EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY: Plasma reactors
SUB-TECHNOLOGY: GlidArc cold plasma
TECHNOLOGY CODE: 3.3.5
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Table of contents

1. Technology

1.1 Description of technology / working principle

The first industrial applications of the electric discharges appear at the beginning of the XIX century. They concerned mostly the domain of chemical fertilizers *via* production of the nitric acid with an electric arc.
According to the type of electric discharge (see Fig. 1) and application, plasma reactors can be classified as:

- Hot plasma reactors (“thermal” plasma", electric arc, plasma torch…); in this case the electric current in the main circuit exceeds 5 A and temperatures are raised up to 10–20 kK. The goal of the majority of hot plasma devices is to achieve such elevated temperatures for metallurgy or intensive heat transfer processes. In this case almost all chemical structure is destroyed.
- Cold plasma reactors with the main circuit current of less than 5 A and bulk temperatures less than 2 kK.
- "Corona discharge" reactors that can be considered as a particular case of very low-current cold plasma.
- "Pulse discharge” reactors that use a source of a very high-current but short impulses.

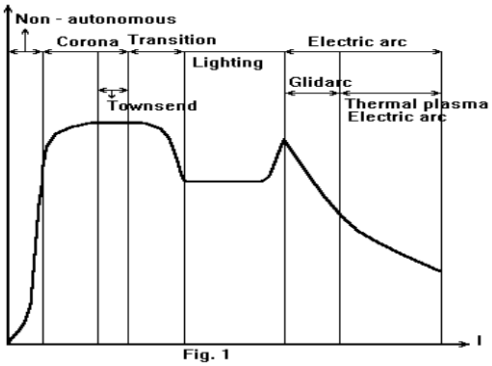
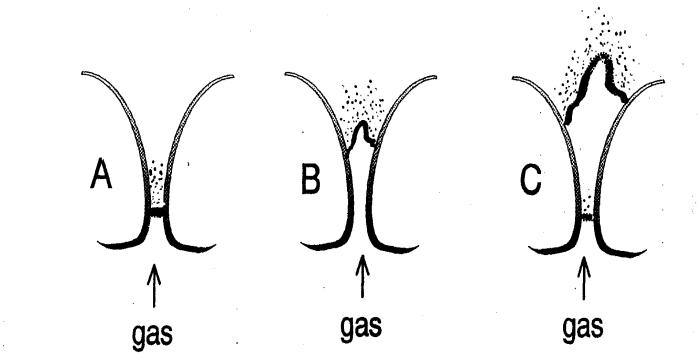


Fig. 1

Fig. 1.General shape of Volt-Ampere characteristic of electric discharges in gases. One can observe that GlidArc is an autonomous discharge situated between the luminescent discharges and the electric arc.

Gliding Arc (GlidArc) devices are a relatively new way (1988's patent) of cold plasma generation. At least two electrodes diverging with respect to each other are placed in fast (typically 10 m/s) gas or vapour flow. A high voltage (5–15 kV) applied between these electrodes creates specific unstable discharges between electrodes and across the flow, see Fig. 2. The discharges start at the spot where the distance between the electrodes is the shortest, and spread by gliding along the electrodes in the flow direction until they disappear after a certain path … to repeat this cycle.



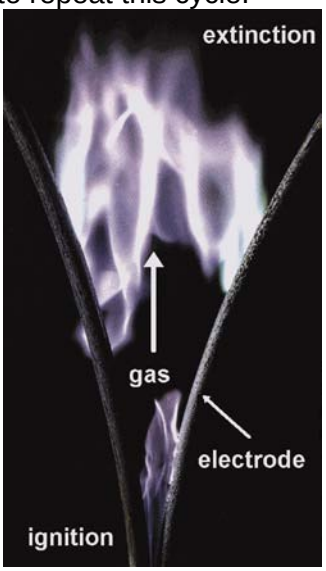


Fig. 2. Principle (up) and time-integrated real picture (right) of a gliding discharge cycle: ignition A, life B, extinction C, and new discharge A.

There are various chemical activations and reactions of decomposition and/or synthesis in fluids that cross the discharges. To get such processes it is necessary to limit the temperature (and energy density) in such plasma through the discharge current limitation below 2 Amps. Consequently the GlidArc has not problem of electrode erosion and/or corrosion (observed in older plasma devices using graphite or intensively water-cooled metallic electrodes). Cooling is no more required - that simplifies GlidArc-based reactors.

The ignition, maintenance and re-ignition of an unstable electrical discharge intended to glide along electrodes does not require a sophisticate power supply; commercial neon-sign 50 or 60 Hz transformers (or any high-inductance high-voltage transformer) can do it at a low cost. For example, a set of three neon-sign mono-phase transformers connected to a 3-phase mains can power a triangular structure of three electrodes or a hexagonal structure of six electrodes for respectively three or six simultaneous discharges, see Fig. 3.

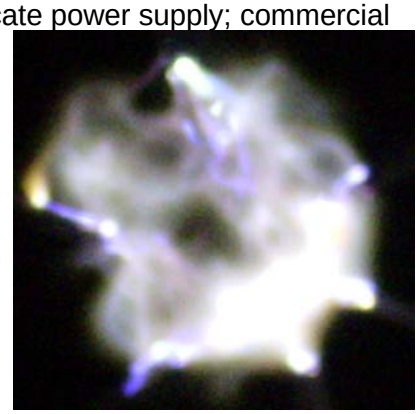


Fig. 3. Front view of GlidArc cold plasma generated between six electrodes.

High power-factor electric supplying of a single- or multiple-electrode GlidArc system can be performed according to 2000's patent. Finally, one high-voltage standard transformer can supply dozens or hundreds electrodes aggregated in a honeycomb structure in order to dissipate high electric power needed to process large flows of fluids, see 2002's patent.

1.2 Types and “versions”

An alternative way of gliding discharges generation using a rotating central electrode (grounded) and connecting it, *via* high-voltage discharges, to several stationary electrodes located around the central electrode is presented in 1997's patent. Such new device called GlidArc-II is presented on Fig. 4 and 5.

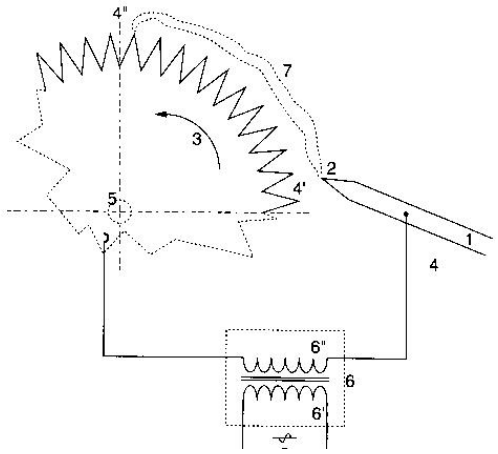


Fig. 4. Principle of the GlidArc-II device: 1 – stationary electrode, 3 – rotating electrode, 6 – power supply, 7 – high-voltage discharge.

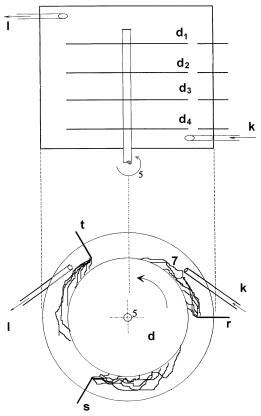


Fig. 5. Multiple-stages and multiple-electrodes GlidArc-II reactor: r, s, and t – three-phase-supplied stationary electrodes, k and l – input and output of the processed gas, d – rotating electrodes.

There are multiple advantages of such structure: The high-voltage discharges generation and the processed gas flow rates are no more self-dependent so that even a very low gas flow rate can be accepted at any power level as there is no more need to accelerate the gas at the proximity of electrodes. The mobile electrodes rotate in the range of 50–1000 rad/s, which are acceptable speeds. The discharges can "touch" several times the same gas flux without any obligation to push the gas between the stages. The reactor is quite compact for even large gas flows. For example one can realise three 2 A and 2 kV discharges for one stage. When adding four stages it makes a 50 kW reactor realised in a 0.3 m diameter cylinder of 0.5 m height (30 L volume). Such reactor can process roughly up to 500 m^3/h of gas.

For specific applications one can inject separately two different fluids into a so-called GlidArc-III patented device (2004) shown on Fig. 6. One fluid (for example air) enters through (5) to a vortex zone (6) that protects a central GlidArc-III electrode (3) while other fluid (for example a liquid) 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. The products of liquid pyrolysis (if any) cannot therefore harm the dielectric support (4) of the central electrode.

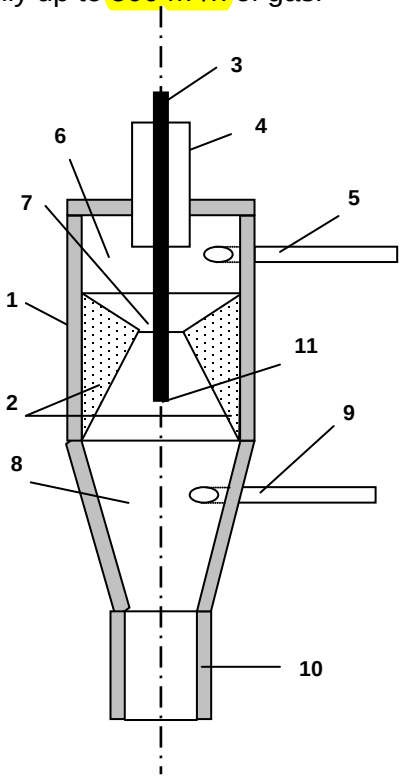


Fig. 6. Principle of the GlidArc-III.

1.3 Potency for Process Intensification: possible benefits

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Low-temperature (cold) plasma	500-2000 K	This range of bulk temperatures is very well adapted for chemical processing of various feeds *via* exothermic reactions (where plasma ignites and then assist such processes) and also for endothermic reactions (where GlidArc supplies a very active energy *via* catalytic species generated directly from the processed feed at thermodynamic non-equilibrium conditions).
High thermal efficiency	~ 100 %	All electric power dissipated in GlidArc discharges is transferred to the processed feed (no electrode cooling).
Simplicity and high efficiency of power supplying	~ 95 %	No high-tech or expensive electric power supplies needed, no active energy dissipated when converting commonly available 50 or 60 Hz mains into 5-15 kV supply voltage at the same frequency.
Wide power range of single discharge	30 W – 10 kW	
High power and large volume *via* multiple discharges	MW range	Dozens or hundreds of GlidArc discharges can be assembled in one reactor to process large feed flow rates.

Ordinary metals and refractories for GlidArc unit manufacturing		Low cost and broad availability (for example stainless steel blades as electrodes and automobile-like spark plugs as high-voltage connectors).
No noble gas, no special carrier gas		No special "plasma-forming" or "carrier" gas needed for GlidArc discharges generation because such discharges are formed directly in the processed gas or vapour.
Corrosive feeds accepted		Short contact time of the low-current discharge roots with electrodes prevents their corrosion even in the presence of highly concentrated corrosive gases like H_2S or Freons.
Dust and/or droplets accepted	< 3 mm	Possibility to generate GlidArc discharge in fluidised or spouted beds for solid matter processing.
Wide pressure range	0.05-12 bar	
Wide feed input temperature range	100-1500 K	GlidArc discharges can be installed in a hot entering feed for better waste heat integration.
Inexpensive way to provide easily controllable energy		This cold and catalytic plasma process at lower energy expense can substitute high energy consuming thermal processes at high temperatures.

1.4 Stage of development

Since the first experiments on gliding discharges (Orleans University) and first patent publication (1988) the progress of this technology was slow; the patent applicant and holder was interested rather to develop its own plasma torches in its own R&D centre. Huge taxpayers money was spent to build and exhibit its classical MW-range plasmatrons. Several trials of their implementation in industry were undertaken but almost nobody remembers them today…
Some preliminary industrial trials of GlidArc technology at a small pilot scale were nevertheless performed in France in early 90': bad-smelling odour removal, afterburning of smoke from explosives destruction, VOC incineration from painting or fibre production as well as waste N_2O recycling into NO_x. Industrial partners of the university team considered however the GlidArc technologies as premature. Nonetheless GlidArc-related teams from the University and from a small local R&D company have been working and presenting their results on physics, chemistry and technology. Based mostly on small contracts and perseverance they got a better understanding of physical and chemical phenomena, achieved some Master and Ph.D. degrees, proposed several GlidArc structures, their powering and applications, and got related patents. During these 20 last years the GlidArc community has crossed French borders and nowadays one can find GlidArc teams or individuals, and studies or emerging applications in almost 20 countries or states.

2. Applications

2.1 Existing technology (currently used)

"Plasma" is a very broad term used for 4th (means ionised) state of Matter; it represents roughly 99 % of the Universe. Several techniques can be used to generate plasma in laboratory or in industry, for example chemical explosion or

adiabatic compression. The easiest way of plasma generation is however an electric discharge in gases.

As indicated on Fig. 1, GlidArc discharge is located somewhere between very-low-current corona and luminous discharges and hot electric arcs. On the left part of this graph the currently used plasma technologies provide light (for example fluorescent tubes), dust removal ("Cottrell" electrostatic precipitator) or ozone production (for water disinfection). Electric arcs on the right part of the graph are used, since more than one century, in metallurgy: melting, extraction, purification, etc. Plasma torches (based on electric arcs of mostly 50-500 A) are used for so-called plasma spraying of refractory metals or ceramic on surfaces…

Nothing covers yet the GlidArc intermediate zone of the graph: relatively low-current (but sufficiently high power) discharges.

2.2 Known commercial applications: None.

2.3 Known demonstration projects

Table 2. Demonstration projects related to the technology (existing and under realisation)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
Chemical weapon	Kobe Steel, Japan	Destruction of toxic exhaust from controlled detonation of old chemical munitions	2007	Successful pre-commercial tests
Industrial Electrical Equipment	Florida Syngas, FL	Industrial “Peak Load Shaving” *via* Distributed Generation equipment (DG)	2008	Successful laboratory experimentation so far
Energy	EmeraChem and McMinnville Electric System, TN	In-situ production of H_2 for catalytic de-NOx of MW-scale power utility	2008	1 kg/h H_2 from the same biodiesel that fuels a 4 MW engine; >96% NOx removal from engine's exhaust
Energy	Biomass Energy Foundation, CO	Conversion of soybean oil into syngas for a spark-ignited engine fuelling	2008	Simple 6-cylinder spark engine can supply a peak-electricity on the farms
Mineral processing	Groupe Chimique, Tunisia	Removal of bad-smelling gases from phosphates production	2009	Successful laboratory experimentation so far
Biofuels production	Aviosol, Sweden	Reforming of methane and light hydrocarbons as well as the tar gasification for synfuels production	2009	Successful laboratory experimentation so far

2.4 Potential applications discussed in literature

Pyrolysis of Natural Gas (NG), see Czernichowski and Czernichowski (2000) was performed in a 2-L six-electrodes GlidArc reactor at atmospheric pressure or at moderate vacuum (down to 0.16 bars) at up to 0.66 m^3(n)/h flow rate and up to 2 kW dissipated power. Two main reactions (both endothermic) were observed:

$$CH_4 = C + 2\ H_2 \text{ and } CH_4 = 0.5\ C_2H_2 + 1.5\ H_2.$$

Up to 40 % of the feed was converted, mostly to H_2 and C_2H_2 (main reaction) and to H_2 and soot (secondary reaction) at very promising energetics of 2.6 kWh per 1 m^3(n) H_2 plus 0.18 m^3(n) C_2H_2 + C_2H_4. Very high selectivity to acetylene (70-90 %) and only 30-10 % selectivity to soot (a very dry and light matter composed of carbon nano-particles) were observed. Such soot may also present a valuable product. An idea of a GlidArc-assisted pyrolysis of the NG for Zero- or Low-Emission-Vehicle is explored as a part of systems supplying pure H_2 for a PEM fuel cell or supplying only partially converted NG (such as a CH_4 + H_2 mix) for piston engines.

Natural Gas (NG) or bio-Methane partial oxidation (POX) into the synthesis gas (syngas, a mixture containing mostly H_2 and CO) was performed in various two-zone reformers presented schematically on Fig. 7, see 1997b patent or Czernichowski (2001) or Czernichowski and Wesolowska (2006). Plasma zone (for example 0.18 L of volume) contains one or more GlidArc discharges. One mixes separate flows of oxidant (air or O_2-enriched air) and NG (or bio-Methane) in a dual-flow injector. Steam can be added to one of the flows preheated in a double-wall of the reformer. The reactants are ignited and ionised in the plasma zone that communicates with a post-plasma zone (for example 0.57 L of volume) filled with refractory granules, see 2004a patent. The flow of partially converted reactants containing long-living active radicals enters this second zone where the conversion is completed by deactivation of excited species. The reformer is thermally insulated from outside to keep two zones hot.

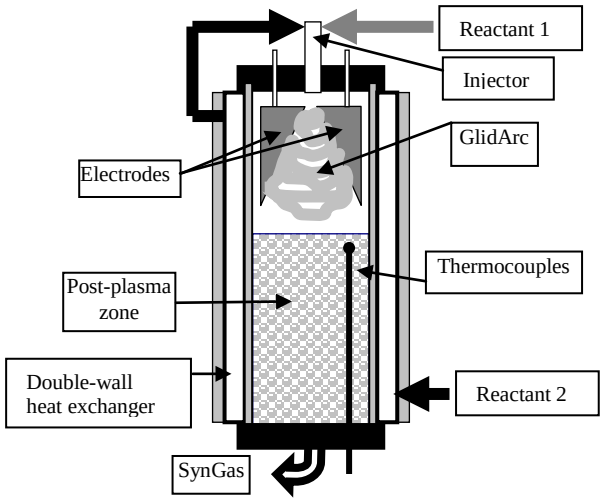


Fig. 7. Principle of the double-zone GlidArc reactor for POX reforming

Natural gas or bio-Methane is reformed at better than 90% energetic efficiency and without soot production. Desired output flow of syngas as well as its quality can be obtained by controlling the supply flow rates of the feed and oxidant. For example a ¾ L reformer (inside volume) can produce up to 5 m^3(n)/h of pure syngas (N_2 and other components not accounted). Electric power assisting such reforming is less than 1 % of the Lower Heating Value (LHV) power of produced syngas stream. Such a low power demand is a worthy compromise: instead using delicate catalysts that ask for a very clean fuel one can dedicate such an almost negligible part of produced syngas power to electrically support a GlidArc-assisted reforming of almost any fuel.

Dry-, steam- or combined dry/steam reforming of light hydrocarbons can be performed by a direct injection of an active electric energy to a mixture of light hydrocarbons (like methane or NG) with CO_2, see 1997a patent or Czernichowski et al. (2003). GlidArc discharges striking in the flow of a poor biogas (containing only 35-50 vol.% of methane) converted it partially into hydrogen and carbon monoxide (syngas). Such upgraded biogas can, for example, be used to fuel an Internal

Combustion Engine, be considered as source of Hydrogen for PEM fuel cells or be consumed in other specific fuel cells. Any level of sulphur impurities in biogas was accepted. The tests were performed in a 1.4-L reactor working at atmospheric pressure. An input of up to 0.6 kW electric GlidArc power was fully sufficient to process a flow of a poor biogas presenting up to 7 kW of LHV thermal power.

GlidArc-assisted POX reforming of other carbonaceous matter (fossil or renewable) into the synthesis gas:

- Liquid Petroleum Gas (LPG, mostly Propane), see Czernichowski et al. (2003a). Feasibility tests with a crude LPG in a 1-L GlidArc reactor at atmospheric pressure and 0.1 kW electric power assistance; generation of a N_2-diluted syngas containing up to 45 % of H_2+CO at the output flow rate corresponding up to 2.7 m^3(n)/h of pure H_2+CO mixture (that is equivalent to LHV output power of 8.6 kW). The LPG was totally reformed at 73 % energetic efficiency and soot absence. A 0.1 % of Sulphur content in LPG was not harmful for the reformer and/or process so that the GlidArc assisted reforming of commercial or waste propane/LPG opens a way for much simpler integrated reformer / Solid Oxide Fuel Cell (SOFC) units without prior desulphurisation step. Such everywhere available LPG can also be considered as feed for pure Hydrogen distribution for PEM fuel cells.
- Gasoline and Diesel Oils, see Czernichowski et al. (2003b). Various commercial diesel oils (including logistic ones that contain up to 4 % of Sulfur) and a gasoline 95 are converted into synthesis gas at atmospheric air. One produces up to 6.9 m^3(n)/h of Nitrogen-diluted syngas containing up to 21 % of H_2 and up to 21 % of CO. It corresponds to 8.4 kW of electric power when such syngas is converted in an ideal Fuel Cell (FC). Power requirement for GlidArc assistance is below 2 % of the FC output. An auxiliary power supplying can therefore be proposed for trucks or buses…
- Rapeseed Oil, see Czernichowski et al. (2003c). A commercial rapeseed oil is converted in a 1-L reformer at atmospheric pressure. Nitrogen-diluted syngas containing up to 40 % of H_2+CO at total feedstock conversion is produced in absence of the soot or coke. The flow of produced syngas corresponds to 11 kW of electric power of an ideal Fuel Cell. These results open a way to other renewable feedstock reforming into the syngas such as other oils, molasses or other secondary or waste products of a food processing.
- Bio-Ethanol, see Czernichowski et al. (2006a). A 50° to 90° Ethanol/water solutions are reformed using air. The feed conversion is total and the produced synthesis gas does not contain soot, coke or tars. The output reformate gas reaches 22 kW power (LHV) at only 1 % of electric power necessary to assist such process. Up to 46 vol.% of H_2+CO syngas mixture is produced (the balance being mostly the N_2) in long runs. A 75 % thermal efficiency of the process is obtained but a large part of remaining heat can be further reused.

Hydrogen sulfide full or partial upgrading, see Czernichowski and Wesolowska (2003d); see also 1989' patent or earlier Czernichowski (1998) paper. Plasma-assisted Hydrogen extraction from H_2S contained in waste gases of oil and gas industry is proposed as alternative to the classical Claus process of H_2S oxidation to H_2O. Various concentrated mixtures of H_2S + CO_2 are processed at atmospheric pressure in small GlidArc reactors, in a 3-steps GlidArc pilot at 60 m^3/h scale, and in a 60-L GlidArc-II pilot plant (see Fig. 8).

Fig. 8. A 36-electrodes 60-L GlidArc-II pilot plant for H_2S processing

Precise mass and energy balances show that such acid gas processing (called SulfArc) can reach the H_2S conversion rate of 99 % providing the Hydrogen and Carbon Monoxide (Synthesis Gas) at a quite low energy consumption.

Conversion of concentrated N_2O into NO_x (or its abatement); see 1993' patent and Krawczyk et al. (1998a). Recycling of concentrated waste N_2O (from Nylon production) into NO and NO_2 in order to re-use these oxides in the same Nylon plants where HNO_3 is needed for the oxidation to the adipic acid was shown. The process:

$$N_2O + 0.5\ O_2 = 2\ NO \text{ and } NO + 0.5\ O_2 = NO_2$$

was performed in a 2.5-L double-wall reactor where the feed was preheated (up to 355°C) before entering the discharge zone. Dry or wet $N_2O/N_2/O_2/CO_2/NO_2$ mixtures (close to the industrial off-gas composition, sometime enriched in oxygen) were processed at atmospheric pressure. The molar percentage of N_2O in the mixtures was 32 to 51 %. The feed flow-rate ranged from 1.3 to 4.9 m^3(n)/h. The electric power of the discharge was 0.62 to 1.2 kW. The total N_2O conversion rate was up to 60 % whereas up to 68 % of reacted N_2O was converted to NO_x. The NO_x concentration in the exit gas was up to 8.9 % (in mass) when no NO_x was present in the entry gas.

Flue-gas SO_2 reduction to elements, see 1992' patent and also Czernichowski et al. (1995). Sulphur dioxide was adsorbed from a diluted air-SO_2 mixture on activated coke bed (60-160°C, 2-8 m^3/h of exhaust per kg of sorbent) then desorbed in a stream of reducing agent (hydrogen or natural gas at 200°C or higher temperatures) and directly converted into liquid sulphur in a GlidArc reactor. Close to 70 % SO_2 conversion was obtained in one-step laboratory scale setup without using any catalyst and at 0.25 kWh electric energy demand per kg of produced sulphur. Desorption and then reduction in GlidArc of SOx and NOx can also be done using coke oven gas, CO, methanol or ammonia.

Polymeric sulphur can be obtained from ordinary sulphur using heating and then quenching of sulphur vapours according to 1996' patent. A stream of 5 m^3/h of nitrogen + 0.5 kg/h of sulphur powder crosses a 3.5 kW GlidArc device and then is quenched in CO_2 at room temperature. One obtains close to 50 % conversion of sulphur into its polymeric state (insoluble in liquid CS_2). Such sulphur has much better properties for tires fabrication.

Chloro- and/or fluoro-organics upgrading

- Partial or total decomposition or de-halogenation of such compounds *via* reduction using hydrogen in GlidArc plasma, see 1994' patent and Krawczyk et al. (1998a). Pure model compounds were mixed with Hydrogen and introduced directly into the discharge under 1 to 2 atm at a total flow-rates up to 2 m^3(n)/h. Acetylene, ethylene, HCl and HF were found in the products as well as some soot. Much better way of steam reforming are therefore proposed below:
- Plasma-catalytic steam cracking of halogen-organic compounds, see 1994 and 1994a patents and/or or Opalska and Czernichowski (2001a). A new steam-cracking conversion of such compounds uses a super-heated and activated steam obtained in GlidArc to initiate and sustain some chemical processes that gives as result CO_2, CO, H_2, concentrated HCl and/or HF, and a residual mixture of clean light hydrocarbons. The process can be carried out the range of 0.05 to 5 bars. Decomposition of some model molecules ($CHCl_3$, $CFCl_3$, CF_2Cl_2, and C_2Cl_4) was tested in three different bench-scale reactors. Up to 100 % conversion of initial CFCs is obtained in the one-step. The specific energy requirement for the process ranged between 0.2 and 15 kWh per kg of completely mineralized CFC.

Hydrogen sulfide and/or mercaptans destruction was already proposed in 1989' patent, see also Czernichowski (1999). Air-diluted sulfides (up to 1 % H_2S or 0.1 % CH_3SH) were processed in gliding electrical discharges at up to 70 m^3(n)/h pilot

scale. Experiments were performed in one or four-stages GlidArc reactors at atmospheric pressure. Each stage contains 3 main electrodes and one ignition electrode. These discharges produce cold plasma, which activates oxidation reactions. Up to 100 % clean-up was obtained at very low energy expense: 1 kWh of injected energy can remove all sulfides from 20 m^3(n) of polluted air independently on initial pollutants' concentration in the range from 1 ppm to 1 %. The process uses a very simple water-washing column: water saturates with the produced SO_2 and captures unprocessed H_2S *via* a wet Claus-like process so that one avoids any SO_2 emission and obtains non-toxic elemental Sulfur as the unique product:

$$3\ H_2S + 1.5\ O_2 = 2\ H_2S + SO_2 + H_2O = 3\ S + 3\ H_2O.$$

It means that only 33 % conversion of the pollutants into SO_2 is sufficient for complete removal of sulphides.

Volatile Organic Compounds (VOC) abatement in flue gases, see 1992a' patent describing how the combustible contaminants in gases extracted from painting booths can be incinerated by passing through a GlidArc device. A multiple-electrode powerful pilot plant was tested for diluted Xylene removal from air, see Fig. 9, but the tests were stopped when it appeared that an excessive amounts of NOx are generated. Duquet and Czernichowski (2001b) find that that drawback can be avoided for pre-concentrated foundry flue gas incineration. Detailed studies of various VOC removals at various GlidArc configurations are presently carried out in China, see Bo et al. (2007).

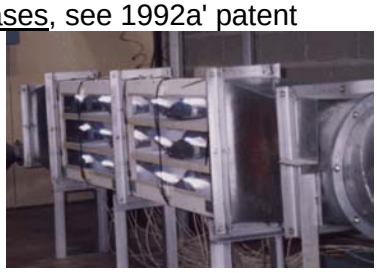


Fig. 9. A 36-electrode GlidArc pilot for VOC removal from exhaust.

GlidArc-Assisted Cleaning of Flue Gas from a Sooting Combustion. Case of Organic Nitrates, see 1993a' patent and Czernichowski et al. (1995a). Multiple-electrode & multiple steps GlidArc was used to clean up highly soot and NOx charged flue gas from an open burning of the Nitro-Benzene at the laboratory scale and the TNT (Tri-Nitro-Toluene) at the pilot scale (see Fig. 10). High cleaning efficiency was achieved at the flue-gas flow-rate up to 200 m^3/h. Almost complete disappearance of soot (and pyrolytic hazardous products adsorbed on it) and substantial lowering of the NOx and CO concentrations were observed. This technology is presently used for chemical weapon destruction at a pre-commercial scale; see Washida and Kitamura (2007a) reporting the capability of their GlidArc Oxidizer to successfully treat detonation off-gases.

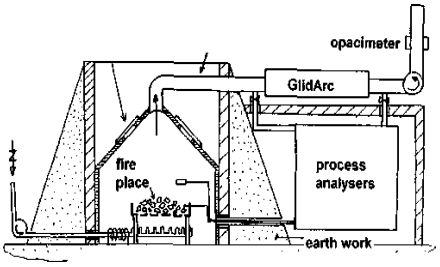


Fig. 10. Explosion-proof pilot plant for burning old munitions.

Solid matter processing

- Activation of solid matter was demonstrated in three cases:
  - Natural wool, see 1993b' patent and Janca and Czernichowski (1998b). An eco-friendly pretreatment of wool fabric with low-temperature GlidArc plasma resulted in a dramatic improvement in fabric hydrophilicity and wettability, the removal of fiber surface material, and creation of new active sites along with improved initial dyeing rate. The nature of the plasma gas governed the final exhaustion percentage of the used acid dyes according to the following descending order: N_2 > N_2/O_2 50/50 > O_2 > Ar ≥ control. Prolonging the exposure time up to 20 minutes resulted in a gradual improvement in the extent of exhaustion.

- Coal, see Holda et al. (1999a): Several crude coal samples were exposed directly or indirectly to GlidArc discharges. An increase of the sorption activity of the samples was found.
- Preheating and activation of powders, see 1998' patent. GlidArc device is used for thermal and/or plasma-chemical treatment of solid particles in the intimate presence of electrical energy dissipated in a mixture of these particles with a neutral or reactive gas. It is therefore possible to realise an intensification of the chemical processes in absence of thermodynamic equilibrium, at a very strong stirring and local dissipation of energy, at very strong velocity gradients and energy densities, and in the presence of extremely active radical species.

o Cleaning

- Metal surface degreasing, pickling or passivation, see 1998a' patent: Process for the treatment of a metal surface involves the generation of several GlidArc discharges between electrodes (at a high voltage) and a grounded metal. Process can be carried out in an active (slightly reducing or oxidising) gas atmosphere in a soft vacuum.
- GlidArc in fluidized or spouted beds was already mentioned in 1998' patent. A specific application was studied by Czernichowski et al. (1998c) for spent moulding sands regeneration by burning the phenolic resins accumulated on their surface. Fig. 11 shows a GlidArc discharge in a spouted bed.

Fig. 11. GlidArc discharge in a spouted bed.

GlidArc discharges to liquid electrodes were initially invented in 1996/1997 by A. Czernichowski (see Fig. 12). More detailed studies of the plasma, liquid, and surface zones were then published by Janca et al. (1999b). The electric field strength was measured, and the gas and electron temperatures and ion composition were estimated for the plasma zone. The cathode fall, water vaporization rate, and active species current yield due to the radiation chemistry mechanism were determined for the surface zone. Chemical action of such gliding discharges between metallic electrodes and conducting (for example aqueous) liquid may have various practical applications for organic or inorganic substances conversion or destruction.

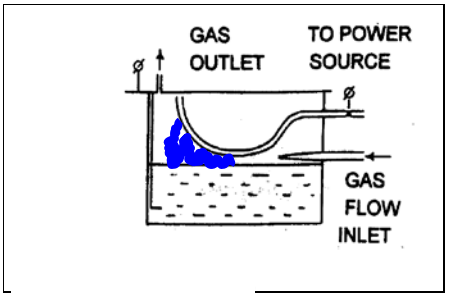


Fig.12. Gliding discharge between metallic and liquid electrodes.

GlidArc for flames activation, overheating, stabilizing or igniting. Electro-burner (in which a part of fuel is substituted by electrical energy) is a very old idea for increasing the temperature of classical burners. When a GlidArc is installed directly in a flame it makes it also more active (better heat-to-target transfer). Fig. 13, see Czernichowski (1997), presents an example of GlidArc-assisted flame.

Fig.13. High-velocity flame of 60 kW (LHV) thermal power assisted by a 3-electrode GlidArc.

A premixed flow of 6 m^3(n)/h of methane + 9 m^3(n)/h air exits a 4-mm nozzle at almost sonic velocity. The mixture is constantly ignited and stabilized with only 0.5 kW added electrical power through 3 electrodes around the nozzle. The flame length is 0.5 m but it cannot burn without GlidArc assistance! Some potential applications of such electric assistance of flames:

- Igniting high-velocity gases,
- Helping to achieve higher flame temperature,
- Allowing a free choice of temperature and red-ox conditions in flames,
- Burning lean gases without any addition of fuel,
- Acting against flame pulsation or extinction.

3. What are the development and application issues?

3.1 Technology development issues

Table 3. Technology development issues

Issue	Description	How and by whom should be addressed?
Engineering & design for commercial-scale devices	GlidArc reactors have been developed at the bench or small-pilot laboratory scales, so far. New designs are needed for commercial-scale reactors with better heat insulation or recycling.	Projects carried at the universities and small R&D-devoted companies, in a tight collaboration with potential end users
Control systems for commercial-scale reactors	Proper control of the plasma chemical processes carried out in the high-voltage reactors is of crucial importance for the reliability and safety of the operation. In most cases such plasma generators have to be used in a continuous (or at least couple-of-hours) way.	Projects carried at the universities and small R&D-devoted companies, in a tight collaboration with potential end users and equipment vendors
Fear	High-voltage devices are generally considered as very dangerous in most of the industries (especially in gas and petroleum ones)	Demonstration projects showing that electric discharges inside closed vessels are safe: they continuously ignite even potentially explosive mixtures so that explosions are avoided

3.2 Challenges in developing processes based on the technology

Table 4. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Pressure increase	Some industrial applications would require a 20 bar pressure range but the GlidArc discharges have tendency to shrink their diameter and convert into less active arc-like form.	Perhaps higher frequency GlidArc powering would solve the problem? A nice field for university studies…
Power increase	Current limitation of a single GlidArc discharge (to avoid its conversion into arc discharge) makes its power limited up to 10 kW range.	Multiple-discharges GlidArc was tested at a bench scale. A simple powering of such discharges has been proposed. Waiting for an industrial scale reactor…

4. Where can information be found?

4.1 Key publications

Table 5. Key publications on the technology

Publication	Publication type (research paper/review/book /report)	Remarks
Czernichowski, A., Lesueur, H., Polaczek, J., Czech, T. and Collin, G., 1995, Cold Plasma Reduction of Sulphur Dioxide to Elemental Sulphur, Erdöl, Kohle, Erdgas, Petrochemie, 48(1), 30-32.	Research paper	Concentrated SO_2 and/or NO_x non-catalytic reduction to elements
Czernichowski, A., Labbe, P., Laval, F. and Lesueur, H., 1995a, 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, American Chemical Society, Washington DC, 1995, Chapter 12, 144-154.	Research paper	Removal of soot from exhaust when burning TNT
Czernichowski, A., 1997, Accroche-flamme électrique, Contribution to "Journée d'Etudes sur la Stabilisation des Flammes", Ecole Centrale de Paris	Oral contribution	Electro-burner and/or igniter
Czernichowski, A., 1998, Plasmas pour valorisation totale ou partielle des gaz contenant de l'H_2S, Revue de l'Institut Français du Pétrole, 53(2), 163-179	Research paper	H_2S into Hydrogen conversion
Krawczyk, K., Ruszniak, J., Młotek, M., Czernichowski, A. and Schmidt-Szalowski, K., 1998a, Decomposition of tetrachloromethane and nitrous oxide under low-temperature plasma conditions, Polish J. of Appl. Chem., 42(2), 151-157	Research paper	CCl_4 and N_2O decomposition
Janca, J. and Czernichowski, A., 1998b, Wool treatment in the gas flow from gliding discharge plasma at atmospheric pressure, Surface & Coatings Technology, 98, 1112-1115	Research paper	Wool activation
Czernichowski, A., Ferenc, Z. and Wandrasz, J.W., 1998c, Odpadowe piaski formierskie źródłem surowców, Ceramika, 50(2), 46-49	Research paper	Recycling polluted moulding sands for foundries
Czernichowski, A., 1999, Plasmas pour la destruction de l'H_2S et des mercaptans, Oil & Gas Science and Technology, 54(3), 337-355	Research paper	Removal of H_2S and mercaptans from gases
Holda, S., Nodzenski, A.,. Musiol, K. and Czernichowski, A., 1999a, Activation of coal with plasma, Journal of Technical Physics, XL(2) 97-102	Research paper	Cheap sorbent

Janca, J., Kuzmin, S., Maximov, A., Titova, J. and Czernichowski, A., 1999b, Investigation of the Chemical Action of the Gliding and "Point" Arcs Between the Metallic Electrode and Aqueous Solution, Plasma Chemistry and Plasma Processing, 19(1), 53-67	Research paper	Gliding discharges to liquids
Czernichowski, A. and Czernichowski, P., 2000, Pyrolysis of natural gas in the gliding electric discharges, 10^{e} Conférence Canadienne sur l'Hydrogène, Québec, 705-711	Conference presentation	Pyrolysis of natural gas to Hydrogen, acetylene and dry soot
Czernichowski, A., GlidArc assisted preparation of the synthesis gas from natural and waste hydrocarbons gases, 2001, Oil & Gas Science and Technology, 56(2) 181-198	Research paper	Summary of earlier works on light hydrocarbons conversion into syngas
Opalska, A. and Czernichowski, A., 2001a, Decomposition of Chlorofluorocarbons in a Gliding Arc Reactor, 15th Int. Symp. on Plasma Chemistry, Orleans, France, VII, 3109-14.	Conference presentation	Upgrading of chlorinated organic compounds *via* steam reforming
Duquet, B. and Czernichowski, A., 2001b, Applications potentielles des plasmas froids au traitement des gaz de fonderie, Fonderie, Fondeur d'aujourd'hui, 205, 9-15	Research paper	GlidArc for foundry flue gas destruction
Czernichowski, A., Czernichowski, M. and Wesolowska, K., 2003, Glidarc-Assisted Production of Synthesis Gas from Biogas, 1st European Hydrogen Energy Conference, Grenoble, France, paper CP1 63, 10 pp	Conference presentation	Newer results on $CH_4 + CO_2$ dry reforming into syngas
Czernichowski, A., Czernichowski, M. and Czernichowski, P., 2003a, Glidarc-Assisted Reforming of Propane into Synthesis Gas, 1st European Hydrogen Energy Conference, Grenoble, France, CP1 66, 7 pp.	Conference presentation	POX reforming of commercial LPG into syngas
Czernichowski, A., Czernichowski, M. and Czernichowski, P., 2003b, Glidarc-Assisted Reforming of Gasoline and Diesel Oils into Synthesis Gas, 1st European Hydrogen Energy Conference, Grenoble, France, CP1 64, 7 pp.	Conference presentation	POX reforming of road gasoline or Diesel oil into syngas
Czernichowski, A., Czernichowski, M. and Czernichowski, P., 2003c, Glidarc-Assisted Production of Synthesis Gas from Rapeseed Oil, 1st European Hydrogen Energy Conference, Grenoble, France, CP1 67, 7 pp.	Conference presentation	POX reforming of commercial Rapeseed oil into syngas
Czernichowski A. and Wesolowska, K., 2003d, Glidarc-Plasma Reactors for Hydrogen Recovery from Waste H_2S, HYPOTHESIS V, Porto Conte, 301-309.	Conference presentation	Hydrogen recovery from H_2S
Czernichowski, A. and Wesolowska, K., POX reforming of bio-methane into synthesis gas, 2006, 232 National Meeting of American Chemical Society, San Francisco, CA, 2 pp abstract.	Conference presentation	Newer results on methane POX reforming into syngas
Czernichowski, A., Wesolowska, K. and Czernichowski, P., 2006a, Synthesis Gas generation from Bio-Ethanol, 16th World Hydrogen Energy Conference, Lyon, France, 8 pp.	Conference presentation	POX reforming of concentrated or diluted ethanol into syngas
Bo, Zh.,. Yan, J. H., Li, X. D., Chi, Y., Cen, K. F. and Chéron, B. G., 2007, Effects of Oxygen and Water Vapor on Volatile Organic Compounds	Research paper	GlidArc-assisted incineration of VOC

Decomposition Using Gliding Arc Gas Discharge, Plasma Chem. Plasma Process (on line), DOI 10.1007/s11090-007-9081-3		
Washida, T. and Kitamura, R., 2007a, Destruction of Old Chemical Bombs using DAVINCH^{TM} at Kanda, Japan, 10th International Chemical Weapons Demilitarisation Conference and Exhibition CWD 2007, Brussels, see http://www.dstl.gov.uk/conferences/cwd/2007/index.php	Conference presentation	Oxidative destruction of toxic exhaust

4.2 Relevant patents and patent applicants

Table 6. Relevant patents

Patent	Patent applicant	Remarks, including names/types of products targeted by the patent
FR 2639172: Dispositif de Génération de Plasmas Basse Température par Formation de Décharges Electriques Glissantes, 1988	Electricité de France	First patent on GlidArc principle
FR 2646099: Procédé de Traitement Electro-chimique d'un Gaz Contenant de l'Hydrogène Sulfuré, 1989 (see also EP 394141 and PL 164357)	BRGM, France	GlidArc for waste H_2S conversion into Hydrogen or destruction
PL 167513: Sposób przemiany dwutlenku siarki z mieszanin gazowych do siarki elementarnej (Sulphur and nitrogen conversion from oxides to elemental form), 1992 (see also FR 2698090 or DE 4336768)	Instytut Chemii Przemysłowej, Poland	Removal of SOx and NOx from exhausts by sorption/desorption and then reduction to elements in GlidArc
FR 2666518: Procédé et dispositif de dépollution de gaz pollués par des solvants, 1992a	GMM and Orleans University, France	Removal of VOC from painting booths
FR 2709748: Procédé de Transformation Plasmachimique de N_2O en NO_x et/ou en ses dérivés, 1993 (see also WO 95/07234, US 5711859 and BR 9405582)	Rhône Poulenc Chimie, France	GlidArc for waste N_2O conversion into concentrated NOx for nitric acid recycling
FR 2709980: Dispositif d'Elimination de Suies Présentes dans des Effluents de Combustion par Décharges Electriques Glissantes, 1993a (see also DE 4432012)	Commissariat d'Energie Atomique, France	Incineration of toxic soot, VOC and NOx from exhaust
CZ 2294-93: Zpusob beleni a zvysovani adhese vlákennych materialu k barvinum (Blending and increasing of adhesivity to dyes of fibrous materials), 1993b, see also FR 2711680	Masarykova Univerzita, Czech Republic	Activation of wool

FR 2724166: Procédé et dispositif de déshalogénation de composés organiques par plasma, 1994	Orleans University, France	Upgrading of CFC in reducing atmosphere
FR 2724806: Procédé et dispositif d'assistance par plasma au vapocraquage non-catalytique de composés hydrocarbonés et halogéno-organiques, 1994a	Pompes Maupu, France	Upgrading of CFC *via* steam-cracking
PL 183985: Sposób wytwarzania siarki nierozpuszczalnej w disiarczku węgla (Method of obtaining sulphur being insoluble in carbon disulphide), 1996.	Instytut Chemii Przemysłowej, Poland	Conversion of ordinary sulphur into its polymeric state
FR 27637778: Procédé et dispositif de production d'un plasma hors d'équilibre, 1997, (see also FR 2775864)	Sunnen Technologies, France	GlidArc-II (rotating central electrode at ground potential)
FR 2758317: Conversion d'hydrocarbures assistée par les arcs électriques glissants en présence de la vapeur d'eau et/ou de gaz carbonique, 1997a (see also US 5993761, ID 23946, OA 10872, ES 2210715, WO 98/30524, EP 0914292, CA 2246878, AP 1038, and AU 735482)	P. Czernichowski and A. Czernichowski, France	Dry, steam or combined dry/steam reforming of light hydrocarbons
FR 2768424: Assistance électrique d'oxydation partielle d'hydrocarbures légers par l'oxygène, 1997b (see also US 6007742, OA 11460, EP 1012113, WO 99/11592, CA 2300962, UA 63966, AU 199891267, and NO 20001013)	A. Czernichowski and P. Czernichowski, France	First patent on GlidArc-assisted partial oxidation of light hydrocarbons
FR 2773500: Dispositifs électriques pour traitement thermique ou plasmachimique de mélanges d'un gaz avec des particules solides, 1998	A. Czernichowski	Heating and/or activating of refractory powders
FR 2774400: Dispositif électrique pour dégraissage, décapage ou passivation plasmachimique de métaux, 1998a	Etudes Chimiques et Physiques, France	Metal surface degreasing, pickling or passivation
FR 2817444: Générateurs et circuits électriques pour alimenter des décharges instables de haute tension, 2000 (see also US 6924608, WO 02/043438, EP 02/043438 and CA 2429533)	Etudes Chimiques et Physiques, France	GlidArc power supplying
FR 2842389: Dispositif modulaire pour générer de multiples décharges électriques glissantes de haute tension, 2002	Etudes Chimiques et Physiques, France	High power supplying for multiple GlidArc clusters

FR 2873306: Générateur GlidArc-III et son application à l'oxydation totale ou partielle de carburants, 2004	Etudes Chimiques et Physiques, France	Principle of GlidArc-III (central high voltage electrode and separate fluids input)
FR 2872149: Conversion plasma-catalytique de matières carbonées, 2004a, see also WO 2007/002719	Etudes Chimiques et Physiques, France	Enhancement of partial oxidation of carbonaceous matter

4.3 Institutes/companies working on the technology

Table 7. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Etudes Chimiques et Physiques Sarl	France	Broad range of research and development activities
Ceramatec Inc.	Utah	Reforming of various fuels into syngas for fuel cells
Breward Research Inc.	Florida	Distributed power and heat generation based on a waste bio-fuel
Kobe Steel Ltd	Japan	Afterburning of toxic flue gases
Aíbmi AB	Sweden	Large GlidArc reformers of various feeds into syngas
Aviosol AB	Sweden	Recycling of residual hydrocarbons into syngas for Fischer-Tropsch synthesis
Politechnika Warszawska	Poland	N_2O upgrading into NOx
EmeraChem Inc	Tennessee	Hydrogen generation from biodiesel for catalytic exhaust cleaning
Biomass Energy Foundation	Colorado	Distributed power generation from crude vegetable oils
Wesco Inc. (former Synergy Technologies Co., Alberta)	Texas	Reformer testing subcontractor

5. Stakeholders

5.1 Suppliers and developers

Table 8. Supplier and developers

Institute/Company	Country	Remarks
Etudes Chimiques et Physiques Sarl	France	Supplies and develops bench- and test-scale GlidArc devices and reactors for a broad range of applications
Breward Research Inc.	Florida	Designs small distributed power and heat generators based on a waste bio-fuel conversion to syngas
Aíbmi AB	Sweden	Designs MW-scale GlidArc reformers for syngas production

5.2 End users

Potential group of end users includes companies operating in the energy and chemistry sector. Gas-to-Liquids and/or Biomass-to-Liquids projects are probably the most important future users.

6. Expert’s brief final judgment on the technology

GlidArc devices present a new and inexpensive way of cold plasma generation, the way to provide easily controllable and very active energy to various processes. A variety of bench- and pilot-scale tests have already confirmed large benefit expectations for GlidArc-based or GlidArc-assisted technologies in several industrial domains. Within next 2-5 years GlidArc-related technologies will certainly participate in the further growth of green distributed electric energy as well as the biofuels production.