Nitrogen Fixation as NOx Using **Air Plasmas** Coupled with Heterogeneous Catalysis

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Outline

- Introduction
- Air plasma for NF: insights from reducing Energy Cost
- Air plasma coupled with heterogeneous catalysis
- Concluding remarks
Introduction: Nitrogen Fixation (NF)

$$\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$$

Biological nitrogen fixation

31% 60m tN

Free-living diazotrophs

Symbiotic diazotrophs

Nitrogenase

$$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$$

1909 Haber-Bosch process

Germany

Nobel Prize Chemistry 1918

POPULATION OF THE EARTH

Number of people living worldwide since 1700 in billions

Introduction: Challenges

- **Energy-intensive**: Reliance on fossil fuels.

- **Huge quantity of H$_2$**: 5% natural gas.

- **Environmental issue**: 0.4 billion-ton CO2/year. \[8\text{NH}_3 \rightarrow 3\text{CO}_2\]

- **Efficiency confined**: 30 GJ/tN $\rightarrow$ 24 GJ/tN.
Introduction: Solutions

A. Nitrogenase

B. Catalysts

C. Plasma ✅

D. Electrocatalysis

Introduction:  N2 — Applied

- Renewable
- Air + Water  Green
- Small scale
Introduction: Birkeland-Eyde process

1903 Birkeland-Eyde process
1906 Notodden Manufactory

N₂ + O₂ → 2NO
NO + 1/2 O₂ → NO₂
2NO₂ + H₂O → HNO₂ + HNO₃
CaCO₃ + 2HNO₃ → Ca(NO₃)₂ + H₂O + CO₂
Ca(NO₃)₂ ‘Norwegian saltpeter’ N fertilizer

Electron
Plasma

Kristian Birkeland (1867-1917)
J. J. Thomson
I. Langmuir

1897 1903 1928

Haber-Bosch; NH₃

1918

Modern Haber-Bosch with steam reforming natural gas

Electric arc; Ca(NO₃)₂ → 250 GJ/tN

1906

Haber-Bosch; NH₃ → 120 GJ/tN

Progress of energy cost for NF

Introduction: Birkeland-Eyde process

In an alternating current (see Fig. 2), all the arcs with a positive direction of current run one way, while all with a negative direction run the opposite way, presupposing the magnetising being effected by direct currents. In this way, a complete, luminous, circular disc is presented to the eye.

Introduction: Nitrogen Fixation in Plasma

Plasma-enabled reaction pathways and historical fertilizer plant
**Introduction: Overview of NO production**

**Y. B. Zeldovich 1947**

\[
\begin{align*}
O + N_2 & \rightarrow NO + N & E_a \approx 3.27 \text{ eV/molecule} \\
N + O_2 & \rightarrow NO + O & E_a \approx 0.3 \text{ eV/molecule} \\
N_2 + O_2 & \rightarrow 2NO & \text{Combustion}
\end{align*}
\]

**A. Fridman, Plasma Chemistry, 2008**

6.1.1. Fundamental and Applied Aspects of NO Synthesis in Air Plasma

The synthesis of nitrogen oxides in air plasma is one of the "old timers" in plasma technology. This endothermic plasma-chemical process is usually presented simply as

\[
\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO, \quad \Delta H \approx 1 \text{ eV/mol.} \tag{6-1}
\]

Henry Cavendish and Joseph Priestly were the first scientists who investigated this process, in the eighteenth century. Industrial implementation of the plasma technology was performed in 1900 by Kristian Birkeland and Samuel Eyde. Birkeland and Eyde developed

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**How to make the plasma process more economical?**

1 atm Air  
Low Energy Cost
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Experimental Setup

Typical FTIR spectrum

Specific energy cost calculation

Calculation of energy cost of plasma nitrogen fixation

\[ E_{Nr} = \frac{P_{\text{dis}} \times t}{V \times \frac{1}{24 \text{ L/mol}}} \times c_{NOx} \times 10^{-6} \times 14 \text{ g/mol} \times 10^{-3} \]

- \(E_{Nr}\) is energy expended per unit of \textbf{reactive N}_r \quad (\text{GJ/tN}) \quad \text{MJ/mol} \quad \text{kWh/kg}
- \(P_{\text{dis}}\) is the \textbf{plasma power consumption} \quad (\text{W}) \quad \text{(only for plasma)}
- \(V\) is the volume of chamber \quad (\text{L}) \quad \text{or gas flow into the chamber}
- \(c_{NOx}\) is the concentration of \textbf{NO}_x \quad (\text{ppm})
Results: DBD (Surface Micro-discharge)

- **Surface Micro-discharge**: Copper, Polytef, Quartz, Metal mesh, CaF₂

- **Plasma**: AC, FTIR

- **Charge (nC)**: -6000 to 6000

- **Voltage (V)**: -8.79 W

- **Power Density vs Time**

- **NOₓ mode**

- **Transition region**

- **O₃ mode**

- **NOₓ species (NO₂, NO and HONO)**

- **GJ/tN**: gigajoules cost per metric ton N produced

- **Pavlovich, M. J., et al. (2014). PSST 23 065036.**
Results: DC glow discharge

- Constant $I_{dis}$ and $V_{dis}$
- High gas temperature $\sim 1800$ K

- Decreases with increasing current (15-45mA)
- Lower energy cost at larger gap distance (2-8mm)
Results: ns pulse spark discharge

After breakdown, $V_{\text{dis}}$ drop quickly, $I_{\text{dis}}$ increase to a high value $\sim 20\text{A}$

Most power dissipated during breakdown period

When voltage across gap drops to $\ll 1\text{kV}$, power decreases, but $\text{NO}_x$ production continues with high current ($\sim 20\text{A}$)

Eagle Harbor Technologies (EHT)
Results: ns pulse spark discharge

- **1kHz, 5mm**
  - 12kV
  - 16kV
  - 20kV
- **1kHz, 20kV**
  - 2mm
  - 5mm
  - 8mm

<table>
<thead>
<tr>
<th>Pulse Width (ns)</th>
<th>100</th>
<th>180</th>
<th>260</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Consumption (W)</td>
<td>4</td>
<td>4.72</td>
<td>4.92</td>
</tr>
<tr>
<td>NOx production rate (ppm/s)</td>
<td>10.75</td>
<td>15.72</td>
<td>18.20</td>
</tr>
<tr>
<td>Energy Cost (GJ/tN)</td>
<td>638</td>
<td>514</td>
<td>463</td>
</tr>
</tbody>
</table>

Most efficient; high $I_{dis}$, low $V_{dis}$

$NO_x$ continues
Results: The Propeller Arc

Rotating cathode, driven by a motor, fixed anodes

Propeller Arc (PA)

- No need forced gas flow
- Low breakdown voltage
- Easy to control, f, L, P
- Simple structure, stable

Gliding Arc

Results: The Propeller Arc

Single electrode

4 electrodes

$f_{\text{dis}} = 15 \text{ Hz}$
Results: **The Propeller Arc**

Large scale PA

Z. Li, J. Liu, X. Lu, Plasma Sources Sci. Technol. 29, 045015
Results: PA energy cost

- Power increases almost linearly with $I_{\text{dis peak}}$.
- Decreases drastically with increasing $I_{\text{dis peak}}$, tends to a saturation value $\sim 250 \text{ GJ/tN}$.

- Energy cost for air is only 13% higher than the lowest value.
Results: PA energy cost

- Specific energy cost (GJ/tN) at different discharge regions
Results: Average electric fields

<table>
<thead>
<tr>
<th>Discharge</th>
<th>Energy cost (GJ/tN)</th>
<th>Gas T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBD</td>
<td>4000-10000</td>
<td>~400</td>
</tr>
<tr>
<td>Glow</td>
<td>500-1000</td>
<td>~1800</td>
</tr>
<tr>
<td>Spark</td>
<td>350-900</td>
<td>~600</td>
</tr>
<tr>
<td>PA</td>
<td>250-1500</td>
<td>~1500</td>
</tr>
</tbody>
</table>

- DBD appears to not be suitable for NO\textsubscript{x} production from the view point of energy cost.

\[
\bar{E} = \int_{t_{bre}}^{\tau} \frac{V_{dis}(t)}{d} dt
\]
Results: The $\chi$ factor

\[ \chi = \frac{\bar{E} \times \bar{T}}{E_r \times T_r} \]

Reference condition

DC glow: 5mm, 45mA, 2slm

\[ E_r = 1.43 \text{ kV/cm} \]

\[ T_r = 1800 \text{ K} \]

Remarkably, there is an almost linear relationship between $\chi$ and energy cost for NO$_x$ production.

$\chi$ factor correlates with the energy cost for strikingly different types of discharges.

Reducing $\chi$ factor, while sustaining the discharge, can be a guiding principle for reducing the energy cost of NO$_x$ production.

Bogaerts et al. (2020)

Wang et al. (1998)
Adamovich et al. (2000)
Namihira et al. (2002)
Korolev et al. (2012)
Kolb et al. (2014)
Janca et al. (2016)
Pati et al. (2016)
Bogaerts et al. (2017)


Vervloesem, E., et al. (2020) ACS Sustainable Chem. Eng 8, 9711–9720 (Gliding Arc Plasmatron)
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Reduce energy cost by coupling with heterogeneous catalysis

Packed DBD plasma reactor

- Gas temperature is low (<~1000 K)
- Easy to combine with catalyst
- Wouldn’t destroy catalyst

~4600 GJ/tN (DBD+catalyst) ~2200 GJ/tN

‘warm’ plasma + catalyst

>~1500 K
~200 GJ/tN

Air plasma combined catalyst for NF

Experiment parameters

- **Current**: 15mA to 75mA;
- **d**: 2mm to 80mm;
- **Flow**: 1L/min to 15L/min
- **Catalyst**: Activated Al$_2$O$_3$
  75 microns, 0.2g

Influence of catalyst

\[ O + N_2 \rightarrow NO + N \]

\[ N_2(v) \quad N_2(E) \]
Influence of catalyst

\[ N_{\text{vib}}, \text{Relative population} \]

100 Torr

\[ \text{time, sec} \]

\[ N_2(\nu) \quad N_2(E) \quad ? \]

\[ N_2(E) + O \rightarrow \text{NO + N} \]

\[ \text{Diffusion time} > 1 \text{ ms} \]

**Figure 7.** Experimental (symbols) and predicted (curves) \( N_2 \) vibrational level populations during the discharge pulse and in the afterglow in nitrogen (a) and in air (b).
Plasma jet coupled with catalyst

Complex process
- $e^-$, $E$, Ions …
- $N_2^*$, $N$
- High $T_g$

$N_2^*$: $N_2$($A$),$N_2$($B$)...

Neutral species
- $N_2^*$, $N$

$N_2^*$ + $O_2$ => $N_2$ + $O$ + O
$N_2^*$ + $O$ => NO + N ...

Shielding gas

Small quantities of $O_2$
Air plasma jet coupled with catalyst

- $n_{N_2^*}$ too low?
- No catalytic effect

Influence of N₂/O₂ ratio

Extremely high N₂ content

0.8% O₂

1.6% O₂

Air

Energy cost (GJ/tN) vs. Iₐₙ (mA)

- 5slm-0.8%O₂ in N₂-free jet
- 5slm-0.8%O₂ in N₂ + Q wool
- 5slm-0.8%O₂ in N₂ + Q wool + Al₂O₃
- 5slm-0.8%O₂ in N₂ + Q wool + Al₂O₃ + heating

- 5slm-1.6%O₂ in N₂-free jet
- 5slm-1.6%O₂ in N₂ + Q wool
- 5slm-1.6%O₂ in N₂ + Q wool + Al₂O₃
- 5slm-1.6%O₂ in N₂ + Q wool + Al₂O₃ + heating

NOₓ/Time (µmol/min) vs. O₂/(N₂+O₂)

- Plasma jet
- On Al₂O₃

Influence of N₂/O₂ ratio

Extremely high N₂ content
Fluidized catalyst + Magnet to stabilize

Concluding remarks

- $\chi$ factor appears to serve as a simple, effective means of correlating NO$_x$ production energy cost across a broad range of discharges, but still poorly understood its physical and chemical mechanisms;

- ‘Warm’ plasma combined with catalyst can reduce the energy cost;

- ‘Fluidized’ catalyst improves the energy efficiency for NOx formation significantly in the air plasma jet system, more work need to do.

- Lowest energy cost for NO$_x$ production in our air plasma system: 210 GJ/tN. (2.9 MJ/mol)
Acknowledgements

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N2 Applied
Thank you for listening!

Plasma

$N_2$ $N_r$