White Paper for *Frontiers of Plasma Science Panel*

Date of Submission:	***06-19-2015***

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Title:	**Plasmas for biomass processing and biofuels production**
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(Limit text to 3-pages including this form. Font Times Roman size 11.
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- ***Describe the research frontier* and importance of the scientific challenge.**

- ***Describe the approach to advancing the frontier and indicate if new research tools or capabilities are required.***

- ***Describe the impact of this research on plasma science and related disciplines and any potential for societal benefit*.**

Plasmas for biomass processing and biofuels production

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The development of methodologies to satisfy needs of the present life without compromising those of future generations is an urgent issue for the modern society affecting the developed and developing countries in order to promote advances in new energy sources, materials, food and the design of new cities.

In the context of energy, despite of significant growth in proven and predicted fossil fuel reserves over the next two decades, notably heavy crude oil, deep water wells, and gas, present great uncertainties in the economics of their exploitation via current extraction methodologies. More crucial is that an increasing proportion of such carbon resources cannot be burned without breaching the UNFCC targets for a 2 ^{0}C increase in mean global temperature relative to the preindustrial level.4,5 There is clearly a rising energy demands, predicted to climb 50% globally by 2040 and the requirement to mitigate current CO_2 emissions and hence climate change.

Similar considerations apply to ensuring a continued supply of organic materials for applications including polymers, plastics, pharmaceuticals, optoelectronics and pesticides, which underpin modern society, and for which significant future growth is anticipated. The quest for sustainable resources to meet the demands of a rapidly rising world population represents one of this century's grand challenges. Our team believes that plasma technologies show significant potential to address the aforementioned challenges.

The processing of biological materials using plasmas is quite wide and it seems that few possibilities have been explored to date. The polymerization of the surface of biological materials has been reported frequently [1]. In reference [2], the authors report a study based on simulations to test the feasibility of using plasma in gas or liquid phase to bleaching and/or delignification of cotton or cellulose. In these applications, there appears to be a wide range of chemical possibilities to manipulate biological materials using plasma for promoting the conversion of organic molecules or macromolecules of little value in high value-added substances.

The gasification of biomaterials for gas synthesis production is a technology already implemented (ex. Westinghouse Plasma Corporation commercial operating facilities in Wuhan, Hubei, China, for biomass gasification and Mepl, Pune, India, for hazardous waste). However, research in this field is still active, with a view to improving energy efficiency, the quality of the gas synthesis and the type of biomass used. One innovation is the possibility of generating gas synthesis in gaseous fuels, using plasmas in liquids [3]. An interesting direction for research in this area is the development of compact burners with high energy density and more efficient, clean ways to generate gas synthesis for applications in urban transport, waste recycling, generators, etc.

Use of ozone-generated plasmas to delignification of biomass was tested in laboratory scale by various groups for different types of biomass as cane sugar bagasse [4], wheat straw [5] and Japanese cedar [6]. The technology is effective superior to conventional pre-treatment methods in terms of conversion efficiency of enzymatic hydrolysis, but more studies about the energy efficiency and economic point of view is needed. In this sense, the research to obtain more effective ozonizers could enable economically viable processes. Ozone interaction mechanism with the biomass is relatively well known [4], but more research is needed to unravel the influence and the role of other radicals (e.g. singlet states of atomic and molecular oxygen, OH, H_2O_2) in biomass degradation processes. Another strategy is to treat the biomass in direct contact with the plasma, both in gas phase [7] or in liquids. In this case, depending on the physicochemical properties of plasma, several types of effect on biomass could be observed in addition to the delignification. Further studies are needed, which could make an important contribution in the field of biomass engineering processes, such as the discovery of new methods for obtaining high added value products. The experimental investigation of plasma interaction mechanisms with biomass is another field to be explored, and experimental techniques of monitoring in real time or retrospectively the effect of plasma on biomass need to be developed.

The work described in [8] reports the conversion of cellulose to simple sugars by plasmas. This result has not been confirmed by other studies yet, but the concept appears to be feasible. Even with this confirmation result, simple sugars are products with a low value for the energy cost of the plasma production so that the most cost effective alternative in this field appears to be the demand for biomass conversion methods into higher-added value products.

While many alternative sources of renewable energy have the potential to meet future demands for stationary power generation, biomass offers the most readily implemented, low cost solution to a drop-in transportation fuel for blending with and/or replacing conventional diesel via the bio refinery concept, illustrated for carbohydrate pyrolysis/hydrodeoxygenation or lipid transesterification. Heterogeneous catalysis has a rich history of facilitating energy efficient selective molecular transformations and contributes to 90% of chemical manufacturing processes and to more than 20% of all industrial products [9]. In a post-petroleum era, catalysis will be central to overcoming the engineering and scientific barriers to economically feasible routes to alternative source of both energy and chemicals, notably bio-derived and solar-mediated via artificial photosynthesis.

The conventional heterogeneous catalysts involved in biodiesel production include mixed metal oxides, alkaline metal oxides, ion-exchange resins, sulfated oxides and immobilized enzymes. Heterogeneous catalysis has emerged as the preferred alternative for biodiesel production because the products are easy to separate, the catalysts are reusable, and the process is environmentally friendly. However, this method suffers from limitations, such as mass transfer problems, high cost and low catalyst stability, that diminish its economic feasibility and low environmental impact on the entire biodiesel process. Carbon nanotubes (CNTs) appear to be a promising catalyst support for biodiesel production due to their ability to overcome the limitations faced by conventional heterogeneous catalysts [9]. Thus, another contribution of this white paper is propose the application of functionalized CNTs as catalyst support in biodiesel production, discussing issues such as the limitations encountered by conventional heterogeneous catalysts, the advantages offered by functionalized CNTs and possible methods to functionalize CNTs to serve as catalyst support in biodiesel production. Another promising catalyst is the graphene sheets [10]. Based on the recent research findings by the authors of this white paper, functionalized CNTs and graphene sheets [11-12] can easily be produced by plasma routes and also hold great potential to be a breakthrough technology in the biodiesel industry.

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