4.48	59.22	19.18
Out		25.49	0.00	0.00	36.47	21.94	1.29	14.80
9 In	303	1.77	2.65	0.53	12.17	4.48	59.22	19.18
Out		24.44	0.00	0.00	33.84	21.60	1.18	18.96

Again, based on precise mass balance we have obtained 4-fold increase of the syngas amount. The conversion rate of CH₄ was also 98% while the conversions of C₂H₆ and C₃H₈ were total. Moreover, the GlidArc-assisted cleaning of wet producer gas acts also as the

¹ H. Lesueur, A. Czernichowski, J. Chapelle, Dispositif de Génération de Plasmas Basse Température par Formation de Décharges Electriques Glissantes, *French Patent 1988*, 2639172.

² M. Czernichowski, P. Czernichowski, A. Czernichowski, Non-catalytical reforming of various fuels into syngas, **2002, France - Deutschland Fuel Cell Conference on "Materials, Engineering, Systems, Applications"**, Forbach, 7 pp.

³ A. Czernichowski, P. Labbe, F. Laval, H. Lesueur, Plasma Assisted Cleaning of Flue Gas from a Sooting Combustion. Case of Organic Nitrates, *ACS Symposium Series No. 607, Emerging Technologies in Hazardous Waste Management V*, Ed. D.W. Tedder & F.G. Pohland, ACS, Washington DC, **1995**, Chapter 12, , pp. 144-154.

⁴ A. Czernichowski, Plasmas pour la destruction de l'H₂S et des mercaptans, *Oil & Gas Science and Technology*, **1999**, 54(3), pp. 337-355.

⁵ A. Czernichowski, T. Opalinska, P. Czernichowski, H. Lesueur, Procédé et dispositif de déshalogénéation de composés organiques par plasma, *French Patent 1994*, 2724166.

⁶ A. Charamel, A. Czernichowski, A. Gorius, Procédé de Transformation Plasmachimique de N₂O en NO_x et/ou en ses dérivés, *French Patent 1993*, 2709748.

⁷ A. Czernichowski, K. Wesolowska, POX reforming of bio-methane into synthesis gas, *232nd ACS, San Francisco, CA, 2006*, 2 pp preprint.

"water-shift" of CO into H₂ so that H₂/CO molar ratio improves from initial value of 0.63 up to even 2.5. Such syngas can now be used as feed for Fischer-Tropsch syntheses.

Preliminary trials including steam and simulated light tars

Dry syngas flow containing (in vol.%) 15.7 H₂, 46.3 N₂, 1.6 CH₄, 29.5 CO, and 6.9 CO₂ was mixed with controlled amounts of water and toluene and preheated to completely vaporize both liquids. Resulting simulated dirty producer gas entered GlidArc-assisted reformer to which we injected 26 L(n)/min of -enriched air (41% O₂). Selected input/output data are presented in Tab. 3.

Table 3. Input/output data of simulated producer gas

Run	Fuel L(n)/min	H ₂ O		Toluene		H ₂ +CO		H ₂ /CO
		IN	OUT	IN	OUT	IN	OUT	
		g/m ³ (n)		% (1)		L(n)/min		
8	103	137	115	0.9	98.9	23	22	0.70
9	103	138	115	1.7	97.9	23	20	0.67
10	116	93	92	2.7	96.7	28	23	0.57
15	105	207	115	1.2	98.5	23	21	0.77

(1) Calculated from mass balance

Selective partial oxidation of toluene contained in simulated producer gas is confirmed. Our proposed method of producer gas cleaning converts close to 99% of toluene mass into the synthesis gas. We observe an increase of H₂/CO ratio (initially = 0.53) in the cleaned syngas from due to some "water shift" acting in parallel. Also the Lower Heating Value (LHV) of the syngas content initially equal to 1.67 kWh/m³(n) slightly lowers to 1.43 kWh/m³(n) which is acceptable (average of here-presented runs).

Conclusions

Our preliminary runs indicate the feasibility of proposed strategy of rather dirty than clean gasification. The scale of GlidArc-assisted tests (less than 10kW of lower heating power of the fuel gas crossing the reformer) was low so that thermal losses of process were quite high. An almost full-scale series of tests is under preparation, this time using the real dirty producer gas from real gasifier of the waste biomass. There is no upper limit of light tars content in the producer gas as even liquid toluene was successfully and totally converted into the syngas without any soot (see ref. 2). There is no limit of such gas upper temperature so that the GlidArc cleaner/reformer can use a residual heat of gasification.

Figure 1 shows the concept of such integrated system of dirty gasification followed by hot producer gas reforming/cleaning.

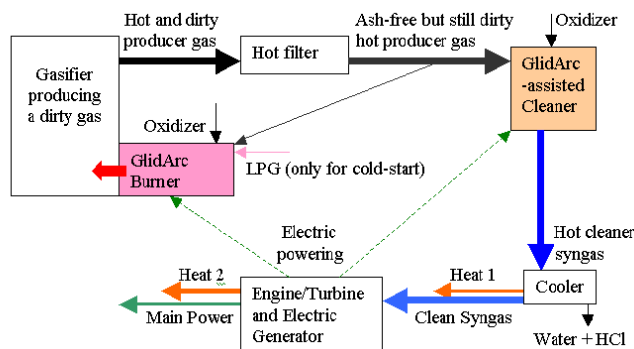


Figure 1. GlidArc-assisted cleaning of dirty producer gas