Monday Afternoon, October 30, 2017

Plasma Processing for Biomedical Applications Focus Topic Room 12 - Session PB+BI+PS-MoA

Plasma Agriculture & Processing of Biomaterials

Moderator: Kristian Wende, INP Greifswald

1:40pm PB+BI+PS-MoA-1 Control for Plant Disease and Development by Atmospheric Pressure Plasma, Gyungsoon Park, Kwangwoon University, Republic of Korea INVITED

Previously, we observed that seeds contaminated with Fusarium fujikuroi (a fungus causing rice bakanae disease) were more effectively disinfected in water by arc discharge plasma than ozone. Efficiency of disinfection was decreased when the distance between seeds and electrodes becomes greater. This indicates that shockwave from arc plasma may play an important role in seed sterilization, and we measured about 50-60 atm shockwave pressure. In addition, seed surface became more hydrophillic after plasma than ozone treatment indicating that water containing ROS and RNS can more easily get inside hull. Ozone level in water was decreased when seeds were present. This is probably due to the chemical reaction of ozone with seed surface molecules and will eventually cause the decrease in efficiency of seed disinfection. We also analyzed the effect of water and buffer treated with microwave plasma generated gas containing nitric oxide (PGNO) on development of spinach. The real time level of nitric oxide in water and phosphate buffer was increased to about 100 μ M after treatment with PGNO for 50 min. Spinach treated with PGNO water seems to become more tolerant to drought stress. Our work was supported by the National Research Foundation of Korea (NRF) grant (No. 2010-0027963), Rural Development Administration (RDA) grant (No. PJ009891) and National Fusion Research Institute (NFRI) grant.

2:20pm **PB+BI+PS-MoA-3 Biomass Pyrolysis Using Low Temperature Plasma**, *Y Gao*, *N Uner*, *J Meyer*, *M Foston*, *Elijah Thimsen*, Washington University in St. Louis

Low temperature plasmas (LTP) are recently being used for processes involving complicated heterogeneous chemistry. Due to their unique nonequilibrium environment and the abundance of reactive radicals, LTPs are expected to bring selectivities and reactivities that are difficult to obtain in systems governed by local thermal equilibrium. In this study, we utilize low temperature plasmas for converting biomass into more valuable chemicals.

Biomass is an abundant and renewable source of carbon. It is recently reported that biomass can be supplied and processed at a scale large enough that is comparable to petroleum [1]. Current research efforts are focused on upgrading biomass into hydrocarbons and valuable aromatic compounds. One common method is to pyrolyze biomass into oils at high pressure. However, the product distribution usually turns out to be very broad, therefore the yields of the desired components are often low. Another common method is to gasify the biomass into syngas, a mixture of CO and H₂. Both pyrolysis and gasification are indirect routes of converting biomass into valuable chemicals. Complicated additional steps are usually required, as in the case of hydrodeoxygenation of pyrolysis oil or production of various paraffins/olefins via Fischer-Tropsch synthesis from biomass-derived syngas. Furthermore, a common drawback for both pyrolysis and gasification methods is the deactivation of catalysts due to coke formation.

In this study, we demonstrate a single-step process without catalysts that generates oxygen-free hydrocarbons with high yield. We will report low temperature plasma conversion of lignocellulosic biomass in a gram-scale radio frequency reactor. Preliminary work shows that the plasma rapidly converts solid feedstock into primarily small chain hydrocarbons. Effects of process parameters such as plasma power, plasma gas composition, operating pressure and biomass feedstock will be presented, along with a techno-economic analysis of the process.

[1] U.S. Department of Energy, "2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy," Oak Ridge National Laboratory, Volume 1, 2016.

2:40pm PB+BI+PS-MoA-4 Growth of Plasma-Treated Corn Seeds under Realistic Conditions, *Chisung Ahn*, *I Shchelkanov*, University of Illinois at Urbana-Champaign; *J Gill*, AgReliant Genetics, LLC; *D Ruzic*, University of Illinois at Urbana-Champaign

Plasma treatments of agricultural seeds have been proposed to enhance germination and improve growth rate by elimination of unwanted microbes, water absorption control, introducing functional groups or other

effects. In particular, making a plasma-activated medium which has nitrogen as its main component can affect the efficiency of water use in the germination phase. There is also a remarkable complementary effect between plasma treatments and biological pre-treatment. To confirm the plasma effects seen in the lab scale, this work seeks to investigate a variety of seed treatments on an industrial agriculture scale.

In this study, various kinds of plasma were introduced for mass treatment of corn seeds to investigate the germination and growth effect. The seed utilized for the experiment is an elite 111 days yellow dent corn hybrid adapted to the US Midwest. Seven experimental treatments were evaluated: Control, Biological treatment only, Plasma Activated Water (PAW) treatment, Atmospheric Pressure DBD Plasma, Microwave Atmospheric Plasma, Vacuum Plasma and Just Vacuum. The corn seeds were treated uniformly by one-layer arrangement on each stage without burning or blackening by the plasma. Each treatment was performed on a total of 1800 corn seeds. Seed of each experimental condition were treated with the recommended rate of Poncho Votivo with Acceleron, a commercial biological seed treatment that helps protect the seeds from fungus, insects, and nematodes after planting. The 1800 seeds were divided evenly into three replications with 100 seeds planted for each replication at six unique locations across central Illinois. The results of germination, growth, and product yield over the 2017 growing season will be presented.

3:00pm **PB+BI+PS-MoA-5** Advanced Control of Plasma Medical Devices, *David Graves*, University of California, Berkeley; *A Mesbah*, *D Gidon*, University of California at Berkeley

Atmospheric pressure plasma jets (APPJs) have widespread use in plasma medicine. This presentation aims to demonstrate the importance of using advanced control strategies for safe, reproducible, and therapeutically effective application of APPJs for dose delivery to a target substrate. Key challenges in advanced control of APPJs arise from: (i) the multivariable, nonlinear nature of system dynamics, (ii) the need to constrain the system operation within an operating region that ensures safe plasma treatment, and (iii) the cumulative, non-decreasing nature of dose metrics. To systematically address these challenges, we propose a model predictive control (MPC) strategy for real-time control of a radio-frequency APPJ in argon. To this end, a lumped-parameter, physics-based model is developed for describing the jet dynamics, and cumulative dose metrics are defined for quantifying the thermal and non-thermal energy effects of the plasma on substrate. The closed-loop performance of the MPC strategy is compared to that of basic proportional-integral control. Simulation results indicate that MPC provides a versatile framework for dose delivery in the presence of system disturbances, while fulfilling the safety and practical constraints of APPJ operation. In addition, we demonstrate the use of advanced control in experimental APPJ systems. Advanced control can lead to unprecedented opportunities for effective dose delivery in plasma medicine.

3:20pm PB+BI+PS-MOA-6 Fingerprinting Different Plasma Sources for Biomedical Applications, *Katharina Stapelmann*, North Carolina State University; *K Wende*, INP Greifswald, Germany; *B Offerhaus*, Ruhr University Bochum, Germany; *C Verlackt*, University of Antwerp, Belgium; *C Klinkhammer*, *F Kogelheide*, *M Havenith*, Ruhr University Bochum, Germany; *A Bogaerts*, University of Antwerp, Belgium; *P Awakowicz*, *J Lackmann*, Ruhr University Bochum, Germany

Cold technical plasmas (CAPs) are under investigation in various fields of industry and medicine. First clinical trials using CAPs for wound healing show promising results. Preliminary results in other fields of plasma medicine, such as cancer treatment, offer promising findings as well. However, the interactions of technical plasmas with biological samples on a molecular level are only partly understood. CAPs generate complex chemical cocktails, having an impact on various biological structures [1]. The impact can vary betweeen different sources, e.g. by employing a DBD in air or a noble gas driven jet. A better understanding of the chemical reactions occuring would allow to tune and adapt plasmas for specific tasks. One prevalent impact of plasma on biological targets has been the chemical modification of thiol groups, which carry out various important tasks in the human body, such as cell signaling and protein structure formation. As thiols are involved in many regulatory and functional processes in tissues, an in-depth understanding of the impact of plasma treatment on thiols is highly relevant for a safe application of plasmas in medicine.

In order to get insight into these interactions, various thiol-containing model substrates, such as the amino acid cysteine and larger target

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substrates, were investigated with different plasma sources [2,3]. By using a standard target substrate, the impact of various plasma sources can be compared not by means of a physical characterization but by their chemical impact. Stepwise increase of sample complexity allows monitoring how thiols are affected by plasma treatment in an ever more complex environment. The combination of experimental evidence and MD simulations permit a comprehensive overview of chemical processes induced by plasma treatment. This combined approach allows a more throughout investigation of modifications on a molecular level and helps to understand fundamental plasma chemistry processes. Furthermore, knowledge about the substrate chemistry enables the use of test substrates as bio-probes for the investigation of plasma chemistry in other industrial fields [4].

[1] Lackmann J-W and Bandow J E 2014 Appl. Microbiol. Biotechnol. 98 6205-13

[2] Kogelheide F et al 2016 J. Phys. D: Appl. Phys. 49 084004

[3] Lackmann J-W et al. 2015 J. Phys. D: Appl. Phys. 48 494003

[4] Offerhaus B et al. 2017, accepted in Plasma Process Polym.

4:00pm PB+BI+PS-MoA-8 Exploring Plasma Coatings Comprising Vertical Chemical Gradients and Multilayers for Biomedical Applications, Dirk Hegemann, M Vandenbossche, M Heuberger, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland INVITED The common definition of "surface" includes surface atoms and molecules, practically extending at the most some three layers - typically one nanometer. This definition is justified by the fact that many surface properties related to symmetry breaking, such as chemistry, wettability or surface charge are determined by the top most surface layer. The common understanding is that this thin surface region also determines how molecules adsorb onto it. Far less explored are effects due to interactions with deeper subsurface layers, i.e. the region extending over several nanometers underneath the "surface". This subsurface region, however, might significantly contribute to molecular adsorption via long-range (i.e. few nm) interaction forces; mainly interactions with fixed dipoles, water structuring and Van der Waals interactions. A key factor to make use of these interaction forces thus lies in the hydration of the subsurface region.

Therefore, stable plasma polymer films made of siloxanes were designed that contain a hydrophilic nanoporous base layer terminated by a hydrophobic top coating, nominally 2-12 nm thick. As a model molecule, bovine serum albumin (BSA) was selected and its adsorption was studied on gradient coatings as well as reference coatings immersed in water or phosphate buffered saline (PBS). As a result, protein adsorption was reduced on hydrated hydrophobic/hydrophilic gradient coatings, while dry or dehydrated films show the same adsorption as the reference hydrophobic plasma polymer film.

Furthermore, double layers made of a terminal a-C:H:O plasma polymer layer (1-5 nm thick) on a-C:H:N base layers were investigated comprising a gradient in carboxylic-to-amino groups. Again conditions were selected to obtain stable plasma polymer films when immersed in aqueous environments. Adsorption using the green fluorescent protein (GFP) on different double layers and reference layers were examined. Enhanced protein adsorption was observed for the 1 nm thick terminal layer of a-C:H:O on a-C:H:N as compared to each reference layer.

Hence the vertical nanostructure of a functional surface implies an additional factor to control adsorption processes. Protein adsorption, selectivity and bioactivity can thus be controlled by using subsurface effects being an important finding for biomedical applications such as e.g. tissue engineering.

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