

Innovation in Chemical Manufacturing: Low-Temperature Solutions for Energy Efficiency and Emissions Reduction

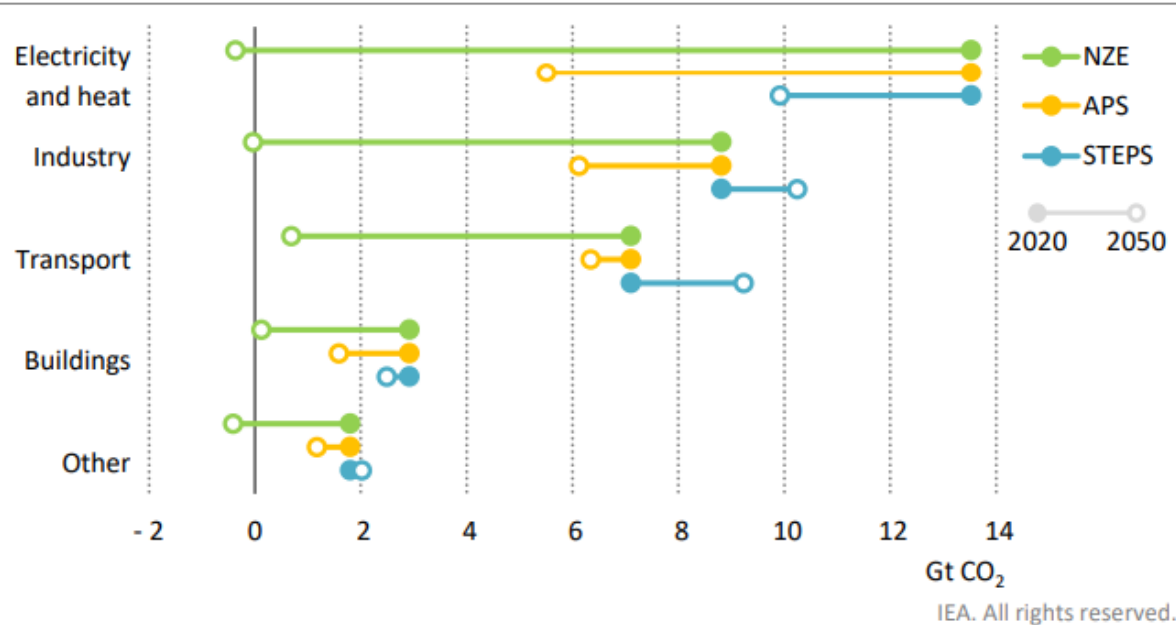
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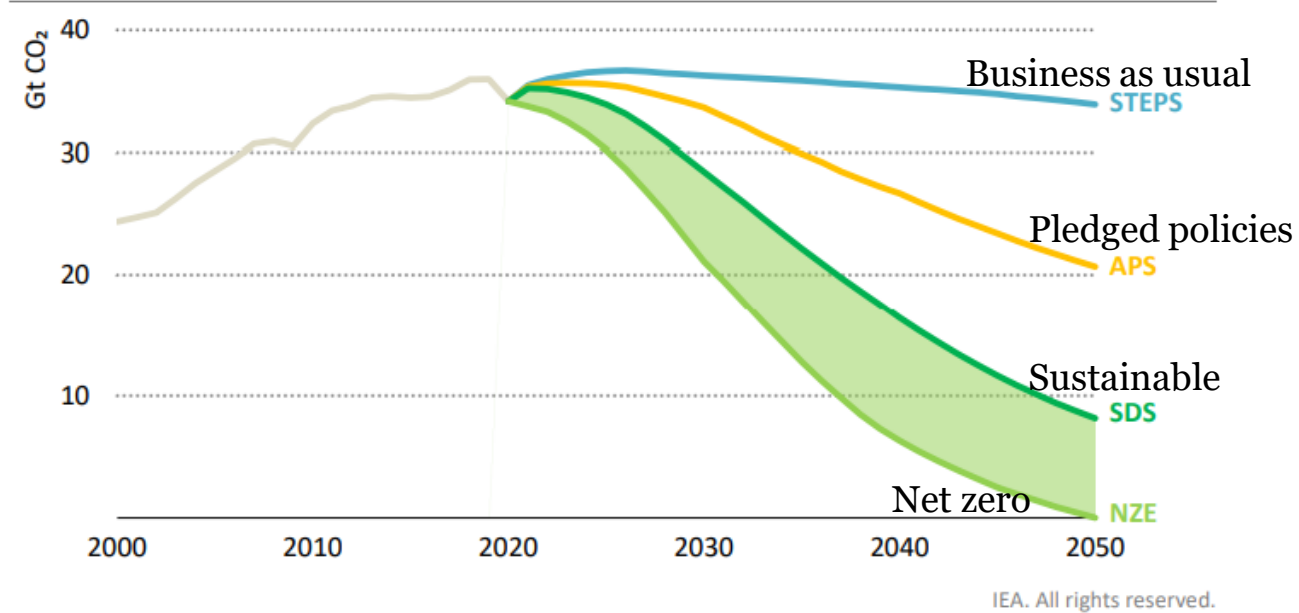
The need for a sustainable chemical industry: Current energy consumption and GHG emissions

Figure 1.1 ▶ CO₂ emissions by sector and scenario



Clean electricity can do a lot of the heavy lifting, but it is harder to bend the emissions curve in industry and transport

Figure 1.4 ▶ CO₂ emissions in the WEO-2021 scenarios over time



The APS pushes emissions down, but not until after 2030; the SDS goes further and faster to be aligned with the Paris Agreement; the NZE delivers net zero emissions by 2050

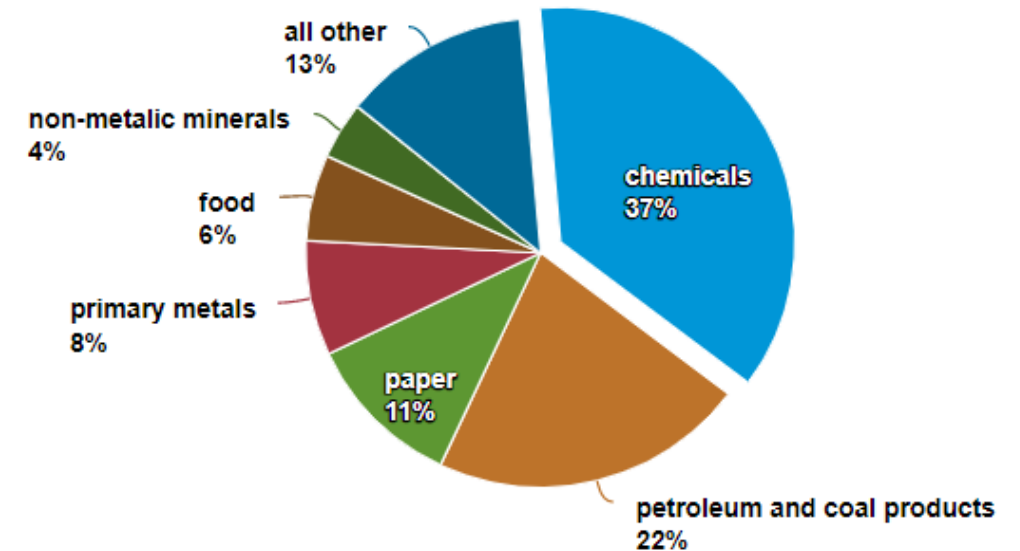
Note: APS = Announced Pledges Scenario; SDS = Sustainable Development Scenario; NZE = Net Zero Emissions by 2050 Scenario. STEPS: Stated Policies Scenario (today's policies)

“There is no guarantee that the emergence of this new energy economy will be smooth, and it is not coming forward quickly enough to avoid severe impacts from a changing climate.”

Chemical industry has the largest energy consumption of U.S. manufacturing sector

Manufacturing energy consumption by subsector and type of energy in 2018 (trillion British thermal units)

Subsector	Fuel	Nonfuel	Total
Chemicals	2,815	4,326	7,141
Petroleum and coal products	3,342	903	4,245
Paper	2,488	3	2,491
Primary metals	1,734	307	2,041
Food	1,511		1,511
Nonmetallic minerals	1,161		1,161
All others	247	599	846
Total	13,298	6,138	19,436



U.S. Manufacturing consumption by major types of manufacturers, 2018. Total=19.44 quadrillion BTU

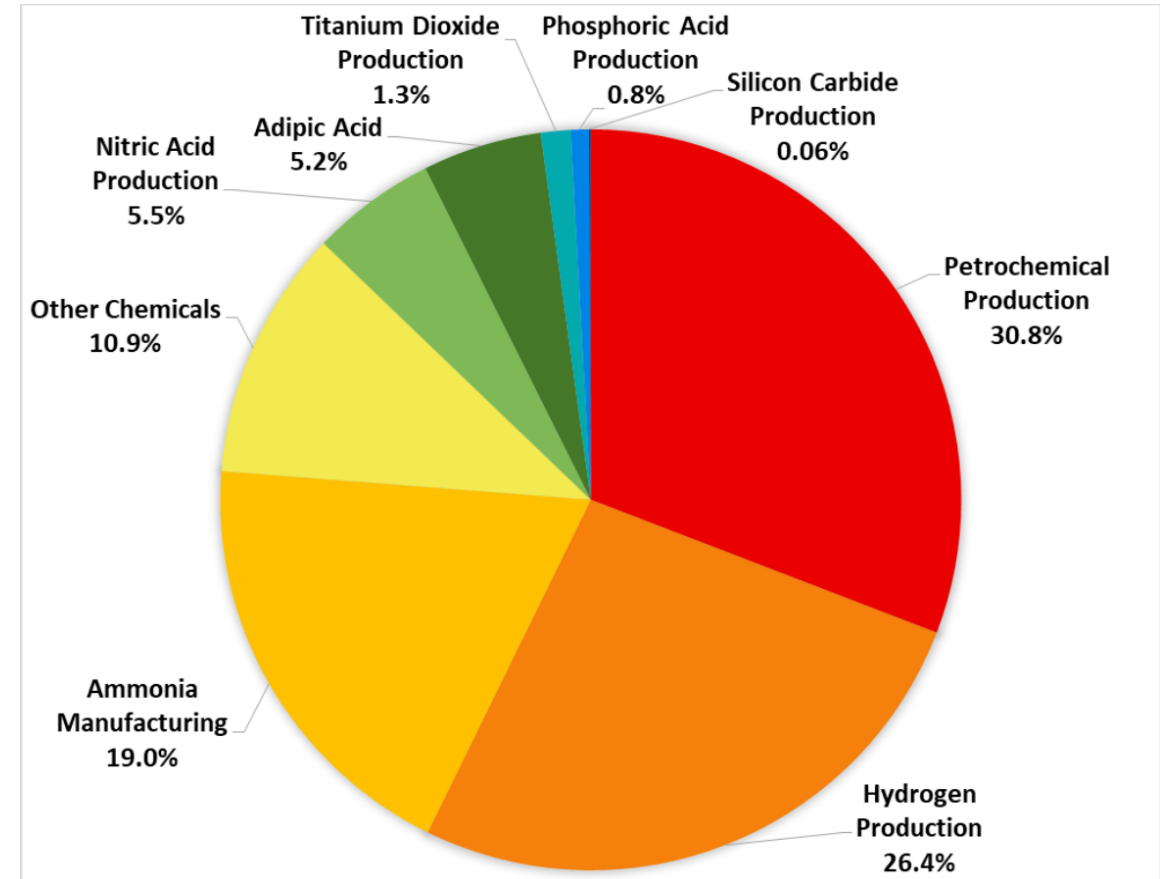
If we were to cut energy consumption in the chemical industry by 50%

- We'll save the equivalent of 31 billion gallon of gasoline/year
- Avoid emission of 262 MT/year of CO₂
- Equivalent to taking 60 million cars off the road!

- ! Assuming 22 miles/gallon and 11,500 miles/year

Hydrogen and ammonia production combined have the largest GHG emissions of the chemical industry

Nitrogen fixation products manufacturing emit as much GHG as hydrogen production



Greenhouse Gas Reporting Program Industrial Profile: Chemicals Sector (Non-Fluorinated), EPA September 2019

Problem: Hydrogen and other chemicals production through thermo-catalysis

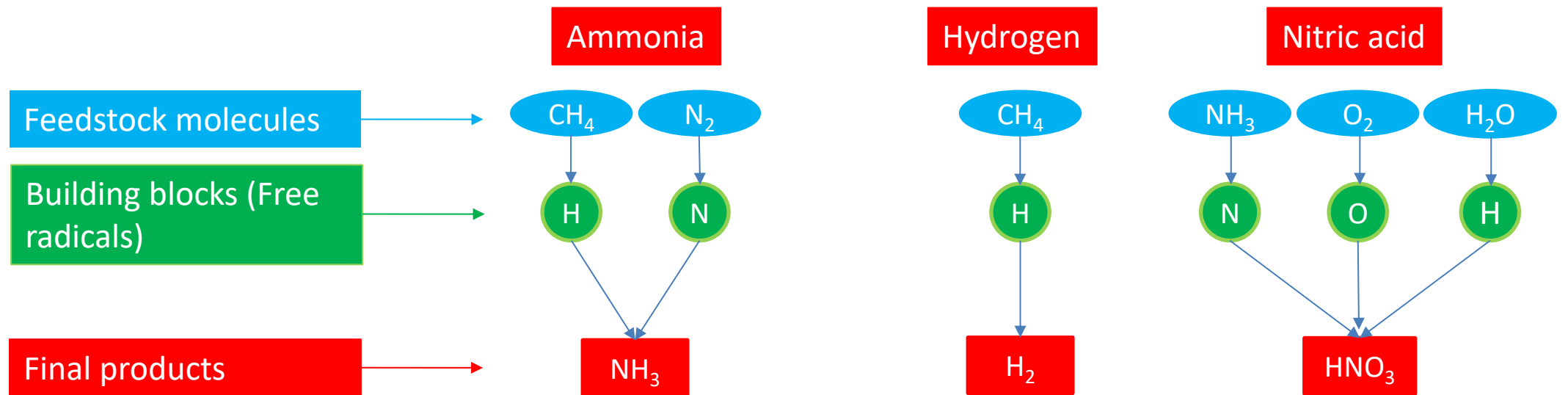
- Mostly thermo catalysis:
 - Methane Steam Reforming (Hydrogen from methane)
 - Claus (Sulfur from hydrogen sulfide)
 - Haber-Bosch (ammonia from nitrogen and methane)
 - Ostwald (nitric acid from ammonia and air)
 - Many others
- Limitations:
 - Energy intensive
 - Very large scale
 - Very large GHG emissions



Thermo-catalysis uses heat to reach the dissociation energy of molecules. Most of the energy consumed is wasted in heat losses

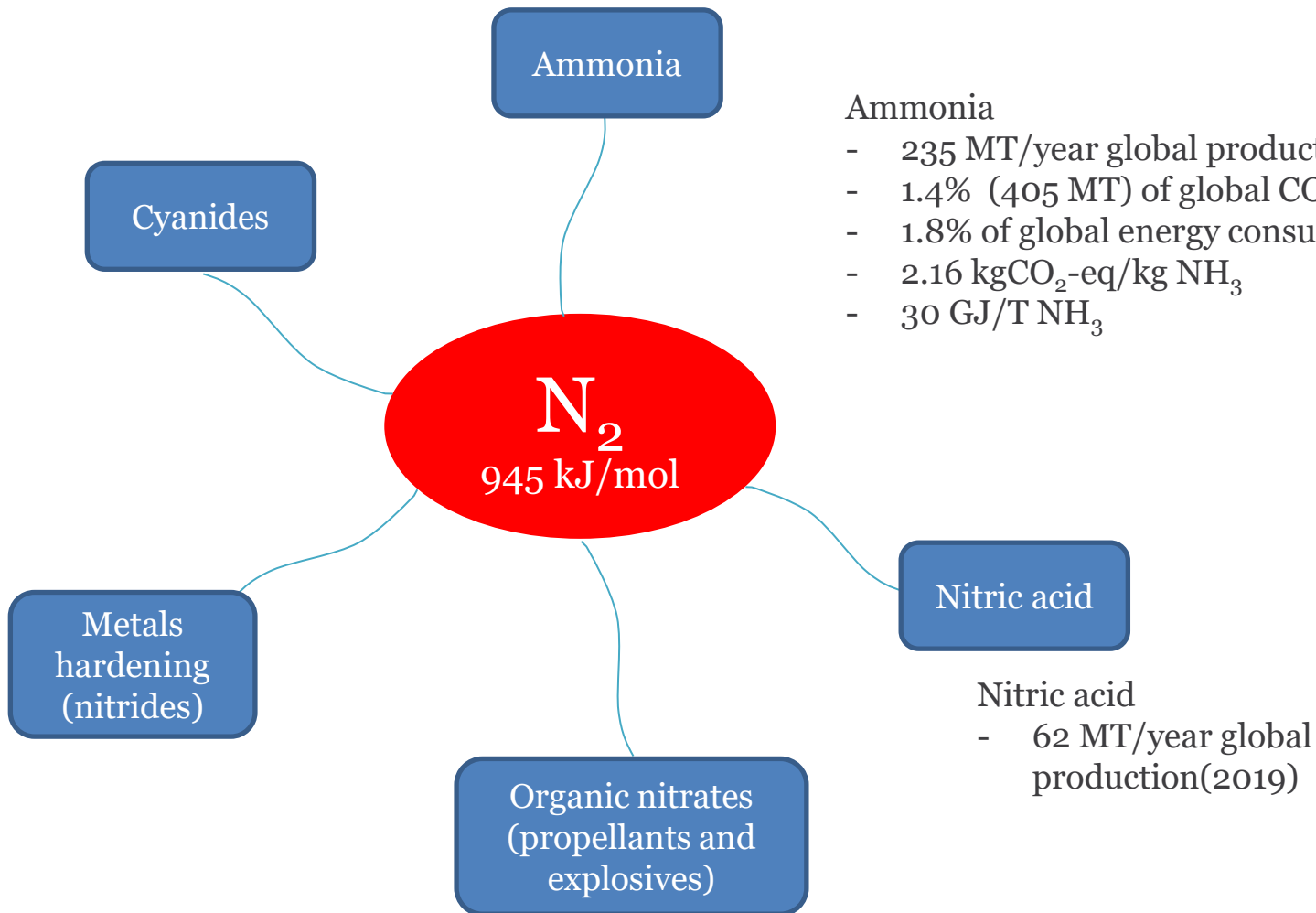
How are these chemicals made?

- Chemical products are made from building blocks (free radicals) that derive from other molecules.



There is a need for producing the building blocks of chemicals at lower energy consumption and lower GHG emissions

Nitrogen



That is the min energy needed when performing thermal dissociation.

Table 1. Bond Dissociation Energies,⁴¹ Energies of Relevant Vibrationally⁴² and First Electronically Excited States,^{42,43} Ionization Energies,⁴¹ and Electron Impact Dissociation Energy Thresholds^{42,44} of N₂, CH₄, and CO₂, All in eV^a

molecule	<i>E</i> _{diss}	<i>E</i> _{vib}	<i>E</i> _{elect}	<i>E</i> _{ion}	<i>E</i> _{diss} ^{e-impact}
N ₂	9.8	0.29 (σ_g^+)	6.2 ($^3\Sigma_u^+$)	15.6	13.0
CH ₄	4.5	0.37 (<i>t</i> ₂)	8.8 (3T_2)	13.0	9.0
CO ₂	5.5	0.29 (σ_u^+)	7.0 (1B_2)	13.8	11.5

Bond dissociation energy is one of the highest.

Methane

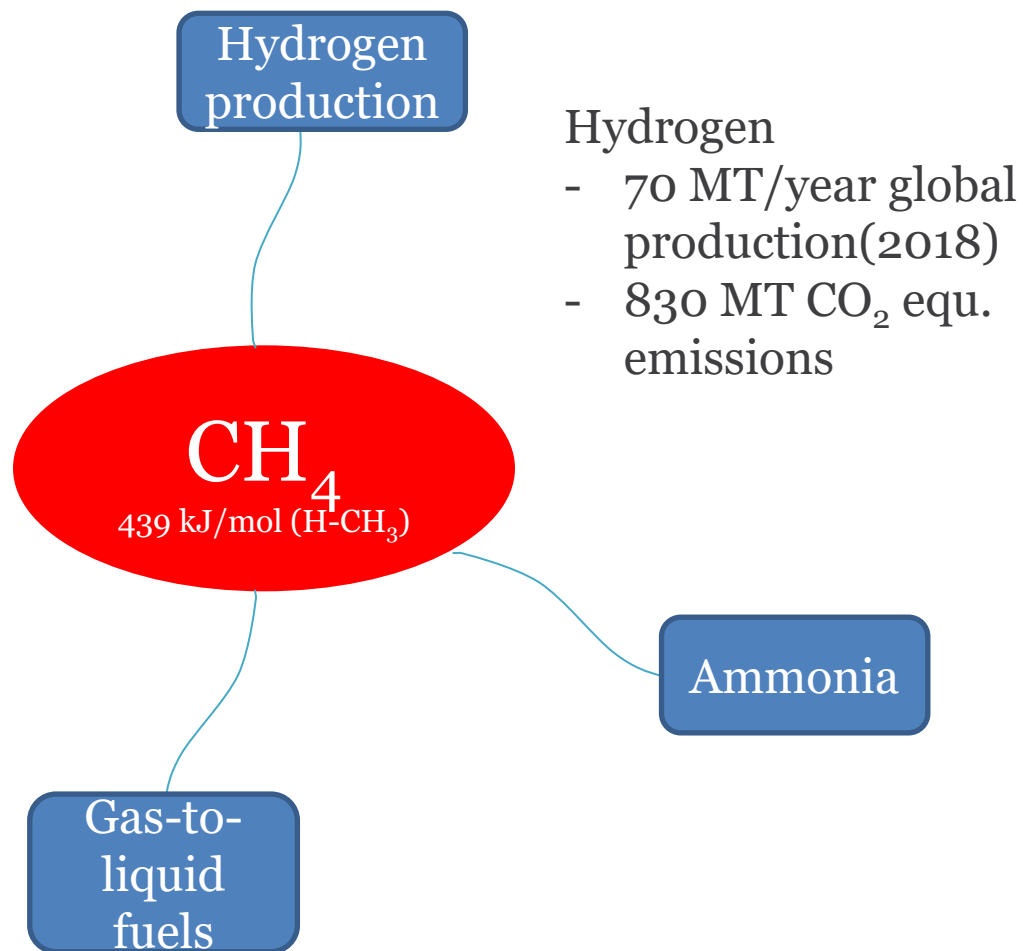


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molecule	E_{diss}	E_{vib}	E_{elect}	E_{ion}	$E_{\text{e-impact}}^{\text{diss}}$
N ₂	9.8	0.29 (σ_g^+)	6.2 ($^3\Sigma_u^+$)	15.6	13.0
CH ₄	4.5	0.37 (t_2)	8.8 (3T_2)	13.0	9.0
CO ₂	5.5	0.29 (σ_u^+)	7.0 (1B_2)	13.8	11.5

Methane-based Haber-Bosch (H-B) process is the most efficient one today for Ammonia production

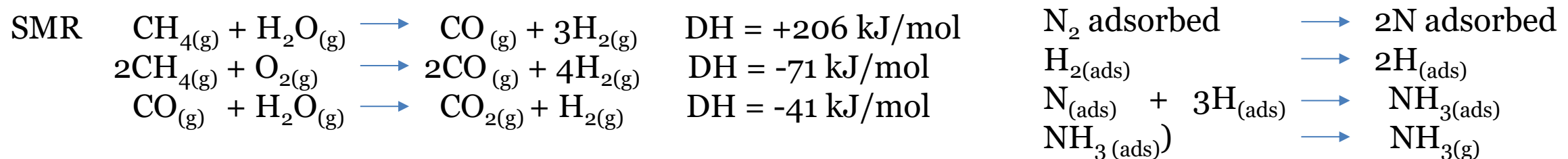
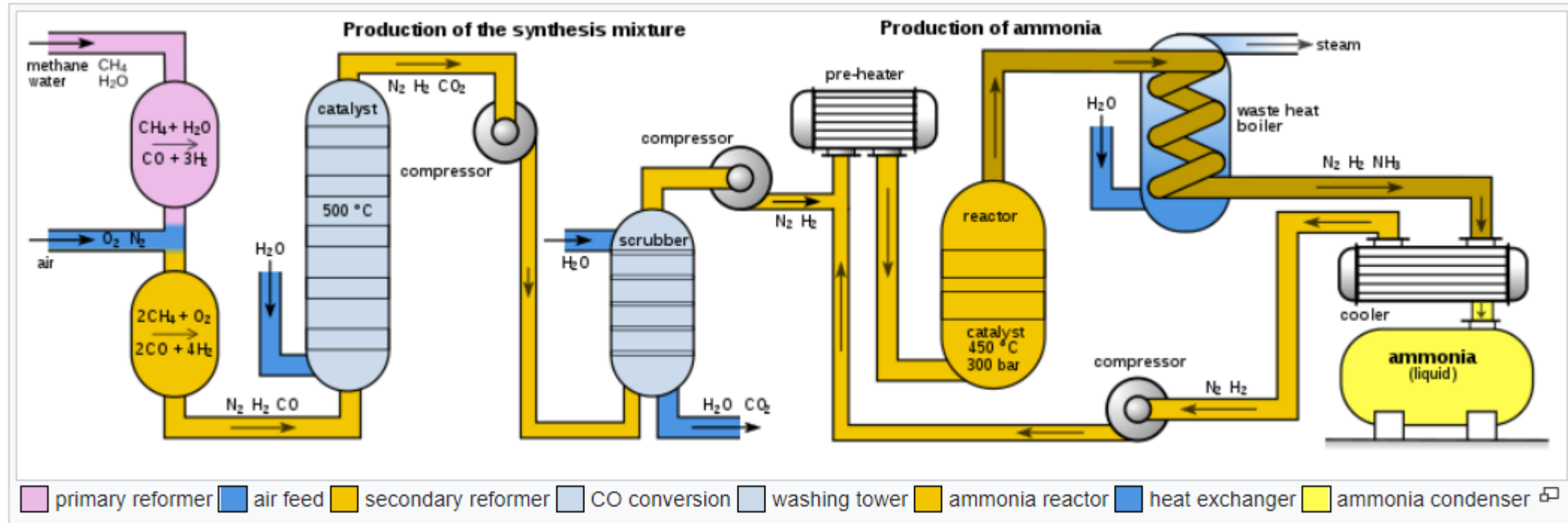


- Catalytic reaction at 150–350 atm., and 450-600 °C
- Equilibrium favors the formation of NH_3 at low temp., but high temp is required to achieve a higher rate of NH_3 formation
- Breaking the N_2 triple bond is rate-limiting
- Iron containing iron oxide, MgO on Al_2O_3 and ruthenium on carbon have been employed as catalysts

CH_4/HB energy consump. MJ/mol	Electro/HB energy consump. MJ/mol	NH_3 energy content MJ/mol	Energy wasted in CH_4/HB MJ/mol
0.48 – 0.6	1.5	0.32	Up to 0.28

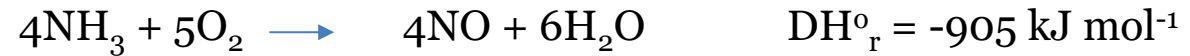
Methane-based H-B is 3x less energy intensive than electro-based H-B process

Schematic diagram for a natural gas-based H-B process



Ostwald process is the most efficient one today for Nitric Acid production

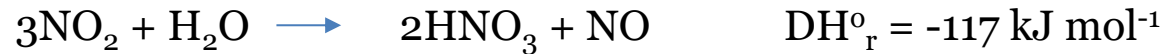
1- Ammonia oxidation to NO:
600C–800C and 4–10 atm, Rh/Pt



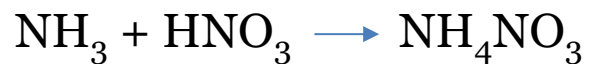
2- NO oxidation to NO₂:
50C



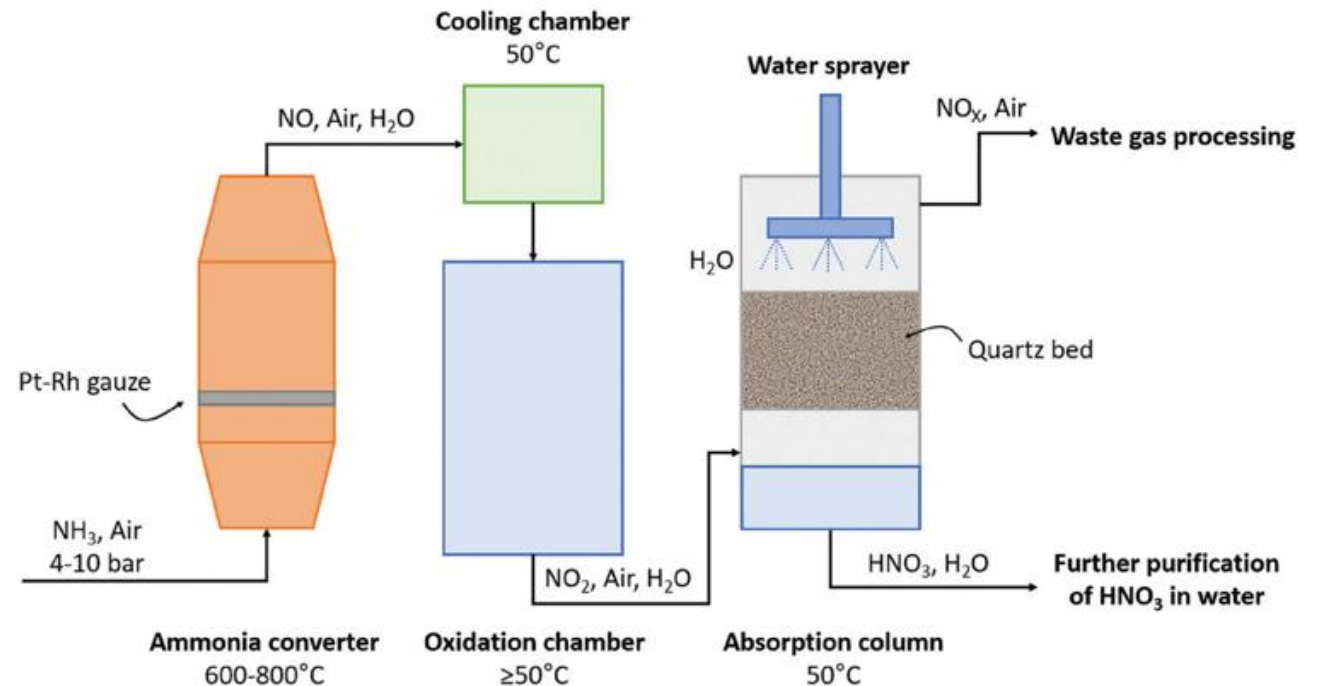
3- NO₂ reaction with water to produce HNO₃



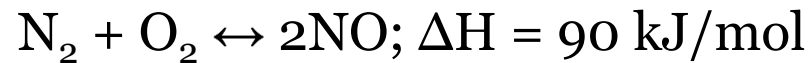
75–80% of the HNO₃ produced is used for ammonium nitrate production



Ostwald process gets nitrogen radicals from ammonia instead of nitrogen molecule due to lower dissociation energy.



Thermal plasma has also been used - Birkeland–Eyde (B-E) process, but not efficient



Zeldovich mechanism:

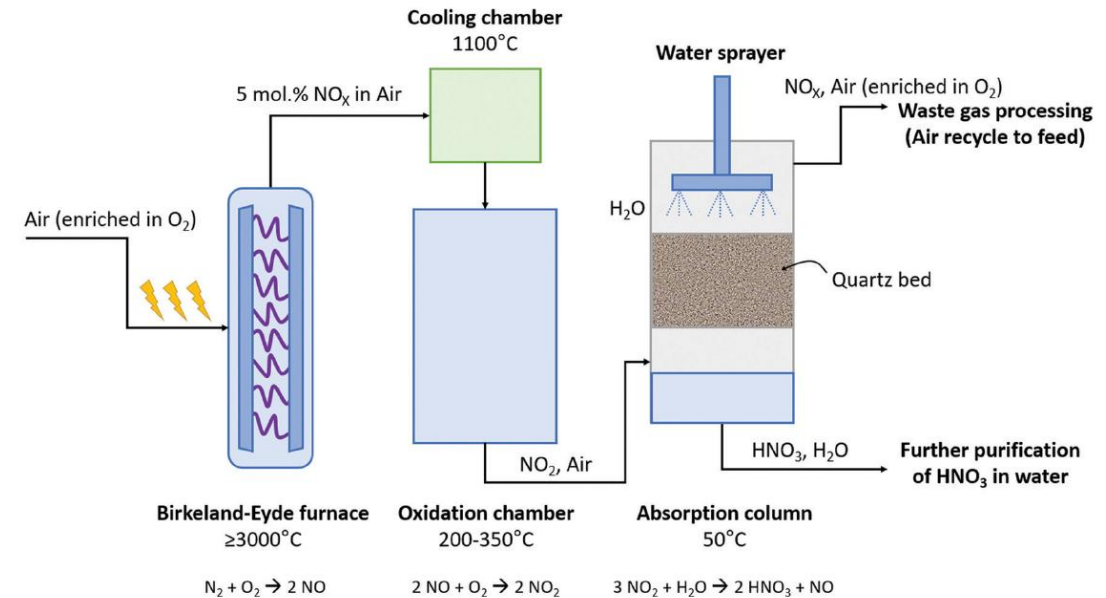


Fig. 2 Process scheme for the Birkeland–Eyde industrial nitrogen-fixation process. Inspired by Patil *et al.*⁹

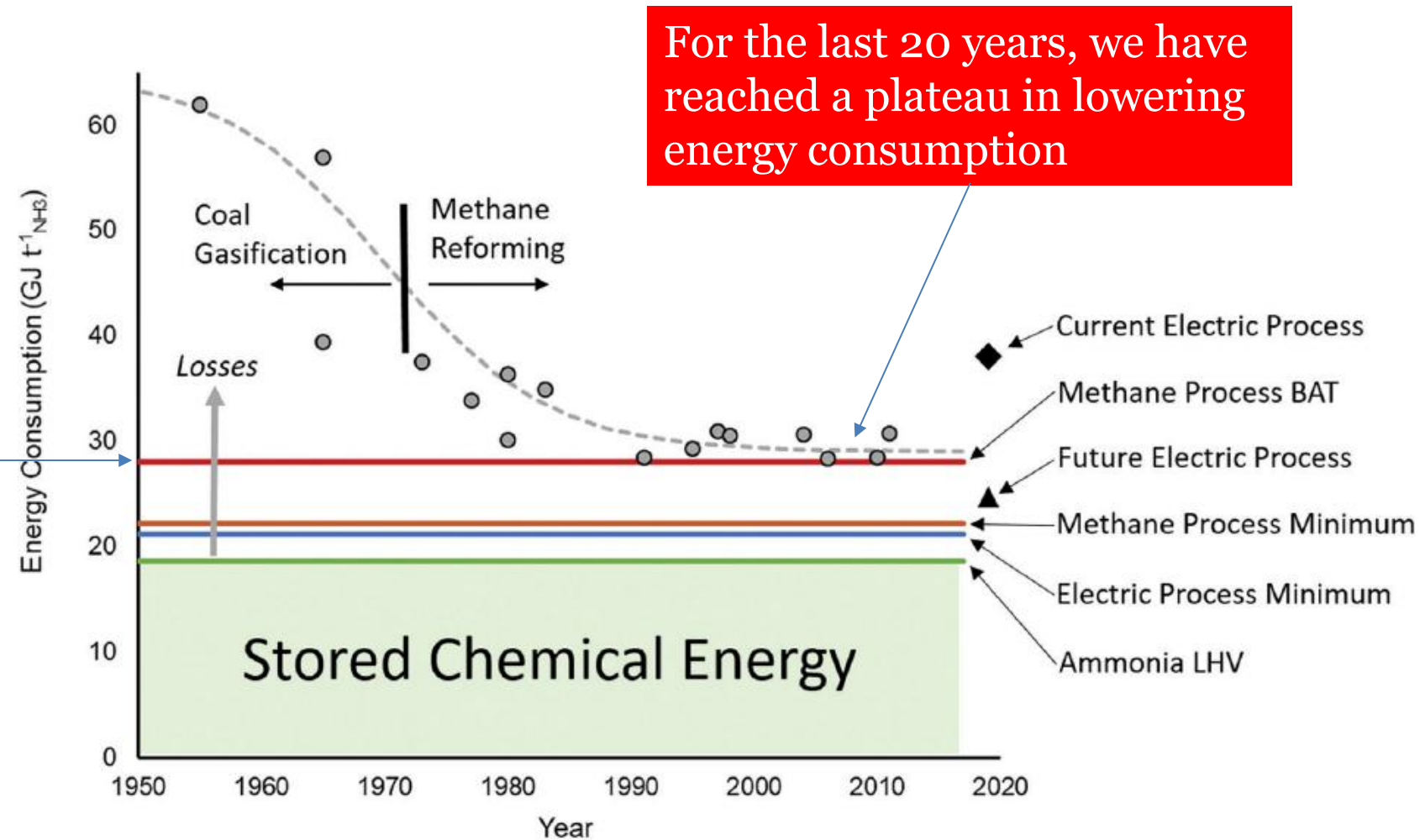
B-E energy consumption MJ/mol	Min theoretical energy consumption MJ/mol	Yield %
2.4 – 3.1	0.72	1 – 2

B-E process is 5 to 8 x more energy intensive than H-B process

What are the limits of current practices?

For ammonia:

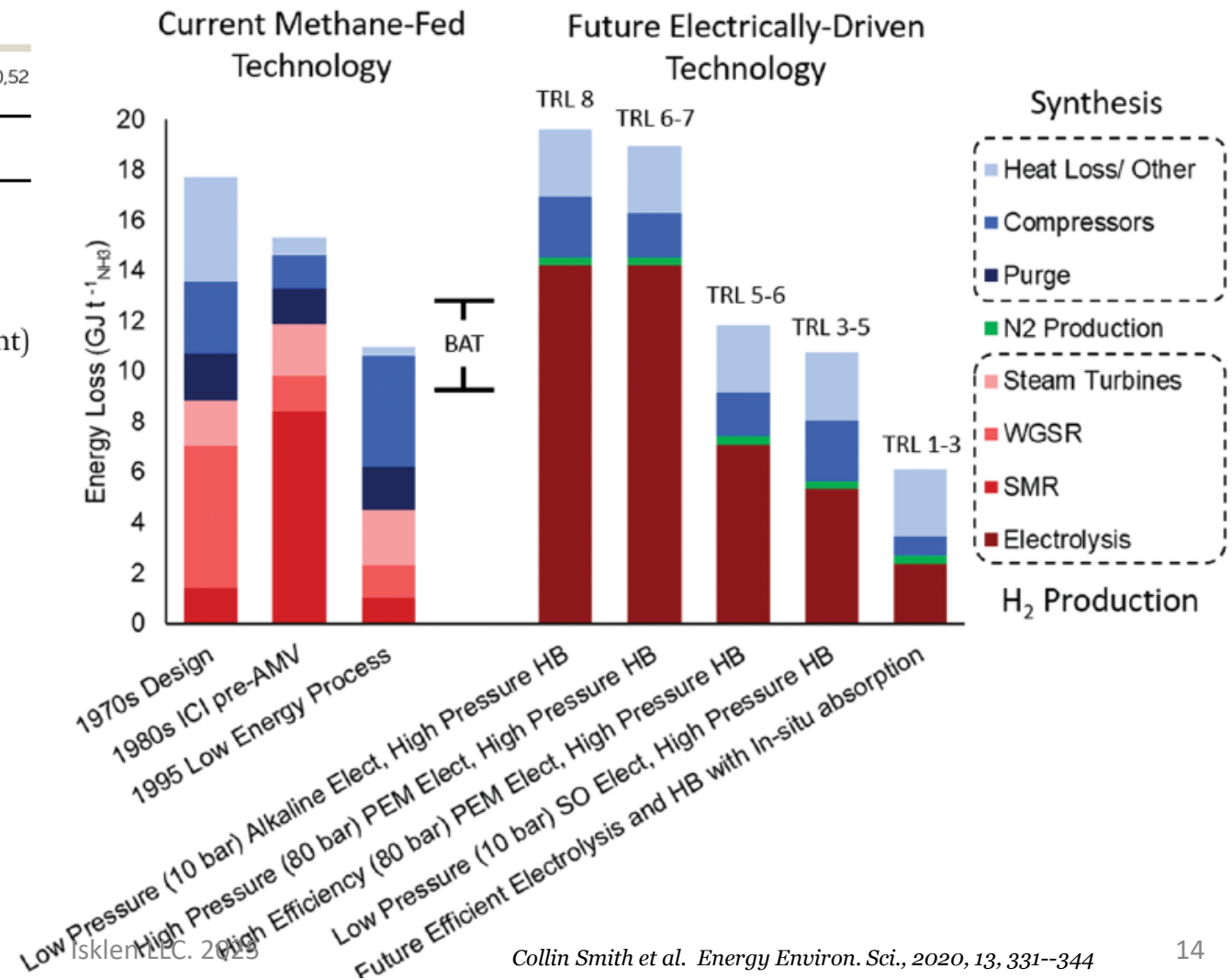
This is where we are today with H-B process



New R&D in ammonia production processes concern mainly electrolysis

Table 1 Summary of main renewable hydrogen production technologies^{50,52}

Hydrogen production technologies	TRL	Feedstock
Alkaline electrolysis	9	H ₂ O + electricity
PEM electrolysis	7–8	H ₂ O + electricity
Solid oxide electrolysis	3–5	H ₂ O + electricity + heat
Biomass gasification	4	Biomass + heat
Biological	1–3	Biomass + microbes (+ light)
Photoelectrochemical	1–3	H ₂ O + light
Thermochemical	1–3	H ₂ O + heat



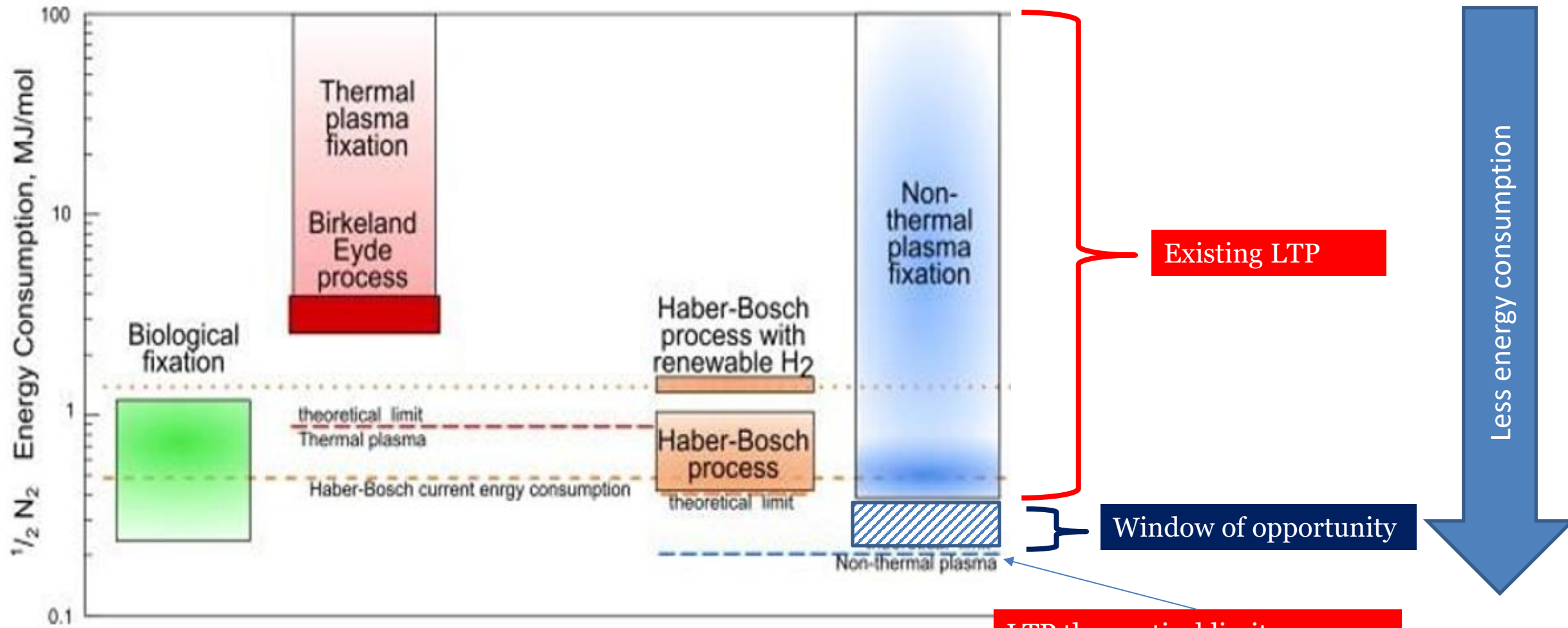
Photocatalysis chemistry

- Syzygy Plasmonics is a **light-powered (photocatalytic) chemical reactor** that uses light instead of heat from combustion to drive chemical reactions (from **Rice University**).
 - Eliminates GHG emissions
 - Low efficiency due to limited efficiency of LEDs (30-40%) and low cross sections for electron-hole creation.

S Y Z Y G Y
P L A S M O N I C S



Low-temperature plasmas have the lowest theoretical energy consumption for nitrogen fixation



Energy consumption by different nitrogen fixation processes.

Modified from: Sirui Li et al. *Processes* 2018, 6, 248; doi:[10.3390/pr6120248](https://doi.org/10.3390/pr6120248)

LTP theoretical limit:
>200% more efficient than
Haber-Bosch

Different types of LTP for N₂ fixation

Table 2 Comparison of energy consumption for NO production in various plasma reactors

Plasma type	Product (concentration)	Energy cost (MJ mol N ⁻¹)
Electric arc (Birkeland-Eyde)	NO (2%)	2.4–3.1
Spark discharge	NO and NO ₂	20.27, 40
Transient spark discharge	NO and NO ₂	8.6
Pin-to-plane ns-pulsed spark discharge	NO and NO ₂	5.0–7.7
Radio-frequency crossed discharge	HNO ₃	24–108
Laser-produced discharge	NO and NO ₂	8.9
(Positive/negative) DC corona discharge	NO and NO ₂	1057/1673
Pulsed corona discharge	HNO ₃	186
Pin-to-plane DC glow discharge	NO and NO ₂	7
Pin-to-pin DC glow discharge	NO and NO ₂ (0.7%)	2.8
Dielectric barrier discharge	NO and NO ₂ (0.6%)	56–140
Packed dielectric barrier discharge	NO and NO ₂ (0.5%)	18
DC plasma arc jet	NO (6.5%)	3.6
Propeller arc	NO and NO ₂ (0.4%)	4.2
Pulsed milli-scale gliding arc	NO and NO ₂ (1–2%)	2.8–4.8
Gliding arc plasmatron	NO and NO ₂ (1.5%)	3.6
Rotating gliding arc	NO and NO ₂ (5.4%)	2.5
Microwave plasma	NO and NO ₂ (0.6%)	3.76
Microwave plasma with catalyst	NO (6%)	0.84
Microwave plasma with magnetic field	NO (14%)	0.28

Kevin H. R. Rouwenhorst et al., *Energy & Environmental Science* · March 2021.

Thermal
plasma

Lowest energy
consumption &
highest NO_x yield at
atmospheric pressure

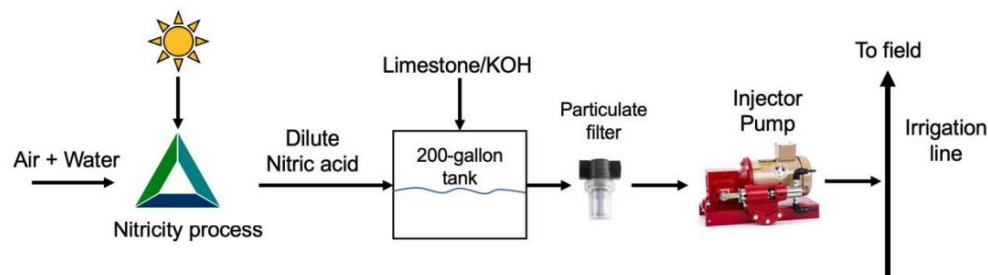
Lowest energy
consumption,
but at low-
pressure

So far, rotating gliding arc has shown the lowest energy consumption and highest yield for N₂ fixation

ARPA-E is funding a small LTP N₂ fixation effort



“Nitricity Inc. is developing an atmospheric **microwave plasma reactor** that uses air, water, and renewable electricity to produce nitrogen fertilizer.



Microwave-Plasma Ammonia Synthesis

• Transportation Fuels

PRINT

West Virginia University

★ Program:
REFUEL

* Award:
\$2,900,000

📍 Location:
Morgantown,
West Virginia

* Status:
ACTIVE

“West Virginia University Research Corporation (WVURC) will develop a process to convert renewable electricity, water, and air into ammonia using plasma excitation **at low temperatures and pressures**.

LTP-assisted catalysis has shown yield enhancement in HN_3 synthesis from N_2/H_2 plasma

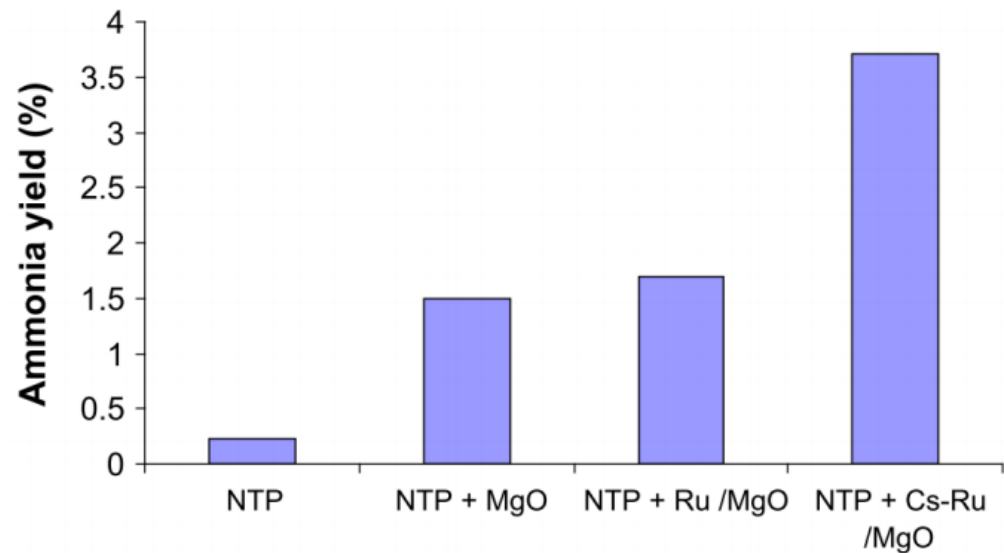
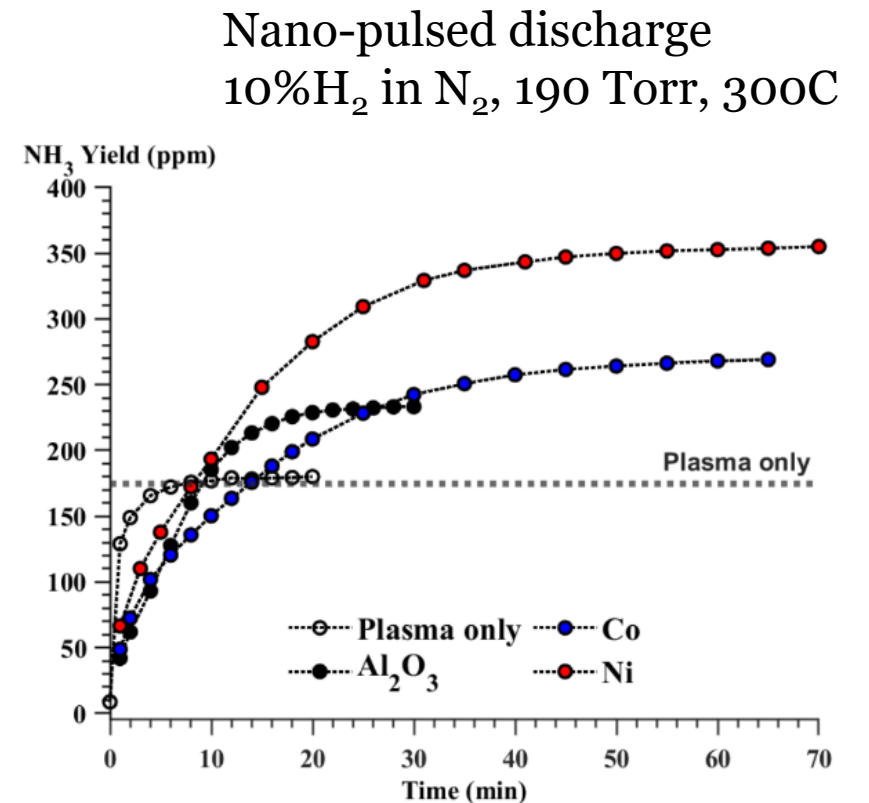


Figure 8. Ammonia synthesis by non-thermal plasma alone, and with different packings ($V_{\text{N}_2}:V_{\text{H}_2} = 3:1$, N_2 and H_2 total flow rate 60 mL/min, voltage 5000 V, frequency 8000 Hz). Reprinted by permission from Springer Nature, Plasma Chemistry and Plasma Processing, “Atmospheric Pressure Ammonia Synthesis Using Non-Thermal Plasma Assisted Catalysis”, Peng et al. [107], [COPYRIGHT] (2018).

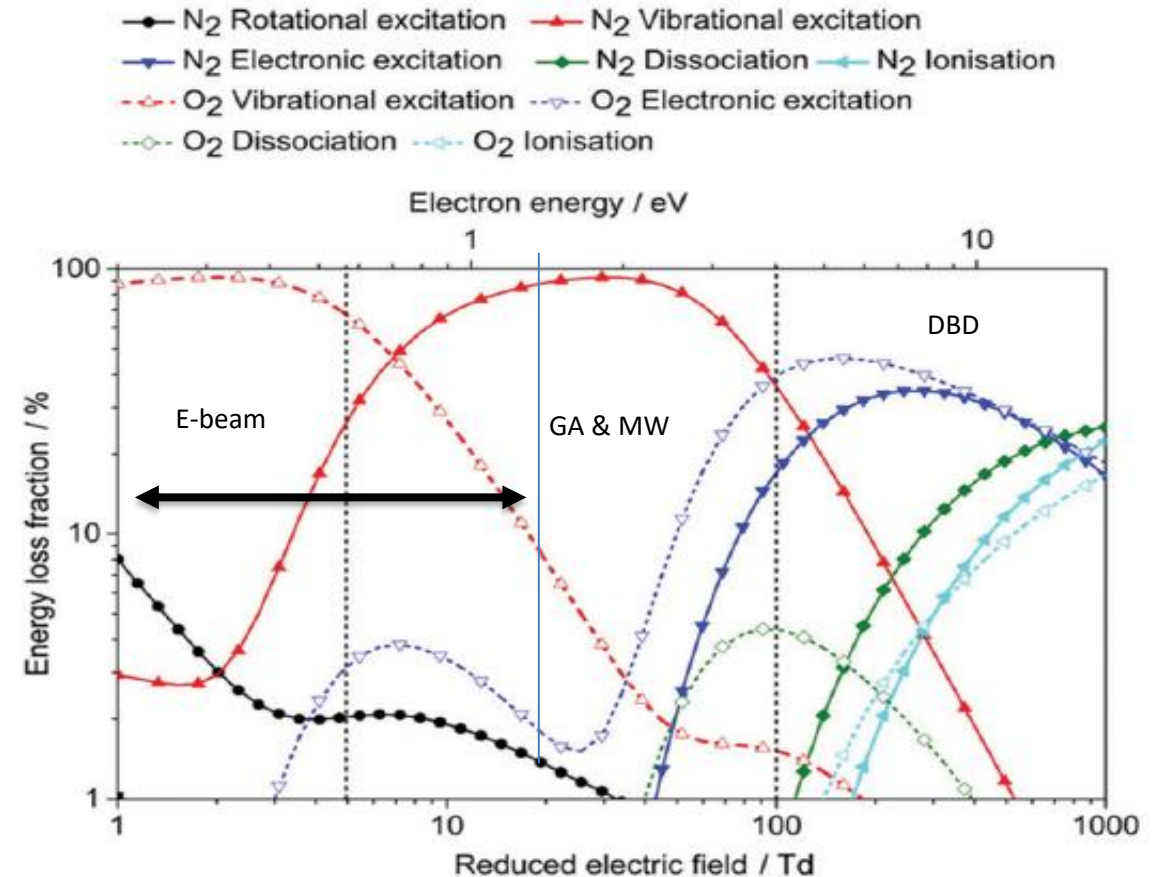
LTP enhances ammonia yield by 15x when used with Cs-Ru/MgO catalyst



Energy dissipating channels in a LTP

- Many energy dissipating channels during a LTP discharge
- What are the channels that lead to dissociation and at what energy expense?

Understanding fundamental physics of LTP is key to improving their efficiency



Fine-tune LTPs to optimize for dissociative vibrational ladder-climbing process

molecule	E_{diss}	E_{vib}	E_{elect}	E_{ion}	$E_{\text{e-impact diss}}$
CO ₂	5.5	0.29 (σ_u^+)	7.0 (1B_2)	13.8	11.5

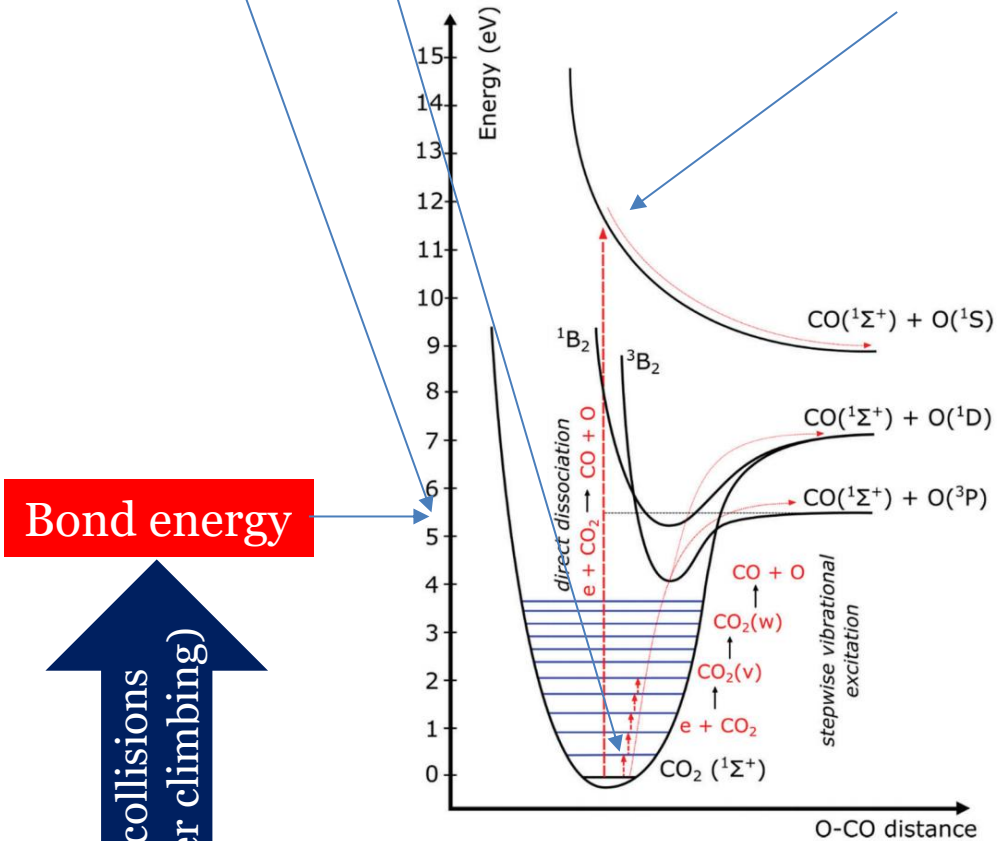


Fig. 12 Schematic of some CO₂ electronic and vibrational levels, illustrating that much more energy is needed for direct electronic excitation-dissociation than for step-wise vibrational excitation, i.e. the so-called ladder-climbing process (reproduced from ref. 91 with permission from the Royal Society of Chemistry).

Current LTPs
(Black box)

Proposed LTPs
(Fine-tuning)
Energy where it is needed
and only min amount needed

Tune plasma to
maximize energy
transfer to vibrational
excitation and
minimize other losses

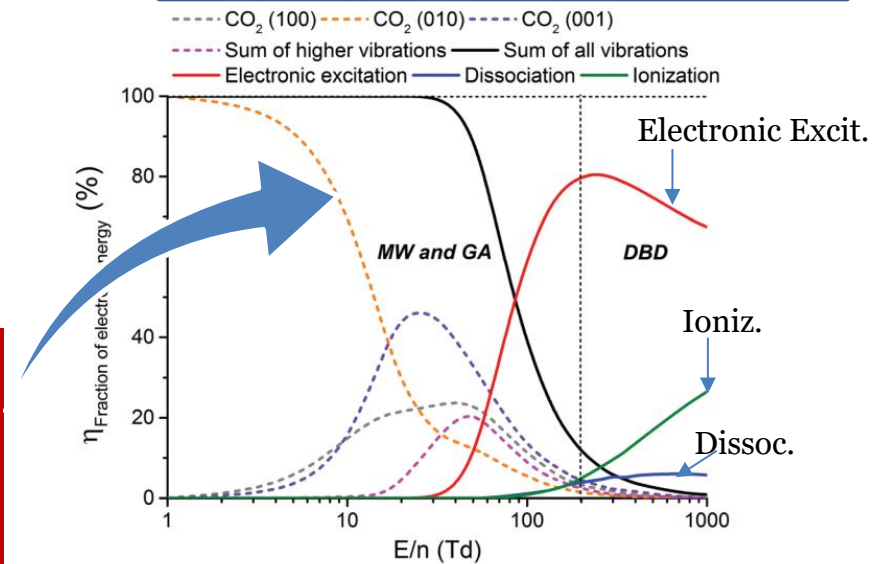


Fig. 11 Fraction of electron energy transferred to different channels of excitation, as well as to the ionization and dissociation of CO₂, as a function of the reduced electric field (E/n), as calculated from the corresponding cross-sections of the electron-impact reactions. The E/n regions characteristic for MW and GA plasma and for DBD plasma are indicated.

Enhanced vibrational ladder-climbing dissociation in a LTP

We maximize the vibrationally-enhanced ladder-climbing dissociation (VELC) process by using a nanopulsed e-field.

Min theoretical energy used by existing thermal technologies

Table 1. Bond Dissociation Energies,⁴¹ Energies of Relevant Vibrationally⁴² and First Electronically Excited States,^{42,43} Ionization Energies,⁴¹ and Electron Impact Dissociation Energy Thresholds^{42,44} of N₂, CH₄, and CO₂, All in eV^a

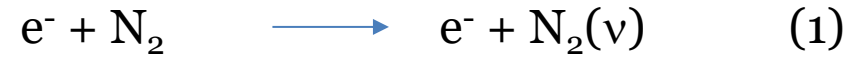
molecule	E_{dis}	E_{vib}	E_{elect}	E_{ion}	$E_{\text{dis}}^{\text{e-impact}}$
N ₂	9.8	0.29 (σ_g^+)	6.2 ($^3\Sigma_u^+$)	15.6	13.0
CH ₄	4.5	0.37 (t_2)	8.8 (3T_2)	13.0	9.9
CO ₂	5.5	0.29 (σ_u^+)	7.0 (1B_2)	13.8	11.5

Min theoretical energy used by existing Non-Thermal Plasmas (NTPs)

Vibrationally-enhanced dissociation: Energy directed only at target molecular bonds to reach min bond energy

Vibrationally-enhanced dissociation has the theoretical potential for min energy consumption

Vibrationally-enhanced Zeldovich mechanism

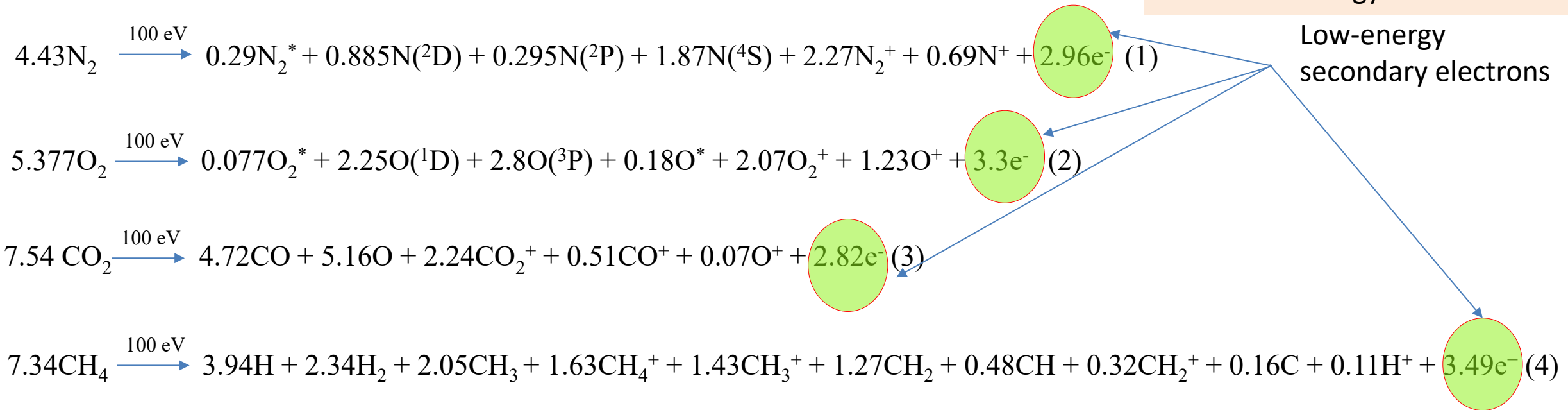


<u>Energy consumption</u> KJ/mol NO Eq (2&3)			NO energy of formation	<u>Energy losses</u> for vibrational dissociation	<u>Energy losses</u> for vibrational + electronic excitation dissociation	<u>Energy losses</u> for thermal dissociation
Only vibrational	Vibrational +electronic excitation	Thermal dissociation	kJ/mol	kJ/mol	kJ/mol	kJ/mol
200	500	722	90	110	610	632
Theoretical LTPs	Current LTPs	Current practice		55%	82%	88%

Can we minimize electronic excitations and maximize vibrational excitations in LTPs?

E-beam LTP G-value for different gases

When an energetic beam of electrons collides with the following gases, for 100eV of energy spent, we get:



For equation (1):

- Total of 3.74 N radicals
- < 2N₂ molecules dissociated
- 26.73 eV/N radical
- ~ 3 low-energy electrons lost

The goal is to precisely control the energy of the secondary electrons to match optimum vibrational excitation energy. Or, give them a second life by accelerating them to produce more dissociation

E-beam enhanced LTP: Act fundamentally to control the chemical reaction pathways

These graphs represent:

- Energy dist. of the electrons in an ebeam plasma
- Different plasma processes for nitrogen

Secondary electrons from the plasma

We want to move this curve to the right, so it overlaps with the excitation curve

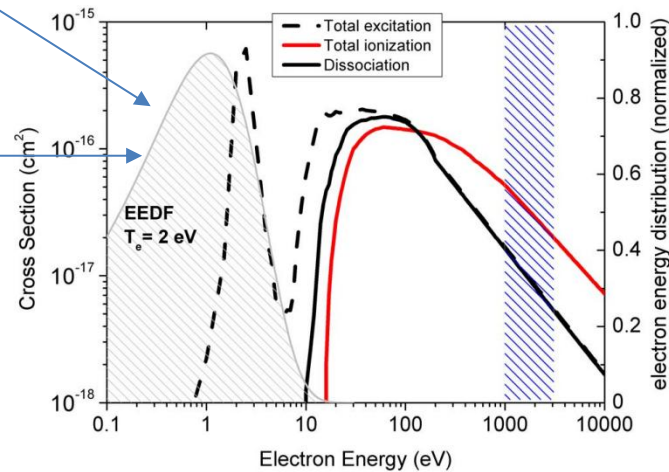
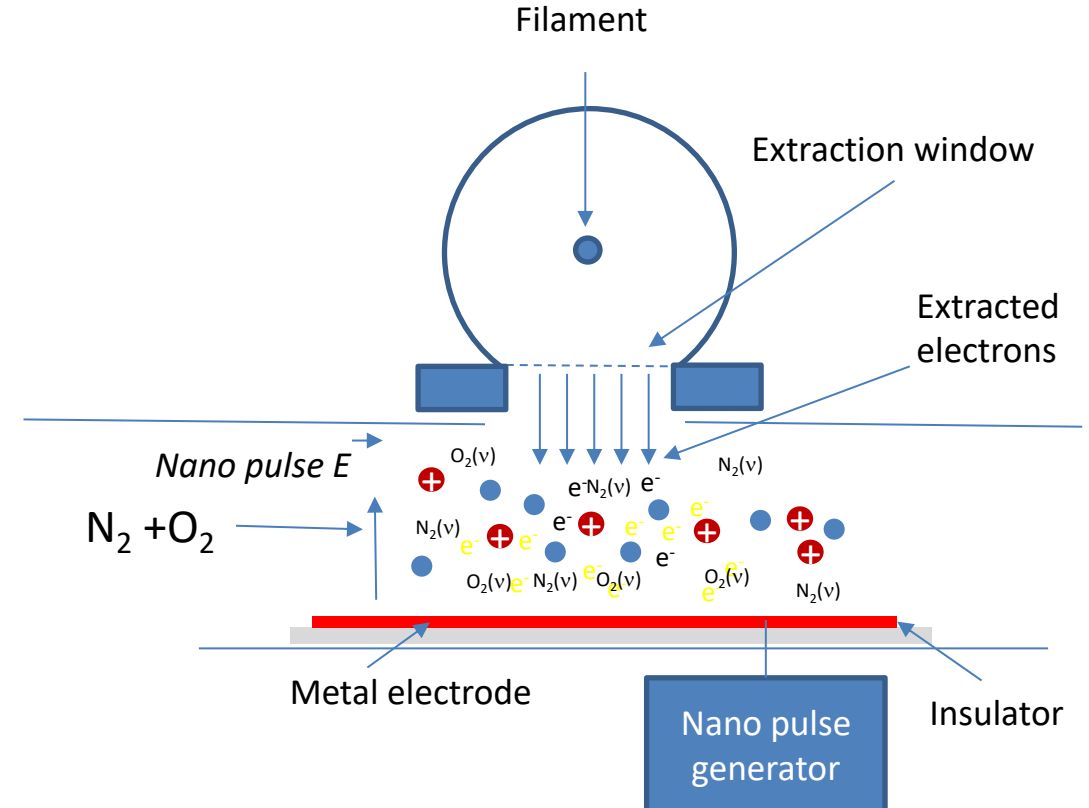


Figure 4. Electron impact cross sections in nitrogen for electron energies up to 10 keV. Also shown is a Maxwellian electron energy distribution function representative of a generic discharge with an electron temperature of 2 eV. Note the drastic difference in cross sections for low-energy plasma electrons and 1–3 keV beam electrons (shaded).



K. Hadidi. US 12,273,987. Apr. 2025

Economics of CH₄ decomposition by current ebeam technology

Kerschert et al. *international journal of hydrogen energy* 46 (2021) 19897e19912

Table 3 – Results of the flowsheet calculations of the electron beam plasma methane pyrolysis processes and comparison with benchmark technologies.

Parameter	Plasma RE input	Electrolysis	Plasma self-sustaining	SMR	SMR w. CCS
Gross H ₂ output	9.0 t/h	–	20.4 t/h	10.0 t/h	10.0 t/h
Net H ₂ output	9.0 t/h	–	9.0 t/h	9.0 t/h	9.0 t/h
Carbon output	26.8 t/h	–	60.8 t/h	–	–
Natural gas input	35.8 t/h	–	81.2 t/h	30.6 t/h	33.6 t/h
Electric energy demand (external)	93.2 MW	–	–	–	–
Specific electric energy demand	0.9 kWh/Nm ³ H ₂	5.0 kWh/Nm ³ H ₂	–	–	–
Electric energy export to the grid	–	–	–	9.9 MW	2.42 MW
Specific direct CO ₂ emissions	–	–	–	9.2 kg CO ₂ /kg H ₂	1.0 kg CO ₂ /kg H ₂
Net efficiency	54.9%	70.8%	28.3%	78.1%	69.6%

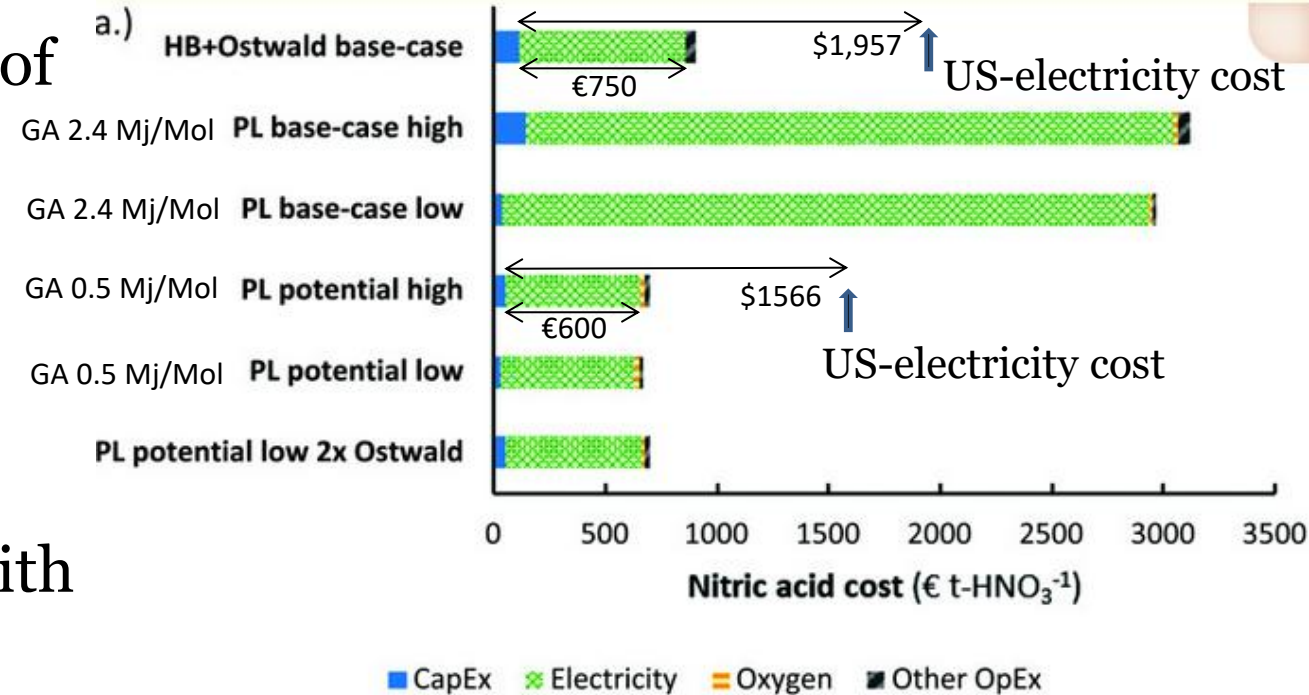
Electricity for the process comes from renewables such as solar

Some of the produced H₂ is used to generate electricity for the process

- **Net efficiency** for producing H₂ from CH₄ using existing e-beam plasma technology combined with renewable electricity input is **54.9%** and **produces no direct CO₂ emissions**
- **Cost of hydrogen between 2.55 Euro/kg H₂ and 5.00 Euro/kg H₂**
- Low-carbon hydrogen production with life cycle emissions between 1.9 kg CO₂ eq./kg H₂ and 6.4 kg CO₂ eq./kg H₂

Reducing energy consumption for LTPs is key to nitrogen fixation

- Assumption (paper): electricity cost of 0.020 €/kWh
- U.S. Electricity cost: \$0.052/kWh*
- CapEx is negligible compared to operational costs for LTP-based process
- Plasma process would be at parity with O/E-HB process at 0.625 MJ/mol N



Kevin H. R. Rouwenhorst, *Energy & Environmental Science* · March 2021. * US Energy Information Administration (EIA)

- Electricity consumption for an LTP-based HNO₃ plant would be the main cost driver
- LTP could be at parity in USA with combined O/E-HB at an energy consumption of 0.625 MJ/mol N

Possible Markets and Applications

Application	Product	Global Production (MT/Y)	Global GHG Emissions (MT/Y)	Total Energy Consumption	Energy Expense (kWh/kg)	Possible Precursors	Previous NTP Works
Nitrogen fixation	Ammonia	235	611	2608 TWh/Y (2% of total energy)	11.1	H ₂ + N ₂	Yes
	Nitric acid	62	192 (CO ₂ _{equ} from N ₂ O)	1.24 GWh/Y	0.4	N ₂ + O ₂	Yes
Hydrogen production	From methane	94	900	4175 TWh/Y (2.5% of total energy)	70	CH ₄	Yes
	From H ₂ S	0				H ₂ S	Yes (H ₂ S decomp)
CO ₂ as feedstock	Adepic acid (C ₆ H ₁₀) ₄)	3	6	60 MWh/Y	38.5	CH ₄ + H ₂	
	Urea (CO(NH ₂) ₂)	180	450	4.5 TWh/Y	20	CO ₂ + NH ₃	
	Acetic acid (CH ₃ COOH)	16.7		417 MWh/Y	10.7	CO ₂ + CH ₃ OH CO ₂ + CH ₄	Yes
	Others						

Summary

- Thermo-catalytic processes have reached their efficiency limits through decades of optimization
- LTP can play a critical role in lowering/eliminating GHG emissions in chemicals manufacturing as they offer different chemical pathways
- Increasing LTP energy efficiency key to making them competitive with existing thermo-catalytic processes
- Controlling LTP at the fundamental level is key to reaching these goals.

Thank you for your attention

Backup Slides

Energy consumption and yield required for an economical plasma ammonia production

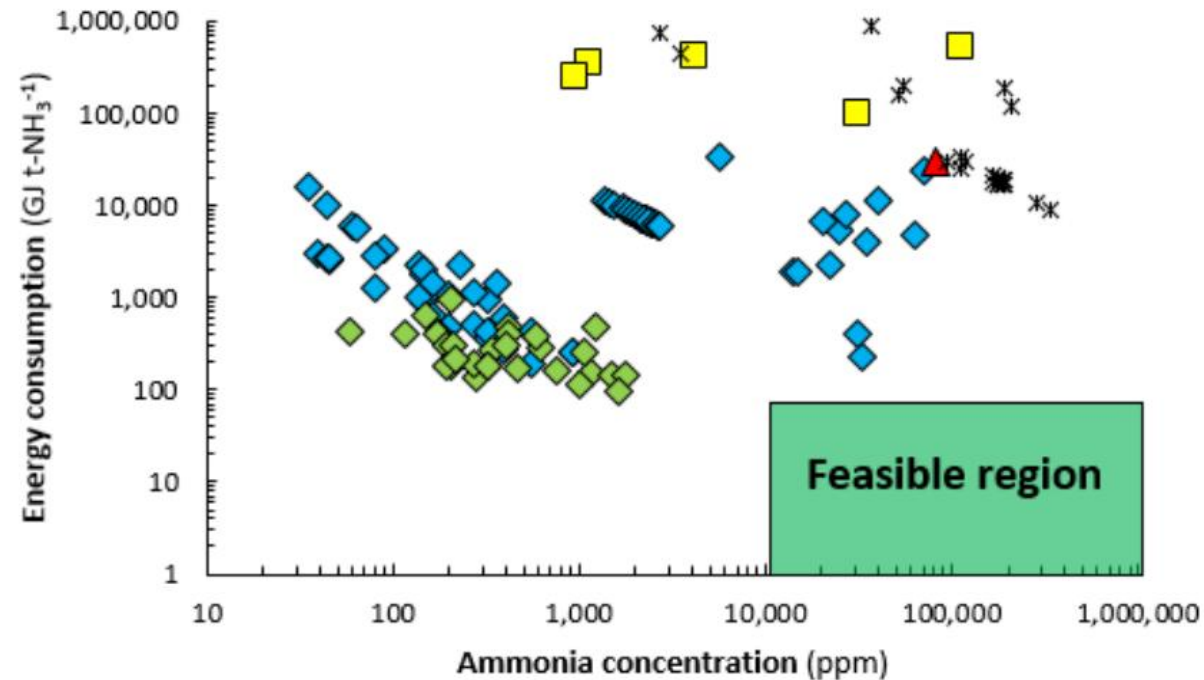


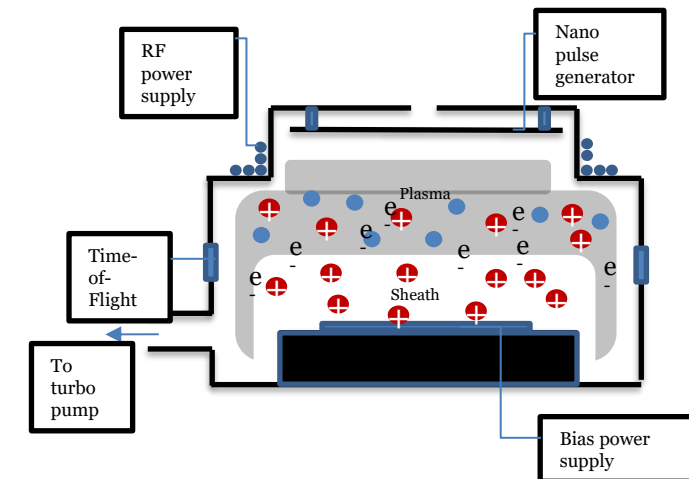
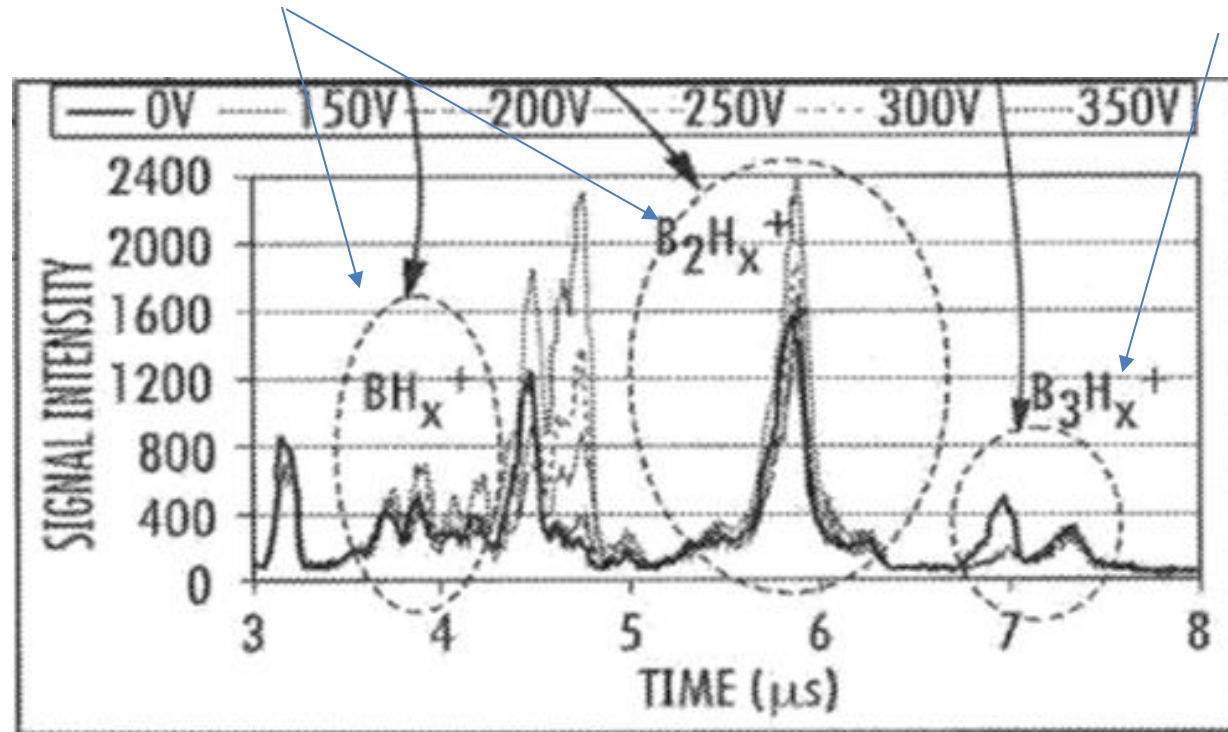
Figure 2. Reported energy yield vs. ammonia concentration at various process conditions. Constructed and extended from [38]. Original references: dielectric barrier discharge (DBD) (alternating current, AC) \blacklozenge [39–52], DBD (pulse) \blacklozenge [43,53], glow discharge \blacktriangle [54], MW \blacksquare [55–59] and radiofrequency (RF) \ast [60–65]. Note that the feed composition varies among the references, and therefore the ammonia yield. In case of a stoichiometric feed ratio, the ammonia outlet concentration is equal to the yield (at 0.0 mol. % NH₃ inlet). The feasible region is discussed in Section 1.2.1.

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Change in plasma chemistry vs nano pulse E-field for semiconductor application

Increase in $B_2H_x^+$ and BH_x^+ with pulse voltage

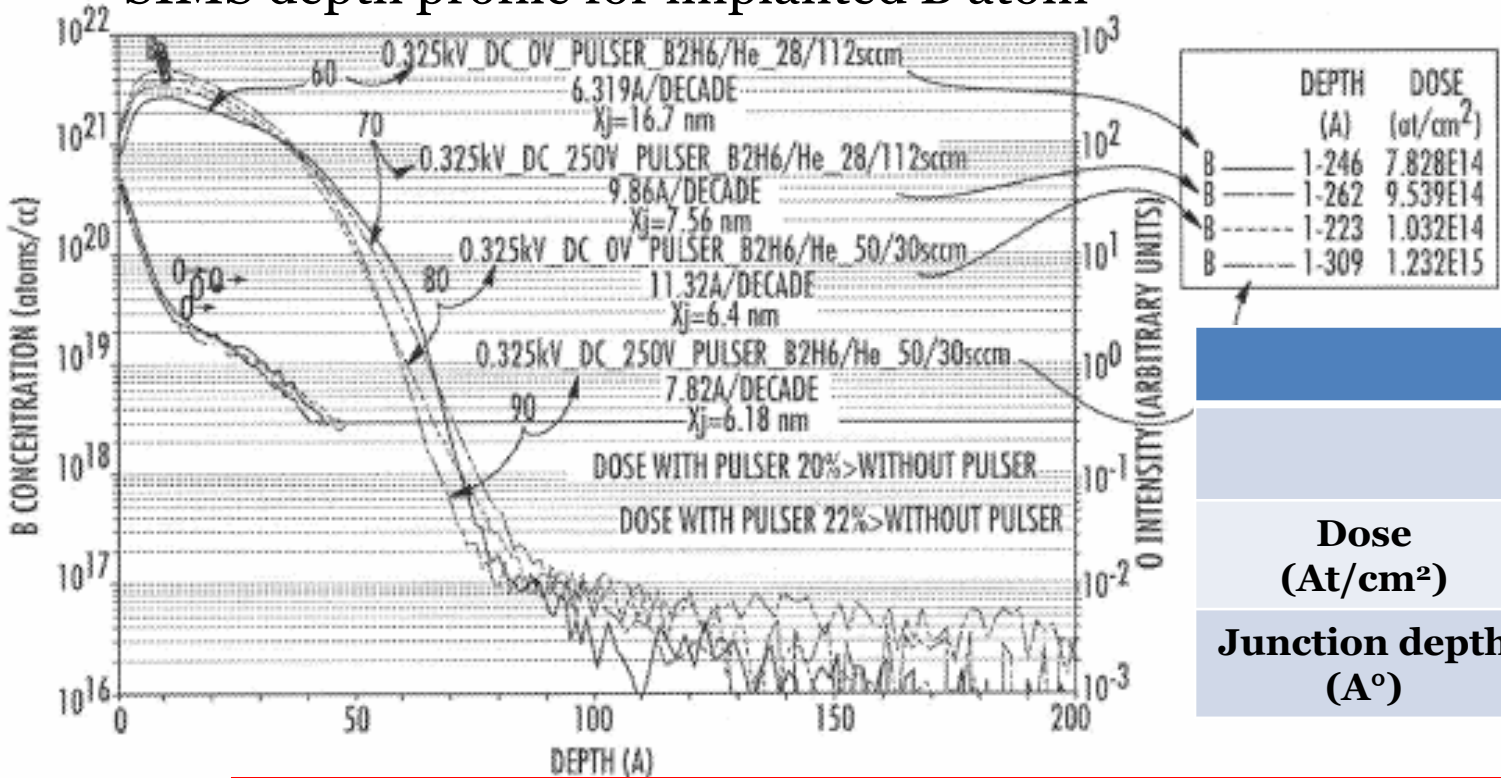
Decrease in $B_3H_x^+$ with pulse voltage ($B_3H_x^+$ come from recombination)



- Increase in RF power would have affected all species the same way
- Increase in nano pulse voltage has different effect on different ion species

Significant change in implanted dose and depth

SIMS depth profile for implanted B atom



Implant voltage: 325 V DC
B₂H₆/He: 0.1% and 0.5%
Nano pulse voltage: 0V and 250V
Nano pulse duration: 1ns

	0.1% B ₂ H ₆			0.5% B ₂ H ₆		
	No Pulse	With Pulse	Change %	No Pulse	With Pulse	Change %
Dose (At/cm ²)	7.828 10 ¹⁴	9.539 10 ¹⁴	20	1.03 10 ¹⁴	1.23 10 ¹⁵	22
Junction depth (Å°)	1.24	1.26	1.6	1.22	1.30	7

- Increase in implanted dose due to higher ion density because of the nano pulse effect on B₂H₆ and other species ionization
- Deeper implant shows a change in the plasma composition with more lighter ions produced because of the nano pulse