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GlidArc Assisted Preparation of the Synthesis Gas from Natural and Waste Hydrocarbons Gases

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Résumé — Arcs glissants pour générer le gaz de synthèse à partir des hydrocarbures légers — Cet article passe en revue l'utilisation des plasmas comme milieu activateur d'une oxydation partielle du gaz naturel ou d'un gaz associé pour produire le gaz de synthèse (H_2 + CO). Cette matière première peut être également convertie en syngaz dans un processus de reformage à la vapeur d'eau *(steam reforming)* assisté par plasmas qui, dans ce cas, exercent un rôle de catalyseurs et, en même temps, fournissent l'énergie très active nécessaire à une telle réaction, endothermique cette fois. Enfin, les mêmes plasmas peuvent être utiles pour effectuer une autre réaction endothermique de conversion directe des gaz hydrocarbonés contenant de fortes teneurs en CO_2 (tels que le biogaz ou certains gaz naturels acides) en syngaz.

Deux réacteurs à plasma à l'échelle du laboratoire sont utilisés pour tester les conversions : un réacteur à arc contrôlé et un réacteur plus récent, à multiples arcs glissants (GlidArc). Dans ce dernier, opérant jusqu'à une pression de 0,4 MPa, on obtient une conversion quasi totale du gaz naturel (1,3 m^3(n)/h) *via* oxydation partielle — avec une dépense d'énergie de seulement 0,11 kWh pour 1 m^3(n) de syngaz de rapport molaire H_2/CO proche de 2 — en utilisant l'oxygène pur comme réactif. Avec l'air enrichi (45 % O_2), la dépense est de 0,24 kWh.

Un pilote de 100 m^3(n)/h de syngaz est actuellement testé sur un champ de gaz naturel.

Mots-clés : GlidArc, arc contrôlé, gaz de synthèse, gaz naturel, gaz associé, biogaz, réacteurs plasma, décharges électriques, carburants synthétiques propres, oxydation partielle, reformage, Fischer-Tropsch.

***Abstract* — *GlidArc Assisted Preparation of the Synthesis Gas from Natural and Waste Hydrocarbons Gases* —** *This article reviews utilisation of plasmas as activation media for the partial oxidation of natural or associated gases to produce synthesis gas (H_2 + CO). These feedstocks can also be converted into syngas* via *plasma-assisted steam reforming. In this case plasmas play a role as catalysts and, at the same time, provide the very active and necessary energy for such reactions, which are endothermic this time. Finally, the same plasmas can be useful for another endothermic reaction, the direct conversion of hydrocarbon gases with high contents of CO_2 (such as biogas or certain acid natural gases) into syngas.*

Two bench-scale plasma reactors were used for the conversion tests: a controlled arc reactor and a more recent, multiple-gliding-arc reactor (GlidArc). In the last one, operating at up to 0.4 MPa pressure, one obtains almost total conversion of the natural gas (1.3 m^3(n)/h) via *partial oxidation—with an energy requirement of only 0.11 kWh for 1 m^3(n) of syngas at a H_2/CO molar ratio close to 2 when using pure oxygen as the reactant. With enriched air (45% O_2), the energy requirement is 0.24 kWh.*

A pilot of 100 m^3(n)/h syngas is currently undergoing field trials on natural gas.

Keywords: GlidArc, controlled arc, synthesis gas, natural gas, associated gas, biogas, plasma reactors, electric discharges, clean synthetic fuels, partial oxidation, reforming, Fischer-Tropsch.

INTRODUCTION

Conversion of light hydrocarbons (HC) into the synthesis gas (*syngas*, a mixture of mainly H_2 and CO) is an important chemical and petroleum activity. Lately applications in metallurgy, H_2-based transport and other domains have also become important. The most important application, however, remains natural gas (NG) conversion into synthetic fuels *(synfuel) via* Fischer-Tropsch (FT) syntheses in which syngas acts as a key intermediate. The results of our research activity in the plasma domain can improve classical technologies of syngas production, making them more energy efficient and environmentally friendly.

Syngas is conventionally produced by NG catalytic steam reforming. Thermal partial oxidation (POX) and CO_2 catalytic reforming of NG into syngas have also begun to attract industrial interest. Hundreds of papers and patents describe all these processes at different conditions and in presence of various catalysts. It would appear that almost all combinations have been evaluated and all strategies have been examined. However significant improvements may be achieved through a new approach: electric plasma assistance.

Electric energy is a very good tool to process any matter without creating a supplementary pollution effect. Specific electrical discharges produce extremely active species (electrons, ions, atoms, radicals, excited molecules like H, H*, H^+, H_2^*, H_3^*, O, O^+, O_2^*, O_2^+, O_2^-, OH, OH*, HO_2, C_2, CH, CH_2, CH_3, CO*, CO_2^*), which can strongly catalyse conversions of feeds of almost any description into more valuable products.

This paper illustrates some of our past results of HC-into-syngas conversion in different plasma reactors and adds new scenarios and experimental results for NG or biogas conversion into syngas. Syngas conversion was followed by conversion into clean liquid fuels performed in our experimental FT reactor. These experiments were conducted at quite a significant scale.

1 CHEMISTRY, THERMODYNAMICS, ENERGETICS

HC gases present in nature are light (almost pure methane) or heavy (as associated petroleum gases with a high content of ethane, propane and butanes), containing more or less of carbon dioxide (see also biogases), containing more or less nitrogen, sweet, or sour if containing H_2S, etc. Let us consider the main HC component of all NG, methane. Three main strategies of the syngas production can be illustrated by the following reactions:

$$CH_4 + H_2O_{vap} \rightarrow CO + 3H_2 \quad (\Delta H° = 205.7\ kJ{\cdot}mol^{-1}) \qquad (1)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (\Delta H° = 246.9\ kJ{\cdot}mol^{-1}) \qquad (2)$$

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \quad (\Delta H° = -36.1\ kJ{\cdot}mol^{-1}) \qquad (3)$$

where $\Delta H°$ are the standard enthalpies (at 298 K and 1 atm = 0.101 MPa).

Steam reforming (1) has two distinct drawbacks: it is strongly endothermic and produces a larger H_2/CO ratio (~ 3) than required (~ 2) for a subsequent FT process. Moreover, steam reforming requires a catalyst, another source of technological problems. Almost the same drawbacks are observed for strongly endothermic catalytic CO_2 reforming (2): too low H_2/CO ratio (~ 1). The mildly exothermic POX reaction (3) produces the syngas at an ideal H_2/CO ~ 2 ratio. Unfortunately, the heat of Reaction (3) is insufficient to keep moving it properly (it represents less than 5% of the full combustion heat) so extra heat and/or catalysts are necessary. For example, an $O_2/CH_4 >> 0.5$ ratio could be used to burn a part of the methane feed. However, this adds steam and CO_2 into the syngas.

Syngas is only an intermediate bridge to liquid synthetic fuels. For simplicity, let us consider only olefins (C_nH_{2n}) and paraffins (C_nH_{2n+n}) from the huge diversity of molecules. The schematic way of gas-to-liquid (GTL) conversion may be written as the following overall exothermic processes:

$$n\ [CH_4 + 1/2\ O_2] \rightarrow n\ [CO + 2H_2] \rightarrow C_nH_{2n} + nH_2O_{liq} \qquad (4)$$

$$nCH_4 + (n-1)/2\ O_2 \rightarrow ... \rightarrow C_nH_{2n+2} + (n-1)H_2O_{liq} \qquad (5)$$

so that only a part of the methane energy is recovered in final products. If we take as a reference the upper heat of CH_4 combustion reaction at the standard conditions:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{liq}\ (\Delta H° = -890.8\ kJ{\cdot}mol^{-1}) \qquad (6)$$

then the energy still conserved in the liquid FT products can be presented as a percentage of the initial energy of the feed. These percentages are between 75% and 74% respectively for C_6 and C_{12} olefins, or between 78% and 75% respectively for C_6 and C_{16} paraffins. It means that in the best GTL process some 22% to 26% of energy are lost in the FT process because of H_2O synthesis. That energy (heat of the FT process at 200-250°C) can be partially recovered.

For the mass balance, the CO molecule is the basic building block for any liquid HC product. Theoretically, starting from 0.571 kg or 0.800 m^3(n) [stands for normal cubic meters at 273 K and 0.103 MPa] of CH_4 feed, one may get at maximum 1.00 kg of CO in syngas and then 0.508 kg of $C_{10}H_{22}$. During such an ideal process one may conserve only 76% of the energy initially contained in the feed. But any real technology will lose much more energy through limited heat exchange, non-adiabatic reactors and compressors, over-oxidation of feed into CO_2 and H_2O, gaseous HC production in the FT step, etc. Such losses can be quantified as the feed mass loss. In whole, the amount of initial feed per mass or volume of the liquid product can quantify a GTL chain, for example as Mscf/bbl [thousands of standard cubic feet of NG per one barrel of synfuel].

As we are going to discuss the feed-into-syngas part of the chain, the energy (or mass) key factor will be defined as the "price" of 1 kg of CO in the syngas. This price can be given in kWh, in kg of O_2, in kg or in m^3(n) of the feed. It does not reflect yet any question about investment costs of the electric energy production, the energy cost of the oxygen supply, etc. However, any skilled engineer will answer such questions for his strategic choice: steam or CO_2 reforming, or POX, other mixed strategies like oxygen-enhanced steam reforming with a waste CO_2 re-use, or low- or high-pressure processes. Or a plasma-assisted conversion can be selected…

A process in which almost all the energy injected into an endothermic reaction in the gas phase, such as Reactions (1) or (2), will only be used to move it towards the products at an initial (low), constant temperature is not yet known. Such an ideal case can be only realised in liquid phase electrolysis. Unfortunately, classical gas endothermic processes always require a much higher heat import which makes the temperature increasing and, as a consequence, chemical equilibria shifting on the product side. One should then separate the products from non-reacted matter at that high-temperature equilibrium. But such separation requires substantially lower temperature operations so that fast quenching is necessary in order to avoid a decomposition of products or reverse reactions. How to recover most of the thermal energy during such a quench in order to limit the energy expense is a major question. Another is, How to preheat an entering feed and reactants at such particular conditions? Let us consider an energy expense for a purely thermal process in which there is no heat recovery. The Gibbs energy minimisation program gives the solution of quite complicated thermodynamic equilibrium equations.

1.1 Steam and/or CO_2 Reforming

In the 300-1300 K temperature range and at 0.1 MPa, the program gives the following main equilibrium products for $CH_4 + H_2O$ in 1/1 molar ratio:

$$CH_4 + H_2O \rightarrow C_s, CO, CO_2, CH_4, H_2, H_2O \quad (7)$$

The presence of CO_2 is not surprising because of the slightly exothermic "water shift" reaction, which takes place at the same time as Reaction (1):

$$CO + H_2O_{vap} \rightarrow CO_2 + H_2 \ (\Delta H^\circ = -41.2\ \text{kJ·mol}^{-1}) \quad (8)$$

We know from our experiments that in fast plasma-assisted steam reforming of methane (and in some other HC plasma-assisted processes) there is not enough time to precipitate significant amounts of solid carbon. We do not consider, therefore, any solid phase in such a quasi-equilibrium calculation. The program calculates also all the energetic properties of the system. Having the specific enthalpy of the whole system and relative amounts of all chemical species one can find a specific energy requirement (SER) to produce them *(Table 1)*. We are mainly interested in the SER for 1 kg of CO or for 1 m^3(n) of syngas (at the given H_2/CO ratio) production. As the energy unit, we propose MJ or the more common "electric" unit of kWh.

The SER for syngas production at 0.1 or 0.5 MPa is equal to 0.96 or 1.02 kWh/m^3(n), respectively.

Similar calculations are made for CO_2 reforming (2) at CH_4/CO_2 = 1/1 molar ratio where the same products were detected. Table 2 shows some outputs for 0.1 and 0.5 MPa.

The syngas production expense (SER) at 0.1 or 0.5 MPa is equal to 1.12 or 1.20 kWh/m^3(n), respectively. One gets more CO than the methane input because of the carbon dioxide import. Such a conversion of waste CO_2 into CO is endothermic. However, if the necessary energy is produced using a "clean" process, then the waste CO_2 can be considered as a carbon raw material to make a fuel.

Both Reactions (1) and (2) produce H_2/CO ratios that are not adapted to the ideal FT process. The energetic expense for CO production from CO_2 (dry) reforming of methane is however two times lower than the expense for CO from the steam reforming. A mixed CO_2/steam reforming of methane is a compromise *(Table 3)*:

$$3CH_4 + 2H_2O_{vap} + CO_2 \rightarrow 4CO + 8H_2 \quad (\Delta H^\circ = 219.4\ \text{kJ per mole } CH_4) \quad (9)$$

One finds the ideal $H_2/CO \sim 2$ ratio and the optimal SER of 8.69 MJ per kg of CO or otherwise 1.00 kWh per m^3(n) of syngas from such a mixed steam/$CO_2 = 2/1$ thermal reforming of methane at 0.1 MPa. This SER value can be compared to the standard enthalpy of Reaction (9) giving us the *minimum minimorum* SER = 5.88 MJ per kg CO. It means that one should use about 48% more heat to achieve that equilibrium at 1070 K.

1.2 Partial Oxidation

No direct heat input is needed for the exothermic reaction (3) to obtain CO. However, one should take into account the energy that should be used somewhere to produce 0.571 kg O_2 of pure oxygen. Let us look at the quasi-equilibrium in O_2/CH_4 = 0.5 system at 0.1 and 0.5 MPa. For such a process one can imagine that all reaction heat is conserved in a thermally isolated reactor kept at a constant pressure. In such a way the temperature of all reactive mixture of methane and oxygen entering at 298 K will increase up to a certain "adiabatic temperature". Table 4 presents such temperatures and corresponding quasi-equilibrium concentrations of products at 0.1 or 0.5 MPa for such an ideal thermal POX process (3). One can see that the methane-into-CO conversion is not yet complete at these adiabatic temperatures.

One can perhaps avoid paying the pure oxygen price using atmospheric air? What is an influence of the nitrogen ballast in such a case? Table 5 presents the outputs when the dry air is used for an ideal thermal POX of methane.

TABLE 1

Quasi-equilibrium composition for H_2O_{vap}/CH_4 = 1/1 reforming at 0.1 and 0.5 MPa and at the temperatures for which the minimum energetic expenses (SER) of CO are expected

Pressure (MPa)	Temperature (K)	SER (MJ/kg)	Moles per 100 initial moles CH_4					H_2/CO (mol/mol)
			CO	CO_2	H_2	CH_4	H_2O	
0.1	1110	11.3	89.8	2.1	278	8.1	5.9	3.09
0.5	1240	12.0	89.0	1.7	274	9.3	7.5	3.08

TABLE 2

Quasi-equilibrium composition for CH_4/CO_2 = 1/1 reforming at 0.1 and 0.5 MPa and at the temperatures for which the minimum energetic expenses (SER) for CO production are expected

Pressure (MPa)	Temperature (K)	SER (MJ/kg)	Moles per 100 initial moles CH_4					H_2/CO (mol/mol)
			CO	CO_2	H_2	CH_4	H_2O	
0.1	990	6.08	159	16.3	142	24.9	8.6	0.891
0.5	1080	6.32	152	17.9	126	30.6	12.7	0.832

TABLE 3

Quasi-equilibrium composition for $H_2O_{vap}/CO_2/CH_4$ = 2/1/3 reforming at 0.1 and 0.5 MPa and at the temperatures for which the minimum energetic expenses (SER) for CO production are expected

Pressure (MPa)	Temperature (K)	SER (MJ/kg)	Moles per 100 initial moles CH_4					H_2/CO (mol/mol)
			CO	CO_2	H_2	CH_4	H_2O	
0.1	1070	8.69	118	4.3	237	11.4	7.1	2.01
0.5	1190	9.16	115	4.1	229	14.0	9.9	1.98

TABLE 4

Quasi-equilibrium composition for the ideal thermal POX of methane at 0.1 and 0.5 MPa and at the adiabatic temperatures of the process when using pure oxygen

Pressure (MPa)	Adiabatic temperature (K)	Moles per 100 initial moles CH_4					H_2/CO (mol/mol)
		CO	CO_2	H_2	CH_4	H_2O	
0.1	1040	81.3	5.6	166	13.2	7.6	2.04
0.5	1135	77.1	5.8	154	17.1	11.3	2.00

TABLE 5

Quasi-equilibrium composition for the ideal thermal air-driven POX of methane at 0.1 and 0.5 MPa and at the adiabatic temperatures of the process

Pressure (MPa)	Adiabatic temperature (K)	Moles per 100 initial moles CH_4						H_2/CO (mol/mol)
		CO	CO_2	H_2	CH_4	H_2O	N_2	
0.1	940	63.3	12.4	140	24.3	11.9	188	2.21
0.5	1015	58.3	12.4	124	29.3	16.9	188	2.13

Again, the conversion of methane into CO at the adiabatic temperatures is insufficient (~ 60%). Certainly, there is somewhere an optimum when using an enriched air. Certainly, one can preheat entering reactants and get higher temperatures and better conversions. One should not forget that, for instance, we are allowing our products to exit at the process temperatures without any heat recovery…

1.3 Zero-Heat Fiction?

One can imagine such a mixed $H_2O/CO_2/O_2$ conversion for which the heat export of POX reaction (3) supplies the necessary energy import of the H_2O/CO_2 reforming (9). The theoretical solution is:

$$\begin{aligned} &100.0CH_4 + 42.9O_2 + 9.4H_2O_{vap} + 4.7CO_2 \\ &\quad \rightarrow 104.7CO + 209.4H_2 \end{aligned} \tag{10}$$

The result is however not attractive as only ~ 5% of a supplementary CO_2 feed can be integrated for CO production.

2 INDUSTRIAL PROCESSES

Steam reforming is performed in a radiation furnace where a catalyst, usually nickel on alumina, is contained in tubes heated by external burners. The temperature of most of the reformers is 700-900°C. Reformers contain a large number of tubes made of exotic high-temperature materials. They are therefore large and expensive units. Recent developments have allowed tube wall temperatures up to 1050°C corresponding to gas exit temperatures exceeding 950°C. Steam is used in large excess (two- to fivefold) to prevent carbon build-up on the catalyst. Pressures can be as high as 4 MPa. Methane conversion is around 80%, limited by the thermodynamic equilibrium. About half of the heat produced by combustion in the burners is transferred through the tube walls and absorbed by the reforming itself. Another half is available in the hot flue gas and partially recovered for preheat duties and to produce the steam.

Thermal POX is mostly carried out in the flame of a burner. The first step of the complete combustion of methane is fast and strongly exothermic, resulting in flame temperatures of more than 2000°C. The subsequent reforming reactions are much slower and strongly endothermic, cooling the resulting gases down to 1100-1370°C. Being slower, the reforming reactions require either a large reaction volume or a catalytic bed downstream of the flame. In a commercial POX, the feed is preheated and then mixed inside a burner. A flame is spontaneously produced with a separate preheat (150°C for O_2 and 480°C for NG). The reactor is a refractory brick-lined vessel. The oxidant can be air, enriched air as well as pure oxygen. If air or enriched air is used, nitrogen appears in the synthesis gas as ballast.

Thermal POX can also be conducted without a flame but in presence of a catalyst, which maintains the reaction and accelerates slower reforming reactions to establish thermodynamic equilibria. However, such a truly thermocatalytic POX has been restricted mostly to laboratory studies.

The hybrid combination of a flame + steam + catalytic bed is called *auto-thermal reforming*. It is a combination of POX and steam reforming, and has the advantage of avoiding the external heat input required in classical steam reforming. However, the catalytic reformer that follows the combustion chamber is exposed to the hot gases (1100-1400°C) so that high thermal stability of the catalyst and its support is required. Gas exits at about 1000°C.

The steam reforming and the thermal POX processes can be combined in series with optional heat integration between the exothermic and endothermic parts. Such a combined reforming optimises the H_2/CO ratio and minimises the manufacturing costs by balancing the cost of an expensive process using a cheap oxidant (steam reforming) with a cheap process using an expensive oxidant (POX). Heat integration between the oxidation and the reforming sections is mainly based on heating the steam reforming pipes with the hot POX products. Effluent gas exits at about 1040°C.

Commercial interest in carbon dioxide catalytic reforming ("dry reforming") originates from some need for the syngas composition with low H_2/CO ratios. Also, some HC gases (natural or biogases) contain too large amounts of CO_2 and would remain therefore unused. In these cases, CO_2 reforming of CH_4 may be the most effective method. Large-scale CO_2 reforming is not yet at a commercial stage because of catalyst deactivation through solid carbon accumulation, sintering of metal particles and/or their reaction with the support. Moreover, steam addition to the feed is required for successful operation.

Combinations of steam and carbon dioxide reforming with a thermal POX may give an interesting combined reforming process for supplying the syngas with a particular composition starting from a particular feed. If inexpensive CO_2 is available at the site, such a combined reforming may result in more favourable syngas composition and in higher conversion efficiency to methanol or synfuels, because the carbon dioxide can also contribute to the final product.

3 ELECTRICALLY ASSISTED SYNGAS PRODUCTION

Can the syngas production be modernised in order to lower feed demand, to avoid problems of catalyst poisoning and/or coking, to minimise the reactor size and weight, etc.? Electrical discharges (like transferred arc, GlidArc or similar) added to the chemical reactions open new ways of exploration and new issues for these problems. Adding and controlling an active electric energy as a supplementary parameter may allow production of syngas at the desired composition, temperature and pressure. The literature review shows some contributions in this field.

3.1 Literature Review

Our review indicates that experiments on plasma-assisted conversion of HC into syngas are quite rare or not disclosed. The principal difficulty has been an oxidative gas composition, which erodes classical electrodes of classical plasma generators.

Peters and Pranschke (1930) tested a reaction of methane with carbon dioxide or water vapour in a 5-6 kV electric discharge under 50 kPa. Gases were almost completely decomposed to CO, C_2H_2… and O_2!

Karl *et al.* (1957) prepared the syngas from propane or butane in an excess (40%) of steam in a glow discharge of 0.17 A at 3-5 kV/cm electric field. About 60% of feed was converted to products containing 25% CO and 61% H_2.

Heaston (1964) tried to operate classical plasma torch directly with methane or steam but extensive erosion of the anode prevented sustained arc operation for more than one minute so that a methane/steam mixture could only be heated in a tail-flame of a torch driven by argon. The Ar-CH_4-steam system worked best at about 2:1:4 mole ratio. The operating parameters were: arc current 400-600 A, DC (direct current) voltage 15-25 V, torch power 8.4-12.5 kW, and feed rate 3.9-5.3 kg/h. The exit gas composition was: 49-68% Ar, 9.2-27% non-reacted methane, 8.7-23% H_2, 1.4-13% CO, 0.4-1.7% CO_2, and some acetylene and ethylene (0.1-1.0%). The best results were: H_2/CO = 1.6-2.5 and the SER ~ 140 MJ per 1 kg of CO. One should add the price of the noble argon gas. No information on further work is found.

Leigh and Dancy (1975) heated a $CH_4/CO_2 \sim 1$ mixture in an argon plasma torch where as much as 70% of injected electrical energy went to the water-cooling. Argon flow rate was 42 L/min. From 20.5 up to 60 L/min of the mixture was injected at the torch plume. The exit gas was composed of H_2, CO, CH_4, CO_2, C_2H_4, C_2H_6, and non-reacted methane. The carbon conversion was between 11% and 74% depending on the mixture flow rate (higher conversion for lower flow rates). The noble argon gas consumption and the process energetics do not make it easy for an industrial application.

Capezzuto *et al.* (1976) studied the methane conversion with CO_2, O_2 or H_2O (at oxidant-to-CH_2 ratio of 1) in a 35 MHz discharge (max. 10 kW) in argon. The reactor at 30 kPa was fed at gas flow rates from 3 to 36 L(n)/min at power densities from 4 to 33 J per cm^3. For all three oxidants, the conversion of CH_4 reached almost 100%. In CO_2/CH_4 system, the main products were H_2, CO, C_2H_2 at a presence of C_2H_4 (< 5%) and traces of C_2H_6 (< 1%). In H_2O/CH_4 system, the main and secondary products were the same (with additional traces of CO_2). In the system $O_2/CH_4 = 1$ (so at twofold oxygen excess), the main products were H_2, CO, CO_2, H_2O and the secondary products were C_2H_2 (< 5%) and C_2H_4, C_2H_6 (< 1%); the typical product composition was: H_2 42%, CO 27%, CO_2 6% and H_2O 25% which corresponds to the equilibrium composition of the water shift reaction at the gas temperature of about 2000 K, much higher than the estimated 800 ± 150 K for the discharge conditions. The noble argon gas consumption, radio-frequency power supply utilisation, and low-pressure reactor chamber make the process non-useful for an industrial application.

Santen *et al.* (1985) have proposed a steam reforming of gaseous HC heated entirely or partially with the aid of plasma generator(s) to temperature exceeding 1200°C without use of classical reformer tubes or catalysts.

Kerker (1987) made a review (with no references) on manufacture of gaseous reductants and syngas using arc plasma processes.

Finally, Kogelschatz *et al.* (1999) investigated theoretically and experimentally a high-power dielectric-barrier discharge in CH_4/CO_2 in full concentration range and observed a synergetic effect caused by free radical reactions. The tested ranges were: 100-800 W power, 0.1-4 L(n)/min gas flow rate at 0.035-0.2 MPa pressure and 80-250°C reactor wall temperature. This technique provided a syngas with different H_2/CO ratios depending mainly on the initial CH_4/CO_2 ratio. The amount of produced syngas rose almost linearly with increasing discharge power. Up to 66 moles of syngas with a H_2/CO ratio of 3.7 were obtained from 100 moles of feed gas in a single pass through the reactor of 31 cm active length. The minimum required specific energy was 48 kWh/m^3(n) for the production of syngas and the highest energy efficiency (electric energy converted to chemical energy in the syngas) reached was about 7%.

3.2 Our Previous Experiments in the "Controlled Arc" Reactor

The production of syngas from methane was demonstrated first in our "controlled arc" as an energy and activation source (Jorgensen *et al.*, 1986). The process used such an arc to provide the endothermic heat for CO_2 dry reforming or an amount of energy just necessary to assist a POX by oxygen. Figure 1 presents a schematic view of the reactor containing a classical plasma torch as the first stage, the feed and oxidant introduction (mixing system), and a controlled discharge chamber with the second anode. The torch had a thoriated tungsten cathode and a copper anode with a hole. Both electrodes were water-cooled. The torch was fed by pure argon and DC power (about 100 A under about 20 V) and provided an ionisation of the two-stage reactor. A plasma jet was injected to the reactor chamber. The second anode (for a transferred arc) was located at 20 to 100 mm from the

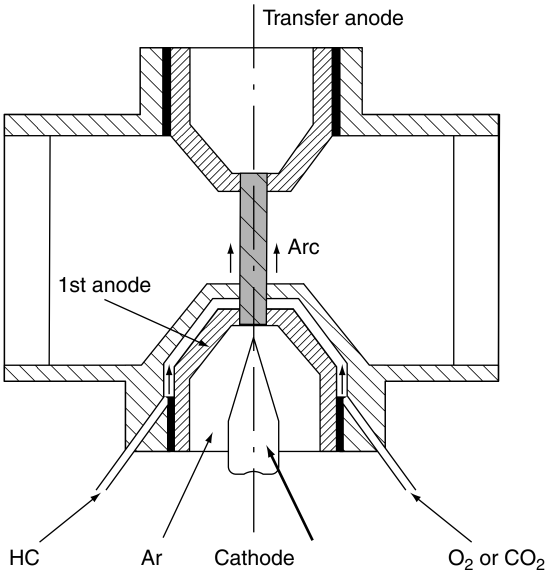

Figure 1

Schematic view of the controlled arc reactor.

first anode and had a hole. The second DC power supply was connected to the common cathode and the second anode through a resistance. In such a way, two power supplies provided the energy simultaneously: the first one for the torch and the second for the transferred arc. Methane (or ethane) and CO_2 or O_2 were introduced separately into argon plasma jet just at the level of the first anode exit. The reactions took place in the transferred arc where the presence of organic carbon and the oxidation process provided some electric conductivity of the gas. This allowed input of a certain amount of electric energy eventually added to the chemical energy of the POX. The gas products were cooled to ambient temperature.

Very interesting static and dynamic plasma characteristics were observed in the jet exiting the primary torch as well as in the main arc column. A Langmuir-like probe put into the transferred arc with CH_4 feed showed a high depression of the electron concentration in the plasma by an electron attachment and negatively charged radical production. It decreased the electric conductivity of the arc column, which allowed us to increase the voltage necessary to pass the electric current through such a column, and therefore to inject more power into the arc. Another probe immersed into the decaying plasma column at 20 cm from the second anode indicated a very high potential difference signalising still active electric charges (ions and electrons).

Static volt-ampere characteristics between two anodes for different plasma forming gases were very different for $CH_4 + O_2$ or $CH_4 + CO_2$ mixtures as compared to non-reactive gases. One observed an instability zone at lower currents where the arcs started to whistle, oscillate and had a tendency to disappear. Under some special arrangements of the electrical supply, we could however quite easily inject and control the power even at the instability region of the characteristics. Our further chemical experimentation has shown that such well-controlled electrical instabilities play a very positive role in the chemical processes efficiency and energetics.

Very different dynamic characteristics were observed when using instruments allowing fast voltage measurement and amperage arc fluctuations. These characteristics showed a strong difference between a non-chemical milieu and a chemical milieu. In pure argon, the voltage fluctuations were very small. A drastically different picture corresponded to the reactive mixture where quasi-periodic (~ 5 kHz) voltage fluctuations of almost 100 V (so about 100% of static voltage value) were detected. This phenomenon is due to the presence of electronegative species in the ionised gas. The electrons are captured by such species from the methane decomposition, which contributes to the whole ionisation (and electro-conductivity) decrease. It gave rise to the voltage and therefore made it easier to re-establish the current. Similar phenomena were observed in CO_2 + Ar mixture where the voltage fluctuations became as high as 60% at about 2 kHz. The presence of fast power oscillations induced very effective mixing and contributed to speed up chemical reactions in the gas. Despite such instabilities, it was possible to finely control the electric energy injected to the discharge.

Several chemical conversions were carried out at pressures up to 0.2 MPa. The methane flow ranged from 10 to 100 L(n)/min. Some tests were also performed with pure ethane at a constant flow of 3.5 L(n)/min. The argon-driven torch was powered at about 2 kW. The second anode for the transferred controlled arc (up to 10 kW) was at about 20 mm from the first one. At the exit from the second anode, the gas temperature ranged from 1100° to 1800°C. Our results underlined that chemical data rather than energetic ones such as the SER for that process can only be considered as rough indications: our reactor was too small, over-cooled and without heat recovery. However, the potential for larger scale projects was observed.

3.2.1 O_2 Reforming of Methane

When 12 L(n)/min of argon were fed into the plasma torch at 2.2 kW dissipated power and 8.0 L(n)/min of CH_4 + 2.2 L(n)/min of O_2 were injected to such non-transferred plasma at 0.18 MPa, the exiting gas analysis showed the following relative concentrations (argon considered as a blend):

$$CH_4:CO:CO_2:H_2:C_2H_2:C_2H_4:C_2H_6:H_2O$$
$$= 0.82:0.45:0.05:1.00:0.09:0.02:0.02:0.35$$

with no apparent soot. It corresponded, however, to only partial (48%) methane conversion. The selectivity of CH_4-into-CO oxidation was only 59% so that the energy expense (SER) for CO production (contained in the synthesis gas at $H_2/CO = 2.2$) was about 46 MJ/kg. One should add to that a cost of about 7.5 kg of argon (to recycle?) for 1 kg of produced CO. When calculated as the SER for the syngas production the expense was equal to 5.0 kWh/m^3(n).

For the same argon-fed torch powered at 3.5 kW level with added transferred arc of 5.7 kW, 7.6 L(n)/min of CH_4 + 2.6 L(n)/min of O_2 at 0.13 MPa, the exiting gas analysis showed the following relative concentrations (argon considered as a blend):

$$CH_4:CO:H_2:C_2H_2:C_2H_4:H_2O$$
$$= 0.01:0.35:1.00:0.09:0.02:0.06$$

with only minor CH_4-into-soot conversion and no apparent CO_2 in the product. It indicated an almost total methane conversion into products. The selectivity of CH_4-into-CO conversion was 61%. The energy expense (SER) for CO production (at $H_2/CO \sim 2.8$) was about 96 MJ/kg. One should add to that a cost of about 3.5 kg of argon per kg of CO. When calculated as the SER of the syngas production the expense was equal to 8.8 kWh/m^3(n).

3.2.2 CO_2 Reforming of Methane

Many more experiments were performed for CO_2 reforming of methane in a small controlled arc reactor (Meguernes *et al.*, 1993). The newest results at 0.1 MPa from the reactor are resumed in Table 6. The test parameters were the following ones:

– argon input	3.5-4.5 L(n)/min
– methane input	6.2-6.4 L(n)/min
– plasma torch power	2.0 kW

TABLE 6

Results of dry reforming of methane in the controlled arc reactor after Meguernes (1998)

CO_2/CH_4	H_2/CO	SER CO (kWh/kg)	SER syngas (kWh/m^3(n))
0.52	1.8	9.3	4.2
0.75	1.2	6.4	3.6
1.04	1.0	4.7	2.9
1.25	0.86	4.7	3.2
1.55	0.71	4.5	3.3
1.75	0.61	4.0	3.1
2.00	0.54	3.7	3.0

Controlled reactors, requiring water cooling and argon for cathode protection, are inconvenient for working with steam (which would condense on all water-cooled parts of the reactor)… All that makes such reactors quite complex for an industrial application. Presently, the similar process can be performed in so-called GlidArc reactors with nearly 100% efficiency of electric-to-thermal energy transfer and without any erosion of electrodes.

4 GLIDING DISCHARGES (GLIDARC)

Production of syngas from natural HC gases or biogases was tested in bench-scale reactors based on gliding arcs (GlidArc) (Lesueur *et al.*, 1988). This powerful and highly active non-thermal plasma source is particularly adapted to chemical processing of gases, vapours, dispersed liquids or solids. Our new GlidArc-II and SynGen reactors have begun to emerge as even more adapted for some processing of HC.

The GlidArc-I reactor has at least two diverging knife-shaped electrodes. These electrodes are immersed in a fast gas flow. The progress of an arc discharge is depicted in Figure 2. A high-voltage and relatively low-current discharge is generated across a gas flow between the electrodes. The discharge forms at the closest point, glides along the electrodes, and disappears. Another discharge immediately reforms at the initial spot. Geometry of the electrodes, flow conditions, and characteristics of the power supply determine the path of the discharge that performs its own maintenance on the electrodes, preventing chemical corrosion and erosion. The electrodes do not need to be cooled so the electrical energy is directly and totally transferred to the processed gas. The voltage can be as high as 20 kV for currents as high as 50 A. Multiple-discharge systems can be installed easily in large gas lines.

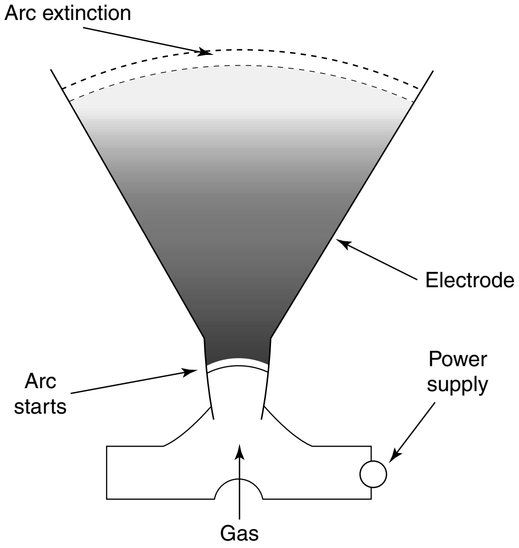

Figure 2

The GlidArc-I principle.

Almost any gas or vapour can be directly processed. Droplets, mists, and powders can be present. A gas of any initial temperature is acceptable. Gases have already been tested successfully at pressures between 5 kPa and 1.2 MPa. The pressure drop in the reactor is negligible. In terms of capital and operating costs, the GlidArc-based processes are inexpensive. Several application tests were performed in laboratory or pilot-scale GlidArc reactors for gases, vapours, flames, and/or condensed matter processing (Czernichowski, 1994). Four main fields have been explored:

- destruction (with or without upgrading) of hazardous gases and vapours like volatile organic compounds (VOC), H_2S, mercaptans, SO_2, chlorofluorocarbon (CFC), and polynuclear aromatic hydrocarbon (PAH);
- advanced chemical syntheses of syngas *(present paper)*, H_2, acetylene, CO;
- stabilisation of flames or over-heating of gases or vapours, like steam drying;
- processing of solid matter, like soot incineration, foundry sand cleaning, metal degreasing or wool activation.

4.1 Steam and/or CO_2 Conversion

Some preliminary tests of the GlidArc-I-assisted conversions were already published (Meguernes *et al.*, 1993; Lesueur *et al.*, 1994). New, more systematic studies of Processes (1) and (2) were recently performed in Orléans for different CO_2/CH_4 mixtures and partially published (Czernichowski, 1998, 1999). The process is illustrated by the conversion of a model-HC "heavy" gas:

– CH_4	91 vol%
– C_2H_6	6.7 vol%
– C_3H_8	1.1 vol%
– C_4H_{10}	0.3 vol%
– N_2	0.9 vol%

A six-phase reactor worked at atmospheric pressure and had six stainless steel, 0.8 mm thick sheet electrodes, 14 cm long, 25 mm wide. The reactor of 80 mm inside diameter had a 1.5 L capacity [a similar reactor is shown in Figure 3, Section 4.2]. Electric power was from 0.6 to 1.1 kW, under 0.1 or 0.2 A (sequential discharges of 1 to 20 ms lifetime). Using a 1.8 mm nozzle, we introduced a gas flow from 0.6 to 1.2 m^3(n)/h so that specific energy input (SEI) ranged from 0.5 to 1.2 kWh per m^3(n) of all entering gas (HC and oxidisers). We did not observe any problem as concerns very long tests; the reactor had excellent stability. It can work at higher pressures up to 0.6 MPa. A quite simple high-voltage power supply is used; its open circuit voltage is 10 kV (average, with respect to a floating zero potential), at the frequency of 50 Hz. Some selected results of our NG-into-syngas experiments are showed in Table 7.

Chemical analyses are made by using classic gas chromatography methods dedicated to CO, CO_2, O_2, N_2, H_2, CH_4, and other HC. The water vapour content in the products is calculated from mass balances or quantified by trapping a known volume of exiting gas.

Forty-four new tests were then performed in newer GlidArc-I reactors at about 0.1 MPa for simulated natural (or bio-) gases containing CO_2. Some parameters of these tests and obtained results were:

Entry:	Gas flow	0.32-0.87 m^3(n)/h
	CO_2 in gas	24-90%
	Added steam	up to 0.42 m^3(n)/h
	Added oxygen	up to 0.12 m^3(n)/h
	SEI	0.46-3.2 kWh/m^3(n)
	Reaction temperature	170-565°C
Exit:	H_2/CO	0.13-2.8 (mol/mol)
	SER for H_2 + CO	2.8-9.5 m^3(n)/h
	Total C conversion	9-59%
	C select. into CO	45-99%

TABLE 7

Steam, dry (CO_2) or mixed steam/CO_2 reforming of a model-HC gas

Example		G1	G2	G3	G4	G5	G11	G12	G21	G22	G23
Input	HC	424	424	424	424	424	328	328	495	484	446
(L(n)/h)	CO_2	0	0	0	0	0	438	438	52	138	138
	steam	473	606	785	803	460	0	0	332	254	177
SEI	kWh/m^3(n)	1.1	1.0	0.90	0.47	1.2	0.75	1.4	1.2	1.1	1.3
Temperature (°C)	preheat	220	215	215	200	250	140	165	240	230	230
	reaction	630	590	560	490	680	290	380	665	660	675
H_2/CO	mol/mol	3.9	3.8	3.8	3.9	4.5	0.84	0.82	3.3	2.6	2.5
SER											
H_2 + CO	kWh/m^3(n)	3.0	3.2	3.3	3.2	3.0	2.6	3.6	2.9	2.9	3.3
CO	kWh/kg	12	12	13	13	13	3.9	5.3	9.9	8.4	9.1
C converted	%	25	24	24	13	24	17	23	23	21	19

Specific observations and partial conclusions are as follows:

- the presence of non-saturated HC in syngas (2.1 to 4.7 vol% of C_2H_2, 1.0% to 2.0% C_2H_4 and 0.05% to 0.15% C_3H_6) is very useful from the point of view of the FT syngas-into-syncrude step *(see below)*;
- the global conversion rate of HC in all experiments was limited to better study the individual conversion phenomena of each NG component; we found that dry reforming of HC heavier than methane along with CO_2 to be easier. The total carbon conversion ("C conv.") can obviously be greater, for example, following an increase of the SEI;
- we have demonstrated a new, non-catalytic HC conversion process assisted only by gliding discharges in the simultaneous presence of steam and CO_2. A wide range of ratios of two oxidisers can be used. One observes $H_2/CO < 1$ ratios when the CO_2 content is higher than 50% at the absence of the steam. The $H_2/CO \sim 4$ ratios are observed for pure steam reforming. For a mixed steam/CO_2 reforming an ideal ratio of 2 can be obtained when playing with the steam addition. As required for a specific process, we can produce a syngas for the syncrude or methanol syntheses, or a syngas very rich in hydrogen for fuel cells or ammonia synthesis, or yet syngas very rich in CO for "oxo" syntheses...;
- no soot, coke or other undesirable products from the conversion of HC were observed in the products;
- for almost the same CO_2/HC gas composition and very similar SEI values one can observe some positive influence of the gas preheat temperature on the energetic expense (SER) for the syngas production;
- H_2/CO ratios are poorer for higher CO_2 concentrations in the feed gas; at the same time the energetic expenses for H_2 + CO production increase…;
- any HC + CO_2 + feed can be converted directly into $H_2/CO \sim 2$ syngas, if CO_2 concentration is less than 40%. For such an endothermic process, the energetic expense for 1 m^3(n) of syngas is about 3.1 kWh and 0.6 m^3 HC per m^3 of product. A part of the CO_2 in the feed is converted into CO. But we have already obtained a lower energetic expense for the H_2 + CO mixture production at a level of 2.8 kWh/m^3(n) for a poor HC gas (66% CO_2) when our new SynGen concept was tested.

Any thermal energy can be integrated to the process in order to preheat the feed and/or oxidant and therefore to lower the electric energy expenses. Such could be a case of a "low-tech" solar heater or, better, more condensed solar radiation flux acting both as a thermal and as a radiative energy source for a direct quanta absorption in the electric discharge in presence of CH_4 and/or CO_2 (Czernichowski *et al.*, 1997). One can therefore imagine producing a biogas from organic wastes (a classical step), which is then totally plasma-converted into the syngas (and then into synfuels) or only partially converted into a syngas-enhanced biogas fuel (Koulidiati and Czernichowski, 1999).

4.2 POX Conversion

Improvements of the GlidArc-I reactor were made in order to work at as high as possible gas preheat temperatures, reactor wall temperatures, pressure, and total gas flow. The reactor /1/ shown in Figure 3 uses six electrodes /2/ in profiled steel sheet, 2 mm thick (only two of the six electrodes arranged symmetrically around the flow axis of the fluid to be processed are shown). Each of the electrodes has a length of 8 cm and a width of 25 mm. The electrodes delimit a nozzle-shaped volume /3/ where gliding discharges /4/ may develop. This reactor contains a simple nozzle /5/ with a diameter of 4 mm, blowing the premixed fluid /6/ to be converted in the space /7/ between the electrodes arranged so that the fluid flows along the central part of these electrodes exposed to the

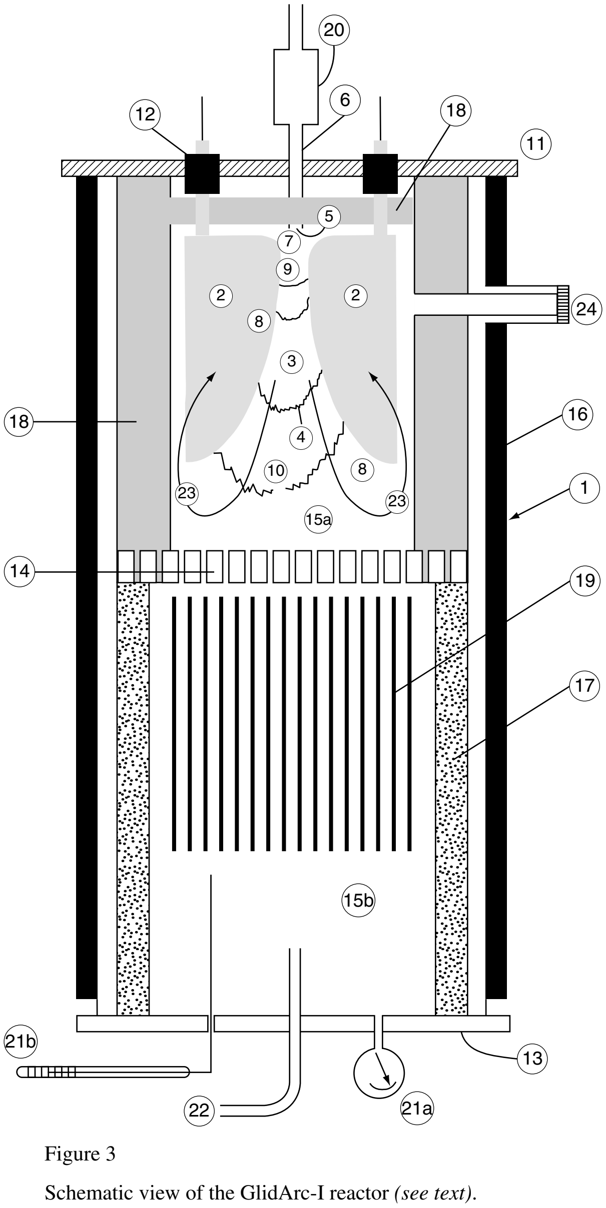

Figure 3

Schematic view of the GlidArc-I reactor *(see text).*

discharges. Another more complex "double nozzle" can also be used; it consists of two concentric pipes through which arrive the HC feed, possibly mixed with steam, and the oxygen, oxygen-enriched air, or atmospheric air, all three being eventually mixed with steam. In this case, the reactants are mixed in such a double nozzle or outside of it, just near the electrodes. Several nozzles may be arranged in the same reactor. The discharges that preionise the gas at the point /9/ (where the distance between the electrodes is the smallest) glide on these electrodes and disappear at the point /10/ near the end of the electrodes, to reappear once again at the initial point. The process is sequential and the lifetime of a discharge /4/ observed ranges from 1 to 20 ms, depending on the linear speed of the fluid in zones /7/, /9/, /3/ and /10/, between the electrodes. Given the moderate temperature (< 1200°C) of the electrodes and a very short contact time of the discharge root /8/ with the electrodes, even in non-cooled steel, we do not observe any deterioration that may prevent the gliding of these current-limited discharges. The discharges have variable characteristics from the point where they are initiated to their extinction with, in particular, dissipation of energy that increases over time. Two covers close the tubular reactor. One of them /11/ supports the electrodes that are isolated electrically with high-voltage connections /12/. The other /13/ closes the reactor on the other side and comprises a product output tube /22/. The entire structure is tight; it supports a pressure of 0.6 MPa. A perforated plate /14/ separates a plasma zone /15a/ and a post-plasma zone /15b/ partially filled with solid material. The two zones are housed within the same reactor. The plate /14/ makes it possible to run products from the plasma treatment to the post-plasma zone. The reactor (outer diameter of 85 mm and height of 88 cm) is insulated externally by a ceramic felt /16/. We packed the inner walls of the post-plasma zone of the reactor with a ceramic tube /17/ with an inner diameter of 55 mm. The plasma chamber is insulated by a heat-resisting felt /18/. The total free volume of the reactor is 1.9 L. The volume of the solid material /19/ inserted in the post-plasma zone /15b/ (in most cases we use metal nickel sticks with a total mass of 1.5 kg) is 170 cm^3, which corresponds to a geometric surface of 1670 cm^2. The ratio between the volumes of solid material inserted in the post-plasma zone and the unfilled volume of this zone is 1:6.5, while the ratio between the volumes of the plasma zone /15a/ and that of the post-plasma zone is 1:2.4. No part of the reactor is cooled in a forced manner. The incoming fluids /6/ may be preheated together (or separately) with a controlled temperature resistance furnace(s) /20/. Two holes in the cover /13/ provide for the connection of a pressure gauge /21a/ and for the insertion of a thermocouple /21b/. The products of the conversion exit the reactor through a tube /22/. With almost punctual injection of the fluid between the electrodes we already provoke a phenomenon of recirculation /23/ of the reactants in the gliding discharge zone. In order to reinforce this recirculation, we also add a separating plate /14/, thus dividing the reactor in two parts. The perforated plate provides for the flow of reactants (partially consumed) and "long-living" active species resulting from the excitation of the gases by the gliding discharges. In the post-plasma zone, the conversion is thus susceptible of being completed in the presence of solid material /19/ and in an environment where the temperature is much lower than that of the walls and electrodes of the plasma zone. The fluid, once in this post-plasma zone, cannot re-enter the plasma chamber. The luminous zone of the gliding electric discharges, as well as part of the wall of the zone, can be observed through a glass /24/ in order to verify the proper operation of the reactor and to determine the temperature in the compartment /15a/. An important information may be derived from the plasma emission spectrum (Koulidiati *et al.*, 1998). The conversion of a NG is generally sufficient with a single run through a single reactor. Otherwise, the products partially converted in one reactor may be reprocessed in several reactors thus described and arranged sequentially.

The presence of the perforated division plate creates a post-plasma reactive zone, where highly active and metastable species (thus having catalytic properties), making it possible to reform HC originating from violent reactions in the plasma zone, can deactivate themselves on other molecules, directly in the gaseous phase or indirectly on the surface of solid material inserted in the zone. It makes possible to advance further the conversion of the reactants as the atomic and molecular species have a lifetime sufficiently long to cover great distances in gas flows, even at atmospheric pressure or higher pressures. This phenomenon is very important for the conversion of HC components known for their fragility. In fact, the action of a non-thermal (or non-equilibrium) plasma makes it possible to avoid the coking of the HC feedstock. Long operating times of the reactor thus built and a good transparency of the glass (all in the presence of HC as fragile as propane and butanes) constitute the best evidence of "soft" transformations that may be carried out in such a reactor.

The reactor is fed by controlled volumes of gas taken from gas cylinders (or other sources) and/or by water vapour originating from a steam generator. The reactor may also be fed with water through the use of a metering pump. The constant flow of water, controlled by a valve and a flow-meter, is thus evaporated in the furnace /20/, and then injected into the reactor, being previously mixed or not with another fluid of the process.

Pure O_2 or an enriched air, both eventually mixed with the steam, was used as the oxidiser. Input parameters of 57 tests are the following:

Electric power	up to 0.98 kW
HC-gas flow	0.25-1.3 m^3(n)/h
Added steam flow	up to 0.78 m^3(n)/h
Added oxygen flow	up to 0.61 m^3(n)/h

Added air flow	up to 0.90 m^3(n)/h
Total input gas flow	0.66-1.6 m^3(n)/h
CO_2 concentration in initial HC gas	0.2-78%
Free O_2 concentration in oxidising gas	43%, 45% or 99%
SEI	up to 0.58 kWh/m^3(n)
Temperature of gas preheat	up to 680°C
Temperature of reaction chamber	up to 1115°C
Absolute pressure	0.13-0.40 MPa

Figure 4 shows some initial tests of POX of a NG (97.3% CH_4, 1.4% C_2H_6, 0.3% C_3H_8 and 0.1% C_4H_{10}). The NG is mixed with pure oxygen according to a constant O_2/NG ratio of 0.48, and then injected into the reactor without preheating. The 1.3 m^3(n)/h flow of the mixture, the pressure in the reactor (0.15 MPa) and the electric supply settings are maintained as constant. The reactor, initially cold at the beginning of the tests, is heated progressively and the exiting products are sampled at naturally increasing post-plasma zone temperatures. The electric power dissipated in the plasma zone varies little so that SEI = 0.29 ± 0.03 kWh/m^3(n). The results show that it is preferable to convert a NG when the post-plasma zone reaches a temperature of at least 480°C since, for lower temperatures, all performance indicators of the process are poorer. By going from 130° to 480°C, we get closer to the desired H_2/CO ratio of 2 (from 0.46 to 1.6), we obtain almost six times more syngas from a unit volume of HC, and this at an energy price over seven times better. These great improvements are also visible from other figures: the conversion of carbon increases by 1.8 times and this rather towards the desired product (CO) than to the undesired molecule (CO_2). By increasing the temperature in the post-plasma zone, we also conserve much more hydrogen H_2 by lowering the relative selectivity of water vapour formation.

Figure 5 shows some tests where a very similar "light" NG is mixed with pure oxygen in variable O_2/HC ratios = 0.49 to 0.65, and then injected into the reactor without preheating. For a constant pressure (0.15 MPa), the flow of the incoming mixture (1.3 to 1.6 m^3(n)/h) and the settings of the electric supply are kept quasi-constant. This time, the entire reactor is closer to its thermal plateau and we keep the SEI values almost constant at a level of 0.15 ± 0.03 kWh/m^3(n). At this level, we add very little energy to the POX of the NG; instead, we "electrify" it. The results of this series of tests inform us that it is preferable to convert a NG when the O_2/HC ratio reaches a value near 0.65. At this level, we obtain very good results of total conversion of carbon and oxygen, we approximate (1.94) the desired H_2/CO ratio of 2.0, we produce 2.6 m^3 of syngas per 1 m^3 of HC feed, all that at the very low energy expense (SER) of 0.11 kWh per 1 m^3(n) of syngas. These results are also readily apparent from the selectivities of the carbon conversion. Curiously, these selectivities evolve rather towards the desired product than towards the parasitic CO_2. Another surprising point is that, by increasing the O_2/HC ratio, we produce more H_2 and the selectivity of water vapour formation decreases.

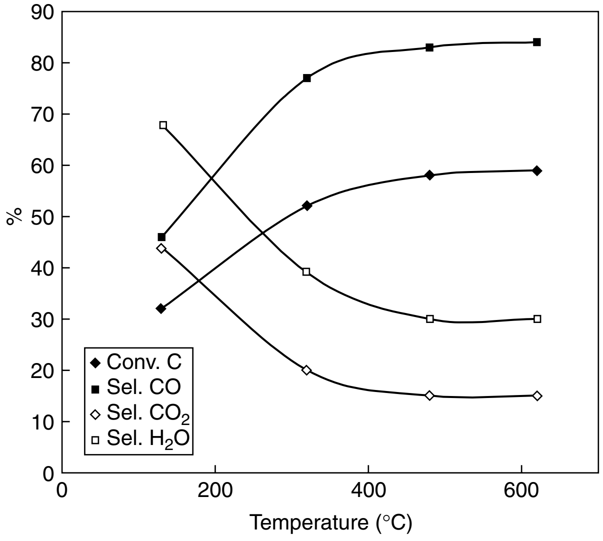

Figure 4

POX of a light NG with pure oxygen at O_2/NG = 0.48 as a function of the reactor wall temperature; 0.15 MPa, GlidArc-I electric settings are maintained constant.

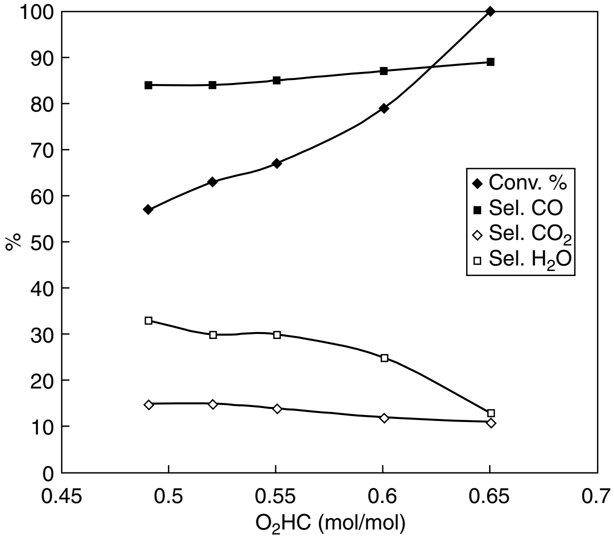

Figure 5

POX of a light NG with pure oxygen at O_2/NG = 0.48 as a function of the O_2/HC ratios; 0.15 MPa, a thermal "plateau" temperature, GlidArc-I electric settings are maintained constant.

Table 8 summarises seven tests of POX of a NG with oxygen and added water vapour. The question was: Can we convert a NG with less oxygen by replacing it with steam, while maintaining a relatively low energy price (SER) for syngas with a composition similar to the H_2/CO ratio = 2? The target NG was heavier: 91.6% CH_4, 6.2% C_2H_6, 1.7% C_3H_8 and 0.5% C_4H_{10}. It was mixed with pure oxygen and steam in variable proportions. Only a light preheating (115-150°C) was used. For a constant pressure of 0.15 MPa, the flow rate of the mixture (1.7 to 2.0 m^3(n)/h) and the electric supply settings were kept almost constant. The reactor was close to its thermal plateau (~ 1030°C for plasma zone and ~ 840°C for post-plasma zone) and we kept almost constant the SEI values at a level of 0.24 ± 0.02 kWh/m^3(n).

The results show us that it is possible to obtain a mixture very close to the ideal mixture of $H_2/CO = 2$, by oxidising the HC feed with a deficit of $O_2/HC = 0.33$, provided that this missing oxidising agent is replaced by steam. The overall limited conversion rate can be brought to almost 100% by increasing the SEI. Analysing individually the conversion rates of each HC component of the NG, we observe that the heavier HC reacts more readily; for example, for an overall carbon conversion rate equal to 32%, the butanes and the propane are fully converted, the ethane is converted at 97%, while the conversion of methane is limited to 19%. Therefore, our POX assisted by gliding discharges could be applied regardless of the HC content of a NG to be converted.

Interesting results are obtained when the POX of a NG with oxygen and added steam is performed in the presence of another material in the post-plasma compartment. In fact, instead of nickel sticks present in the zone during the previous tests, we filled this zone with large pieces of a ceramic brick to study an influence of the nature of the solid introduced in the post-plasma zone. A "heavy" NG (90.7% CH_4, 6.9% C_2H_6, 1.9% C_3H_8, and 0.5% C_4H_{10}) was mixed with pure oxygen and steam in variable (molar) proportions: $O_2/HC = 0.22$ to 0.58, $H_2O/HC = 0.72$ to 1.22. A light feed preheating (150°C) was used. For a constant pressure of 0.15 MPa, the flow of the mixture (1.6 to 2.1 m^3(n)/h) and the electric supply settings were kept almost constant. The reactor was at its thermal plateau (~ 990°C for plasma zone and ~ 890°C for post-plasma zone) at almost constant SEI values of 0.24 ± 0.04 kWh/m^3(n). The results show that it is possible to obtain a mixture very close to the ideal mixture of $H_2/CO = 2$, by oxidising the HC feed with a deficit of $O_2/HC = 0.22$, provided that this missing oxidising agent is replaced by steam. We create a lot of ethylene and acetylene in the syngas as the selectivity of carbon conversion into C_2H_4 and C_2H_2 reaches 25% and 5% respectively. This indicates the possibility of controlling closely the ethylene and acetylene contents in the syngas depending upon the nature of the solid material placed in contact with the flow of gas resulting from the electro-treatment in the plasma zone of gliding discharges. The relatively high SER, up to 1.4 kWh/m^3(n), is not surprising as it does not take into account the syntheses of two very energy intensive products. In our definition, the SER is the quantity of electric energy (in kWh) consumed to produce 1 m^3(n) of syngas so that other products such as acetylene or ethylene are not taken into account and considered as "gratis".

Table 9 summarises seven tests of POX of a NG with O_2-enriched air and eventually mixed with water vapour. The questions were: Can we convert a NG with such enriched air (for example, of membrane separation origin and thus much less expensive and more readily available than the pure oxygen of cryogenic origin)? Can we obtain a syngas at a reasonable SER expense, while also having a H_2/CO ratio of approximately 2? The target NG was similar to the previous one. It was mixed with enriched air containing 43% oxygen and eventually with steam in variable proportions. A light preheating (170-180°C) was used. The pressure ranged from 0.16 to 0.19 MPa for incoming mixture flow comprised between 1.9 and 2.6 m^3(n)/h. The reactor was close to its thermal plateau (plasma zone at ~ 1050°C) at almost constant SEI of 0.22 ± 0.04 kWh/m^3(n).

The results from this series of tests show us that it is possible to obtain a mixture very close to the ideal mixture of $H_2/CO = 2$ by partially oxidising the HC feed with enriched

TABLE 8

O_2/steam reforming of a heavy NG (all ratios are given in mol/mol)

O_2/HC	H_2O/HC	H_2/CO	Syngas/HC	SER (kWh/m^3(n))	C conv. (%)	Selectivities (%)		
						CO	CO_2	H_2O
0.64	0.58	1.92	1.9	0.28	76	79	21	0.3
0.64	1.0	2.04	1.5	0.39	67	67	32	0.6
0.56	1.0	2.04	1.4	0.46	61	69	30	0.9
0.48	1.0	2.05	1.2	0.45	54	69	30	1.3
0.41	1.0	2.19	0.99	0.55	44	65	32	2.9
0.33	1.0	1.89	0.83	0.69	40	67	27	5.7
0.25	1.0	1.80	0.61	0.98	33	62	24	14

TABLE 9

Enriched air (43% O_2) and steam reforming of a heavy NG (all ratios are given in mol/mol)

O_2/HC	H_2O/HC	H_2/CO	Syngas/HC	SER (kWh/m^3(n))	C conv. (%)	Selectivities (%)		
						CO	CO_2	H_2O
0.94	0	1.50	2.2	0.33	95	84	15	32
0.85	0	1.58	2.3	0.30	94	85	13	27
0.74	0	1.66	2.2	0.31	86	85	12	23
0.69	0	1.72	2.2	0.31	82	86	12	21
0.73	0	1.74	2.3	0.18	87	85	15	20
0.73	0.28	1.91	2.4	0.23	90	81	19	15
0.73	0.66	2.06	2.3	0.25	88	76	24	13

air (43% O_2) and by adding a small amount of water vapour. We obtain very good syngas/HC volume ratios, a sufficient carbon conversion and very reasonable selectivities towards all valuable products. The energetic expense SER is also approximately twice that of the tests performed with pure oxygen, but it remains at a very low level of approximately 0.24 kWh/m^3(n). We observe that the addition of water vapour generates very well the reaction (8) of "water shift" (lower selectivity towards H_2O, greater selectivity towards CO_2). Moreover, the pyrolysis of HC into ethylene and acetylene was blocked. In spite of a strong nitrogen ballast (28-38 vol% in the incoming flow), we are able to maintain, thanks to the added energy and active species, a reactive environment that promotes the development of the reactions of HC POX.

A strong ballast (up to 40% by volume) of carbon dioxide present in some NG that we also tested does not prevent the smooth conversion of HC into syngas. Such ballast can be compared to the ballast of inert nitrogen, although a fraction of CO_2 may actively escape through Reaction (2) or (9), upon the conversion of the original HC carbon into CO, which increases the content of this valuable product. We also observe that the CO_2 present in the mixture to be converted plays a positive role by preventing the formation of soot by the following reaction:

$$C + CO_2 = 2CO \qquad (11)$$

Other series of tests were carried out with atmospheric air mixed with a light NG. This entire mixture was subjected to the action of gliding discharges in another "shortened" reactor (30 cm total length), with a thermal insulation. All other details of the equipment were the same, except that the reactor only had one large hole to separate the plasma zone from the post-plasma zone. Some results of these tests are presented in Table 10.

This time, at 0.11 MPa and with significant energy losses preventing the reactor from increasing its temperature, which would have made it possible to ensure a sufficient build-up of thermal energy from exothermal reactions, we did not obtain very good results. However, these tests show us the viability of a POX of HC with atmospheric air. This oxidation may even be carried out with a very strong deficit of oxygen but it is only possible in the presence of gliding discharges, otherwise the purely auto-thermal process would stop very quickly (here the inertia of the reactor is quite small). We must point out the strong influence of the material introduced

TABLE 10

Air reforming of a light NG in a presence of solids in the post-plasma zone
(a shorter reactor; A and B are two different stainless steels)

O_2/C	SEI (kWh/m^3(n))	Post-plasma zone		H_2/CO	SER (kWh/m^3(n))	Selectivities (%)			
		filled	°C			CO	CO_2	C_2H_4	C_2H_2
0.36	0.73	A	560	1.43	3.9	58	24	16	0
0.36	0.61	Cu	730	0.59	8.3	51	34	13	0
0.36	0.72	brick	440	1.86	3.9	69	18	11	1.5
0.32	0.57	none	390	2.40	2.3	51	11	16	22
0.23	0.60	none	390	3.05	2.7	49	12	7.5	31
0.31	0.56	B	440	1.73	2.9	50	34	14	1.1
0.23	0.58	B	450	1.99	2.9	51	37	12	1.5

in the post-plasma zone on the chemical composition of the products. We can thus obtain more or less unsaturated HC, almost block the production of hydrogen on large pieces of metallic copper, regulate the H_2/CO ratio, etc.

By comparing this section's tables and figures, one observes that it is possible to partially oxidise and pyrolyze a light or heavy NG, with or without the addition of water vapour, within a very wide range of O_2/HC and H_2O/HC ratios. These reactions are carried out in the presence of an initially non-catalytic metal or ceramic material in the post-plasma zone, in order to obtain a syngas with more or less of ethylene and acetylene. A free choice of the solid material in contact with the post-plasma flow and the free choice of its temperature provide us with wide possibilities for directing the composition of the exiting product according to the process requirements, depending on the composition of the HC feed, the availability of oxygen, etc. Also, by injection of more or less electric energy directly into the discharges we can convert more or less HC into syngas. For example, we can obtain a NG that is only seeded with hydrogen and carbon monoxide, in order to improve its combustion in piston engines or for its transportation *via* a traditional gas pipeline to a location where the CO and/or H_2 would be extracted for a more valuable use than fuel. We could also convert the entire HC feed and then send it to a FT synthesis... Everything indicates that a combination of the auto-thermal process with electric discharges provides a new opportunity for producing more interesting products (presence of ethylene and acetylene), obtained from the light or heavy feed of HC, partially oxidised by oxygen or by enriched air, or even by the atmospheric air, all that at a low pressure of less than 0.6 MPa.

We thus arrive at a very important question: Is it really our gliding electric discharge that produces such a smooth production of syngas? And, what would happen if we completely shut down the electric supply of these discharges, causing their complete disappearance once that the reactor reaches its steady operating condition? The items included in Table 11 answer this question.

The tests without discharges performed in the "long" and very well insulated reactor follow some minutes later those performed with discharges, without modifying any of the initial settings. It should be noted that this reactor is quite massive and cools slowly. We observe oxidation processes a long time after the shutdown of the electric discharges, but, in these cases, all indicators of the quality of the conversion of NG into syngas are lower. Without plasma the temperature in the post-plasma zone increases (!) progressively, reaches a maximum (at which point we sample the product for the analysis), and finally falls quickly to a threshold below which the conversion stops. However, at the beginning, the temperature of the solids in the post-plasma zone (nickel or brick) increases due to the side reaction (6) that is highly exothermic (the selectivities towards CO_2 and H_2O increase for all tests without plasma). In spite of this temperature increase, the oxygen conversion becomes stagnant or even decreases. Without electric discharges assisting the conversion, we will find, in spite of a large surplus of fuel, a high content of elemental oxygen, which, if not separated, would exhaust the catalysts of a FT process for which the syngas is produced.

Everything indicates that it is indeed the presence of gliding discharges immersed in a rich fuel/oxidant mixture that provides for the smooth execution of the process. Furthermore, the still active flow of intermediate products exiting the plasma zone undergoes a post-plasma conversion in the presence of a ceramic or a metal (Ni) known for its catalytic properties, provided that it is highly dispersed. Given the ridiculous surface of the metal (1670 cm^2 per 1.5 kg), only one conclusion can be drawn: the inert or quasi-inert material introduced in the post-plasma zone plays the role of a catalyst only in the presence of the flow of products exiting the plasma. Without this constant flow from the plasma, this material deactivates itself very quickly and even begins to play a reverse role from the desired reaction.

TABLE 11

Air reforming of a heavy NG in a presence of solids in the post-plasma zone
(A and B are two different stainless steels)

Post-plasma zone	O_2/HC	H_2O/HC	Temperature in zones (°C)		SEI (kWh/m^3(n))	H_2/CO	SER (kWh/m^3(n))	Conv. (%)		Selectivities (%)		
			pl.	post				C	O_2	CO	CO_2	H_2O
Ni	0.40	0		775	0.10	1.40	0.21	38	98.7	73	23	44
Ni	0.40	0		840	0	1.34	0	34	98.6	63	32	49
Ni	0.63	0	1030	690	0.14	1.66	0.11	84	99.3	85	14	25
Ni	0.63	0	975	770	0	1.65	0	81	99.8	83	17	27
Ni	0.25	1.00	965	860	0.27	1.80	0.98	33	97.0	62	24	24
Ni	0.25	1.00	< 600	900	0	0.84	0	21	82.1	49	25	51
Brick	0.22	1.22	930	900	0.33	1.73	1.87	30	97.1	47	20	32
Brick	0.22	1.22	< 600	990	0	1.34	0	27	91.4	47	18	39

Our preferred material would be nickel, although other materials may be even more advantageous. The free (gas) volume of the reactor zone housing the nickel welding sticks is 660 cm^3. Under the conditions of our tests, this volume is covered by a flow of products of approximately 6.6 m^3/h (at the pressure and temperature of the zone). This gives a surprisingly high space velocity of approximately 10 000 h^{-1}.

Other conclusions are the following:

- exothermic POX with pure oxygen or ~ 45% O_2 "enriched air" of a low-CO_2 feed costs less. A production of H_2/CO ~ 2 syngas requires 0.11 kWh, 0.38 $m^3(n)$ of HC and 0.25 $m^3(n)$ of O_2 or 0.24 kWh, 0.43 $m^3(n)$ of HC and 0.70 $m^3(n)$ of such an enriched air per $m^3(n)$ of product. Oxygen conversion rate reaches 99% while the methane slippage may be close to zero;
- the methane content of the HC feed ranged from near 100% down to about 90%. We can process much heavier HC such as flared associated gases of any kind. Hydrogen sulphide will not interfere.

5 NEW DEVELOPMENTS

New SynGen reactors of type are under development for a large-scale process. They are based on the multiple-discharge GlidArc-I systems. Another version of SynGen integrates a new principle of GlidArc-II brush-like, multiple-electrode and multiple-stage electric discharges. Our recent, large laboratory tests indicate already that the SER expenses of syngas production are about half of those obtained with the GlidArc-I structure. Higher temperatures inside the reactors are found very favourable concerning the syngas energetic price so that relatively cold gliding electric discharges are now installed inside a wall's high-temperature section. The SynGen reactors are intended to process any gas at any initial temperature and at pressure up to several bars, transferring active electric energy directly and almost totally into process. They input new possibilities to the previous reactors:

- a solid, apparently non-catalytic matter can be added to the discharge;
- the processed gas flow rate has almost no influence on discharge's behaviour;
- at the same average SEI to converted gases, the SynGen spreads the energy of diffused electric discharges in a more uniform way so that the non-equilibrium plasma effects are enhanced.

6 LINK TO THE FISCHER-TROPSCH PROCESS

Our plasma-assisted syngas technology is devoted mainly to the NG upgrading into the best-grade liquid fuel through the FT synthesis step. Such a step may be, for example, performed using special cobalt FT catalysts developed in Moscow's *Zelinsky Institute of Organic Chemistry* for fixed-bed reactors and tested in Novocherkassk's plant at 30 000 t/y scale. Liquid HC (mostly of diesel range) can be produced from the rich-CO_2 and rich-N_2 syngas using new Russian chain-limiting FT cobalt catalysts. Some of these catalysts can accept the presence of acetylene and/or ethylene content in the syngas.

In fact, C_2H_2 and/or C_2H_4 act as homogeneous phase catalytic promoters, especially at the initial step of the HC chain development. Indeed, we are able to produce a syngas with a considerable amount of such unsaturated HC so that one can enhance the FT synthesis using these catalysts making profitable use of initial =C=C= and/or –C≡C fragments from C_2H_2 and/or C_2H_4 as "initiating" bricks.

In order to test different FT catalysts under different conditions (syngas composition, space velocity, pressure, temperature, etc.) we have built in Orléans a 1 L capacity (~ 0.5 kg of FT catalyst), fixed-bed reactor supporting up to a 2 MPa pressure. This pilot reactor is based on a 1 in diameter, 4 m length steel tube, similar to the tubes used in industrial reactors. We performed a series of preliminary tests of three type catalysts under different H_2/CO ratios, gas blends, temperatures, etc. All tests gave us very clean, paraffinic liquids (without aromatics or waxes) that we analysed by chromatography by ourselves. The carbon distribution over the typical product ranges mostly between C_5 and C_{20} paraffins with some olefins. The maximum distribution is around C_{11} *(Fig. 6)*. Based on our laboratory results, a simulation has been carried out to evaluate the whole GTL process, as it would apply to a real situation. The product will be virtually free from aromatics, with an average carbon of about 11.2

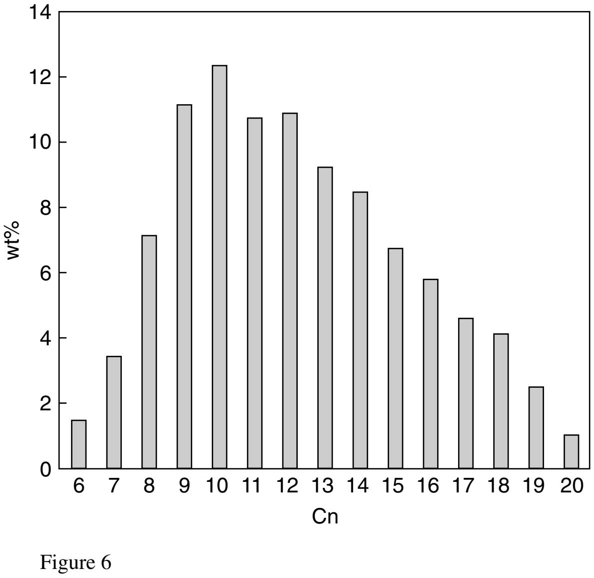

Figure 6

FT synthetic paraffinic oil composition (in wt%) as synthesised in Orléans in November 1998 using 1 L tubular 1 in reactor at 1.0 MPa and a chain-limiting catalyst; Cn is a number of carbon atoms in paraffin molecule.

and it will be colourless. The liquid HC fraction obtained from the equipment could be characterised as follows:

– *n*-alkanes	40-70% (wt)
– isoalkanes	20-50%
– alkenes	10-13%.

CONCLUSIONS

One can find in literature the thought that a combination of steam reforming, carbon dioxide reforming and thermal POX may give an interesting combined reforming supplying the syngas with a particular composition starting from a particular feed. Such a combined reforming should result in more favourable syngas composition and in higher methane-based conversion efficiency to syncrude or methanol, because the CO_2 carbon will also contribute to the final product.

Our experiments show such a feasibility of the GlidArc-assisted conversion of CO_2-rich NG into syngas of variable compositions. The precise balance shows that up to 40% of input electric energy goes into such endothermic combined reforming, without using a catalyst. We have in fact something like a "gas-phase electrolyser". Co-generated cheap electrical energy will be accessible to run the SynGen plasma reactors from energy recovery from the highly exothermic FT process. We have proved through an additional comparative study that one really needs plasma-produced species to assist the HC conversion into the syngas. Without plasma, but at the same other conditions, one gets much worse results for both endothermic and exothermic conversions. In addition for the POX case, our active electric discharges act as a non-blow-out igniter, a flame stabiliser, and as a source of condensed energy. Our catalytic species simply prevent any risks of explosion. Moreover:

- GlidArc can be easily integrated into almost any process; very compact equipment may be installed in restricted areas (for example, on offshore petroleum platforms for the conversion of associated gases);
- our system can be modularised and sized utilising multiple-electrode configurations;
- GlidArc can process material containing poisons, liquids or solids, and can directly produce very reactive medium allowing for efficient gas processing;
- GlidArc is inexpensive, powerful, and easily controllable; the gliding discharges have no thermal inertia, therefore they respond immediately to the control signals;
- an increase of the inlet gas temperature allows for better integration of the GlidArc-assisted process into a whole industrial process;
- the proposed GlidArc process can be a substitute for high-energy consuming and/or troublesome classical processes with lower energy costs;
- the technology does not require noble materials but rather utilises classical steels;
- the electric power supply is non-sophisticated thus operator-friendly.

POST-SCRIPTUM

A new SynGen pilot plant *(Fig. 7)*, of more than 100 m^3(n)/h of SynGas from NG is being commissioned in Alberta, Canada, by *Synergy Technologies Corporation* (see more details at www.synergytechnologies.com website). The author currently serves as a consultant to *Synergy Technologies Corporation* in ongoing development of plasma technology. US trademark protection has been applied for the designation "SynGen".

Figure 7

Overview (2000) of the SynGen pilot converting natural gas into more than 100 m^3(n)/h of synthesis gas at Bantry Plant, Alberta, Canada.

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GlidArc reactors and SynGen processes are protected by French and US patents. International patents are in progress. US patents granted to date include 5,993,761 and 6,007,742.

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