Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
Nationales Metrologieinstitut

TÉCNICO LISBOA

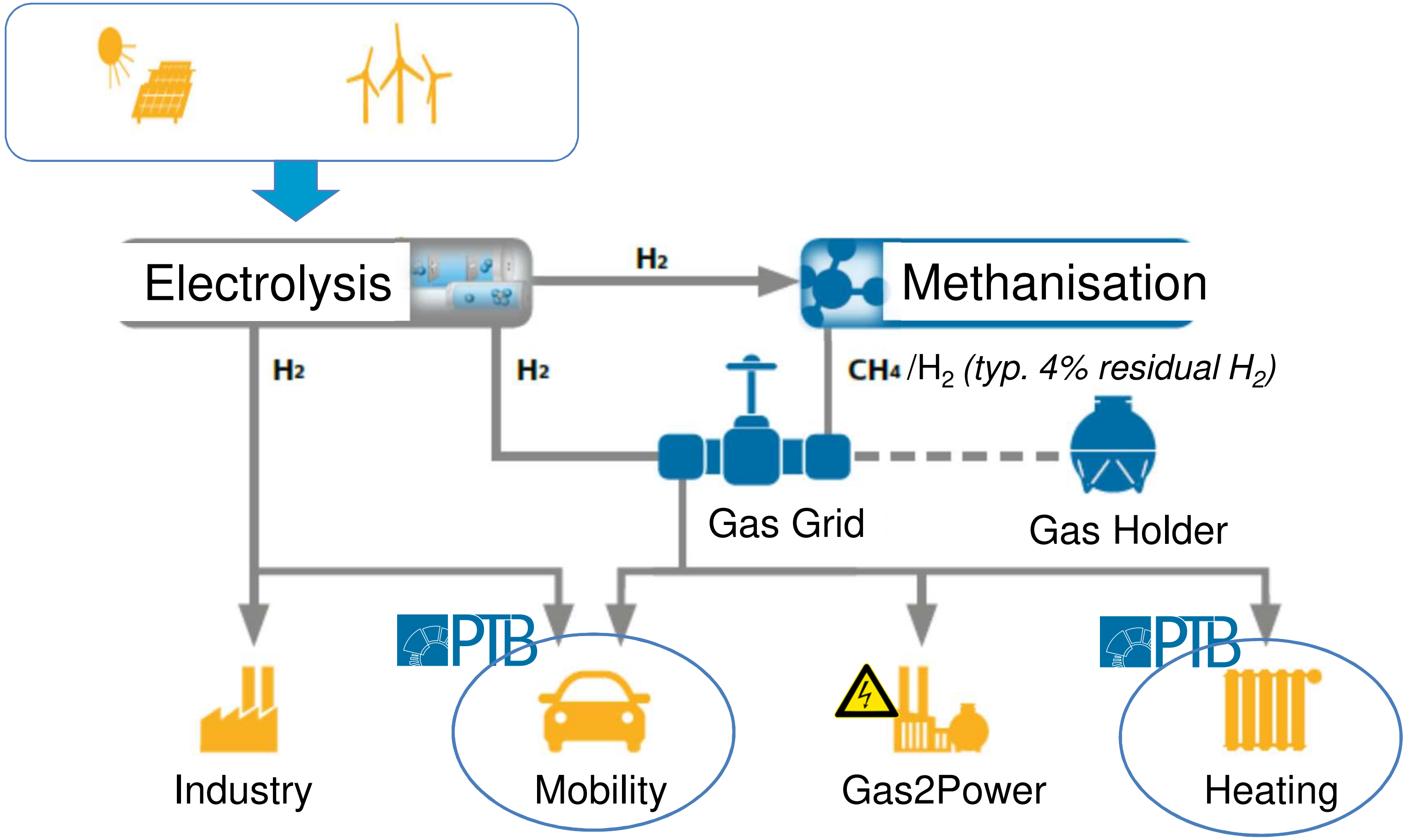
Auto-ignition kinetics of Ammonia at low temperatures and high pressures

Xiaoyu He[1,3], David Nascimento[2], Bo Shu[1], Kai Moshammer[1], Mario Costa[2] and Ravi Fernandes[1,3]

1. Thermophysical Quantities, Physikalisch Technische Bundesanstalt (PTB), Germany
2. Institut Superior Tecnico (IST), Lisbon, Portugal
3. Institute for Combustion Engines, Technical University of Braunschweig

Motivation

Ammonia is a hydrogen carrier produced from renewable sources



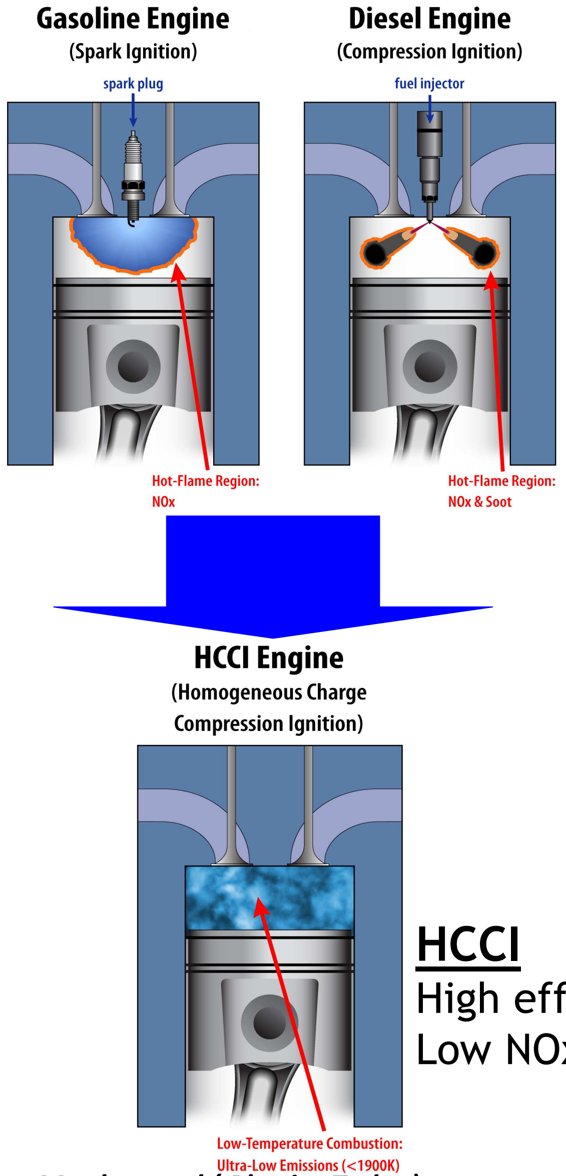
Adapted from: German Energy Agency (DENA): Power to Gas. Eine innovative Systemlösung auf dem Weg zur Marktreife (2013)

Motivation

- Emission control has become stringent
- Promising alternative clean fuels need to be investigated and established in the market
- Ammonia has good energy density and being carbon free, is being identified as promising alternative fuel and green energy storage carrier

Combustion properties of ammonia have not been fully understood and need to be investigated

Advanced engine concepts with alternative fuels (ammonia) offer new opportunities towards clean and efficient energy conversion

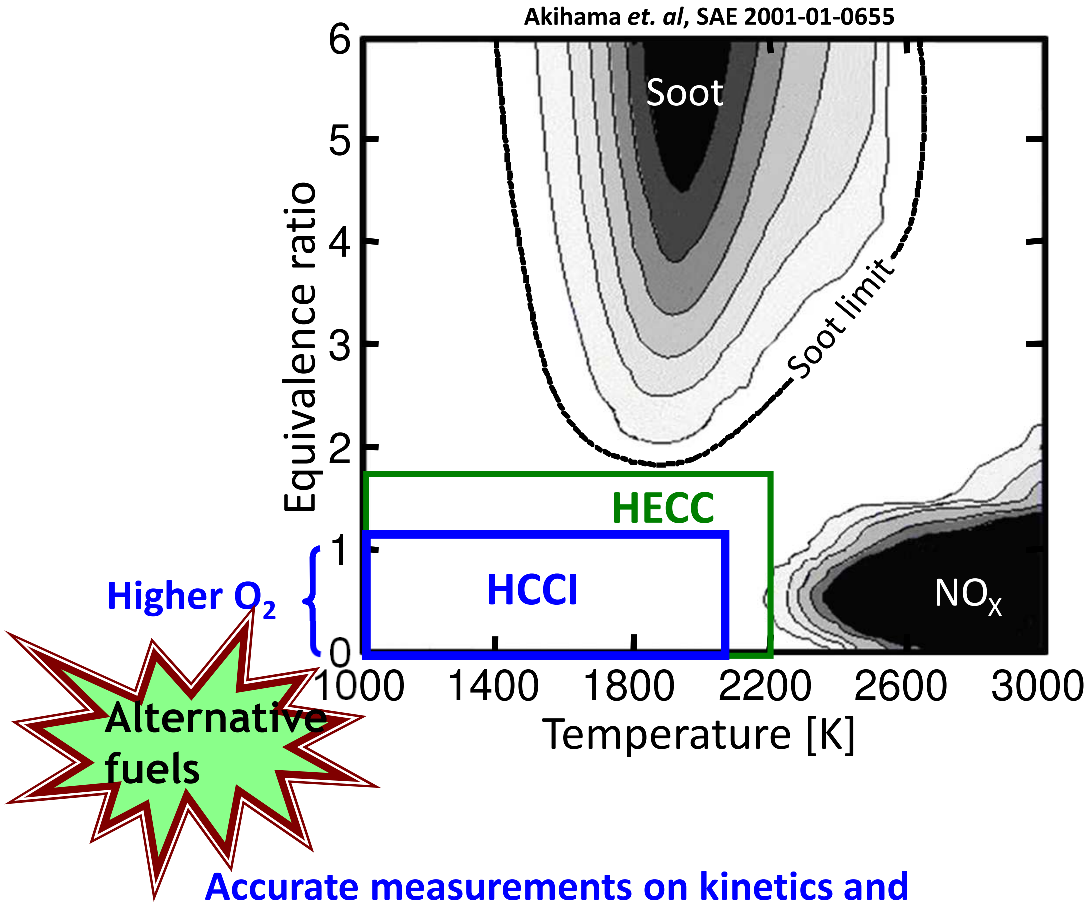


Manley et al (Physics Today)

HCCI

High efficiency

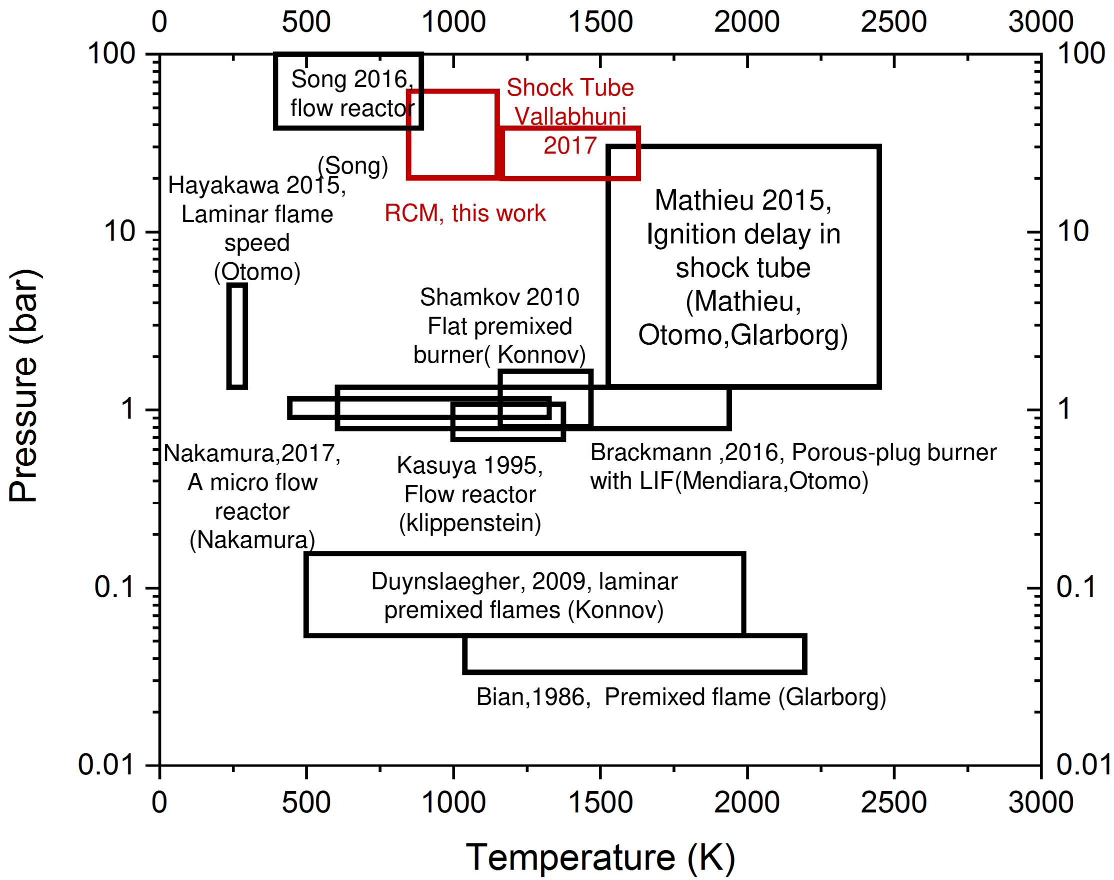
Low NOx and emissions



Accurate measurements on kinetics and thermophysical quantities play a central role

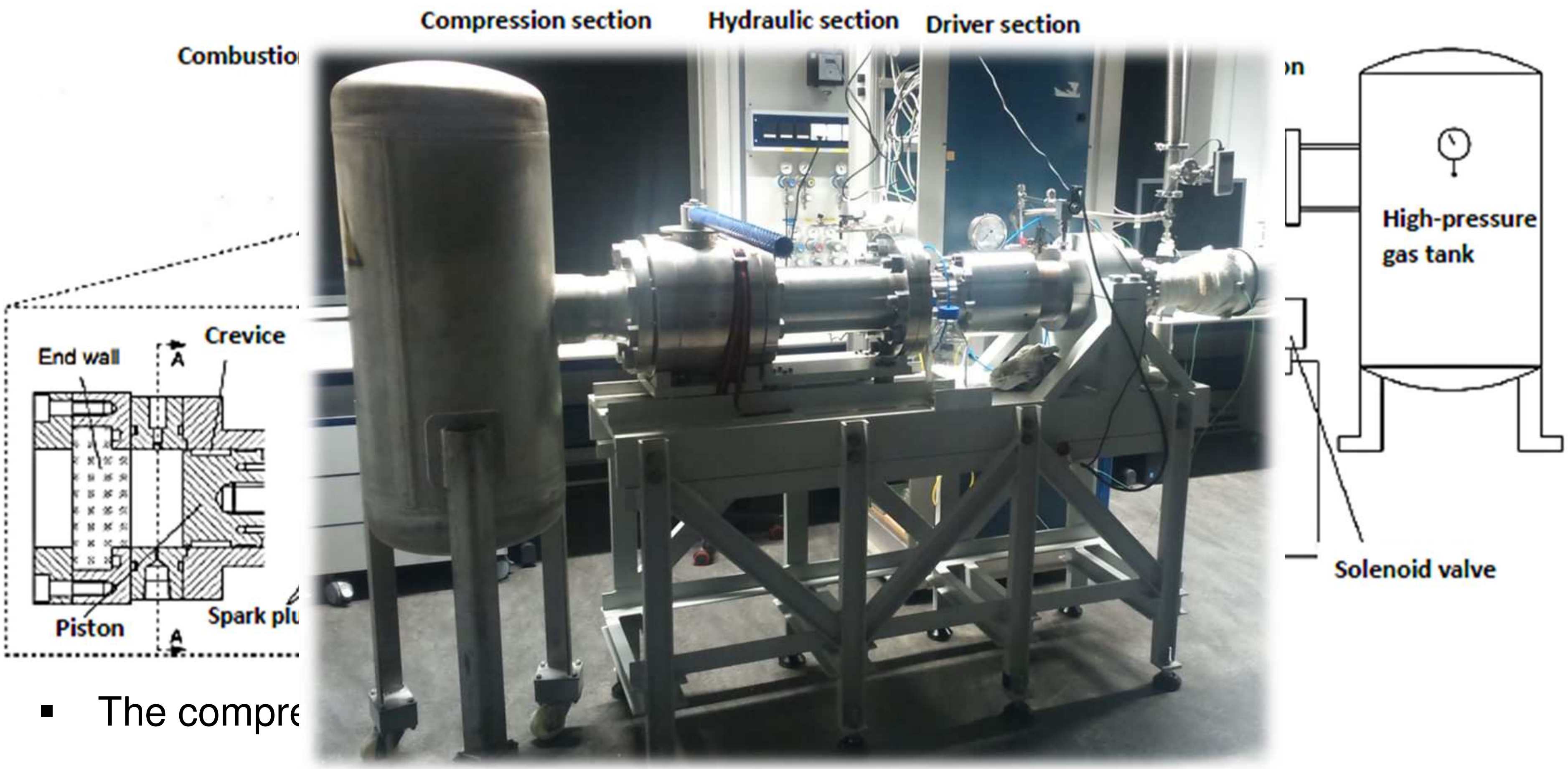
Density, viscosity, surface tension, calorific values
Composition (fuel quality),
Reaction Kinetics parameters
Flow properties

Research on ammonia combustion: bridging the gaps



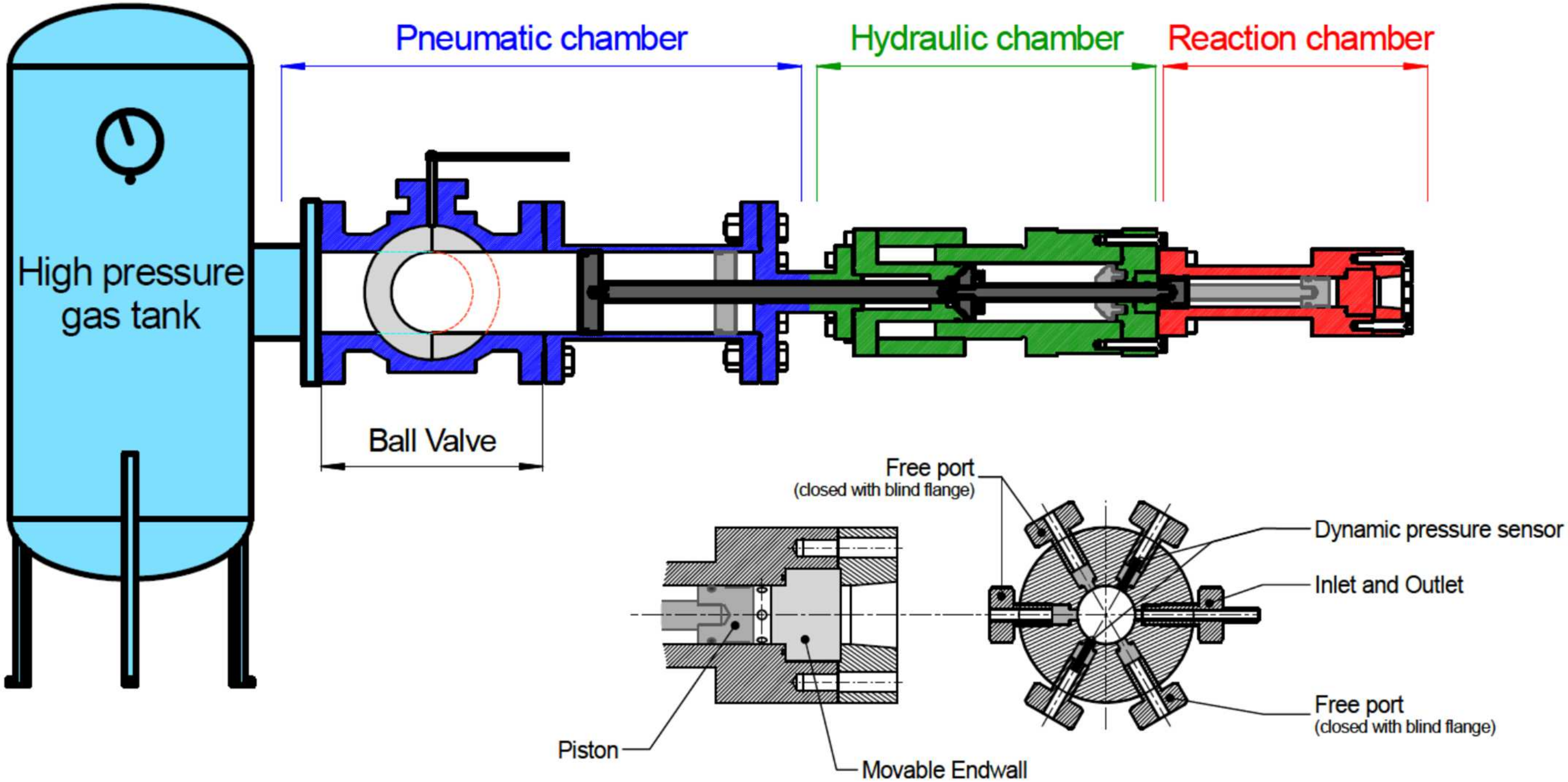
- Studies of ammonia oxidation at intermediate temperatures and at high pressure are scarce.

Autoignition studies using a Rapid compression machine (RCM)



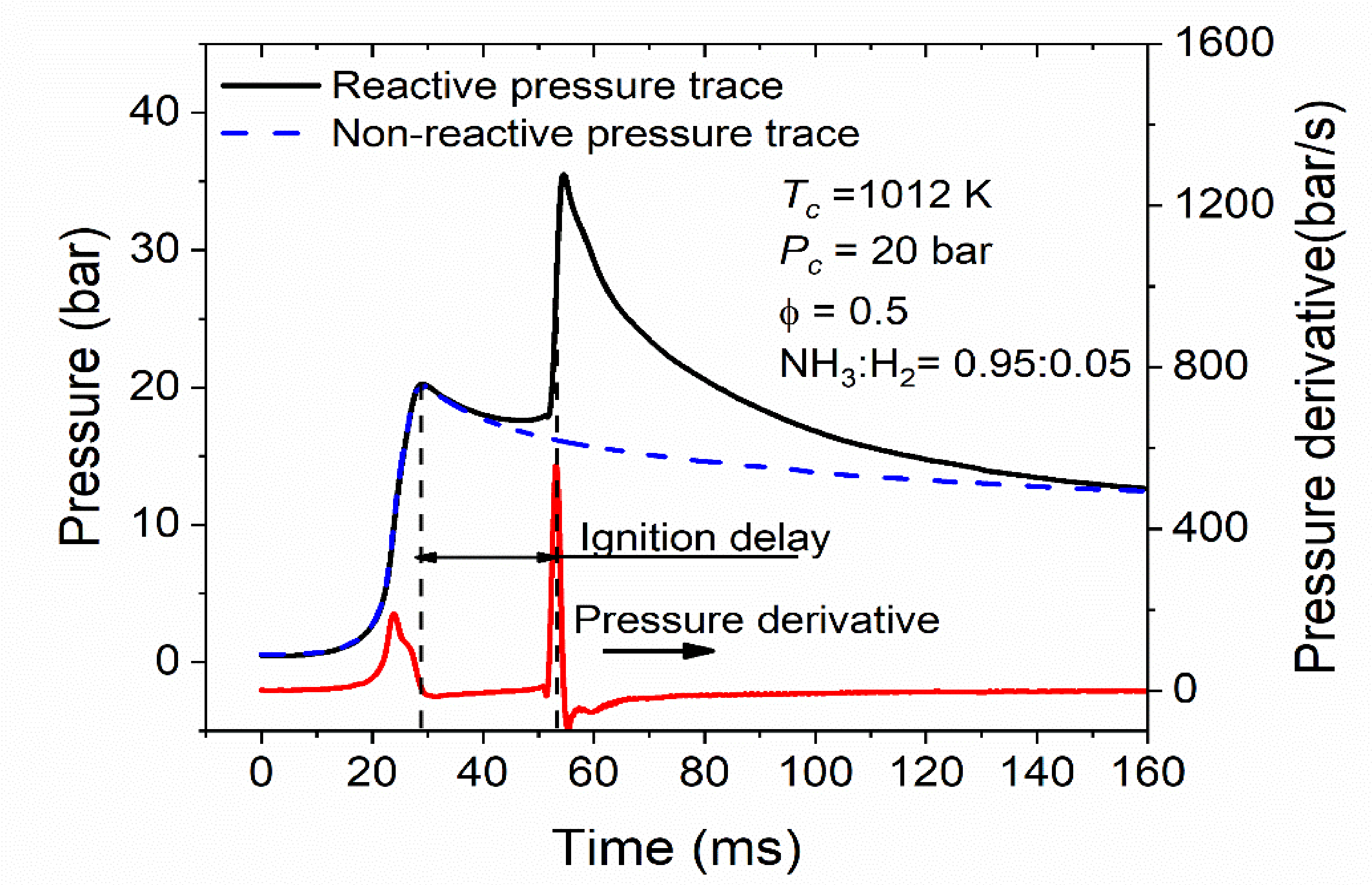
- The compre

Rapid compression machine (RCM) at PTB



Pressure time histories indicate ignition time delays

- T_c : 950 – 1150 K, P_c : 20, 40, 60 bar
- Ignition delay time: pressure trace

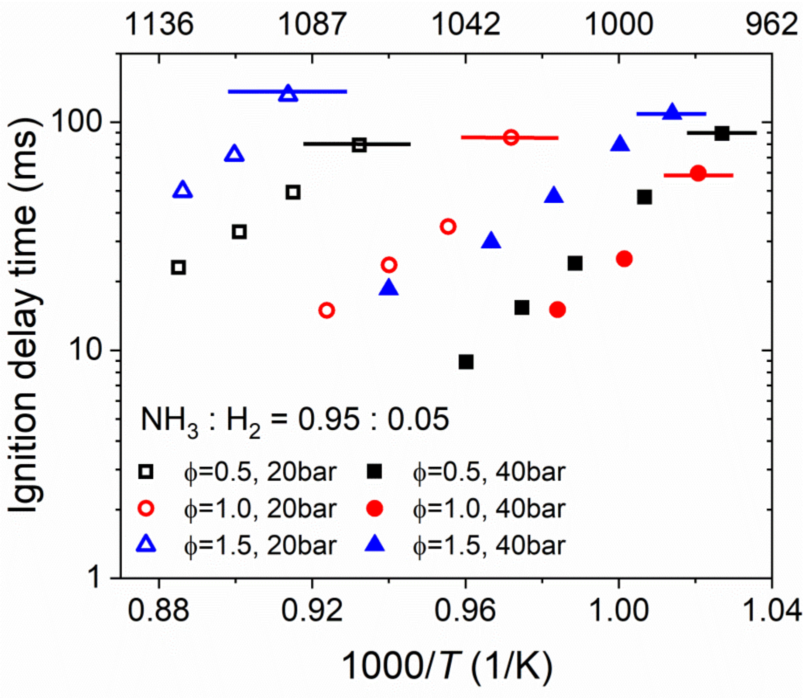


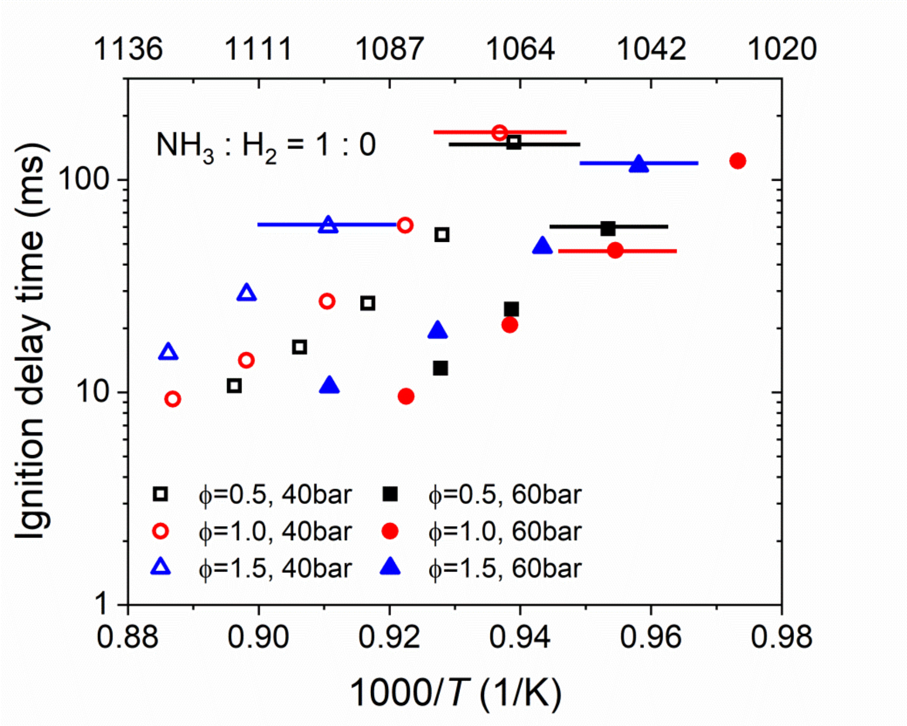
Investigated mixtures

- T_c : 950 – 1150 K

No.	% of H_2 in fuel	Equivalence ratio	Dilution	$Ar:N_2$ in dilution	EOC pressure(bar)
1	20%	0.5	70%	90:10	20
2	20%	1.0	70%	90:10	20
3	20%	1.5	70%	90:10	20
4	10%	1.0	70%	90:10	20
5	5%	0.5	70%	100:0	40
5b	5%	0.5	70%	90:10	20
6	5%	1.0	70%	100:0	40
6b	5%	1.0	70%	90:10	20
7	5%	1.5	70%	100:0	20, 40
8	5%	2	70%	100:0	40
9	1%	0.5	70%	90:10	40
10	1%	1.0	70%	90:10	40
11	1%	1.5	70%	90:10	40
12	0%	0.5	70%	100:0	40, 60
13	0%	1.0	70%	100:0	40, 60
14	0%	1.5	70%	100:0	40, 60

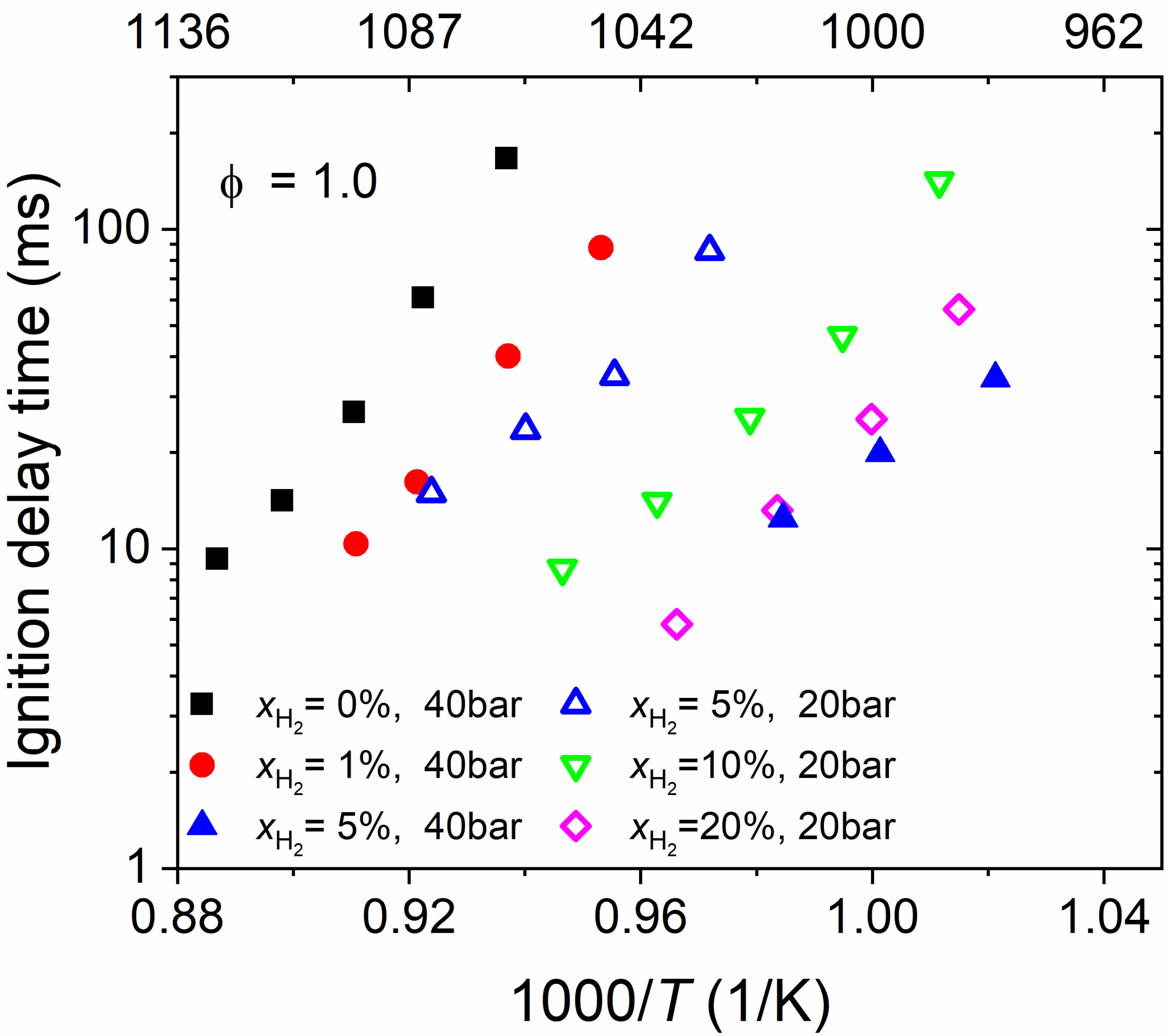
Effect of Pressure on ignition delay times





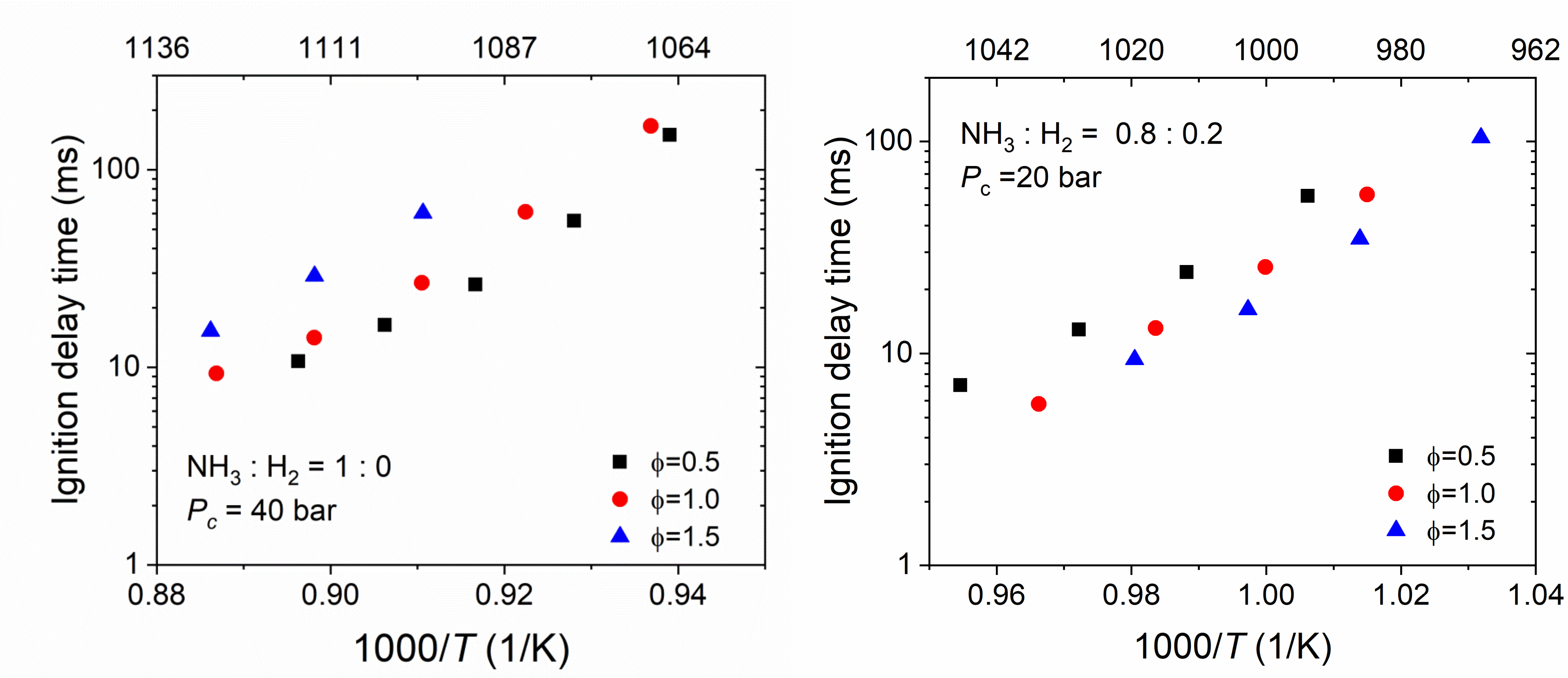
- The uncertainty of compressed temperature is ±1.38~1.07% at 20~60 bar.
- Higher pressures lead to higher concentration of reactants and increase the reaction rates.

Effect of NH3-H2-ratio on ignition delay time



- Higher hydrogen percentage decreases the ignition delay time.

Effect of equivalence ratio on ignition delay time



- For pure ammonia, leaner mixtures have shorter ignition delay times.
- For the mixture with 20% H_2 in fuel, the equivalence ratio dependence is reverse.

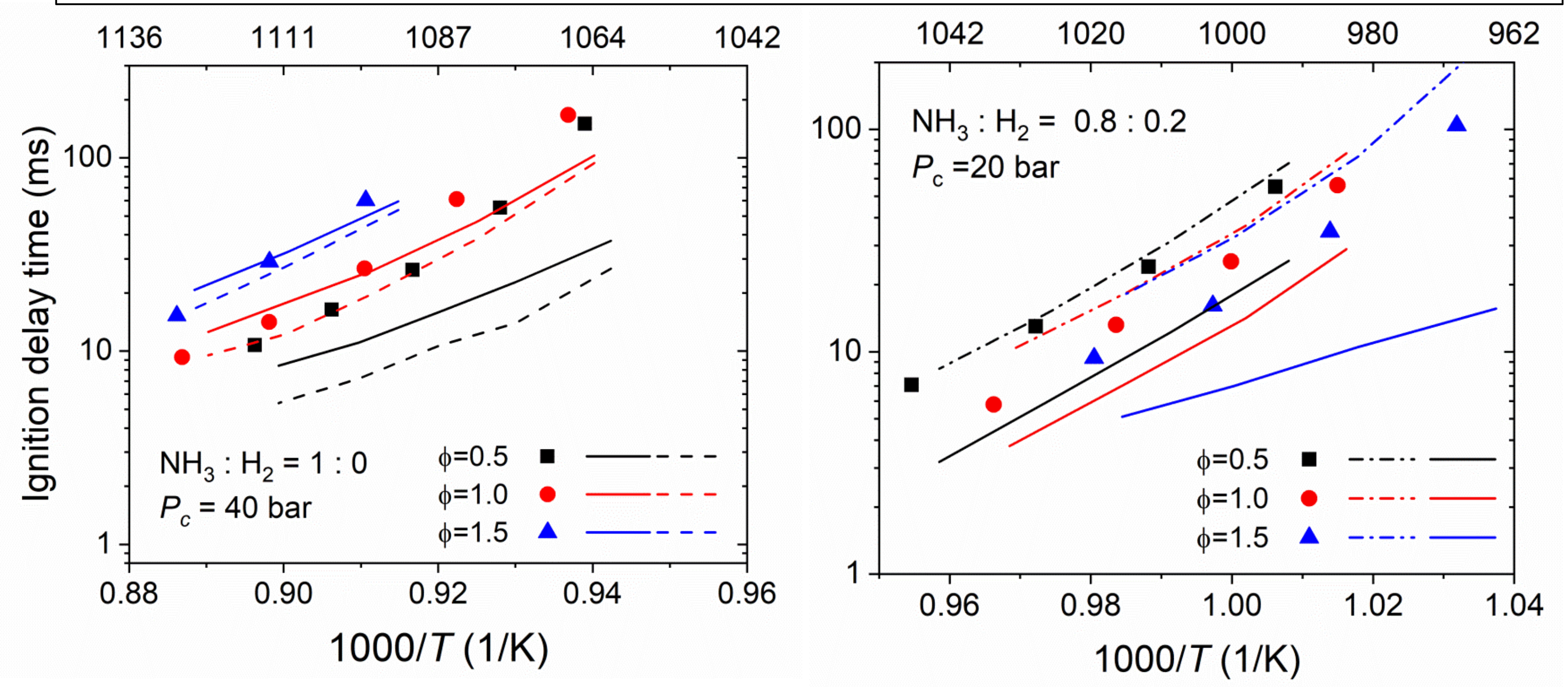
Kinetic model

- The three mechanisms of Mathieu et al., Klippenstein et al. and Glarborg et al. are adopted.

NO.	Author	Species number	Reaction number	Year	comments
1	Dagaut et al.	25	135	2008	
2	Mendiara et al.	31	191	2009	
3	Konnov	31	242	2009	
4	Klippenstein et al.	31	202	2011	
5	Song et al.	32	204	2015	improvement of No.4
6	Mathieu et al.	30	159	2015	improvement of No.1
7	Otomo et al.	33	222	2017	improvement of No.5
8	Nakamura et al.	32	224	2017	combination of No.3 and 6
9	Glarborg et al.	33	211	2018	improvement of No.4

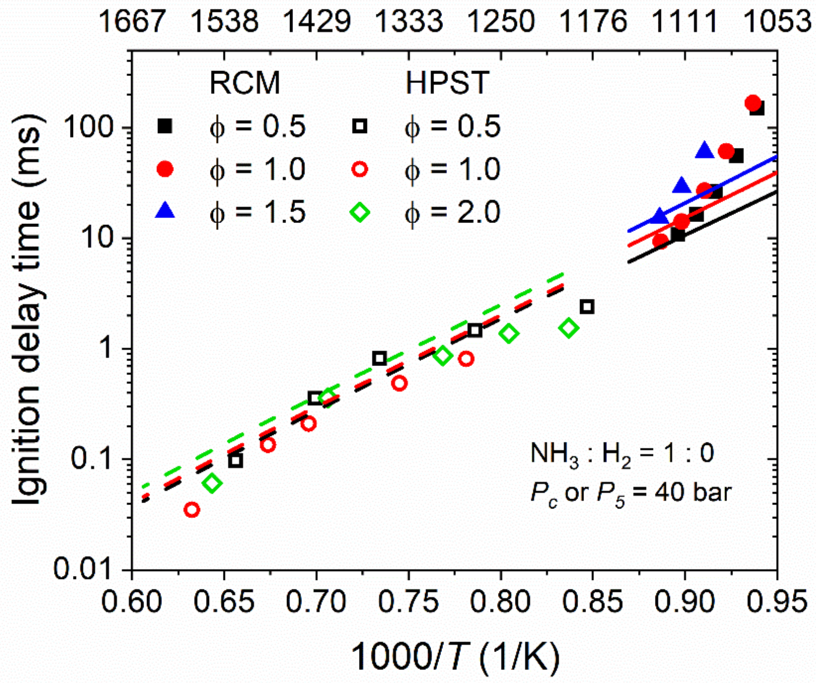
Effect of equivalence ratio on ignition delay time

solid lines: Glarborg et al., dash-dot lines: Klippenstein et al., dash lines: Mathieu et al.

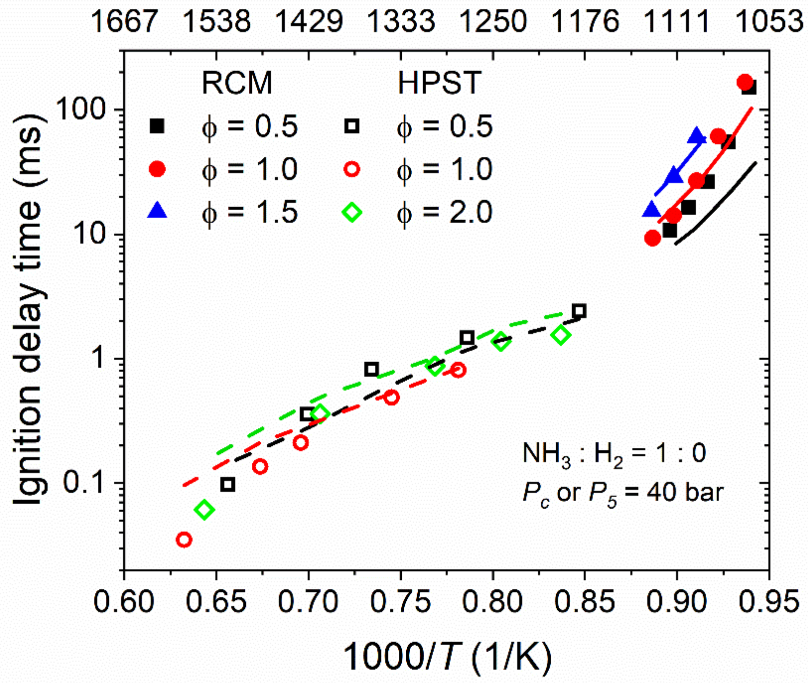


- In general, the mechanism from Glarborg et al. works best.

Comparison between the ignition delay time of pure ammonia in RCM and HPST



Simulation with constant volume solver



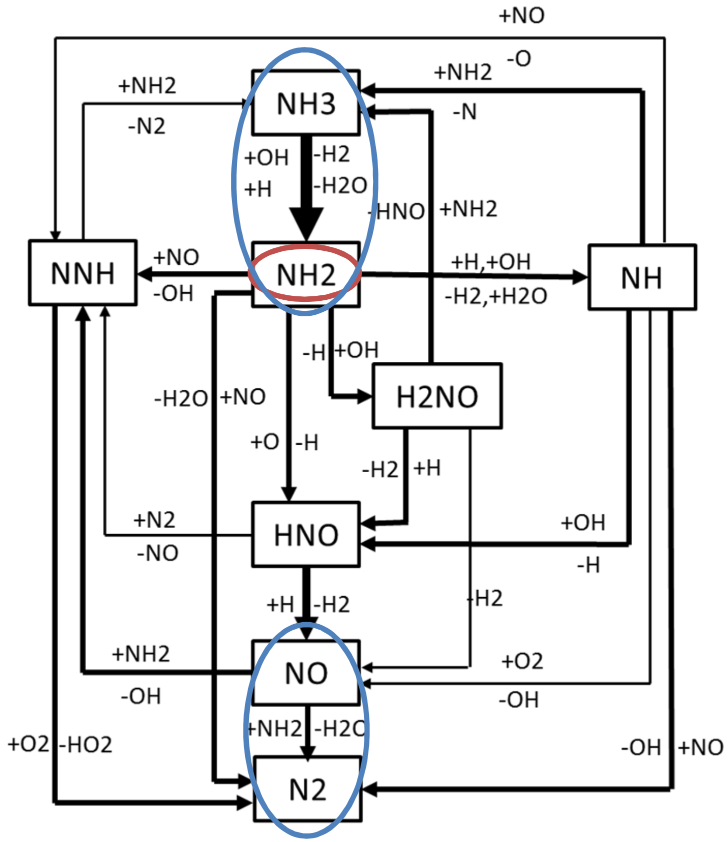
Simulation considering facility effects

- The model with Glarborg et al.'s mechanism reproduces the ignition delay time in whole temperature range satisfactorily.

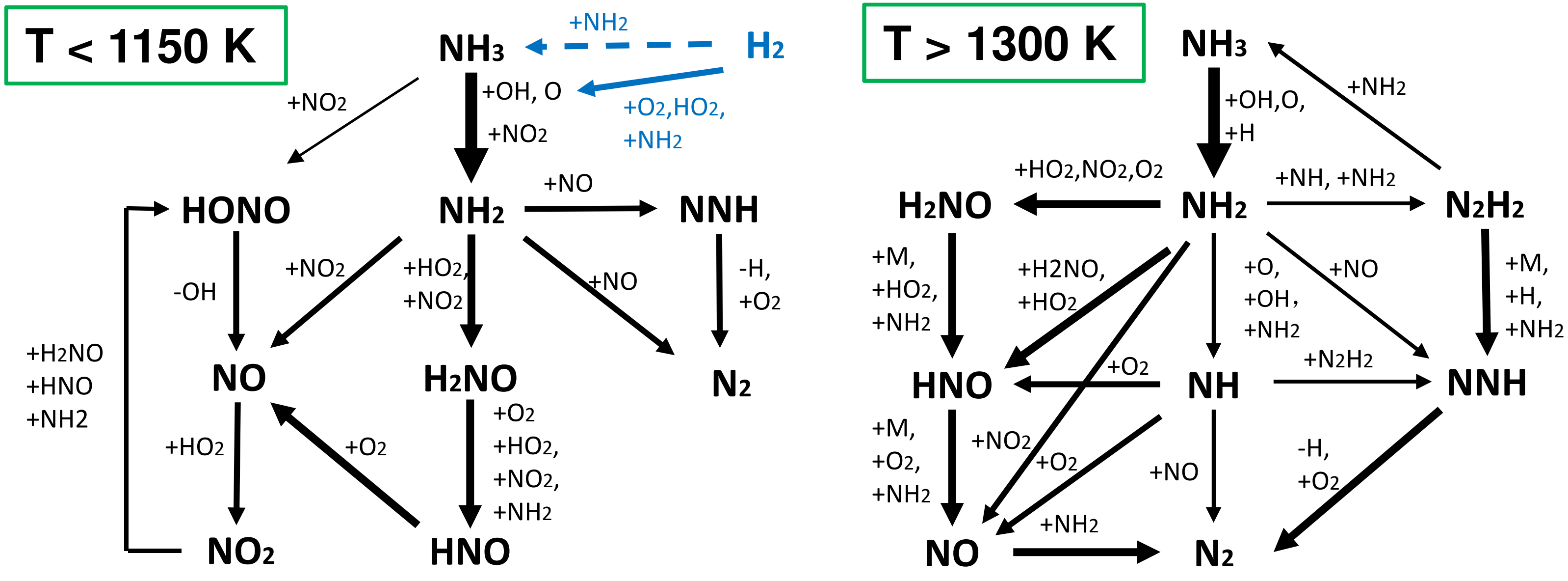
Reaction path analysis

Reaction pathway:

- φ = 2.0, *T* = 1200 K, *p* = 20 bar
- NH_2 is the key radical in the radical pool
- NO and unburned NH_3 are the most significant emissions
- NO and NH_3 can potentially be converted to N_2 and H_2O



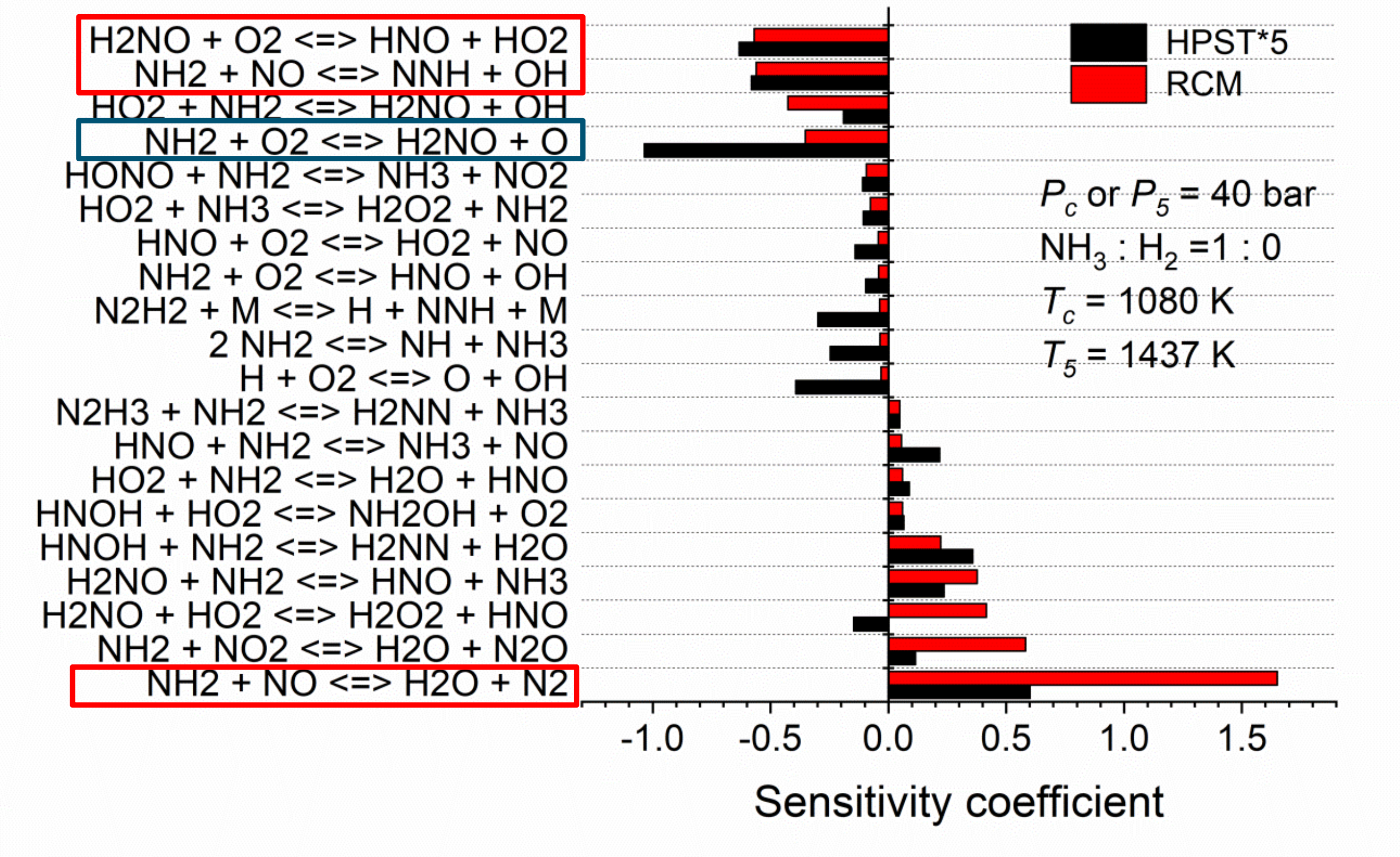
Reaction path analysis



- NH_3->NH_2->H_2NO->HNO is the main pathway at elevated pressures and intermediate temperatures.
- The additional hydrogen does not change the reaction pathway of ammonia oxidation
- At high temperature range, the pathway NH_2->NH/N_2H_2->NNH becomes also important.
- The competition between two pathways of amine radicals (NH_2/NH), i.e. reacting with HO_2/O_2 or with NO, determines the selectivity for forming NO or N_2 in oxidation of ammonia.

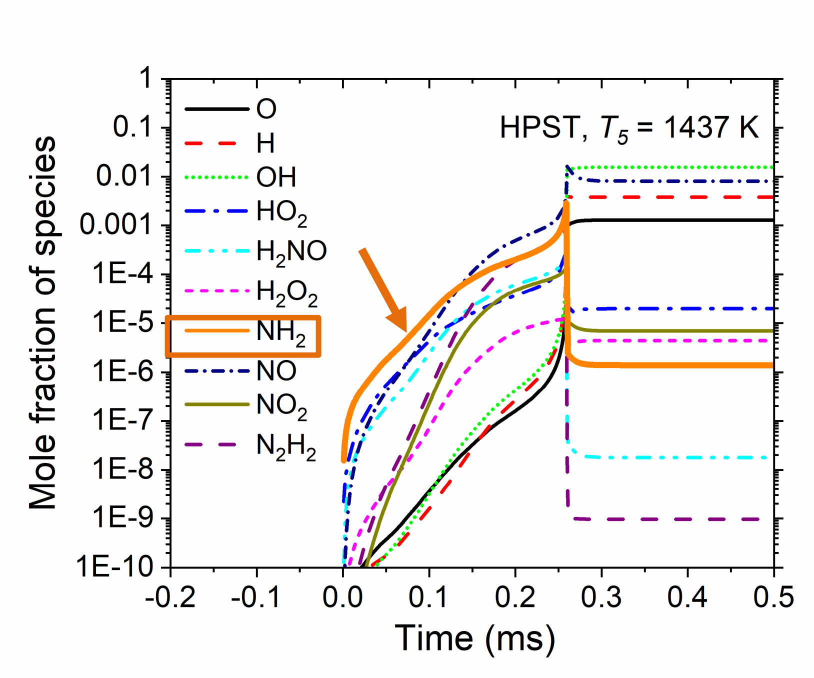
Mechanism: P. Glarborg et al., Prog. Energy Combust. Sci. 67(2018), 31-68

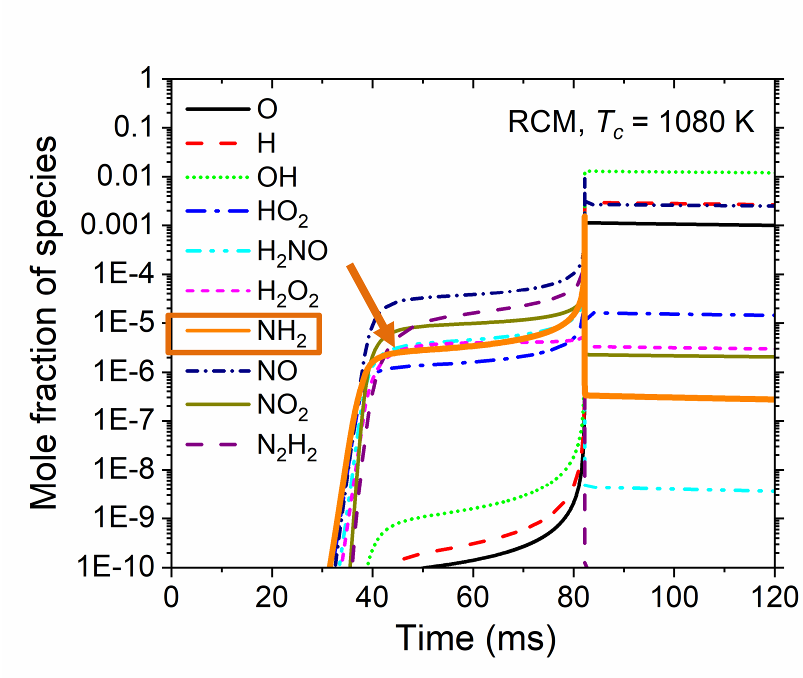
Sensitivity analysis for ignition delay time



- Chemistry of NH_2+NO and H_2NO+O_2 is essential for ammonia oxidation at both temperature range.

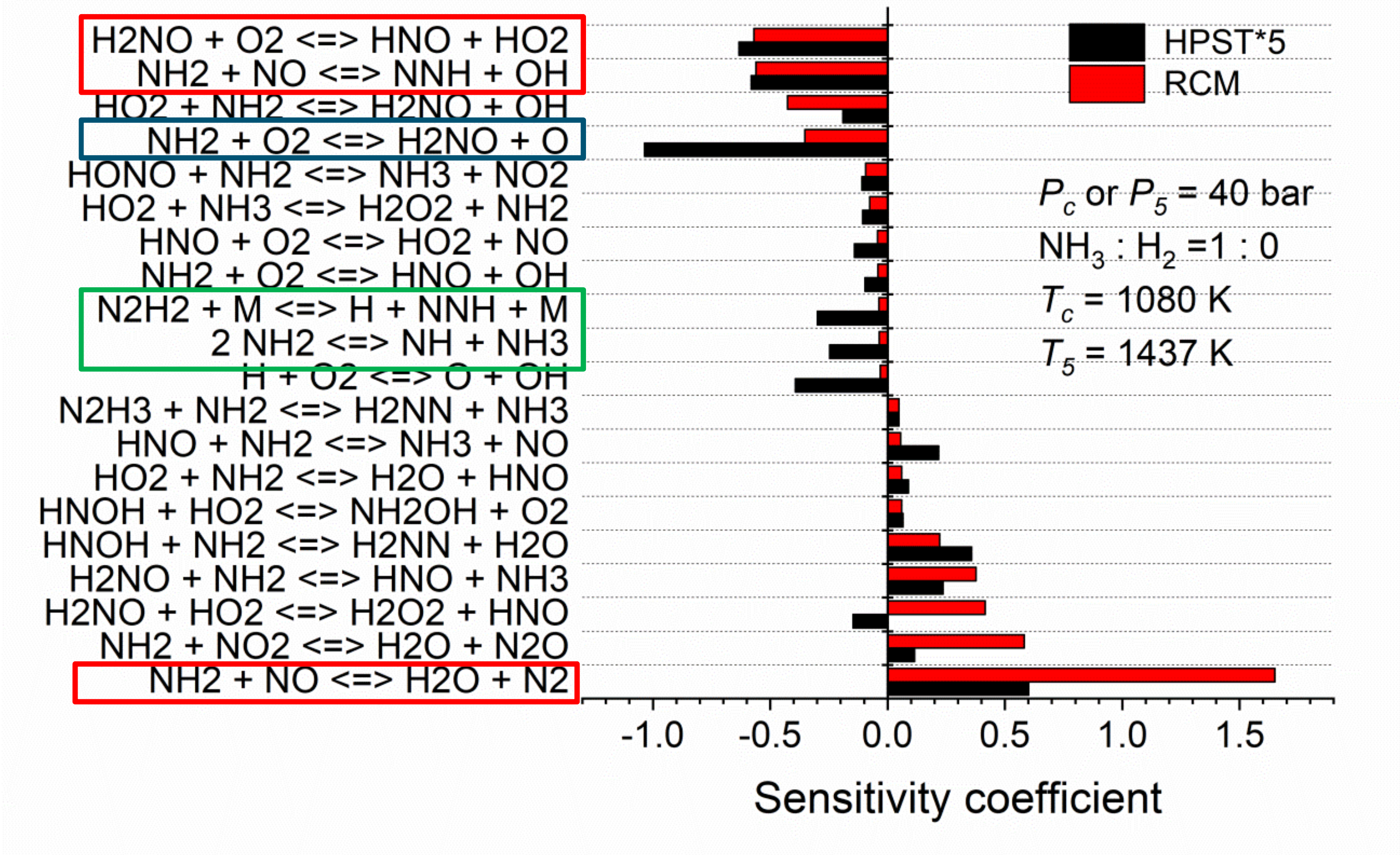
Mole fraction profiles of intermediates in RCM and HPST





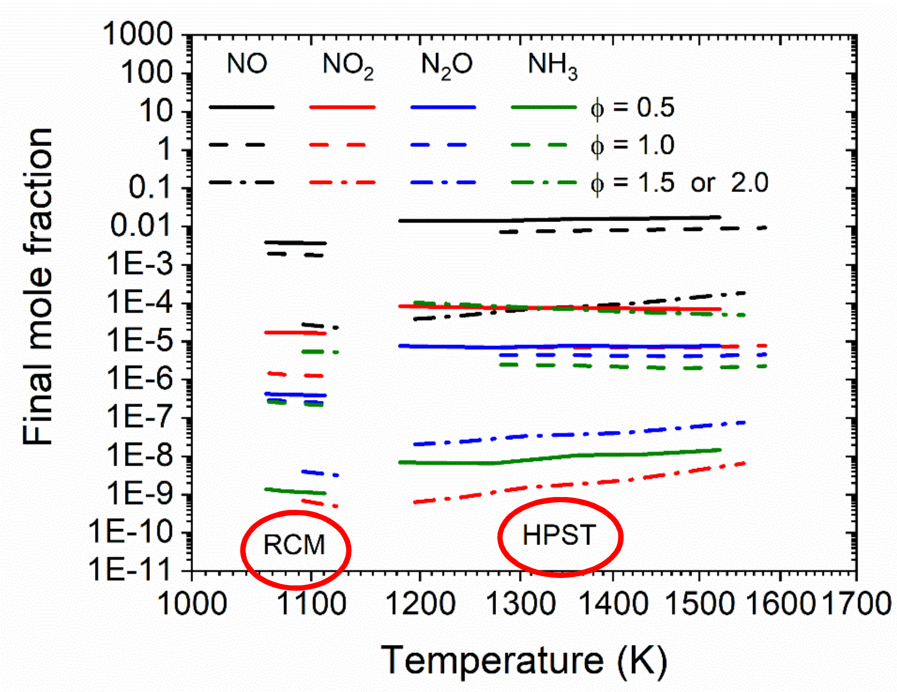
- In the first half of the induction time NH_2 has the highest mole fraction among all the radicals at high temperature.
- At intermediate temperature the mole fraction of NH_2 is moderate compared with the species, such as NO and NO_2.

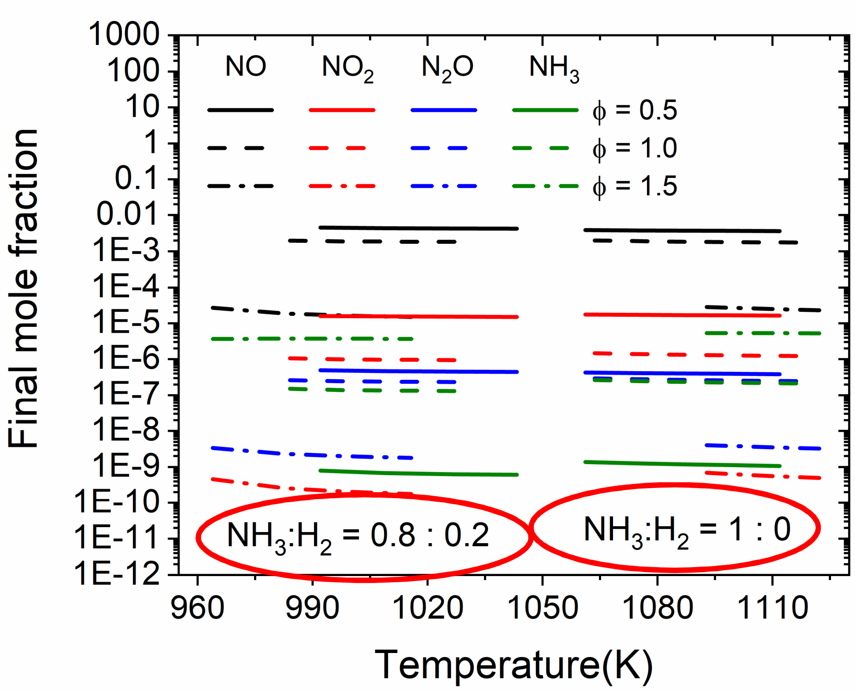
Sensitivity analysis for ignition delay times



- Chemistry of NH_2+NO and H_2NO+O_2 is essential for ammonia oxidation at both temperature range.

Emissions of ammonia combustion





- The emissions are strongly dependent on the equivalence.
- The values in RCM conditions are overall lower than in HPST conditions
- Hydrogen has almost no effect on the final emission.

Conclusions

- We investigated the ignition properties of Ammonia under advanced combustion conditions (low T, high P)
- Detailed kinetic model was developed and validated with experimental results of ignition delays
- The validated detailed model was also used to predict the emission (NH3, Nox, N2O) characteristics of ammonia under varied operating conditions
- Experimental results and validated model indicate a very good performance of NH3/H2 for a wide operating conditions
- Future measurements will focus on blends with other fuels as well as direct emission measurements.

Thank you for your attention !

Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
Bundesallee 100
38116 Braunschweig

Prof. Dr. Dir.u.Prof. Ravi Fernandes
Thermophysical Quantities

Telefon: 0531 592-3300
Fax: 0531 592-3305
E-Mail: ravi.fernandes@ptb.de
www.ptb.de

Stand: 10/18