Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia

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Supplementary Material

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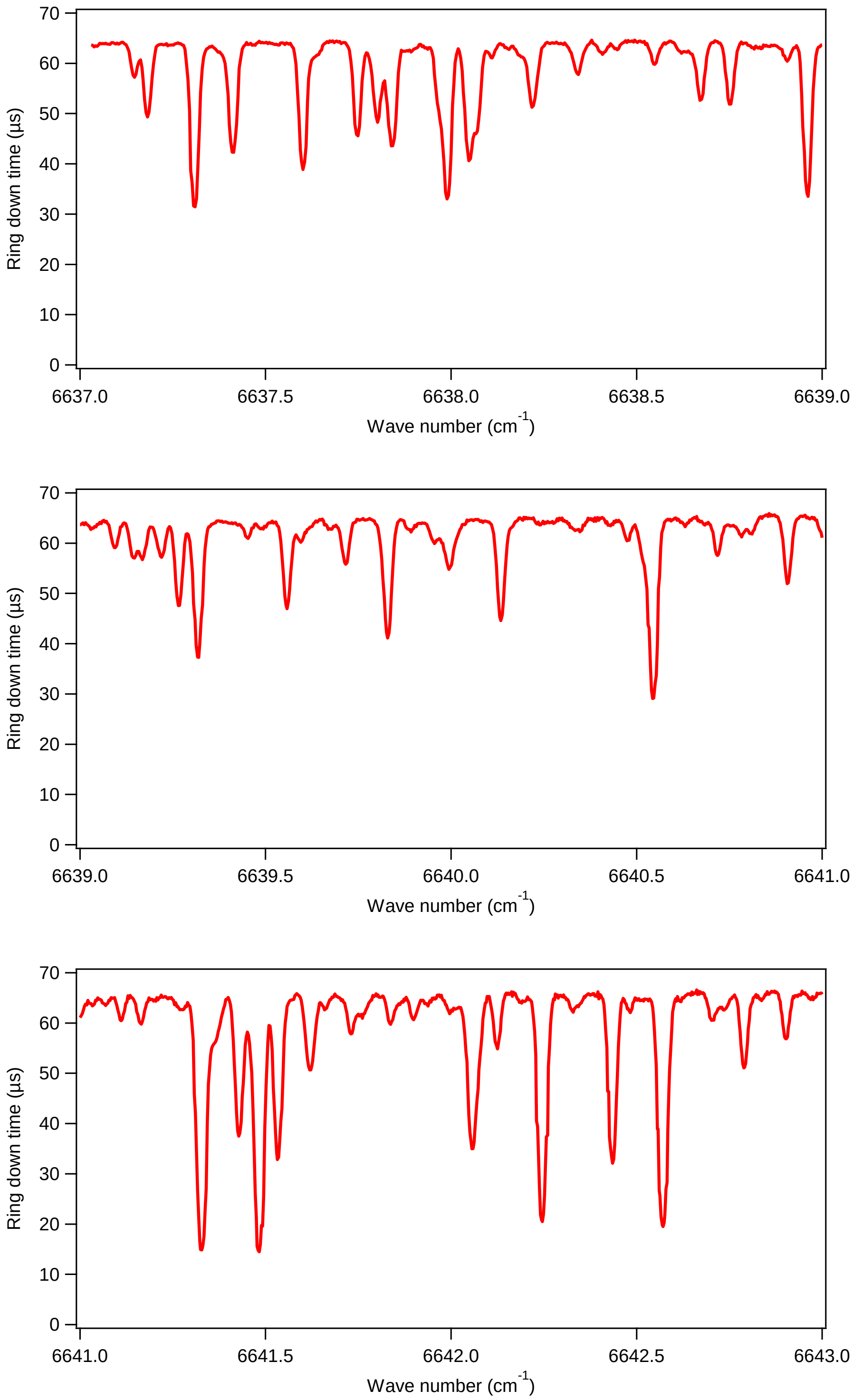
1 Ammonia CRDS infrared spectrum



CRDS infrared spectrum recorded during the oxidation of ammonia under unreactive conditions (φ = 1, 500 K) over the range 6637-6643 cm^{-1}.

2 Validation of the kinetic mechanism

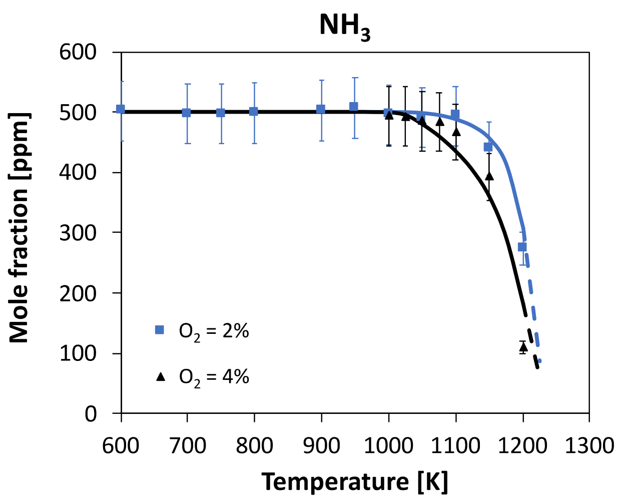
2.1 Jet Stirred Reactor

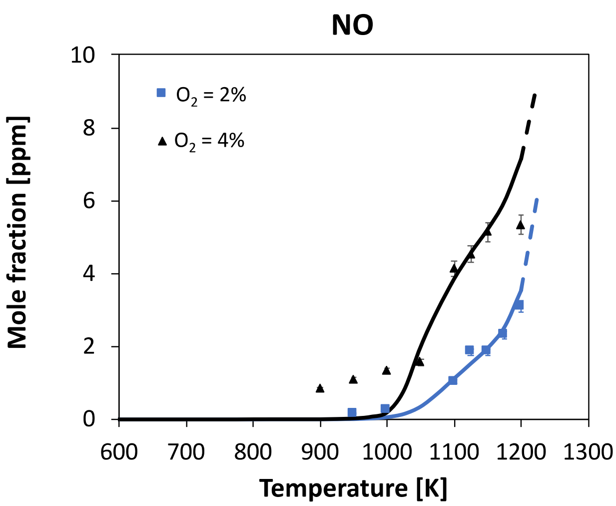
2.1.1 Present work

<u>Type</u>: isothermal Jet Stirred reactor

<u>Model</u>: Isothermal Perfectly-Stirred reactor

- 500 ppm NH_3 – 2-4% O_2
- Balance gas: He
- P = 800 torr
- τ = 1.5 s



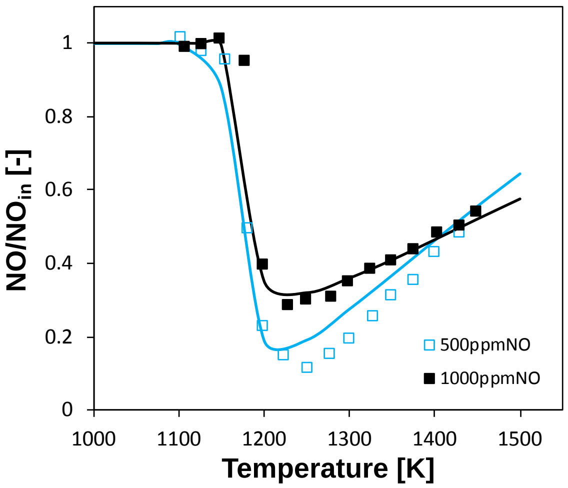


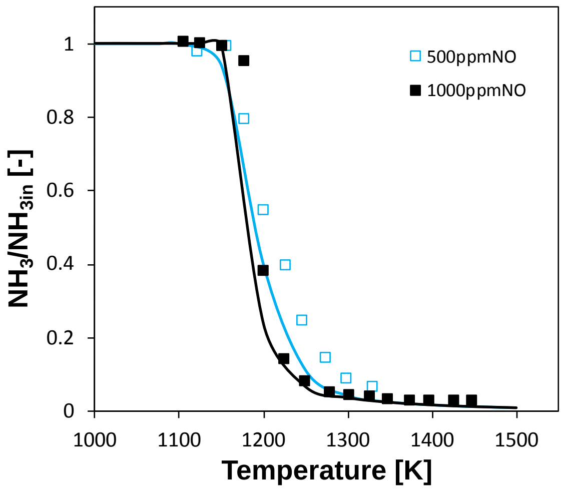
2.1.2 Dagaut et al. [1]

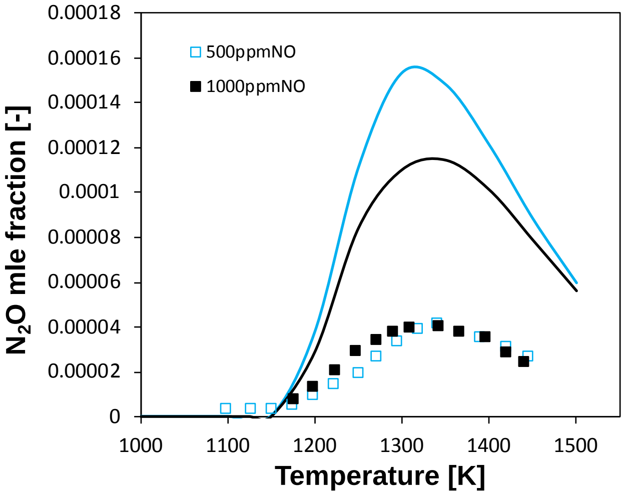
<u>Type</u>: Isothermal Jet Stirred reactor

<u>Model</u>: Isothermal Perfectly-Stirred reactor

- 1000 ppm NH_3 – 12500 ppm O_2 – 500-1000 ppm NO
- Balance gas: N_2
- P = 800 torr
- τ = 0.1 s







2.1.3 Rota et al. [2]

Type: isothermal Jet Stirred reactor

Model: Isothermal Perfectly-Stirred reactor

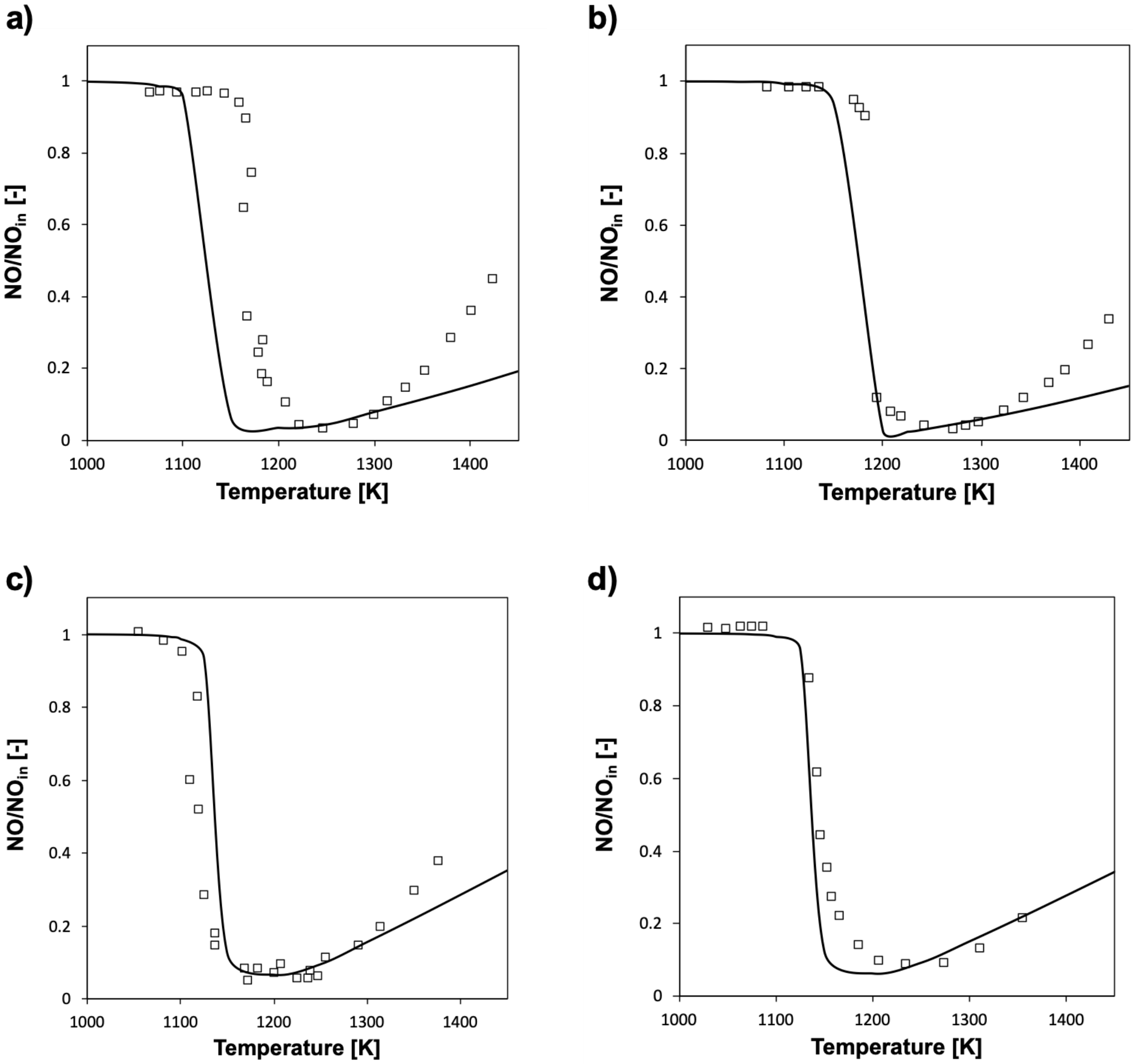
- Balance gas: N_2
- P = 1 atm
- $\tau = \frac{374}{T[K]}$ [s]

a) 7200 ppm NH_3 – 3000 ppm NO – 6000 ppm O_2

b) 7200 ppm NH_3 – 3000 ppm NO – 2000 ppm O_2

c) 1920 ppm NH_3 – 800 ppm NO – 2000 ppm O_2

d) 1920 ppm NH_3 – 800 ppm NO – 1600 ppm O_2


a)
b)
c)
d)
NO/NO$_{in}$ [-]
Temperature [K]
0
0.2
0.4
0.6
0.8
1
1000
1100
1200
1300
1400

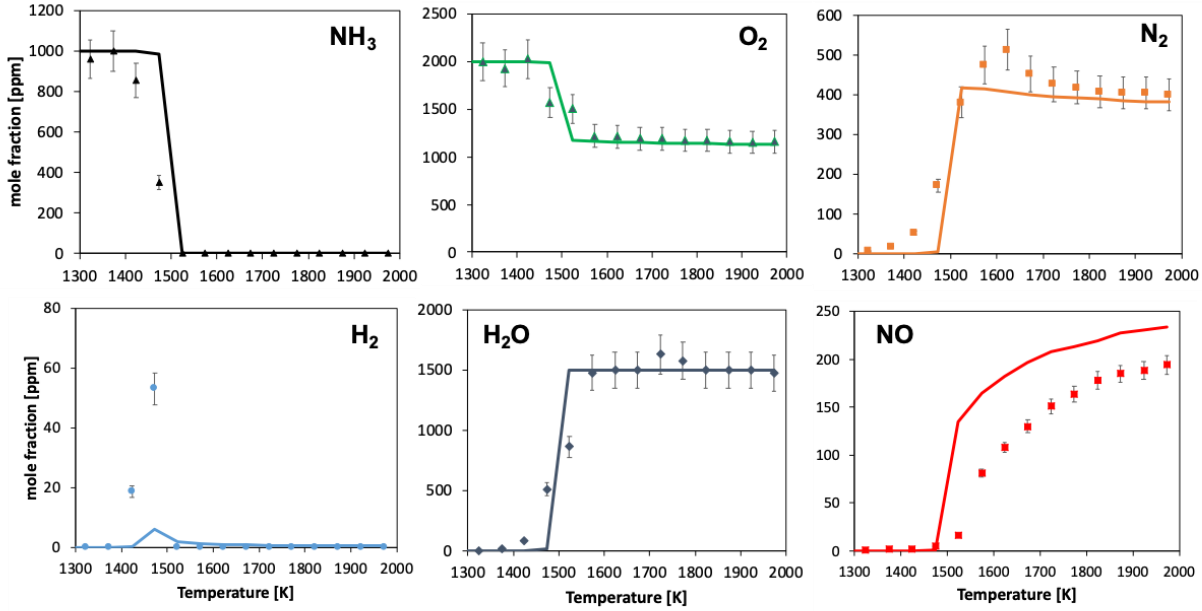
2.2 Flow reactor

2.2.1 Present work

<u>Type</u>: Flow reactor with assigned temperature profile

<u>Model</u>: Plug-flow reactor with assigned temperature profile

- 1000 ppm NH_3 – 2000 ppm O_2
- Balance gas: He
- P = 925 torr
- τ = 50 ms (in the reactive zone)

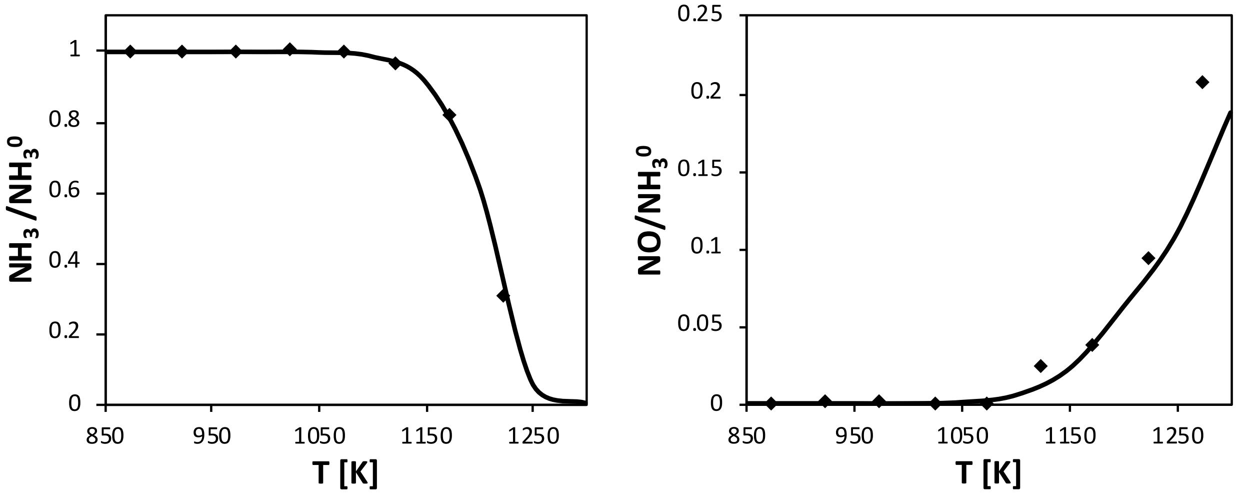


2.2.2 Wargadalam et al. [3]

Type: Isothermal flow reactor

Model: Isothermal Plug-flow reactor

- 242 ppm NH_3 – 10 % O_2
- Balance gas: N_2
- P = 1 atm
- $\tau = 339/T[K]$ s



2.2.3 Song et al. [4]

Type: Flow reactor with assigned temperature profile

Model: Plug-flow reactor with assigned temperature profile

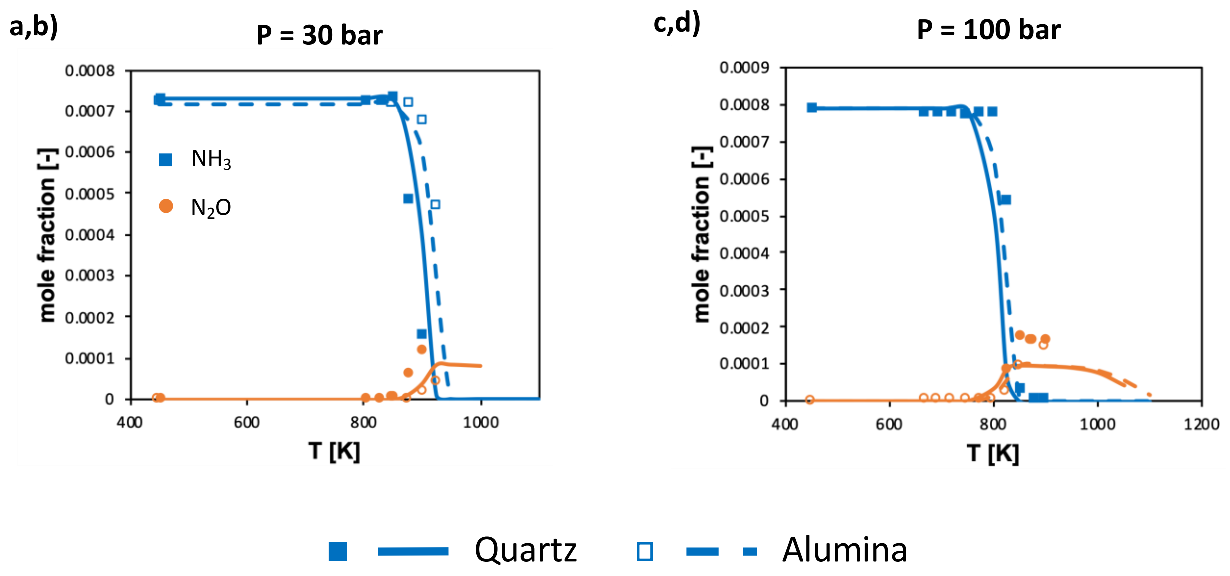
- Balance gas: He

a) P = 30 bar – 729 ppm NH_3 – 3.95% O_2 – $\tau = \frac{3100}{T[K]}$ [s] (in the reactive zone) – Quartz

b) P = 30 bar – 719 ppm NH_3 – 4.03% O_2 – $\tau = \frac{1984}{T[K]}$ [s] (in the reactive zone) – Alumina

c) P = 100 bar – 789 ppm NH_3 – 4.07% O_2 – $\tau = \frac{10330}{T[K]}$ [s] (in the reactive zone) – Quartz

d) P = 100 bar – 789 ppm NH_3 – 4.07% O_2 – $\tau = \frac{6610}{T[K]}$ [s] (in the reactive zone) – Alumina

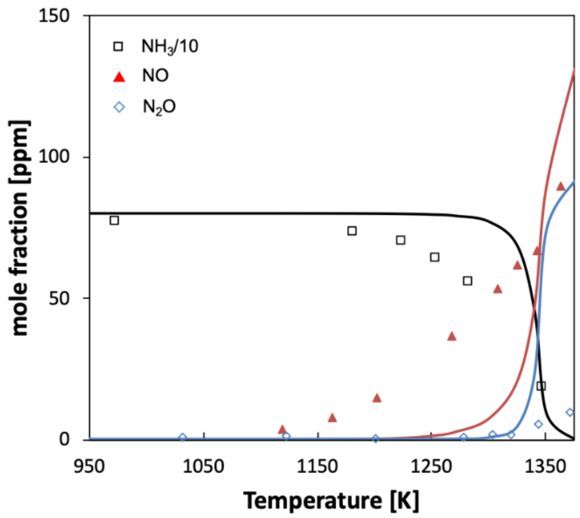


2.2.4 Hulgaard and Dam-Johansen [5]

Type: Isothermal flow reactor

Model: isothermal plug-flow reactor

- 800 ppm NH_3 – 2.5 % O_2
- Balance gas: N_2
- P = 106 kPa
- $\tau = 71/T[K]$ s



2.3 Shock tube

2.3.1 Davidson et al. [6]

Model: constant-volume batch reactor

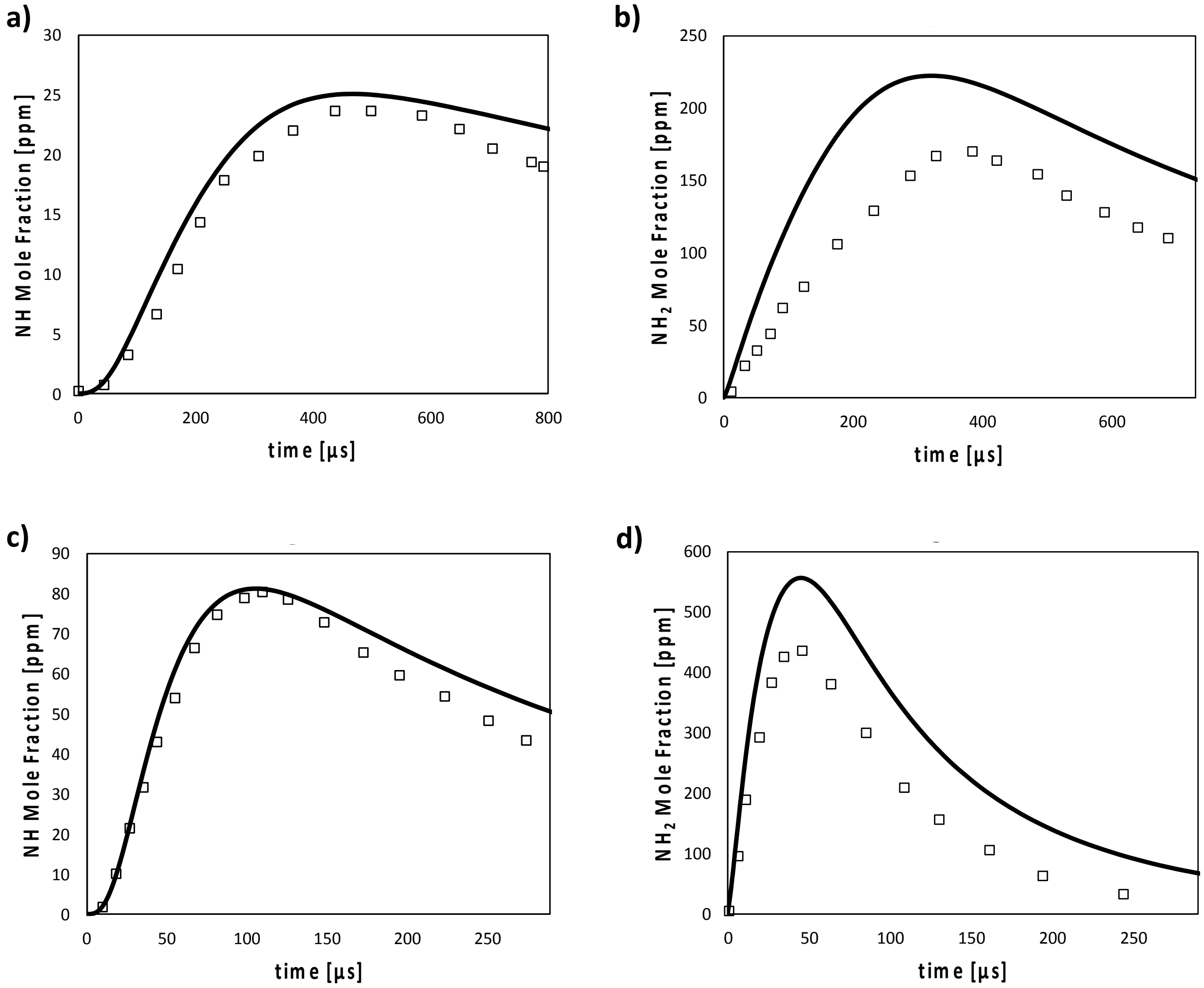
- Ammonia pyrolysis
- Balance gas: Ar

a) T = 2294 K – P = 0.986 atm – 3000 ppm NH_3

b) T = 2301 K – P = 1.028 atm – 2700 ppm NH_3

c) T = 2652 K – P = 0.876 atm – 3000 ppm NH_3

d) T = 2781 K – P = 0.902 atm – 2700 ppm NH_3


a)
NH Mole Fraction [ppm]
time [µs]
0
5
10
15
20
25
30
0
200
400
600
800
b)
NH2 Mole Fraction [ppm]
time [µs]
0
50
100
150
200
250
0
200
400
600
c)
NH Mole Fraction [ppm]
time [µs]
0
10
20
30
40
50
60
70
80
90
0
50
100
150
200
250
d)
NH2 Mole Fraction [ppm]
time [µs]
0
100
200
300
400
500
600
0
50
100
150
200
250

2.3.2 Mathieu and Petersen [7]

Model: constant-volume batch reactor

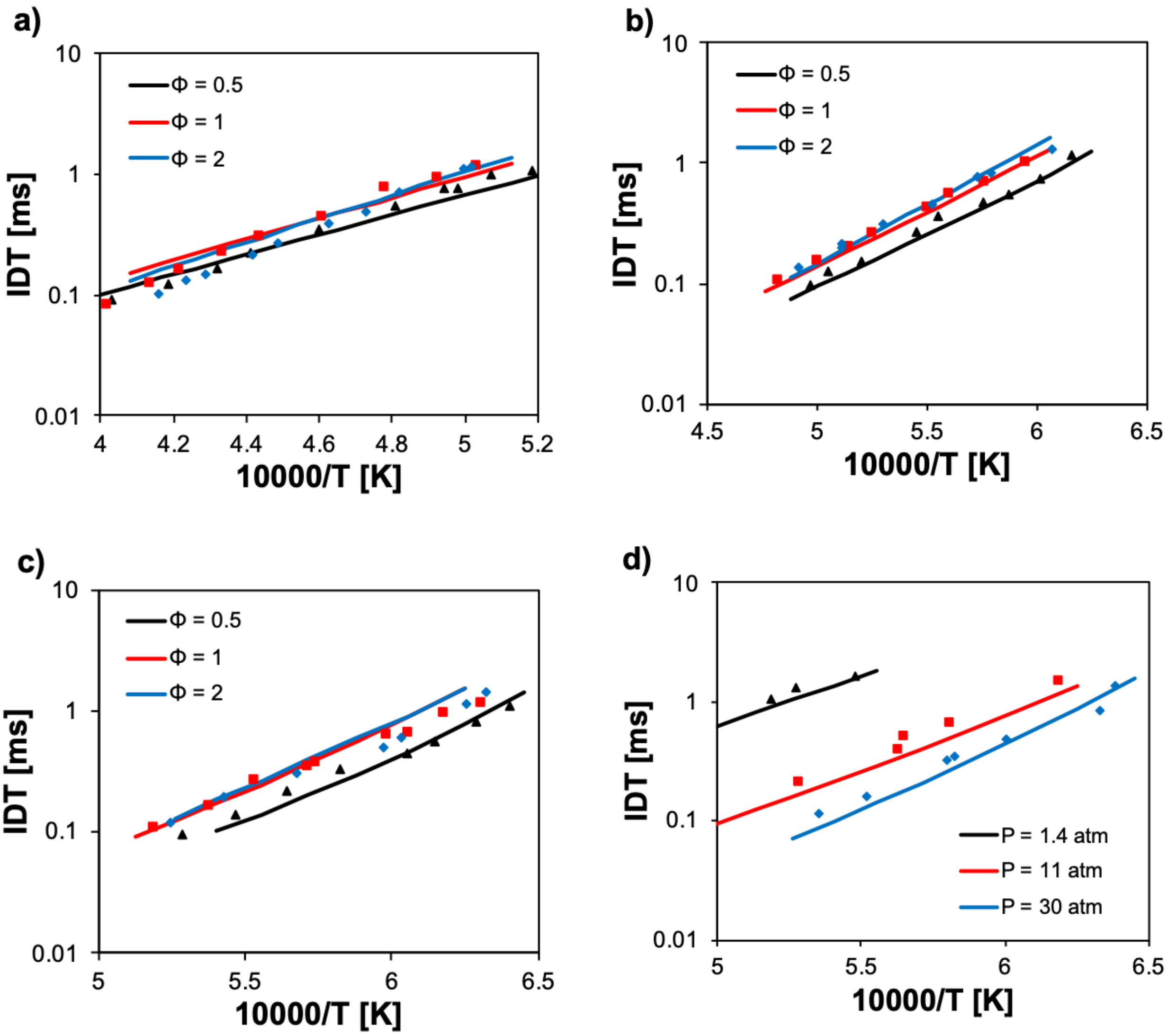
- Balance gas: Ar

  a) P = 1.4 atm – 99% Ar

  b) P = 11 atm – 99% Ar

  c) P = 30 atm – 99% Ar

  d) ϕ = 1 – 98 % Ar


a)
b)
c)
d)
IDT [ms]
10000/T [K]
Φ = 0.5
Φ = 1
Φ = 2
P = 1.4 atm
P = 11 atm
P = 30 atm

2.3.3 Shu et al. [8]

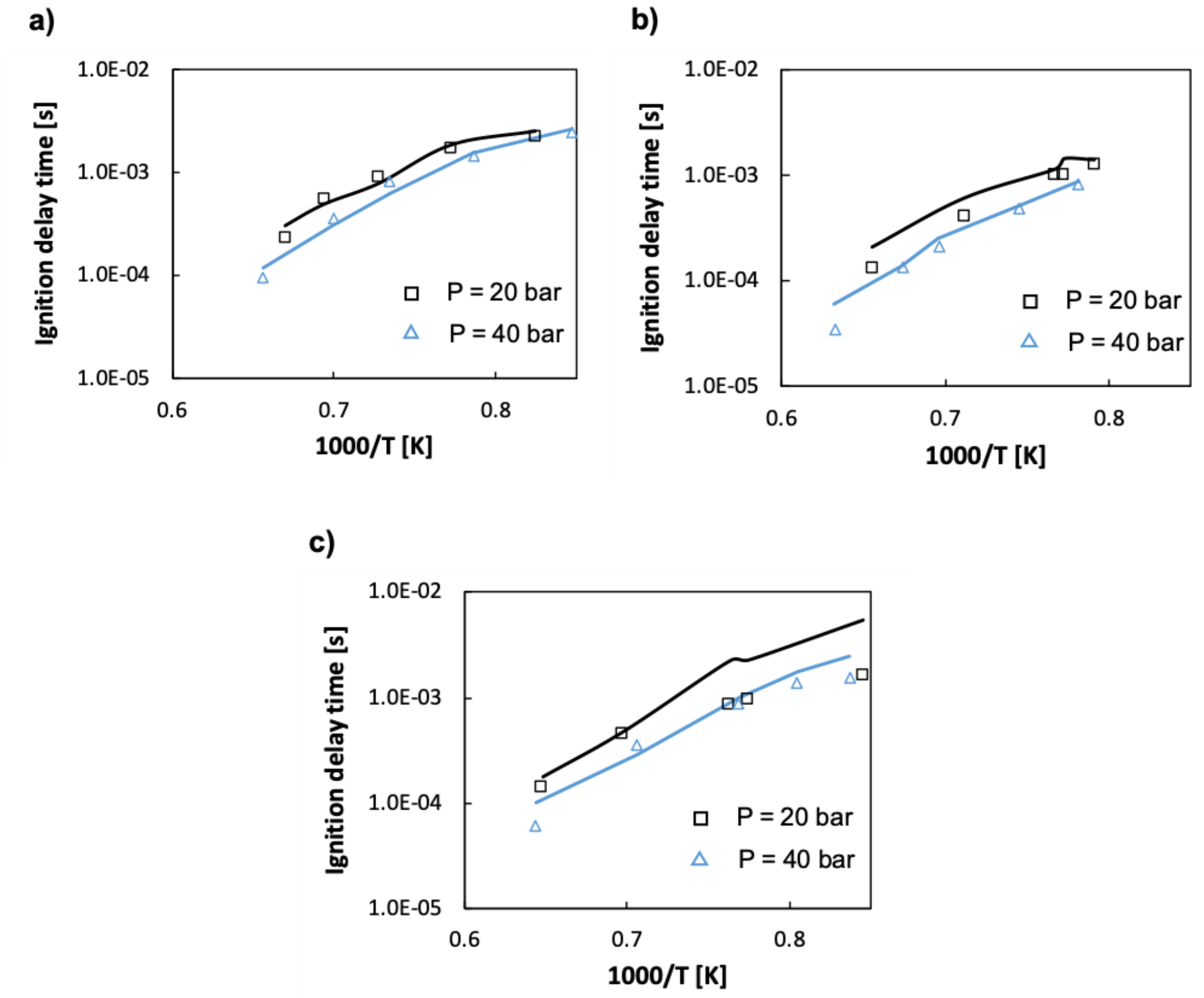
<u>Model</u>: Batch reactor with assigned volume profile (converted from experimental pressure trace)

- NH_3/Air

  a) ϕ = 0.5 – P = 20-40 bar

  b) ϕ = 1 – P = 20-40 bar

  c) ϕ = 2 – P = 20-40 bar

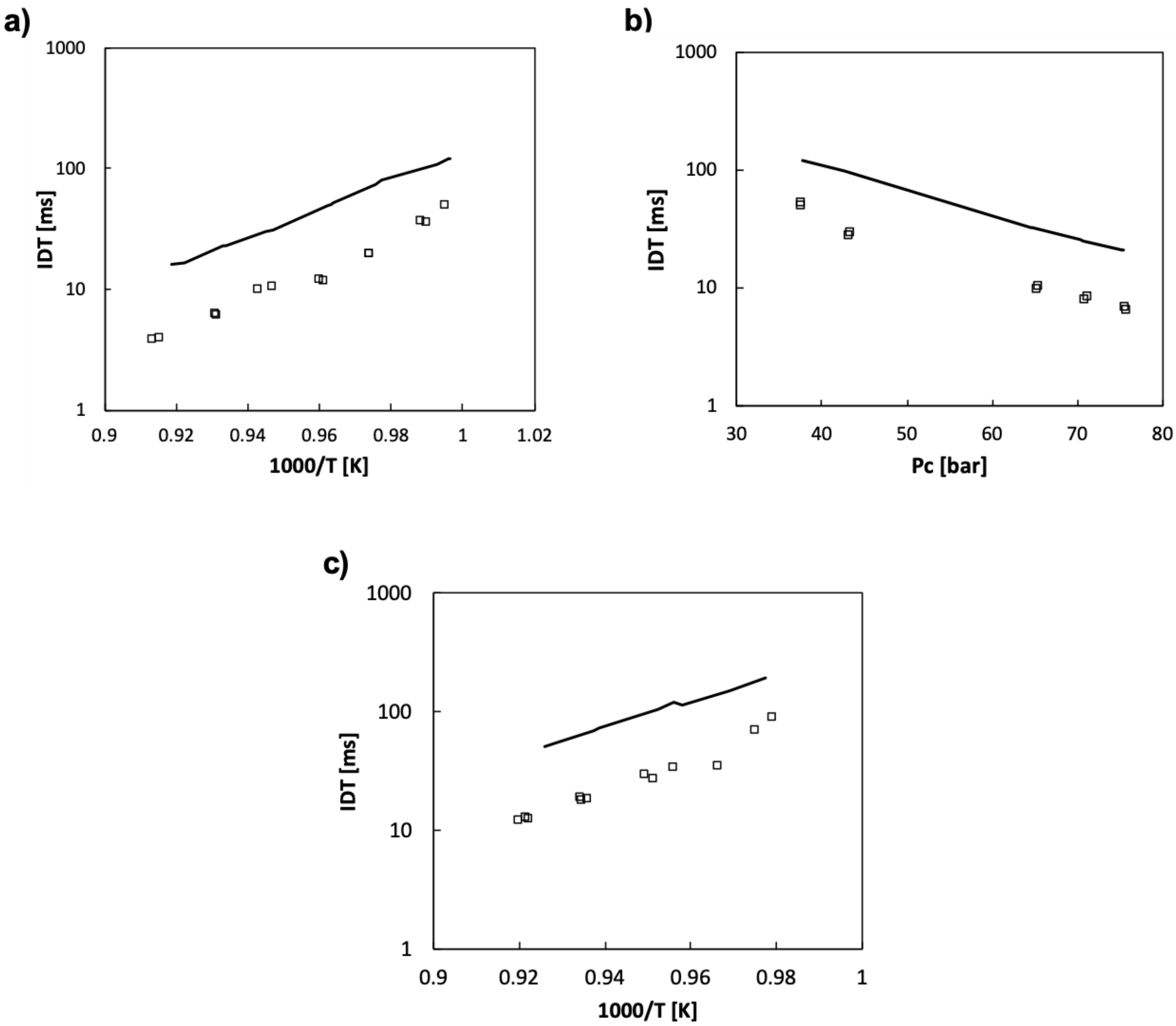


2.4 Rapid-compression machine

2.4.1 Pochet et al. [9]

Model: Batch reactor with assigned volume profile (converted from experimental pressure trace)

- 8.93% NH_3 – 19.13% O_2 – 61.15% N_2 – 10.79% Ar
    a) P_c = 65.5 bar
    b) T_{in} = 353 K
    c) P_c = 43.4 bar


a)
1000
100
10
1
IDT [ms]
0.9
0.92
0.94
0.96
0.98
1
1.02
1000/T [K]
b)
1000
100
10
1
IDT [ms]
30
40
50
60
70
80
Pc [bar]
c)
1000
100
10
1
IDT [ms]
0.9
0.92
0.94
0.96
0.98
1
1000/T [K]

2.4.2 He et al. [10]

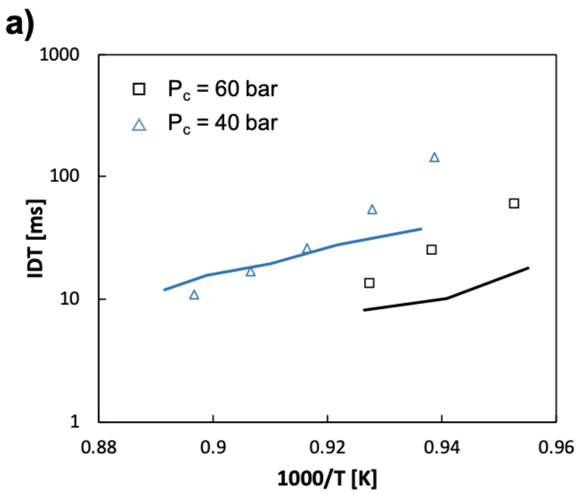
Model: Batch reactor with assigned volume profile (converted from experimental pressure trace)

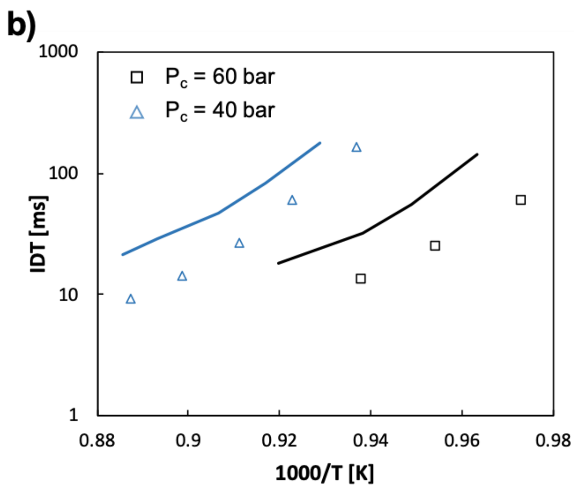
- Balance gas: Ar
- T_c = 310-370 K

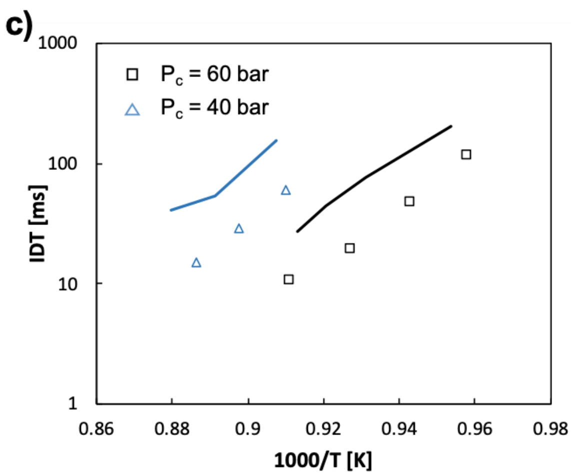
a) ϕ = 0.5

b) ϕ = 1

c) ϕ = 1.5





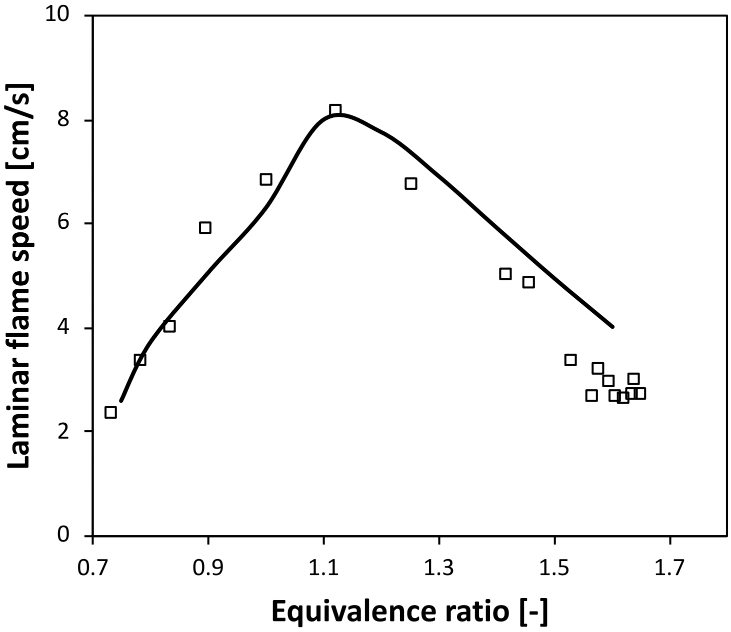


2.5 Laminar flame speed

2.5.1 Ronney [11]

<u>Model</u>: Premixed 1D laminar flame – radiation accounted for by optically-thin model

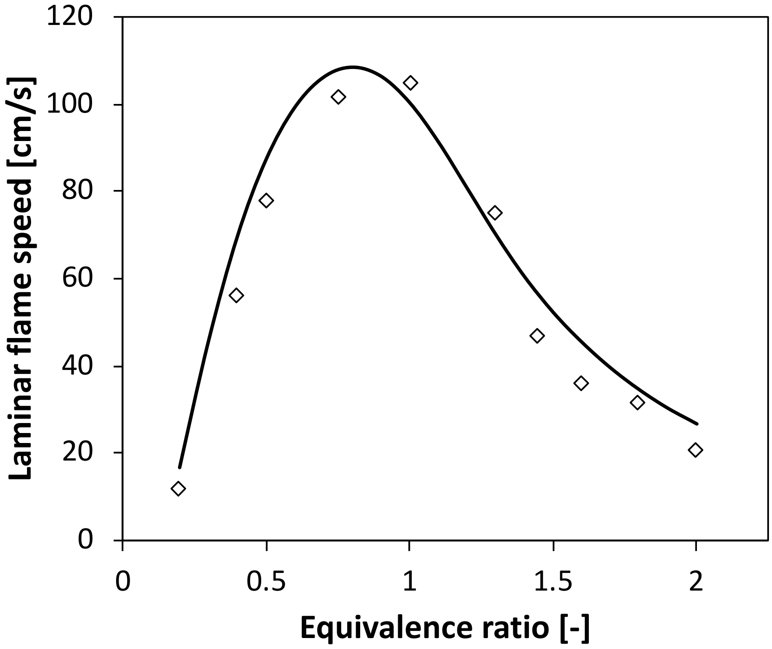
- NH_3/Air
- T_{in} = 298 K
- P = 1 atm



2.5.2 Liu et al. [12]

Model: Premixed 1D laminar flame – radiation accounted for by optically-thin model

- NH_3/O_2
- T_{in} = 298 K
- P = 1 atm



2.5.3 Mei et al. [13]

Model: Premixed 1D laminar flame – radiation accounted for by optically-thin model

- NH_3/O_2
- T_{in} = 298 K

  a) 35% O_2 – 1 atm

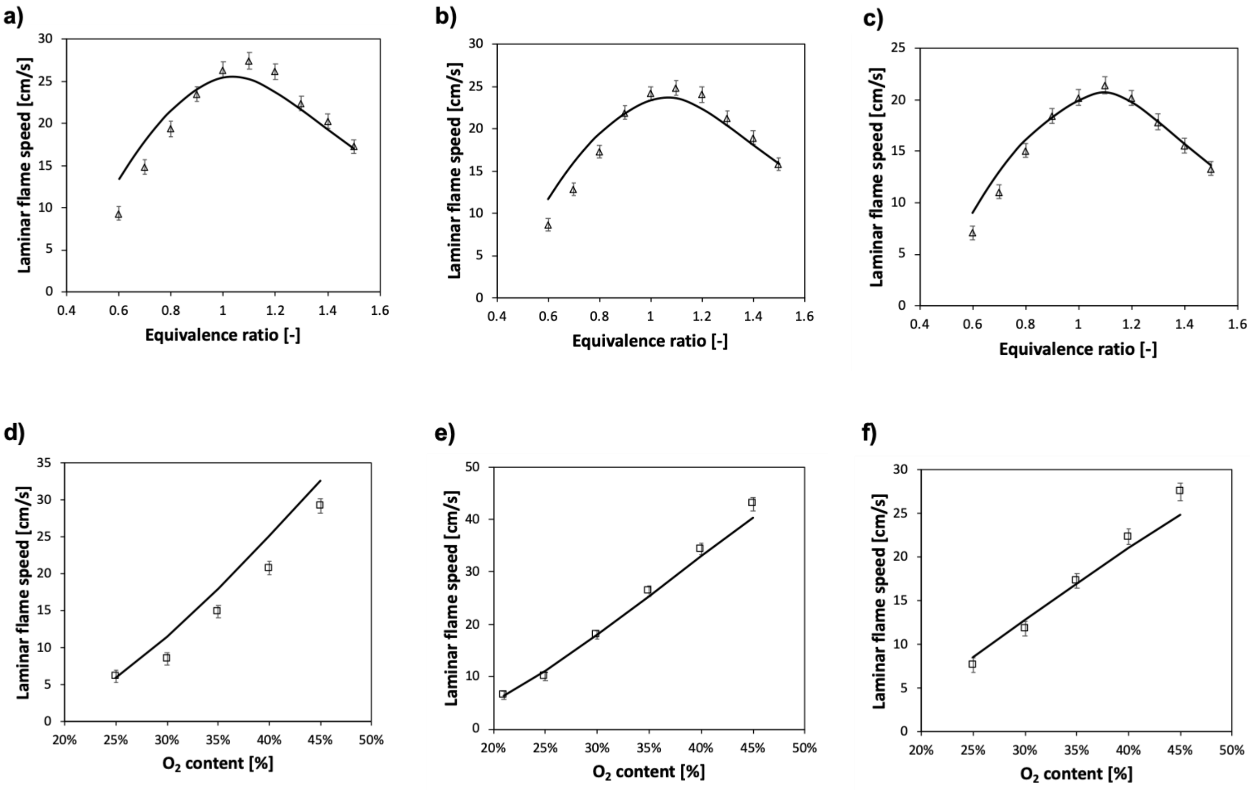
  b) 35% O_2 – 21 atm

  c) 35% O_2 – 5 atm

  d) ϕ = 0.7 – 1 atm

  e) ϕ = 1 – 1 atm

  f) ϕ = 1.5 – 1 atm



2.6 Burner-stabilized flame

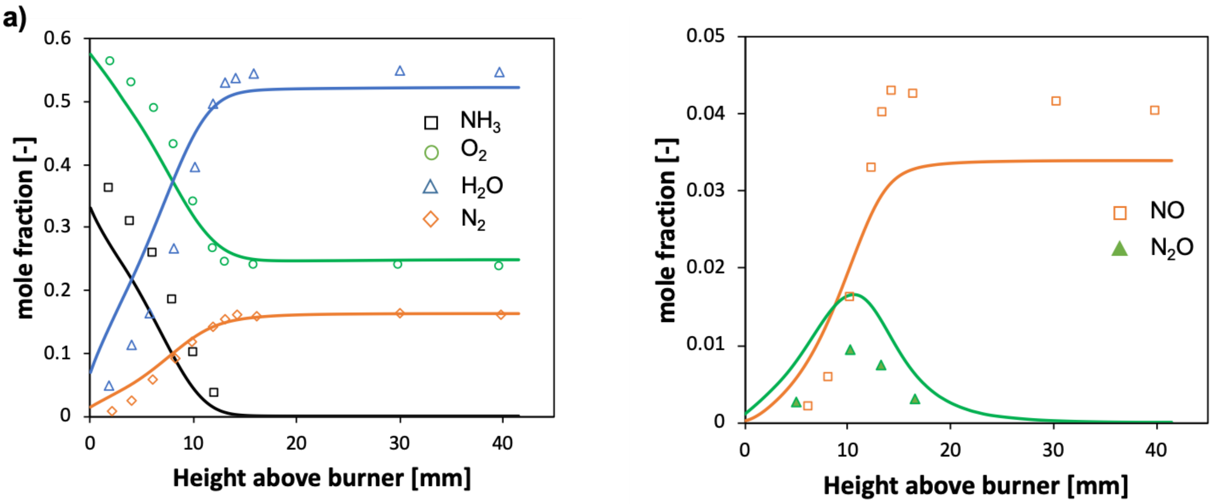
2.6.1 MacLean et al. [14]

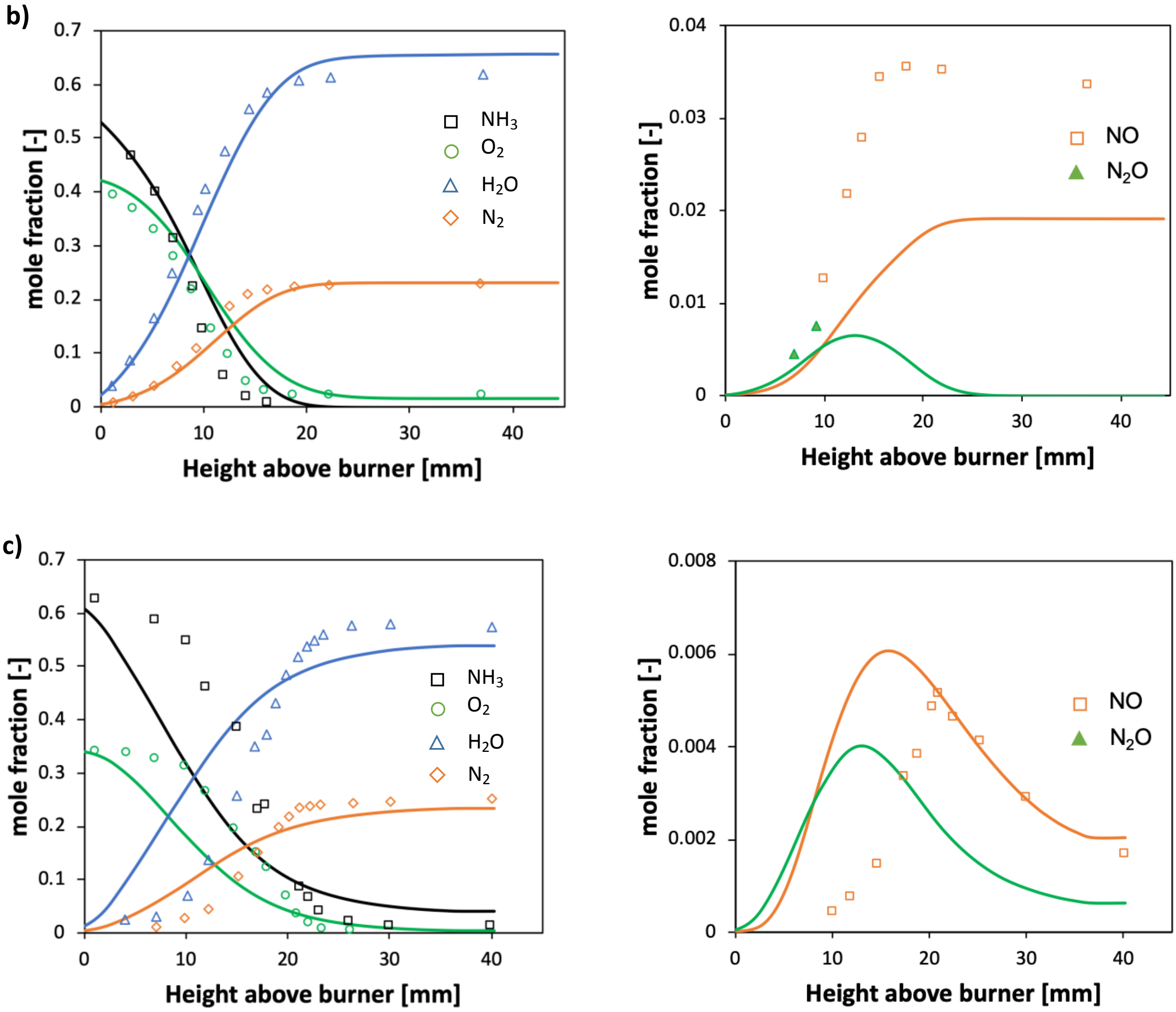
- NH_3/O_2
- P = 20 torr
- v0 = 60.5 cm/s

a) 40% NH_3 – 60% O_2

b) 57% NH_3 – 43% O_2

c) 65% NH_3 – 35% O_2




b)
c)
mole fraction [-]
Height above burner [mm]
NH3
O2
H2O
N2
NO
N2O

3 References

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