

### 3. PLASMA REACTORS FOR POWDER MODIFICATION

As it has been already presented one of the main objectives of this work is to modify surface activity by means of treating CB with plasma techniques. In this chapter the different plasma types and reactor that have been used are described and the advantages and drawbacks of each system are evaluated.

Although some phenomena related with plasma had already been described before, plasma was first defined by W.Cookes in 1879 as electrically charged gas molecules or ions. However, it was Langmuir in 1923 who gave the name plasma to the 4th state that occurred when a gas at low pressure was submitted to an electric field. Since then many efforts have been done in order to understand better the plasma state but also in order to use plasma as a tool for processing technology. Microelectronics industry has been the first drive force in order to develop plasma processes since 1960's but nowadays many other fields such as biomedical, automotive, textile, lightening and many others applications that deal with surface modification have already adopted this technology (BMBF, 2001).

Although generally defined plasma is a partially ionized gas very rich in charged and reactive species, there are different types of plasma regarding to its temperature and pressure (Fig. 3. 1). One of the most used classifications corresponds to equilibrium and non-equilibrium plasmas. The word equilibrium is referred to thermal equilibrium among the species present in the plasma state. Non-equilibrium plasmas are commonly known as cold plasmas while equilibrium are known as thermal plasmas.

As shown in Fig. 3. 2, equilibrium plasmas known as thermal plasmas, are those in which temperature is the same for all the species present in the plasma. The energy to ionize and activate the gas comes from the thermal heating which can reach above 10000°C. A well known example in nature is the solar corona. These type of plasmas are mainly used in plasma spray, plasma torches, waste destruction and welding applications.

On the other hand, the non-equilibrium known also as cold plasmas, do not present a unique temperature. In these type of plasmas electrons have a much higher temperature (around 30000°C) which allow them to activate other species and produce ionization, excitation of present species and dissociation of molecules (H. Yasuda 1985). Because ions, atoms and molecules can not interchange heat with electrons, due to their fast movement of the last, these species are kept almost at room temperature. As a consequence this plasma might present temperatures similar to room temperature, sometimes slightly higher but generally lower than 100°C.

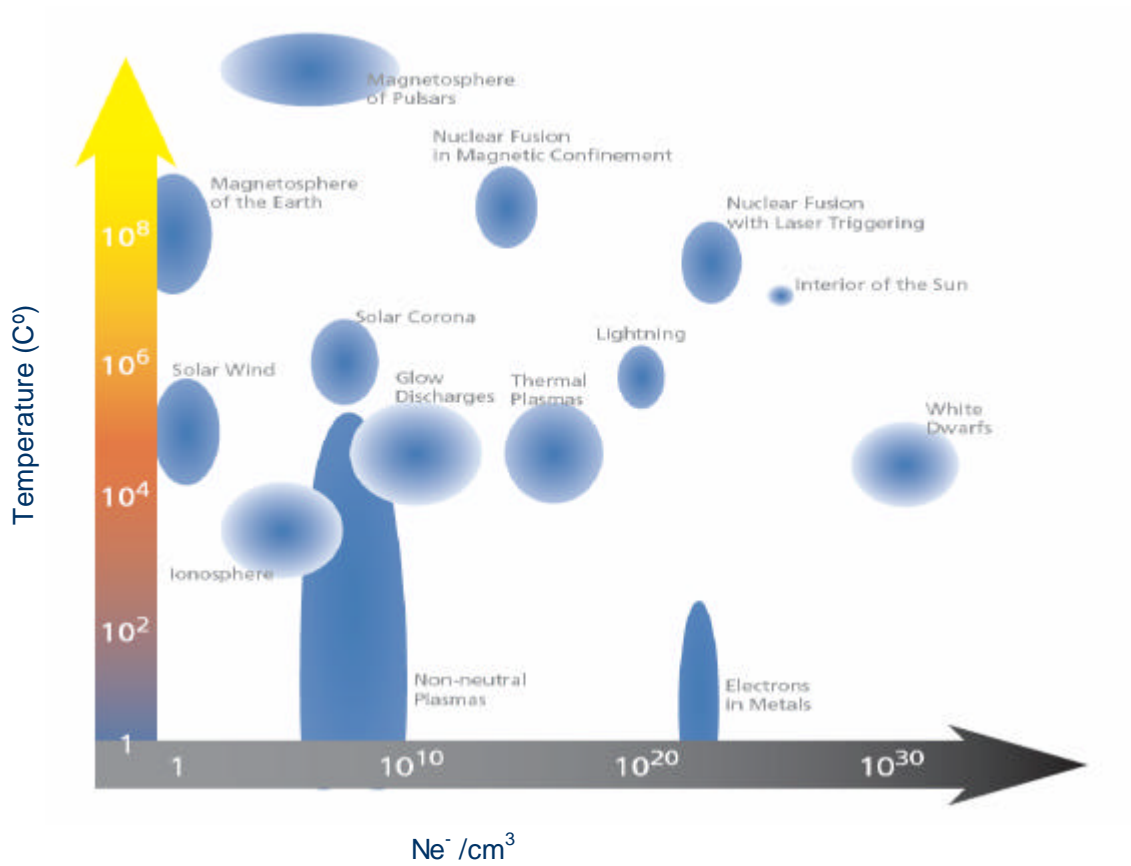


Fig. 3. 1 Plasma classification as function of e- density and temperature (BMBF, 2001)

For these type of plasmas the generation of an electric field at low pressure is usually needed in order to be able to activate the plasma. Before the electric field is applied, there are not many free electrons ( $10^{-11}$ - $10^{-12}$ ), but the number increases once the voltage is applied to the system. The electrons are accelerated and produce excited species and molecular fragments, including new electrons ( $10^{-5}$  to  $10^{-7}$ ). If pressure is too high there are many collisions and ion and excited species can not be formed or lifetime will be too short to generate a stable plasma. Therefore, it can be said that plasma is a steady state due to the production of ionized and excited species and the recombination of these activated species. A natural cold plasma is created during the phenomena known as Aurora Borealis or Northern Lights.

However, there have been recent developments that have been successful in achieving glow discharges at atmospheric pressures under specific conditions (Kanazawa et al 1988). Although their temperature is higher than the former presented cold plasmas, they are far away from the thousand degree Celsius for the thermal plasmas. Despite the restrictions presented by these systems may present certain restrictions as it will be presented, they are presented as one of the main breakthroughs from the industry point of view (VDI Technologiezentrum GmbH, 2004).

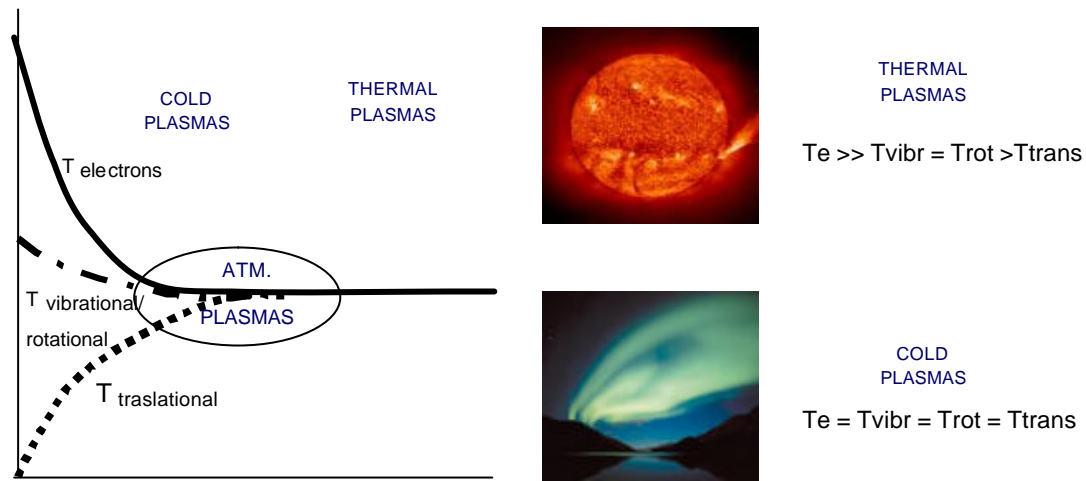


Fig. 3. 2 temperature distribution in Cold and Thermal plasmas (P.Favia, 2003)

Which are the advantages of using non-equilibrium plasmas seem clear: they allow to treat materials that present low thermal resistance and that would be damaged by other modification techniques, needless to say by thermal plasma.

On the other hand, being a gas, plasma allows treating materials that present different shapes and complex geometries including webs, tubes and powders (I. Hudec et al. 2006, F.Bretagnol 2004, and D. Pappas et al. 2006). It presents also a very high reactivity and unique chemistry which allows to obtain final surface properties which could not be achieved by any other process. Moreover the absence of solvents, and the use of very allow amount of chemicals make them one of the most preferred treatment as far as the environmental aspect is concerned. Due to the presented reasons, these types of plasmas have been widely used during the past years.

But which kind of modification is possible to obtain using plasma modification? Mainly a division in three different groups can be presented;

- 1) etching or ablation: it provokes removing of the substrate material. It can be used to obtain specific patterning and is mainly produced by the positive ions in the plasma (D.P. Norton et al. 2005). As shown in Fig. 3. 3 dotted line represents initial surface and continuous line final surface after etching.
- 2) plasma deposition: also known as Plasma Enhanced Chemical Deposition (PECD) occurs when plasma contains reactive species, which are able to react between themselves on the top of the substrate and form thin films (H. Yasuda 1985).
- 3) plasma functionalization: in this case plasma species do not react among themselves but with the substrate surface on determined positions. It allows to have new functionalization retaining initial surface structure (A. A. Meyer-Plath).

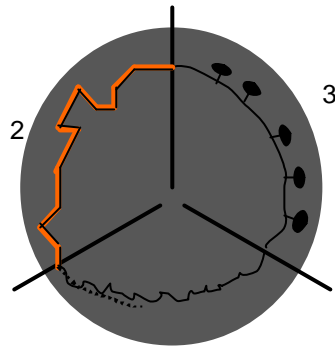


Fig. 3. 3 Scheme of processes possible to happen in a plasma reactor:  
1) etching 2) plasma deposition, 3) plasma functionalization

The properties that can be modified by using plasma treatments due to the three former mentioned processes are presented in Table 3. 1

Table 3. 1 Surface properties that can be changed by means of plasma treatment (R. D'Agostino, 2003)

• adhesion
• Barrier characteristics and permeability
• Biocompatibility
• Chemical inertness
• Color
• Degree of repellence of biorganic matter
• Dielectric constant
• Dyability
• Electrical conductivity
• Hardness
• Microroughness and flatness
• Resistance to bacteria adhesion
• Reactivity
• Refractive index
• wettability

It is easy to treat flat surfaces and even very successful systems to treat foils and webs have been described using non-equilibrium plasma (B. Gupta et al. 2000, I. Hudec et al. 2006). However, not so much work has been done on powder materials mainly due to a more difficult process and system complexity. Because the present work deals only with this type of substrate, in the next pages plasma modification description will be focused on powder materials.

### **3.1. Low Pressure Plasma (LPP)**

As for all type of cold plasma reactors, reactors designed to treat powders have a number of internal parameters that define plasma activity. These internal parameters shown in Table 3. 2 are determined by the external parameters imposed to the plasma reactor operation conditions (also presented in the same table). It is important to remember that in order to obtain reproducibility in different systems, external parameters have to be selected in order to obtain the same internal parameters.

Table 3. 2 Internal and External parameters for cold plasma characterization

Internal Parameters	External Parameters
<ul style="list-style-type: none"> <li>- Fragmentation degree of the gas</li> <li>- Density of neutrals</li> <li>- Density of electrons and electron Energy Ionization degree</li> <li>- Residence time of the species</li> <li>- Process homogeneity</li> <li>- Positive ion bombardment, sputtering</li> <li>- Deposition, etching, treatment rate</li> <li>- Contaminations</li> </ul>	<ul style="list-style-type: none"> <li>- Pressure</li> <li>- Feed composition, flow rate, leaks</li> <li>- Field frequency,</li> <li>- Power density</li> <li>-Reactor configuration, materials, electrode geometry</li> <li>- Substrate position</li> <li>- Duty cycle %, time on, time off in pulsed plasmas</li> <li>- Substrate temperature</li> <li>- Substrate bias potential</li> </ul>

Feed composition, flow rate, power density and substrate position are the most frequently studied parameters for a given reactor system which consequently will effect internal parameters such as fragmentation degree, residence time of the species, ion bombardment among other internal parameters.

But in order to better understand this information, Fig. 3. 4 presents a scheme of the different parts that usually compose a LPP reactor.

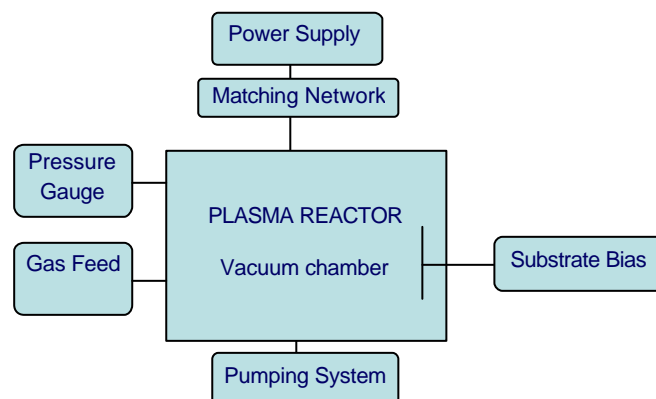


Fig. 3. 4 Scheme of components of a low pressure plasma reactor

As it has been mentioned, in order to create the electric field that is able to generate the plasma a generator is needed. Most plasma sources use radiofrequency at 13,56 MHz or

27 MHz. Another source that is also commonly used are microwaves at 2.53 GHz. Microwaves allow to work at higher pressures and give higher plasma densities. On the other hand audiofrequency plasmas (KHz) cause a higher bombardment and radiation damage which is often no desired for the application.

Concerning the electrodes used to apply the electric field different types can also be found. Electrodes can be present at the inner part of the reactor, that's the case for all metallic, reactors or outside the reactor which are mainly used in Pyrex and quartz reactors. In the case of powder treatment the outer position is preferred as it avoids the powder of getting in direct contact with the electrodes. Another useful configuration when dealing with powders is the use of a copper coil inductively coupled to the generator. In all cases the need of a matching box is needed in order to effectively generate the plasma inside the reactor and minimize the reflected power.

It is also worth to remember that any surface inside the plasma is covered by an electron sheet developing a negative bias. This effect produces the plasma bulk potential to be higher than the surfaces in the reactor. Therefore electrons are not accelerated to the surfaces but positive ions are. These accelerated ions may produce etching and surface ablation. In order to minimize this effect the substrates and desired surfaces may be grounded or connected to another RF generator avoiding this potential difference and minimizing the ion impact effect (F. Fracassi 2005). This possibility is not possible when using powders and therefore the etching and ablation effect of positive ions may be an important effect to take into account.

As a consequence of the above explained effect sample position is another important factor to take into account. The sample can be placed in the zone were the plasma is generated, in this case plasma effect is characterized by a high ion bombardment and high fragmentation. But the sample can also be place remote to the plasma generation region, in this case the bombarding effect turns to be very low, treatments are less severe and when using monomers its structure retention becomes much higher (S. Borros 1999)

#### **3.1.1 Powder Modification by Cold Plasma Reactors:**

Cold plasma reactors are mainly designed to treat flat surfaces as already mentioned. However, some type of reactors have also been designed and adapted to treat powder materials. The first type of powders that were first attempted to modify by plasma techniques were pigments in order to improve their dispersion (K.Tsutsui et al.1988, T. Ihara 1986). Many other type of powder materials have been treated by LPP until today, both plasma deposition and plasma functionalization treatments have been described as it will be shown further on in this section. It is worth to point out that the main powder characteristics that have to be taken into account in order to achieve a successful modification are particle size and geometry, density, agglomeration and reactor capacity.

The different plasma reactors configuration, which have been used in powder modification, as well as the treated materials are presented next. Special attention will be given to the carbonaceous powders such as active carbon, carbon black, carbon nanofibers and carbon nanotubes that have been treated by means of such reactors.

### 3.1.1.1 Bell Jar Reactor

The simplest attempts to modify powder materials in plasma reactors have been carried out by using a Petri dish, or similar element, containing the powder. In some cases the powder is just well spread while in others the sample holder to a vibration system which shakes the sample in order to obtain a more homogeneous treatment. As it will be presented, maximum amounts of 1 g of powder materials have been modified using such equipment.

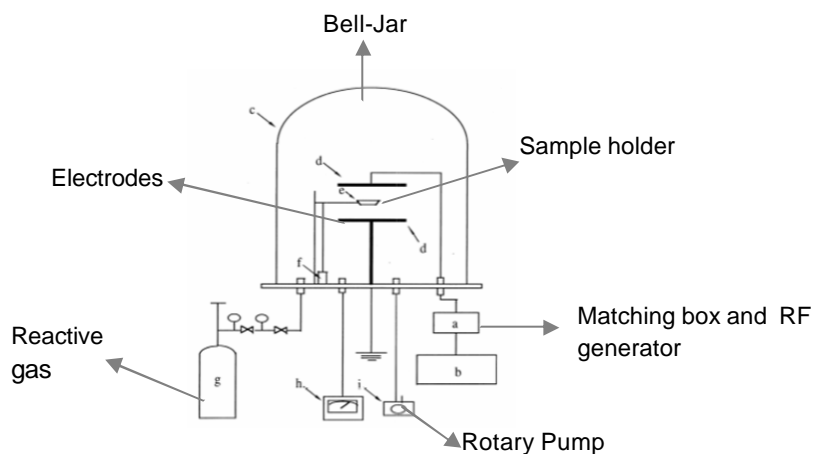


Fig. 3. 5 Bell-Jar reactor with vibrating device (X. Li et al. 2000)

The Bell-Jar reactor type has been used by the group of Tascon et al. in order to modify different types of carbonaceous powders as for example active carbon (A. B. García 1998, J.P. Boudou 2000). In both studies 1g of active carbon was treated in a microwave reactor at 150W with oxygen plasma at several treatment lengths. The same experimental conditions were also used in order to modify 1g of graphitized carbon black (L.E. Cascarini de Torre et al. 1998) and 0.5g of pristine CB (J.I. Paredes et al. 2005).

The same group performed a recent study in order to compare the effect of oxygen plasma versus molecular oxygen on 46 different carbons and coals including graphite, carbon fibres, carbon black, active carbon and coals among others. In this case 0.1g of the carbon substrate were used. Microwave plasma was also used in this case and carbon powder was previously sieved in order to obtain a fraction with a smaller diameter than 63 $\mu$ m (A. Cuesta et al. 2001).

It should be said that for all above mentioned cases the carbon sample was only spread on a Petri dish and no vibration was applied. Vibrating sample holders were used by T. Takada et al and Xu Li et al. in order to study the effect of oxygen plasma on carbon black samples (T. Takada et al. 1996 and Xu Li et al. 2000). Both studies utilized an RF plasma at 13.56 MHz. In the first case CB was pulverized in order to obtain particles below 200 mesh (74  $\mu\text{m}$ ) and 200 mg were treated. No information about CB size and quantity is given for the second study. Soon Jin- Park et al tested also an RF plasma system but in this case  $\text{N}_2$  plasma was used as reactive media to modify 200 mg of CB (S.J. Park et al. 2001).

But not only active carbon and carbon black have been plasma treated using this reactor system. In the recent years other materials such as carbon nanotubes have also become very popular. For some basic studies carbon nanotubes were placed on a double side Scotch tape and placed in a RF plasma reactor (A. Felten et. al 2005, Q. Chen et al. 2001).

As already mentioned above, it is important to keep in mind that the exposed plasma treatments are only able to modify small amounts of powdery materials, and that in some cases homogeneity of the treatment could be doubtful specially in those cases where sample is not shaken during the treatment. It is also worth to notice that in this case the sample is usually placed in between of the electrodes, which means that the sample is in contact with the most reactive plasma species.

#### *3.1.1.2 Down-Stream Reactor*

Another type of plasma reactor suitable for powder modification is the so-called down-stream reactor. In this type of reactor the sample is not in direct contact with the glow discharge zone. This fact prevents the sample from high positive ion impact and it also promotes the functionalization retention when trying to deposit polymers onto the powders as it has been already presented. In this type of reactor the sample is vigorously stirred by mechanical methods in order to obtain homogeneity. One of the main advantages of this reactor design, is that particle size can be as small as in the nanometre scale and also fibres can be treated; only precautions during the pumping down time need to be taken to avoid powder travelling to the pump.

As it can be seen in the picture in Fig. 3. 6 this type of reactor does not present two electrodes to generate the plasma but a copper coil which is inductively coupled to the RF Generator. Being placed at the outer part of the reactor the copper coil prevents the powder to be deposited on internal electrodes. The number of turns of the copper coil has to be adjusted depending on the reactor impedance and the copper coil diameter.



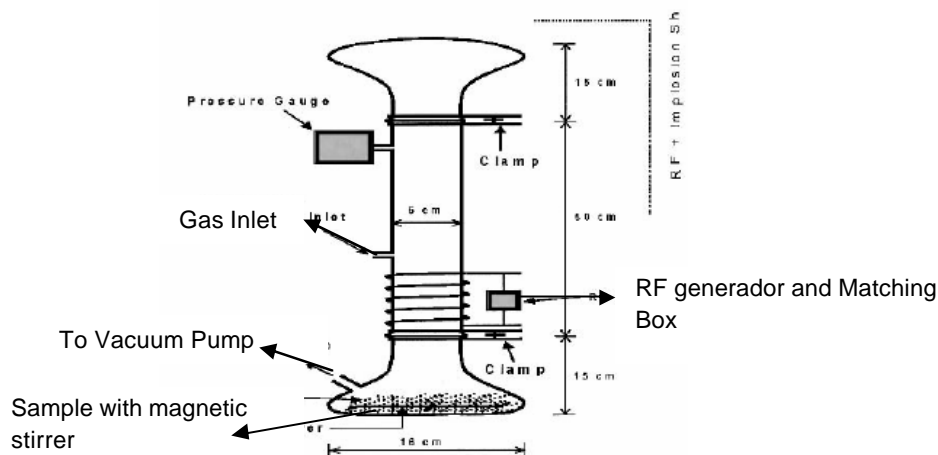


Fig. 3. 6 Down Stream plasma reactor (D.Shi et al. 2002a)

The mentioned reactor has been used by the research group of W. Van Ooij in order to study several powder modification based on plasma deposition of thin films on nanopowders. All works were performed under RF at 13,56 MHz. ZnO nanoparticles of 50 nm were coated with acrylic acid in order to promote metal ions removing from aqueous media (D.Shi et al. 2002a). Films thicknesses of 15nm were obtained for 40 gram batches. Higher structure retention of the monomer structure was obtained at powers below 30W while resistance to water increased above 60W. Treatment time was 240 min.

Another interesting work was based in coating  $Al_2O_3$  with polypyrrol thin films in order to facilitate the sintering process which could be carried out at much lower temperatures after the particle coating. In this case a wide range of particles from 10nm to 150nm were treated, this fact points out the capacity of the present reactor to treat powders with wide dispersion size (D.Shi et al. 2002b). In this case, films of 2nm of polypirrole where obtained for a treatment at 10W for 240 min in a 40 g. batch.

Previous collaboration of our research group with W. Van Ooij lead to the treatment of sulphur powders in order to coat them with thin polymer films. tetrafluoromethane, ethane and acrylic acid (AA) were used as monomers. As a result sulphur activity during the vulcanization reaction was modified achieving shorter scorch time for coated sulphur with AA and longer scorch times with fluoropolymer coatings. This is a very important achievement in order to control the kinetics of the vulcanization reaction (Borros et al. 2000)

In one of their last works, pigments were coated in order to use them as corrosion inhibitors. Cerium acetate and sodium vanadate were coated with perfluorohexane and octafluorotoluene thin films (L. Yang, 2005). Plasma conditions were 80W for 30 to 60 minutes in a 10 g batch.

When focusing the work on carbonaceous powdery materials it has been found that only carbon fibres have been reported to have been submitted to plasma modification in this type of plasma reactor. Carbon nanotubes were coated with thin films of polypyrrole. A thin film between 2 and 7 nanometres was uniformly deposited both at the outer and the inner surfaces of the carbon nanotubes (D.Schi et al. 2002c). Carbon nanofibres were also coated using the down-stream LPP reactor in order to enhance dispersion and interfacial bonding in polymer composites. Fibres presented diameters between 70-200nm and 50-100 $\mu$ m length. Polystyrene was used as monomer for the plasma deposition which presented a final thickness of 3nm. Composites containing coated carbon nanofibres presented better fracture behaviour and tensile strength properties (D.Shi et al., 2003).

Another research group developed also a reactor in which powders are placed in a bottom vessel which is stirred by means of an electromagnet. The plasma is coupled into the reactor through a quartz glass window by a copper coil (Fig. 3. 7). The reactor dimensions are (250mm x 250mm x 140 mm) which allowed 1 gram of fibres to be treated each batch. The position of the monomer inlet or vacuum connexion are not specified.

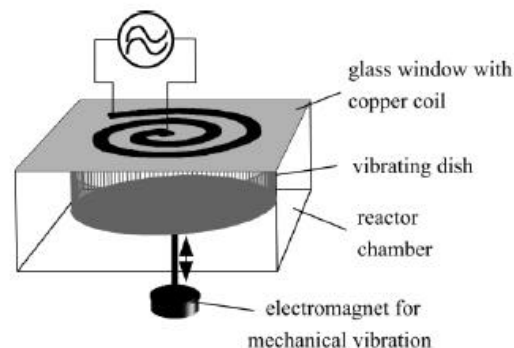


Fig. 3. 7 Plasma reactor for powder treatment developed by Brüsser et al. (Brüsser 2004)

Using this reactor Carbon nanofibres with a diameter range of 50-200nm and length between 100-200 $\mu$ m were modified in a RF plasma reactor using oxygen, argon and carbon dioxide as plasma gases (S. Habier et. al. 2003).

### 3.1.1.3 Rotary Drum Reactor

Another useful reactor design in order to treat powder in LPPs is the rotary reactor. In this case a vessel is coupled to a motor in order to be rotated and consequently the powder is stirred inside. Those models are known since the 80's but still are an option to be considered in order to modify large amounts. These reactors were the first type used for

pigments surface modification in order to change their polarity by means of oxygen plasma on diazine blue and phthalocyanine blue improving gloss and Newtonian flow of final pigments (T. Ihara et al. 1986). Oxygen, air, nitrogen and ammonia RF plasmas have been also reported on Quinacridone red changing the heat of immersion both in water and hexane improving the dispersion in the final resins (K. Tsusui et al. 1988).

More recently, polymer surface modification has also become a very interesting topic. Although polymers present very interesting bulk properties, many times adhesion, wear, reactivity and wettability at their surfaces need to be improved. In 2001 S.P. Godfrey et al used a rotary type plasma reactor in order to modify the surface of polystyrene beads by means of  $\text{CF}_4$  RF plasma (S.P. Godfrey et al. 2001). Non porous beads  $40\mu\text{m}$  size, mesoporous beads  $30\mu\text{m}$  and microporous beads  $300\text{-}800\mu\text{m}$  size were used for this study using 0,5 g of polymer for each treatment.

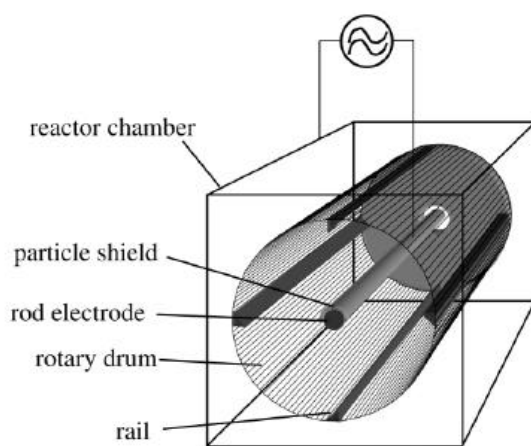


Fig. 3. 8 Scheme of a rotary drum reactor (V. Brüsser et al.2004)

Rotary drum reactors have also been used to treat carbonaceous powders. The group of Donnet et al, used this type of reactor to modify of carbon black with several reactive plasma gases. After the treatment, both the surface energy and surface topology by STM of the CB's were studied (J.B. Donnet, 1994, W. Wang 1993). The amount of modified material was 0.2g per batch.

L.I. Schukin et al. were able to modify 0.1 g of several active carbon coming from 8 different precursors in a rotating reactor with oxygen plasma in order to study the influence of active carbon origin (L.I Schukin et al, 2002)

On the other hand three different types of CB's were treated using this type of system to obtain a fluorinated surface, the amount of treated sample however is not revealed (A Tressaud et al. 2002), but they found fluorination leave to be dependent on CB surface structure. It is worth mentioning that recently a study performed by Favia et al. (P. Favia et al. 2006), used this type of reactor to modify carbon black granules in order to be able to tune its surface acidity/basicity, In this case up to 500g of carbon black were able to be

modified at each batch with oxygen and ammonia RF plasma. The size of carbon granules was in the range between 0.1-2mm which probably facilitated to work with such large quantities.

Fibres such as carbon nanofibres have also been modified by V. Brüsser et al. whose RF plasma reactor scheme is shown at Fig. 3. 8. The reactor diameter is 250mm and length is 390 nm, and treatments were performed on 1 gram of carbon nanofibres of 100-300nm diameter and 10-100 $\mu$ m length. Several plasma treatments on carbon nanofibres including oxygen plasma, water, ammonia and formic acid treatments have been described by this group (Brüser et al 2004)

#### 3.1.1.4 Fluidized Bed Reactor

Another useful reactor design in order to treat powders is the fluidized bed reactor which has become very popular since the 90's in the plasma field. In this case, a fluidized bed at low pressure is generated by passing a flow of a determined gas through a bed of powder which is placed on a porous support. For this type of reactor particle size is one of the critical parameters and due to this fact 4 different fluidization behaviours have been described regarding this parameter (Fig. 3. 9)

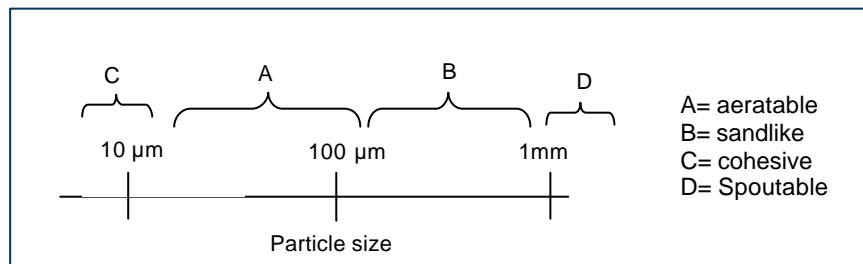


Fig. 3. 9 Geldart's Classification for powder fluidization

Particles belonging to groups A, B and D have been successfully used in fluidisation systems by many authors as it will be presented next. However, particles in the C group have not been still present many problems and fluidisation remains more like an art. However, in some cases particles in the low limit of the micron range trend to agglomerate during fluidization helping the process to happen (A. W. Pacek et al. 1990). Although it could give the impression that agglomeration would lead to the treatment of the whole agglomerate, this is a dynamic state between formation and disintegration of the agglomerates during the fluidization process (H.O. Kono et al. 1987). Agglomeration depends mainly on the Van der Waals forces between adjacent particles, while the disintegration is governed by the shearing force due to bubble movement (J. Visser 1989). When gas is not enough in order to help fluidization, mechanical vibration of the bed can be a very helpful option.

One of the main drawbacks presented by this type of reactor is therefore that in order to have a good fluidization behaviour, particles should not present smaller diameters than 40 microns (L.G. Gibilaro et al. 1988). It should be also pointed out that in order to obtain good fluidization particle size should present a narrow particle distribution in order to avoid stratification of the treated powders.

A review about fine particle fluidization in 1990 based in work done in Japan shows how by that time already several fine powders had been modified in cold plasma systems (S. Morooka et al. 1990). It can be found that SiC, TiO<sub>2</sub> and Ni in the nanometre range naturally form agglomerates in a fluidized bed even at the reduced pressures imposed by the cold plasma conditions allowing to obtain a good fluidization regime.

But since the 90's many studies have been done on powder modification by plasma in fluidized bed reactors. Special attention has been given to the modification of polymer powders as it was already said when presenting rotary drum systems.

The group of S. Done et al. works mainly on high density polyethylene (HDPE) powders with 230µm diameter and a density of 956 kg·m<sup>-3</sup>. The powder has been treated with oxygen and tetrafluoromethane plasmas (S.H. Park et al. 1994 and S.H. Park et al. 1998). Similar experiments were reported by the group F. Arefi-Khonsari et al., modification of low density polyethylene (LDPE) powders with 350µm diameter and a density of 920 kg·m<sup>-3</sup>. The scheme of the reactor utilised for this study is shown in Fig. 3. 10 showing that the plasma was generated by two external electrodes coupled to an RF generator.

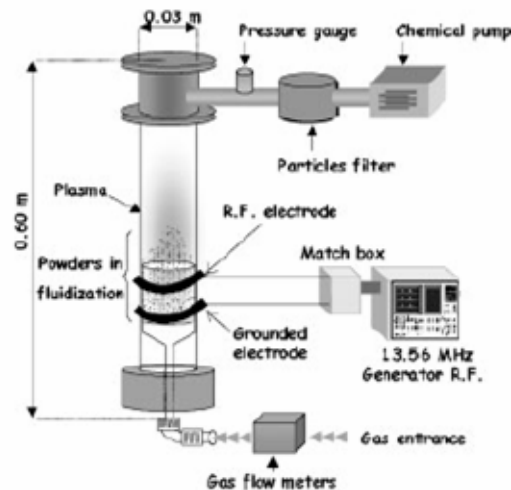


Fig. 3. 10 Plasma fluidized bed reactor (F. Bretagnol et al. 20004)

The same reactor was used by the former group in order to modify polystyrene (PS) beads 200 µm diameter and the previously presented LDPE by means of an allylamine/argon plasma obtaining thin deposited films on the polymer powders (M. Tatoulian et al. 2005 and F. Arefi-Khonsari et al. 2005)

In all previous presented studies, the plasma is generated at a higher position than the bed height without fluidization. When the particle bed is fluidized, the particles at the higher point are inside the plasma glow. Other studies place the plasma generation in a region up stream from particle fluidization. In this last case the gas is ionized and after ionization the gas fluidizes the powder, the remaining active species are the ones which will react with the powders. This is the case for the studies presented by the group of Mutel et. al. who treated polyethylene powder (diameter 280  $\mu\text{m}$  and density 960  $\text{kg m}^{-3}$ ) using a microwave plasma in an  $\text{N}_2$  and  $\text{O}_2$  (5%) atmosphere which allowed the remote cold plasma to the treatment area (J.B. Leroy 2003 and B. Mutel. 2004)

Very few has been described about carbonaceous powders being modified plasma fluidized bed reactors. In this area, work is focused on carbon nanofibres modification. The first work based on this type of material was presented in 1990 where milled carbon black fibres were treated with plasma oxygen. To help fluidization, glass beads of 141 $\mu\text{m}$  were also placed in the bed. The reactor consisted of a Pyrex column 27.5mm internal diameter and 75cm long (Kawamura et al 1990). The second known work utilizes a modification of the regular fluidization bed reactor shown in Fig. 3. 11 In this case, carbon nanofibres are fed from a reservoir by means of a screw system, the flow of gas forces the powder to go throw the plasma and collected at the end of the reactor tube (M Heintze et. al. 2003). In the case of carbonaceous material their high electrostatic properties can make the plasma treatment by fluidization even more difficult as they may stick on to the wall and avoid plasma generation inside the reactor column.

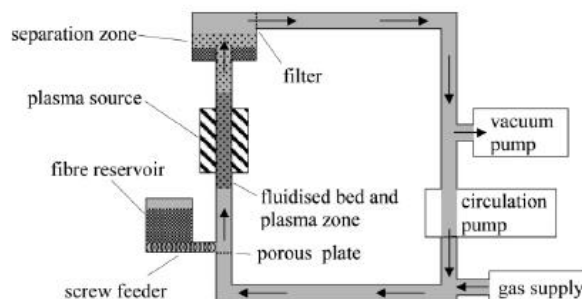


Fig. 3. 11 Cold plasma reactor designed by M. Heintze et. al 2003

One very recent type of cold plasma reactor that it is thought to be worth to mention is the one designed by the group of Asparagus et al. This reactor could remind the above presented but working in the opposite direction. In this case the powder is placed in a reservoir at the top of the reactor. The powder is fed through a metering screw which pushes the powder to go down to the reactor bottom while passing through the plasma zone. The reactor operates at RF and two half shell copper electrodes, fit to the outer shape of the reactor, capacitively couple the plasma. HDPE with an average diameter of 56  $\mu\text{m}$  and a density of 950  $\text{Kg m}^{-3}$  were modified by means of an  $\text{O}_2/\text{Ar}$  plasma. The powder was in contact with the plasma less than 0.1 second and the powder throughput

was kept at 5 Kg/hr while operation times were between 1 to 5 min depending on the amount of modified powder desired (C. Asparagus et al. 2005).

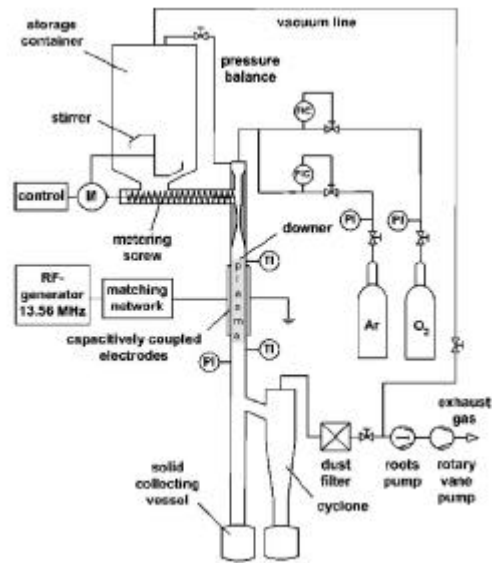


Fig. 3. 12 Scheme of the reactor designed by Arpagaus et. al (C. Arpagaus et. al 2005)

### 3.1.1.5 Circulating Reactor

One last type of reactor which will be here presented is the circulating bed reactor shown in Fig. 3. 13. In this case the powder is circulated in the reactor while going through a plasma zone.

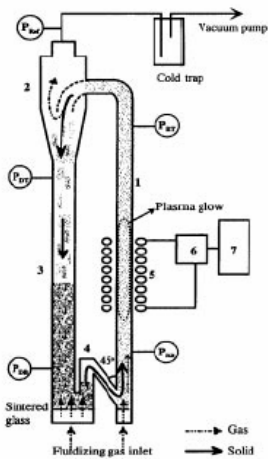


Fig. 3. 13 Circulating Bed plasma reactor by S.H.Jung et al. 2001

The already presented group of S. Done et al. used the same experimental conditions as in the former presented fluidized bed reactor studies. An external copper coil (12 turns 4,8mm outer diameter) was utilized to couple the plasma in the reactor by means of an RF generator. Oxygen as well as tetrafluoromethane plasma treatments have been reported using this reactor ( S.H. Jung et. al 2001 and S.H. Jung et. al 2004) The group of Rudolph

von Rohr also carried out powder modification using this system, in this case NaCl and glass beads powders with 210 $\mu$ m and 125  $\mu$ m diameter respectively were coated with hexamethyldisiloxane (HMDSO), in this case a MW generator was used allowing to work at higher pressures (M. Karches et. Al 1999 and 2001).

One of the main disadvantages of the circulating reactor is that particles should be in the hundreds of the micron scale, as separation of powder and gas would be too difficult in the nanometric region. There is no evidence that fluidised neither circulating systems have been used in order to modify carbon black, probably the size and the electrostatic properties are the main drawbacks to use such type of reactors to modify this powder.

To sum up the presentation of the different plasma reactor types Table 3. 3 presents the different exposed systems with the optimum particle size range to be modified in each reactor as well as the capacity of the different described reactors. In the last column the suitability of each of these systems to treat carbon black powders is commented.

Table 3. 3 Particle size and reactor capacity of each cold plasma reactor.

Reactor type	Particle Size	Reactor capacity	CB treatment
Bell-Jar	Micron scale (polydispersed)	mg	Low performance
Down-Stream	Nanometer (polydispersed)	1-40g	Able to treat fluffy CB
Rotating drum	Micron-mm (polydispersed)	100g	Able to treat pellets
Fluidized Bed	Micron (monodispersed)	5g	Able to treat small agglomerates
Circulating Bed	Micron (monodispersed)	5g	Difficult due to electrostatic deposition on the reactor walls

The prior examples show that there is a lack in the field of reactors able to modify a suitable amount of CB to make studies in applications which need large amounts and also to improve homogeneity of the treatment. Due to this reason two different cold plasma reactors were designed in order to achieve the mentioned goals.

The first of them, a down-stream reactor which allows to treat considerable amounts of Carbon Black in Fluffy state (diameter below 10  $\mu$ m). This reactor is very convenient in order to have a maximized amount of treated surface and therefore to observe easily the effect produced by the plasma treatment.

On the other hand a fluidized bed reactor was also set up, In this case although particles should be in the micron range, the reactor allows the particles to get in direct contact with the plasma and enhance the plasma effect. Whether agglomeration of fluffy carbon black particle occurs or small size pellets above 50  $\mu$ m was also an interesting point for this study.



### **3.1.2 Experimental Part (LPP Reactors)**

#### **3.1.2.1 Down-Stream Reactor**

##### ***3.1.2.1.1 Reactor Description***

The first presented reactor that has been set up to fulfill the aim of this study was a down-stream LP reactor type. As shown in Fig. 3. 14 the reactor is composed of 3 different glass parts and was designed following the reactor of Van Ooij research group. However, some interesting modifications were introduced in order to improve working conditions, versatility and performance. These changes consist in the relocation of the vacuum exit in upper part of the reactor contrary to the position used by V. Ooij et al. where it is done in the downer vessel. A flexible inlet position has also been designed in order to be able to control reaction activity in each reactor zone. First a description of the reactor is given followed by the optimization of the system.

The reactor, as mentioned, has three different Pyrex pieces: the central tube (1) 10 cm wide 60 cm height is where plasma is generated by means of a copper coil (4) which is 8 mm inner diameter and has 8 turns. The lower round flask is where the powders are located for their modification (2). In order to have a good reproducibility and homogeneous treatment a magnetic stirrer is introduced in the powder container (11). Contrary to the down stream reactor described in section 3.1.1.2, the upper round flask and not the bottom is connected to the vacuum system. The vacuum pump is a rotary pump (Boc Edwards V12) which is protected by a double cold trap filled with acetone\_CO<sub>2</sub> during reaction. Traps help to achieve lower background pressures but also to retain some powder that might outside the reactor. However the upper exit to the vacuum contains also a powder filter. A Pirani gauge is used to measure the pressure inside the reactor (6).

The RF generator at 13,56 MHz is inductively coupled to the copper coil already presented. A wattmeter shows the refracted power which is kept at minimum by means of a matching box (7)

On the other hand, position 5 shows the plasma gas inlet position which as it has been explained is not fixed. A plastic tube (PP) goes through inside the compression fitting, and can be located at different height in the reactor as will be shown later with more detail.

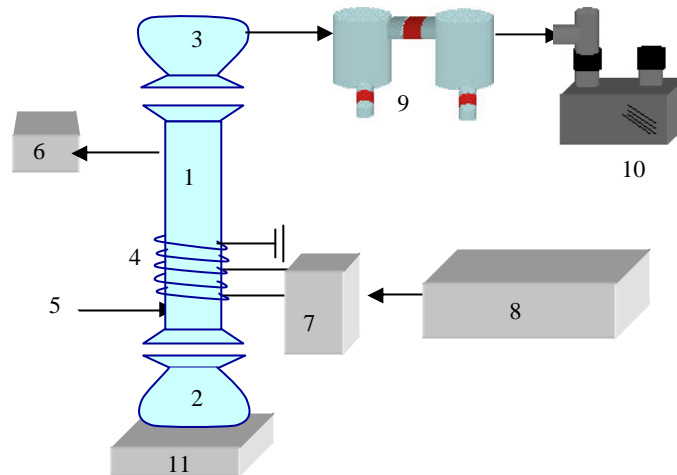


Fig. 3. 14 Scheme of the downstream plasma reactor

In order to prevent any risk do to implosion of the glass during working at vacuum conditions, the reactor was placed in a PMMA box. The box was covered with a metal foil with helped to avoid radiofrequency dispersion as well as protection against plasma radiation. Small window was left uncovered in order to be able to observe the reaction under working conditions. A picture of the whole system is shown in Fig. 3. 15

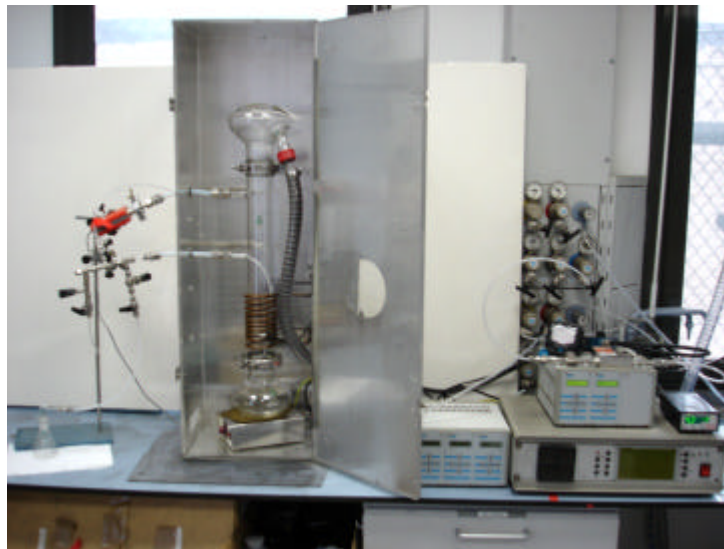


Fig. 3. 15 Picture of the down-stream plasma system

### 3.1.3.1.2 Reactor Optimization

As it has been presented before, the inlet position of the reactive gas which will be used in order to treat the powder, can be modified by changing the length of the plastic tube that conducts the gas inside the reactor. Fig. 3. 16 presents a picture of the different positions that have been evaluated during this work. Position 1 introduces the gas in the zone above the copper coil, position 2 introduces the gas just in the middle of the copper coil, while position 3 introduces the gas below the copper coil. The plasma reactivity in each zone of the reactor when using each position was studied as it is here described.

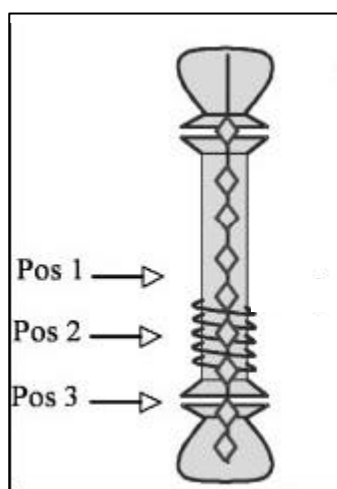


Fig. 3. 16 Inlet positions which have been studied for the reactive gas.

In order to be able to compare the plasma activity in each reactor zone when changing the inlet position, a nylon string containing glasses at different heights was hung from the top to the bottom of the reactor (Fig. 3. 16). Afterwards, a polymer deposition reaction using pyrrole as reactive monomer was carried out. The plasma conditions used during the experiments were:  $0.2 \cdot 10^{-2}$  mbar background pressure, 0.4 mbar working pressure, 30 W, and 30 min. The intensity degree of the yellow colour of the plasma deposited pyrrole film onto the small glass pieces, allowed to define rapidly the most reactive zone in the reactor without the need to further analyze the samples. The more intense the colour, the greater the reaction between the plasma and the organic feed. Although it is not very precise to know the reaction rate this method is very convenient determine whether plasma reaction was taking place in the vessel were the powders should be placed as the change in the vacuum position could bring all the plasma species up-stream without having the chance to get in contact with the powder placed in the downer vessel. Fig. 3. 17 shows one of the glass-pieces containing string which were used to evaluate reactivity in the reactor after one of the trials. The difference in colour between each glass-piece is easily observed.



Fig. 3. 17 Glass-pieces used to determine reactive plasma zone in the down-stream reactor

The experiment was performed at three different positions for the monomer inlet. The results presented in Fig. 3. 18 show the reactivity obtained in each reactor zone for each monomer inlet. It is possible to observe that changing the monomer inlet the more reactive zone in the reactor can be controlled. However, it is also possible to observe that inlet position 3 is the one giving a maximum plasma activity near to the zone where the powders are placed for modification.

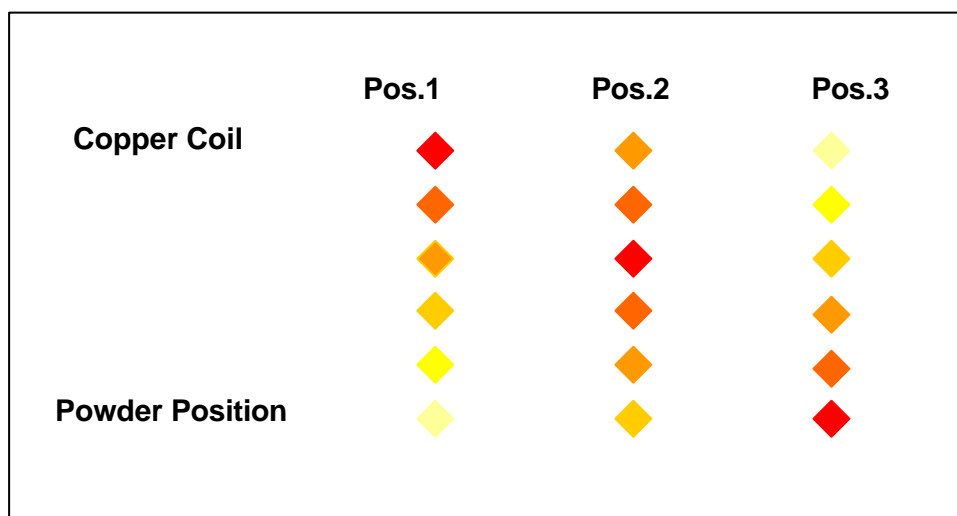


Fig. 3. 18 Results for (pyrrole) plasma reactivity in the downstream reactor changing inlet monomer position

It is obvious, that changing monomer and flow rate conditions would not lead to exactly the same deposition results. For this reason a rough method (changing in colour) has been chosen to establish the inlet position that gives maximum plasma activity. Although the intensity would probably change under other conditions, a higher activity in the powder-containing vessel would be expected when using inlet position 3 than when using the two other inlets. As a result this position was used for the experiments performed on CB modification.

On the other hand the maximum amount of fluffy CB that could be introduced and stirred in the vessel was also determined. Although the reactor was able to stir up to 30 grams the best behaviour was found when introducing 15 g of the powder inside the lower vessel. Therefore this amount was used in order to further study the modification of CB in this system.

### 3.1.2.2 Fluidized bed reactor

#### *3.1.2.2.1 Reactor description*

The second reactor that has been set up in order to modify powders and more precisely CB during the present work is a fluidized LPP reactor type.

The scheme of the fluidized bed reactor is shown in Fig. 3. 19 . The central part is a glass (Pyrex) column (30mm wide 600mm long). The sample is supported on a porous plate, the size of the porosity determining its performance. However, the porous plate is not attached directly to the mentioned glass column but to another inner glass tub. Special connection at the lower end of the reactor (5) allows the porous plate to move easily at different heights. As a consequence the powder sample may be position at several distances from the copper coil that generates the plasma

The copper coil in this case has a diameter of 2mm and consists of 9 turns around the outer glass tube. The tube is connected, in the upper part, to the pressure gauge on one side and to the cold trap and the vacuum pump on the other. The cold trap (8) is specially designed to prevent the entrance of the powder in case it escapes from the reactor. The matching system is the same as used in the reactor explained above. One or two different type of gases can be mixed with the help of two flow meters before the total gas flow is used to fluidize the powder located on the porous plate.

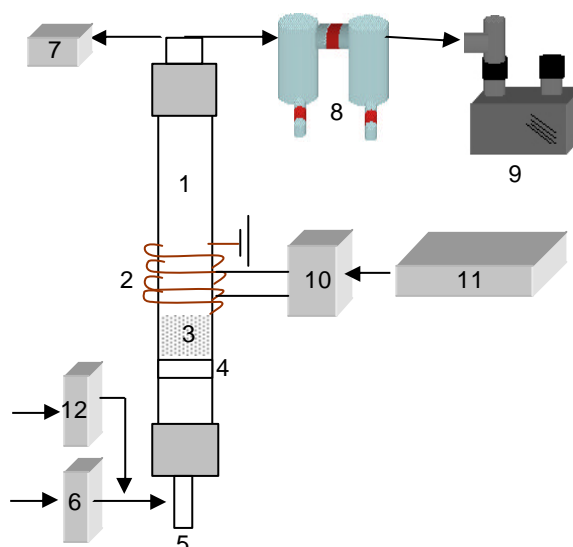


Fig. 3. 19 Scheme of a fluidized bed plasma reactor

A picture of the final system is presented in Fig. 3. 20



Fig. 3. 20 Picture of the Fluidized bed Plasma reactor

#### 3.1.3.2.2 Reactor optimization

In order to test the ability of the system to fluidize powders and let them flow into the plasma region in order to provoke surface modification some tests were carried out. Because Fluffy Carbon Black presents many drawbacks such as a very low density and very small particle size (some microns), polystyrene powders were used for the first trials.

Some of parameter effects such as powder distance to the plasma generation coil, powder support porosity and fluidization flow where evaluated.

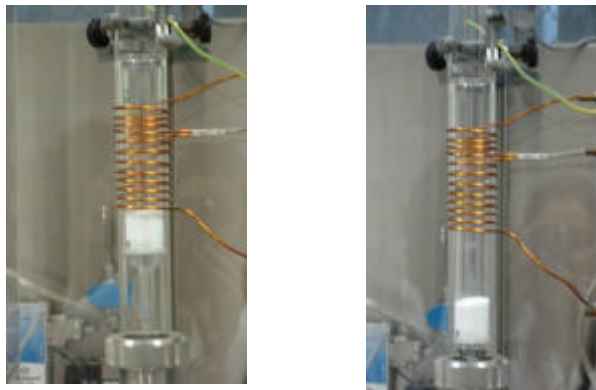


Fig. 3. 21 Modification of Polystyrene beads at different distance from the copper coil

Polystyrene (PS) powder from Goodfellow was used (nominal size of 200 $\mu\text{m}$ ). 8 grams of the powder were placed in the reactor which was pumped down to 5 $\cdot 10^{-3}$  mbar prior to fluidization.

Three different porosities for the support were tested as shown in Table 3. 4. Optimal fluidization process was found for the smallest porosity (1-5 microns), however, diminishing porosity increased considerably the time needed to achieve the mentioned initial pressure. Fluidization gas flow rate changed slightly when the porosity of the support was modified. It should be also mentioned that zirconia beads about 40 microns were also very nicely fluidised by an Ar flow of 20 ml/min. The perfect round shape of such beds helps to facilitate the fluidization of powders as it was observed during this experiment.

Table 3. 4 Support Porosity studies on fluidization behaviour

Support porosity	50-100 microns	20-50microns	1-5 microns
Fluidization behaviour	Bad, preferent channels	Good	Very Good
Fluidization rate	11ml/min	12ml/min	14ml/min
Time needed to achieve background pressure	15 minutes	20 minutes	2 hours



Fig. 3. 22 Polystyrene beads in a water-containing beaker before and after oxygen plasma modification Left and right respectively

In order to determine changes in the final modification of the material due to different sample position, pH of a PS suspension measured before and after oxygen plasma modification (40W ,10 min.) was measured. The results presented in Table 3. 5 show that changing the position of the powder did affect the final pH value. Position 1 corresponds to the powder at the farther position from the coil and 2 to the closest. In the picture above the PS water suspension used in order to measure pH is shown. Clear differences due to the oxygen groups which transform PS surface into a hydrophilic surface are observed.

Table 3. 5 pH measurement after PS modification

	pH
<b>Original PS</b>	7.8
<b>Modified PS pos 1</b>	5.2
<b>Modified PS pos2</b>	3.7

In order to ensure a good mixing and circulation of the powders in the fluidized bed, the following test was performed. Some pigment powders (nominal size 100 $\mu$ m) both black and white were located in the reactor in two different layers. After pumping down to 10<sup>-5</sup> mbar, argon flow was increased in order to observe the fluidization behaviour. After one minute after fluidization started, no difference could be observed between the two different colours and a final grey mixture was obtained. Although it is a preliminary test it allows to confirm that it is possible to treat powders in an homogeneous way.

Some trials with CB powders were done using the fluidised bed reactor. Grinded N134g with size about 100 microns was modified with oxygen plasma showing a decrease in pH from 9 to 5. However it has to be mentioned that some sparks were observed in the system which increased with oxygen content. On the other hand, fluidisation of fluffy CB was not achieved. Powders are in the C domain described by Geldart's classification which has been presented in section 3.1.1.4, which was described as the most difficult powder size to fluidize. However, the hope that CB may agglomerate and help to the fluidization process was not accomplished and CB would just go up to the top of the system. Further work is being developed in order to achieve fluidization of such material.

On the other hand, both LPP reactor (down-stream and fluidized bed systems) have been used by our group in order to modify hydroxyapatite powders with acrylic acid successfully (E.Garreta et al.2006).

It is important to say that from now on in this work, further results about CB modified by means of LPP treatments are related to the down-stream plasma system.

### **3.2 Atmospheric Pressure Plasma (APP)**

As it has been presented, LPP presents many important advantages in order to treat surfaces and some reactors have already been adapted to modify powder materials. The high versatility of this type of reactors being able to change gas feed ratios, flow, time treatment, power density among others allow to tailor surface properties in a wide range.

On the other hand, this technique presents an important drawback at industrial levels as it requires low pressure to achieve the plasma state which usually means a higher cost but also that it increases the difficulty to obtain continuous processes



The presented inconveniences and a very wide new area of applications are making the APP field a very hot topic in the plasma research field. The main advantages are the elimination of vacuum systems, reduction of costs, the possibility to use continuous systems and treatment of materials which present high vapour pressure. On the other hand, these systems present also some drawbacks being the glow stability and the homogeneity of final treated surfaces as two main examples. Despite these problems APP has been successfully used already in some fields such as etching, surface activation, ozone production and decontamination among others (U. Kogelschatz 2003 and Th. Lampe et al. 2003)

Contrary to LPP, which are all defined as glow discharges although they can be generated in different reactors configurations, several type of plasma nature have been described as APPs. Their classification is still nowadays quite confusing although some efforts to make it more clear have already been done (P. Napartovich 2001 and A. Friedman 2005). The main types of APP could be divided in two main regimes the microdischarge or filamentary plasma and the atmospheric pressure glow (APG).

Microdischarges and filaments are obtained always when corona systems are used. In a corona system one electrode has a thin and sharp configuration which produces the discharge (Fig. 3. 23). Corona description is beyond the scope of this work but detailed information may be found in several reviews (A. Friedman et al. 2005 and B. Eliasson et al. 1991a). In the case of corona treatment air is used as plasma gas. This system is very useful to modify foils and has been widely used to modify polymeric films surface energy (K. Akutsu et al. 2000) however the treatment is restricted to surface oxidation and leaning.

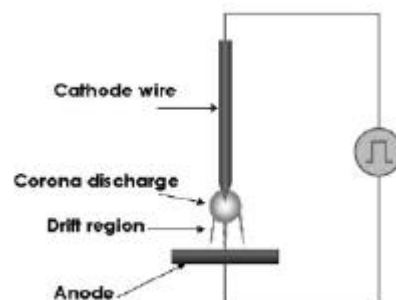


Fig. 3. 23 Corona plasma reactor configuration

Another well known configuration for APP treatments is the dielectric barrier discharge (DBD) In this case one of the electrodes, or both are covered by a dielectric layer in order to minimize electricity intensity and avoid arcing between the two electrodes. This problem is solved in the corona systems by using very low powers and pulsed energy, which usually provokes insufficient modification and lack of treatment homogeneity. DBD systems are much complex than corona systems and can present both microdischarges

(also known as silent discharges) and APG plasmas. The first is composed by cylindrical plasma channels of about  $100\mu\text{m}$  radius which take place in the nanosecond time scale, while the second one is very similar to the one obtained at low pressure conditions (U. Kogelschatz 2002)

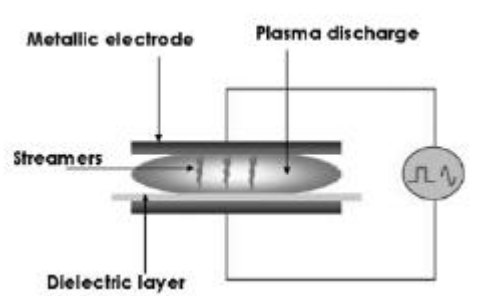


Fig. 3. 24 DBD plasma reactor configuration

Many studies have been carried out to determine which conditions are necessary to obtain APG and which may favour the formation of microdischarges. Gas type, has been defined as the most determining factor in order to obtain one or the other plasma type together with frequency of excitation and voltage. When the gas molecule presents a low ionization energy and therefore a low electronegativity the microdischarges present larger diameter and a diffuse plasma glow is obtained (B. Eliasson et al. 1991b). Gases can be grouped in the following order from thinnest to wider streamer channels and therefore from a more microdischarge plasma type to a more APG plasma type:

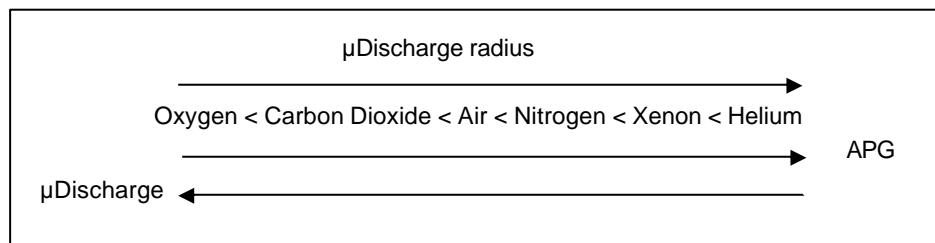


Fig. 3. 25 Influence of the plasma gas in the microdischarge radius and plasma nature

This is the reason why systems using He as plasma gas are described as APG plasmas. The first studies using these gases were carried out by Kanazawa using He and were confirmed by other studies (S.Kanazawa et al 1988, T Yokoyama et al 1990, D. Trunec et al 1998, F. Massines et al. 1998a, S. Guimond et al 2002). Although some authors have described the obtainment of APG in rich oxygen plasmas (S. Okazaki et al. 1993, M. Laroussi et al. 2003), other authors confirm the presence of microdischarges when oxygen content is higher than the 0.1 % (K.V. Kozolov et al. 2005, S. F. Mirala et al. 2000, F.Massines 1998b). For nitrogen plasmas the situation stays in the limit and both glow and filamentary have been described (K.V. Kozolov et al. 2005 N. Gherardi 2000 and F. Massines 2003).

DBD systems have been used in a very wide range of applications: excimer lamps, ozone production, surface treatment, CO<sub>2</sub> lasers and plasma panels (U. Kogelschatz 2003). In the field of surface treatment, which is closer to the final aim of this work, activation of polymer surfaces but also the deposition of SiO<sub>x</sub> or diamond-like carbon films are the two main topics described in literature (Y. Sawada et al. 1995, K. Pochner et al. 1995, M.J. Shenton et al. 2001, Y. Tsuchiya et al. 1998, R. Prat et al. 2000).

The most commonly used DBD configurations are the “planar configuration” with two parallel electrodes, or the cylindrical configuration where the dielectric is placed between two concentric electrodes, in both cases the gap between the electrodes is in the millimetre range. Therefore, one of the main disadvantages of this system is the difficulty to treat large objects as the electrode gap usually is presented in the millimetre range. To solve this problem another configuration was developed which received the name of plasma jet. In this type of system, a high flow of gas is blown through a nozzle where plasma is generated and brought to the open air due to the high gas flow. Moreover, the jet configuration also makes it easier to treat materials in a continuous way. Plasma jets are created out of several type of plasma types, DBD's, DC, microwave and RF discharges.

In this case, in order to avoid sparks and arcs in this type of APP reactor, high gas flows (3-10 slm approximately) and cooling systems are used. Due to this fact, one of the main disadvantages of this type of reactor is the high cost when a high flow of He are used.

As it was the case for DBD's both APG and microdischarges have been described in the plasma jets. APG discharges have been described when using RF excitation frequency, this type of reactor that was developed by J.Y. Jeong et al. and J. Park et al. is commonly known as Atmospheric Pressure Plasma Jet (APPJ) (J. Y. Jeong et al. 1998 and J. Park et al. 2000). Studies about the type of plasma obtained in a plasma jet were carried out by W.C.Zhu et al. using RF frequency in a He/O<sub>2</sub> gas mixture (W.C.Zhu et al. 2005).

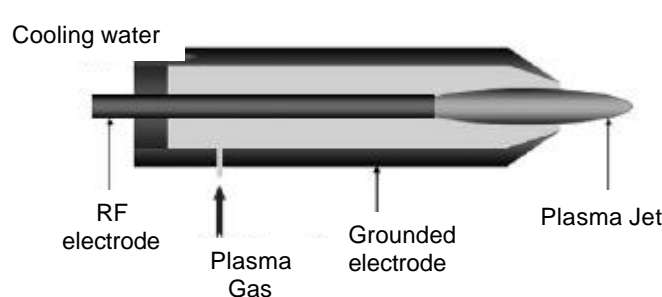


Fig. 3. 26 RF Plasma jet (APPJ) (C.Tendero et al. 2005)

However, there are many other plasma jet configurations which are presented next page at Fig. 3. 28, a detailed classification of the plasma jets described up to day is presented in a review by Tendero et al. (C. Tendero et al. 2006)

APP Jets have been used for etching purposes (K. Ionomata et al. 1995 and J.Y. Jeong et al. 1998), deposition of oxide films such as  $\text{SiO}_2$ ,  $\text{CeO}_x$  and  $\text{TiO}_2$  (S.E. Babayan et al. 1998, L. Bardos et al.1997 and R. Foest et al. 2005), diamond-like films deposition (D.W. Park et al. 1999), surface activation (Z. Hubicka et al. 2002), decontamination (H.W.Herrmann et al 1999), surface cleaning (J.M. Thiebaut et al. 2003) and surface modification in biomaterial to promote cell adhesion and growth (E. Stoffels et al 2002)

Finally it should be said that in the last 5 years, low powered arc plasma torches have been commercialized, they use homogeneous low-powered current-carrying arc plasma jet, and are commonly used in order to prepare surfaces prior to joining, coating and painting. Opposite to the classical arc plasma torches, the discharge generates very little heat, which allows the surface treatment of various materials including polymers. These pencil-like torches are classified as non-equilibrium plasmas. One of these systems is the one commercialized by Plasmacreat (Open Air System ®) which was used during this work to modify carbon black. This system will be presented in more detail further on. Other commercialized pencil-like plasma torches are: Plasmapen® (PVA-TEPLA) and Plasma-Jet® (Corotec Corporation). One of the advantages of these systems is the possibility to use air and nitrogen as plasma active gases reducing the costs of the treatment. The current carrying jet (Fig. 3. 27 a) allows to treat also polymers which are not so easily treated in transferred arc (Fig. 3. 27b)

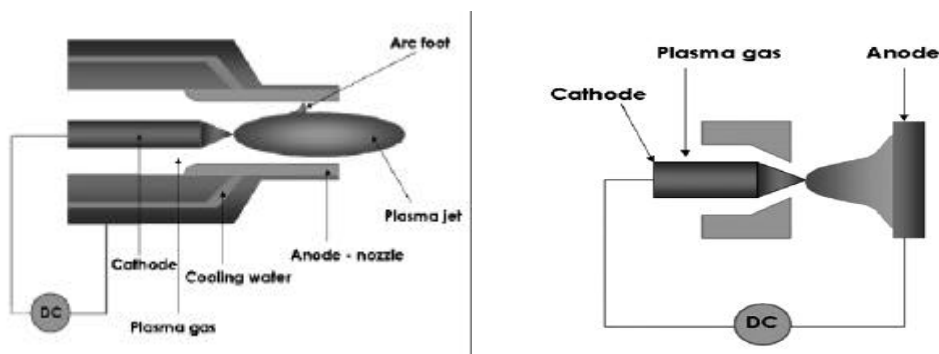


Fig. 3. 27 a) Carrying current ( plasma and b) transferred arc atmospheric plasma (C. Tendero 2006)

Characteristics of atmospheric plasma sources

Excitation	Source	Plasma properties	Operating conditions
<i>Industrialized sources</i>			
DC/Low frequency	Arc torch	$T_e = T_h \approx 8000 - 14,000 \text{ K}^s$ $n_e = 10^{21} - 10^{26} \text{ m}^{-3}$	Gas: Ar /He Gas flow: 10–150 slm Power: 10–100 kW
	Plasmatreat®	$T_h < 700 \text{ K}$	Gas: air Gas flow: 117 slm
Pulsed DC/Low frequency	Corona [19]	$T_e = 40,000 - 60,000 \text{ K}$ $T_h < 400 \text{ K}$ $n_e = 10^{15} - 10^{19} \text{ m}^{-3}$	Gas: air
	DBD [43]	$T_e = 10,000 - 100,000 \text{ K}^m$ $T_h < 700 \text{ K}$ $n_e \approx 10^{18} - 10^{21} \text{ m}^{-3}$	Some 100 W Plasma gas: 5–40 slm
Radio frequency	ICP [5,123]	$T_e = T_h = 6000 - 11,000 \text{ K}^s$ $n_e = 10^{21} - 10^{26} \text{ m}^{-3}$	Gas: Ar/He Gas flow: 10–200 slm Power: 50–700 kW
Pulsed radio frequency	IST [41]	$T_h < 400 \text{ K}$	Gas: surrounding air No gas flow Power: 20 kW
Microwave	Cyrannus [72]	$T_h < 700 \text{ K}$	Gas: Ar/O <sub>2</sub> Power: 6 kW
<i>Still in laboratory development sources</i>			
DC	Microplasma	–	Power: 500 V; 250 μA
Radio frequency	APPJ [19]	$T_e = 10,000 - 20,000 \text{ K}^s, m^1$ $T_h < 600 \text{ K}$ $n_e = 10^{17} - 10^{18} \text{ m}^{-3}$	Gas: O <sub>2</sub> /He Gas flow: 50–90 slm Power: some 100 W
	Cold plasma torch [19]	$T_e = 10,000 - 20,000 \text{ K}^s, 1$ $T_h < 700 \text{ K}$ $n_e = 10^{17} - 10^{18} \text{ m}^{-3}$	Gas: Ar Gas flow <1 slm Power: 100 W
	Hollow cathode [48,49]	$T_e = 3000 - 11,000 \text{ K}^s$ $T_h < 800 \text{ K}$ $n_e \approx 10^{17} - 10^{18} \text{ m}^{-3}$	Gas: Ar, He Gas flow <2 slm Power: some 100 W
	Microplasma CCμP [12]	$T_e = 1850 - 2300 \text{ K}$	Gas: Ar Gas flow: <0.2 slm Power: 5–25 W
Microwave	TIA [125]	$T_e = 13,000 - 14,000 \text{ K}^s$ $T_h = 2400 - 2900 \text{ K}^s$ $n_e \approx 10^{21} \text{ m}^{-3}$	Gas: He Gas flow: 2–6 slm Power: 100 W–2 kW
	MTD [62]	$T_e = 17,000 - 20,000 \text{ K}^s$ $T_h = 1500 - 4000 \text{ K}^s$ $n_e = 10^{20} - 10^{21} \text{ m}^{-3}$	Gas: N <sub>2</sub> Gas flow: 1–3 slm Power: 100 W–400 W
	MPJ [63]	$T_e = 12,000 - 17,000 \text{ K}^s$ $T_h = 5000 - 10,000 \text{ K}^s$ $n_e \approx 10^{22} \text{ m}^{-3}$	Gas: Ar Gas flow: 2–7 slm Power: 2–5 kW
	MPT [126,127]	$T_e = 16,000 - 18,000 \text{ K}^s$ $T_h = 3000 - 3500 \text{ K}^s$ $n_e \approx 10^{20} - 10^{21} \text{ m}^{-3}$	Gas: Ar Gas flow <1 slm Power: some 100 W
	Baeva et al. [70]	$T_e \approx 7000 \text{ K}^s$ $T_h \approx 7000 \text{ K}^s$ $n_e \approx 10^{19} \text{ m}^{-3}$	Resonant cavity Pulsed MW power supply Gas: N <sub>2</sub> Gas flow: 30 slm Power: 800 W
	Sugiyama et al. [128]	$T_e \approx 90,000 \text{ K}^s$ $T_h \approx 1000 \text{ K}^1$ $n_e \approx 10^{17} \text{ m}^{-3}$	Ignition by perovskite powder Gas: Ar/H <sub>2</sub> Gas flow: 0.3–1.2 slm Power: some 100 W

<sup>s</sup>: temperatures calculated from spectrometric measurements.  
<sup>m</sup>: temperatures calculated from models.  
<sup>1</sup>: temperatures calculated from Langmuir probe measurements.  
<sup>†</sup>: temperatures measured by thermocouple.

Fig. 3. 28 Plasma Jet classification by C. Tendero et al. 2005

### 3.2.1 Powder modification by APP treatment

Concerning powder modification using APP techniques, the number of published works is much lower than for LPP systems. The difficulty to handle powders in open air systems and make them flow through the APP region seems to be the main drawback. However some interesting works should be presented.

In order to treat powders some additional handling problems have to be considered. In continuous processes such as the one presented in this work, the need of powder fluidization to obtain an homogeneous treatment at the plasma zone, as well as the maximal recovery amount of the CB after the modification are two important points that should be studied in detail. Blockage of the system caused by the agglomeration of the filler on the walls should obviously be avoided. Although some systems have been described using plasma at atmospheric pressure they have only been able to treat small amounts of filler using batch reactions and they are briefly here described.

The group of Kogoma, which has been presented as one of the pioneers in the advances in the APG reactors were also one of the first to treat powders using this technique (Y. Sawada and M. Kogoma 1997). They used a circulating APG reactor to treat Silica particles (average diameter 152 $\mu$ m). In this case the glass tube works as the dielectric layer. Helium was used as plasma gas (3000sccm) with 1 percent of tetrafluoroethylene (30sccm). The reactor worked at a frequency of 15 KHz and 10 W of Power. Each batch reaction was able to treat 2 grams of the mentioned powder. The same group used the APG reactor in Fig. 3. 29 a) to treat Fe<sub>3</sub>O<sub>4</sub> pigments with He:TEOS (500sccm:10mg min<sup>-1</sup>) at 13,56 MHz and 250-300W (T. Mori et al 1998). In 2001 they used the reactor in Fig. 3. 29 b) in order to coat amorphous magnetic powders (Co<sub>70.3</sub> Fe<sub>4.7</sub> Si<sub>10</sub> B<sub>15</sub>) with zirconia ZrO<sub>2</sub> operating at RF 13,56MHz and 400W. A mixture He:O<sub>2</sub> (6500sccm:15sccm) was utilized for this purpose. In order to obtain the ZrO<sub>2</sub> coating, butyl zirconate was previously adsorbed on the magnetic powder which had an average diameter of 50  $\mu$ m (S. Ogawa et al. 2001).

Other groups used also the APP plasma circulating reactors to modify powders. This is the case of Alumina powders (60  $\mu$ ) coating in an RF reactor (13.56 MHz) by S.H Jung et al. (S.H Jung et al. 2004). In this case a powder eight of about 50 grams was used for each experiment. A mixture of He, Ar, O<sub>2</sub> and TEOS with a total flow of 1200sccm was used. In the all the described experiments till this point, the glow state of the discharge was achieved by using high flows of Helium which consequently makes the treatment quite expensive.

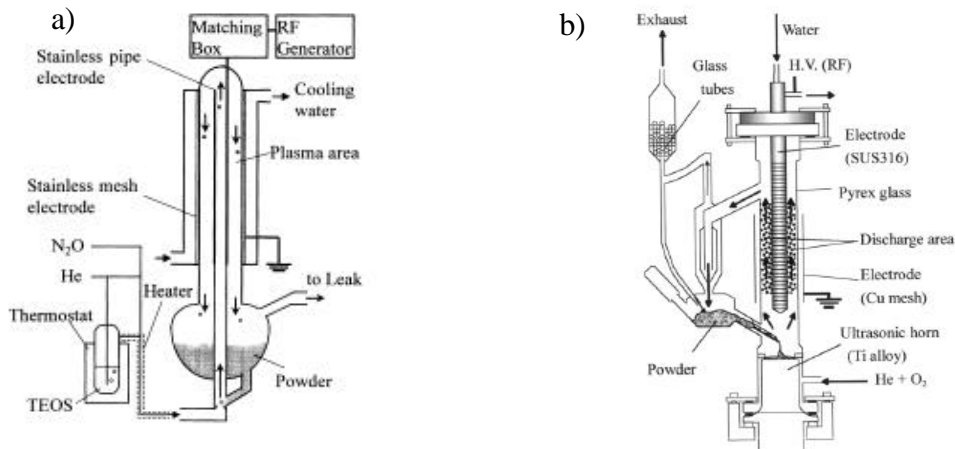


Fig. 3.29 Circulating APP reactors designed by the group of Kogoma (a) T. Mori et al. 1998 and b) S. Ogawa et al. 2001

The use of a fluidized bed in order to modify silica particles has also been reported. In this case particle average size was  $900\mu\text{m}$  which ensures a good fluidization behavior as has been explained before. A plasma jet (gliding arc) was adapted to fluidize the particles as shown in Fig. 3.30. Nitride deposition from the precursor chlorides ( $0.2\text{g}\cdot\text{min}^{-1}$ ) in a nitrogen ( $40\text{sccm}$ ) /hydrogen plasma was carried out. Higher temperatures are measured in this case ( $600\text{-}900\text{K}$ ) (I. Sanchez et al. 2001).

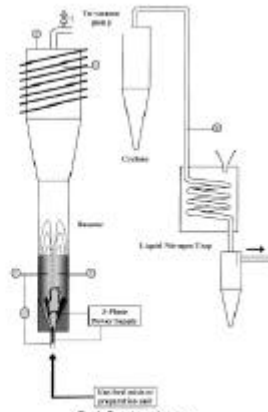


Fig. 3.30 Fluidized bed APP system (I. Sanchez et al. 2001).

Another system which has been recently described by H Yasuda is a combination between APP and LPP. A plasma jet is injected into an expansion chamber under low pressure, 1 torr or less, the flame extends about 1 m. depending on working conditions Usually monoatomic gases such as Ar or He are used as carrier gas but other reactive gases may be introduced in different positions. In such a process, particles are dropped into the horizontal of the jet a few centimeters away from the nozzle, and blown to the downstream of the expansion chamber and separated from the gas stream. Such system

could treat large amounts of powder in a short time (about 10Kg/hour), The determining step of this system is the powder feeding, whereas that in conventional plasma is the mixing of powder to enhance the exposure of powder surface to the luminous gas phase. No particular cases are described.

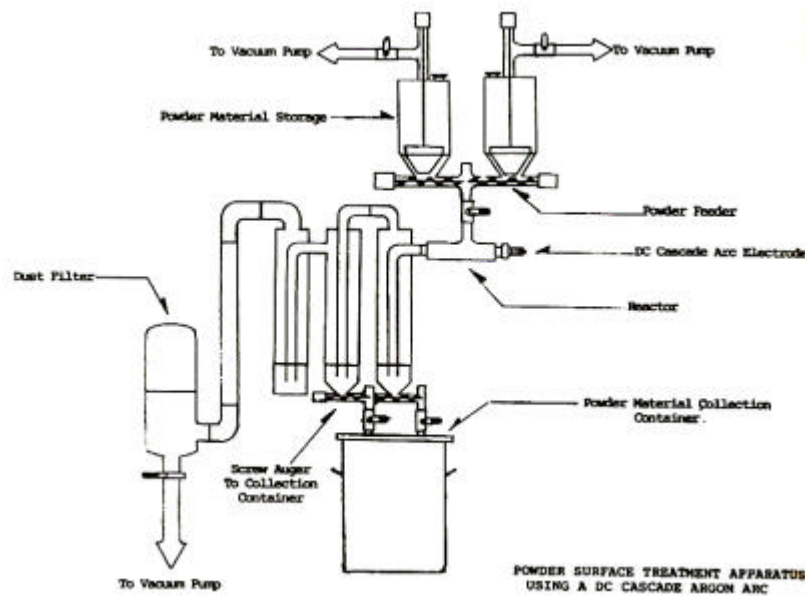


Fig. 3. 31 System described by Yasuda DC jet coupled to a LPP system (H. Yasuda 2005)

A very similar idea to the one proposed by Yasuda was developed during the current work as will be seen in the following section.

Some type of carbon powders have been in the last years also been treated using APP techniques. The first work done by T. Hanabusa et al. used a fluidized bed coupled to a plasma jet in order to coat activated carbon granules (average diameter (440 $\mu$ m) (T. Hanabusa et al, 1996). Argon was used as carrier gas (50 sccm) and temperature was kept at 298K. Reactant gases were SiH<sub>4</sub> (100sccm) and CH<sub>4</sub> (50 sccm) and C<sub>2</sub>H<sub>4</sub> (50sccm), which were injected through a couple of gas injection located 5.5mm away from the plasma nozzle end.

However, in some cases the powders were just deposited on the lower electrode of a DBD system. This is the case of the work of S. Kodama et al. who studied the oxidation of activated carbon in a DBD planar system (S. Kodama et al 2002). 0,3g of activated carbon were treated under a probably filamentary oxygen plasma (10 sccm). The plasma was generated at a frequency of 15 KHz. Ozone was determined to be the main plasma specie responsible for the activated carbon oxidation. Increase in Cu and Zn adsorption on the modified activated carbon was reported. The same method was used by D. Lee et al, in this case activated carbon was modified by a mixture of He:O<sub>2</sub> (5000 sccm: 0-200 sccm), in this case and enhancement of Fe adsorption was the aim of the treatment (D. Lee et al.



2005). In another study activated carbon was modified using three different APP reactors: DBD parallel-plate reactor (0,4g), plasma jet reactor (1g), DBD coaxial type (1g) also in a mixture of He:O<sub>2</sub>. The changes in the point of zero charge was used to determine the final effect of each type of reactor (S. Kodama and H. Sekiguchi 2006).

Carbon nanotubes have also been modified by means of a DBD system in the filamentary state (T.I.T. Okpalugo et al. 2005). Air was used as reactive plasma gas and carbon nanotubes were placed on a variable speed moving tray that was used as lower electrode. A similar system was used by S.J Park et al. in order to modify carbon fibers in a mixture of Ar:O<sub>2</sub> (1%) (S.J. Park et al. 2004). 1 gram of fibers were treated using RF at 13,56MHz and 300W. The total flow was 5000sccm which probably allowed to obtain a stable glow discharge.

Taking into account the presented facts, the scope of this work is to adapt an APP reactor for the treatment of CB in order to modify the surface chemistry of the filler. The changes of the filler surface chemistry as well as the effects on the polymer-filler interaction are evaluated after modifying the CB under different conditions (being plasma gas the most important).

### **3.2.2 Experimental Part (APP Reactor)**

#### *3.2.2.1 Open Air System ® (Pasmatreat GmbH)*

The plasma reactor corresponds to a plasma jet commercialized by Plasmamatreat GmbH. A Single Jet PFW10-PTF269 (Fig. 3. 34), electrode voltage 3-5KV. The Plasma generator FG 1001 working frequency 20 kHz. Plasma power is in the range of 500 to 1000W. The jet is described to be reactive in a distance from 4 to 20 mm from the plasma nozzle. Until the present moment this system has been used to improve polymer adhesion, aluminum etching, and improvement of wettability in order to improve printability. A scheme of the commercialized equipment is shown in Fig. 3. 32

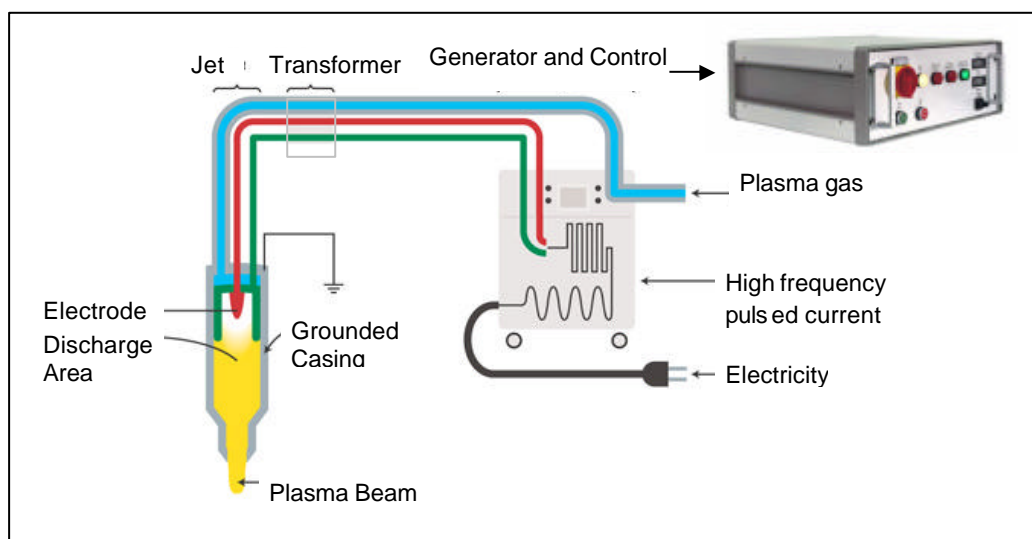


Fig. 3. 32 Scheme of the equipment provided by Plasmamatreat GmbH

### 3.2.2.2 Reactor description

The first step to achieve the surface modification was to set up an equipment able to perform the treatment. For this finality several modifications were introduced in the Plasmatreat equipment presented above. A scheme of the final APP system is presented in Fig. 3. 33 and will be described in detail bellow.

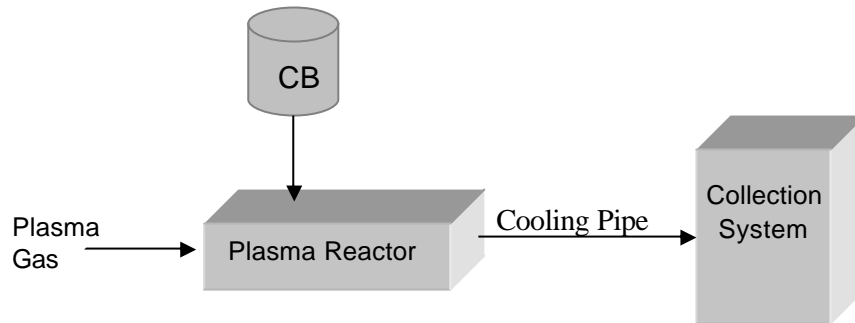


Fig. 3. 33 Scheme of the proposed system to modify powders using an atmospheric plasma jet

The equipment parts are described as following:

#### 1- The plasma torch

As already presented, consists in a nozzle through which a high flow of a gas is run, for example air and nitrogen were used in the present case. This gas is ionized by a discharge generating the plasma state which is present in a 2 cm zone from the nozzle. Next figure shows a scheme and a picture of such plasma torch.

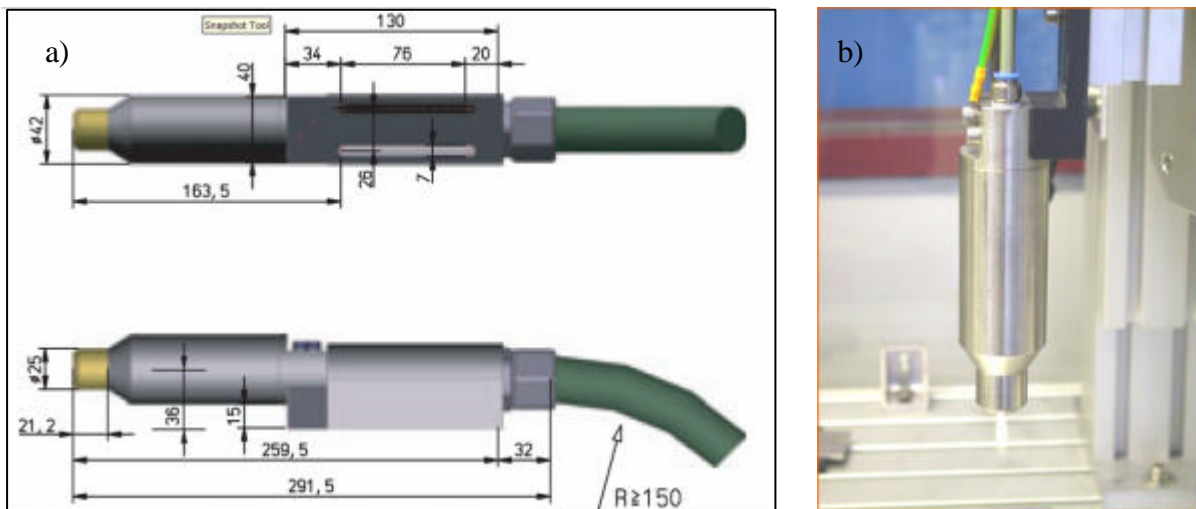


Fig. 3. 34 a )Detailed scheme of the plasma Torch b) Picture of the plasma torch

## 2- CB modification reactor:

A steel stainless cylinder was built in order to make the CB go through the plasma torch and achieve its modification. This reactor has a special geometry adaptable to the presented plasma torch. In order to introduce CB two different inlets were designed at 5 and 10 mm from the origin of the torch in order to be sure that CB. The residence time in the plasma region has been estimated from gas flow and plasma region length to be from 5 to 10 ms. A third inlet was placed downstream (40 mm) which was used to introduce reactive gases such ammonia that could react with the CB surface after being activated by the plasma treatment. The total length of the reactor was 200 mm (Fig. 3. 35).

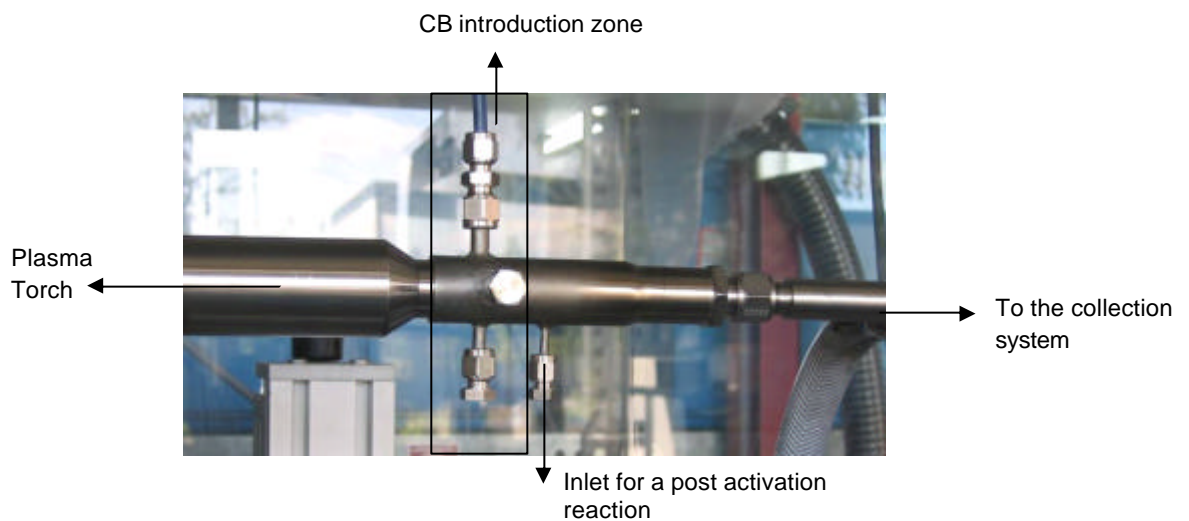


Fig. 3. 35 Picture of the reactor designed to modify CB by the atmospheric plasma jet

The inner diameter of the reactor was 5mm in order to be sure that the plasma flame was present homogeneously in the reactor. The activity of the plasma flame in this range (5-10mm length and 5mm with) was tested by modifying a polymer (SBR) sheet using a treatment distance of 10mm, afterwards the change in polarity was measured by means of inks of known surface tension, provided by Plasmatreat. Using both air and nitrogen as reactive plasma, the results showed that a treatment on SBR increased its surface energy from 60 to 120 mJ/m<sup>2</sup>, in a strip of 1,5cm width. Therefore it can be stated that inside the designed reactor plasma is present in the entire treatment zone.

In order to bring the modified CB to the collection system a pipe was connected at the end of the reactor. Further detail about this part of the system is given further on, in the results about the performed temperature studies.

### 3. CB introduction in the plasma reactor

Direct injection of CB by gravity through a funnel caused pipe obstruction and clogging due to the agglomeration of the powder, this problem could also cause the treatment to be inhomogeneous due to agglomerate formation. In order to solve this problem the idea of introducing the CB in gas suspension was taken into consideration and a convenient system was designed (Fig. 3. 36).

In order to introduce the filler in the plasma system CB is placed in a vessel where a fluidized bed is created by mechanical stirring. A flow of carrier gas (nitrogen) allows the introduction of the filler in the plasma reactor. It has to be said that other gases or mixtures could also be used for this purpose in order to obtain desired reactive species in the plasma zone. A flow of 2L/min was used in order to introduce the carbon black in the reactor. A scheme of the system is presented in fig. 3.36.

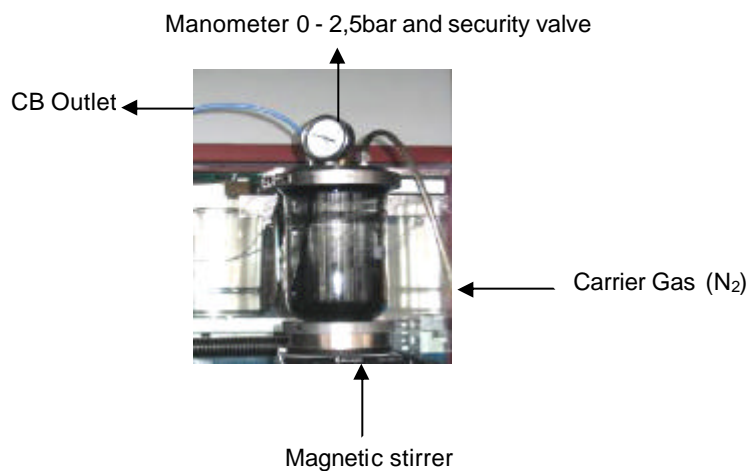


Fig. 3. 36 CB reservoir designed to introduce the powder in the plasma active zone

Glass vessel capacity was 2,5L with a 20cm diameter. Because the glass vessel is designed to work in a pressure range lower than 1 bar a manometer and a security valve, which opened at 0,75 bar, were also installed at the top of the vessel. A metallic top with all the necessary connections was also designed and adapted to the vessel through a DN 20 flange. In order to introduce CB after fluidization, a PTFE tube connected the vessel with the reactor. Two inlet sizes were tested 4 and 6 mm. although PTFE diminished adhesion of CB onto the walls the 6mm inlet was used in all experiments as many less blocking problems were found as for the 4mm tube.

### 4. Collecting system

The CB was collected in one of the filter bags used to collect the filler during the CB production. This bag was adapted and placed in a plastic barrel to avoid CB going into the atmosphere, as 2% of the filler is not retained. This barrel was connected to an exhaust system in order to remove the unretained filler.



Fig. 3. 37 Barrel were the textile bag to collect CB is placed at the end of the system

Fig. 3. 38 shows the amount of CB that was recovered in the collection bag after the treatment. In order to obtain this information a known amount of CB was blown through the system and weighted after the experiment. From these experiments it could also be observed that the average velocity of treatment was not constant as the carrier gas flow was not controlled giving a mean treatment velocity of 1g/min. However, controlling the carrier gas at 2L/hr a 3g/min rate was achieved as will be later explained.

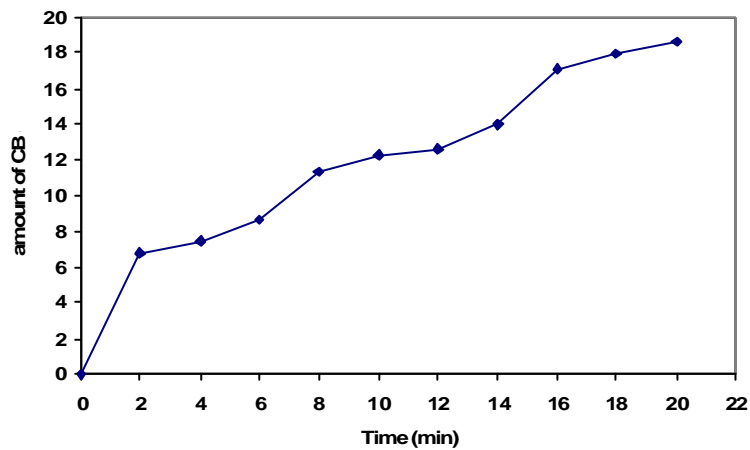


Fig. 3. 38 Amount of CB going through the system (not controlled carrier gas flow)

A global picture of the APP reactor which is adapted to treat powders and all the corresponding zones are shown in Fig. 3. 39. As it can be observed the APP torch itself is located also in a metacrylate box connected to the vacuum in case some toxic species are created during the plasma functioning.



Fig. 3. 39 Picture of the final APP system for powder modification 1:CB container, 2: plasma reactor, 3: cooling pipe, 4: collection system

After the set-up of the system, and due to the lack of information as no previous equipment like this had been described, several studies were performed to know better the working conditions. The studies were focused on the internal pressure of the system, the temperature and the gas composition.

### 3.2.2.3 Pressure Studies

As it has been mentioned, the plasma torch utilizes a high flow of plasma gas in order to keep a low temperature. Because the described system has the exit of the total gas through the presented collecting bag system, it could be thought that if the plasma gas could not get out of the system fast enough the pressure would increase preventing the carbon black to go into the system and maybe provoking the security valve of the glass vessel to open.

Therefore the relative pressure was measured at the inlet position of the carbon black by means of a water manometer. When a lower pressure was present in the system the water column would raise from its initial position, on the other hand if overpressure was built the water column would go down from the initial position. It was found that when no carbon black was present in the system, due to the high flow going through the plasma torch a Venturi effect was observed and consequently suction of gas through the CB inlet took place. This effect was maintained as long as the high plasma flow was present.

However, once CB was loaded in the system the pressure behaviour was different. As it can be observed in Fig. 3. 40 pressure at the inlet of the CB was dependent on the

amount of CB in the system. As it can be observed in the figure where pressure the relative water column movement is represented versus the CB amount in the system, it can be said that the larger the amount of CB in the system the lower is the suction effect in the CB inlet and after 13 grams a positive pressure is present at this point of the reactor. As a consequence, after reaching this point no more CB would enter the system. This effect is explained due to the CB covering the collecting bag. The CB clogs the textile pores and difficult the exit of the gas provoking an increase of the pressure in the system. This effect could also be observed when opening the collecting system. When CB was present in the bag, the bag was inflated due to the presence of the gas unable to leave the system, this effect was not observed when CB was not present.

To avoid CB velocity of entrance to the system dependence with changing inner pressure, a flow of 2 L/min of the carrier gas was forced to go through the vessel by increasing the pressure of the gas bottle. A total of 20 grams could be treated before the pressure reached 0,5bar which was considered the end of the treatment. However, opening the system to load more CB in the vessel was enough to decrease the inner pressure and perform a second treatment step. A total of 100 grams of CB could be treated without removing the filler from the collecting bag. It should be pointed out that some small engineering improvements are needed to convert this equipment in a fully continuous system.

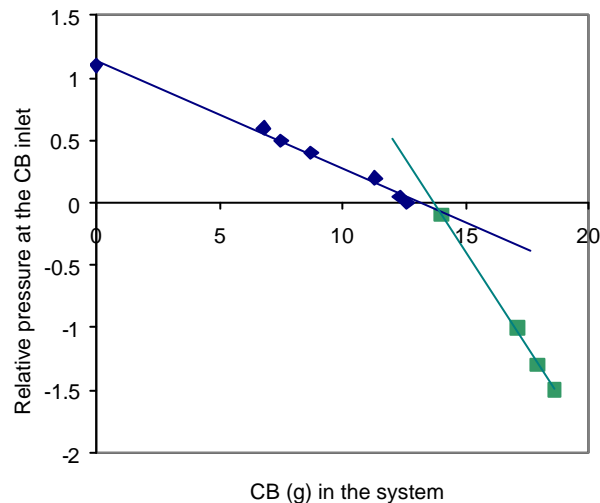


Fig. 3. 40 Relative Pressure at the CB inlet as a function of CB amount in the system

#### 3.2.2.4 Temperature Studies

In order to have more information about the temperature inside the system the temperature was measured at two different points of the system, at the end of the reactor zone (about 20 cm downstream from the plasma flame) and at the end of the cooling pipe.

Fig. 3. 41 shows the temperature variation in the mentioned regions. As it can be seen temperature increased steeply during the five first minutes. After ten minutes the temperature was stabilized around 300°C. This temperature should be kept in mind as it could influence the species formed in the reaction zone and consequently the final composition of the material.

On the other hand, two different systems were used in order to cool down the gas before entering the collecting device. In a first attempt a copper pipe was connected to both the reactor and the collecting bag. A home-made external copper coil was around the pipe and water was used in order to cool down the temperature. In this case gas temperature at the end of the pipe was 180°C. The lack of a good contact between the copper pipe and the copper coil was thought to be the main cause of still having rather high temperatures in the collection system.

In a second attempt a stainless steel pipe with cooling jacket was used to cool down the gas. The pipe was designed and manufactured by Iberfluid S.A. In this case a much lower temperature around 100°C is observed at the end of the cooling region. This temperature was thought to be low enough to avoid any post-treatment effect due to the heat during material collection.

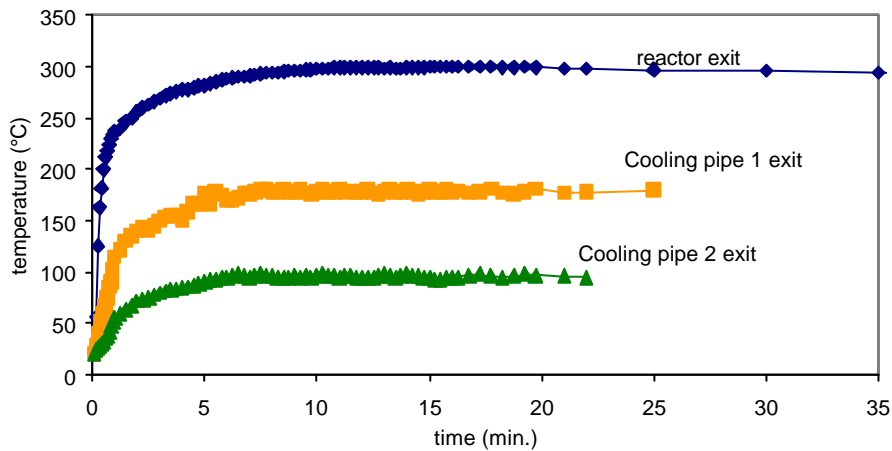


Fig. 3. 41 Temperature monitoring in the APP system

### 3.2.2.5 Gas Composition Studies

#### Gas Analysis

The gas composition in the system was tested in two different positions, at the plasma flame zone and after the cooling system just before the collection filter. In order to achieve the gas probes, an over pressure was created by means of a valve located at the end of the cooling pipe, which allowed to control the flow coming out at the two studied positions. When using air plasma different pressures of the gas at the plasma torch inlet were tested:



1,5, 2 and 3 bars (increasing gas flow). The flow variation influence could not be studied using nitrogen plasma as higher values than 1,5 cause instability of the plasma torch while lower flows are not sufficient to create the plasma.

As a first test, the gas coming from the plasma region was bubbled into 100ml. water and the pH change was determined. pH of water was checked to be between 6-6,5 before the test. For the gas coming from the air plasma torch a change in pH can be clearly observed. Gas taken at the end of the cooling system presents a slightly lower pH as the one taken from the plasma torch (Fig. 3. 42). In the case of nitrogen plasma the change in pH was not so important. pH changes caused from the gas coming in the reactor zone were not detected while at the end of the cooling system pH was found to be 5,8 after 10 minutes bubbling.

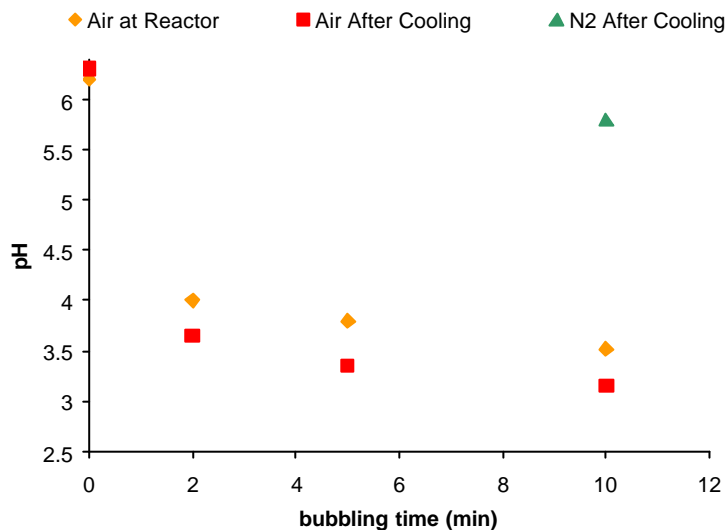


Fig. 3. 42 Water pH change after bubbling plasma effluent from Nitrogen and Air Plasma

The presence of soluble species in water such as  $\text{NO}_x$  and  $\text{CO}_2$  are probably responsible for the presented results. It should also be remembered that OH radicals (due to ambient and air humidity) in the plasma, may convert NO and  $\text{NO}_2$  molecules in  $\text{HNO}_2$  and  $\text{HNO}_3$  respectively.

In order to confirm  $\text{NO}_x$  presence a known volume of the plasma gas coming from the torch was bubbled into a dibutylamine solution. During the gas bubbling N-nitosodibutylamine (NDBA) was formed when  $\text{NO}_x$  was present. NDBA extracted from water to an organic solvent (dichloromethane). The final amount of nitrosamine was detected using a TEA detector after gas chromatography separation. Quantification was done with the help of N-nitrosodiisopropylamine (NDIPA) as an internal standard (CEN/TC 252 WG5/TG3). More detailed information and Chromatograms can be found in [annex 3](#).

Values for the  $\text{NO}_x$  concentration in air plasma are presented in Fig. 3. 43. The values are dependent on the position in the system and gas flow. Higher amounts are found at the end of the cooling system as the excited species created in the plasma have already recombined leading to stable ones. As far as flow is concerned, lower flows produce a higher amount of  $\text{NO}_x$  in the system due to a higher residence time in the reactor system. In the case of nitrogen plasma no  $\text{NO}_x$  was detected by means of this analysis technique. This result is consistent with the above presented result where pH was almost not modified after bubbling the nitrogen plasma effluent gas into water.

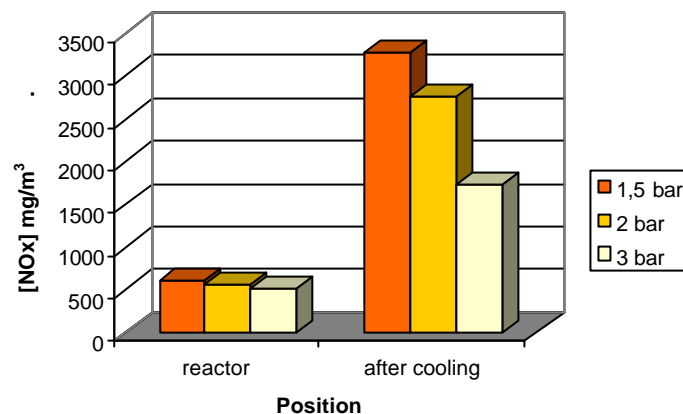


Fig. 3. 43  $\text{NO}_x$  concentration in 2 positions of the plasma system at different plasma flow

On the other hand, ozone presence was also studied due to its high oxidative and toxic properties. The presence of this specie has been already described by many authors in several DBD's systems (B. Eliasson et al. 1987, I.A. Kossyi et al. 1992, M. Kogoma et al. 1994, I. Stefanovic et al. 2001 J. Chen et al. 2002, U. Kogelschatz 2003). However, it has not been so much studied in plasma jets (J. Jeong et al 1998).

Ozone was tested by iodometry (annex 4), as explained above two positions and different pressures were also tested. The results for the air plasma show that there is a high concentration of ozone in the reactor system (Fig. 3. 44). Concentrations are much higher at the end of the cooling system as in the reactor zone itself. This phenomenon is probably because the conditions at 5mm of the plasma torch are not optimal for the ozone production and stability. On the other hand at the end of the cooling system all the ozone produced in previous regions of the system can be collected. It should also be said that higher pressure in the plasma torch lead to lower ozone concentrations due to the shorter residence time of the molecules in the system. This effect was also found in a DBD system, (J. Chen at al. 2002). On the other hand, low temperatures (below  $200^\circ\text{C}$ ) also favor the ozone formation and stability while increasing temperature from  $27^\circ\text{C}$  to  $220^\circ\text{C}$  has been reported to diminish the ozone presence in a 44%. However, ozone is detected up to  $500^\circ\text{C}$  (J. Chen et al. 2002).

In the case of nitrogen plasma no ozone was detected, neither in the reactor zone nor at the end of the cooling process.

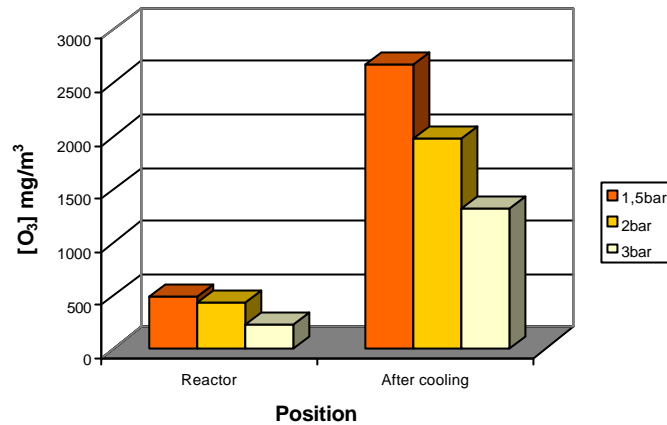
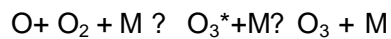


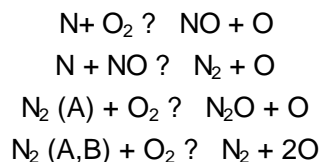
Fig. 3. 44 Ozone concentration in 2 positions of the plasma system at different plasma flow

The presented results agree with the studies performed on the ozone formation which is described by the following equations



Where M is a third collision partner : O<sub>2</sub>, O<sub>3</sub>, O, or in the case of air as is the one here presented, also N<sub>2</sub>

It is also well known that in air discharges, the presence of nitrogen ions N<sup>+</sup>, N<sub>2</sub><sup>+</sup>, nitrogen atoms and excited atoms and excited atomic and molecular species add complexity to the system. A variety of nitrogen species are generated: NO, N<sub>2</sub>O, NO<sub>2</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (B. Eliasson et al. 1987, I.A. Kossyi et al. 1992). Excitation and dissociation of nitrogen molecules, lead to a number of additional reacting paths involving nitrogen atoms and the excited molecular states (N<sub>2</sub>(A<sup>3?</sup> +<sub>u</sub>) and N<sub>2</sub>(B<sup>3?</sup> +<sub>g</sub>)) that can produce additional oxygen atoms for ozone generation.



Therefore, the presence of nitrogen influences the ozone production, it has been described that In a DC Corona Discharge half of the ozone is generated by the N<sub>2</sub> excited species and 1/3 by the O<sub>2</sub> excited species. The destruction of O<sub>3</sub> is mainly due to the presence of NO (J. Chen et. Al 2002).

Concerning to the ozone and NO<sub>x</sub> level detected in the presented APP system, the values are in the range of those obtained by Stefanovic et al. for mixtures of N<sub>2</sub> and O<sub>2</sub> in a DBD system (I. Stefanovic et al. 2001). When comparing it to the study of J.Y. Jeong in a plasma Jet, although in this case only 0.8% of oxygen was used, a proportional amount of Oxygen was also found (between 26 and 56 ppm) (J.Y: Jeong et al. 1998)

Both ozone and NO<sub>x</sub> are very strong oxidative substances. As a conclusion from the gas composition in the system obtained when using air plasma, it can be said that the oxidation, takes not only place in the plasma torch zone but also is followed during residence time in the system by O<sub>3</sub> and NO<sub>x</sub>. On the other hand, no ozone or NO<sub>x</sub> species have been detected nitrogen plasma, which leads to the conclusion that mainly nitrogen excited species are present in the reactor.

As a conclusion of this chapter it can be said that a down stream reactor has been redesigned for LPP modification of powder materials. The vacuum exit was relocated, and the reactive gas inlet was carefully positioned to allow surface modification of the materials down, in and up-stream of the plasma generation zone. On the other hand, a fluidized bed reactor for LPP of powders has been designed. The reactor has shown its versatility in terms of plasma position, size and shape of the treated powder. However, more experiments should be done in order to use this type of reactor in order to modify fluffy CB as it low apparent density and small size prevented to obtain a good fluidization behavior. Finally an APP device has been designed to be connected to a commercial AP torch from Plasmatrete GmbH, the reactor is able to treat fluffy CB in a velocity between 1-3g of CB/min in an almost continuous way.

Both the Down-stream LPP reactor and the APP reactor have been used to treat the selected CB grades in different gases and conditions that will be presented in next chapter.

**REFERENCES:**

- R. d'Agostino, Lecture at International Symposium on Plasma Chemistry (ISPC 17), Low Pressure Plasma Summer School, August 2005
- K. Akutsu, A. Iwata, and Y. Triyama, Surface Modification of Polymeric Films by atmospheric plasma treatments. *Journal of Photopolymer Science and Technology*, 13 (2000) 75
- F. Arefi-Khonsari, M. Tatoulian, F. Bretagnol, O. Bouloussa, F. Rondelez, Processing of polymers by plasma technologies. *Surface and Coatings Technology* 200 (2005) 14
- C. Arpagaus, A. Rossi, R. von Rohr, Short-time plasma surface modification of HDPE powder in a Plasma Downer Reactor - process, wettability improvement and ageing effects. *Applied Surface Science* 252 (2005) 1581
- S. E. Babayan, J. Y. Jeong, V. J. Tu, J. Park, G. S. Selwyn and R. F. Hicks, Deposition of silicon dioxide films with an atmospheric-pressure plasma jet, *Plasma Sources Sci. Technol.* 7 (1998) 286
- L. Bardos, H. Barankova, S. Berg, Thin film processing by radio frequency hollow cathodes, *Surface and Coating Technologies* 97 (1997) 723
- BMBF, German Federal Ministry of Education and Research "Plasma Technology: Process Diversity and Sustainability", Bonn 2001.
- Borros, S.; Picazo, Li.; Ferrer-Anglada, N.; Takhtoukh, Y.; Esteve, J. Plasma polymer thin films obtained by plasma polymerization of pyrrole. *Journal de Physique IV: Proceedings* 9 ( Proceedings of the 12th European Conference on Chemical Vapour Deposition, 1 (1999) 461
- J. P. Boudou, A. Martinez-Alonzo, J. M. D. Tascon, Introduction of acidic groups at the surface of activated carbon by microwave-induced oxygen plasma at low pressure. *Carbon* 38 (2000).
- W. Brandl, G. Marginean, Functionalisation of the carbon nanofibres by plasma treatment. *Thin Solid Films* 447 (2004) 181
- F. Bretagnol, M. Tatoulian, F. Arefi-Khonsari, G. Lorang, J. Amouroux, Surface modification of polyethylene powder by nitrogen and ammonia low pressure plasma in a fluidized bed reactor. *Reactive & Functional Polymers* 61 (2004) 221
- V. Brüser, M. Heintze, W. Brandl, G. Marginean, H. Bubert, Surface modification of carbon nanofibres in low temperature plasmas. *Diamond and Related Materials* 13 (2004) 177

- L. E. Cascarini De Torre,; E. J Bottani,.; A.Martinez-Alonso,; A.Cuesta,; A. B Garcia,.;J. M. D. Tascon, Effects of oxygen plasma treatment on the surface of graphitized carbon black. *Carbon* 36 (1998) 277
- CEN/TC 252 WG5/TG3 Methods for determining the release of N-Nitrosamines and N-Nitrosable substances from Elastomer and Rubber Teats and soothers, European Comitte for Standarization 1996
- COROTEC: [www.corotec.com](http://www.corotec.com) (18.01.2007)
- A. Cuesta, A.Martinez-Alonso and J. M. D. Tascon, Carbon reactivity in an oxygen plasma: a comparison with reactivity in molecular oxygen. *Carbon* 39 (2001) 1135
- Q. Chen, L.Dai, M. Gao, Sh. Huang and Albert Mau Plasma Activation of Carbon Nanotubes for Chemical Modification *J. Phys. Chem. B* 105 (2001) 618
- J. Chen and J.H. Davidson Ozone Production in the Positive DC Corona Discharge: Model and Comparison to Experiments, *Plasma Chemistry and Plasma Processing* 22 (2002) 495
- J.B. Donnet, W.D. Wang, and A. Vidal Observation of plasma treated Carbon Black Surfaces by scanning tunnelling Microscopy, , *Carbon* 32 (1994) 199
- B. Eliasson M. Hirth and U. Kogelschatz , Ozone synthesis from oxygen in dielectric barrier discharge, *J. Phys. D: Appl. Phys.* 20 (1987) 142
- B. Eliasson and U. Kogelschatz Nonequilibrium Volume Plasma Chemical Processing, *IEEE transactions on plasma science*, 19 (1991a) 1063
- B. Eliasson and U. Kogelschatz Modeling and Applications of Silent Discharge Plasmas *IEEE Transactions on plasma science*, 19 (1991b) 309
- P. Favia; N. De Vietro,; R. Di Mundo, F. Fracassi,; R.d'Agostino, Tuning the acid/base surface character of carbonaceous materials by means of cold plasma treatments. *Plasma Processes and Polymers* 3 (2006) 66
- P. Favia, Lecture at International Symposium on Plasma Chemistry (ISPC 17), Low Pressure Plasma Summer School, August 2005
- A. Felten, C.Bittencourt, , J. J Pireaux. G.Van Lier and J. C Charlier,. Radio-frequency plasma functionalization of carbon nanotubes surface O<sub>2</sub>, NH<sub>3</sub>, and CF<sub>4</sub> treatments. *Journal of Applied Physics* 98 (2005) 4308/1
- R. Foest, E Kindel, A. Ohl, M. Stieber and K-D Weltmann Non-thermal atmospheric pressure discharges for surface modification, *Plasma Physics and Controlled Fusion* 47 (2005) B525
- F. Fracassi, Lecture at International Symposium on Plasma Chemistry (ISPC 17), Low Pressure Plasma Summer School, August 2005

- A Fridman, A Chirokov and A Gutsol, Non-thermal atmospheric pressure discharges J. Phys. D: Appl. Phys. 38 (2005) R1–R24
- A. B García, A. Martínez-Alonso, C. A. Leon, J. M. D Tascon, Modification of the surface properties of an activated carbon by oxygen plasma treatment. Fuel 77 (1998) 613
- N. Gherardi, G. Gouda, E. Gat, A. Ricard and F. Massines, Transition from glow silent discharge to micro-discharges in nitrogen gas, Plasma Sources Sci. Technol. 9 (2000) 340
- L. G. Gibilaro, R. Di Felic and P. U. Foscolo on the minimum bubbling voidage and the Geldart classification for gas-fluidised beds *Powder Technology*, 56 (1988) 2.
- S.P Godfrey, E.J Kinmond, J.P S Badyal, I. R Little, Plasmachemical Functionalization of Porous Polystyrene Beads. Chemistry of Materials 13 (2001) 513
- S. Guimond, I. Radu, G. Czeremuskin, David J. Carlsson and Michael R. Wertheimer Biaxially Oriented Polypropylene (BOPP) Surface Modification by Nitrogen Atmospheric Pressure Glow Discharge (APGD) and by Air Corona, Plasmas and Polymers, 7 (2002) 71
- B.Gupta, J.Hilborn Ch. Hollenstein, C.J.G.Plummer, R.Houriet, N. Xanthopoulos, Surface modification of polyester films by RF plasma. Journal of Applied Polymer Science 78 (2000) 108
- S. Haiber, X. Ai, H. Bubert, M. Heintze, V. Brueser, W. Brandl and G. Marginean Analysis of functional groups on the surface of plasma-treated carbon nanofibers. Analytical and Bioanalytical Chemistry 375 (2003) 875
- T. Hanabusa, S. Uemiya and T. Kojima, Surface modification of particles in a plasma jet fluidized bed reactor. Surface and Coatings Technology 226 (1997) 88
- M. Heintze, V. Bruser, W. Brandl, G. Marginean, H. Bubert, and S. Haiber, Surface functionalization of carbon nano-fibers in fluidized bed plasma. Surface and Coatings Technology 174-175 (2003), 831
- H. W. Herrmann, I. Henins, J. Park, and G. S. Selwyn, Decontamination of chemical and biological warfare .CBW. agents using an atmospheric pressure plasma jet .APPJ. Physics of Plasmas 6 (1999) 2284
- Z Hubicka, M. Cada, M. Sicha, A. Churpita, P. Pokorny, L. Soukup and L Jastrabik, Barrier-torch discharge plasma source for surface treatment technology at atmospheric pressure Plasma Sources Sci. Technol. 11 (2002) 195
- I. Hudec and M. Jaso, Influence of plasma polymerization on Adhesion of Polyester Cords to Rubber Matrix, presented at the KHK, Hannover, Germany November 2006.

- T. Ihara, S. Ito, M. Kiboku, Low temperature plasma oxidation treatment of several organic pigments. *Chemistry Letters* 5 (1986) 675.
- K. Inomata, H. Koinuma, Y. Oikawa and T. Shiraishi, Open air photoresist ashing by a cold plasma torch: Catalytic effect of cathode material *Applied Physical Letters* 66 (1995) 2188
- J Y Jeong, S E Babayan, V J Tu, J Park, I Henins, F Hicks and G S Selwyn Etching materials with an atmospheric-pressure plasma jet, *Plasma Sources Science and Technology* 7 (1998) 282
- S. H. Jung, S. H. Park,; Dong Hyun Lee,; S.D. Kim, Surface modification of HDPE powders by oxygen plasma in a circulating fluidized bed reactor. *Polymer Bulletin* 199 (2001) 47
- S. H. Jung,; S. H. Park,; S.D. Kim, Surface treatment of polymeric fine powders by CF<sub>4</sub> plasma in a circulating fluidized bed reactor. *Journal of Chemical Engineering of Japan* 166 (2004) 37
- S.H. Jung and S. H. Park *Ind. Eng. Chem.. Res.* 43 (2004) 5483 Surface Modification of Fine Powders by atmospheric Pressure Plasma in a Circulating Fluidized Bed Reactor
- S. Kanazawa, M. Kogoma, T. Moriwaki and S. Okazaki (Stable glow plasma at atmospheric pressure) *J. Phys. D:Appl. Phys.* 21 (1988) 838
- M. Karches, Ch. Bayer, Ph. R. Von Rohr, A circulating fluidized bed for plasma-enhanced chemical vapor deposition on powders at low temperatures *Surface and Coatings Technology* 116 (1999) 879
- M. Karches and Ph. R. von Rohr Microwave plasma characteristics of a circulating fluidized bed-plasma reactor for coating of powders *Surface and Coatings Technology* 142 (2001) 28
- H. Kawamura, T. Okubo, K. Kusakabe and S. Morooka Plasma surface treatment of milled carbon fibre in a fluidized-bed reactor *Journal of Material Science Letters* 9 (1990) 1033
- S. Kodama, H. Habaki, H. Sekiguchi, J. Kawasaki Surface modification of adsorbents by dielectric barrier discharge *Thin Solid Films* 407 (2002) 151
- S. Kodama and H. Sekiguchi, Estimation of point of zero charge for activated carbon treated with atmospheric pressure non-thermal oxygen plasmas. *Thin Solid Films* 506 (2006) 327.
- U. Kogelschatz, Filamentary, Patterned, and DiffuseBarrier Discharges, *IEEE transactions on plasma science.* 30 (2002) 1400



- U. Kogelschatz, Dielectric-Barrier discharges: their history, discharge physics, and industrial applications, *Plasma Chemistry and Plasma Processing*, 23 (2003) 1
- M. Kogoma and S. Okazaki Raising of ozone formation efficiency in a homogeneous glow discharge plasma at atmospheric pressure *J Phys. D Appl Phys.* 27 (1994) 1985
- H.O. Kono C.C. Huang, E. Morimoto T. Nakayama and T. Hikosaka, Segregation and agglomeration of Type C powders from homogeneously aerated Type A–C powder mixtures during fluidization *Powder Technology*, 53 (1987) 163
- I A Kossyi, A Yu Kostinsky, A A Matveyev and V P Silakov, Kinetic scheme of the non-equilibrium discharge in nitrogen-oxygen mixtures, *Plasma Sources Sci. Technol.* 1 (1992) 207
- K V Kozlov, R Brandenburg, H-E Wagner, A M Morozov and P Michel Investigation of the filamentary and diffuse mode of barrier discharges in N<sub>2</sub>/O<sub>2</sub> mixtures at atmospheric pressure by cross-correlation spectroscopy *J. Phys. D: Appl. Phys.* 38 (2005) 518
- Th. Lampe, S. Eisenberg, E. Rodríguez Cabeo, Plasma surface engineering in automotive industry-trends and future. *Surface and coating technology*, 174 (2003) 1
- M. Laroussi, X. Lu and Ch. M. Malott A non-equilibrium diffuse discharge in atmospheric pressure air. *Plasma sources Science and Technology* 12 (2003) 53
- D. Lee, S. H. Hong, K.H. Paek, W-T Ju, Adsorbability enhancement of activated carbon by dielectric barrier discharge plasma treatment *Surface & Coatings Technology* 200 (2005) 2277
- J. B Leroy, N. Fatah, B.Mutel, J Grimblot, Treatment of a Polyethylene Powder Using a Remote Nitrogen Plasma Reactor Coupled with a Fluidized Bed: Influence on Wettability and Flowability. *Plasmas and Polymers* 8 (2003) 13
- X.Li, and K. Horita, Electrochemical characterization of carbon black subjected to RF oxygen plasma, *Carbon* 38 (1999)133
- A. A. Meyer-Plath, K. Schröder, B. Finke and A. Ohl Current trends in biomaterial surface functionalization—nitrogen-containing plasma assisted processes with enhanced selectivity 7 (2003) 391
- F. Massines, A. Rabehi, P. Decomps, R. Ben Gadri, P. Segur and C. Mayoux Experimental and theoretical study of a glow discharge at atmospheric pressure controlled by dielectric barrier *J. Appl. Phys.* 83 (1998a) 2950
- F. Massines, R. Messaoudi, and C. Mayoux Comparison Between Air Filamentary and Helium Glow Dielectric Barrier Discharges for the Polypropylene Surface Treatment *Plasmas and Polymers*, 3 (1998b) 43

- 
- F. Massines, P. Ségur, N. Gheradi, C. Khamphan, A. Ricard, Physics and chemistry in a glow dielectric barrier discharge at atmospheric pressure: diagnostics and modelling. *Surface and Coatings Technology*, 174 (2003) 8
  - S. F. Mirala, E. Monette, R. Bartnikas, G. Czeremuszkina, M. Latreche and M. R. Wertheimer Electrical and Optical Diagnostics of Dielectric Barrier Discharges (DBD) in He and N<sub>2</sub> for Polymer Treatment, *Plasmas and Polymers*, 5 (2000) 63
  - T. Mori, K. Tanaka, U. T. Inomata, A. Takeda, M. Kogoma, Development of silica coating methods for powdered pigments with atmospheric pressure glow plasma in *Solid Films* 316 (1998) 89
  - S. Morooka, T. Okubo and K. Kusakabe, Recent work on fluidized bed processing of fine particles as advanced materials. *Powder Technology* 63 (1990) 105
  - M. Mutel, H. Bigan and P. Vezin Remote nitrogen plasma treatment of a polyethylene powder optimisation of the process by composite experimental designs *Applied Surface Science* 239 (2004) 25.
  - A. P. Napartovich, Overview of Atmospheric Pressure Discharges Producing Nonthermal Plasma, *Plasmas and Polymers* 6 (2001) 1
  - S. Ogawa, A. Takeda, M. Oguchi, K. Tanaka, T. Inomata, M. Kogoma, Zirconia coating on amorphous magnetic powder by atmospheric pressure glow plasma. *Thin Solid Films* 213 (2001) 386
  - T. I. T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, N. M. D. Brown, Oxidative functionalization of carbon nanotubes in atmospheric pressure filamentary dielectric barrier discharge (APDBD). *Carbon* 43 (2005) 2951
  - S. Okazaki, M. Kogoma, U. Uehara and Y. Kimura, *J. Phys. D: Appl. Phys.* 26 (1993) 889
  - J. I. Paredes, M. Gracia, A. Martinez-Alonso and J. M. D. Tascon Nanoscale investigation of the structural and chemical changes induced by oxidation on carbon black surfaces: a scanning probe microscopy approach. *Journal of colloid and interface science* 288 (2005) 190
  - D. P. Norton and S. Pearton, Dry Etching of Electronic Oxides, Polymers, and Semiconductors, *Plasma Process Polym.* 2 (2005) 1
  - W. Pacek and A. W. Nienow, Fluidisation of fine and very dense hardmetal powders, *Powder Technology* 60 (1990) 145 .
  - D. Pappas, A. Bujanda, J. D. Demaree, J. K. Hirvonen, W. Kosik, R. Jensen and S. McKnight Surface modification of polyamide fibers and films using atmospheric plasmas, *Surface and Coatings Technology*, 20 (2006) 4384

- S. H. Park and S. D. Kim, Plasma surface treatment of HDPE powder in a fluidized bed reactor. *Polymer Bulletin* 33 (1994) 249
- S. H. Park and S. D. Kim Oxygen plasma surface treatment of polymer powder in a fluidized bed reactor. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* 133 (1998) 33
- J. Park, I. Hennins, H.W. Herrmann, G.S. Selwyn, J. Y. Jeong, R.F. Hicks, D. Schim, C.S. Chang, An atmospheric plasma source, *Appl. Phys. Lett.* 76 (2000) 288
- S.J. Park and J.S. Kim Influence of Plasma Treatment on Microstructures and Acid-Base Surface Energetics of Nanostructured Carbon Blacks: N<sub>2</sub> Plasma Environment. *Journal of Colloid and Interface Science* 244 (2001) 336
- S.J. Park and K. Byung-Joo,. Influence of oxygen plasma treatment on hydrogen chloride removal of activated carbon fibers. *Journal of Colloid and Interface Science* 275 (2004) 590
- D.-W. Park, J.-S. Yun, Structural characterization of diamond thin films prepared by plasma jet, *Thin Solid Films* 345 (1999) 60
- Plasmatreat GmbH: [www.plasmatreat.com](http://www.plasmatreat.com) (18.01.2007)
- K. Pochner, W. Neff, R. Lebert, Atmospheric pressure gas discharges for surface treatment, *Surface Coatings Technology* 74(1995) 394
- R. Prat, Y. J. Koh, Y. Babukutty, M. Kogoma, S. Okazaki, M. Kodama, Polymer deposition using atmospheric pressure plasmaglow (APG) discharge, *Polymer* 41 (2000) 7355
- PVA-TEPLA: [www.pvatepla.com](http://www.pvatepla.com) (18.01.2007)
- I.Sanchez, G.Flamant, D.Gauthier, R.Flamand, J. M Badie and G Mazza, Plasma-enhanced chemical vapor deposition of nitrides on fluidized particles, *Powder Technology* 120 (2001) 134
- Y. Sawada, S. Ogawa and M. Kogoma: *J. Phys. D. Appl. Phys.* 28 (1995) 1661-1669  
Synthesis of plasma-polymerized tetraethoxysilane and hexamethyldisiloxane films prepared by atmospheric pressure glow discharge
- L. I. Schukin, M. V. Kornievich, R. S. Vartapetjan, S. I. Beznisko, Low-temperature plasma oxidation of activated carbons. *Carbon* 40 (2002) 2028
- M.J. Shenton, M. C. Lovell\_Hoare and G.C. Stevens, Adhesion enhancement of polymer surfaces by atmospheric plasma treatment *Journal of Applied Physics* 34 (2001) 2754

- D. Shi, P. He, S. X. Wang, W. J. van Ooij, L. M. Wang, J. Zhao, and Z. Yu, Interfacial particle bonding via an ultrathin polymer film on Al<sub>2</sub>O<sub>3</sub> nanoparticles by plasma polymerization *J. Mater. Res.* 17 (2002b) 981
- D. Shi, J. Lian, P. He, L. M. Wang, W. J. van Ooij, M. Schulz, Y. J. Liu, and D. B. Mast, Plasma deposition of Ultrathin polymer films on carbon nanotubes *Appl. Phys. Lett.* 81 (2002c) 5216
- D. Shi, J. Lian, P. He, L. M. Wang, W. J. Van Ooij, M. Schulz, Y. J. Liu, and D. B. Mast, Plasma coating of carbon nanofibers for enhanced dispersion and interfacial bonding in polymer composites *Appl. Phys. Lett.* 83 (2003) 5301
- D. Shi, P. He, J. Lian, L. M. Wang and W. J. Van Ooij, Plasma deposition and characterization of acrylic acid thin film on ZnO nanoparticles *J. Mater. Res.* 17 (2002a) 2555
- I Stefanovic, N K Bibinov, A A Deryugin, I P Vinogradov, A P Napartovich and K Wiesemann Kinetics of ozone and nitric oxides indielectric barrier discharges in O<sub>2</sub>/NO<sub>x</sub> and N<sub>2</sub>/O<sub>2</sub>/NO<sub>x</sub> mixtures *Plasma Sources Sci. Technol.* 10 (2001) 406
- E Stoffels, A J Flikweert, W W Stoffels and G M W Kroesen Plasma needle: a non-destructive atmospheric plasma source for fine surface treatment of (bio)materials *Plasma Sources Sci. Technol.* 11 (2002) 383
- Y. Swada and M. Kogoma, Plasma-polymerized tetrafluoroethylene coatings on silica particles by atmospheric-pressure glow discharge *Powder Techn.* 90 (1997) 245
- T. Takada, M. Nakahara, H. Kumagai and Y. Sanada Surface Modification and Characterization of Carbon Black with oxygen Plasma, *Carbon* 34(1996) 1087
- M. Tatoulian, F. Bretagnol,; F. Arefi-Khonsari,; J. Amouroux, O. Bouloussa, F. Rondelez, A. J. Paul, R. Mitchell, Plasma deposition of allylamine on polymer powders in a fluidized bed reactor *Plasma Processes and Polymers* 2 (2005) 38
- C. Tendero, C. Tixier, P. Tristant, J. Desmaison and P. Leprince Atmospheric pressure plasmas: A review, *Spectrochimica Acta Part B* 61(2006) 2
- J.M. Thiebaut, T. Belmonte, D. Chaleix, P. Choquet, G. Baravian, V. Puech, H. Michel, Comparison of surface cleaning by two atmospheric pressure discharges, *Surf. Coat. Technol.* 169– 170 (2003) 181
- A. Tressaud, T. Shirasaki, G. Nanse, E. Papirer, Fluorinated carbon blacks: influence of the morphology of the starting material on the fluorination mechanism. *Carbon* 217 (2002) 40
- D. Trunec, A. Brablec and F. Stastny Experimental study of atmospheric pressure glow discharge *Contrib. Plasma Phys.* 38 (1998) 435

- Y. Tsuchiya, K. Akutu, A. Iwata, Surface modification of polymeric materials by atmospheric plasma treatment *Progress in Organic Coatings*, 34 (1998) 100
- K. Tsusui, K. Nishizawa and S. Ikeeda, Plasma Surface Treatment of an Organic Pigment., *Journal Coatings of Technology* 69 (1988) 107
- VDI Technologiezentrum GmbH, "Evaluierung Plasmatechnik" Düsseldorf 2004.
- E. Vidal-Escales, E.; Borros, S. Influence of carbon black surface activity on vulcanization reaction. *Gummi, Fasern, Kunststoffe* 56 (2003) 38
- J. Visser, Van der Waals and other cohesive forces affecting powder fluidization *Powder Technology*, 58 (1989) 1
- W.Wang, A.Vidal and J. -B Donnet, M.J. Wang, Study of surface activity of carbon black by inverse gas chromatography, Part III. Superficial plasma treatment of carbon black and its surface activity. *Kautschuk Gummi Kunststoffe* 46 (1993) 933
- L. Yang, H. Manian and W.J. van Ooij, "Plasma-coated pigments for use as corrosion inhibitors in organic coatings" resented at the ISPC 17, Toronto, August 2005
- H.Yasuda, *Plasma Polymerization*, Academic Press London (1985)
- H.Yasuda, *Luminous Chemical vapour deposition and Interface Engineering* p.359-360 Marcel Dekker, New York (2005)
- T Yokoyama, M Kogoma, T Moriwaki and S Okazaki The mechanism of the stabilisation of glow plasma at atmospheric pressure *J. Phys. D: Appl. Phys* 23 (1990) 1125
- W. Zhu, B. Wang, Z. Yao and Y. Pu, Discharge characteristics of an atmospheric pressure radio-frequency plasma jet, *J. Phys. D: Appl. Phys.* 38 (2005) 1396

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