

# **Plasma Chemistry for Nitrate Formation**

## **Notes**

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**Note:** Parts of the material reviewed here have been or will be published in the following documents. Please do not distribute this document and treat as business confidential.

- 1) Locke, B. R., P. Lukes and J.-L. Brisset, Elementary Chemical and Physical Phenomena in Electrical Discharge Plasma in Gas-Liquid Environments and in Liquids, in *Plasma Chemistry and Catalysis, From Pollution Control to Energy Conversion*, V. I. Parvulescu, M. Magureanu, P. Lukes (Eds.), Wiley-VCH Verlag, 2012, ISBN 978-3-527-33006-5 (print edition).
- 2) S. Mededovic-Thagard and B.R. Locke, Electrical Discharge Plasma for Water Treatment, Chapter 12, in *Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications*, M. Stefan, ed., IWA Publishing, London, UK, 2016 (in production, 2017).

## INTRODUCTION

It has been estimated that in order to meet the demand for food of a projected world population of 9 billion people by the years 2025 to 2050 and beyond, mankind will need to increase food production by 70 to 100%. [1, 2] The increase in demand is driven not only by increased population but also by increased standards of living which leads to the desire for higher quality foods made in environmentally sustainable ways. [1] While past experiences during the Green Revolution of the 1960 to 1980 period suggests that increased food production is possible through improved technology (e.g., intensive application of synthetic fertilizers and crop strain improvements by genetic engineering and other methods) [3], the environmental impact of agriculture is already creating major local, regional, and global problems related to soil fertility, air/water pollution, and global climate change. [4, 5] Worldwide in 2005 there was 1200 Mha of land used to produce 4.5 Gt of food using 160 Mt of fertilizer. Nitrogen, the limiting nutrient in the production of many crops [6], is one of the key nutrients in plant fertilizers (along with potassium and phosphorous). Mankind releases 160-170 Mt/yr of nitrogen to the environment, of which 100 Mt come from the Haber-Bosch process of ammonia synthesis and a large amount of the remaining release comes from combustion. [4, 6-9] Human intervention in the global nitrogen cycle has therefore been profound with the total anthropogenic release of nitrogen about double the natural release. [10] It has been estimated that only 18-49% of nitrogen in fertilizer is taken up by crops after application, and in some foods the efficiency of nitrogen incorporation has decreased over the last 40 years. [4] Of the 100 Mt of N produced by the Haber-Bosch process only 17 Mt end up in plant and animal products. [4] The remaining nitrogen released to the soil, air, and water in the forms of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_3^-$  leads to many problems such as water eutrophication, soil nutrient depletion, and global warming. [7] Similar air and water pollution problems exist with the application of synthetic pesticides, herbicides, and fungicides. [4] In addition to the environmental impacts, the effects of many modern agricultural practices, including heavy synthetic fertilizer and excessive pesticide use, on human health are profound. [11] Nevertheless, improvements in efficiency of agriculture can mitigate some of the environmental impact. [2, 12]

Nitrate production by the Haber-Bosch process consumes 3-5% of the natural gas production and 1 to 2 % of the world's energy supply. The efficient commercial production of nitrate by the Haber Bosch process requires large scale, high temperature and pressure reactors, and the primary feedstock component, ammonia, requires large amounts of energy and natural gas to produce hydrogen [13]. Smaller amounts of nitrate salts, including potassium nitrate, are still mined and used in specialty fertilizers and other applications. With increasing world population and demand for high quality foods, there is an increasing need for efficient and environmentally safe methods to produce nitrate.

Although high temperature thermal plasma processes were used to produce nitrates at the end of the 19<sup>th</sup> century and beginning of the 20<sup>th</sup> century, the high energy and operating costs were not competitive with the Haber process, and further these *thermal arc plasma* processes (like the Haber Bosch process) require relatively large scale systems, e.g., high capital costs, to be effective. It is important to note that the many advances in technology and science as well as environmental issues since that time allow us to revisit the problem of nitrate formation with plasma discharges. Some of these reasons include

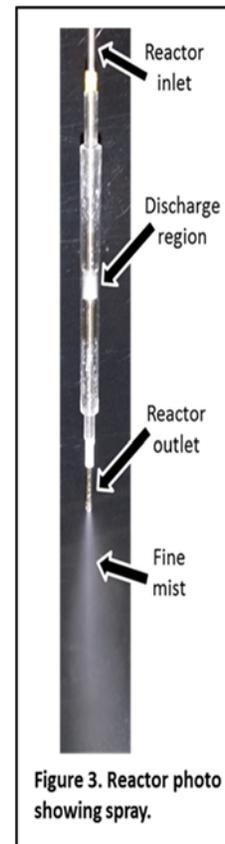
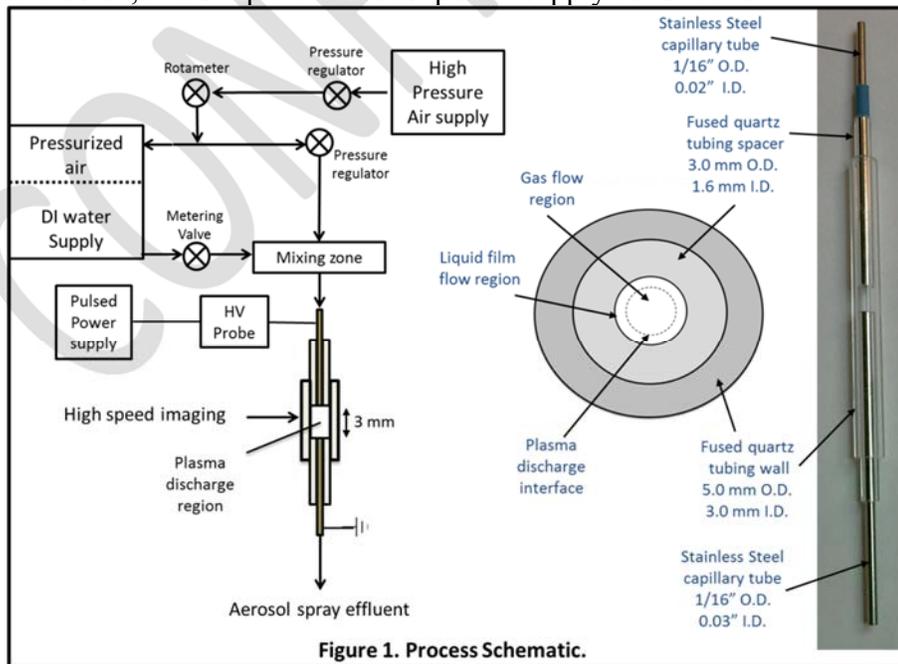
- 1) Improved electrical energy delivery technology.
- 2) Improved understanding of plasma processes and chemistry.
- 3) Advances in novel areas of plasma contacting liquid water.

- 4) Environmental concerns of the Haber Bosch process.
- 5) Potential advantages of distributed production of nitrate by farmers.

The field of *non-thermal plasma* processes have been under intensive investigation for nitrogen oxide control and removal from combustion processes over the last 25 years and such plasma processes have been successful in converting waste pollution into fertilizer products (e.g., ammonium sulfate, ammonium nitrate)[14] and other environmental applications.[15] In a non-thermal atmospheric pressure plasma process energy from a large electric field is directed to increasing the kinetic energy of free electrons in such a manner that the energy of the remaining gas phase species is close to ambient (i.e.,  $T_e \gg T_i = T_g$ , where  $T_e$  temperature of electrons,  $T_i$  temperature of ions, and  $T_g$  temperature of background gas).[16] A key factor to utilizing a plasma process to perform chemical synthesis is to suppress reverse reactions that tend to destroy the desired products through degradation reactions with ions, radicals, and other species formed in the plasma.

In previous and current work, we have shown that atmospheric pressure low temperature plasma formed by pulsed power in an electric discharge (figures 1, 2, and 3) with flowing inert gas and liquid water aerosols and films provides an efficient means to produce hydrogen peroxide.[17-22] The highest energy yield for hydrogen peroxide formation with a plasma processes [23] was obtained with water droplets at about 80 g/kwh with pulsed plasma discharge and water spray injection. The thermal energy of the plasma in that system was not sufficient to vaporize the flowing water, and the liquid water droplets provide both a large source of water to generate hydroxyl radicals (which recombine to make hydrogen peroxide) and secondly a condensed phase which acts to sequester the highly water soluble product, thus removing it from the plasma environment, and thereby reducing the effects of the degrading reverse reactions[17].

We have also found that nitrate can be formed effectively in such a reactor when the flowing *air* contacted liquid water (figures 4, 5, and 6). Other key advantages of this reactor system are the low operating power, thus causing negligible electrode erosion, and simple and robust power supply construction.



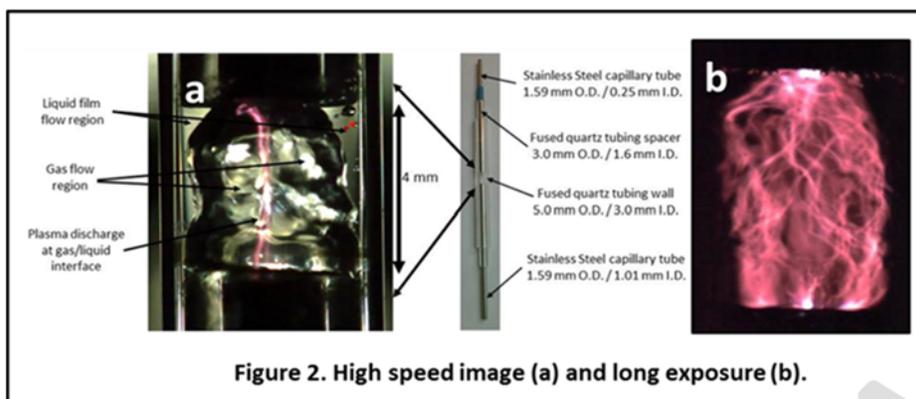


Figure 2. High speed image (a) and long exposure (b).

## BACKGROUND

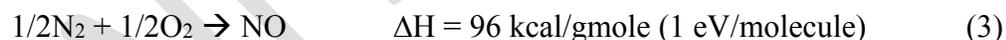
The overall reaction to form nitrate (as nitric acid) from water, oxygen, and nitrogen is exothermic and is given by



The pathway and mechanism that lead to products depend upon the type of process (e.g., catalytic, thermal, plasma) and, indeed, depending upon the system, other overall reactions are possible, for example[24, 25]



The Birkeland–Eyde process utilized a thermal plasma arc for the generation of nitrate for use in fertilizers at the beginning of the 20<sup>th</sup> century. This process operated commercially for about 20 years before being supplanted by the high temperature Haber catalytic process [26, 27]. The plasma arc first generated nitric oxide (NO) by the overall and limiting endothermic reaction



Downstream of the plasma reactor in the original process the above reaction was followed by the two exothermic, non-plasma, reactions involving first high temperature oxidation with oxygen and then reaction with water



The generation of NO from N<sub>2</sub> and O<sub>2</sub> in a plasma reactor has been extensively reviewed [24, 25, 27] and the energy cost for production of NO by the Birkeland-Eyde process was 25 eV/molecule. This result corresponds to a 4% energy yield based upon the enthalpy of reaction. Thermal plasma systems at very high pressure (20–30 atm) and temperature (3000–3500 K) have subsequently been found to lead to an energy efficiency of 11% (9 eV/mol) and very fast quenching rates (large temporal gradients, 10<sup>8</sup> K/s, in the plasma temperature to the ambient) are needed to achieve this efficiency. The energy costs by plasma process for the formation of some reactive nitrogen species are summarized in Table 1. It is important to note that the energy yields in Table 1 only include the electrical costs of the plasma and not the feed costs, capital

costs, or other costs (e.g., cooling, magnetic fields, catalysts). For comparison, the Haber Bosch process requires 4.8 to 9.0 eV/molecule. Typical costs of nitrogen are \$0.4 to 0.48/pound which gives approximately 5 eV/molecule assuming \$0.1/kWh equivalent.

Table 1. Summary of processes for nitrogen oxide formation by plasma and the Haber Bosch process.

Process	Prod.	Feed	Conditions	Energy Yield	Ref.
				eV/molecule	
Birkeland and Eyde	NO	N <sub>2</sub> , O <sub>2</sub>	thermal plasma arc	12 to 25	1900's
Thermal plasma	NO	N <sub>2</sub> , O <sub>2</sub>	20-30 atm, 3000-3500 K	9	1980's – Russia
Microwave non thermal plasma	NO	N <sub>2</sub> , O <sub>2</sub>	with magnetic field, cooled walls with liquid nitrogen	3	1980's – Russia
Low pressure	NO	N <sub>2</sub> , O <sub>2</sub>	with catalyst	9 to 23	1980's - France
Rotating disk	NO	air	injected water	33	1980's - Poland
Plasmatron gliding arc	NO <sub>3</sub> <sup>-</sup>	air with water	240 Watts	3100	Present – Drexel
Glow discharge	NO <sub>3</sub> <sup>-</sup>	air with water	420 W 162 MHz	5700	Present - North Carolina State
AC gliding arc over water	NO <sub>3</sub> <sup>-</sup>	air with water	2 electrodes 300 W	360	2000's - Our lab
AC gliding arc over water	NO <sub>3</sub> <sup>-</sup>	air with water	3 electrodes 600 W	430 to 2000	2000's - Our lab
Bubbling in water	HNO <sub>3</sub>	air with water	underwater pulsed discharge with bubbles	1900	Present - Chinese group
Pulsed corona	NO <sub>3</sub> <sup>-</sup>	air with water	300 W over water discharge	120	Present - Eindhoven
Pulsed plasma water film	NO <sub>3</sub> <sup>-</sup>	air with water	Atm. Pressure, 1 to 5 W	190	Present - FSU
Haber Bosch	NH <sub>3</sub>	N <sub>2</sub> , CH <sub>4</sub>	High temperature catalysis	4.8 to 9.0	[28]

For comparison, the commercial production of ozone from oxygen, one of the most successful applications of non-thermal plasma in industrial processes, has an energy yield of about 10% of thermodynamic limits, but experimental systems can reach over 60% of the thermodynamic limit[29]. Table 2 summarizes more recent selected work showing the maximum achieved ozone energy yields by various plasma processes. The thermodynamic limit based upon the enthalpy of reaction for ozone generation in dry oxygen is 1220 g/kWh.[30] As shown in Table 2 laboratory studies with nanosecond pulse discharges have achieved the highest energy yields of approximately 60% of the thermodynamic limit (725 g/kWh or 4x10<sup>-6</sup> mole/J).

On the other hand, typical commercial energy yields are 25 to 50 g/kWh and 50 to 70 g/kWh for air and oxygen fed ozonizers, respectively.[27, 30] Kogelschatz and Eliasson note that approximately ½ of the operating costs for ozone synthesis commercially is from the supply of oxygen, and it can also be noted that most sources do not account for the cost of oxygen in reporting ozone energy yields.[30] Fridman discusses earlier literature including studies where the highest yields obtained were for cases of cryogenic cooling of the reactor walls giving energy yields as high as 400 g/kWh; however, the cost of the cooling was not included.[27] It is also useful to note that ozone generated by electrochemical cells in various water electrolytes generally have much lower efficiencies than the plasma processes.

Table 2 Summary of selected ozone generation by various plasma processes.

Gas	Ozone conc. gO <sub>3</sub> /m <sup>3</sup>	Ozone prod. rate gO <sub>3</sub> /h	Ozone yield g/kWh	Discharge type	Ref.
Oxygen	15	0.9	725	Neg. ns pulse 60 kV, 5 pps	[31]
Oxygen	10, 30	0.6, 1.8	570, 400	2 ns pulse, 40 and 50 kV	[32]
Oxygen	5.8	0.7	274	Hybrid silent surface discharge	[33]
Oxygen	16.6	3.5	202	Pulsed DBD	[34]
Oxygen	48	0.9	185	Silent discharge	[35]
Oxygen	61	3.7	173	Packed bed dielectric barrier	[36]
Oxygen	17	0.2	85	Micro-channel arrays of DBD	[37]
Oxygen	10-50	0.2-0.9	120-250	Shielded sliding discharge (+/-)	[38]
Air	4-13	0.07-0.2	75-110	Shielded sliding discharge (-)	[38]
Air			150-300	DC discharge, 50-122 Torr 700-4600 V	[39]
Air	Up to 4		Up to 350	50 Hz, AC	[40]
Air	Up to 18	Up to 1000	Up to 239	ns pulse, 50 kV, 20 pps	[29]
Electrolytes in water			6 to 21	Various electrochemical cells	[41]

In plasma with dry air the oxygen is dissociated through either dissociative attachment or direct electron dissociation (in addition to other electron collision reactions with molecular oxygen). [42]



The Zeldovich mechanism through vibrationally excited nitrogen (generically shown here as N<sub>2</sub>\* and formed by electron collisions with molecular nitrogen) has two steps, the first a limiting endothermic reaction (reaction (8) with ΔH = 291 kcal/gmole or 3 eV/mol) and the second an exothermic reaction.



Key reactions that suppress the formation of NO and thus limit the achievable energy efficiencies are the in-plasma and outside-of-plasma reverse reactions



The latter, reaction (11), occurs strongly at temperatures above 1500 K and the former, reaction (10), combined with the branching reaction



lead to high atomic oxygen in the plasma resulting in high ozone concentrations.[27] Typically ozone does not co-exist with NO [43, 44] due to the rapid reaction (13), but if all NO and NO<sub>2</sub> are converted to further products there may be some ozone. For the production of nitrate the formation of NO<sub>2</sub> in the plasma would be desirable, and ozone and atomic oxygen can further oxidize both NO and NO<sub>2</sub>.



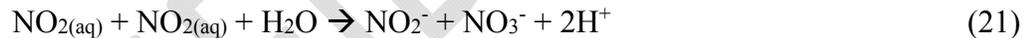
The addition of water vapor leads to the formation of hydroxyl radicals through water dissociation (and other [45]) reactions with electrons.



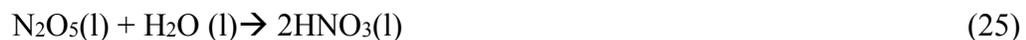
A wide range of reactions with nitrogen oxides and hydroxyl and hydroperoxyl radicals lead to the formation of nitrite and nitrate.



In humid oxygen/nitrogen mixtures reactions 13a and 14a through dissociated oxygen formed by reactions 6 and 7 are perhaps more likely than direct ozone reactions, however the roles of these and the other reactions must be more fully assessed through the combination of experimental and modeling approaches. In the presence of liquid water NO and NO<sub>2</sub> can directly dissolve in water and react by the follow reactions.



A very successful commercially viable approach for removing NO<sub>x</sub> from *combustion gases* uses the ozone reaction pathway (reactions (13) and (14)) where ozone is made in a separate ozone generator fed with pure oxygen and reaction (23) forms N<sub>2</sub>O<sub>5</sub> in the gas phase coupled with a gas-liquid scrubber where reactions (24) and (25) lead to nitrate (see also for this and various other techniques in NO<sub>x</sub> control using plasma, ozone, and absorbents [46-50]).



It was also found that an optimal ratio of NO/NO<sub>2</sub> could lead to nitrite production. To make nitrate from air or nitrogen/oxygen mixtures, rather than from waste gas containing nitrogen oxides, such a process requires a source of NO which is the limiting reaction as discussed above. Our plasma process synthesizes the NO as well as the ultimate nitrate product in one low temperature, atmospheric pressure reactor.

We have found high efficiency for hydrogen peroxide in a water spray plasma reactor [17, 51] and a water film reactor using only argon and water (see figures 1-3)[52], and we have found very good energy efficiency for the formation of nitrate using pure air feed with deionize water sprayed into the same plasma reactors. The highest yield efficiency was found for air at 20 mL/min and corresponds to approximately 39 eV/mol. This reactor uses 1 to 5 W of power under ambient temperature and pressure conditions and the thermal energy input is not sufficient to vaporize or significantly heat the liquid water sprayed into the plasma.[17] Hydrogen peroxide and nitrate have very high Henry's Law constants ( $7.5 \times 10^4$  and  $2.1 \times 10^5$  M/atm) in comparison to NO, NO<sub>2</sub>, N<sub>2</sub>O, OH, and HNO<sub>2</sub> ( $1.9 \times 10^{-3}$ ,  $1.0 \times 10^{-2}$ ,  $2.5 \times 10^{-2}$ , 25, and 49 M/atm) [53], and thus under atmospheric conditions the former two species are rapidly absorbed into the liquid phase; although some H<sub>2</sub>O<sub>2</sub> exists in the gas phase and no HNO<sub>3</sub> is expected in the gas phase all the other species remain in the gas. This commonality in high water solubility for nitrate and hydrogen peroxide suggest a common reason for the high efficiencies of nitrate formation and hydrogen peroxide with the water film reactor.

For combustion gas treatment containing NO in the feed, Mok et al. [54] and Hu et al. [55] found decreases in NO conversion with increasing water vapor. Mok found that increasing H<sub>2</sub>O decreases the production of ozone by  $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ , and that in this reactor ozone generally causes NO oxidation by reaction (13). He also found that the energy delivered by the pulsed corona decreases with increasing water and this result is consistent to that of Hu et al. [55] (both groups used pulsed corona wire cylinder type discharges). In our discharge, because of the high water content we may have sufficient OH radicals so that the reaction of NO with OH predominates over the ozone pathway. Yin et al [56] found in dielectric barrier discharge (DBD) that there was no effect of H<sub>2</sub>O on discharge power but there was a reduced NO conversion in the N<sub>2</sub>/NO/H<sub>2</sub>O plasma with up to 2% water vapor; however, the simultaneous effects of oxygen were not reported. This reduced conversion of NO with the addition of water is also consistent with reported *increased* NO production in an inductively coupled radio frequency (ICRF) plasma by reaction (28) [57]



Such increases in NO are not desirable in many of the applications for NO<sub>x</sub> removal by plasma in pollution control; however, in our system we are interested in producing NO *and* converting the formed NO into nitrates in one reactor. Reaction (28) could provide significant enhancement of NO formation by the N formed in reaction (8) and (15). Thus, we believe that the literature and our work suggests that the addition of sufficient water through the liquid film can enhance both the formation of NO and the conversion of NO into nitrate.

Yan et al [58] found that gas phase water concentrations over 10% enhance NO removal in N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O/NO mixtures and suggested that reactions (17) and (19) with OH radicals and further reactions (22) and (25) through N<sub>2</sub>O<sub>5</sub> can be enhanced in the presence of liquid water which absorbs the reaction products. It is possible that the production of N<sub>2</sub>O from



may also be suppressed in our reactor due to rapid conversion of NO<sub>2</sub> by OH radicals.

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