Plasma processing of nano and microparticles in Gliding Arc Tornado device

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The Gliding Arc Tornado (GAT) is a device operating a near atmospheric pressure discharge with optimized hydrodynamical properties compared to those of gliding arcs reactors. The name points to the reverse vortex flow configuration, a tornado, of the gas-phase in the discharge region. In practice, this is implemented through a tangential gas injection from the lateral surface of a cylinder hosting the process chamber. This ensures an optimal mixing and much longer residence times respect to an axial laminar flow [1]. It provides also, normally a better insulation of the device walls from the discharge. It was also observed that a higher level of non-equilibrium characterizes the plasma gas-phase than in arcs. We have developed and used a kind of these devices for the treatment of lignin by plasmas [2]. Particles in powder, such as lignin, can be easily injected in the gas flow, separated and exposed to the plasma gas-phase while they are transported by the hydrodynamical flow. So optimal interaction with the discharge gas-phase could be achieved. Here we will present some results concerning the characterization of the discharge and of the plasma gas-phase. We discuss briefly also the prospect of plasma processing and its optimization, we have studied during a dedicated application, the POLISTE project [3].

The laboratory device was already described [2], see Figure 1. Here the anode is a three turns tungsten coil, with a diameter almost equal to that of the pyrex chamber hosting the tornado. It is supplied by a high-voltage dc generator (SHV9000 by Alintel), 6 kV and 2 A maximum. The grounded cathode is a hollow stainless steel disk through which the reverse flow jet is ejected. A residence

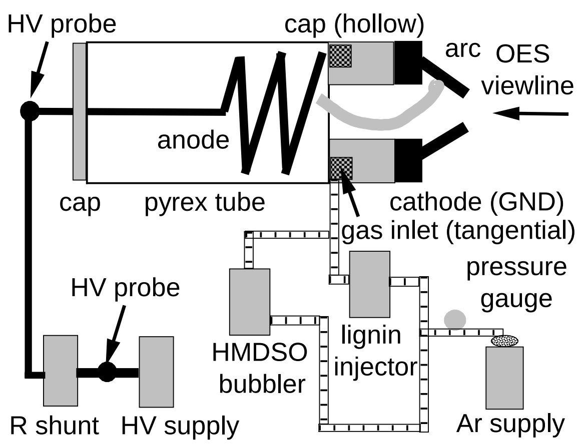

Figure 1 – Experimental setup

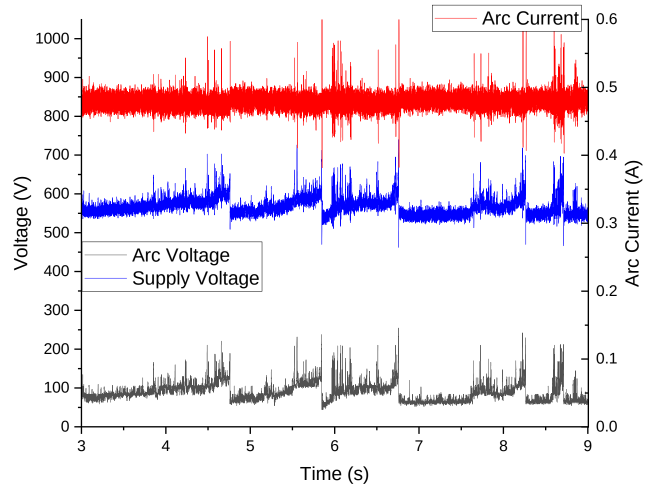

Figure 2 – Electric characteristics of Ar GAT.

time of a few milliseconds and outflow velocities of some tens of m/s have been estimated. A dust injector and a bubbler upflow, can be used to prepare a gas and vapour mixing that constitutes the initial gas-phase of the discharge. In the experiments described here a Soda Grass lignin was used (Protobind 1000 by Tanovis AG, Switzerland). Gel Permeation Chromatography (GPC) and SEM imaging show that lignin powder is composed by a wide range of irregular particles whose sizes cover the nanometer to micrometer scales. Mesh filters downstream the jet exiting along the tornado axis, can capture up to 80% of the particles. As a carrier gas we used argon whereas hexane and HMDSO were considered as vapour precursors.

The electrical characteristics of the discharge are controlled by selecting on the HV supply a value of the mean current intensity. As shown in Figure 1, a set of 16 high voltage, high power resistances, with a global resistance of 1 kΩ, is inserted before the anode. Two HV sensors at the load ends provide measurements the instantaneous values of the voltages on a digital scope and are used to estimate the electric current flow. At low current setting, the discharge displays an intermittent spark character [4]. Above a certain threshold of the setting, slightly depending on the inlet flow pressure and gas mixture composition, a stable arc is established, as shown in Figure 2. Despite the almost steady state, the arc is continuously sliding and reforming along the anode. The transition between the spark and arc regimes happens as the average current exceeds some threshold value, of the order of a few hundreds of milliamperes. Its value is a rising function of both the pressure load driving the tornado and of the electrodes gap distance. Vapour addition, as well as that of lignin particles, affects only slightly the electrical characteristics, in particular the transition among the two regimes.

More detailed information on the plasma gas-phase can be obtained by investigating the emission light from the discharge. Optical Emission Spectroscopy was performed using a wide band (180-850 nm), low resolution (0.4 nm) spectrometer (PS2000 by Ocean Optics) and an UV enhanced optical fiber, see Figure 1 [5]. A typical spectrum is shown in Figure 3 for discharges in pure argon and in an argon and hexane mixture. Spectra of the light emitted from the discharge show a broad continuum peaking at about 500-550 nm, with superimposed a rich structure of lines. In pure argon, the emission lines from electrons in the 4p excited levels (the $2p_n$ system in Paschen notation) dominates the spectrum. This feature could be exploited to extract the local electron (excitation) temperature, from the pattern of line intensities. $R_n = (I_n / b_n) / \left[k_n(T_e)\left(1 - \sum x^*\right) + \sum k_n^*(T_e) x^* \right]$, where I is the measured intensity of the selected n-th emission line and b is the branching ratio of that particular transition from the upper excited level involved, could be evaluated. In the above formula k and k* are the electron impact collision rate to the excited level corresponding to the n-th emission lines, respectively from the ground state and from the two metastable states, while x* are their concentrations. Minimization respect to the parameters allows to extract the electron temperature and the two metastable concentrations [6]. The addition of a small flow of vapour, in this case hexane, reduces strongly the argon emission. New broad lines appear, emitted from the optical active fragments of the hydrocarbon molecules. In particular the bands (not resolved by the low resolution spectrometer) of the vibrational states of excited C_2 radicals, can be observed. Also emission from CH and H atoms could be spotted. Again their relative intensity respect to reference argon lines, could be used to extract informations about the dissociation of the vapour precursor.

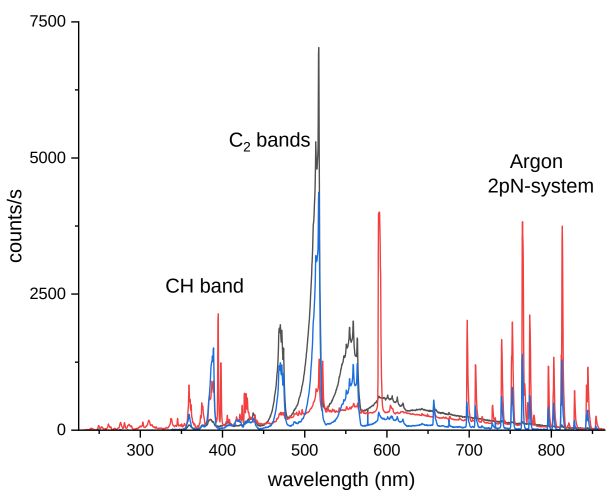

Figure 3 – OES spectra of Ar/Hexane GAT.

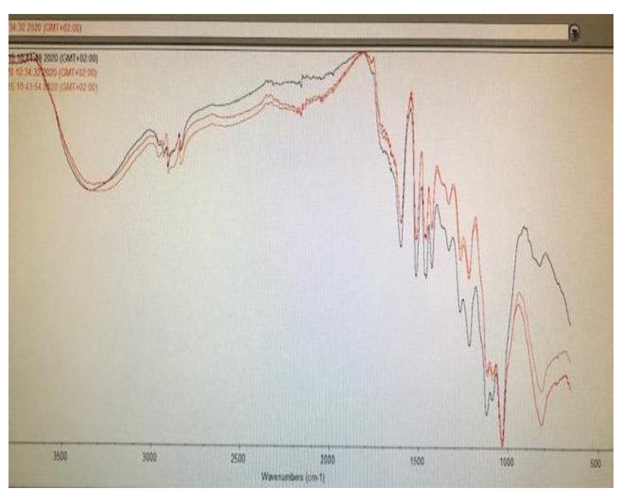

Figure 4 – FTIR of plasma treated Lignin.

The absence of the readily observable CO bands proves that no significant oxidation happens and back-mixing from external air does not contaminate the arc discharge.

As already stated, our main aim was to treat small size particles advected through the discharge by the reverse flow vortex [1]. As mentioned above, mesh filters have been employed to capture the lignin exiting the discharge region along the central axis jet. Here, we only notice that such dust collecting procedure does not alter significantly the dimensional distribution of the initial sample. Our first aim was to impart a hydrophobic character to the lignin particles. To this purpose we have considered the grafting and covering of the lignin by an organic silicon oxide deposition, starting form HMDSO precursor [7]. Fourier Transform Infrared Spectroscopy (FTIR) can be used to reveal the chemical groups and molecular structure of organic polymers. Untreated lignin, see Figure 4, has a broad band due to OH (around 3400 cm^{-1}) and a number of narrow peaks (2926, 1711, 1615, 1513 and 1120 cm^{-1}) due to C-H, C-O and C=O vibrations. After treatment in HMDSO containing GAT, lignin shows a new peak at 835 cm^{-1} similar to $Si\text{-}(CH_3)_3$ peak in pure HMDSO, supporting the evidence of grafting of organic silicon groups on the lignin. This is also complemented by the increase of the water contact angle, measured on lignin tablets (from 89.6° to 124.6°). There was also a strong increase of the signal of phenoxy radicals by Electron Paramagnetic Resonance (EPR) spectroscopy [8]. Both demonstrate the potential of plasma modification of the lignin particles surface.

We have presented some results describing the use of a GAT discharge for the treatment of nano and micro particles of lignin. Measurements aimed to the characterization of the plasma have been discussed, as well as a few analysis of the modifications observed at the particle surfaces.

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