PRODUCTION AND CHARACTERIZATION OF CARBON BLACK FROM PLASMA PYROLYSIS OF NATURAL GAS

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Many traditional methods for production of carbon black and hydrogen release CO_2. An alternative method that does not release CO_2 and produces carbon black and hydrogen simultaneously is the plasma torch process with natural gas as one of the input gases. In this process the natural gas is pyrolised at high temperatures, and the main reaction is CH_4 + Energy = C + $2H_2$. A plasma torch of non-transferred arc with two vortex chambers was developed. Nitrogen gas, injected tangentially in the first chamber, was used as a secondary input gas to protect the cathode from erosion. In the second chamber, the natural gas was injected radially. We have carried out experiments with the following ratios between the flow rates (NL/min) of natural gas and nitrogen: 20/91, 59/102, 92/107, 129/114. We have obtained gaseous and solid products. The gaseous products, characterized by mass spectroscopy, showed the formation of hydrogen with small amounts of C_2H_2 and HCN. The produced solid phase materials, collected in several parts of the reactor, were characterized by elemental analysis, surface area measurements, XRD and electron microscopy. The materials can be classified as carbon blacks with specific BET surface area values up to 290 m^2/g. The XRD measurements showed broad lines typical of non crystalline materials. The electron microscopy results showed the presence of particles with diameter of the order of 100 nm.

Keywords: Carbon black, Pyrolysis, Carbon clusters

Introduction

Changes in the atmospheric abundance of greenhouse gases and aerosols, in solar radiation and in land surface properties alter the energy balance of the global climate system. A recent report of the Intergovernmental Panel on Climate Change (IPCC, 2007; Solomon et al., 2007)) has pointed out that warming of the climate system is unequivocal. Carbon dioxide (CO_2) is the most important anthropogenic greenhouse gas. The global atmospheric concentration of CO_2 has increased from a pre-industrial value of about 280 ppm to 379 ppm in 2005. The primary source of the increased atmospheric concentration of CO_2 since the pre-industrial period results from fossil fuel use, with land-use change providing another significant but smaller contribution. Many studies and applications have been developed with the objective of minimizing the emissions of CO_2. The mains focus of these studies are the search for energy alternatives to substitute part of the fossil fuel use, as well as the development of industrial processes involving reduced CO_2 emission. Hydrogen (H_2) is considered one of the potential substitutes of fossil fuels, though many traditional methods for H_2 production (such as steam reform) also release CO_2. An alternative method that does not involve the release of CO_2 and produces carbon black and hydrogen simultaneously is the plasma process. Along the last decades several studies were accomplished using this method, however in laboratory scale (Jordan et al 1967, Lahaye and Prado, 1978; Idonov et al 1986; Shakourzadeh et al 1986; Cristofides 1993;). Now due to the recent environmental concerns and the improvements and progresses in the technology of plasma, a new phase in the production of carbon black and hydrogen has emerged through the Kværner Carbon Black & Hydrogen (CB&H) process, (Lynum, 1994) and through the 3-phase AC plasma process (Schwob, 1993).

Carbon black is an industrially manufactured colloidal carbon material in the form of spheres and of their fused aggregates with sizes below 1000 nm with a high specific surface area (Donnet, 1993; Fitzer, 1995 and Taylor, 1997). Carbon black is often used as a pigment and reinforcement in rubber and plastic products, with its most common use (about 70%) being in automobile tyres. Carbon black particles are also employed in inks, printer toners, rubber and plastic industries. Today, apart from the plasma torch processes, about 95% of carbon black is produced by the incomplete combustion of carbon hydrogen compounds by the furnace process, releasing CO_2. In this work, we have investigated the carbon black and hydrogen production, without CO_2 emissions, through the pyrolysis of natural gas and nitrogen using a DC plasma torch of non-transferred arc with tungsten cathode and two vortex chambers. The process involves basically the thermally (plasma) assisted decomposition of methane, through the overall reaction $CH_4 \rightarrow C + 2H_2$, where C is mainly carbon black. The gaseous products were characterized by mass spectroscopy and gas chromatography, and the produced carbon blacks were characterized by elemental analysis, surface area measurements, X-ray diffraction, and electron microscopy.

Experimental

Figure 1 shows schematically the plasma torch used in the present work. Nitrogen gas (N_2) was injected tangentially in the first chamber to stabilize the electric arc and to protect the tungsten cathode from erosion caused by natural gas (NG), which was injected radially in the second chamber. In the absence of N_2, the direct contact of NG with tungsten would lead to a reaction producing tungsten carbide, leading to the erosion of the cathode and reducing drastically its lifetime. The pyrolysis reactions of NG occur mainly inside the second anode (made of copper) and in the central region of the plasma immediately after the exit of the torch, which correspond to the regions of highest temperatures. The plasma torch is connected directly to a water refrigerated cylindrical reactor. The gas flow and the produced solid particles are quickly cooled in the reactor, going next to the filters, measurement units, sampler point, and incinerator. The gases generated in the process are analyzed directly in real time by a mass spectrometer, connected as shown in Figure 1.

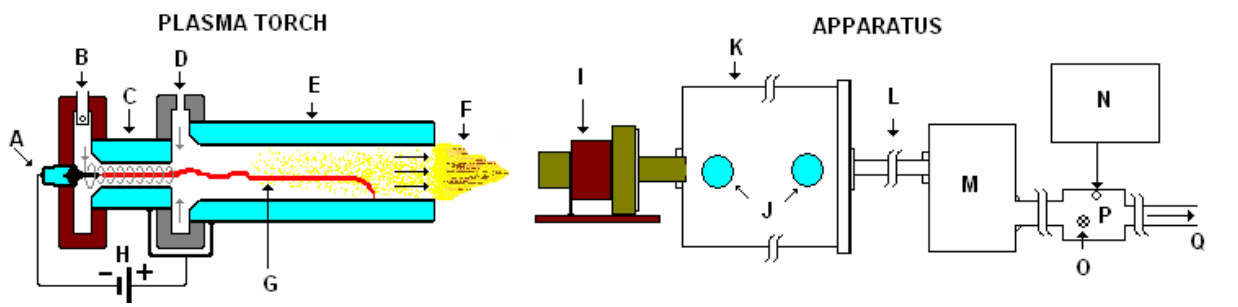

Figure 1: Scheme of the plasma torch and the apparatus used in this study. A) cathode, B) vortices chamber1, C) anodo1, D) vortices chamber2, E) anodo2, F) plasma, G) electric arc, H) power supply, I) plasma torch, J) quartz window, K) reactor, L) pipe cool, M) filter, N) mass spectroscopy, O) sampler point, P) span block, Q)incinerator.

Four tests were carried out with the following ratios between the flow rates (NL/min) of NG and N_2: 20/91, 59/102, 92/107, and 129/114. The NG was injected shortly after the stabilization of the plasma, when the concentration of residual atmospheric oxygen (monitored by the mass spectrometer) in the reactor was below 3% (1 to 3 min). The duration of NG injection was the same for all the tests, approximately 15 min. All experiments were carried out keeping the plasma power at about 50 kW and the N_2 flow from 91 to 114 NL/min.

The characterization measurements were conducted in the following equipments: elemental analysis in a Perkin-Elmer CHN 2400; x-ray diffraction (XRD) in a Rigaku Geigerflex Cu-Kα (λ = 1.5418 Å); BET specific surface area in a Quantachrome Quantasorb; mass spectrometry in a OmniStar Balzers; scanning electron microscopy (SEM) in a Jeol 35A; and coupled gas chromatography - mass spectrometry (GC-MS) in a Schimadzu QP-5050.

Results and discussion

As shown in Figure 2, the mass spectrometry results showed that most of the NG was completely pyrolized, with exception of the fourth test where the NG flow was larger than the N2 flow. All the experiments confirmed the H_2 production. The largest yield of H_2 was obtained in the third test (NG/N_2 flow rate ratio = 92/107). The experiments also showed the formation of small amounts of acetylene (C_2H_2) and hydrocyanic acid (HCN).

The solid material, produced in all the tests, was collected at two different regions of the apparatus: inside the reactor and in the filter. The total mass of the collected solid material was 10, 45, 75 and 120 g for the tests 1, 2, 3 and 4 respectively. Elemental CHN analysis yielded the results C = 82 ± 2%, H = 1.6 ± 0.5% and N = 1.0 ± 0.3% for the samples collected in the reactor, and C = 90 ± 3%, H = 1.9 ± 0.2% and N = 1.0 ± 0.3% for the samples collected in the filter. These results were determined through the averaging of the four tests.

The BET surface area measurements for the samples collected in the reactor or in the filter yielded similar results. However, these values were different for each test, which indicates that the variation of the NG flow is very important to determine the properties of the produced material. The obtained results (in m^2/g) for the tests 1, 2, 3 and 4 were respectively 179, 253, 278 and 175 for the samples collected in the reactor, and 173, 246, 292 and 216 for the samples collected in the filter. It can be observed that the largest values for the surface area were obtained for the material produced in the third test, which coincides with the test of highest yield of H_2.

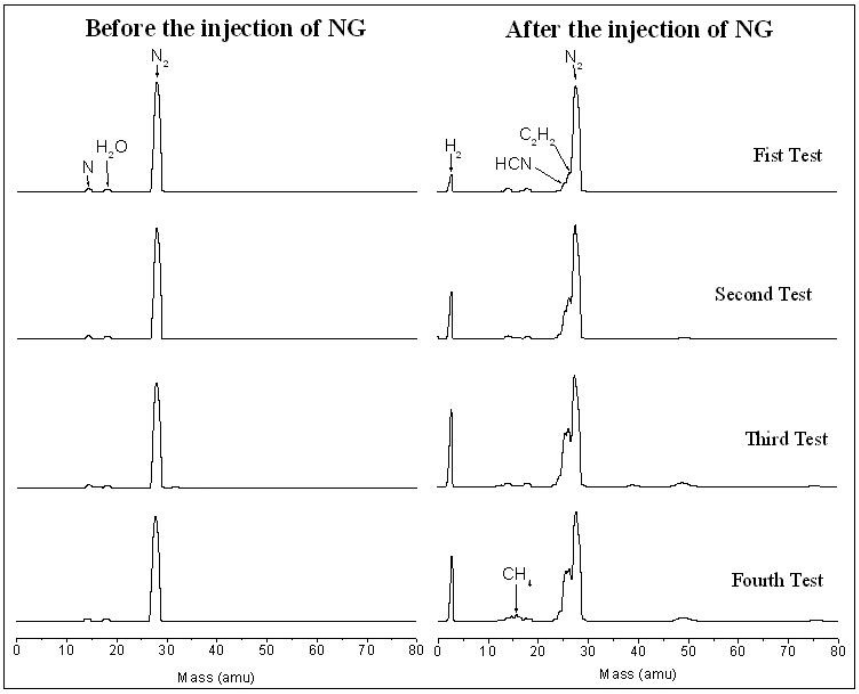

Figure 2. Mass spectra of the tests.

The XRD patterns for the samples collected in the reactor and in the filter in the second test are shown in Figure 3. The results were similar for the four tests. The presence of a broad line, typical of amorphous materials, centered at $2\theta \approx 18°$ is cleared observed. Other two lines (with reduced intensity) can be observed (especially for the samples collected in the reactor) for 2θ around 26° and 43°, which coincide with the characteristic positions expected for turbostratic carbon.

The solid materials collected in the reactor and in the filter were submitted to a Soxhlet extraction process, using three different solvents (dichloromethane, hexane and ethanol). It is observed in Fig. 3 that the amorphous broad line centered at $2\theta \approx 18°$ disappears for the solid residue obtained after extraction, remaining just the typical lines of turbostratic carbon with interlayer spacing from 3,45 ± 0.05 Å. A similar result was found for a solid material produced after a process of purge under nitrogen flow at 300°C. The Soxhlet extracted material, after separated from the solvents, was analyzed through coupled gas chromatography - mass spectrometry (GC-MS). Several aromatic substances (fluorene, phenanthrene, pyrene, anthracene, and coronene, among others) were found. However, no nitrogenated compounds were detected in the extracted fraction.

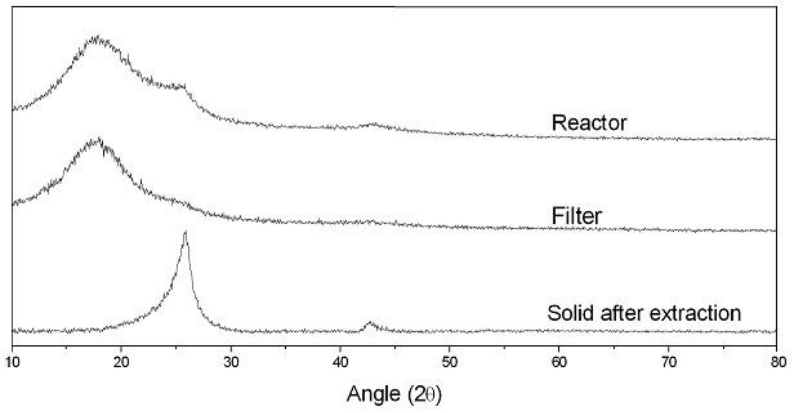

Figure 3. XRD powder patterns for the materials collected in the reactor and in the filter.
It is also shown the pattern corresponding to the solid residue obtained after Soxhlet extraction.

Scanning electron microscopy (SEM) images are shown in Fig. 4 for some typical samples collected in the reactor. A highly disordered and non-homogeneous matrix composed of particles (of about 100 nm) and aggregates of different sizes is observed in all cases. For the samples collected in the filter, the low resolution of the recorded images precluded a reliable evaluation of the size of the particles.

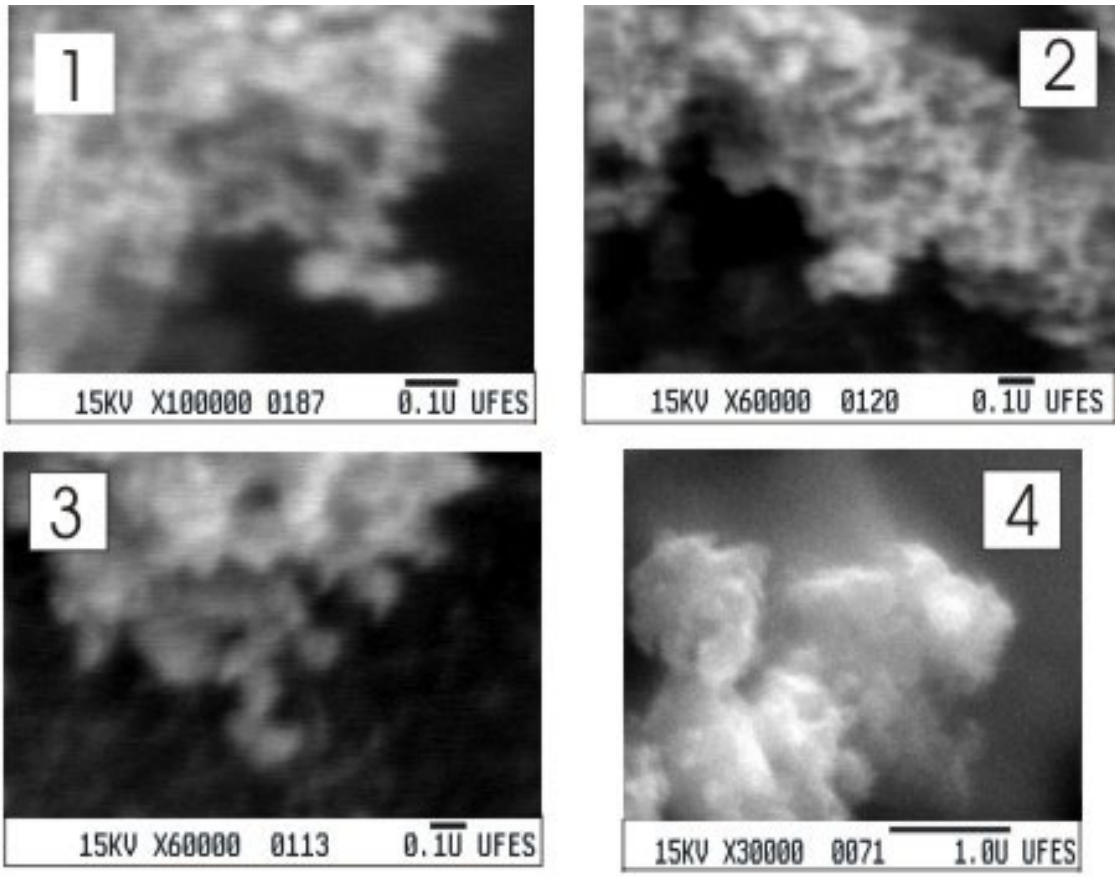

Figure 4. SEM images of the materials collected in the reactor in tests 1, 2, 3 and 4.

Conclusions

The plasma torch used in this work (with the electric power limited to 50 kW) was able to pyrolize natural gas with high efficiency (close to 100% in the tests 1, 2 and 3), leading simultaneously to the production of carbon black and hydrogen, without release of CO_2. It was observed that the NG flow rate is an important parameter for the quality of the produced carbon black. The highest value for the surface area was obtained when the concentration of NG in the gas mixture approached that of N_2. The produced carbon black needs subsequent treatment stages for purification and improvement of its physicochemical characteristics, because a great number of aromatic substances are found dispersed in the material. It is worth mentioning that no nitrogenated compounds were detected in the Soxhlet extracted fraction of the produced materials, in spite of the use of nitrogen gas in the plasma apparatus. The studies are in progress and several factors still need to be investigated to optimize the process and to better characterize the obtained solid products.

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