

# Wednesday Afternoon, November 8, 2023

## Plasma Science and Technology Division Room A106 - Session PS1+AS-WeA

### Plasma Chemistry, Catalysis and Applications for the Environment and Sustainability

**Moderators:** Michael Gordon, University of California at Santa Barbara, Kenji Ishikawa, Nagoya University

#### 2:20pm PS1+AS-WeA-1 Synthesis of Hydrogen and Structural Carbon Materials from Methane Using Radiofrequency Nonequilibrium Plasma, *Elijah Thimsen*, Washington University in St. Louis **INVITED**

The production of hydrogen from methane by dehydrogenation of carbon is up to 6 times less energy intensive than water splitting and involves no intrinsic CO<sub>2</sub> byproduct. If hydrogen were used as a fuel at societal scale, billions of tons per year of carbon co-product would be produced. Steel and concrete are manufactured goods that are used at a scale of billions of tons per year, for structural applications. To avoid massive waste, the carbon co-product from hydrogen production could be used in structural applications, perhaps to displace concrete and steel. In this talk, I will focus on the use of radiofrequency capacitively coupled electrodeless discharges in a tubular flow-through configuration for methane dissociation. The plasma step of our process currently operates in the pressure range from 0.025 to 0.125 bar, and the goal is to synthesize an equimolar mixture of C<sub>2</sub>H<sub>2</sub> + HCN from CH<sub>4</sub> + N<sub>2</sub>. The mixture of C<sub>2</sub>H<sub>2</sub> + HCN is an intermediate between the plasma and a downstream thermocatalytic reactor. The downstream thermocatalytic reactor synthesizes acrylonitrile, which is a critical precursor to structural carbon fiber, from the C<sub>2</sub>H<sub>2</sub> + HCN mixture that elutes from the plasma. Remarkably, the plasma synthesis of C<sub>2</sub>H<sub>2</sub> + HCN from CH<sub>4</sub> + N<sub>2</sub> is highly selective. We have been able to achieve >95% methane conversion with >90% nominal yield of a stoichiometric mixture of C<sub>2</sub>H<sub>2</sub> + HCN. Downstream of the plasma in the thermocatalytic reactor, selectivity is somewhat challenging, but yields of the desired acrylonitrile in the range from 20 to 40% based on C<sub>2</sub>H<sub>2</sub> + HCN have been achieved at the time of writing. For technoeconomic context, the results will be compared against the industrial standard SOHIO ammoxidation process for the synthesis of acrylonitrile. Furthermore, I will take this opportunity to reflect on the prospect of running a gas-phase synthesis process at a reduced pressure of approximately 0.1 bar and a production rate of minimum 10,000 tons per year.

#### 3:00pm PS1+AS-WeA-3 Kinetics of Hydrocarbon Decomposition in Plasmas Operating Up to 5 bar, *Norleakvisoth Lim, M. Gordon*, University of California at Santa Barbara

Hydrogen is a promising energy carrier to replace fossil fuels in response to the rise in global warming from CO<sub>2</sub> greenhouse gas emissions. Unfortunately, hydrogen is predominantly produced industrially via steam methane reforming, where the reaction itself and process heating requirements generate CO<sub>2</sub>. Direct methane pyrolysis for hydrogen generation has recently regained interest due to its potential for net zero CO<sub>2</sub> emission. This process requires high operating temperatures due to high C-H bond energies (4.55 eV for methane) and collateral issues such as catalyst poisoning via coking. As an alternative, plasma-based conversion of methane to hydrogen and carbon (as well as other hydrocarbons) is an attractive process due to its potential ability to generate reactive species that can overcome activation barriers, improve CH<sub>4</sub> conversion, and use less energy than required for water electrolysis. Thus, understanding the mechanism and kinetics of CH<sub>4</sub> dissociation in thermal and non-thermal plasmas is a crucial step to evaluate the efficacy of plasma conversion of hydrocarbons.

This talk will highlight conversion, selectivity, and kinetics measurements of plasma-based decomposition of CH<sub>4</sub> and C<sub>2</sub> hydrocarbons using various plasma excitation schemes (AC arc and nanopulse) at pressures up to 5 bar in a batch configuration with different electrode gaps. H<sub>2</sub> selectivities up to 80% were observed in AC-excited thermal arcs, with specific energy requirements (SER) decreasing with increasing pressure to ~300 kJ/mol CH<sub>4</sub>. In general, plasma-based conversion has fast rates and seems to not encounter the typical pseudo-equilibrium limit, i.e., due to hydrocracking of products back to CH<sub>4</sub>, that is typically encountered with thermal pyrolysis of CH<sub>4</sub> at temperatures from 900-1300 °C. Other CH<sub>4</sub> decomposition products (<30 mol %) observed include C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, and plasma-decomposition of C<sub>2</sub>H<sub>4</sub> was also studied. Product distribution with pressure and various CH<sub>4</sub>:H<sub>2</sub> ratios will be discussed, along with characterization and management of the solid C product. This work suggests that higher

operating pressures can potentially improve the efficiency of plasma conversion of hydrocarbons.

#### 3:20pm PS1+AS-WeA-4 Plasma Pyrolysis of Liquid Hydrocarbons to Produce H<sub>2</sub> and Solid Carbon, *N. Lim, Michael Gordon*, University of California at Santa Barbara

Understanding and engineering reacting systems that enable more sustainable use of our natural resources is central to both reducing the risks associated with CO<sub>2</sub> emissions and making the long-term transition to a more circular, sustainable, and electrified economy. Moreover, developing technologies to leverage the energy density of liquids to produce clean H<sub>2</sub> and solid carbon without CO<sub>2</sub>, could be game changing. In this work, we investigate the potential of directly exciting plasmas in liquid hydrocarbons to create unique, multi-phase reaction environments, i.e., environments where plasma (ionized gas), gaseous H<sub>2</sub>, gaseous and liquid hydrocarbons, and solid carbon are all present simultaneously, to produce clean H<sub>2</sub> and carbon. The ultimate target is direct transformation of liquid hydrocarbons to gaseous H<sub>2</sub> and solid, easy-to-separate carbon using electricity that can be provided from any source and/or points of use.

As a proof of concept, we have recently demonstrated that it is indeed possible to strike and sustain plasma discharges in liquid hydrocarbons such as hexane, to simultaneously generate gaseous H<sub>2</sub> and solid carbon at high rates. Significant H<sub>2</sub> generation along with small amounts of other light hydrocarbons was observed. Initial, un-optimized experiments have been promising: a single pin-to-pin AC-driven, high voltage plasma discharge running at ~18 W (estimated from the plasma current-voltage transient) in liquid hexane produced ~80-100 sccm of H<sub>2</sub>, which is equivalent to an energetic input of ~240 kJ/mol H<sub>2</sub> = 33 kW\*hr/kg H<sub>2</sub>. This energy requirement for an un-optimized system is considerably lower than for water electrolysis (40 kW\*hr/kg H<sub>2</sub> (theoretical), but 60 kW\*hr/kg H<sub>2</sub> in practice), and promisingly competitive with other plasma-based hydrocarbon conversion processes. Preliminary experiments show that (i) the plasma is not simply vaporizing the liquid - so the system's specific energy input (SEI) is preferentially driving hydrocarbon cracking; (ii) small amounts of C<sub>2</sub>-C<sub>4</sub> products are also produced, where selectivity depends on plasma operating conditions; and (iii) the liquid hydrocarbon phase immediately turns yellow and then quickly black due to rapid formation of suspended carbon particulates. Hydrocarbon conversion, reaction rates, and characterization of the gas (MS), liquid (GC/MS), and solid (C/H analysis, SEM, Raman) phase products as a function of plasma operating conditions and hydrocarbon source will be discussed.

#### 4:20pm PS1+AS-WeA-7 Plasma-Surface Interaction in CO<sub>2</sub> Containing Plasmas, *Olivier Guaitella, E. Baratte*, Ecole Polytechnique - CNRS, France; *V. Guerra*, Instituto Superior Técnico, Portugal; *D. Sadi, S. Bravo, C. Garcia-Soto*, Ecole Polytechnique - CNRS, France; *T. Silva*, Instituto Superior Técnico, Portugal **INVITED**

The use of Non Thermal Plasmas to convert CO<sub>2</sub> is a very promising way of meeting environmental challenges. However, there are two main obstacles to their use and optimisation:

- the complexity of the kinetics of these plasmas makes it very difficult to predict their chemical reactivity,
- while it is relatively easy to dissociate the CO<sub>2</sub> molecule in a plasma, it is difficult to avoid reverse reaction mechanisms that reduce the energy efficiency of conversion.

To address the first point, complementary experimental set-ups have been developed in this work to enable step-by-step validation of 0D kinetic models including electronic, vibrational and chemical kinetics. This systematic approach relies on discharges as simple as pulsed glow discharge and radiofrequency discharges in batch reactor, monitored with in situ time resolved absorption spectroscopy. Thanks to these studies, models of pure CO<sub>2</sub> but also, CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> have been thoroughly validated against a large range of experimental conditions. Once these plasma sources have been well characterized, they can be used to study the fundamental mechanisms of plasma-catalyst interaction. The combination of a cold plasma and a catalyst is indeed the solution most often proposed to overcome reverse reaction processes and improve selectivity and energy efficiency. However, the design of materials truly capable of benefiting from the vibrationally or electronically excited species of the plasma relies on an understanding of these mechanisms.

In addition to plasma-catalysis, new concepts are currently emerging for continuously shifting chemical equilibria in the plasma phase, thereby improving yields. The use of ionic membranes (perovskite or Yttrium

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Stabilized Zirconia) or water used as solvent opens up new routes for improving plasma CO<sub>2</sub> conversion processes, but once again raises the question of how these plasmas interact with complex surfaces. Examples of these approaches will be given.

5:00pm **PS1+AS-WeA-9 Study of Plasma-Catalyst Surface Interactions for Methane Dry Reforming**, *Michael Hinshelwood, G. Oehrlein*, University of Maryland, College Park

Plasma enhanced dry reforming of methane (DRM) at atmospheric pressure is a promising technique for converting greenhouse gases (CH<sub>4</sub> and CO<sub>2</sub>) into syngas (H<sub>2</sub> and CO), which can be further used for producing fuels and chemicals. The exact mechanism of enhancement of DRM due to plasma is not fully understood, however plasma-generated reactive species are thought to play an important role. Enhancement in DRM can take the form of increased product formation or reduced carbon coking which can deactivate the catalyst. We use a remote plasma-catalysis setup that enables the study of certain plasma-catalyst interactions by infrared spectroscopic methods [1]. Species adsorbed on the catalyst surface are analyzed in-situ using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase products from the interaction are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). The catalyst used is Ni, commonly used for dry reforming reactions, on a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> support. The catalyst is exposed to either Ar/CO<sub>2</sub> or Ar/CH<sub>4</sub> plasma, while other gas mixtures are introduced into the reaction chamber downstream from the plasma. This allows for evaluation of the effect of reaction species specific to either gas. DRIFTS measurements reveal that exposure to CH<sub>4</sub> plasma results in the buildup of CH<sub>2</sub> (2930 cm<sup>-1</sup>) and CH<sub>3</sub> (2960 cm<sup>-1</sup>, 2860 cm<sup>-1</sup>) containing species on the catalyst surface. Build-up of such species also occurs during catalyst coking and deactivation. Exposure to CH<sub>4</sub>/Ar plasma may be able to replicate coking at low temperatures where reaction rates are lower and surface mechanisms easier to resolve. If CH<sub>n</sub> (n=1-3) buildup at room temperature is followed by Ar plasma exposure, the CH<sub>2</sub> and CH<sub>3</sub> surface coverages are reduced at similar and temporally decreasing rates, but not eliminated. Comparing the effect of Ar plasma and Ar/CO<sub>2</sub> plasma on surface CH<sub>n</sub>, is used to evaluate the potential of Ar/CO<sub>2</sub> plasma to reduce catalytic deactivation during dry reforming. Our setup allows for variation of the catalyst temperature to test the impact of plasma on DRM at various degrees of catalyst activity. Increased understanding of the time-dependent relationship between downstream products (FTIR) and surface adsorbed species (DRIFTS) will shed light on the plasma enhancement of DRM to inform development of future systems.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under award number DE-SC0020232.

1.Y. Li, J. Jiang, M. Hinshelwood, S. Zhang, P. J. Bruggeman, and G. S. Oehrlein, "Characterization of plasma catalytic decomposition of methane: role of atomic O and reaction mechanism," *J. Phys. D: Appl. Phys.*, 55, 155204, (2022). doi: 10.1088/1361-6463/ac4728.

5:20pm **PS1+AS-WeA-10 Silver Nanoparticle Synthesis in Low-Pressure Plasmas: The Roles of Free Electrons and Photons**, *Chi Xu, J. Held, H. Andaraarachchi, U. Kortshagen*, University of Minnesota

The interactions of plasmas with liquids enable considerable electron and vacuum ultraviolet (VUV) photon fluxes to the solution surface, contributing to subsequent reduction processes and emerging as a novel technique of nanomaterials synthesis. To date, the solvated electrons were mostly proposed to be the critical reducing agent while the effect of photon-driven reactions on nanoparticle synthesis has not been fully understood. In this work, we use glycerol, a major co-product of biodiesel production as the solvent. Using this solvent, we investigate the silver nanoparticle formation in silver nitrate (AgNO<sub>3</sub>)-glycerol solutions delivered as droplets to a low pressure nonthermal plasma, opening new synthetic pathways over previous bulk reactions. We demonstrate that this system allows the formation of monodispersed sub-20 nm silver nanoparticles. By inserting crystal filters having various cut-on wavelengths between the plasma and the glycerol droplet, UV radiation from the plasma-liquid emission at wavelength ranges between 150 and 280 nm is differentiated, while plasma-generated electrons are prevented from reaching the droplet. To quantify the nanoparticle yield, the final silver ion concentration was measured using a colorimetric method. We find that UV radiation contributes ~ 70% of the integral plasma effect in reducing silver ions to atoms, likely driven by H radicals attributed to the photodissociation of glycerol with an energy threshold of ~ 5 eV. The UV emission was traced to

originate from carbon species released into the plasma from the glycerol solvent. The effects of aldehydes are minimal, which was evaluated by scavenger study and colorimetric assay kit, respectively. Using water as the solvent instead, silver nanoparticle formation in aqueous solutions instead of glycerol does not exhibit a strong dependence on UV emission under the same operating conditions.

The research was sponsored by the Army Research Office and was accomplished under Grant No. W911NF-20-1-0105.

5:40pm **PS1+AS-WeA-11 Plasma Synthesis of Hydrogen from Ethanol Solution**, *D. Lojen*, Université libre de Bruxelles, Belgium; *T. Fontaine*, Université libre de Bruxelles/ University of Mons, Belgium; *L. Nyssen*, Université libre de Bruxelles/Ghent University, Belgium; *D. Petitjean*, Université libre de Bruxelles, Belgium; *R. Snyders*, University of Mons, Belgium; *N. De Geyter*, Ghent University, Belgium; **Francois Reniers**, Université libre de Bruxelles, Belgium

In the quest for green energy sources, hydrogen is often presented as the fuel of the future. However, as such, hydrogen must be synthesized. Among the many synthesis routes, those which don't directly produce CO<sub>2</sub> are privileged. In this regard, water electrolysis, plasma splitting or pyrolysis of methane are intensively explored, sometimes already at the industrial or preindustrial scale. However, all routes present advantages and drawbacks. For instance, plasma splitting of methane has to deal with the removal of solid carbon from the reactor, and water electrolysis suffer from the high intrinsic energy cost to break the water molecule into H<sub>2</sub> and O<sub>2</sub>. In this paper, we present preliminary results of the plasma induced splitting of liquid ethanol, using a nanopulsed generator, as this route could be an intermediate between the high energy cost of water splitting, and the solid carbon problem evidenced in CH<sub>4</sub> plasma. Moreover, ethanol could be from renewable sources origin, and according to previous studies, its main oxygenated degradation product could be CO, which is useful for the chemical industry. The plasma reactor consists of a pin-to-plate electrode geometry, with the plate electrode being submerged in ethanol. The gases produced are quantified using atmospheric mass spectrometry (Hiden) and the discharge is characterized using a high speed photron camera, and electrical measurements. The main body of the reactor is glass-based, with selected entries for OES, mass spectrometry, gas inlet and outlet. Results show that the thickness of the liquid ethanol layer over the plate electrode plays a tremendous role as it generates two plasma regimes: up to 2.5 mm, the plasma is hot, with a high current and a reasonable peak voltage, whereas above 2.5 mm, the plasma changes to a DBD-like configuration, with ethanol playing probably the role of a dielectric. This induces an increase in voltage and a drop in current. Hydrogen production is directly related to the current injected in the discharge. In the hot plasma configuration, hydrogen is produced with 55% selectivity, dropping to <50 % at higher ethanol thicknesses. A change in the byproducts selectivities is also observed (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO), with the change in plasma regime. Results also show the effect of the nanopulse duration and frequency and the electrode polarity.

Acknowledgements:

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