Nitrogen Removal and Energy Recovery Through N_2O Decomposition

Yaniv Scherson, Brian Cantwell, Craig Criddle
Aeronautics and Astronautics , Civil and Environmental Engineering, Stanford University

Background

With **a global warming potential (GWP) 310 times greater than CO_2** [1], N_2O is a powerful greenhouse gas (GHG) that accounts for approximately 5.3% of total U.S. GHG emissions[2] and approximately 8% of total GHG emissions[1] worldwide. Human alteration of the nitrogen cycle via the Haber process, intensive crop cultivation, and fossil fuel use has approximately **doubled the rate of nitrogen input to the terrestrial nitrogen cycle**[3]. Loss of anthropogenic nitrogen to natural systems has led to an array of environmental and public health problems, including ammonia toxicity to aquatic life, eutrophication of nutrient limited natural water bodies, oxygen depletion, and vast dead zones in the ocean margins.

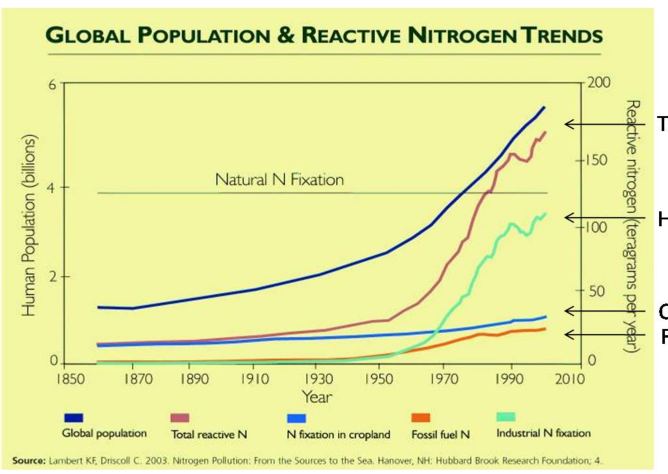
While N_2O is commonly considered as a greenhouse gas, it is often overlooked as a **clean source of energy**. N_2O is an energetic nitrogen compound that releases heat when decomposed catalytically or combusted with a fuel such as methane. In fact, N_2O is a more powerful oxidant that oxygen and releases an additional 329 kJ/mol when combusted with methane.

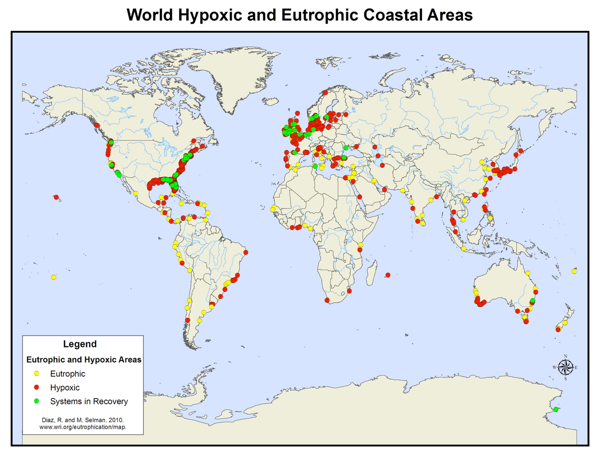
$$N_2O \rightarrow \tfrac{1}{2}O_2 + N_2 \qquad \Delta H^\circ_R = -82\ \text{kJ/mol}$$

$$CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O + 4N_2 \qquad \Delta H^\circ_R = -1{,}219\ \text{kJ/mol}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^\circ_R = -890\ \text{kJ/mol}$$

The Threat to the Nitrogen Cycle





CANDO

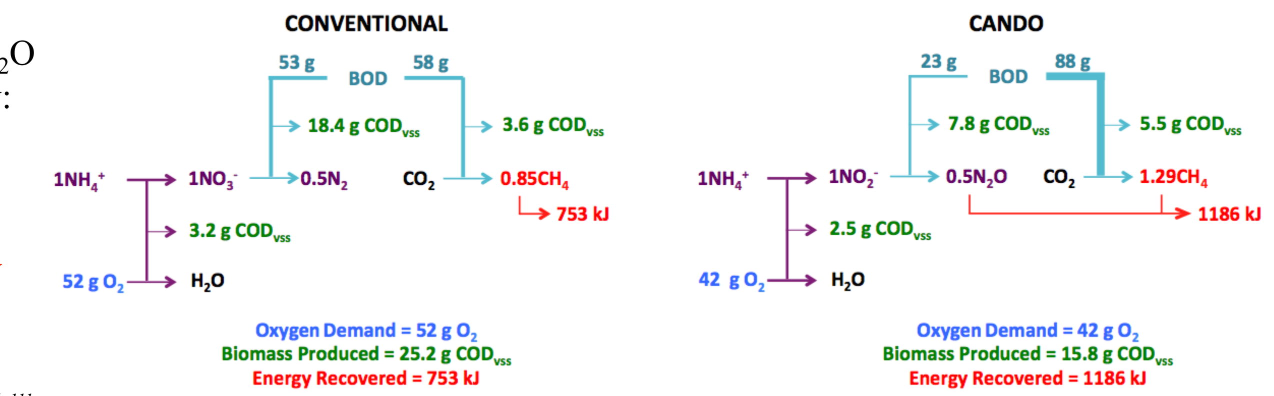
The Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO) converts the most common form of reactive nitrogen, Ammonium (NH_4^+) into gaseous nitrogen while simultaneously generating power and potentially recovering phosphorus. CANDO involves 3 principal steps: (1) biotic conversion of ammonia to nitrite, (2) abiotic/biotic conversion of nitrite to nitrous oxide, (3) decomposition or combustion of nitrous oxide to nitrogen, oxygen, and energy.

Partial oxidation of ammonia to nitrite and N_2O decomposition/combustion are well-established processes. The focus of this work is the yet unproven step of efficient conversion of nitrite to nitrous oxide. Two "partial-denitrifying" strategies are presented involving an abiotic reaction of ferrous iron and nitrite to form nitrous oxide and a biotic pathway utilizing heterotrophic denitrifying organisms.

Conventional N-Treatment vs. CANDO

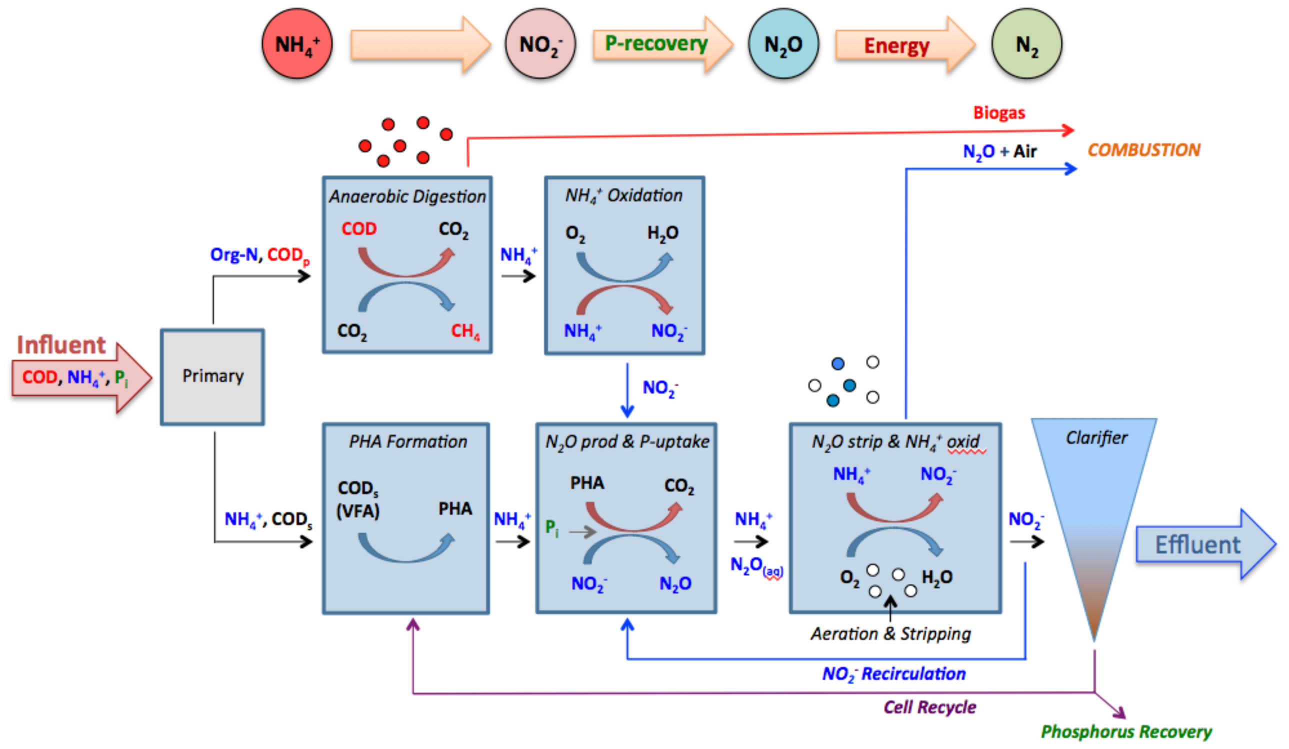
As compared to conventional treatment, nitrogen treatment via N_2O offers a potential for approximately:

- 20% savings in O_2 demand
- 40% reduction in biomass
- 60% increase in energy recovery



Note: Analysis assumes complete treatment of 1 mole of ammonia with 111 grams of available BOD_L (typical of U.S. medium strength wastewater)

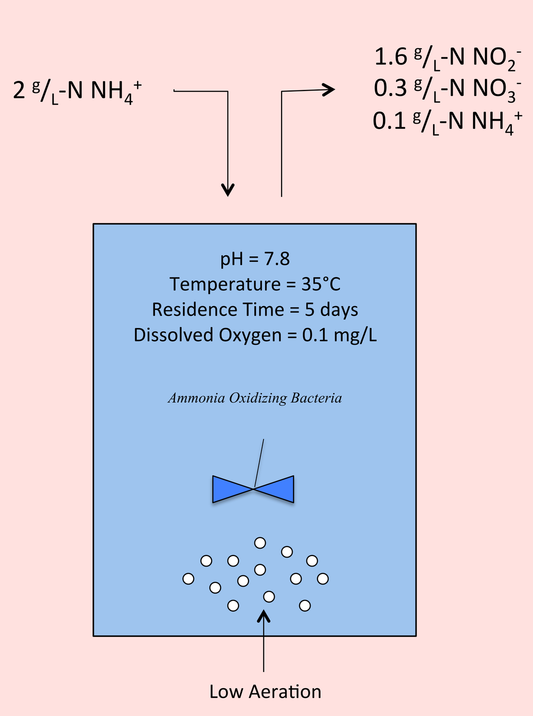
Potential CANDO System Diagram



Successful Lab-Scale Demonstration of CANDO

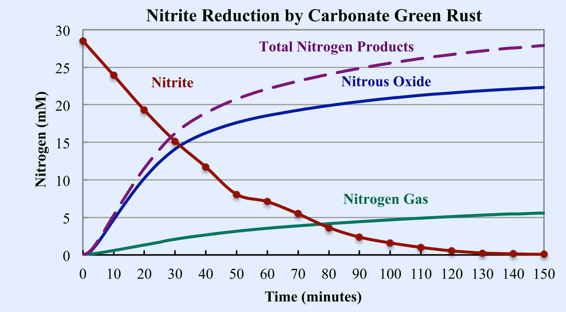
$NH_4^+ \rightarrow NO_2^-$	$NO_2^- \rightarrow N_2O$	$N_2O \rightarrow N_2$ + Energy

≈ 80% Conversion Ammonia to Nitrite

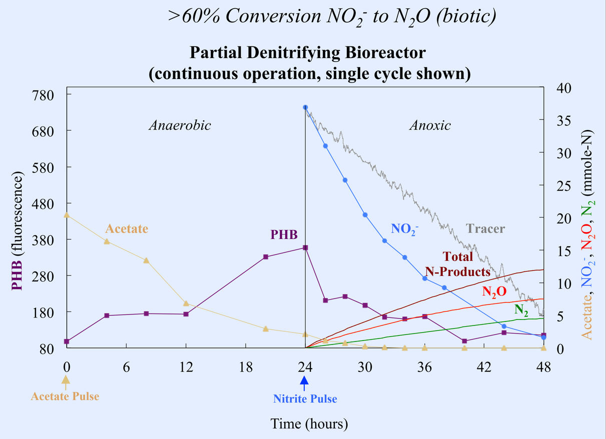


Operation of Nitritation Bioreactor

>90% Conversion NO_2^- to N_2O (abiotic)

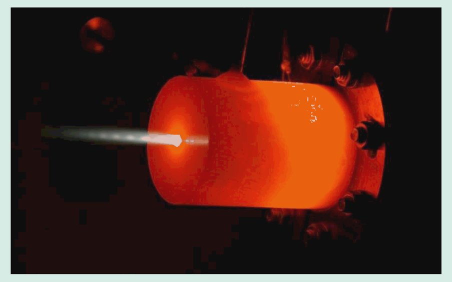


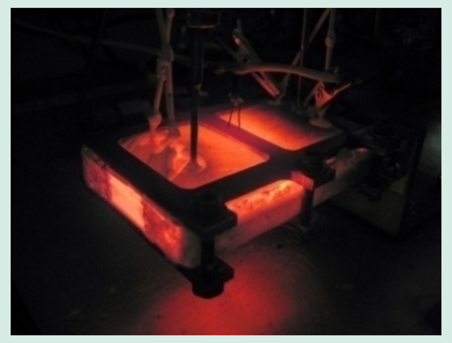
>60% Conversion NO_2^- to N_2O (biotic)



Partial Denitrification (abiotic & biotic)

Complete Decomposition of Nitrous Oxide





N_2O Decomposition Devices

Benefits of CANDO

For wastewater treatment, CANDO offers the following potential benefits as compared to conventional nitrification/denitrification of waste nitrogen:

Methane
- Increased CH_4 production.
- Approximately 60% increase in energy recovery.

Oxygen
- Reduce O_2 requirement by at least 20%.
- Aeration is highest operational cost for WWT (≈50%).

Biomass
- At least 40% decrease waste biomass.
- Biomass disposal is 2nd greatest operational cost for WWT.

Robustness
- Resistant to upsets.
- Fast kinetics, low capital cost.

Nitrogen
- Direct energy generation from waste nitrogen.
- Eliminates the release of nitrous oxide.

Phosphorus
- Potential for phosphorus recovery through anoxic PHB oxidation.

How Does CANDO Compare?

	Conventional N-Removal	State-of-Art CANON	CANDO
GHG Emissions	[red]	[green]	[green]
Energy Production	[red]	[yellow]	[green]
Aeration Cost	[red]	[green]	[yellow]
Biomass Production	[red]	[green]	[green]
Operational Complexity	[green]	[red]	[yellow]
Startup Time	[green]	[red]	[green]
Reactor Footprint	[red]	[yellow]	[green]

Legend	Worst	Neutral	Better

Summary

Nitrogen removal and energy recovery via N_2O presents a potential alternative in the treatment of waste nitrogen. Nitrogen treatment through N_2O may improve the efficiency of wastewater treatment by lowering oxygen demand, reducing biomass production, and increasing energy recovery from organic matter and reactive nitrogen. CANDO is still in preliminary development and the true benefits at practical scale remain unclear. CANDO will be tested next at the pilot-scale.

CANDO is patented through Stanford University (Pub. No. US 2011/0207061).

Acknowledgments

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[1] US-EPA. Global Anthropogenic Non-CO_2 Greenhouse Gas Emissions: 1990-2020. Office of Atmospheric Programs, Climate Change Division. Washington, DC. 2006.
[2] Energy Information Administration. Emissions of Greenhouse Gases in the United States 2007. DOE/EIA-0573(2007). Washington, DC. 2008.
[3] Fields, S. Global Nitrogen: Cycling out of Control. *Environ. Health Perspect.* 112, A557 (2004).

Further Information

Feel free to direct questions and/or comments to Yaniv Scherson at yaniv@stanford.edu