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Air plasma for nitrogen fixation: an old idea with new promise

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Abstract: This paper focuses on the generation of 'fixed' or 'reactive' nitrogen using air plasma, and offers a vision for how the technology might be used for sustainable agriculture. Air plasma generates nitrogen oxides that when dissolved in water create aqueous nitrate and nitrite. NH_3 formed from bacterial degradation of animal manure or urine will react with this solution to create ammonium nitrate. This creates a high N content organic fertilizer and reduces the pollution associated with NH_3 emission. Electrical power to run the air plasma reactor and associated facilities will come from distributed, renewable solar or wind sources. Fundamental plasma science is needed to help bring this vision to reality.

Keywords: air plasma, nitrogen fixation, nitric acid, ammonia volatilization, recycling, manure, organic waste

1. General

This paper focuses on the generation of 'fixed' or 'reactive' nitrogen using air plasma, and offers a vision for how the technology might be used in sustainable agriculture. The currently dominant method for nitrogen fixation, the Haber-Bosch (HB) method, is a catalytic process of combining H_2 and N_2 into NH_3. It has been estimated that close to 50% of world population is alive today only because of the increased agricultural productivity associated with the use of N-based fertilizers made from HB-manufactured NH_3 [1]. However, there are important environmental problems associated with inefficient N-fertilizer use [2]. In this talk, we show that air plasma formation of nitrogen oxides can potentially help increase nitrogen use efficiency by treating N-containing organic waste, creating high-value organic fertilizer. In addition, air plasma technology is ideally suited to exploitation of renewable, distributed forms of energy generation such as wind or solar.

The basic idea is to create nitric oxide (NO) in air plasma then allow the NO to react with O_2 in the air to create NO_2. Dissolving NO_2 into water creates nitric and nitrous acid, or equivalently nitrate and nitrite ions. When bacteria degrade animal waste products such as manure and urine, much of the organic N content is converted to volatile ammonia (NH_3). If this NH_3 is lost to the environment, a series of environmentally damaging reactions will occur [2]. However, if the NH_3-containing waste is treated with the nitric acid solution, non-volatile ammonium nitrate (NH_4NO_3) is formed. This greatly increases the N-fertilizer potency of the organic waste and minimizes the environmental problems associated with gaseous NH_3 release. The proposed process would reduce, but probably not eliminate, the need for fixed nitrogen created by HB.

In order to be practically feasible, however, the energy cost of creating NO from air must be kept as low as possible.

Some aspects of this idea were used commercially in the early 20th century, but HB quickly replaced the air plasma approach for various economic reasons, mostly associated with excess energy use in the air plasma process [3]. However, recent theoretical and experimental results show that air plasma has an unrealized potential waiting to unfold. The minimum theoretical enthalpy requirement for nitric oxide (NO) production is only 6.4 GJ/tN (~ 1 eV/molecule) starting from air, assuming 100% excess energy recovery in the form of heat. If NO formation kinetics is governed by non-equilibrium, electron-impact creation of excited states of N and O rather than purely thermal kinetics, the energy barrier is about 20 GJ/tN. The practical limits for recovery of excess thermal energy is currently about 60% from gas temperatures on the order of 2500 K. This leads to the conclusion that practical air plasma systems could operate with a net energy consumption of 36 GJ/tN, or 10 kwh/kgN. The best current air plasma technology, however, uses ~ 90 GJ/tN. Under current environmental regulations in most of the world, with no cost associated with release of reactive N into the environment, economic analysis suggests that economically practical air plasma systems will require energy efficiency of less than ~40 GJ/tN. The challenge for the plasma research community is to design plasma devices that can approach the lowest value possible for energy use per mass of fixed nitrogen generated.

Lowering the specific energy consumption down to the target of 36 GJ/tN can initially be divided into two separate paths:

a) Reduce energy input for a given NO concentration; and/or
b) Increase NO concentration by increasing energy input and energy recovery.

Both paths are viable. Path a) can be achieved by finding non-equilibrium plasma conditions to create N_2 excited state precursors for NO formation, thought to be ~ 20 GJ/tN. Path b) involves applying more energy in order to increase the concentrations of N and O in the plasma to reach higher NO concentrations. This increase in specific energy input can be compensated by capturing some of the heat generated in the intense plasma and using it to heat the incoming air.

Path a) can be pursued through several non-equilibrium plasma approaches. The most promising appear to be plasma excitation through certain microwave and radio wave sources, including rotating, magnetized arcs. Laboratory experiments (and associated patents) have reported 70GJ/tN by producing relatively low concentrations NO from air plasma. Dielectric barrier discharges seem unable to crack the nitrogen molecule at sufficient rates. Nano-pulsed plasma sources (e.g., as used in breakdown and recombination studies) have achieved greater success.

One challenge in using non-equilibrium plasma sources is to suppress the reverse reactions: NO is lost when it re-converts to N_2 and O_2. The lower energy barrier associated with excited state, non-equilibrium pathways works both ways, representing both a theoretical and practical disadvantage.

Path b) aims to approach thermal equilibrium conversions to NO from the high dissociation, non-equilibrium side. The method has been patented in various forms. In 1929 Harry Pauling [4] summed up the state of the art with reference to experiments by Nernst who claimed an equilibrium concentration of 10% NO at 4400 K and an energy efficiency of 120 GJ/tN. With a reduced electrode loss the efficiency was brought down to 90 GJ/tN.

Fundamental plasma research has a key role to play in this field. One important experimental challenge is to measure the short-lived, excited state plasma components. This is essential in order to improve air plasma models and to advance general understanding of the plasma. Trial and error testing has a limited ability to really advance the field. Simplified theories often can be far away from realistic practical conditions, thus limiting their value.

The development of improved analytical capability has the potential to reveal critical steps in NO formation as well as in avoiding the destruction of the formed NO.

The nature of the plasma non-equilibrium, especially the processes responsible for accelerating electrons with a minimum overall energy consumption, is not fully understood. The NO yield measurements at the reactor outlet can be strongly affected by the post-plasma reactions in the flowing afterglow. Destruction of NO and recombination to N_2 and O_2 must be better understood.

Fully self-consistent air plasma modeling with all its chemical components and their associated reactions and transport is still challenging under practically realistic conditions Understanding the physical and electrical properties of the plasma is as important as plasma chemistry. The very strong gradients near bounding walls as well as wall interactions are notably difficult issues.

Progress has been made recently in developing deeper fundamental understanding of air plasma and NO kinetics [5, 6].

Encouraging progress in developing new materials with improved functionalities like heat resistance, oxygen and nitrogen permeability and catalytic effects offer hope for significant process improvements. Materials with higher temperature oxygen permeability will enable gas separation and process intensification. A plasma process is able to generate very high driving forces in terms of heat and mass transfer. This will reduce the need for large traditional unit processes. Such a new process regime will, however, require new process engineering competence and standards.

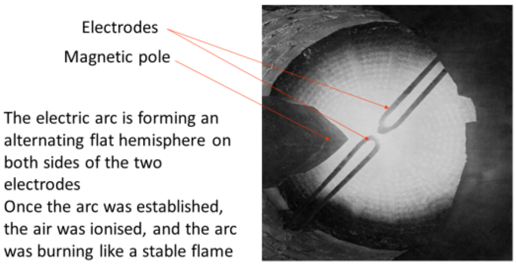
‘Process intensification’ is the science of combining unit operations into a high intensity chemical process step where the scale of the equipment can be reduced by a factor of thousands. An example of process intensification from traditional fertilizer industry is combining neutralisation, evaporation, and particulation into a reaction-nozzle in a fluid-be-granulator. The neutralisation, evaporation and solidification from the nozzle onto a granule is completed in a few milliseconds. Plasma conditions offer several similar opportunities.

Since the beginning of the industrial revolution, the world has taken advantage of the abundance of concentrated chemical energy stored in fossil fuels. The technology and knowledge built up over the last ~150 years has been based on exploiting relatively cheap hydrocarbons that combine both energy source and energy carrier in order to drive endothermic chemical processes. Chemical energy and chemical building blocks often went hand-in-hand in elegant processes. Examples include methane-based ammonia technology and oil- and gas-based polymer production.

A paradigm shift is required in our rapidly emerging post-fossil era. We need to base chemical technology on renewable energy, utilizing chemical building blocks with lower free energy. This implies a new way to approach process and plant engineering.

In the post-fossil era, we foresee a sort of reverse engineering, where for example CO_2 may become an important building block and electricity acts as the renewable energy carrier. Plasma technology has the potential to make a dramatic change in how we generate both intermediates and final products from waste, water and air.

In this vision, small-scale, process-intense, clean and safe technologies will replace large scale ‘mega-industrial’ units where economies of scale and high-risk capital are the winning recipe. The generation of reactive nitrogen via renewable energy for agriculture may become the leading example of this new paradigm.



Birkeland Eyde electric arc in operation

The electric arc is forming an alternating flat hemisphere on both sides of the two electrodes

Once the arc was established, the air was ionised, and the arc was burning like a stable flame

2. References

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