Classification and Generation of Atmospheric Pressure Plasma and Its Principle Applications

(Review Article)

[1]Zahidur Rahman, [2]Hafijur Rahman, [3]Md. Atikur Rahman

[1, 2,3]Department of Physics, Pabna University of Science and Technology, Pabna-6600, Bangladesh

Abstract: **This paper provides a general discussion of atmospheric-pressure plasma generation, classification, and applications. There are two distinct categories of atmospheric-pressure plasmas: thermal and nonthermal. Thermal atmospheric-pressure plasmas include those produced in high intensity arcs, plasma torches, or in high intensity, high frequency discharges. Although nonthermal plasmas are at room temperatures, they are extremely effective in producing activated species, e.g., free radicals and excited state atoms. Thus, both thermal and nonthermal atmospheric pressure plasmas are finding applications in a wide variety of industrial processes, e.g. waste destruction, material recovery, extractive metallurgy, powder synthesis, and energy conversion. One of the most fascinating applications of atmospheric pressure plasmas is its use for biomedical applications because of its capability of producing various biocidal agents including reactive species, UV radiation, and charged particles.**

Keywords: **Atmospheric pressure plasma, Classification and generation of plasma, Applications.**

1. INTRODUCTION

Plasma is a gas with enough energy to ionize a significant fraction of its atoms or molecules, forming equal numbers of positive ions and electrons. Plasmas exhibit some properties of gases, but differ from gases in being good conductors of electricity and being affected by magnetic fields. Although there are free charges and ambipolar pairs in plasmas, overall the negative and positive charges compensate each other. Therefore, plasmas are electrically neutral, a property known as quasi-neutrality. Plasmas cover a wide range of pressures, temperatures, and electron densities; the classification of plasmas is shown in Figure 1 [1].

There are two main types of plasmas, atmospheric pressure and low pressure. For atmospheric pressure plasmas, the mean free paths between electrons and heavy particles are extremely short and, therefore, the plasma is collision dominated. Under such conditions, local thermodynamic equilibrium (LTE) may prevail, which includes kinetic equilibrium ($T_e \approx T_h$ where T_e = electron temperature and T_h = heavy particle or sensible temperature) as well as chemical equilibrium, i.e. particle concentrations in LTE plasmas are only a function of temperature. In contrast, in low pressure plasmas, the mean free paths are much longer and, therefore, collisions between particles are much less frequent. Under these conditions, the electron temperature is much higher than the heavy particle temperatures, i.e. $T_e \gg T_h$ (Figure 2) [1]. Even though ionization in low pressure plasmas is very high, the gas density in this type of plasma is extremely low. Therefore, thermal equilibrium cannot be achieved between electrons and heavy particles during collisions. Consequently, the heavy gas particles remain cold after collisions. Plasmas produced in various types of glow discharges, in low intensity high frequency discharges, and in corona discharges are typical examples of cold plasmas.

Within atmospheric-pressure plasmas, there are two distinct categories, thermal and nonthermal. A thermal plasma also called hot plasma is one which approaches a state of local thermodynamic equilibrium (LTE). In thermal plasmas $T_e \approx T_h$ (LTE exists). The core gas temperatures in thermal plasmas are well above 10,000 K and the gas is significantly ionized. A non-thermal plasma also called cold plasma is one in which the thermal motion of the ions can be ignored. Consequently there is no pressure force, the magnetic force can be ignored, and only the electric force is considered to act

on the particles The atmospheric nonthermal plasmas have very high electron temperatures, T_e, while the sensible temperatures, T_h, remain ambient. Atmospheric nonthermal plasmas have a low degree of ionization and the density of charged species is low.
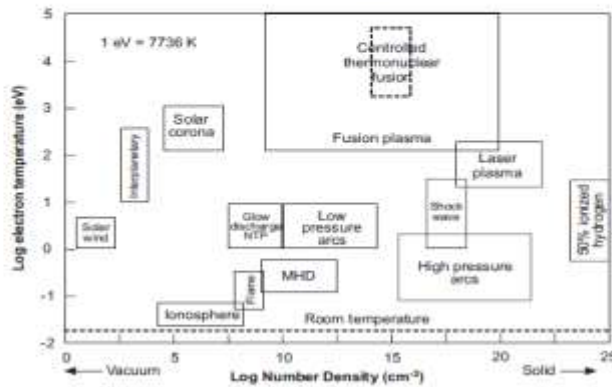

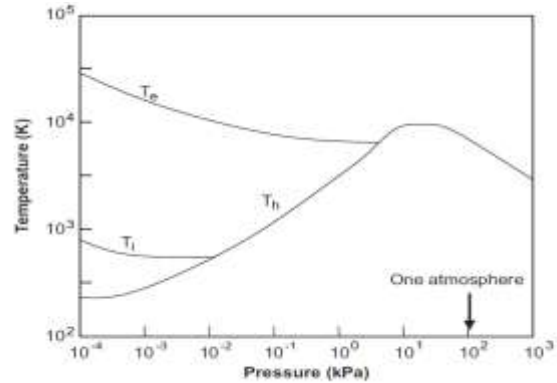
Fig.1: Classification of plasmas.	Fig.2: Variation of electron and heavy particle temperature with pressure.

The electrons and ions never achieve local thermodynamic equilibrium. For this reason, the gas is at room temperature. However, atmospheric nonthermal plasmas have a high density of activated species, i.e. reactive free radicals and excited state atoms. Thus, nonthermal plasmas are very reactive. Plasma technology has become an ideal solution for many industrial chemical, metallurgical and mechanical processes (Venkataramani, 2002). Thermal plasma powered systems are typical used for their unique characteristics such as high energy densities, high temperatures, small installation sizes, rapid startup and shutdown features, controlled process chemistry and use of electrical energy as a heating source resulting in decoupling the heat source from the oxygen flow rate (Heberlein J. et. al., 2007). Depending on the nature of the main plasma forming gas used, thermal plasma systems offer a high temperature heating source coupled with a highly reactive plasma plume rich in free radicals and ions which promote otherwise hard to drive chemical reactions, as well as high heat transfer rates. Atmospheric-pressure plasmas have a wide variety of potential industrial applications. They are used in extractive metallurgy; metal recovery; novel nanomaterial synthesis; refractory and wear resistant coatings deposition; chemical synthesis; energy conversion; industrial, medical, and nuclear waste destruction; engine combustion enhancement; and exhaust gas pollutants clean up. This paper presents an overview of the use of atmospheric-pressure plasma processes in several of these areas.

2. ATMOSPHERIC-PRESSURE PLASMA GENERATION

Plasma is generated by the passage of an electric current through a gas. Since gases at ambient temperatures are excellent insulators, a sufficient number of charge carriers have to be generated to make the gas electrically conducting. Passing an electrical current through an ionized gas leads to phenomena known as gaseous discharges. Such gaseous discharges are the most common, though not the only, means for producing plasmas. Thermal plasma may be generated by passing a gas through a high intensity electric arc discharge, which will heat the gas by resistive and radiative heating to very high temperatures within milliseconds, or through high intensity and high frequency arc discharges. The arcs are initiated by electron emission through a process known as thermoionic emission. The thermoionic emission of bonded electrons from a solid surface is caused by supplying a large amount of heat to the surface. If the surface temperature of the emitter is not high enough for pure thermoionic emission of electrons, a strong field is used to pull out the electrons. This process is called thermoionic plus field emission of electrons. Arc initiation by a high frequency arc starter belongs to this process. Plasma generators are classed as direct current (DC), alternating current (AC), radio frequency (RF), or microwave (MW) plasma generators. The DC and AC-generated plasmas are electrode-discharged plasmas, while RF- or MW-generated plasmas are referred to as inductively-coupled plasmas. The inductively-coupled plasmas are electrodeless discharged plasmas. Finally, thermal plasmas may also be produced by heating gases (vapors) in a high temperature furnace or in a combustion flame. Due to the inherent temperature limitations, this method is restricted to metal vapors with very low ionization potentials. In a flame-ionized gas, only the metal vapor is ionized, not the gas molecules, so the flame-ionized gas is not a real thermal plasma. Atmospheric nonthermal plasmas include the corona discharge, dielectric barrier

discharge, and surface plasma discharge. These discharges are generated by electron avalanche and streamer formation mechanisms. Ionization in nonthermal plasmas is not very high, but it is very effective in generating high concentrations of reactive radicals.

3.   APPLICATIONS OF ATMOSPHERIC PRESSURE PLASMA

3.1 Waste destruction and material recovery with thermal plasmas:

The destruction of toxic and hazardous wastes is a serious concern for this country. Manufacturing industries, communities, hospitals, farming operations, and educational and research institutions all produce hazardous wastes [2]. Nuclear operations, particularly at the Department of Energy sites, have produced high-level radioactive waste from the nuclear materials separation process, materials contaminated with transuranics, and low-level radioactive wastes. For example, the wastes at the Idaho National Laboratory (INL) [3] include solid combustibles, organic and inorganic sludge, hazardous organic compounds, structural metals, construction debris, and soil contaminated with long-lived radionuclides. There are also large stockpiles of toxic military wastes worldwide that present an environmental hazard. There are three main options for waste disposal: (1) burial, (2) treatment followed by burial, and (3) recycling to recover raw material and energy followed by disposal of residues [4]. With the amount of available land shrinking, burial is becoming a less viable option. Incineration was once a treatment option, but it has technological limitations, e.g., treatment of large offgas volumes and fly ash. Recently, attention has focused on developing thermal plasmas for the destruction of hazardous wastes and stabilization of nuclear wastes. Thermal plasmas possess several favorable characteristics for waste destruction: (1) very high temperatures, (2) very high energy density, (3) very fast process kinetics, (4) homogeneity and readily controlled, (5) turn key system, (6) very small footprint, and (7) useful material recovery. Since the late 1980s, plasma waste destruction systems significantly greater than 0.5 MW have been commercialized in Europe and North America. Several examples of plasma waste destruction and material recovery are given below; interested readers should refer to the excellent review of thermal plasma waste destruction technology by J. Heberlein [5]. Toshiba Corporation [6] investigated an RF plasma process to detoxified fly ash and recover useful materials. Using a ZnO and PbO feed, they demonstrated that Zn metal can be recovered and auto-separated from the fly ash by controlling the condensation temperature. The Toshiba plasma process for fly ash destruction and metal recovery is shown in Figure 3.
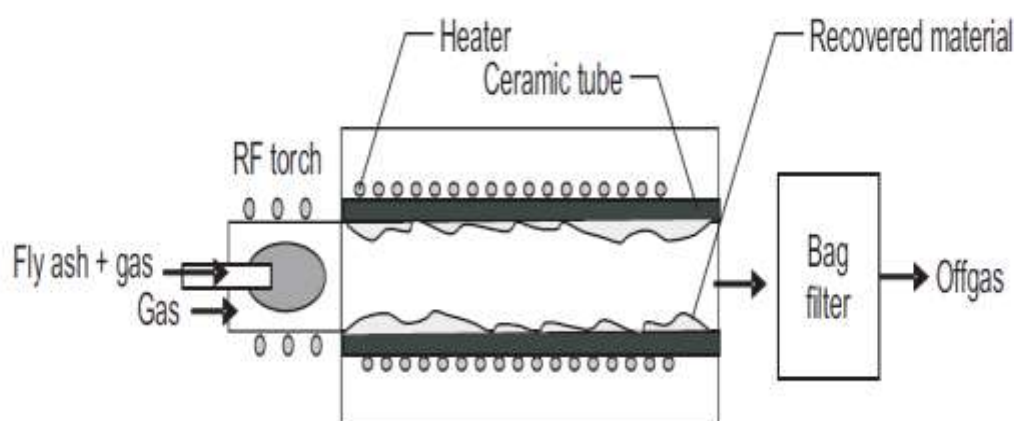

Fig.3: Schematic of Toshiba's RF plasma detoxification and recovery system.

Plasma cold hearth and plasma arc centrifugal furnaces have been investigated for waste treatment. The goals are to thermally destroy the combustible parts, reduce metal oxides, melt and pour the metals, and vitrify inorganic residue into a leach resistant slag. A plasma cold hearth furnace [7] employing two swivel torches that also rotate (Figure 4), was investigated for treating scrape metal, dross, dust and sludge, spent catalysts, laminates, and electronic scraps. In this furnace, waste material is fed to the first hearth for combusting, reducing, and melting under the first plasma torch. The melt then flows into the second hearth and is continuously heated by a second plasma torch. The second hearth is withdrawn to cool the melt to form an ingot. A large pilot-scale plasma arc centrifugal furnace [8,9] employed a nontransfer plasma torch to destroy hazardous and radioactive wastes (Figure 5). In this system, material to be treated is fed into a sealed, rotating (15–50 rpm) treatment chamber. A plasma torch melts the material that falls into the rotating tub. At regular intervals feeding is interrupted and rotation is slowed so vitrified material can be tapped.
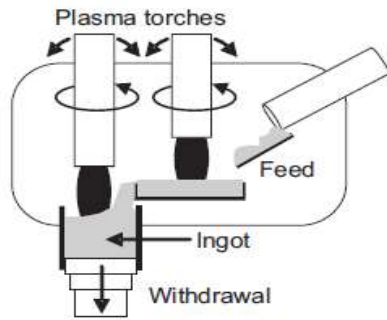
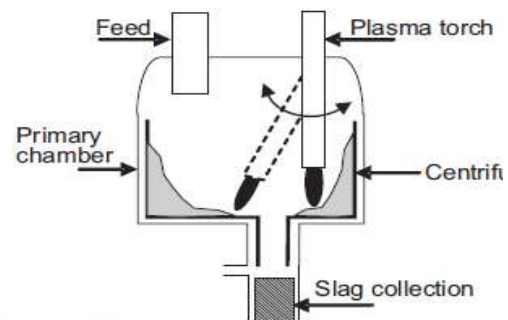**Fig. 4: Plasma cold hearth furnace.**   **Fig. 5: Plasma arc centrifugal furnace.**

Westinghouse and Barton developed a 1-MW mobile nontransfer plasma pyrolysis reactor for liquid waste [10,11]. The Westinghouse torch consists of two cylindrical water-cooled electrodes; the air plasma gas is injected through a narrow gap between the electrodes (Figure 6). A magnetic field rotates the arc root attachment on the electrodes, reducing the electrode wear. The liquid waste stream is injected into the jet immediately downstream of the torch. The system was tested with various wastes including PCBs (polychlorobiphenyls). The PCBs were destroyed at a rate up to 12 L/min and at a torch power of 0.85 MW. A destruction efficiency of eight 9s was attained, with particulate and acid emission well below the U.S. Environmental Protection Agency guidelines. The entire process is self-contained; the equipment is mounted on a trailer so that it can be moved easily from one waste site to another.
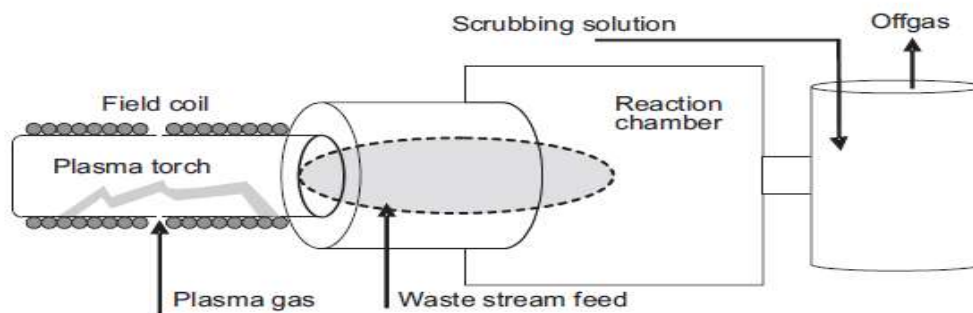

Fig. 6: Schematic of the Westinghouse 1 MW plasma pyrolysis reactor.

A laboratory-scale reverse-polarity plasma electrolysis process was developed by Taylor and Wang [12] to recover chromium from slag without using coke as a reducing agent (Figure 7). Two slag compositions, SiO_2-CaO-Al_2O_3-Cr_2O_3-Na_2O and SiO_2-CaO-Cr_2O_3-Na_2O, were used in the development. In each case, chromium oxide was successfully reduced to chromium metal. Aluminum was also reduced from alumina. The energy requirement for the reverse-polarity process is much less favorable than the normal polarity reduction process with coke; the significance of this process is production of carbon-free aluminum and chromium metals as well as no carbon dioxide emission. Taylor and Pirzada [13] give an in-depth review of plasma technology in extractive and process metallurgy covering the last several decades.
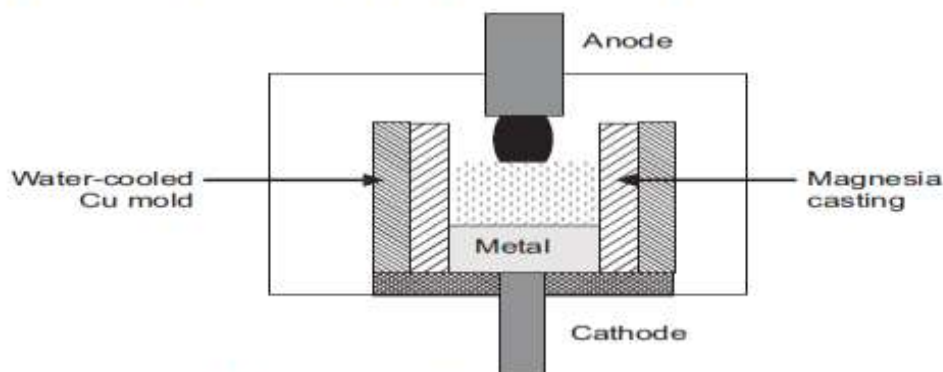

Fig. 7: Reverse-polarity plasma electrolysis reactor for metal recovery.

Recently, a process using thermal plasma with/without steam for pyrolysis of waste tires to produce carbon black and other gaseous products came out of China [14]. When the tire particles are injected into the plasma, volatile matter is released and cracked, yielding H_2, CO, C_2H_2, other light hydrocarbons, and solid residue. The solid residue contains primarily pyrolytic carbon black and a few percent of inorganics. Steam injection during plasma pyrolysis significantly enhanced the production of H2 and CO. This process may be attractive for syn-gas production from waste tires.

3.2 Nonthermal plasma destruction of wastes:

Plasma aftertreatment is a possible reduction method for nitrogen oxides, volatile organic compounds, and particulate matters in automotive exhaust. Nonthermal plasmas can induce a host of new chemical reactions due to the abundant production of radicals and excited state molecules. Corona-discharge or barrier-discharge plasmas could be used in such applications. Whatever type of nonthermal plasma is employed, all plasma aftertreatment technologies rely on high local electric fields that directly produce energetic electrons. The energetic electrons influence the chemistry, even in the ambient collision dominated regime, because they do not lose much energy in elastic collisions due to their small mass. Instead, they bounce around and transfer most of their energy to molecules, either dissociating, ionizing, or exciting them. The excitation and radical production can cause vast changes in reaction rates. A combination of oxidation and reduction reaction pathways is possible. Oxidation leads to compounds such as NO_2 and nitric acid; reduction leads to dissociative attachment, eventually forming N_2. In two review papers, Hammer [15] and Chae [16] discuss different plasma conditions for NO and HC (hydrocarbon) reduction. Nonthermal plasmas are also finding applications in destroying hazardous liquid wastes and chemical weapons. These applications will be briefly discussed. Rosocha et al. [17] developed a two-stage thermal and nonthermal waste treatment pilot process for hazardous organic waste at Los Alamos. The technology consists of a packed bed reactor (PBR) in the first stage to volatilize and/or combust liquid organics and a dielectric barrier discharge (DBD) reactor to remove entrained hazardous compounds from the offgas (Figure 8). The PBR and DBD technologies have been tested individually and in combination over a range of operating temperatures with a variety feed streams. At moderate energy density in the combined mode (PBR and DBD), the plasma reactor destroys the unburned hydrocarbons and chlorocarbons in the PBR effluent.

Safely demilitarizing the U.S. military's large stockpiles of chemical warfare agents is a high priority for the U.S. Department of Defense. The nerve agents, GB (also called Sarin) and VX, are extremely toxic organophosphorous compounds.
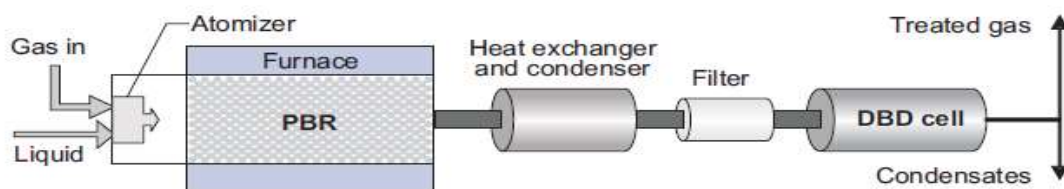

Fig. 8: Two-stage thermal and nonthermal waste treatment system.

Rosocha [18] investigated applying the PBR/DBD technology to destroy these agents. The two-stage thermal packed-bed and nonthermal plasma waste treatment system (Figure 9) was tested with methyl ethyl ketone and Malathion as surrogates. The test results, shown in Table I, established the technical basis for applying the PBR/DBD to chemical warfare agents. Destruction of chemical warfare agents requires a DRE (destruction removal efficiency) of at least six 9s. The U.S. Army sponsored a study to compare nonthermal plasma and hot gas decontamination (HGD) of chemical weapon shell surfaces [19]. The nonthermal plasma system destroyed up to 99.98% of 1.0 g TNT on an 8-mm shell in a one-step treatment. The treatment time is very short, about 10–15 minutes. A comparison between the plasma and HGD processes is shown in Table II. It is clear that nonthermal plasma outperforms the HGD process.
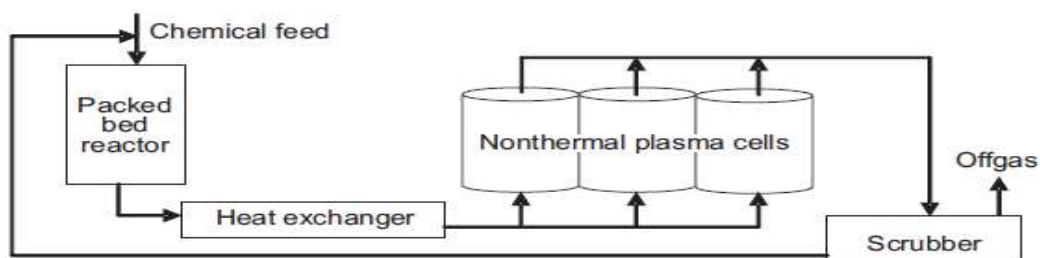

Fig. 9: Advanced oxidation technology for chemical demilitarization

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Table I. Destruction Efficiency of the PBR/BDB System on Chemical Agent Surrogates [18]

Configuration	DRE methyl ethyl ketone	DRE Malathion
PBR only	99.998783–99.999983	99.998780–99.999642
PBR closed-loop	99.999947	-----
PBR/DBD open-loop	99.999989	99.996423–99.999902

Table II. Cost, Environmental, and Performance Advantages of Nonthermal Plasma Process over HGD Process [19]

		Nonthermal Plasma	HGD
Cost	Operating	< $30.00/metric ton	$60.87/metric ton
	Fuel requirement	No	Yes
Environmental	Exhaust emission	<0.004 ft^3/min	~2,000 ft^3/min
	Fuel NO$_x$	Yes, but reduced	Yes
	Thermal NO$_x$	No	Yes
Performance	Cycle time	<1 hr	24 - 60 hr
	Nonmetal and intricate parts	Yes	No
	Temperature shell exposed to	Low (<100°C)	High (260–370°C)

3.3   The new functional treatment for nonwovens:

Textile manufacturers and end users alike have been searching for ways to improve the surface properties of natural and synthetic fibers. Specifically, there is a need to improve adhesion, wettability, printability, dyeability, as well as to reduce material shrinkage. Methods of modifying fiber properties to make polypropylene dyeable, including the process of copolymerization with polymers which can be dyed, have been evaluated. Traditional latex systems and primers with low melt points have been used to coat fabrics to promote ink adhesion, heat-sealing and thermoforming performance. Polypropylene nonwovens have especially been the focus of research to enhance colorfastness properties for the material because of its excellent chemical resistance, high melting point, low cost, and adaptability to many fabrication methods. To date, the poor dyeability of polypropylene nonwovens has limited optimization of its applications in the manufacturing of knitted yarns and fabrics, upholstery fabrics and industrial fabrics within the textile industry. Fibers with polar functional groups can be dyed more easily than non-polar fibers since polar groups will chemically bond with dye molecules. Because the molecular chains of polypropylene are non-polar and its surface is hydrophobic, the dye molecules will not chemically bond to the fibers. Polypropylene fibers also are highly crystalline, which also restricts its dyeability.

Plasma technology has been shown to improve fiber surface properties without affecting the bulk properties of these fibers. However, low-pressure plasma systems have required expensive vacuum equipment in order to increase surface hydrophilicity. Functional groups can be introduced onto the surface of fibers by using gas plasma treatments. By creating a polar layer on the fiber surface in reaction with functionality introduced, wettability of the fiber for dyeing is enhanced. A novel atmospheric plasma treatment (APT) process has been developed using glow discharge (APGD) technology as a result of studying the reaction mechanisms between plasma and fiber surfaces to optimize industrial system applications. The atmospheric plasma treatment apparatus does not require any vacuum systems, produces a highdensity plasma, and provides treatment of various nonwoven substrates at low temperature while operating at atmospheric pressure. This system also has the flexibility to be manufactured and used as a reduced ozone corona system and a controlled gas chemistry corona system with chemical corona. The wettability of various synthetic and natural fibers has been

dramatically increased by this process. Electron microscopy has shown that the surface of fibers after atmospheric plasma treatment is uniform and consistent; suggesting that the atmospheric plasma surface treatment is homogeneous.

Plasma is an ionized form of gas and can be created using a controlled level of AC or DC power and an ionizing gas medium. The plasma, commonly referred to as the fourth state of matter [20], that is created is an ensemble of randomly moving charged atomic particles with a sufficient particle density to remain, on average, electrically neutral. Plasmas are used in very diverse applications, ranging from manufacturing integrated circuits used in the microelectronics industry, through treating polymer films, to the destruction of toxic waste [21-23]. Plasma processes can be grouped into two classes, low density and high density, and are often displayed in an electron temperature versus density phase-space plot (Figure10) [21]. Low-density, direct-current and radio-frequency glow discharges are usually non-equilibrium, i.e., the electron and heavy particle (ions, neutral) temperatures are not equal. Low-density plasmas have hot electrons ($T_e > 10^4$ K) with cold ions and neutrals. Energetic electrons collide with, dissociate and ionize low-temperature neutrals, creating highly reactive free radicals and ions. These reactive species enable many chemical processes to occur with low-temperature feed stock and substrates. Low-density plasmas are usually associated with low material-throughput processes such as surface modification. Low density plasmas are used in a variety of processes such as: surface treatment, physical sputtering, plasma etching, reactive ion etching, sputter deposition, plasma enhanced chemical vapor deposition, ashing, ion plating, reactive sputter deposition, and a range of ion beam-based techniques, which all rely on the formation and properties of plasmas.
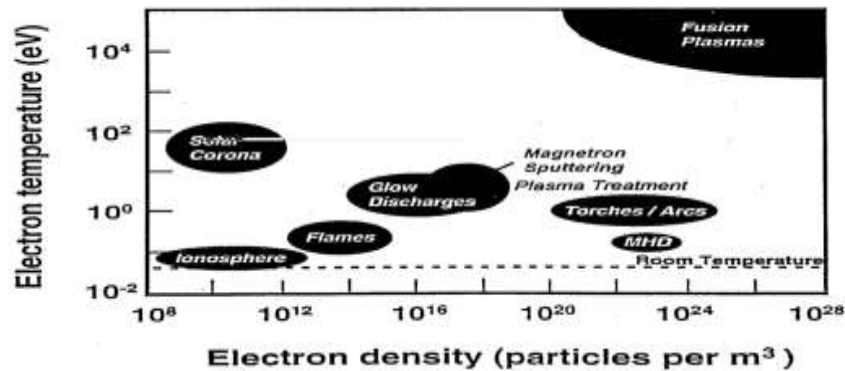

Fig. 10: Classification of plasmas, electron temperature vs. electron density [21].

The types of plasmas encountered in surface treatment processing techniques and systems are typically formed by partially ionizing a gas at a pressure well below atmosphere. For the most part, these plasmas are weakly ionized, with an ionization fraction of 10-5 to 10-1. Electron cyclotron resonance (ECR) plasmas can have higher ionization at high power [25]. Low-density plasmas can be established by AC or DC power input, and these systems can have many different types of geometry's depending upon the application. Since these systems are run at low pressures, vacuum chambers and pumps are needed to create and contain these plasma processes.

Atmospheric Plasma Treatment (APT) Process:

The APT process was developed for treating/functionalizing a wide range of materials and has unique advantages over the presently used technologies of corona, flame, and priming treatment. The APT system allows creation of uniform and homogenous high-density plasma at atmospheric pressure and at low temperatures using a broad range of inert and reactive gases. The APT process treats/functionalizes material surfaces in the same way as the vacuum plasma treatment process. APT production equipment testing has been successfully performed for the treatment of various materials, including polypropylene fibers, polypropylene and polyethylene nonwovens, polyester fiber, Tyvek®, nylon, wool, textile yarns, oriented polypropylene (OPP) film, polyethylene (PE) film, polyethylene teraphthalate (PET) film, and polytetrafluoroethylene (PTFE) film. The surface energies of the treated materials increased substantially (without any backside treatment), thereby enhancing their wettability, printability, and adhesion properties. In the Atmospheric Plasma Treatment (APT) process, plasma is generated at atmospheric pressure and at low temperatures using an AC power source, a proprietary designed electrode, a dielectric layer between the electrodes, and an appropriate gas mixture as the plasma medium is used. The electrode is connected to the AC power supply, while the rotating treater roll is grounded and acts as the other electrode. A general overview of the APT treater is shown in Figure 11.
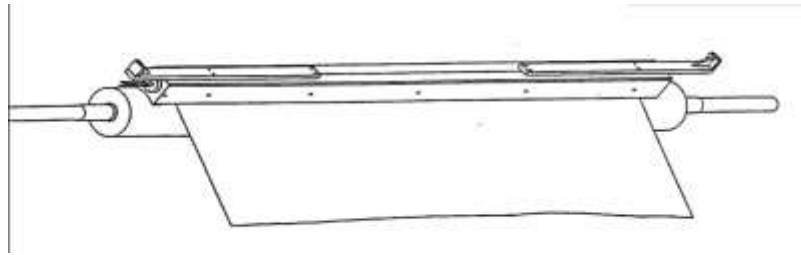
Fig. 11: A general overview of the atmospheric plasma treatment apparatus.

Attributes of the atmospheric plasma process:

The atmospheric plasma system can be used for treating and modifying the surface properties of both organic and inorganic materials. The plasma system can be used for a very wide variety of applications including, treatment of fabrics, wool, paper, foils, polymer films; plasma grafting and plasma polymerization; ashing various materials in microelectronics industry; barrier layer deposition for packaging industry, and sterilizing biologically contaminated materials. The Atmospheric Plasma Treatment (APT) process has the following attributes:

➢ Produces uniform and homogenous plasma at atmospheric pressure and low temperatures.
➢ A variety of process gases can be used
➢ Ideal for treating nonwovens, wovens, fibers, and films
➢ Uniform treatment
➢ Enhances surface energy of the films thereby improving wettability, printability and adhesion
➢ No backside treatment
➢ No need of vacuum chamber and pumps
➢ Available in all sizes
➢ Simple and rugged construction
➢ Automatic control and indicators

Modes of operation:

The APT atmospheric plasma system can be manufactured to operate in the following modes of operation:
➢ Plasma "Cold Flame" with controlled chemistry
➢ Reduced ozone corona
➢ Corona with controlled gas chemistry, called Chemical Corona™

Atmospheric plasma system can also be effectively used for cleaning, functionalization, and grafting of substrates such as fabrics, fibers, wool, films and papers.

Treatment results on nonwovens:

Several polypropylene nonwovens with a 0.40 mil. thickness were treated by the plasma treater at atmospheric conditions. These nonwovens were treated on webs sized from 27 – 60 inches in width. The key treatment parameters were input power, gas type, flow and the ratio of the gas mixture. Surface tension of the treated nonwovens was determined by surface tension test fluids markers (ASTM D-2578). The surface energy of these nonwovens was substantially enhanced after the plasma treatment. The nonwovens were then printed with an image of the American flag in four color process using photopolymer printing plates on a Mark Andy press with Akzo Nobel Hydrokett 3000 water-based ink. The anilox roll was 700 line screen with a 2.1 cell volume. The nonwoven material was printed in roll form at 200 fpm. The ink was dried in-line with a forced air at a temperature of 140 degrees F. Untreated, corona treated and plasma treated protocols for these nonwovens were then evaluated to determine the adhesion of the ink. A tape test was performed for each protocol using a ½ inch x 2 inch tape peel test using fresh transparent (clear) pressure-sensitive tape. The tape was applied to the printed side of the film and allowed to remain for 60 seconds. During the peel test, the untreated and printed nonwoven exhibited total ink adhesion failure, with all image ink removed with the tape. The corona treated nonwoven retained approximately 90% of the image ink at its surface. The APT-treated nonwoven displayed 100% ink adhesion, with no residue being removed from the surface. The trial supports the role and efficiency of atmospheric plasma in functionalizing the surface of polypropylene nonwovens for improved water-based ink adhesion.

A second test was performed to assess the "hold-out" of the ink from the nonwoven fiber structure. Since absorption of ink into printed substrates can diminish the surface perception of the pigments used, promoting ink hold-out on printed substrates can serve to increase the depth of color within the image. A comparison was made of untreated, corona treated and plasma treated polypropylene nonwoven material relative to the reflectance on light off of the aforementioned four color process image using a spectrophotometer. Spectrophotometers measure light reflected from an object at each wavelength. This spectral data is displayed in the Figure 12 graph form below:
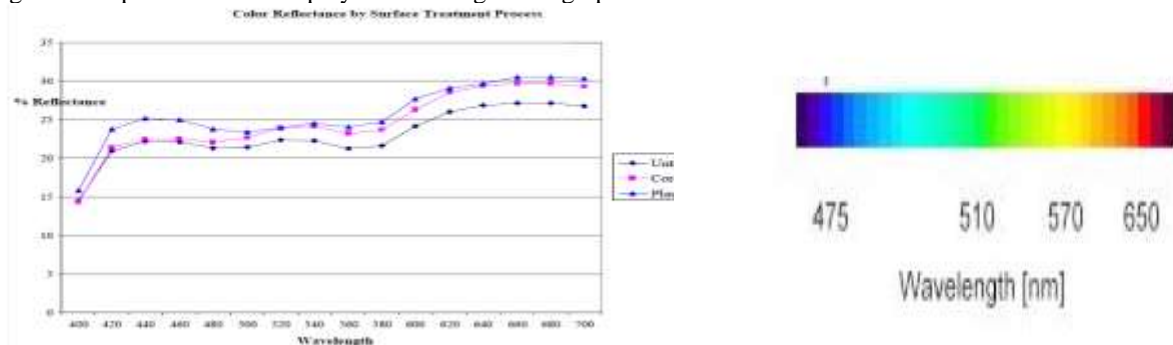

Fig. 12: Spectrophotometer measurements of light reflectance by wavelength.

Comparing the chart data in Figure 12 to the above wavelength spectrum, the plasma-treated nonwoven significantly increased the reflectivity of the flag image's primary blue and red tones beyond the reflectivity created by the untreated or corona-treated nonwoven. Additional APT trials on spunbond PET nonwoven materials utilizing gas chemistries have lead to improved dyeability using water-soluble inks and dyes. Although not a direct predictor of pigment adhesion, dyne levels of greater than 70 have been achieved for spunbond PET nonwovens.

3.4 Atmospheric pressure plasma treatments for repellent textiles:

Plasmas are formed when electromagnetic energy is coupled to a process gas to generate a mixture of ions, electrons, photons, and free radicals. This diverse collection of particles and energy can be used to clean, etch, activate, or coat surfaces. Treatment of textile substrates with plasmas has until recently been limited to batch processes involving vacuum conditions. Low pressure plasma processes use mature technology requiring high vacuum conditions. These processes are best suited for high-value, non-commodity products. Innovations in plasma generation and control have led to the development of atmospheric pressure plasma systems—systems that can treat textiles continuously at atmospheric pressures and room temperature. Chemical coatings, [26-32] surface energy modifications, [33-40] desizing enhancement [41-44] and dyeing properties [45, 46] after atmospheric pressure plasma treatment have all been topics of scientific study. Atmospheric pressure plasma processes require less capital investment than vacuum plasma processes and are well suited for high volume products such as textiles. The three major types of atmospheric pressure plasma are corona discharge, dielectric barrier discharge, and atmospheric pressure glow discharge [47].

Corona Discharge:

Corona discharges are plasmas formed from the application of a high voltage electric field (direct current, or continuous or pulsed alternating current) to asymmetric conductive electrodes. A typical arrangement for textile use is a thin wire electrode opposing a large diameter cylinder (Fig. 13). Plasmas generated by corona discharges are non-uniform and require narrow spacing between the electrodes. The free electron density in corona discharges is approximately 10^8 electrons/cm^3. A typical commercial corona discharge unit is shown in Fig. 14. These units have a relatively low power density of < 0.1 W/cm^3.
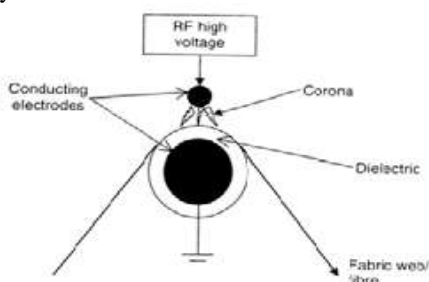

Fig. 13: Corona discharge.

Fig. 14: Commercial corona discharge unit.

Dielectric Barrier Discharge:

Plasmas are generated by dielectric barrier discharge when an alternating (1–100 kHz) high voltage (~ 20 kV) is applied across two fl at electrodes that are covered with a dielectric coating. A helium atmosphere is required to prevent arcing between the electrodes. A typical dielectric barrier discharge system is shown in Fig. 15. Plasmas formed by dielectric discharge frequently use a continual flow of helium for enhanced stability. Other gases such as oxygen or ammonia can be added in small amounts to the helium flow for enhanced surface reactions. Vinyl, acrylic, methacrylic, and other free radical polymerizable monomers can be injected into the plasma as fi ne droplets which then polymerize and attach to the fabric surface. Dielectric barrier discharge plasmas have an approximate electron density of 10^{10} electrons/cm^3 and a power density of about 0.1 W/cm^3.
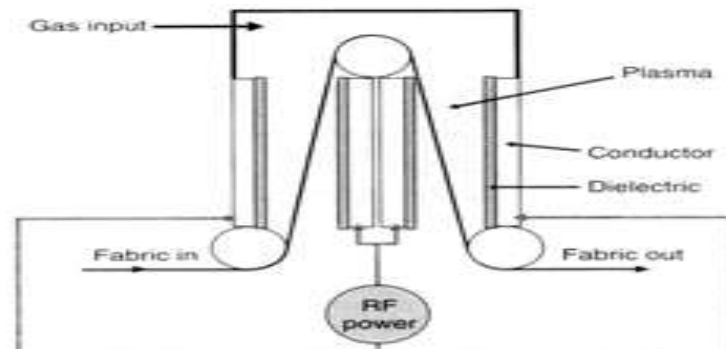

Fig. 15: Dielectric barrier discharge.

Atmospheric Pressure Glow Discharge:

Atmospheric pressure glow discharges generate plasmas by applying a relatively low voltage (~ 200 V) across two fl at metal electrodes at high frequency (13.56 MHz). Just as with dielectric barrier discharges, a flow of helium is necessary to prevent arcing. One typical atmospheric pressure plasma setup is given in Fig. 16. In this particular configuration, monomers polymerizable by free radicals can be applied to the fabric prior to entry into the plasma. Other gases can also be added to the helium flow for special surface treatments. Plasmas formed with atmospheric pressure glow discharge have an electron density of 10^{12} electrons/ cm^3, the highest of all atmospheric pressure plasma systems. These plasmas also have the highest power densities, > 10 W/cm^3. A commercial atmospheric pressure glow discharge unit is shown in Fig. 17.

A comparison of the times required for equivalent plasma power exposure for the three types of atmospheric pressure plasmas is given in Table III. Atmospheric glow discharge plasma requires the shortest time for equivalent power exposure, leading to the fastest production speeds.
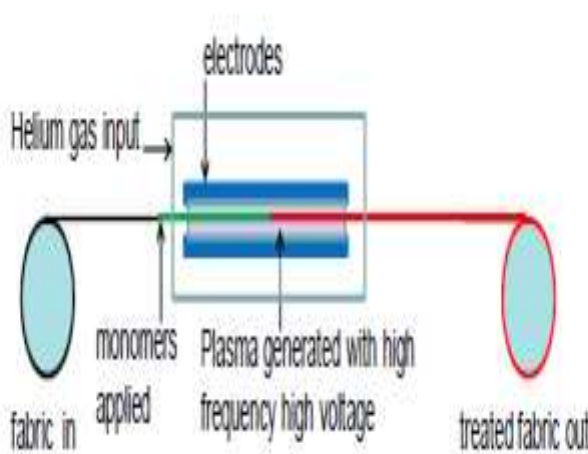

Fig. 16: Atmospheric pressure glow discharge.   **Fig. 17: Atmospheric pressure glow discharge unit.**

**Table III: Times for equivalent plasma power exposure**

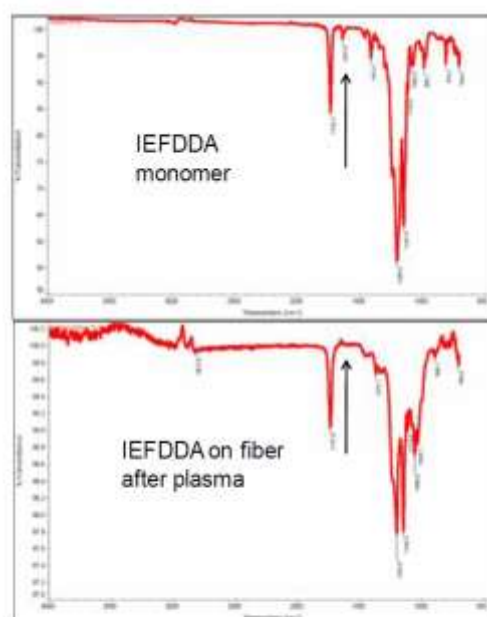|	
Corona Discharge	1000 s (~17 min)
Dielectric Barrier Discharge	100 s (~1.5min)
Atmospheric Pressure Glow Discharge	1 s

Plasma Treatments:

A laboratory atmospheric pressure plasma unit (Fig. 18), APPR Model 300-13 from APJeT [49] was used for fabric treatments. This unit operates on the atmospheric pressure glow discharge principle and was operated at 675 W and 13.56 MHz. A helium gas flow of 40 L/min. was used to maintain the plasma. The liquid monomers were mixed in a 10:1IEFDDA: PETA mole ratio and pumped at flow rates of 0.6–2.0 mL/min. into the APPR evaporator chamber where they are vaporized in an argon atmosphere at 165°C. The monomer vapors were then pushed into the 175°C applicator with Argon flow (1 L/min.) and allowed to condense on the room temperature fabric immediately prior to the fabric entering the plasma. Fabric samples (12-in × 12-in.) were exposed to the plasma for 4, 9, 13, or 23 s. FTIR analysis (Fig. 19) demonstrated that polymerization had occurred at the fiber surface. The infrared absorbance at 1637 cm^{-1}

present in the monomer spectra has disappeared after plasma exposure. Selected repellency results are summarized in Table IV. Repellency results from the conventional repellent finish are given in Table V.

As can be seen from the data tables, the plasma-applied repellent finish is comparable to the conventional pad-dry-cure repellent finish with the highest possible ratings for water/alcohol repellency. The exposure of the monomer treated fabric to a plasma clearly produced polymerization on the fabric surface. An exposure to plasma prior to monomer application (sample 3C) provided slightly higher oil repellency, possibly due to free radicals already being on the fiber surface when the monomers were applied.
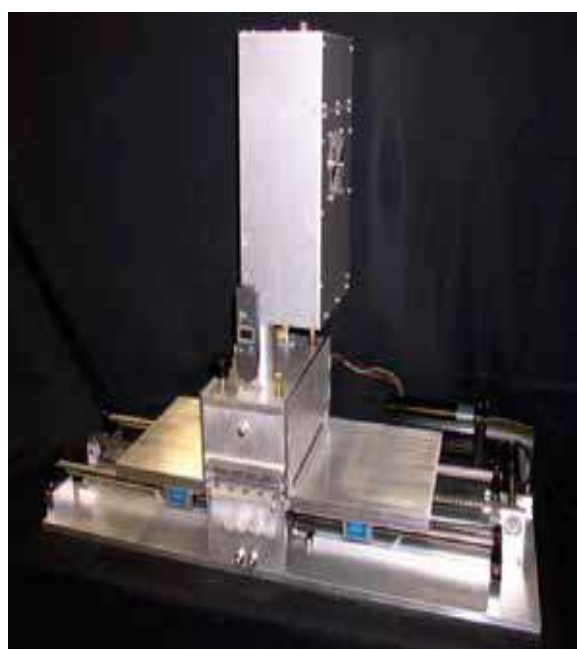
Fig. 18: Laboratory plasma unit.   **Fig. 19: FTIR spectra of monomer and polymer on fiber.**

Table IV: Repellency data from plasma treatments

Sample	Exposure Time (s)	Flow Rate (mL/min)	AATCC 127 (mm)	AATCC 118 (0–8)	AATCC 193 (0–8)
7	23	0.8	21.5	8B	8A
3C*	23	2	Not evaluated	8A	8A

* This sample was treated with plasma prior to and after monomer application.

Table V: Repellency data from conventional treatments

Sample	AATCC 118	AATCC 193
Conventional pad-dry-cure fluorocarbon repellent (~ 4% solids add-on)	6.5A	7.5A

3.5 Biomedical applications and diagnostics of atmospheric pressure plasma:

The choice of the plasma system used for treatment is usually guided by the kind of samples that are treated and the effect these plasmas are intended to have on the samples. The desire to use plasma for in-vivo treatments have made it necessary that several requirements for plasma sources be met. Necessarily, plasmas have to operate at atmospheric pressure if they are to be used for medical treatment of living organisms. At the same time, one needs non-equilibrium plasmas in order to achieve separation of electrons on the one side, and ions and neutrals, on the other. It is an advantage that no expensive vacuum systems are needed, while, on the other hand, it is much more difficult to achieve non-equilibrium (non-thermal) mode of operation at higher pressures. The sensitivity to heat of biomedical samples narrows the choice of non-thermal plasmas. There are many types of plasmas that can be generated under ambient pressure and temperature conditions suitable for treatment of sensitive samples [50,51,52]. The motivation is to develop new medical techniques, as plasma offers some possibilities for inducing desired processes with minimum damage to the living tissue [50-53]. While the first results seemed quite impressive, including effects on tumor cells and even active tumors [54], tooth decay treatment and tooth cleaning [55], wound healing [54], treatment of fungi and spores and even treatment of ulcers and blood vessels, one can still not rule out negative effects that have not been studied over a sufficiently long time scale. Th preliminary results, however, show a large degree of selectivity. Some of the well-known small-size atmospheric-pressure plasma sources are: plasma needle [56,53], μAPPJ [57], plasma bullet [58], plasma torch [59] and floating electrode dielectric barrier discharge plasma [60]. Their electrode configuration, voltages and excitation frequencies are very different; some of them work at microwave frequencies, some at 13.56 MHz and others at 5-120 kHz in sine or pulse regime. Yet, all is not understood about their physics and while models are being developed mainly based on low pressure plasmas, the reliable experimental data are limited due to the limited availability of diagnostic techniques that are suited for such plasmas. Here we will present several diagnostics techniques suited for atmospheric pressure plasmas and the operation of several different plasma systems working at atmospheric pressure.

Atmospheric pressure discharges – different experimental set-ups:

Achieving non-equilibrium at atmospheric pressure is difficult since the ionization growth is very fast at such a high pressure. The high degree of ionization on the other hand enables transfer of energy between electrons and ions through Coulomb collisions. Furthermore, heating of the background neutral gas is achieved through collisions between ions and neutrals. Thus, all schemes to produce non-equilibrium plasmas revolve around some form of control of the ionization growth. It can be achieved either by an inhomogeneous field as in corona or by employment of a dielectric barrier which turns the field off after a space charge is deposited on the dielectric. Ionization growth limiting may also be achieved by a time-varying field. Another approach is to operate at the *pd* value corresponding to the Paschen minimum, i.e. at microscopic dimensions and high pressures. In that case, the breakdown voltage is below the threshold for streamer development and thus a glow discharge may be achieved. If the electronegative nature of the gas is increasing the breakdown and operating voltages, one may mix in an inert gas. The discharge is thus initiated in the inert gas and then the atmospheric gas is mixed to produce chemically active radicals. In most cases, however, atmospheric pressure plasmas have small dimensions making it very difficult to perform standard diagnostics. Some of the plasma devices designed for in-vivo treatments are the μ-APPJ and the plasma needle, which operate at 13.56 MHz at atmospheric pressure. A micro-atmospheric plasma jet was developed by Schultz van der Gathen and coworkers [61]; this plasma source is interesting both for applications as well as for the study of its basic properties. The micro-atmospheric pressure plasma jet [μ-APPJ] consists of two symmetrical electrodes of equal length (34 mm) made of stainless steel. The distance between the electrodes can be adjusted with good precision from a few mm up to several hundred micrometers. In all our experiments, the distance between the powered and the grounded electrode was 1 mm. One of the electrodes was powered by a signal generator at 13.56 MHz while the other electrode was grounded. The measurements were made at powers of 40-80 W fed by a RF power supply. Plasma is ignited along the entire length of the electrodes (figure 20); for certain combinations of

power/gas-flow parameters, effluent of plasma coming out of the cuvette can be formed. The main advantage of this design is that both the discharge volume (plasma core) and effluent region are accessible for diagnostics, such as optical emission spectroscopy (OES) and two-photon absorption laser-induced fluorescence (TALIF) [57]. Also, the plane parallel geometry of the electrodes adds to the simplicity when it comes to modeling this type of discharge.
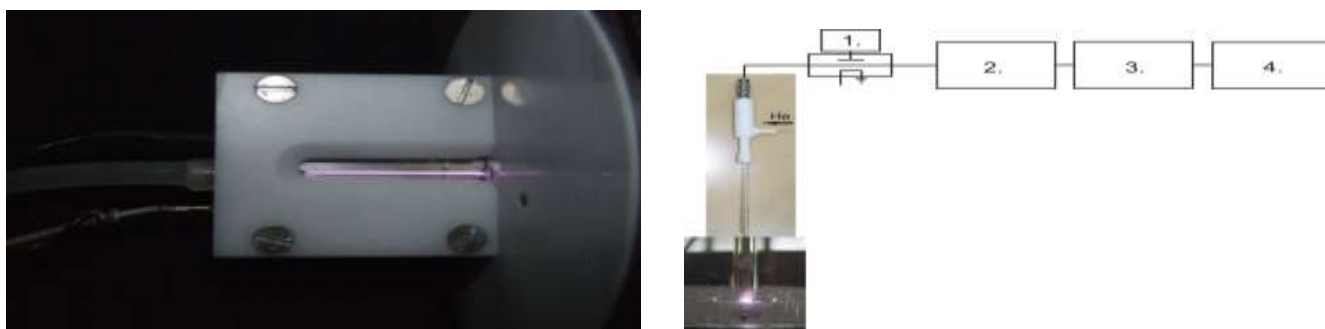

Fig. 20: μ-APPJ with formed plasma and plasma needle system set-up.

Another plasma source that meets all the necessary conditions for treatment of organic materials and living tissues is the plasma needle (figure 21, picture on the right-hand side). Most importantly, in such a discharge gas the heating is minimized, while the effects on the tissue and bacteria have been clearly shown to be significant. The needle consists of a central electrode made of tungsten insulated almost to the tip by a slightly larger ceramic tube, both being placed inside a glass tube. The needle body is made of Teflon. We used helium as a buffer gas at several different flow rates. The central electrode is powered by a 13.56 MHz signal generator through an amplifier and a matching network. Both for the plasma needle and for the μ-APPJ, we have derivative probes and a Hiden HPR60 mass/energy analyzer in order to determine the power applied to plasma and the composition of the discharge, respectively. In both of these systems, inert gas is used to reduce the breakdown voltage and achieve stable non-equilibrium plasma formation. Yet these plasmas have shown several modes of operation and further studies are required to fully understand their operation and make further optimizations. Another type of atmospheric pressure plasma relies on mixing the inert gas carrying the plasma created by external electrodes with atmospheric gas mixture. It is the so-called plasma jet. The operating frequencies of plasma jets are in the region of several tens of kHz which are much lower frequencies then those used for the plasma needle and μ-APPJ (in MHz). It has been shown that micro jet plasma is not always continuous but often is formed by a train of fast travelling bullets which only appear to be continuous to the human eye. The atmospheric pressure plasma jet/bullet that we constructed was made of a Pyrex glass tube with the electrodes made of a thin copper foil wrapped around the glass tube. The distance between the powered and the grounded electrode was 13.5 mm and their width was 13 mm. One of the electrodes (the left electrode, see figure 21) was grounded. The other electrode, closer to the end of the glass tube, was the powered one (see figure 21). In all experiments the buffer gas was helium. We used a signal generator connected to the custom-made amplifier to power the micro jet. The highest voltages that we could obtain from the amplifier were up to 1 kV, which was not enough to ignite the plasma. In order to the increase the applied voltages to more than 5-6 kV, we had to use an additional homemade transformer. The operating frequency was 80 kHz and the applied voltage was sinusoidal in the range of 6-10 kV$_{peak-to-peak}$. Micro jets with plasma bullets have been constructed with a range of different geometries, frequencies and shapes of applied voltage. The effect of bullets seems to be quite universal for an optimum range of electrode sizes and flows, while the frequencies and voltage shapes vary a lot. Plasma bullets, however, still need to be fully understood and properly modelled. We will focus here on the plasma jet diagnostics, while at the same time showing some results on the sterilization achieved by a plasma needle.
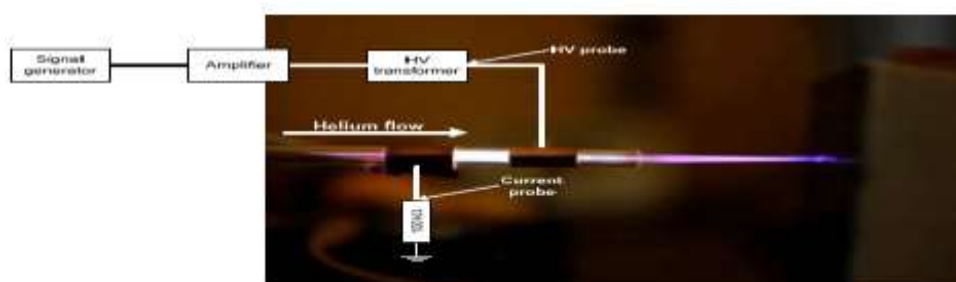

**Fig. 21: Atmospheric plasma bullet.**

Plasma diagnostics:

It has been reported only quite recently that the plasma jets formed by the source operating at low excitation frequency is not continuous. Instead it consists of small plasma packages that are formed in positive and/or negative half cycle of the period [62]. Amazingly these little bullets are formed and travel outside the plasma jet where there is no applied electric field. The velocity of these packages are larger than the speed of the flowing feed gas by several orders of magnitude. Several theories of bullet formation have been proposed [62-67] but to date a definite explanation of the physical mechanisms involved in creation and propagation of plasma bullet are still not fully understood. For the current and voltage measurements, we used two commercial probes. The current and voltage waveforms when the plasma is formed and without discharge are shown in figure 22. When the plasma is off, the phase difference between the current and voltage is close to 90°. In this case, we have a capacitive impedance of several MΩ, corresponding to a capacitance of about 0.5 pF. On the other hand, when the plasma is formed, the current signal is larger, deformed and shifted in phase overlapping more with the voltage signal. The plasma ignition changes the slopes of the V_{RMS}–I_{RMS} curves (see figure 23). The mean power calculated increases with the increase of the applied voltage; it was in the range from 1 to 8 W in all measurements. Integral and time-resolved images of the plasma jet system were obtained by an ICCD camera. For exposure times larger than the cycle period (12.5 μs), the plasma appears to be continuous, like a plume (see figure 21 LHS picture). The length of the plasma plume is up to five centimeters, depending of the flow rate and the voltage applied. For the time-resolved images, we had to use integration on the chip because the light emission in a single shot is not sufficient to obtain clear images with gate widths less than 50 ns. This was facilitated by the high reproducibility of the pulses and the small jitter. Figure 24 shows the plasma bullet images obtained for several different flows of working gas. We can see that with the decrease in the He flow, the plasma bullet starts to be elongated, deformed and its intensity is much smaller. Eventually, bullets are not formed at the very small flows.
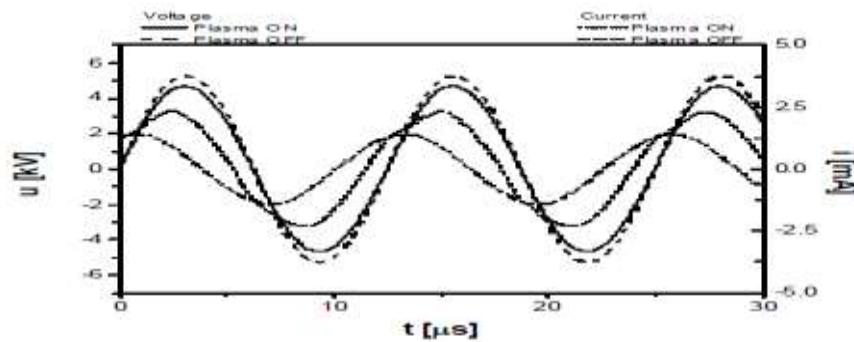
Fig. 22: Current and voltage waveforms for helium flow rate of 3 slm. The dashed lines represent the case when discharge is OFF, the solid lines, when discharge is ignited [19].
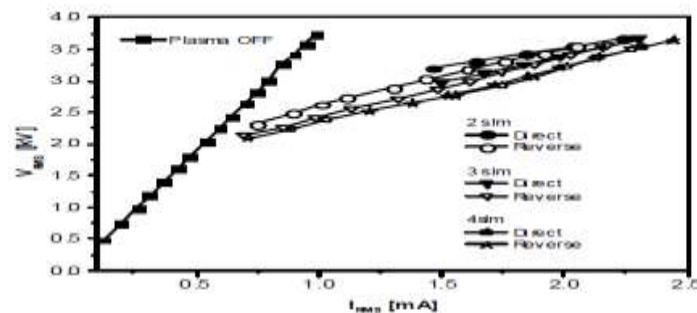
Fig. 23: Current-voltage characteristics for three different flows of helium [19].

Figure 25 shows the development of the plasma over the entire period of applied voltage (12.5 μs). All images are scaled to the same maximum intensity and thus can be compared. One can see that when the current and voltage signals are close to zero, the plasma is not visible. In the negative part of the current and voltage waveforms, the plasma is confined between the electrodes. During the positive part of the waveforms, the plasma is first confined between the electrodes (rising slope) and then, near the maximum of the curves, it leaves the glass tube in the form of a bullet. The dimensions of the bullet are of the order of a few millimeters. We calculated the speed of the bullet at ~20 km/s, depending on the position away from the end of the glass tube. The plasma bullet is much faster than the speed of the buffer gas flow (1 to 7

m/s). Thus we can conclude that our plasma source was not continuous, it consisted of very small plasma packages that traveled at a high speed. By varying the plasma parameters, the length and intensity of the plasma coming out of the tube can be adjusted. For the two plasma devices operating at a much higher frequency (13.56 MHz), the diagnostics was made by using homemade derivative probes in order to determine the power transmitted to the plasma and the operation mode of the discharge. The derivative probes were very sensitive; a numerical procedure for subtracting the displacement current based on accurate calibration of the system was performed so that it was possible to measure powers of the order of 0.1 W or less even with displacement current a couple of orders of magnitude larger than the plasma current. Besides derivative probes, we used mass spectrometry to analyze the plasma products formed by a µ-APPJ [68] and by a plasma needle [69]. Several problems occurred during the setting up of the experiment; they are described in detail elsewhere [68.69].

The analysis of the composition of neutrals and ions was motivated by the need to check which species are formed in the discharge. These results may be used as a test of plasma chemical models, to identify radicals and ions (that may be used after acceleration to induce damage to the tissue). The performance of the mass analyzer was tested and techniques were developed to produce data without the uncertainty induced by a contribution of the ionizer to possible dissociation. It was found that the predominant ions created by the plasma are O_2^+, O+, H_3O^+, N_2^+, N^+, NO^+, OH^+ [19]. When it comes to plasma treatment of samples of biological origin, the chemically active species that are of interest are O, metastables O and O_2, OH, N, H_2O_2 and NO.

Plasma sterilization:

The entry point for most groups dealing with plasma medicine is a study of sterilization. The effects on bacteria may be shown quickly, although it requires expertise in biomedicine. The benefit is that direct potential applications may be developed outside the realms of strict medical regulations. Yet, in situ sterilization, for example, treatment of wounds to prevent infection would be a much more important goal. Following preliminary work on sterilization in microwave plasma, albeit at low pressure, we reinitiated the studies of plasma sterilization as a part of our plasma medical project. So far, a plasma needle has been used to induce killing of Streptococcus mutans and Escherichia coli bacteria in the form of planktonic samples. Also, we have the plasma interaction with normal, living cells; for these experiments we used human peripheral blood mesenchymal stem cells (hPB-MSC) as a model system to predict the degree of possible damage to the
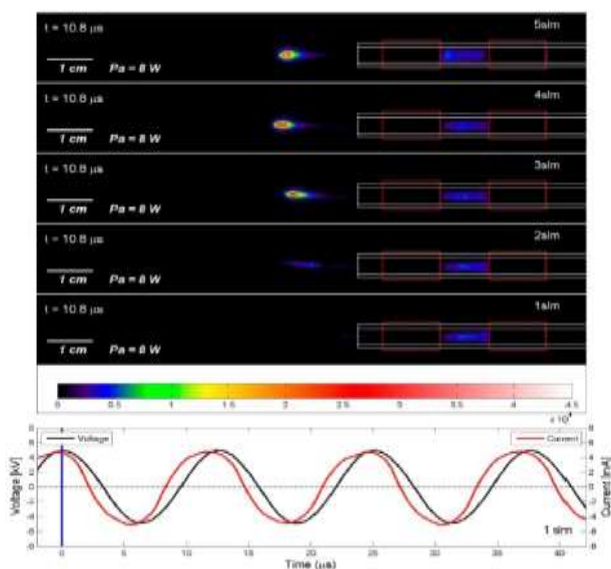

Fig. 24: Plasma jet for 1, 2, 3, 4 and 5 slm of He flow. Exposure time 2 ms, gate width 25 ns, gate delay 10.8 μs [68].
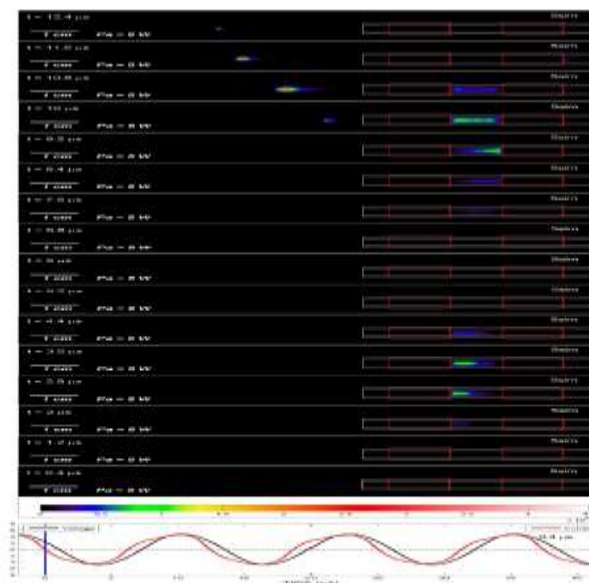
Fig. 25: Plasma jet at 5 slm, exposure time 2 ms, gate Width 25 ns and gate delay from 0.4 to 12.4μs [68].

cell responses [70]. Many factors are responsible for bacterial inactivation. Direct exposure of the bacterial samples to the plasma appears to be more effective than remote exposure. Another factor that determines the efficiency of the specific treatment is the type [71] of bacteria, gram positive or gram negative. Very importantly, we studied the sterilization of bacteria in planktonic samples, where bacteria are dissolved in a small amount of liquid that would otherwise give it some protection from other agents. We showed that efficient sterilization of planktonic samples is not only possible, but may be

efficient depending on the initial population [70]. One of the most serious problems in the hospital environment is bacterial contamination of surfaces with methicillin-resistant Staphylococcus aureus (MRSA) responsible for significant nosocomial infections. The pathogenic contaminants form biofilms, which are difficult to treat with routine biocides. The biofilm is not just a secured shelter but a defense mechanism and a nutrition depot for pathogens. We show below the preliminary results of plasma treatment of the MRSA bacteria samples in the form of a biofilm.
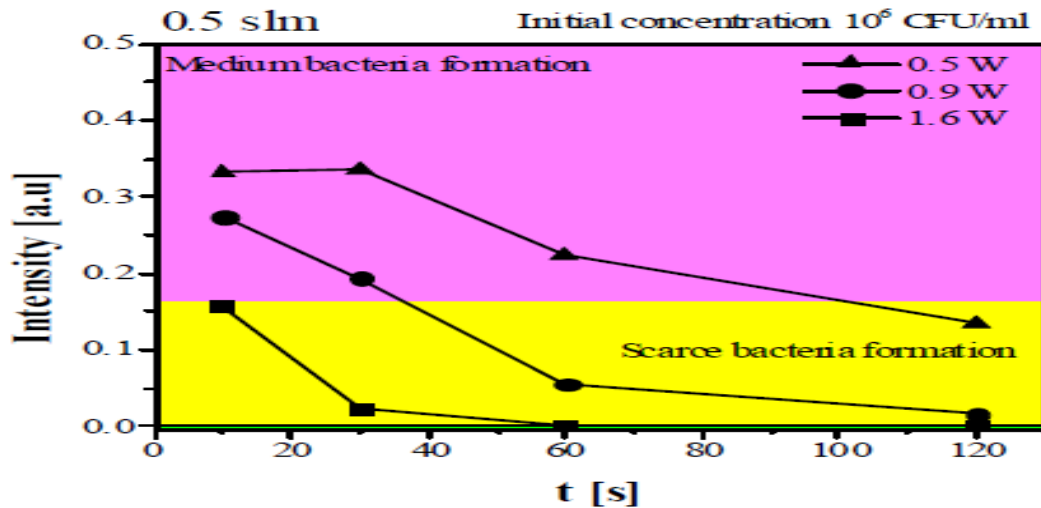
Fig. 26: Treatment of MRSA biofilms of Staphylococcus aureus (ATCC 25923) by using plasma needle. Untreated sample showed STRONG bacteria formation (control intensity 0.65 a.u). Initial concentration of bacteria used was 106 CFU/ml.

In figure 26, we show the optical density of bacteria samples after plasma treatment for several different treatment times (10, 30, 60 and 120 s). The initial concentration of the samples was 106 CFU/ml, which corresponds to a measured optical density of 0.65 a.u. The buffer gas flow was 0.5 slm, but studies were also made as a function of the flow rate. The treatment efficiency increases with the increase of the treatment time and the mean power deposited to the plasma. For the highest power and only for the shortest treatment time of 10 s, there was scarcely bacteria formation; for the longer treatment, no bacteria formation was observed after the plasma treatment and yet there was very little or no heating of the gas.

3.6 Thermal plasma torches for metallurgical applications:

Advances in thermal plasma torches have resulted in this technology becoming a commercially viable solution for chemical and metallurgical processes. The main advantages of plasma are its ability to control process chemistry and to build small footprint reactors due to its high energy density and reactivity of the free radicals that are produced. This paper focuses on thermal plasmas produced by DC torches and their applications for waste treatment, production of high purity metals, and nanomaterials. Industrial plasmas can be broadly classified as thermal plasmas and non thermal plasmas. Thermal plasmas are atmospheric pressure plasmas characterized by local thermodynamic equilibrium (Boulos et. al, 1994). Thermal plasmas are typically established between any two current conducting electrodes separated by an insulator. A plasma forming gas is blown between the two conducting electrodes resulting in a high temperature plasma plume. A plasma torch generates and maintains an electrically conducting gas column between the two electrodes: a cathode (negative electrode) and an anode (positive electrode) (Camacho,

1988). If both electrodes are housed in a single housing, resulting in an arc enclosed inside the plasma torch, then such plasma generating torches are termed as non-transferred (NT) plasma torches, whereas, if the second electrode is external to the torch, creating an arc transferred between the cathode and the working piece, then such plasma torches are termed as transferred (T) plasma torches. Depending on the source of the electricity which can be either direct current (DC), alternating current (AC) at main network frequency or at radio frequency (RF), the plasma torches are classified as DC, AC or RF plasma torches.

Steam plasma torch and its typical application:

This plasma torch consists of three electrodes namely, a pen shaped refractory metal lined copper cathode, a tubular copper ignition electrode and a tubular copper anode. All three electrodes are water cooled using high pressure deionised

water flowing in a closed circuit. A stainless steel body houses the co-axially mounted electrodes along with the water cooling channels and gas flowing conduits, carved out of high temperature plastic such as UltemTM. A self sustaining plasma column is ignited between the cathode and the ignition electrode and is transferred to the working anode. Any oxygen free inert gas such nitrogen and/or argon is used as a shroud gas to protect the refractory metal lined cathode. The steam plasma torch is ignited on air and then gradually switched to steam torch. The main plasma forming is introduced between the ignition electrode and the working anode, through a swirl generator, consisting of tangentially drilled holes. Powered from a DC source, this plasma torch works with super heated steam as the plasma forming gas and can operated between 50 kW to 150 kW gross power. This plasma torch design offers many advantages such as:

i) a wide range of torch power turn down ratio ranging from 50 kW gross power to 150 kW gross power,

ii) long electrode life with electrodes lasting over 200 hrs for the anode and 1000 hrs for the ignition electrode and the cathode.

This plasma torch design was originally developed for destruction of hard to destroy hazardous substances such as halogenated hydrocarbons such as chlorofluorocarbons and brominated hydrocarbons.

PCI has successful demonstrated that the steam plasma torch can be used to destroy R-12 refrigerants to a destruction and removal efficiency of 99.9999%. Other potential applications of steam plasma torch include, steam reforming (Zhu et. Al., 2011), coal gasification, steam arc cutting rapid decontamination of large surfaces.

Air plasma torch and its typical application:

This plasma torch consists of three electrodes namely, a pen shaped refractory metal lined copper cathode, a tubular copper ignition electrode and a tubular copper anode. All three electrodes are water cooled using high pressure deionised water flowing in a closed circuit. A stainless steel body houses the co-axially mounted electrodes along with the water cooling channels and gas flowing conduits, carved out of high temperature plastic such as Ultem^{TM}. A self sustaining plasma column is ignited between the cathode and the ignition electrode and is transferred to the working anode. Any oxygen free inert gas such nitrogen and/or argon is used as a shroud gas to protect the refractory metal lined cathode. The main plasma forming which is air is introduced between the ignition electrode and the working anode, through a swirl generator, consisting of tangentially drilled holes. The shroud gas typically represents 10% by volume of the main plasma forming gas. Powered by a DC source, this plasma torch typically works with compressed air as the main plasma forming gas.

This plasma torch design offers many advantages such as:

i) high thermal efficiency reaching up to 70%,

ii) a wide range of torch power turn down ratio ranging from 50 kW gross power to 500 kW gross power,

iii) long electrode life with electrodes lasting over 1000 hrs for the cathode and ignition anode, 600 hours for the main anode.

4. CONCLUSIONS

Thermal plasmas have found increasing applications in waste destruction, material recovery, extractive metallurgy, powder synthesis, coating deposition, and energy conversion. Plasma treatment of automotive exhausts has been the main thrust of nonthermal plasma research and development, though limited research has been performed on using nonthermal plasmas for demilitarization, other waste treatment, energy conversion, and material synthesis. A plasma treatment system has been developed which can be operated at low temperatures and at atmospheric pressure, thereby eliminating the need for any vacuum chambers or pumps, yet provides the unique advantages which plasma technology has over the existing technologies for surface treatment of nonwovens.

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