

CHARACTERIZATION OF A 3 - PHASE AC PLASMA REACTOR FOR CARBON BLACK SYNTHESIS FROM NATURAL GAS

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ABSTRACT

A new plasma reactor, using a 3 Phase AC plasma arc for Carbon Black synthesis from methane is operating since March 1994. Carbon nanostructures have shown, as a result of high temperatures reactions, an important graphitic organisation similar to *Acetylene Blacks*.

Research of optimal operating parameters led to model the thermoconvective field into the reactor. In a first approach, the case of an inert gas flow (Ar and N₂) in the absence of CH₄ is presented. Results of a 2D steady state numerical model are analysed and compared with experiments.

INTRODUCTION

Carbon black (CB) describes a wide group of industrial carbon products which consist in more or less organised carbon nanostructures, [1]. The total world production is about 6 millions tons per year [2]. Most of the production goes in the rubber industry, the other important fields of CB application are ink industry and electrochemistry (dry cells). Processes of CB manufacturing may be classified into two main categories : processes based on incomplete combustion of an hydrocarbon and processes based on thermal decomposition of an hydrocarbon.

Processes which belong to the first category, furnace processes, are far most important. Since hydrocarbon feedstocks have a negative energy content, it is necessary to compensate this deficit by burning a part of it or using an auxiliary flame. Thus the reaction zone is a non homogeneous complex flame. As a consequence, main characteristics of such processes are : poor carbon yields (30 to 40 %), low value and high pollution level of off-gases (CO₂, NO_x, V.O.C., SO₂,...), high dispersion of product characteristic. Although a valuable commodity, the hydrogen is lost.

Among the second category, the case of Acetylene Black is very singular since pure acetylene is continuously introduced into a furnace where adiabatic decomposition occurs, [3], as a consequence of the high energy content of the

feedstock. The black is very well defined its characteristics depending only loosely on the technical production parameters. The carbon yield approaches 100 % and pure H₂ can be recovered in the off gases.

The idea of making simultaneously CB and H₂ by cracking an endothermic hydrocarbon using an external energy supply has been patented in France in 1980, [4], and several studies have been dedicated to this subject, [5], [6], [7]. Now, because of new environmental concerns, [8], and improvements in plasma technology, this idea is being bought up to date again. In particular, a large scale pilot plan has been set up in Norway by Kværner Engineering a.s., [9].

In collaboration with industry, a research program has been initiated in France. The new process uses a 3 phase AC. plasma source with graphite electrodes, [10].

EXPERIMENTAL SET UP

The pilot is mainly composed of (Fig. 1).

- a 3 phases A.C. source with graphite electrodes, located at the top of the device (P : 100 - 200 kW)
- a high temperature zone in which CH₄ is introduced
- an insulated reacting chamber , 2 meters high
- a tail filter in which CB and H₂

External parts of the pilot are water cooled.

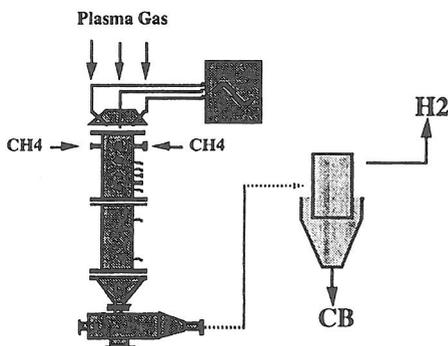


Figure 1: Scheme of the pilot

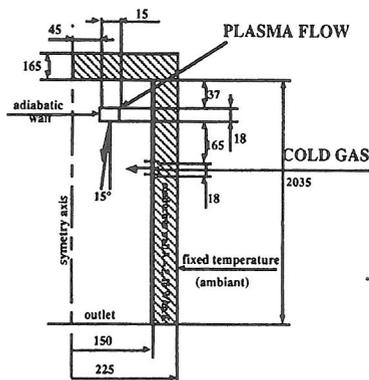


Figure 2: Geometry and boundary conditions

FLOW MODELING

The modeling of the thermo-convective field into the reactor has been initiated. In a first approach, the case of the plasma gas flow alone is presented (Ar and N₂ without CH₄). In a second step, the case of the mixing with a cold gas (same as plasma gas) is considered. The mathematical model is mainly based on the following assumptions.

1. The system is in steady state and axially symmetric. The resulting model equations are two-dimensional.
2. The flow is turbulent. The plasma jet is assumed to be in LTE.
3. All the thermodynamic and transport properties are temperature dependent; chemical reactions (dissociations and ionisations) are only taken into account via this dependence.
4. Electric and electromagnetic effects are neglected.
5. Radiation is neglected (gas and walls).
6. Gravity is taken into account.

Based on these assumptions, the conservation equations are expressed in terms of cylindrical coordinates. The turbulent flux (Reynolds) equations of conservation of mass, momentum, enthalpy, turbulent kinetic energy k and turbulent energy dissipation ϵ , can be written in general form :

$$\frac{1}{r} \left[\frac{\partial}{\partial x} (\rho r u \Phi) + \frac{\partial}{\partial r} (\rho r v \Phi) - \frac{\partial}{\partial x} (r \Gamma_{\Phi} \frac{\partial \Phi}{\partial x}) - \frac{\partial}{\partial r} (r \Gamma_{\Phi} \frac{\partial \Phi}{\partial r}) \right] = S_{\Phi}$$

Where Φ represents the two velocity components (u and v for respectively x and r axis) as well as the other variables already mentioned; Γ_{Φ} exchange coefficient and S_{Φ} source term. Detailed expressions of these variables are given by DILAWARI and SZEKELY, [11] as well as the values of constants used in the k - ϵ model. Geometry and boundary conditions are presented in Fig. 2.

Despite both the facts the thermal conductivity of Ar is lower than N_2 one and plasma temperature is higher for Ar, the outlet flow of N_2 is warmer. This phenomenon may be explained by the higher input enthalpy for the N_2 case (about twice the Ar case). We can notice in both situations that, while the thermal insolation (wall conductivity : $2.16 \text{ W.m}^{-1}.\text{K}^{-1}$), losses to walls remain very important since most of the input enthalpy is lost in the first meter of the reactor. (Fig. 3 and Fig. 4).

The velocity fields for Ar and N_2 are much alike, with swirls on each side of the inlet jets due to the sharp widening of the section just after the nozzle. This phenomenon results in increasing the hot gas residence time in the upper part of the reactor and explains the high thermal exchange to the walls at the top. The velocity profile becomes flat before the half the height of the pilot. (Fig. 5 and Fig. 6).

In the case of a cold gas radial injection, we present results related to N_2 for two flow rates of cold gas respectively equal and double of the hot gas flow rate. In all the situations, we can notice a bad mixing between the two flows due to differences of viscosity with temperature. The hot gas remain confined above the cold gas injection. Downstream, the cold gas insulates the wall from the hot flow in the center. (Fig. 7 and Fig. 8).

Figure 3 : Temperature profile, N_2 plasma gas, input : velocity : 12,7 m/s, input temperature : 7600 K, output temperature : 300 K.

Figure 4 : Temperature profile, Ar plasma gas, input : velocity : 12,7 m/s, input temperature : 13 000 K, output temperature : 300 K.

Figure 5 : Velocity profile, N₂ plasma gas, input : velocity : 12,7 m/s, input temperature : 7600 K, output temperature : 300 K.

Figure 6 : Velocity profile, Ar plasma gas, input : velocity : 12,7 m/s, input temperature : 13 000 K, output temperature : 300 K.

Figure 7 : Temperature profile, mixing of N₂ axial flow (input : velocity : 12,7 m/s, input temperature : 7600 K) with a radial N₂ injection (same massic flow, temperature : 300 K).

Figure 8 : Temperature profile, mixing of N₂ axial flow (input : velocity : 12,7 m/s, input temperature : 7600 K) with a radial N₂ injection (double massic flow, temperature : 300 K).

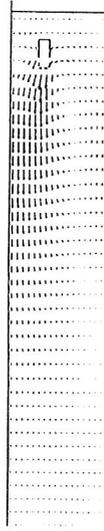
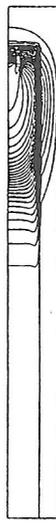
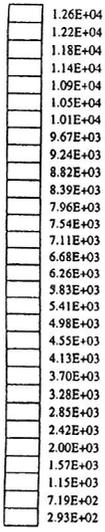
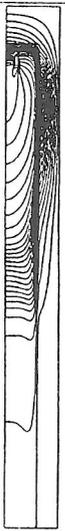
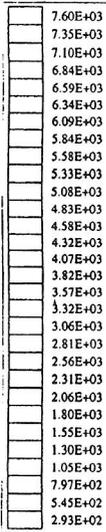


Figure 3

Figure 4

Figure 5

Figure 6

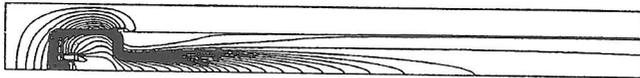


Figure 7



Figure 8

EXPERIMENTAL RESULTS

Every experiment begins by heating the reactor with a plasma gas flow until the system reaches its steady state. Once the thermal steady state, CH₄ is radially injected downstream the arc zone. The time constant - evaluated from heat balance analysis of the cooling loops - varies between one to two hours.

Lower voltages are observed for the Ar plasma process, and for N₂ the situation is the opposite, and the consumed electric power is higher. CH₄ injection in a N₂ plasma flow increases drastically the voltage and the same phenomenon is observed with Ar. In both cases when increasing, this voltage influences the stability of the plasma, and points out that the species coming from the reactive zone (H₂, H,...) modify the electric resistance in the arc.

Several dozen experiments with CH₄ injection have been made under different operating conditions, using Ar, N₂ and CH₄ as plasma gas. In all the experiments, the resulting carbon yields were about 50 %. These poor yields, which should theoretically reach 100 % due to autocatalytic effect of carbon, are the result of a bad mixture of the plasma flow with the CH₄.

All the samples have been analysed. The main characteristics of the products are : a high carbon purity, a clear graphitic organization, a specific area varying between 50 to 80 m² / g. These analysis have shown that the products were, as a result of the high temperature reactions, closer to *acetylene blacks* than to *furnace blacks*. These conclusions have been confirmed by X. BOURRAT from T.E.M. analysis of the samples [12], [13]. We give in the following figures, micrographies related to typical nanostructures. The first micrography (Fig. 9) shows that the texture brings up a concentric organisation. Agregats are not, as in the case of *furnace blacks*, made of a set of spheroidal particules. On the contrary, they look like a "giant fullerene", similar to a *hollow ball*. On the other micrography (Fig. 10), we can observe the atomic organization of the layer. Actually, the structure is not continuous but the length of graphene shell and the dimension of carbon crystallites remain small.

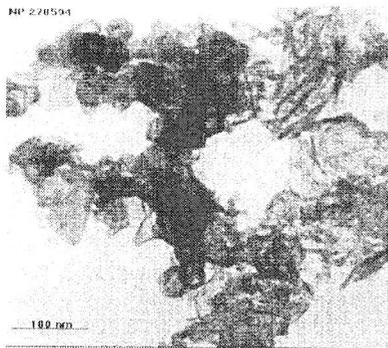


Figure 9 : T.E.M micrography of a typical plasma black agregat (X. BOURRAT)

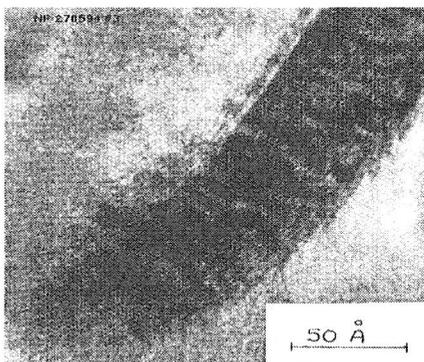


Figure 10 : T.E.M.detail of the atomic structure of typical plasma black (X. BOURRAT)

CONCLUSION

A new pilot, using a 3 phase A.C. plasma device, for making CB from CH₄ is operating. First experiments have shown that the products, as a result of the high temperature, had very specific properties. In particular the important graphitic organization let predict interesting qualities for electrochemistry applications (cells). On a qualitative way, the poor carbon yields obtained, have required the study of the cold gas injection into the pilot. Research of optimal operating parameters led to modeling the thermo-convective field into the reactor. In a first approach, the case of an inert gas flow (Ar and N₂) with the absence of CH₄ has been investigated. Despite the arc zone was not taken into account in a first step, results obtained with a 2D steady state numerical model have been very instructive and have confirmed experimental observations. Next step will consist in improvement of the model by taking into account the CH₄ injection and modeling the arc zone.

References

- [1] L. FULCHERI, Y. SCHWOB, Comparison between two carbon nanostructures : furnace and acetylene blacks, NANOS 94, Int. Workshop on nanostructured materials, 6-8 January 1994, Odeillo FRANCE, to be published in High Temp. Chem. Process.
- [2] J. B. DONNET, Carbon Black, 2nd Edition, H. DEKER, N. YORK, 1993.
- [3] Y. SCHWOB, Acetylene Black: Manufacture, Properties and Applications, Chemistry and Physics of Carbons, a series of advances, edited by P.L. WALKER, vol 15, 110-227, 1979.
- [4] ARMINES, Procédé et dispositif de fabrication de noir de carbone et noir de carbone obtenu. B.F. 8000981, Janvier 1980.
- [5] N.A. IDONOV, Y. M. KOROLEV, L.S. POLAK, V.T. POPOV, Plasma chemical production of dispersed carbon. Phase composition study, Khim. Vys. Energ. 20(2), 174-80, 1986.
- [6] K. SHAKOURZADEH, J. AMOUROUX, Reactor design and energy concepts for a plasma process of acetylene black production, Plasma Chem. Plasma Process., 6(4), 335-348, 1986.
- [7] C. CRISTOFIDES, V.J. ILBERSON, Processing Hydrocarbons in a thermal R.F. plasma reactor, ISPC-6 Montreal, July 1983, paper A-8-2.
- [8] J.W. BOYD, Air Quality Issues for Carbon Black, Intertech conferences, The Global Outlook for Carbon Black, February 23-24, 1993, Houston, Texas USA. Intertech Conferences, 170 US Route one, Portland Maine 04105 USA.
- [9] CO₂-free Hydrogen from Hydrocarbons, The Kværner CB&H Process, 10th World Hydrogen Energy Conference, Cocoa Beach, Florida, June 1994.
- [10] L. FULCHERI, A 3-Phase A.C. Plasma Process for Carbon Black Production from Methane, Thermal Plasma Processes, 19-21 Sept. 94, Achema Germany, to be published in High Temp. Chem. Process.
- [11] A.H. DILAWARI, J. SZEKELY, Some perspectives on the modeling of plasma jets, plasma chemistry and plasma processing, 7, n° 3, 1987.
- [12] X. BOURRAT, Contribution à l'étude de la croissance du carbone en phase vapeur, thèse de Doctorat d'Etat, soutenue le 7 septembre 1987, université de PAU, FRANCE.
- [13] X. BOURRAT, Personnel communication.