18AIChE
Annual Meeting, Pittsburgh, PA

NH3 FUEL ASSOCIATION

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Israel Institute of Technology

Ignition of an Aqueous Ammonia/Ammonium Nitrate Fuel

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31/10/2018

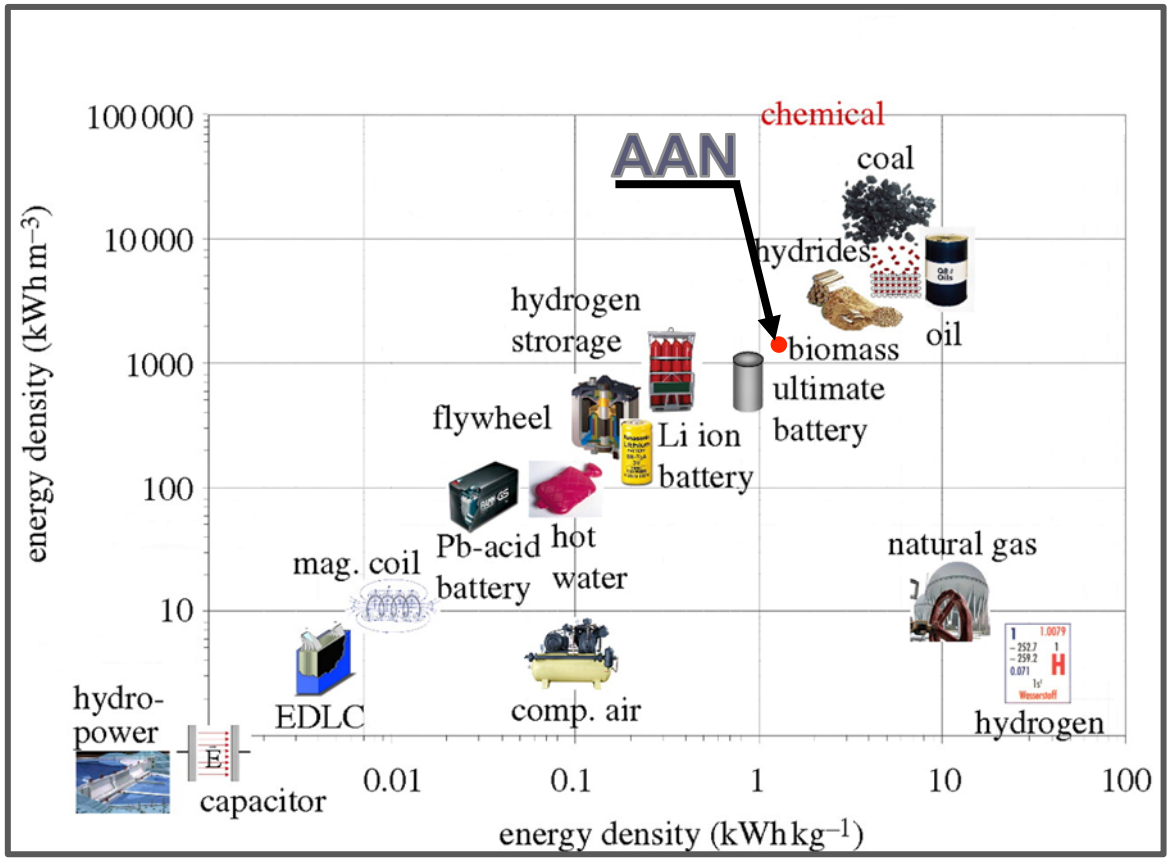
AIChE Annual Meeting 2018

Introduction

- Aqueous ammonia/ammonium nitrate (AAN) is a **carbon free** nitrogen-based monofuel
- Composed from mass-produced fertilizers
- Principal combustion products are N_2 and H_2O:

$$3NH_4NO_{3\,(aq)} + 2NH_4OH_{\,(aq)} + 4H_2O \rightarrow 4N_2 + 15H_2O$$

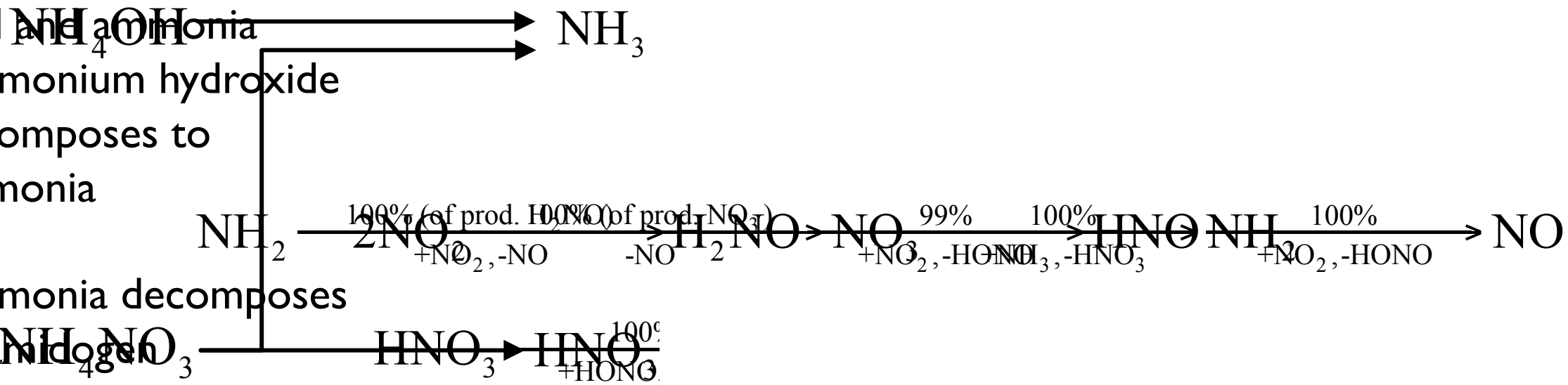
- Volumetric energy density close to CNG at distribution pressure (90 bar)
- Compatible with current fuel infrastructure
- **No PM, VOC, CO_2 and CO emissions**



R. Lan, J.T.S. Irvine, T. Shanwen, Int. J. Hydrogen Energ., 37 (2), 1482-1494, 2010

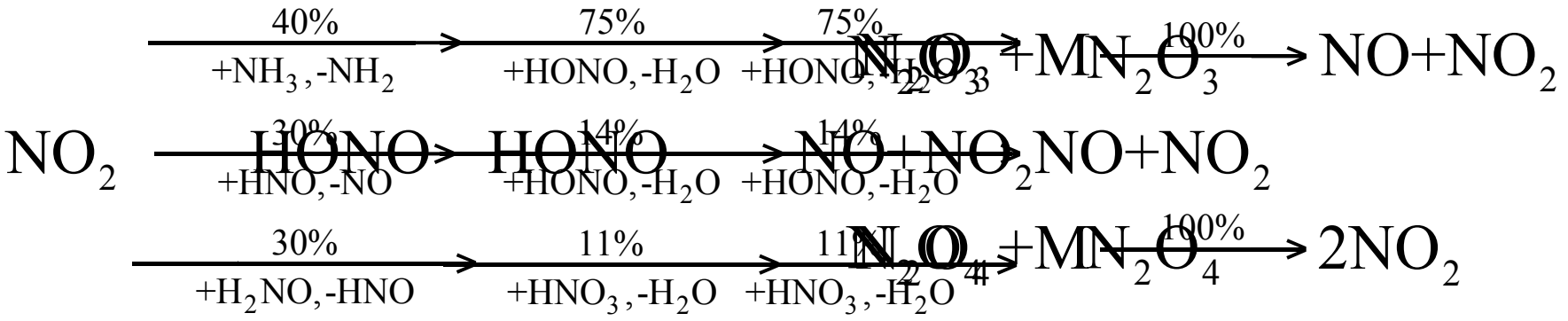
Pre-ignition Mechanism

- Ammonium nitrate decomposes to nitric acid and ammonia
- Ammonium hydroxide decomposes to ammonia
- Ammonia decomposes to amidogen
- Nitric acid decomposes to nitrogen dioxide



Pre-ignition Mechanism

- Nitrous acid is formed by nitrogen dioxide



- And decomposes to a mix of nitric oxide and nitrogen dioxide

Heat Sources and Sinks

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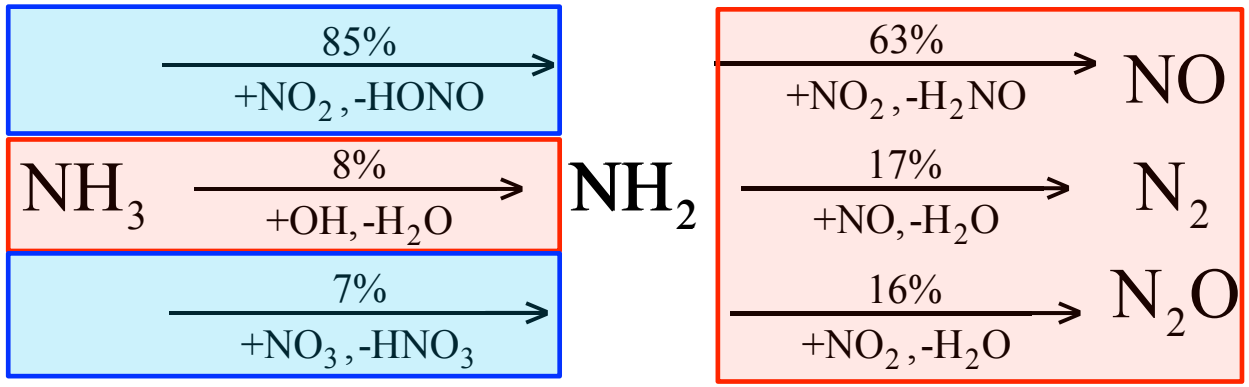
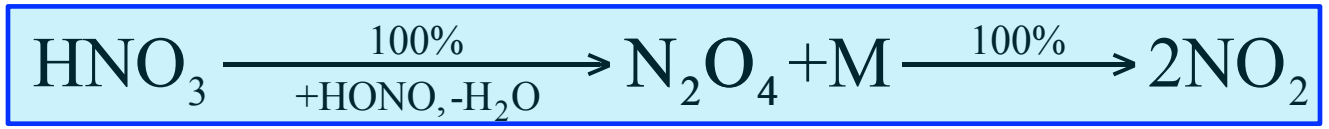
Pre-ignition heat sources:

- Ammonia reacting with hydroxyl
- Amidogen reacting with high oxidation NOx



Pre-ignition heat sinks:

- Ammonia reacting with high oxidation NOx
- Nitric acid decomposition to nitrogen dioxide



Ignition heat sources are amidogen oxidation by nitric oxide & nitrogen dioxide

Take-Home Messages

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- Ammonia reacts with hydroxyl and NOx to form amidogen
- Amidogen reacts with NOx to form low oxidation NOx and N_2
- Nitric acid reacts with nitrous acid to form nitrogen dioxide
- Nitrous acid is generated from nitrogen dioxide and produces NOx by propagation

- A molecular nitrogen yield of 5% is achieved prior to ignition
- Higher yields are achievable by high pressures and catalysts

Acknowledgements

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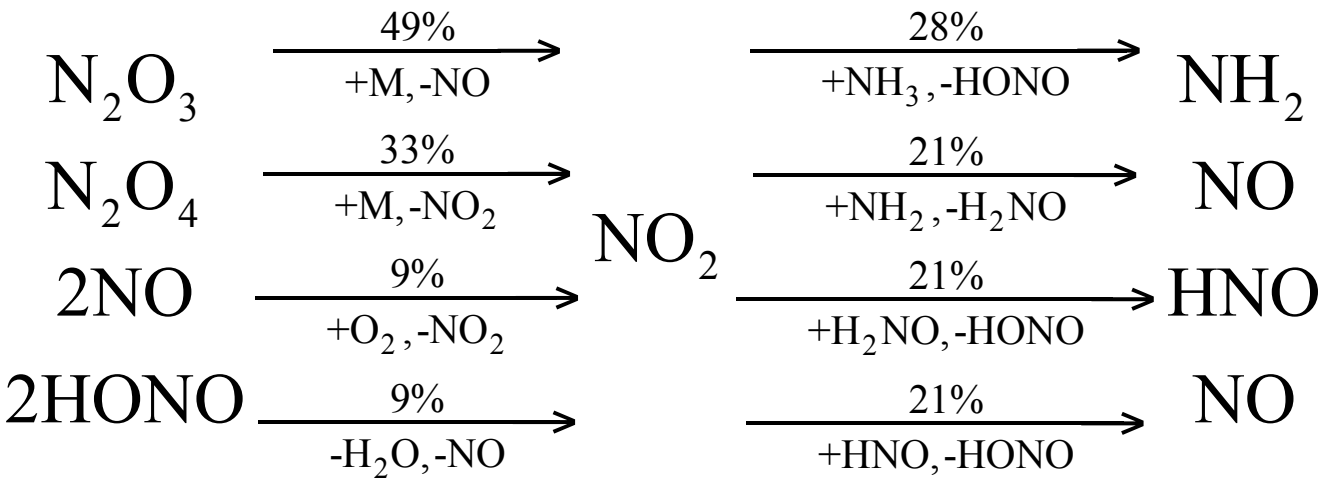
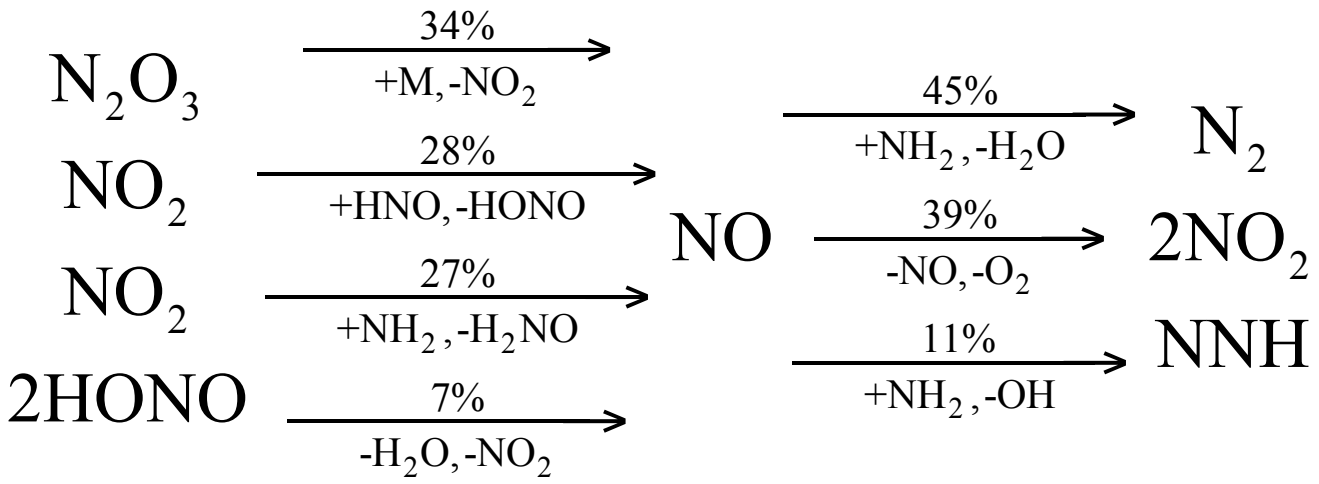
GTEP
Grand Technion Energy Program

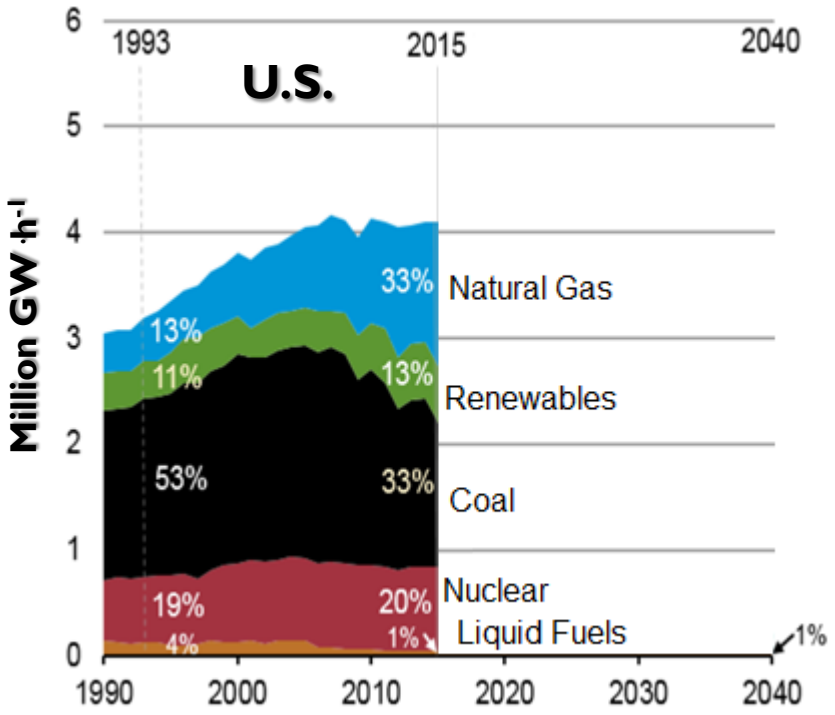
The Ed Satell Family Nitrogen-Based Alternative Fuels Reaction Research Laboratory

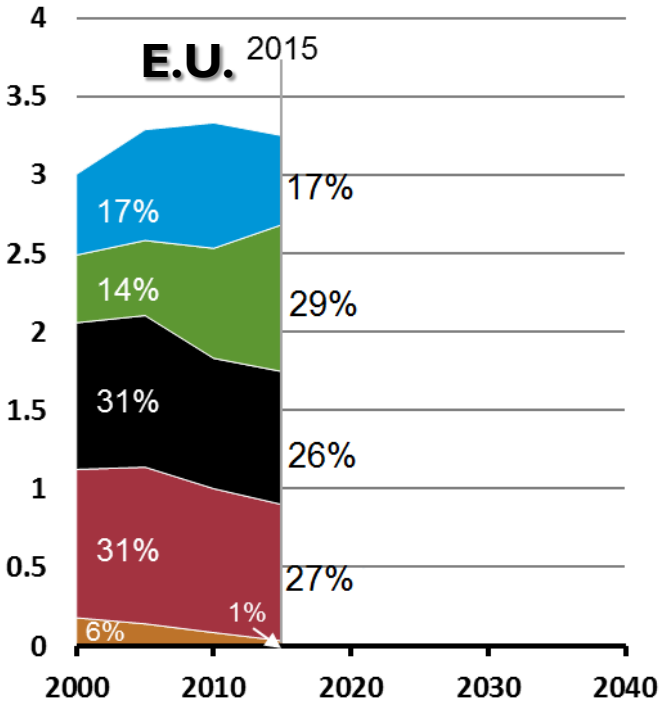
Pre-ignition Mechanism



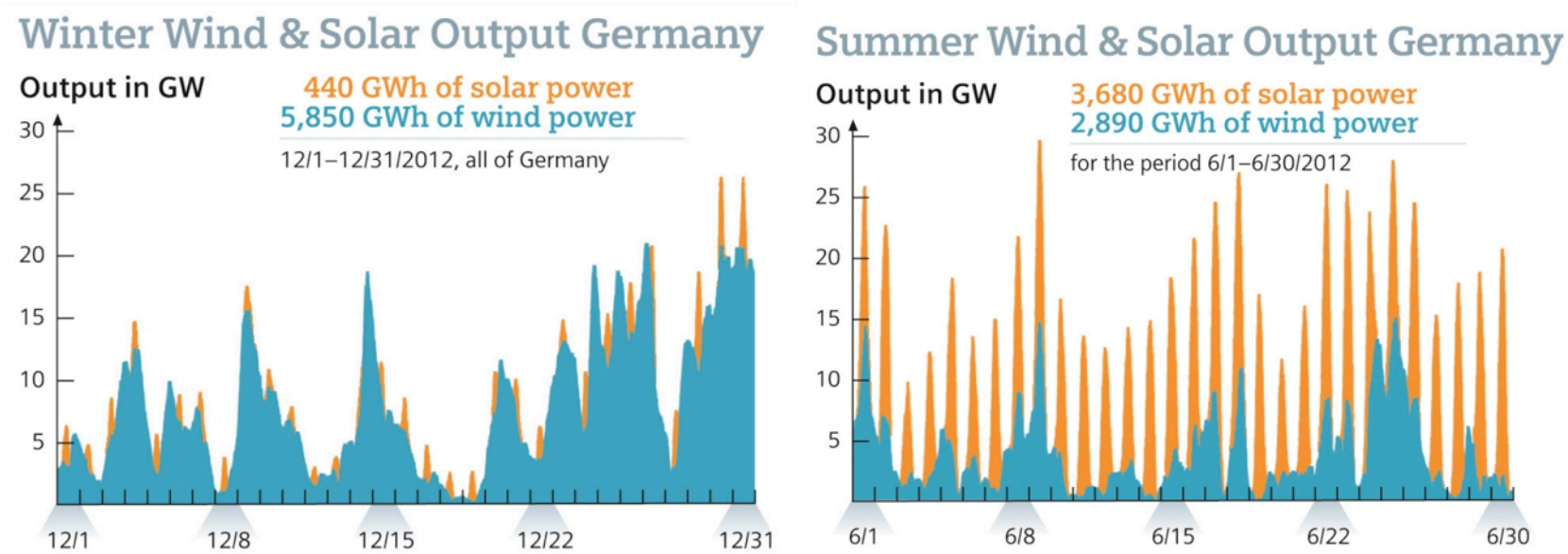


Motivation


U.S.
1993
2015
2040
Million GW·h⁻¹
6
5
4
3
2
1
0
1990
2000
2010
2020
2030
2040
33%
Natural Gas
13%
11%
13%
Renewables
53%
33%
Coal
19%
20%
Nuclear
4%
1%
Liquid Fuels
1%


E.U.
2015
4
3.5
3
2.5
2
1.5
1
0.5
0
2000
2010
2020
2030
2040
17%
17%
14%
29%
31%
26%
31%
27%
1%
6%

Motivation



Dates (month/day)

Motivation

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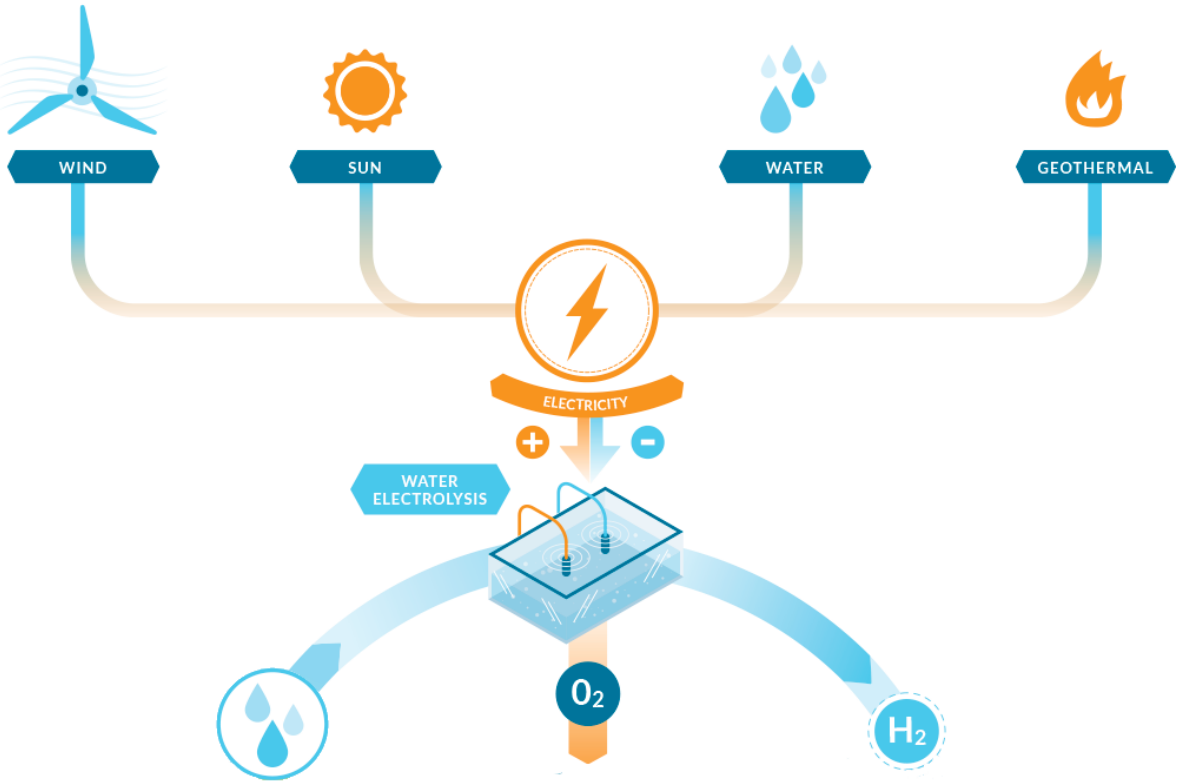

Motivation

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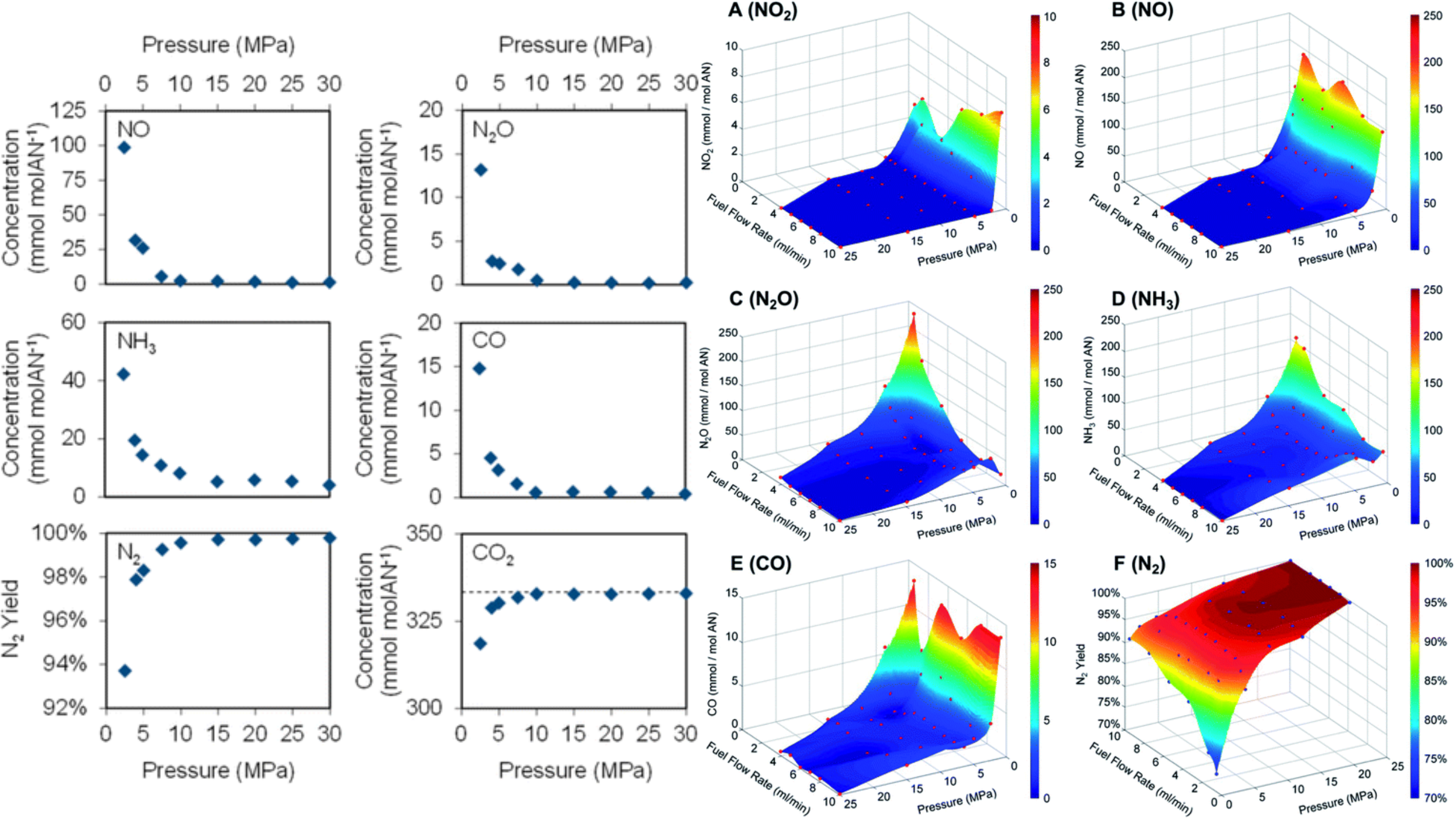
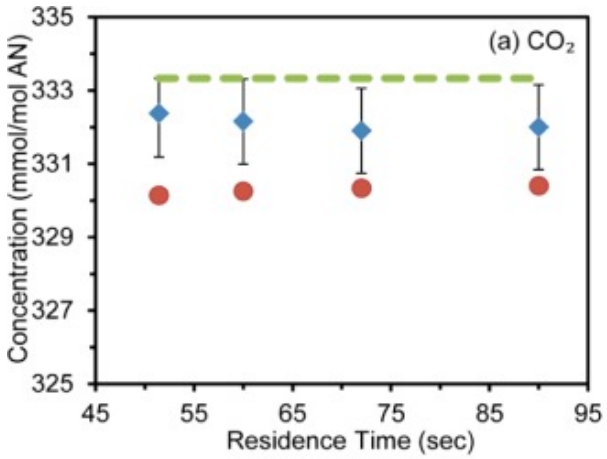
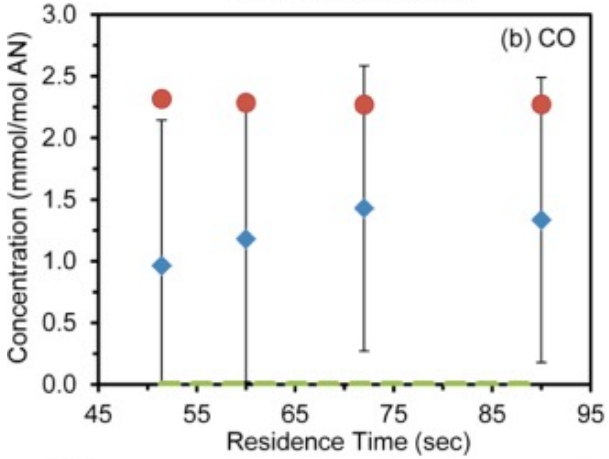
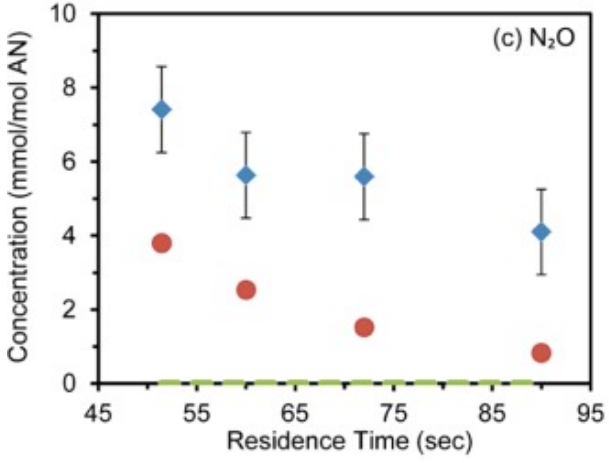
Fuel	Air separation[a,b]	Water splitting[a,c]	Synthesis energy[a,d]	Distribution[a,e]	Energy density[f] [GJ t^{-1}]	$\eta_{combustion}$[g]	PFP^{atm} [h]
methane	0.326	1.64	0.022	0.027	55.5	%54.1	27%
MeOH	0.382	1.44	0.202	0.005	23.7	54%	27%
DME	0.398	1.50	0.274[i]	0.005	31.7	50%	23%
ammonia	0.008	1.43	0.071[i]	0.008	22.5	53%	35%
aq.AHU	0.138	1.58	0.162[i]	0.011	9.2	50%	27%
aq.AAN	0.018	3.12	0.235[i]	0.023	3.7	47%	14%
aq. UAN	0.235	3.27	0.376[i]	0.022	3.3	48%	12%

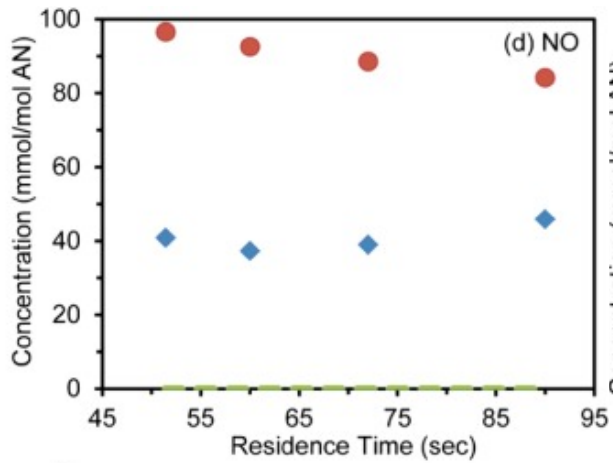
1.[a] Energy values are in an equivalent work basis (see text). [b] Required energy for separating N_2, CO_2, or both from the atmosphere as feedstock.[12, 70] [c] Based on a future prediction for central grid electrolysis evaluated as 180.72 GJ $(t\ H_2)^{-1}$. [86] [d] Values represent state-of-the-art required synthesis energy. [e] Calculated as in Table S3. [f] Taken as high heating value. [g] Calculated as in Table S2. [h] Calculated according to Equation (E2). [i] See Sections 8 and 9 of the Supporting Information for detailed calculations. [j] Average literature value.[48, 49, 87]

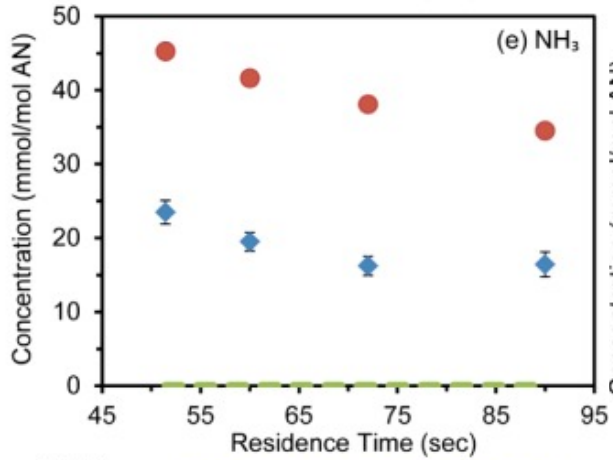

Pressure (MPa)
Concentration (mmol molAN-1)
NO
N2O
NH3
CO
N2
CO2
N2 Yield
A (NO2)
B (NO)
C (N2O)
D (NH3)
E (CO)
F (N2)
Fuel Flow Rate (ml/min)
NO2 (mmol / mol AN)
N2O (mmol / mol AN)
NH3 (mmol / mol AN)
CO (mmol / mol AN)

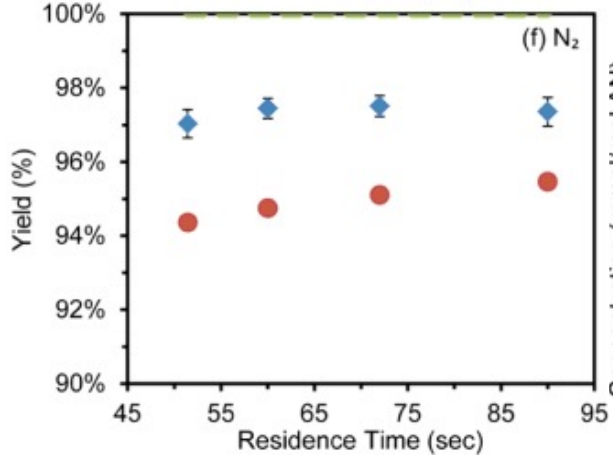

(a) CO_2
Concentration (mmol/mol AN)
Residence Time (sec)

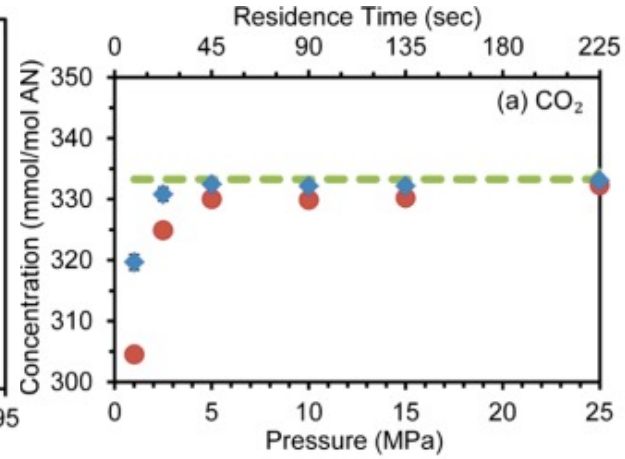

(b) CO
Concentration (mmol/mol AN)
Residence Time (sec)

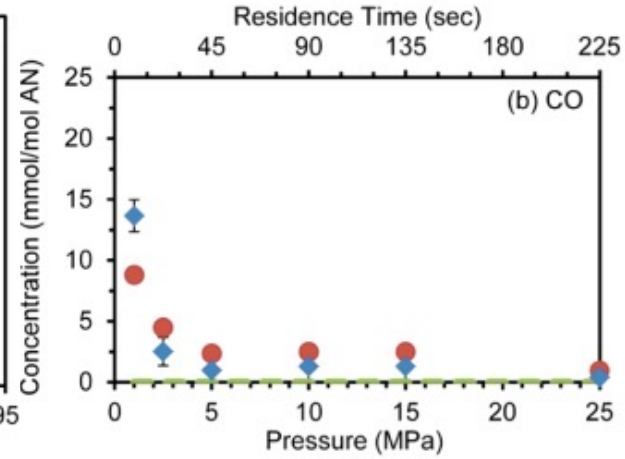

(c) N_2O
Concentration (mmol/mol AN)
Residence Time (sec)

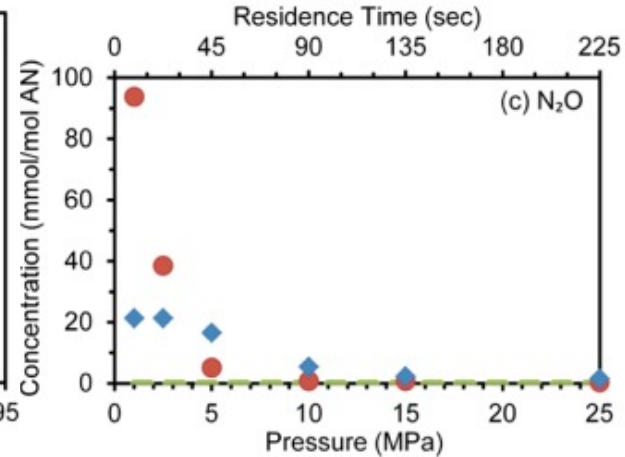

(d) NO
Concentration (mmol/mol AN)
Residence Time (sec)

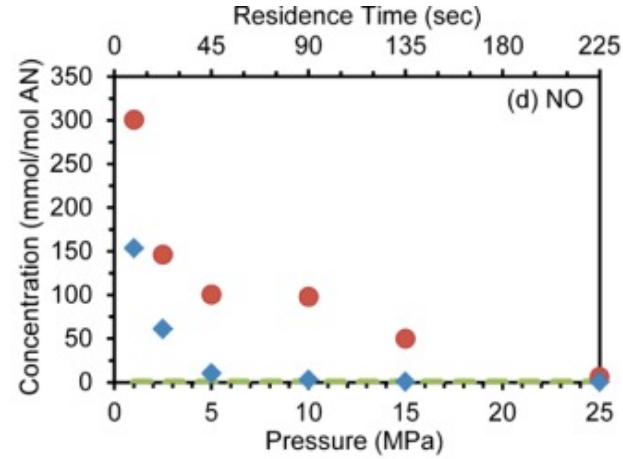

(e) NH_3
Concentration (mmol/mol AN)
Residence Time (sec)

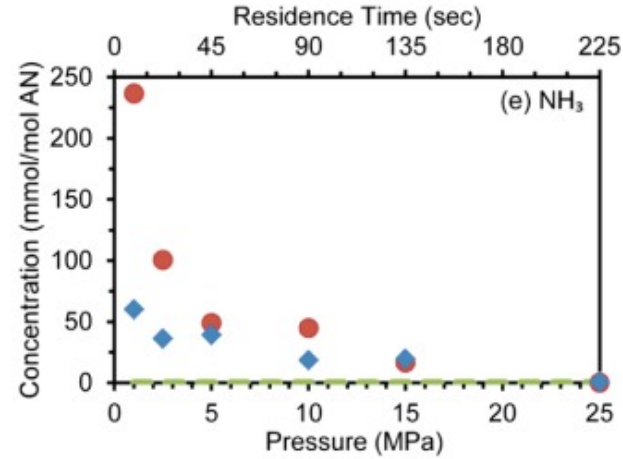

(f) N_2
Yield (%)
Residence Time (sec)

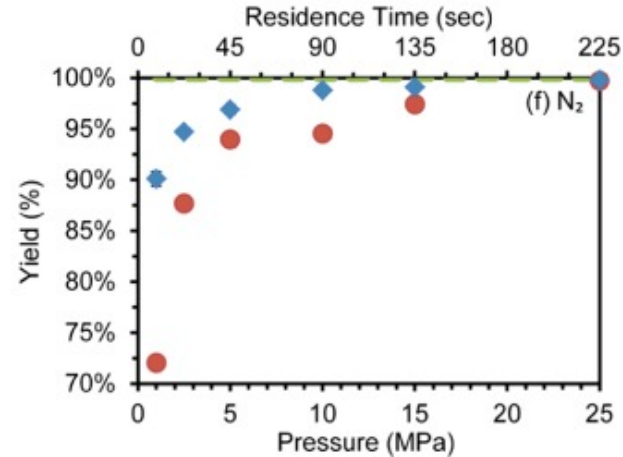

(a) CO_2
Concentration (mmol/mol AN)
Residence Time (sec)
Pressure (MPa)


(b) CO
Concentration (mmol/mol AN)
Residence Time (sec)
Pressure (MPa)

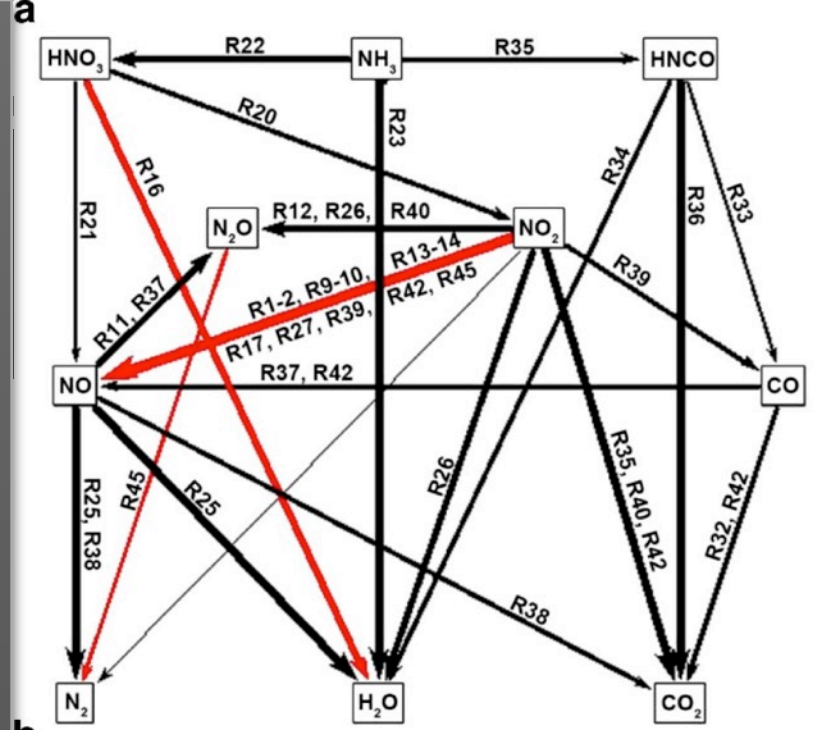

(c) N_2O
Concentration (mmol/mol AN)
Residence Time (sec)
Pressure (MPa)

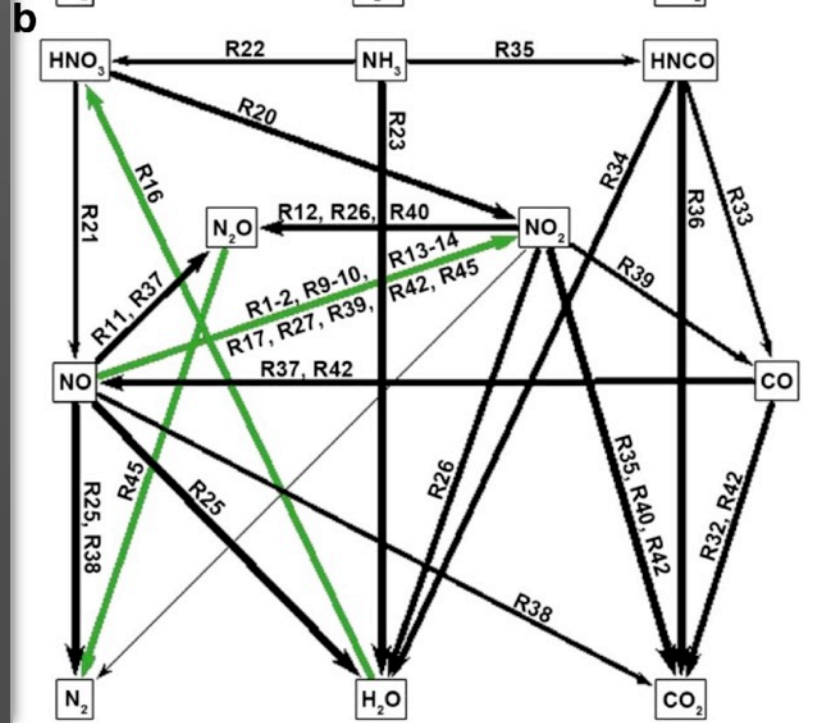

(d) NO
Concentration (mmol/mol AN)
Residence Time (sec)
Pressure (MPa)

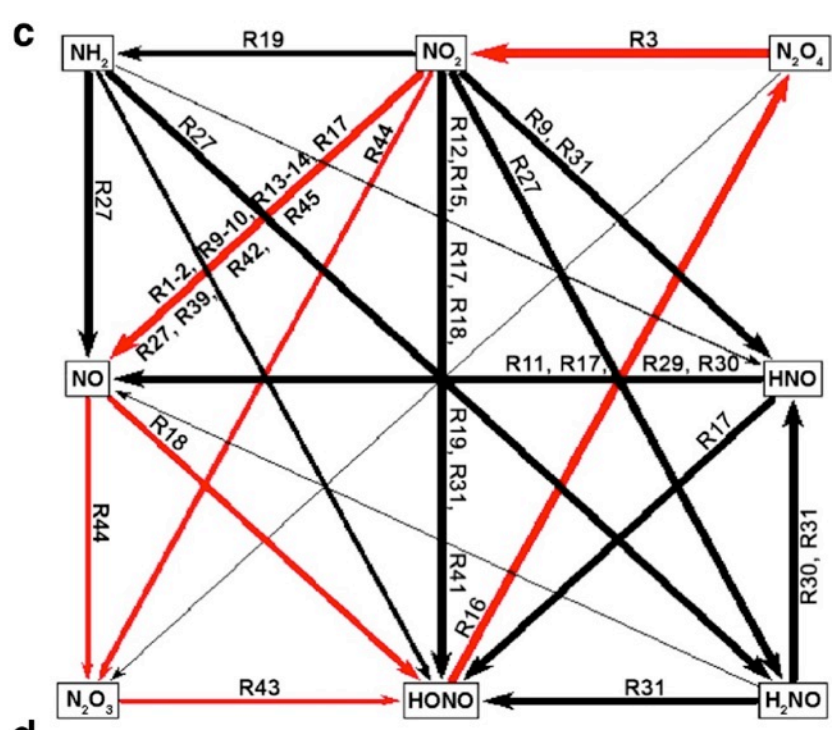

(e) NH_3
Concentration (mmol/mol AN)
Residence Time (sec)
Pressure (MPa)

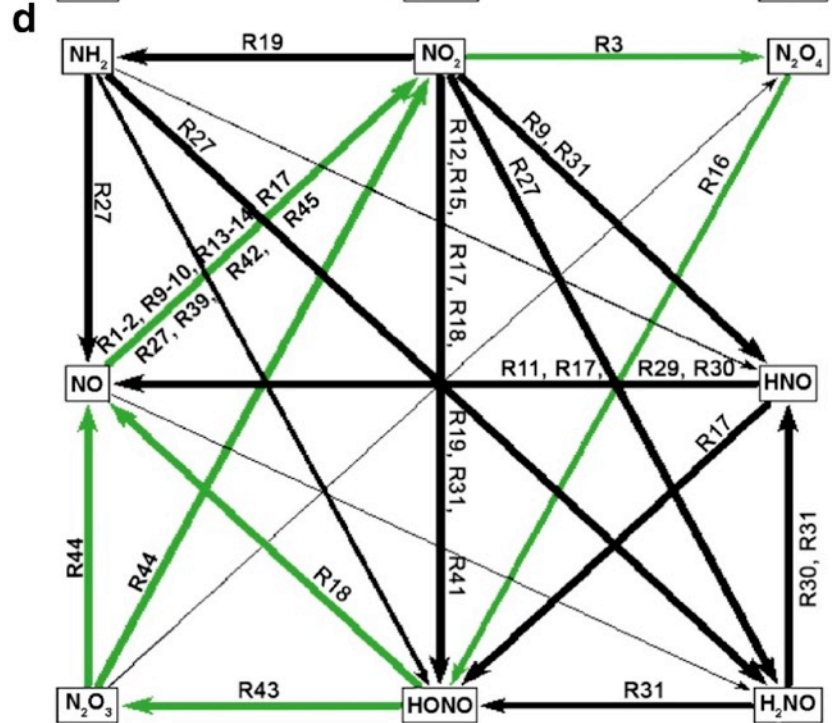

(f) N_2
Yield (%)
Residence Time (sec)
Pressure (MPa)

R1	$NO_2+NO_2 \leftrightarrow NO+NO+O_2$
R2	$NO_2+NO_2 \leftrightarrow NO+NO_3$
R3[a,b]	$N_2O_4(+M) \leftrightarrow NO_2+NO_2(+M)$
--	Low Pressure Limit:
R4	$NNH+M \leftrightarrow H+N_2+M$
R5	$N_2H_3+M \leftrightarrow H+N_2H_2+M$
R6	$N_2H_3+N_2H_3 \leftrightarrow NH_3+NH_3+N_2$
R7	$N_2H_3+N_2H_3 \leftrightarrow N_2H_2+N_2H_4$
R8[c]	$N_2H_4(+M) \leftrightarrow NH_2+NH_2(+M)$
-	Low Pressure Limit:
R9	$HNO+NO+NO \leftrightarrow HNNO+NO_2$
R10	$HNNO+NO \leftrightarrow NNH+NO_2$
R11	$HNNO+NO \leftrightarrow HNO+N_2O$
R12	$HNNO+NO_2 \leftrightarrow HONO+N_2O$
R13	$H+NO_2 \leftrightarrow NO+OH$
R14	$NO_2+OH \leftrightarrow HO_2+NO$
R15	$HO_2+NO_2 \leftrightarrow HONO+O_2$
R16	$H_2O+N_2O_4 \leftrightarrow HNO_3+HONO$
R17	$HNO+NO_2 \leftrightarrow HONO+NO$
R18	$HONO+HONO \leftrightarrow H_2O+NO+NO_2$
R19	$HONO+NH_2 \leftrightarrow NH_3+NO_2$
R20	$NO_2+OH+M \leftrightarrow HNO_3+M$
R21	$HO_2+NO+M \leftrightarrow HNO_3+M$
R22	$HNO_3+NH_2 \leftrightarrow NH_3+NO_3$
R23	$NH_3+OH \leftrightarrow H_2O+NH_2$
R24	$NH_2+NO \leftrightarrow NNH+OH$
R25	$NH_2+NO \leftrightarrow H_2O+N_2$
R26	$NH_2+NO_2 \leftrightarrow H_2O+N_2O$
R27	$NH_2+NO_2 \leftrightarrow H_2NO+NO$
R28	$N_2H_3+O_2 \leftrightarrow HO_2+N_2H_2$
R29	$N_2H_3+NO \leftrightarrow HNO+N_2H_2$
R30	$H_2NO+NO \leftrightarrow HNO+HNO$
R31	$H_2NO+NO_2 \leftrightarrow HNO+HONO$
R32	$CO+OH \leftrightarrow CO_2+H$
R33	$HNCO+H \leftrightarrow NH_2+CO$
R34	$HNCO+OH \leftrightarrow H_2O+NCO$
R35	$HNCO+NH_2 \leftrightarrow NH_3+NCO$
R36	$HNCO+NO_2 \leftrightarrow HNNO+CO_2$
R37	$NCO+NO \leftrightarrow N_2O+CO$
R38	$NCO+NO \leftrightarrow CO_2+N_2$
R39	$NCO+NO_2 \leftrightarrow NO+NO+CO$
R40	$NCO+NO_2 \leftrightarrow N_2O+CO_2$
R41	$NCO+HONO \leftrightarrow HNCO+NO_2$
R42	$NO_2+CO \leftrightarrow CO_2+NO$
R43	$H_2O+N_2O_3 \leftrightarrow HONO+HONO$
R44[d,e]	$NO+NO_2(+M) \leftrightarrow N_2O_3(+M)$
--	Low Pressure Limit:
R45	$N_2O+NO \leftrightarrow N_2+NO_2$









UAN Catalytic Combustion

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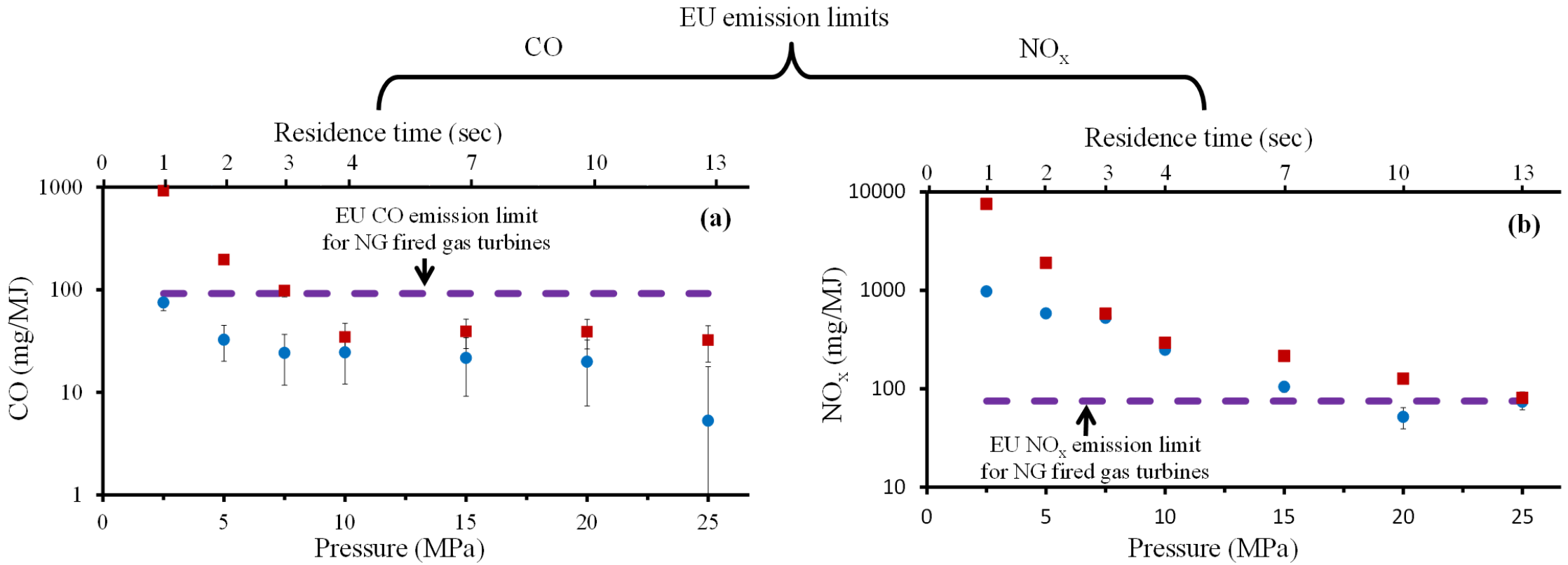
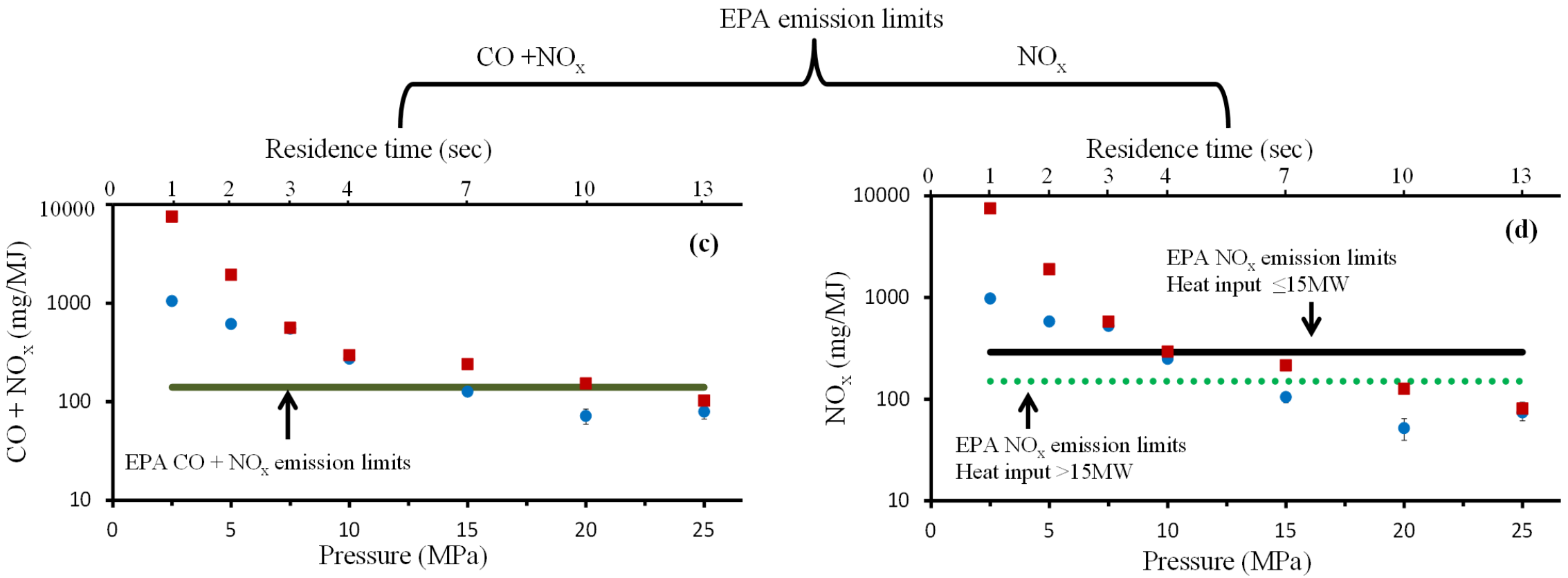
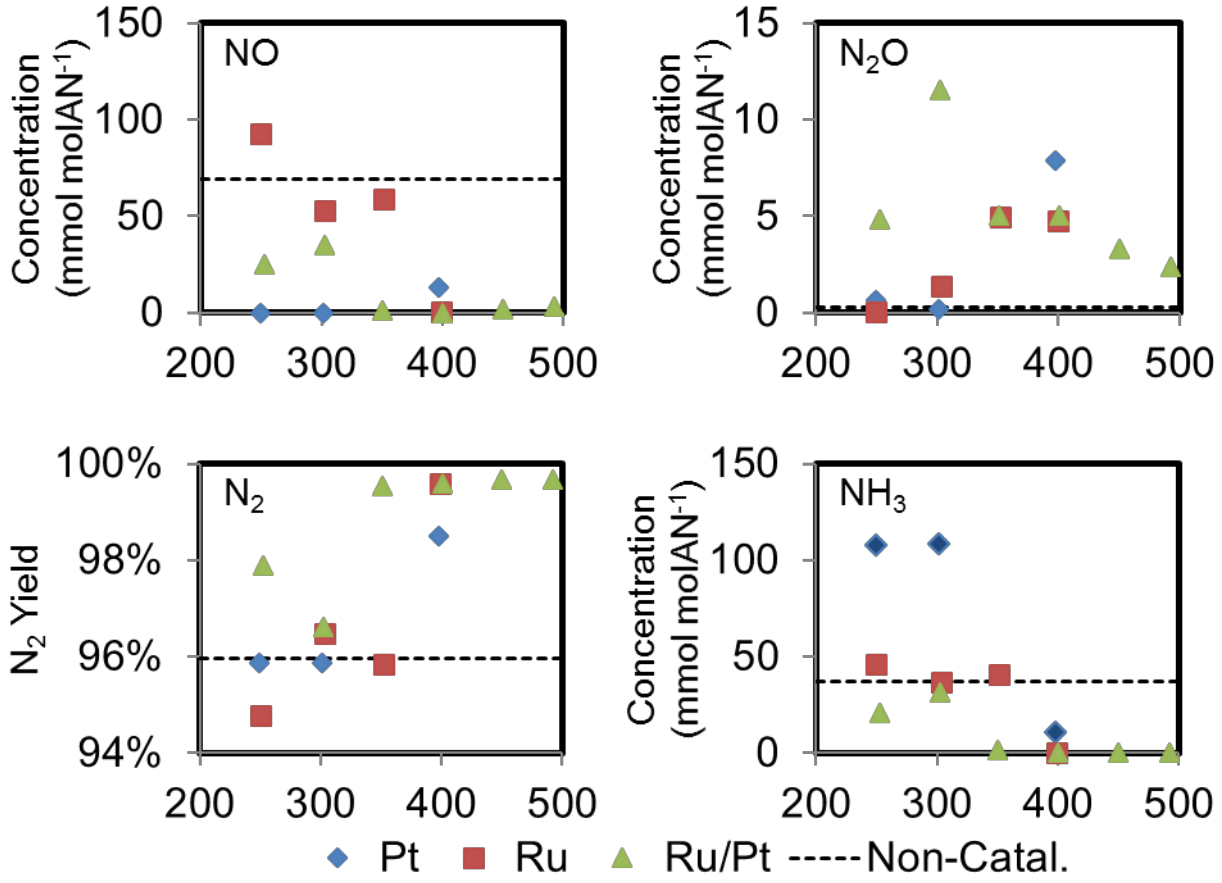


UAN Catalytic Combustion



UAN Catalytic Combustion



Liquid Flow Characterization

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$$Re = u \cdot d_H \cdot \rho / \mu = 2.659 \cdot 10^{-2}\ (m/s) \cdot 2.825 \cdot 10^{-3}\ (m) \cdot 1{,}330\ (kg/m^3) / 5.000 \cdot 10^{-3}\ (kg/m \cdot s) \cong 6.152$$

(Laminar) (Eq. S1)

Where: u - fluid velocity (m s^{-1}); d_H - hydraulic diameter (m); ρ - density (kg m^{-3}); μ - dynamic viscosity (kg m^{-1} s^{-1}).

The density of UAN was previously measured to be 1,330 kg m^{-3}

Viscosity values for UAN at different AN to urea ratios indicate strong interaction between the solutes (μ~5 kg m^{-1} s^{-1})

Gas Flow Characterization

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$$Q = n \cdot Z\downarrow m \cdot R \cdot T / P \quad (Eq. S2)$$

Where: $\dot{Q}$ - volumetric flow rate ($m^3\ s^{-1}$); $\dot{n}$ - mole flow rate ($mol\ s^{-1}$); Z_m - average compressibility factor; R - gas constant ($m^3\ MPa\ K^{-1}\ mol^{-1}$); T - temperature (K); P - pressure (MPa).

Table S1. Critical parameters for immediate decomposition/combustion products.

Assumption	Species	T_c (K)	P_c (MPa)	Mole Fraction
Decomposition products	HNCO	460.1	7.56	7.37%
	NH_3	405.5	11.3	29.5%
	HNO_3	520.0	6.89	22.1%
	H_2O	647.1	22.1	41.0%
Combustion Products	CO_2	304.2	7.38	5.39%
	N_2	126.2	3.40	21.6%
	H_2O	647.1	22.1	73.1%

Gas Flow Characterization

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Table S2. The ignition, peak and outlet temperatures at each working pressure

P (MPa)	T_{ig} (K)	T_{peak} (K)	T_{out} (K)
1	550	1,172	805
2.5	578	1,268	844
5	587	1,383	754
10	656	1,243	725
15	656	1,212	719

Table S4. Partial and average compressibility factors for the main combustion products, using Dalton's law.

P (MPa)	T (K)	Z_{CO_2}	Z_{N_2}	Z_{H_2O}	Z_m
1	550	1.00	1.01	0.97	0.98
1	1,172	1.00	1.01	1.00	1.00
1	805	1.00	1.01	1.00	1.00
2.5	578	1.00	1.01	0.94	0.96
2.5	1,268	1.01	1.02	1.00	1.00
2.5	844	1.01	1.02	0.99	1.00
5	587	0.99	1.01	0.87	0.91
5	1,383	1.02	1.02	1.00	1.01
5	754	1.00	1.02	0.96	0.98

Table S3. Partial and average compressibility factors for the immediate decomposition products, calculated using Dalton's law.

P (MPa)	T (K)	Z_{HNCO}	Z_{NH_3}	Z_{HNO}	Z_{H_2O}	Z_m
1	550	0.98	0.98	0.97	0.97	0.97
1	1,172	1.00	1.00	1.00	1.00	1.00
1	805	1.00	1.00	1.00	1.00	1.00
2.5	578	0.95	0.98	0.91	0.94	0.95
2.5	1,268	1.01	1.00	1.00	1.00	1.00
2.5	844	1.00	1.00	0.98	0.99	0.99
5	587	0.96	0.97	0.82	0.87	0.90
5	1,383	1.01	1.01	1.00	1.00	1.00
5	754	0.98	1.00	0.94	0.96	0.97

Gas Flow Characterization

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Table S5. Average compressibility factors for immediate decomposition/main combustion products calculated using Kay's law.

P (MPa)	T (K)	Z_m (Decomposition products)	Z_m (Combustion products)
5	587	0.90	0.94
5	1,383	1.00	1.00
5	754	0.97	0.98
10	656	0.88	0.92
10	1,243	1.00	1.00
10	725	0.92	0.94
15	656	0.82	0.87
15	1,212	1.00	1.00
15	719	0.88	0.91

Table S6. Volumetric gas flow rates and velocities at the investigated system conditions.

P (MPa)	T (K)	Decomposition products		Combustion products	
		Q (m^3 s^{-1})	u (m s^{-1})	Q (m^3 s^{-1})	u (m s^{-1})
1	550	3.34E-05	5.33	1.00E-04	16.0
1	1,172	7.32E-05	11.7	6.90E-05	11.0
1	805	5.03E-05	8.03	1.90E-05	3.02
2.5	578	1.37E-05	2.19	4.36E-05	6.95
2.5	1,268	3.17E-05	5.06	2.88E-05	4.59
2.5	844	2.09E-05	3.34	9.11E-06	1.45
5	587	6.59E-06	1.05	9.28E-06	1.48
5	1,383	1.73E-05	2.76	2.37E-05	3.78
5	754	9.14E-06	1.46	1.26E-05	2.01
10	656	3.61E-06	0.58	5.16E-06	0.82
10	1,243	7.77E-06	1.24	1.06E-05	1.70
10	725	4.17E-06	0.66	5.83E-06	0.93
15	656	2.24E-06	0.36	3.25E-06	0.52
15	1,212	5.05E-06	0.81	6.91E-06	1.10
15	719	2.64E-06	0.42	3.73E-06	0.60

Gas Flow Characterization

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$$\rho = m.w\downarrow av \cdot P/Z\downarrow m \cdot R \cdot T \quad (Eq. S3)$$

Where: ρ - density (kg m^{-3}); $m.w_{av}$ - average molecular weight (gr mol^{-1}); P - pressure (MPa); Z_m - average compressibility factor; R - gas constant (m^3 MPa K^{-1} mol^{-1}); T - temperature (K).

Table S7. Gas densities for immediate decomposition/main combustion products

P (MPa)	T (K)	Decomposition products	Combustion products
		ρ (kg m^{-3})	ρ (kg m^{-3})
1	550	6.64	4.81
1	1,172	3.03	2.21
1	805	4.41	3.22
2.5	578	16.2	11.7
2.5	1,268	7.00	5.09
2.5	844	10.6	7.70
5	587	33.6	23.9
5	1,383	12.8	9.35
5	754	24.3	17.6
10	656	61.5	43.0
10	1,243	28.6	20.9
10	725	53.3	38.1
15	656	99.0	68.2
15	1,212	43.9	32.1
15	719	84.2	59.5

Gas Flow Characterization

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$$\mu = 2.6693 \cdot 10^{-6} \sqrt{m.w \cdot T} / \sigma^2 \cdot \Omega_\mu \quad (Hirschfelder-Curtiss-Bird) \quad (Eq.\ S4)$$

Where: m.w - molecular weight (gr mol^{-1}); T - temperature (K); σ – collision diameter (Å); Ω_μ – viscosity collision integral.

Collision diameters were extracted from the literature where possible (H_2O - 2.65, N_2 - 3.68, CO_2 - 4.00) and calculated using the Brokaw relation for polar species (Eq. S5) in other cases (NH_3 - 2.04, HNO_3 - 2.49, HNCO - 3.20).

$$\sigma = (1.585 \cdot V_b / 1 + 1.13 \cdot \delta^2)^{1/3} \quad (\text{Brokaw Relation}) \quad (Eq.\ S5)$$

Where: σ – collision diameter (Å); V_b – atomic diffusion volume (cm^3 mol^{-1}); δ – polarity parameter.

Gas Flow Characterization

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$$\delta = 1940 \cdot \mu_p^2 / V_b \cdot T_b \quad (Eq.\ S6)$$

Where: δ – polarity parameter; μ_p – dipole moment (D); V_b – atomic diffusion volume ($cm^3\ mol^{-1}$); T_b – normal boiling temperature (K).

Atomic diffusion volumes were extracted from the literature where possible (NH_3 - 14.9, H_2O - 12.7) and calculated using the Fuller-Schettler-Giddings increment method in other cases (HNO_3 - 24.1, HNCO - 29.7).

Table S8. Viscosities of immediate decomposition/ main combustion products.

T (K)	μ_{H_2O} (Pa s)	μ_{N_2}(Pa s)	μ_{CO_2}(Pa s)	μ_{NH_3}(Pa s)	μ_{HNO_3}(Pa s)	μ_{HNCO}(Pa s)
550	2.95E-05	2.73E-05	2.49E-05	4.16E-05	2.44E-05	2.69E-05
1,172	5.48E-05	4.54E-05	4.29E-05	8.70E-05	5.25E-05	5.32E-05
805	4.04E-05	3.51E-05	3.28E-05	6.00E-05	3.55E-05	3.80E-05
578	3.07E-05	2.82E-05	2.58E-05	4.36E-05	2.56E-05	2.81E-05
1,268	5.78E-05	4.79E-05	4.52E-05	9.30E-05	5.65E-05	5.64E-05
844	4.20E-05	3.63E-05	3.39E-05	6.30E-05	3.73E-05	3.97E-05
587	3.11E-05	2.85E-05	2.61E-05	4.42E-05	2.60E-05	2.85E-05
1,383	6.09E-05	5.07E-05	4.77E-05	9.91E-05	6.07E-05	5.96E-05
754	3.82E-05	3.36E-05	3.12E-05	5.62E-05	3.32E-05	3.57E-05
656	3.40E-05	3.07E-05	2.82E-05	4.91E-05	2.89E-05	3.15E-05
1,243	5.71E-05	4.73E-05	4.47E-05	9.15E-05	5.55E-05	5.56E-05
725	3.70E-05	3.27E-05	3.03E-05	5.41E-05	3.19E-05	3.44E-05
656	3.40E-05	3.07E-05	2.82E-05	4.91E-05	2.89E-05	3.15E-05
1,212	5.61E-05	4.65E-05	4.39E-05	8.96E-05	5.42E-05	5.46E-05

Gas Flow Characterization

$$\mu_{mix} = \sum_{i=1}^{n} \frac{x_i \cdot \mu_i}{\sum_{j=1}^{n} x_j \cdot \phi_{ij}} \quad \text{(Wilke Formula)}$$

(Eq. S7)

Where: μ_{mix} – mixture viscosity (Pa s); x_i – molar fraction; ϕ_{ij} – empirical expression.

$$\phi_{ij} = \frac{\sqrt{\Omega_{\mu i}/\Omega_{\mu j}} \cdot \Omega_{\mu ij} \cdot \sigma_i \cdot \sigma_j}{\sqrt{\sigma_i^2 \cdot \Omega_{\mu i} \cdot \sigma_j^2 \cdot \Omega_{\mu j}}} \cdot \left(4 \cdot \frac{m.w_i \cdot m.w_j}{(m.w_i + m.w_j)^2}\right)^{0.25} \cdot \sqrt{\frac{m.w_j}{m.w_i}} \cdot \left[1 + \frac{m.w_i}{m.w_j} - \frac{(m.w_i/m.w_j)^{0.45}}{2 \cdot \left(1 + \frac{m.w_i}{m.w_j}\right)} + 1 + \frac{(m.w_i/m.w_j)^{0.45}}{1 + \left(4 \cdot \frac{m.w_i \cdot m.w_j}{(m.w_i + m.w_j)^2}\right)^{0.25}}\right]$$

(Eq. S9)

Where: ϕ_{ij} – empirical expression; Ω_{μ} – viscosity collision integral; $\Omega_{\mu ij}$ – viscosity collision integral of mixture; σ – collision diameter (Å); $m.w_i$ – molecular weight (gr mol^{-1}).

Gas Flow Characterization

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Table S9. Mixture viscosities of the immediate decomposition / main combustion products

T (K)	Decomposition Products	Combustion Products
	μ_{mix} (Pa s)	μ_{mix} (Pa s)
550	6.28E-05	6.62E-05
1,172	1.25E-04	1.16E-04
805	8.74E-05	8.80E-05
578	6.54E-05	6.86E-05
1,268	1.35E-04	1.23E-04
844	9.14E-05	9.12E-05
587	6.62E-05	6.95E-05
1,383	1.46E-04	1.30E-04
754	8.23E-05	8.37E-05
656	7.27E-05	7.54E-05
1,243	1.33E-04	1.21E-04
725	7.94E-05	8.12E-05
656	7.27E-05	7.54E-05
1,212	1.30E-04	1.19E-04
719	7.89E-05	8.07E-05

Table S10. Reynolds numbers and related data for the immediate decomposition/main combustion products mixtures.

T (K)	Decomposition Products				Combustion Products			
	u (m s^{-1})	ρ (kg m^{-3})	μ (Pa s)	Re	u (m s^{-1})	ρ (kg m^{-3})	μ (Pa s)	Re
550	5.33	6.64	6.28E-05	1,590	16.0	4.81	6.62E-05	3,280
1,172	11.7	3.03	1.25E-04	798	11.0	2.21	1.16E-04	592
805	8.03	4.41	8.74E-05	1,140	3.02	3.22	8.80E-05	312
578	2.19	16.2	6.54E-05	1,530	6.95	11.7	6.86E-05	3,350
1,268	5.06	7.00	1.35E-04	740	4.59	5.09	1.23E-04	537
844	3.34	10.6	9.14E-05	1,100	1.45	7.70	9.12E-05	346
587	1.05	33.6	6.62E-05	1,500	1.48	23.9	6.95E-05	1,440
1,383	2.76	12.8	1.46E-04	682	3.78	9.35	1.30E-04	768
754	1.46	24.3	8.23E-05	1,220	2.01	17.6	8.37E-05	1,190
656	0.58	61.5	7.27E-05	1,380	0.82	43.0	7.54E-05	1,320
1,243	1.24	28.6	1.33E-04	755	1.70	20.9	1.21E-04	830
725	0.66	53.3	7.94E-05	1,250	0.93	38.1	8.12E-05	1,230
656	0.36	99.0	7.27E-05	1,380	0.52	68.2	7.54E-05	1,330
1,212	0.81	43.9	1.30E-04	775	1.10	32.1	1.19E-04	838
719	0.42	84.2	7.89E-05	1,270	0.60	59.5	8.07E-05	1,250

Liquid Dispersion

The molecular diffusion coefficient of aqueous urea in water at the experimental concentration (3.32 M) is $1.1890 \cdot 10^{-9}$-$1.1425 \cdot 10^{-9}$ m^2 s^{-1}. While no data is available for aqueous AN, diffusion coefficient values for ammonium and nitrate ions in water are available ($1.86 \cdot 10^{-9}$ and $1.70 \cdot 10^{-9}$ m^2 s^{-1}, respectively). Therefore, average molecular diffusion on the order of **$1 \cdot 10^{-9}$-$2 \cdot 10^{-9}$ m^2 s^{-1}** was assumed.

Using the Taylor expression for the dispersion coefficient (Eq. S11), the dispersion value was estimated to be between 1,180-2,360 m^2 s^{-1}. Therefore the extent of dispersion ($D_{disp.} \cdot u^{-1} \cdot L^{-1}$), calculated using the fluid velocity, reactor length (0.8 m) and diffusion coefficient, was in the range of $4.70 \cdot 10^{-8}$-$9.40 \cdot 10^{-8}$.

$$D\downarrow disp.\uparrow Taylor = u\uparrow 2 \cdot d\downarrow H \uparrow 2 / 192 \cdot D\downarrow diff. \quad (Eq. S11)$$

Where: $D_{disp}{}^{Taylor}$ – Taylor's expression for the dispersion coefficient; u – fluid velocity (m s^{-1}); d_H – hydraulic diameter (m); D_{diff} – molecular mass diffusion coefficient (m^2 s^{-1}).

Gas Dispersion (Pair Diffusion)

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$$D\downarrow diff\downarrow AB = 0.001858 \cdot T\uparrow 1.5 \cdot \sqrt{\square}1/m.w\downarrow A + 1/m.w\downarrow B \; / P \cdot (\sigma\downarrow A + \sigma\downarrow B /2)\uparrow 2 \cdot \Omega\downarrow D\downarrow AB \quad (Eq. S12)$$

(Hirschfelder-Curtiss-Bird)

Where: D_{diff} – mass diffusion coefficient; T – temperature (K); m.w – molecular weight (gr mol^{-1}); P – pressure (atm); σ – pair collision diameter (Å); Ω_D – diffusion collision integral.

Table S11. Diffusion collision integrals and pair molecular mass diffusion coefficients for the main combustion products.

T (K)	P (atm)	N_2+CO_2		H_2O+CO_2		H_2O+N_2	
		Ω_D	D_{diff} (m^2 s^{-1})	Ω_D	D_{diff} (m^2 s^{-1})	Ω_D	D_{diff} (m^2 s^{-1})
550	9.87	0.875	4.55E-06	1.0547	5.83E-06	0.9558	7.66E-06
1,172	9.87	0.766	1.62E-05	0.8572	2.23E-05	0.7975	2.86E-05
805	9.87	0.805	8.77E-06	0.9515	1.15E-05	0.8595	1.51E-05
578	24.67	0.863	1.99E-06	1.0415	2.55E-06	0.9422	3.35E-06
1,268	24.67	0.751	7.43E-06	0.8410	1.02E-05	0.7896	1.30E-05
844	24.67	0.799	3.79E-06	0.9387	4.98E-06	0.8494	6.55E-06
587	49.35	0.860	1.02E-06	1.0373	1.31E-06	0.9379	1.72E-06
1,383	49.35	0.723	4.39E-06	0.8251	5.95E-06	0.7819	7.47E-06
754	49.35	0.814	1.57E-06	0.9693	2.04E-06	0.8743	2.69E-06
656	98.69	0.837	6.20E-07	1.0074	7.96E-07	0.9087	1.05E-06
1,243	98.69	0.755	1.79E-06	0.8449	2.47E-06	0.7915	3.14E-06
725	98.69	0.820	7.35E-07	0.9803	9.49E-07	0.8839	1.25E-06
656	148.04	0.837	4.13E-07	1.0074	5.31E-07	0.9087	7.00E-07
1,212	148.04	0.760	1.14E-06	0.8501	1.58E-06	0.7940	2.01E-06
719	148.04	0.821	4.84E-07	0.9824	6.24E-07	0.8857	8.24E-07

Gas Dispersion (Mix Diffusion)

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$$D\downarrow diff\downarrow mix=(\sum i=1\uparrow n\blacksquare x\downarrow i/D\downarrow diff\downarrow Ai)\uparrow-1 \quad (Eq.S13)$$

Where: $D_{diff,mix}$ – mixture mass diffusion coefficient; x_i – molar fraction; $D_{diff,Ai}$ – pair/mixture mass diffusion coefficient.

Table S12. Mixture mass diffusion coefficients for the main combustion products.

T (K)	H_2O+mix	N_2+mix	CO_2+mix	Mixture
	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})
550	2.68E-05	9.33E-06	5.79E-06	1.67E-05
1,172	1.00E-04	3.46E-05	2.17E-05	6.26E-05
805	5.27E-05	1.83E-05	1.13E-05	3.29E-05
578	1.17E-05	4.08E-06	2.53E-06	7.32E-06
1,268	4.58E-05	1.57E-05	9.97E-06	2.85E-05
844	2.29E-05	7.96E-06	4.91E-06	1.43E-05
587	6.02E-06	2.10E-06	1.30E-06	3.77E-06
1,383	2.64E-05	9.08E-06	5.82E-06	1.65E-05
754	9.38E-06	3.27E-06	2.02E-06	5.86E-06
656	3.66E-06	1.28E-06	7.90E-07	2.29E-06
1,243	1.11E-05	3.81E-06	2.41E-06	6.90E-06
725	4.37E-06	1.52E-06	9.41E-07	2.73E-06
656	2.44E-06	8.52E-07	5.27E-07	1.53E-06
1,212	7.08E-06	2.44E-06	1.54E-06	4.41E-06
719	2.87E-06	1.00E-06	6.19E-07	1.80E-06

Gas Dispersion (Polar Inter.)

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$$\Omega_{D,AB} = \Omega_{D,AB}^{0} + 0.196 \cdot \delta_{AB}^{2} / T_{AB}^{*} \quad (Eq. S14)$$

Where: Ω_D – diffusion collision integral; Ω_{D0} – diffusion collision integral parameter; δ – polarity parameter; T* – dimensionless temperature.

$$\Omega_{D,AB}^{0} = 1.06036 / T_{AB}^{*0.15610} + 0.19300 / e^{0.47635 \cdot T_{AB}^{*}} + 1.03587 / e^{1.52996 \cdot T_{AB}^{*}} + 1.76474 / e^{3.89411 \cdot T_{AB}^{*}} \quad (Eq. S15)$$

Where: Ω_{D0} – diffusion collision integral parameter; T* – dimensionless temperature.

Gas Dispersion (Pair Diffusion)

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Table S13. Molecular pair mass diffusion coefficients for the immediate decomposition products.

T (K)	$HNCO+NH_3$	$HNCO+HNO_3$	$HNCO+H_2O$	NH_3+HNO_3	NH_3+H_2O	HNO_3+H_2O
	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})
550	6.30E-06	3.32E-06	5.76E-06	5.76E-06	8.80E-06	5.34E-06
1,172	2.82E-05	1.52E-05	2.43E-05	2.77E-05	3.99E-05	2.46E-05
805	1.36E-05	7.24E-06	1.21E-05	1.28E-05	1.91E-05	1.17E-05
578	2.79E-06	1.47E-06	2.54E-06	2.56E-06	3.90E-06	2.37E-06
1,268	1.31E-05	7.06E-06	1.12E-05	1.30E-05	1.85E-05	1.15E-05
844	5.97E-06	3.18E-06	5.29E-06	5.66E-06	8.41E-06	5.15E-06
587	1.44E-06	7.62E-07	1.31E-06	1.32E-06	2.02E-06	1.23E-06
1,383	7.71E-06	4.16E-06	6.56E-06	7.71E-06	1.09E-05	6.76E-06
754	2.39E-06	1.27E-06	2.13E-06	2.24E-06	3.36E-06	2.05E-06
656	9.03E-07	4.78E-07	8.15E-07	8.36E-07	1.27E-06	7.71E-07
1,243	3.16E-06	1.70E-06	2.71E-06	3.12E-06	4.46E-06	2.76E-06
725	1.10E-06	5.85E-07	9.88E-07	1.03E-06	1.55E-06	9.46E-07
656	6.02E-07	3.19E-07	5.43E-07	5.57E-07	8.44E-07	5.14E-07
1,212	2.01E-06	1.08E-06	1.72E-06	1.98E-06	2.83E-06	1.75E-06
719	7.24E-07	3.84E-07	6.49E-07	6.76E-07	1.02E-06	6.21E-07

Gas Dispersion (Mix Diffusion)

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Table S14. Mixture mass diffusion coefficients for the immediate decomposition products.

T (K)	HNCO+mix	NH_3+mix	HNO_3+mix	H_2O+mix	Mixture
	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})	D_{diff} (m^2 s^{-1})
550	5.42E-06	1.03E-05	7.55E-06	1.14E-05	9.31E-06
1,172	2.39E-05	4.79E-05	3.46E-05	5.15E-05	4.24E-05
805	1.16E-05	2.27E-05	1.65E-05	2.48E-05	2.03E-05
578	2.40E-06	4.59E-06	3.35E-06	5.06E-06	4.13E-06
1,268	1.11E-05	2.23E-05	1.61E-05	2.39E-05	1.97E-05
844	5.09E-06	9.98E-06	7.25E-06	1.09E-05	8.91E-06
587	1.24E-06	2.37E-06	1.73E-06	2.61E-06	2.13E-06
1,383	6.49E-06	1.32E-05	9.49E-06	1.41E-05	1.16E-05
754	2.04E-06	3.97E-06	2.89E-06	4.34E-06	3.55E-06
656	7.73E-07	1.49E-06	1.09E-06	1.64E-06	1.34E-06
1,243	2.66E-06	5.37E-06	3.87E-06	5.76E-06	4.74E-06
725	9.43E-07	1.83E-06	1.33E-06	2.00E-06	1.64E-06
656	5.16E-07	9.95E-07	7.26E-07	1.09E-06	8.93E-07
1,212	1.69E-06	3.41E-06	2.46E-06	3.66E-06	3.01E-06
719	6.19E-07	1.20E-06	8.75E-07	1.32E-06	1.08E-06

Gas Dispersion (Coefficient)

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$$D_{disp.}^{Aris} = D_{diff.} + u^2 \cdot d_H^2 / 192 \cdot D_{diff.} \quad (Eq. S16)$$

Where: D_{disp}^{Taylor} – Taylor's expression for the dispersion coefficient; D_{diff} – molecular mass diffusion coefficient ($m^2\ s^{-1}$); u – fluid velocity ($m\ s^{-1}$); d_H – hydraulic diameter (m).

Table S15. Bodenstein numbers, appropriate dispersion expressions, dispersion coefficient values and extents of dispersion for the immediate decomposition and main combustion products.

T (K)	Decomposition Products				Combustion Products			
	Bo	Expres.	D_{disp} ($m^2\ s^{-1}$)	D_{disp} uL^{-1}	Bo	Expres.	D_{disp} ($m^2\ s^{-1}$)	D_{disp} uL^{-1}
550	64.7	Taylor	1.44E-01	0.034	76.6	Taylor	5.11E-01	0.040
1,172	29.2	Aris	1.74E-01	0.019	14.1	Aris	1.27E-01	0.014
805	43.6	Taylor	1.46E-01	0.023	7.35	Aris	4.22E-02	0.017
578	59.7	Taylor	5.45E-02	0.031	76.0	Taylor	2.20E-01	0.040
1,268	26.9	Aris	7.18E-02	0.018	12.9	Aris	5.32E-02	0.014
844	41.1	Aris	6.37E-02	0.024	8.14	Aris	1.92E-02	0.017
587	55.5	Taylor	2.43E-02	0.029	31.4	Aris	2.32E-02	0.020
1,383	24.7	Aris	3.73E-02	0.017	18.4	Aris	4.54E-02	0.015
754	45.5	Taylor	2.76E-02	0.024	27.4	Aris	2.89E-02	0.018
656	48.1	Taylor	1.15E-02	0.025	28.8	Aris	1.22E-02	0.018
1,243	27.5	Aris	1.78E-02	0.018	19.7	Aris	2.08E-02	0.015
725	45.1	Taylor	1.25E-02	0.023	27.2	Aris	1.33E-02	0.018
656	44.8	Taylor	6.68E-03	0.023	27.2	Aris	7.41E-03	0.018
1,212	28.2	Aris	1.17E-02	0.018	20.0	Aris	1.36E-02	0.015
719	43.5	Taylor	7.62E-03	0.023	26.5	Aris	8.37E-03	0.018

Fitting (NH_2+NO→PRODUCTS)

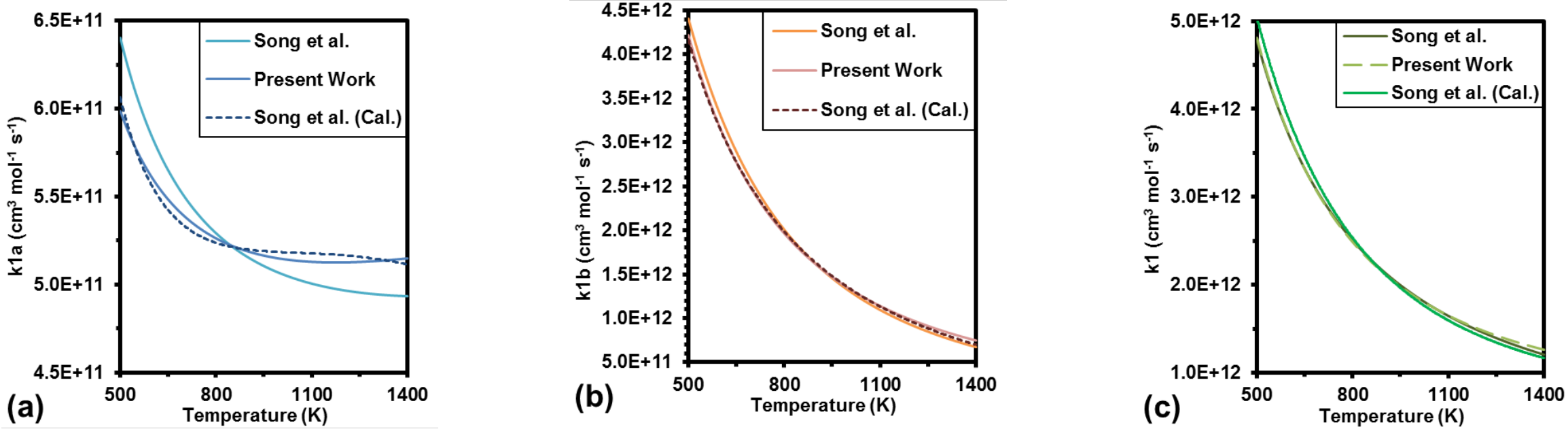

Figure S1. The reaction rates from the overall reaction kinetic data by Song et al., the individual reaction kinetic data by Song et al. (calculated), and those fitted in this work as a function of temperature for the reactions: (a) NH_2+NO=NNH+NO, (b) NH_2+NO=N_2+H_2O and (c) NH_2+NO=Products.

Fitting ($NH_2+NO \rightarrow PRODUCTS$)

The reaction rates proposed by Song et al. for reactions RS1a and RS2b had $R^2=0.1818$ and $R^2=0.9919$, respectively, at 500K–1400K. Therefore, the kinetic data for RS1a and RS1b was refitted to the modified Arrhenius equation: $\mathbf{k_{1a}=4.10\cdot10^{10}\cdot T^{0.313}\cdot exp(368\cdot T^{-1})}$ and $\mathbf{k_{1b}=7.16\cdot10^{17}\cdot T^{-1.886}\cdot exp(-161\cdot T^{-1})}$. These kinetic constants resulted in an average absolute error of 1.00% $R^2=0.9995$ for the overall reaction rate, and $R^2=0.9671$ and $R^2=0.9994$ for RS1a and RS1b, respectively, at 500K–1400K.

Reactor Temperature

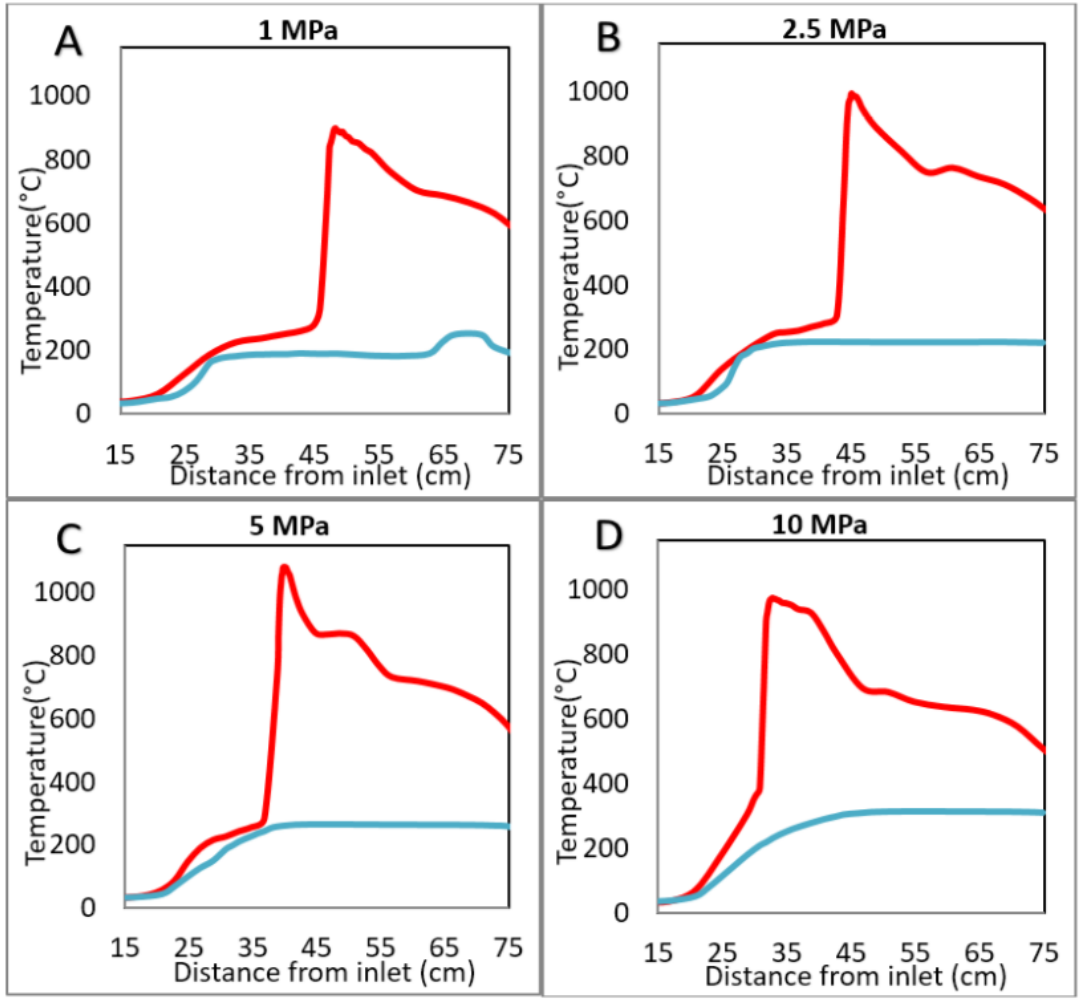

Figure S5. Fuel (red) vs water (blue) temperature profile comparison at (A) 1 MPa, (B) 2.5 MPa, (C) 5 MPa and (D) 10 MPa.

Sensitivity Analyses (React.)

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HNCO			Pressure		
Reaction	1 MPa	2.5 MPa	5 MPa	10 MPa	15 MPa
(R5) $HNCO+H_2O=NH_3+CO_2$	-4.43E+00	-4.84E+00	-4.12E+00	-4.75E+00	-6.12E+00
(R12) $NH_3+OH=H_2O+NH_2$	-1.41E-01	-6.64E-01	-9.34E-01	-7.41E-01	-1.79E+00
(R13) $HONO+NH_2=NH_3+NO_2$	2.40E-01	-6.63E-01	-6.39E-01	-1.27E+00	-2.29E+00

HNO_3			Pressure		
Reaction	1 MPa	2.5 MPa	5 MPa	10 MPa	15 MPa
(R13) $HONO+NH_2=NH_3+NO_2$	-4.43E+00	-4.84E+00	-4.12E+00	-4.75E+00	-6.12E+00
(R27) $HO_2+NO+M=HNO_3+M$	-1.76E+01	-3.13E+01	-2.86E+01	-2.60E+01	-2.05E+01

NH_3			Pressure		
Reaction	1 MPa	2.5 MPa	5 MPa	10 MPa	15 MPa
(R13) $HONO+NH_2=NH_3+NO_2$	-1.17E+00	-1.68E+00	-1.70E+00	-2.52E+00	-3.72E+00
(R12) $NH_3+OH=H_2O+NH_2$	-6.71E-01	-6.49E-01	-9.27E-01	-7.56E-01	-8.44E-01
(R24) $NH_2+NO=NNH+OH$	-3.89E-01	-4.32E-01	-1.14E+00	-1.28E+00	-1.79E+00
(R25) $HNO+OH=H_2O+NO$	2.93E-01	3.47E-01	4.95E-01	5.74E-01	4.74E-01
(R26) $H_2NO+NO=2HNO$	-2.73E-01	-4.92E-01	-5.28E-01	-4.29E-01	-3.27E-01
(R27) $HO_2+NO+M=HNO_3+M$	-2.61E-01	-2.88E-01	-2.94E-01	-4.21E-01	-6.19E-01

Sensitivity Analyses (Prod.)

Technion
Israel Institute of Technology

N_2			Pressure		
Reaction	1 MPa	2.5 MPa	5 MPa	10 MPa	15 MPa
(R5) $HNCO+H_2O=NH_3+CO_2$	4.92E+02	9.67E+02	6.50E+02	-1.94E+04	1.84E+04

H_2O			Pressure		
Reaction	1 MPa	2.5 MPa	5 MPa	10 MPa	15 MPa
(R13) $HONO+NH_2=NH_3+NO_2$	4.32E-01	6.86E-01	7.33E-01	1.49E+00	2.99E+00
(R27) $HO_2+NO+M=HNO_3+M$	9.67E-02	1.18E-01	1.27E-01	2.58E-01	4.97E-01
(R24) $NH_2+NO=NNH+OH$	5.71E-02	6.92E-02	6.24E-02	6.13E-02	5.34E-02

CO_2			Pressure		
Reaction	1 MPa	2.5 MPa	5 MPa	10 MPa	15 MPa
(R5) $HNCO+H_2O=NH_3+CO_2$	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
(R13) $HONO+NH_2=NH_3+NO_2$	2.49E-01	-5.19E-01	-5.63E-01	-1.17E+00	-2.17E+00

$$\rho u A \frac{dY_k}{dx} = W_k \omega_k A$$

$$\omega_k = \sum_i \nu_{ki} q_i$$

$$k_{fi} = A_i T^{\beta_i} \exp\left(\frac{-E_i}{RT}\right)$$

$$k_{ri} = k_{fi} / K_{ci} = k_{fi} / K_{pi} \left(\frac{P_{atm}}{RT}\right)^{\sum_{k=1}^{K} \nu_{ki}}$$

$$K_{pi} = \exp\left(\frac{-\Delta_r G^o}{RT}\right) = \exp\left(\frac{\Delta S_i^o}{R} - \frac{\Delta H_i^o}{RT}\right)$$

$$\rho u A \left(\sum_{k=1}^{K} h_k \frac{dY_k}{dx} + C_p \frac{dT}{dx} + u\frac{du}{dx}\right) = -a_e Q_e \qquad \frac{\Delta S_i^o}{R} = \sum_{k=1}^{K} \nu_{ki} S_k^o / R \quad \frac{\Delta H_i^o}{RT} = \sum_{k=1}^{K} \nu_{ki} H_k^o / RT$$

h_k-specific enthalpy of species k, C_p-mean heat capacity per unit of mass of the gas, a_e-surface area per unit of length of wall, Q_e - heat flux from wall temperature

$$C\downarrow pk\uparrow o /R = a\downarrow 1k + a\downarrow 2k\, T\downarrow k + a\downarrow 3k\, T\downarrow k \uparrow 2 + a\downarrow 4k\, T\downarrow k \uparrow 3 + a\downarrow 5k\, T\downarrow k \uparrow 4$$

$$H\downarrow k\uparrow o /RT\downarrow k = a\downarrow 1k + a\downarrow 2k /2\, T\downarrow k + a\downarrow 3k /3\, T\downarrow k \uparrow 2 + a\downarrow 4k /4\, T\downarrow k \uparrow 3 + a\downarrow 5k /5\, T\downarrow k \uparrow 4 + a\downarrow 6k /T\downarrow k$$

$$S\downarrow k\uparrow o /R = a\downarrow 1k\, lnT\downarrow k + a\downarrow 2k\, T\downarrow k + a\downarrow 3k /2\, T\downarrow k \uparrow 2 + a\downarrow 4k /3\, T\downarrow k \uparrow 3 + a\downarrow 5k /4\, T\downarrow k \uparrow 4 + a\downarrow 7k$$

$$S\downarrow k\uparrow o = \int 298 \uparrow T\downarrow k \, \square C\downarrow pk\uparrow o / T\, dT + S\downarrow k\uparrow o\,(0)$$

$$H\downarrow k\uparrow o = \int 0 \uparrow T\downarrow k \, \square C\downarrow pk\uparrow o \, dT + H\downarrow k\uparrow o\,(0)$$