NITROGEN FIXATION BY GLIDING ARC PLASMA: BETTER INSIGHT BY CHEMICAL KINETICS MODELLING

Significance Statement

Nitrogen is an important building block for almost all forms of life considering that it is needed to biosynthesis basic components of plants and other living organisms. Living organisms can consume nitrogen in usable forms that are obtained by chemical reaction with hydrogen and oxygen. For this reason, nitrogen compounds can be found in amino acids, nucleic acids, plant cells, and proteins.

Nitrogen is in abundant supply in the atmosphere; about 78.08% of air is composed of nitrogen. Unfortunately, this abundant nitrogen source is not available to a good number of living organisms in view of the extreme difficulty in breaking its triple bond as well as its stable electronic configuration. Therefore, this makes the initial reaction step of the conversion energy demanding.

Nitrogen fixation that converts molecular nitrogen into simple compounds including ammonia and nitric oxide can be used further for the preparation of more complex molecules. Unfortunately, this is the most challenging step of nitrogen utilization by living organisms. The Haber-Bosch process, binding nitrogen with hydrogen to produce ammonia at high pressure, is perhaps the most efficient process for fertilizer production. However, industrial ammonia preparation is the most energy intensive chemical process.

For this reason, there is a need to come up with sustainable processes for nitrogen fixation. Several alternatives have been investigated including biological nitrogen fixation and nitrogen fixation with metallocomplex homogeneous catalysts under ambient pressure. Plasma technology, and particularly gliding arc plasma, is a promising candidate in this industry. However, much is still unknown regarding the underlying mechanism.

Belgian researchers at University of Antwerp, Weizong Wang, Stjin Heijkers and Annemie Bogaerts, in collaboration with Bhaskar Patil and Volker Hessel at Eindhoven University of Technology, studied the NOx production in a pulsed-power gliding-arc plasma reactor by a chemical kinetic model. They performed experiments to benchmark the model, and reasonable agreement was reached between the computed and measured NO and NO_2 yields. Their research work is published in *ChemSusChem* (with the highlight of very important paper) and it was also featured as cover story of the journal.

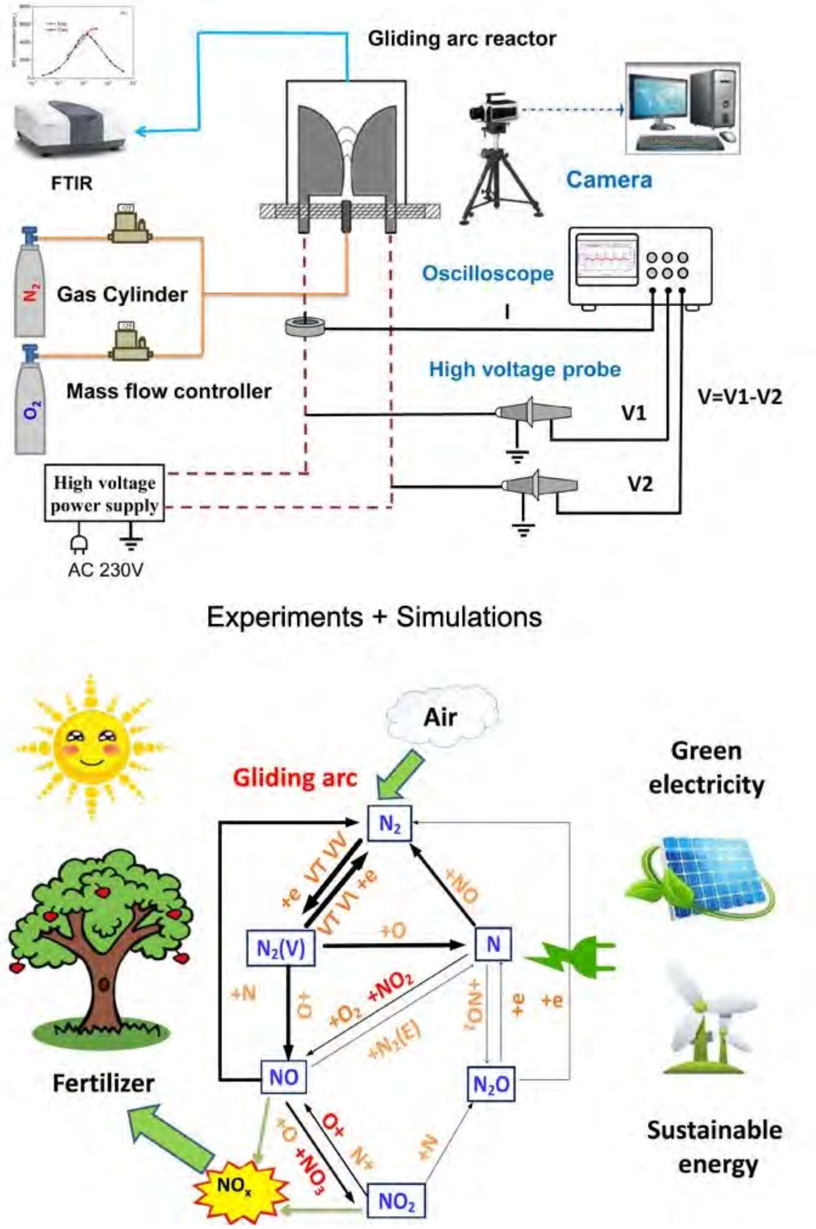
The research team wanted to get an in-depth understanding of nitrogen fixation via NOx production in gliding arc plasma by means of combined experiments and a zero-dimensional kinetics model. They compared their experimental outcomes with the predictions of the model and found good agreement for NO, NO_2 and the total NOx production, NO_2 and NO selectivity, energy consumption, and energy efficiency for the whole range of N_2/O_2 ratios in the mixture. This indicated that the proposed model could be implemented to elucidate the most dominant reaction pathways for the production of NOx.

Their study also revealed that vibrational excitation of nitrogen could help to overcome the reaction energy barrier of the non-thermal Zeldovich mechanism, and could therefore improve NO production. This provided an energy efficient approach for NO formation in the gliding arc. The outcomes of the study also indicated that the most important reaction for nitrogen oxide formation was the oxidation of NO by oxygen atoms.

The researchers also compared their experimental results with those of thermal NOx production. The NOx yield and energy efficiency obtained in the gliding arc were much higher than the thermal values, due to the non-equilibrium properties of the plasma, since the chemistry of the conversion is initiated by energetic electrons.. Although the energy consumption achieved is still higher than for the Haber-Bosch process, indicating that further improvements are necessary, the authors believe that the gliding arc is a promising building block for industrial-scale nitrogen fixation.

The authors believe the new plasma process open doors to new windows of opportunity concerning distributed fertilizer manufacturing. This had a social dimension as this is needed mostly in less developed regions with large transport distances such as in Africa. Thus IT contributes to the megatrend resources (hunger). Hunger is given despite having Haber-Bosch.

There are a lot of applications for this technology. For example, farmers in remote areas will be able to create mineral fertilizers on site with wind or solar energy as a sustainable alternative to current conventional fertilizers. This certainly opens up opportunities in developing countries and regions where renewable energy is currently underused.



About the author

Dr. Weizong Wang received double Ph.D. degrees in electrical engineering from Xi'an Jiaotong University in Xi'an (China) and University of Liverpool (United Kingdom) in 2013. His PhD thesis investigates the dynamic characteristics and decaying behaviour of SF6 Arcs in switching applications. After that, he worked at Qian Xuesen Laboratory of Space Technology, China Aerospace Science and Technology Corporation (CASC) and studied advanced spacecraft (electric) propulsion. In 2015, he entered the PLASMANT research group at the University of Antwerp in Belgium supported by the European Marie Skłodowska-Curie (MSCA) Individual Fellowship and studied plasma based gases conversion into value added products.

His main interests concern the fundamental physics, chemistry and applications of low temperature plasmas. Dr. Wang has authored over 40 publications in peer-reviewed journals and received the National Excellent Patent Award of China in 2013 and Excellent Doctoral Dissertation Award of Shaanxi Province in China in 2014 as well as IOP Journal of Physics D: Applied Physics Outstanding Reviewers Award in 2016. He is also serving as advisory board member of IOP Journal of Physics D: Applied Physics.

About the author

Prof. Dr. Annemie Bogaerts received her M.Sc. and Ph.D. degrees in chemistry, in 1993 and 1996, respectively, from the University of Antwerp in Belgium. After some postdoctoral research years, she became a professor of Physical Chemistry in 2003 at the University of Antwerp, and in 2012 she became full professor. She is the head of the interdisciplinary research group PLASMANT, which counts 38 members. She is also head of the Chemistry Department at the University of Antwerp. From 2013 till 2016 she had a prestigious mandate as Francqui Distinguished Research Professor.

Her current research activities include the study of plasma chemistry, plasma reactor design and plasma-surface interactions, by numerical modelling and experiments, for various applications, especially environmental applications (CO_2 conversion into value added chemicals and renewable fuels, and nitrogen-fixation from the air for the production of small chemical building blocks) as well as medical applications (mainly cancer treatment).

She is author of more than 400 publications, and she has more than 9000 citations (Web of Science; h-index 47) and 13,000 citations (Google Scholar; h-index 58). She gave more than 200 invited talks at international conferences and research institutes. She is editor of Spectrochimica Acta B, responsible for the review papers, and guest editor for 10 special issues in several journals. She is also in the advisory/editorial board of several journals, and in the international scientific committee of many international conferences. In 2015 she was the Chair of the International Symposium on Plasma Chemistry (ca. 600 participants), and she is also member of the Board of Directors of the International Plasma Chemistry Society.

About the author

Prof. Dr. Volker Hessel investigates flow chemistry with process chemistry focus, plasma-based chemical processing and nanomaterial synthesis, and sustainability of process designs of process intensification approaches at industrial scale. He studied chemistry at Mainz University (PhD in organic chemistry, 1993). In 1994 he entered the Institut für Mikrotechnik Mainz GmbH (1996: group leader microreaction technology). In 2002, Prof. Hessel was appointed Vice Director R&D at IMM and in 2007 as Director R&D. In 2005 and 2011, Prof. Hessel was appointed as part-time and full professor at Eindhoven University of Technology, respectively, for the chair of "Micro Flow Chemistry and Process Technology". He is honorary professor at TU Darmstadt, Germany, and guest professor at Kunming University of Science and Technology, China.

Prof. Dr. Hessel is (co-)author of more than 420 peer-reviewed publications and 11 books (h index 50, Scopus). He received the AIChE Award "Excellence in Process Development Research" in 2007, the ERC Advanced Grant "Novel Process Windows" in 2010, and the IUPAC ThalesNano Prize in Flow Chemistry in 2017, and the FET Open and ERC Proof of Concept Grants in 2016 and 2017, respectively. In the same year, he got granted as coordinator the FET OPEN project ONE-FLOW. He is Editor-in-Chief of the journal "Green Processing and Synthesis". He was authority in the 35-man teamed Enquete Commission "Future of the Chemical Industry" of the parliament of Germany's state Nordrhein-Westfalia and is advisor for GSK for the Green Chemical Manufacturing Programme in Singapore.

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Reference

Weizong Wang, Bhaskar Patil, Stjin Heijkers, Volker Hessel, and Annemie Bogaerts. **Nitrogen Fixation by Gliding Arc Plasma: Better Insight by Chemical Kinetics Modelling.** ChemSusChem 2017, 10, 2145 – 2157.

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