

Principles of Ammonia combustion

Prof Christine Mounaïm-Rousselle

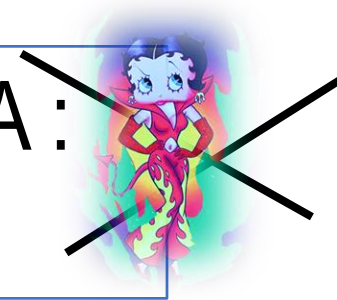


ACTIVATE
SEMINAR 2021

RELEVANCE OF NH₃ AS FUEL FOR ICE

- No CO₂, CO nor PM emissions
- Good energy density
- Potential for high compression ratios (CR)
- **Combustion promoter**
 - to boost performance

ICE fueled with AMMONIA :
Challenge !



BUT

Fuel-bound nitrogen: NO_x and NH₃

- Mitigation strategy required for pollutants
 - corrosive (copper, alloy, plastic, rubber, teflon...)
 - toxic (300 ppm < air)



RELEVANCE OF NH₃ AS FUEL FOR ICE

	H ₂	Methane	Methanol	gasoline	NH ₃	Diesel fuel
Boiling Point (°C) at Patm	-253	-162	65	27-225	-33	
Density (20°C, 1 bar) (kg/m ³)	0,08	0,66	790	740	0,71 (G)	
Storage	Gas, Liquid	gas	liquid	liquid	gas ou Liquid	liquid
Liquid pressure at 20°C	700	250	1	1	8.6	3
Density at storage conditions(kg/m ³)	39.7	194	790	740	610	800
Energy density at storage conditions (MJ/l)	4.76	9.70	15.72	32	11.47	34,9
Latent heat of vaporization(kJ/kg)	461	510	1168	180-350	1370	400

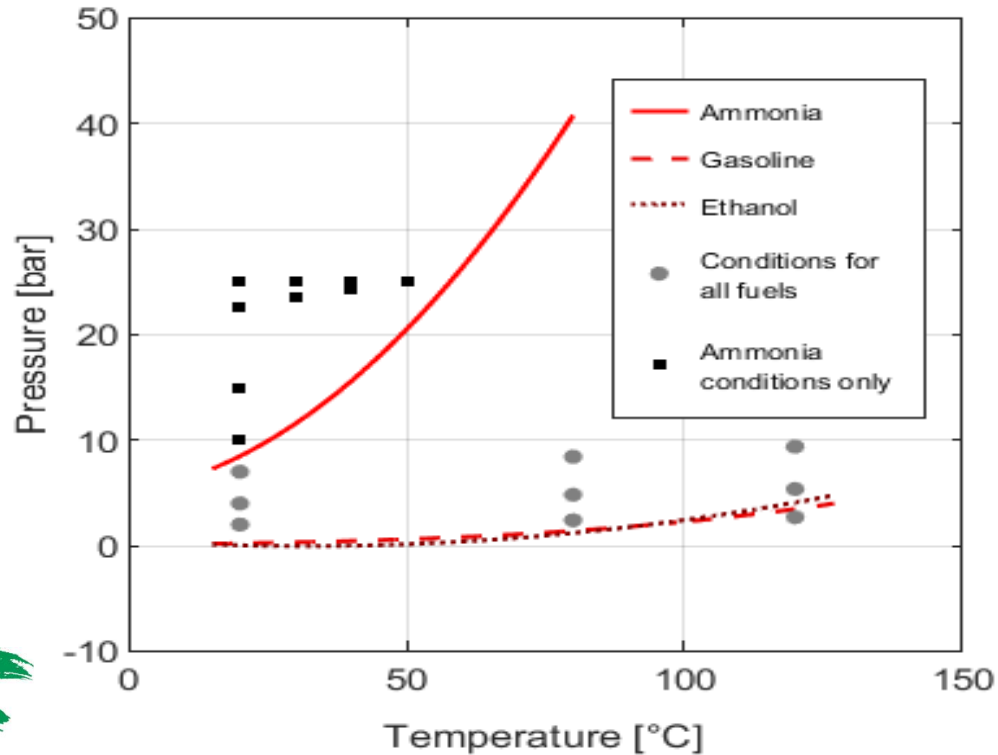
More > H₂, similar « classical » fuel

3 * > LPG ! , > methanol

Very high ! as methanol

Ammonia injection : unknown

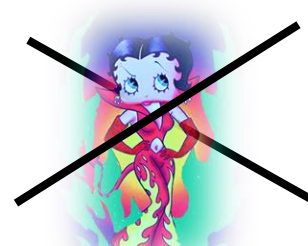
- Flash-boiling ?
- Accuracy of vaporization model/CFD



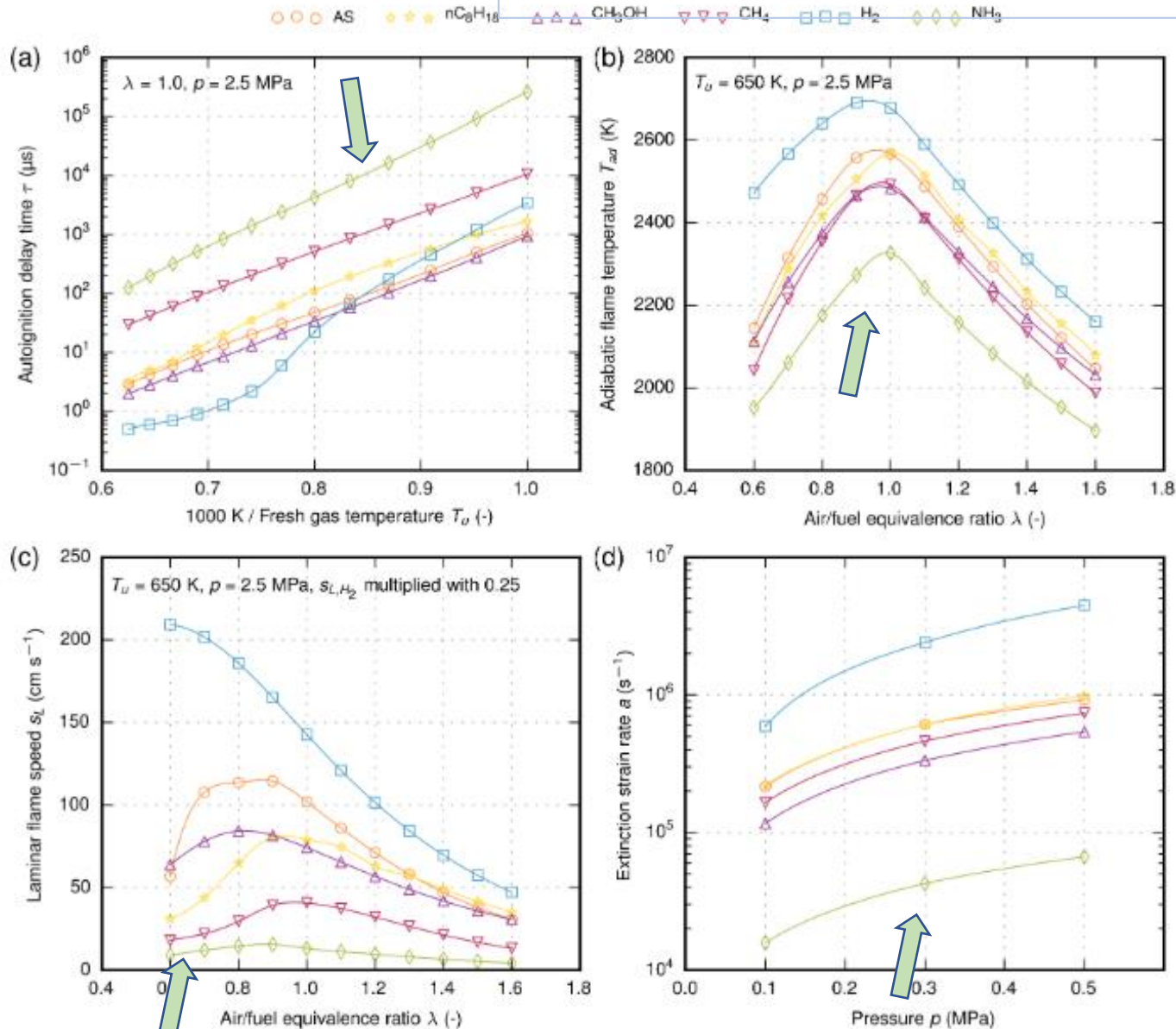
ρ_{air}, T_{air}	Ammonia		Gasoline	
	Liquid	Liquid + Vapor	Liquid	Liquid + Vapor
2,38 kg/m ³ 20°C				
2,38 kg/m ³ 80°C				
2,38 kg/m ³ 120°C				
8,32 kg/m ³ 20°C				
8,32 kg/m ³ 80°C				
8,32 kg/m ³ 120°C				

Global ammonia combustion characteristics

	Hydrogen	Methane	Methanol	Gasoline	Diesel Fuel	Ammonia	consequences
Low Heating Value (MJ/kg)	120	49	19.9	44	45	43,2	Similar
Air/Fuel ratio at stoichiometry (kg/kg)	34.2	17.65	6.46	14.6	14.6	6.06	High fuel consumption
Flammability limit in air (vol.%)	4.5-75	5-15	6.7-36	1.3-7.6	1-6	15-30	Low risk
Laminar flame speed (cm/s)	210	38	40	~40		7	Difficult propagation
Auto-ignition Temperature(°C)	537	595	465	275	225	651	Difficult ignition
Octane Number (-)	>120	120	109	88-98		>120	Low knock occurency ?
Adiabatic flame temperature (°C)	2519	2326	2228	2392		2107	Colder flame
Quenching distance (mm)	0.64	2		3	7	7	Lower heat wall loss



Ammonia combustion characteristics



High ID, Low Adiab Temp, Low Laminar burning speed, Low extinction strain rate



Article

A Study on Electrofuels in Aviation

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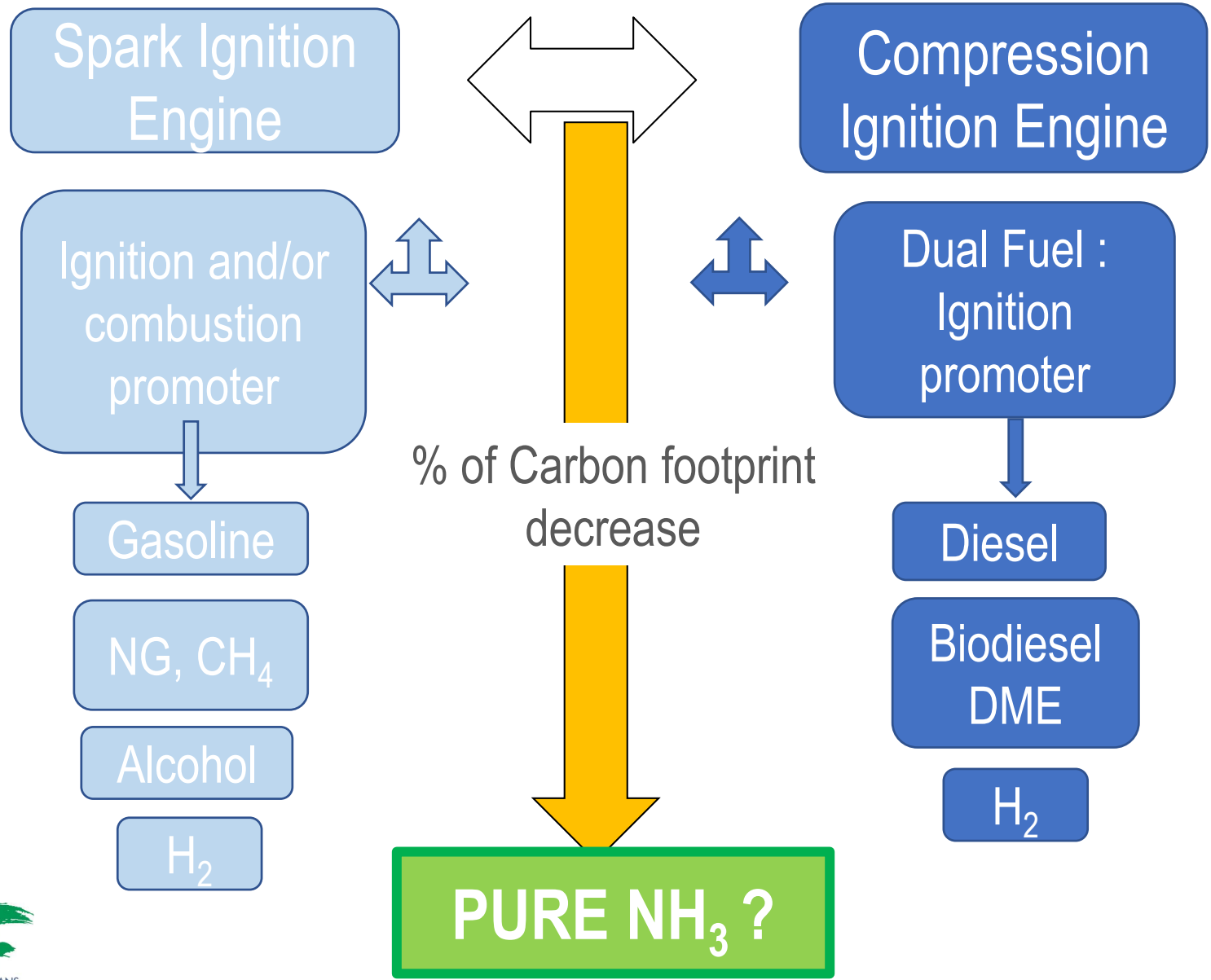
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Challenges for Ammonia fuel in ICE

CHALLENGES	Technical Impact	Fundamental needs
High latent heat of vaporization + different saturated vapor curve	Injection sytem	Flash boilling ? Supercritical ? Atomization process
Difficult Auto-Ignition	Ignition range, cold starts Compression ratio, boosted conditions ? Ignition system : reactive fuel pilot injection ? Igniter ?	Auto-ignition delay (T,P, lambda, reactive fuel addition ?) Accurate full kinetics mechanism Reduced kinetics mechanism for CFD use
Narrow flammability range	Combustion stability Operating conditions range (lambda)	flame/stretch, extinction, Neat NH3 + other fuels
Low reactivity/ low flame propagation speed	Efficiency ? Thermodynamics conditions	Flame speed database (T, P, Phi, pilot fuel ..) Kinetic mechanism (neat ammonia+ more reactive fuel ? ...) Flame-turbulence interaction, stretch, wall heat transfer
Fuel nitrogen	Exhaut pollutant : NO, NO2? N2O ? Unburnt NH3, Exhaust post-treatment	Reduced Kinetic mechanism for CFD ?

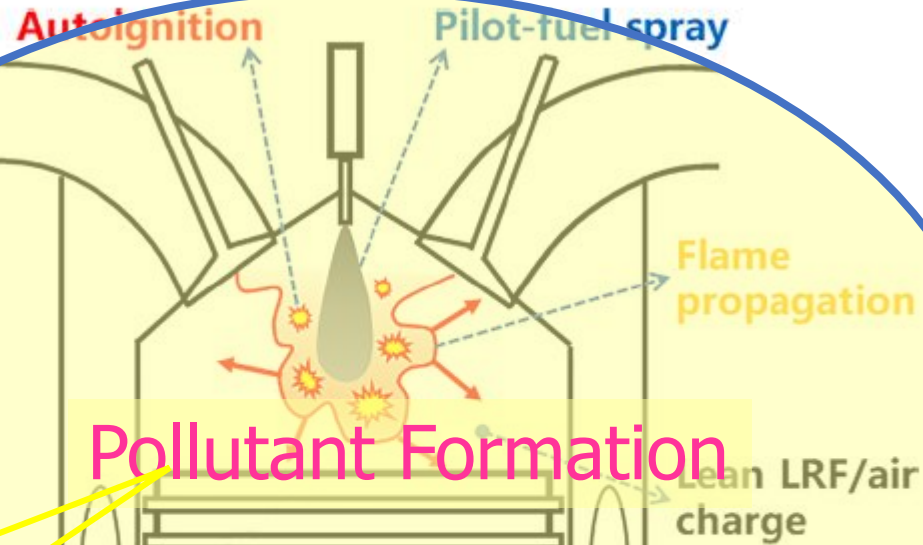
NH₃ AS FUEL FOR POWERTRAIN



« Reactive »
fuel pilot injection

Ignition site

Flow fields



Combustion
Development

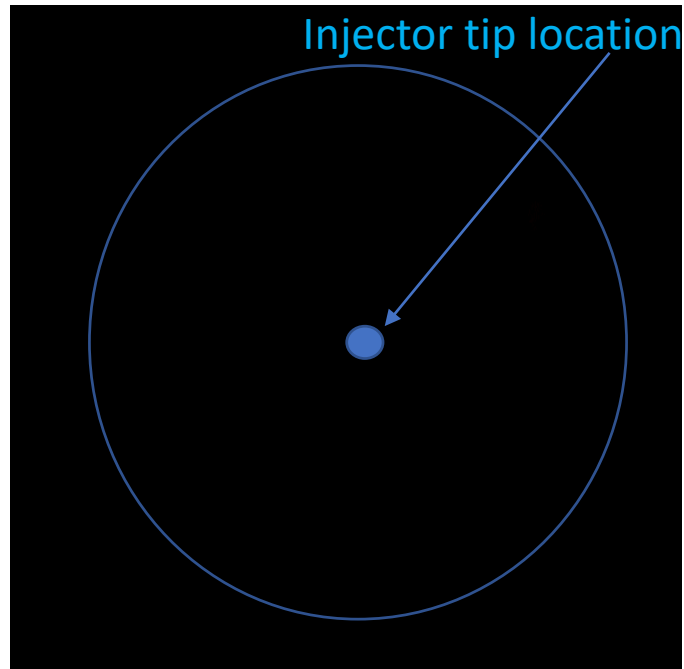
Local Air/fuel
Mixture

Wall-heat
Transfer

Fig. 1. Multiple combustion modes and transition in typical DF engines.

First visualisation of ammonia flame propagation in ICE

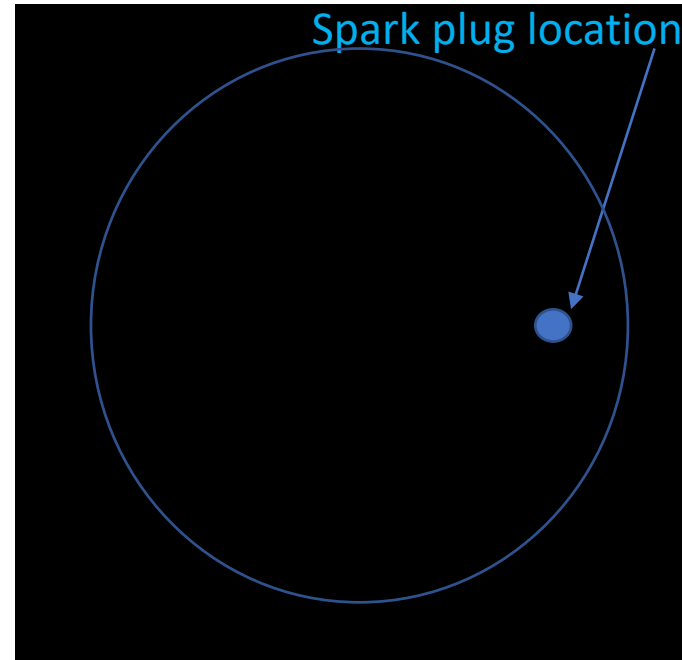
DUAL FUEL NH₃ -Decane



-10 CAD to 57 CAD ATDC

- Start of Injection -22 CAD, duration 6 CAD $P_{inj} = 600$ b, % decane/total fuel = 11% in Energy input
- E.R. total = 1.07, 'higher' IMEP = 7.4 b

Spark Ignition NH₃

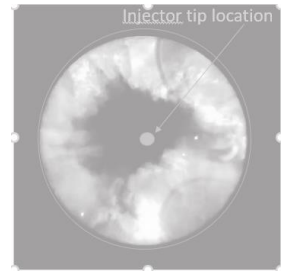


-40 CAD to 27 CAD ATDC

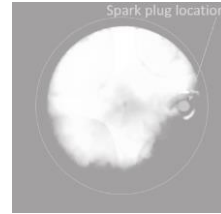
- Spark timing : -40 CAD
- IMEP = 6.7 b

3 images/CAD, during 67 CAD

First visualisation of ammonia flame propagation In ICE

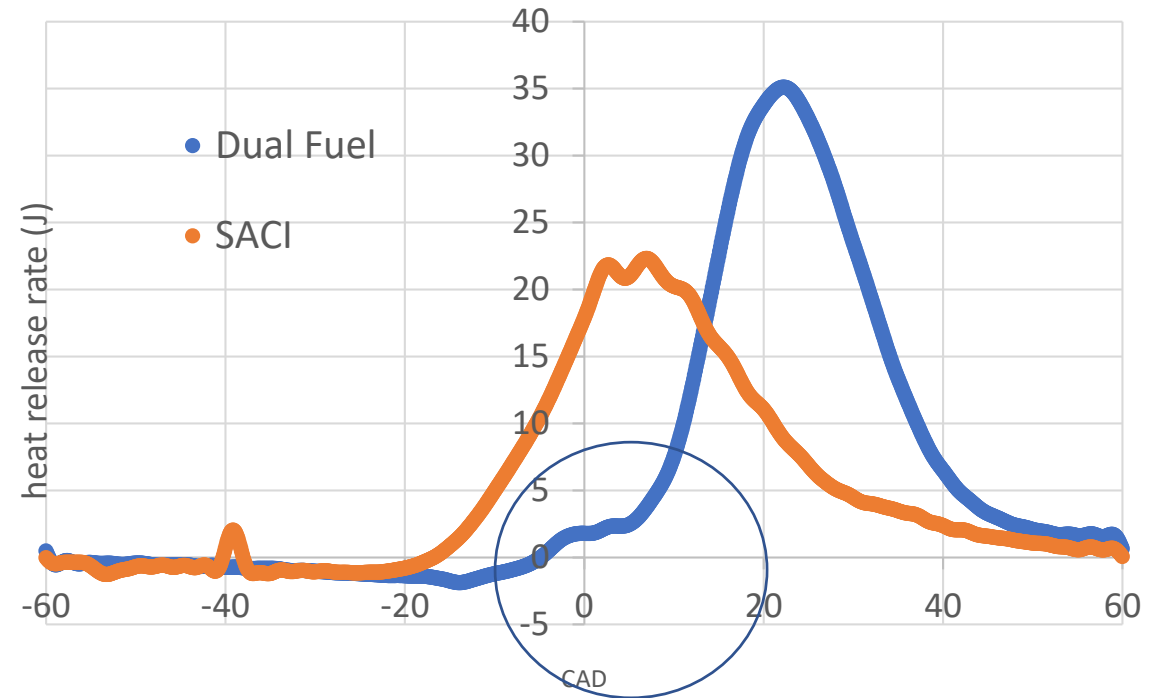
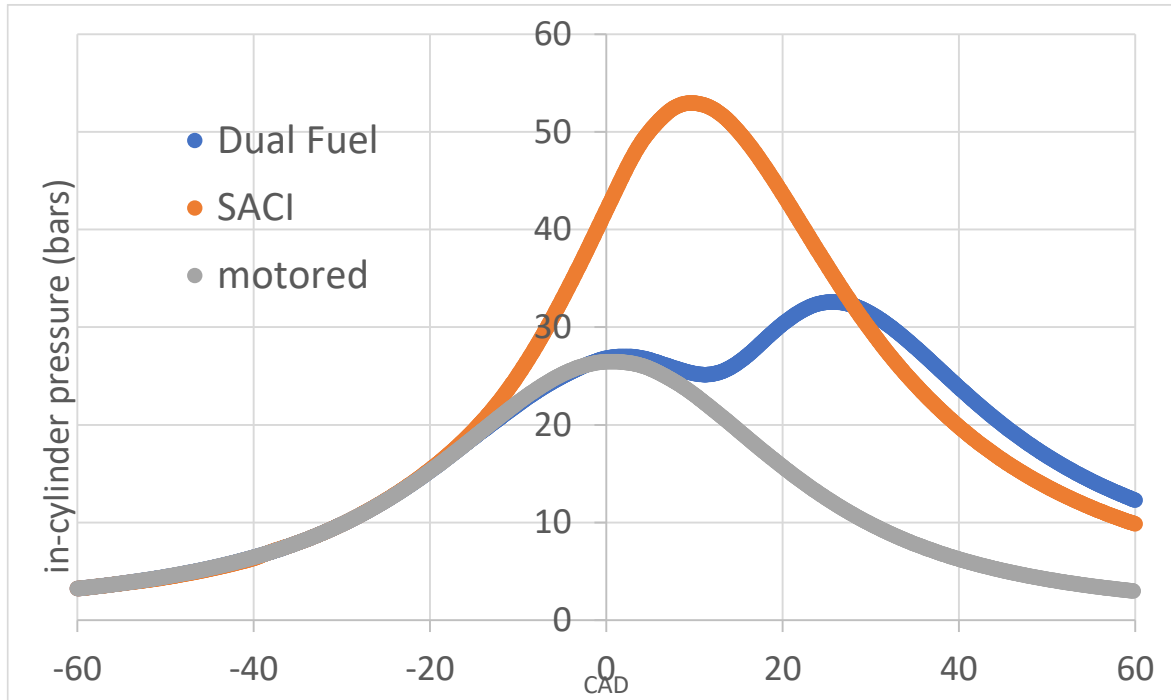


DUAL FUEL NH₃ -Decane



Spark Ignition NH₃

- CR = 16, PSA_DW10 : 0.5 l,
- Engine speed : 1000 rpm,
- Intake pressure = 0.9 bar
T_{intake} = 35°C
- **ER NH₃ = 0.9**



Similar for ER NH₃ = 0.7

First visualisation of ammonia flame propagation In ICE

Decane with ammonia :SOI 22 CAD bTDC

Minimum decane quantity : no OH from decane flame

Decrease of decane quantity : NOTHING _ no IGNITION

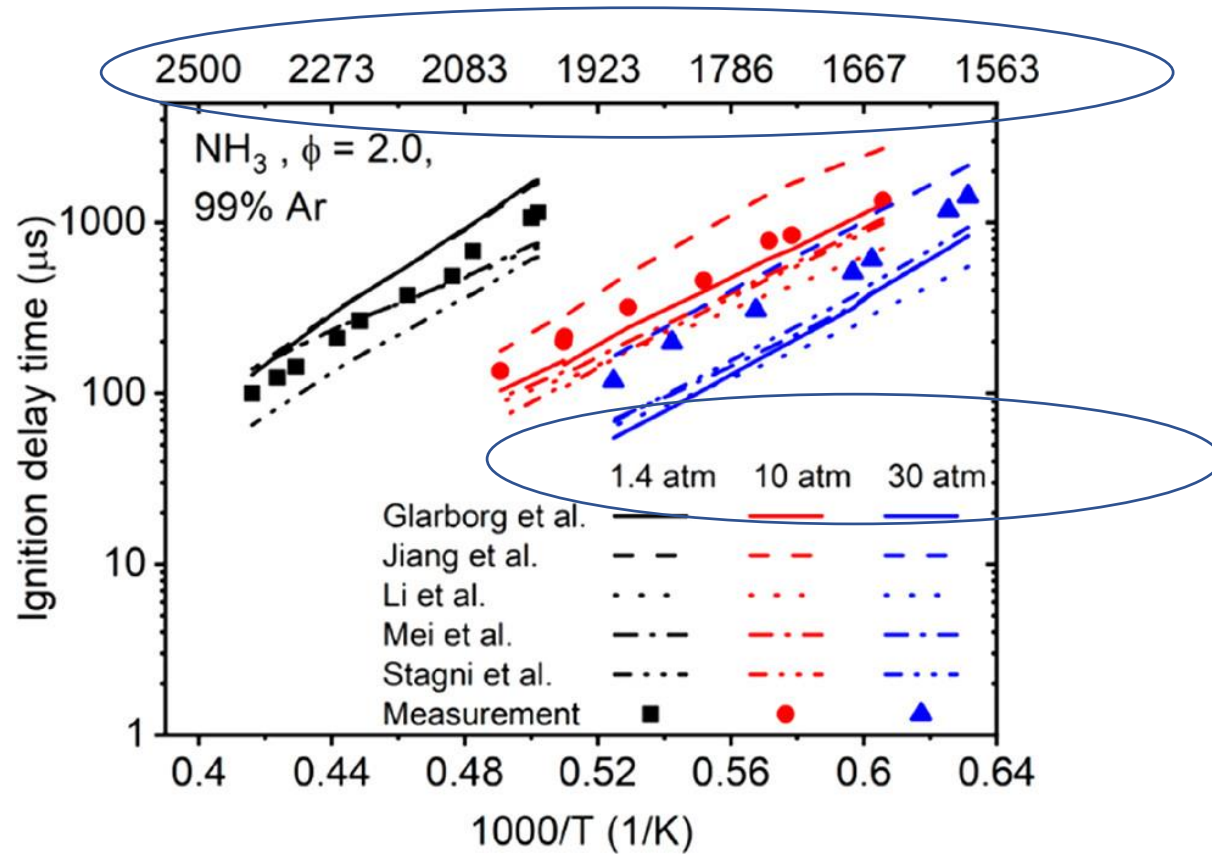


blue = OH, Red = NH

ammonia replaced by N₂
IGNITION OF the pilot

Possible to simulate accurately ?

Auto-Ignition delay



Comparison between simulation results with the selected mechanisms and the measurement from Mathieu and Petersen(70) for ignition delay times of fuel-rich $\text{NH}_3/\text{O}_2/\text{Ar}$ mixtures with at shock tube conditions. Lines, simulation; symbols, measurement.

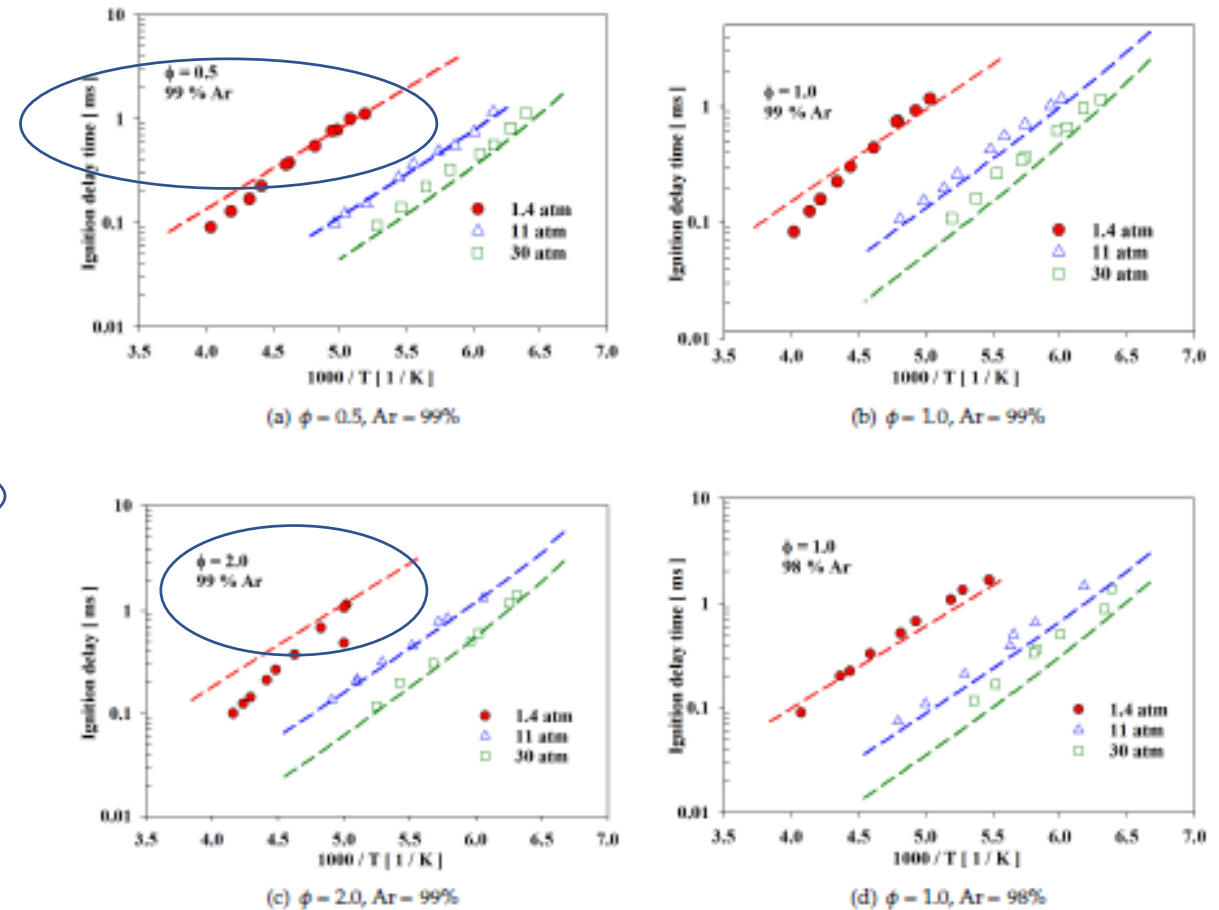
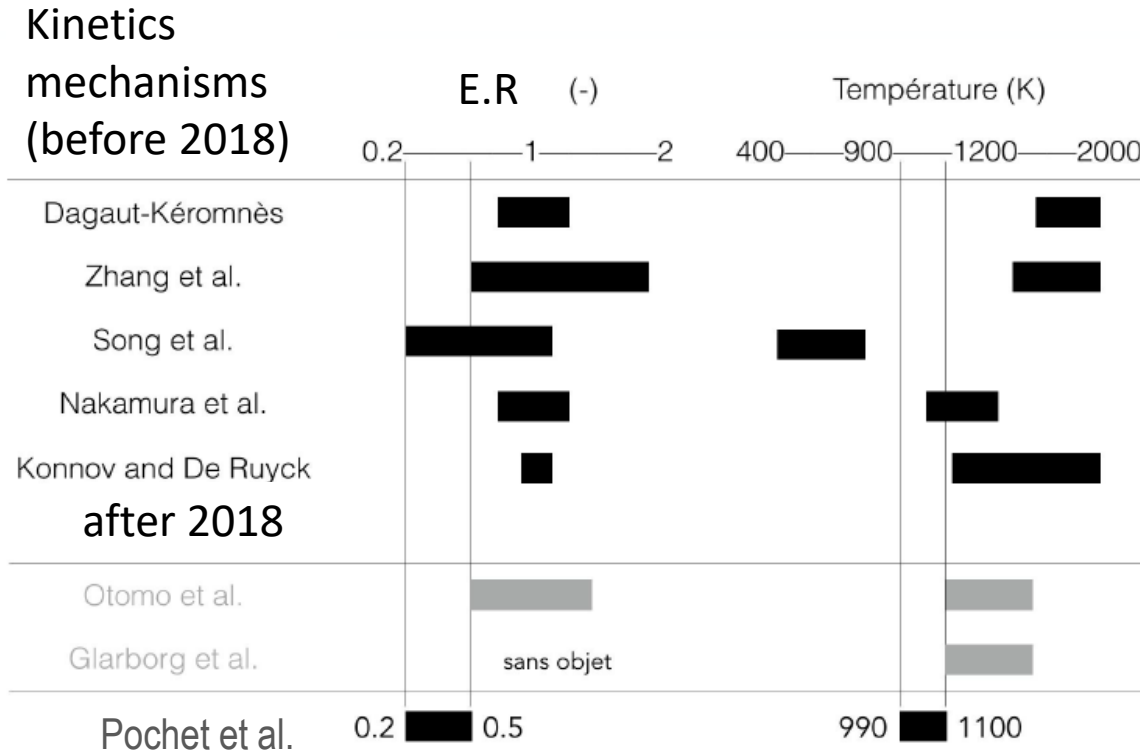


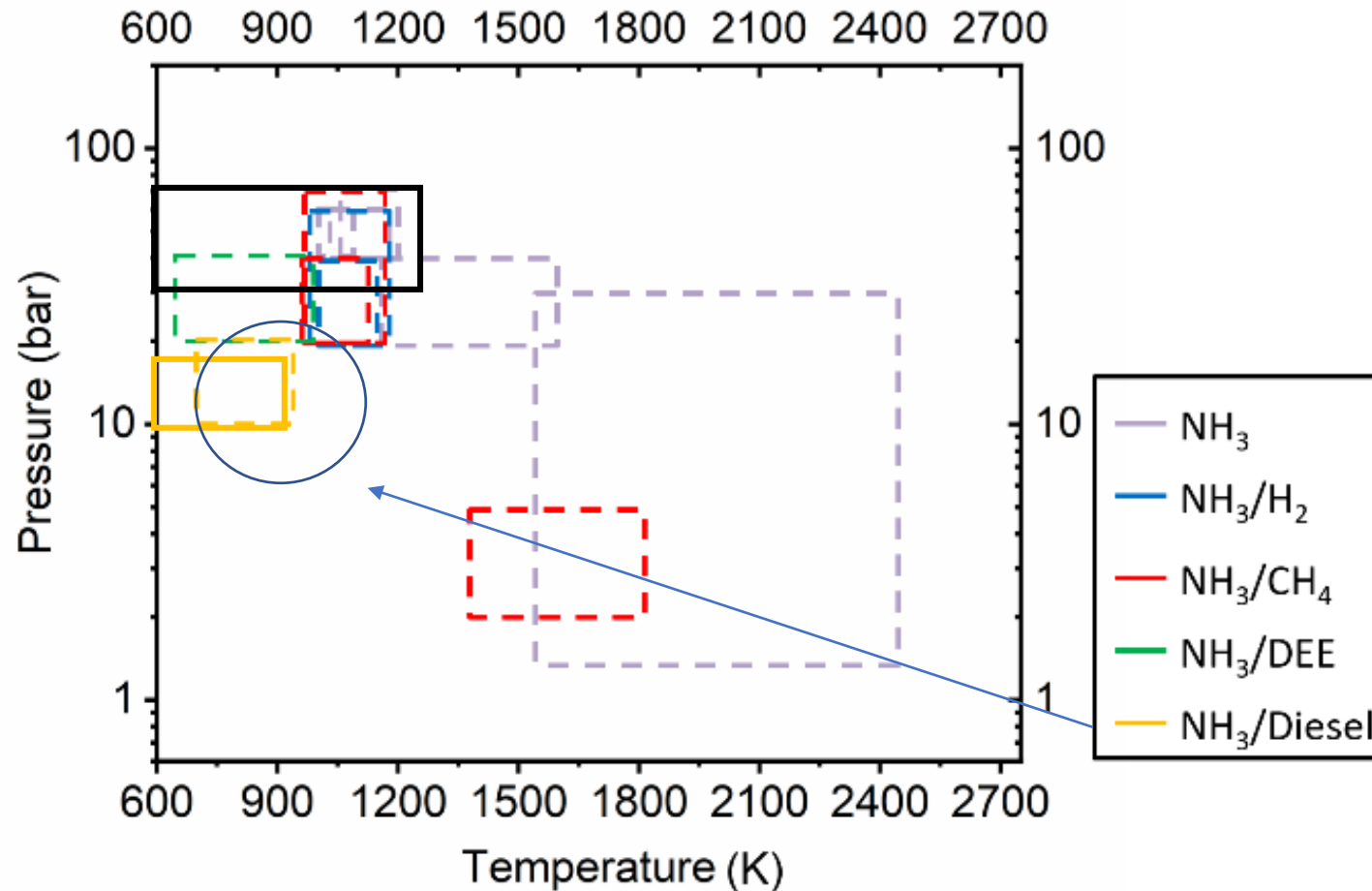
Figure 70: Ignition delay time of $\text{NH}_3/\text{O}_2/\text{Ar}$ at $\phi = 0.5, 1.0$ and 2.0 and at pressure of $1.4, 11$ and 30 atm. Symbols: experimental data from [59], lines: this work.

□ Summary of the conditions of ignition delay time measurements of pure ammonia



- Lack of data
- Lack of predictivity of kinetics mechanism

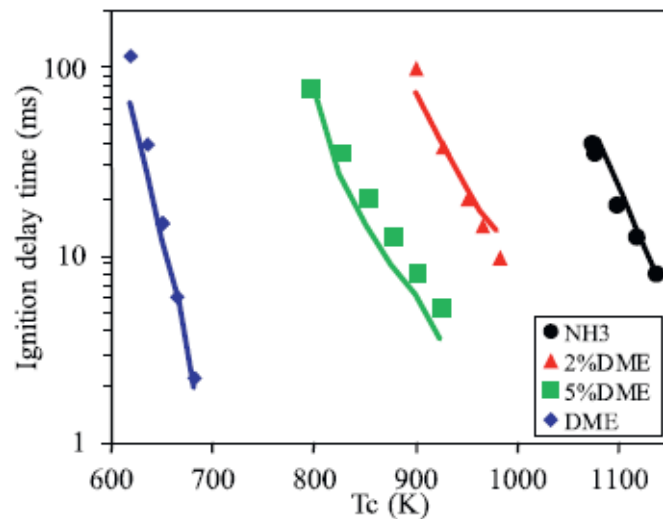
□ Summary of the conditions of ignition delay time measurements of mixtures containing ammonia



— NH₃/n-heptane (2021)

— NH₃/DME (2021)

Impact of DME on ammonia ID



(a) $\phi = 0.5, P_c = 60$ bar

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journal homepage: www.elsevier.com/locate/combustflame



Ignition delay times of NH_3 /DME blends at high pressure and low DME fraction: RCM experiments and simulations

Liming Dai^{a,1}, Hamid Hashemi^b, Peter Glarborg^b, Sander Gersen^c, Paul Marshall^d, Anatoli Mokhov^a, Howard Levinsky^{a,*}

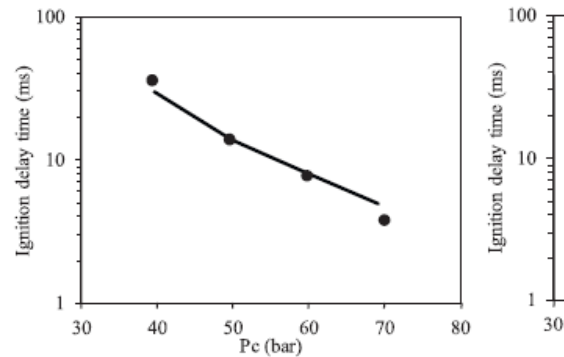
^aEnergy and Sustainability Research Institute, University of Groningen, Nijenborgh 6, 9747 AG Groningen, the Netherlands

^bDepartment of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby DK-2800, Denmark

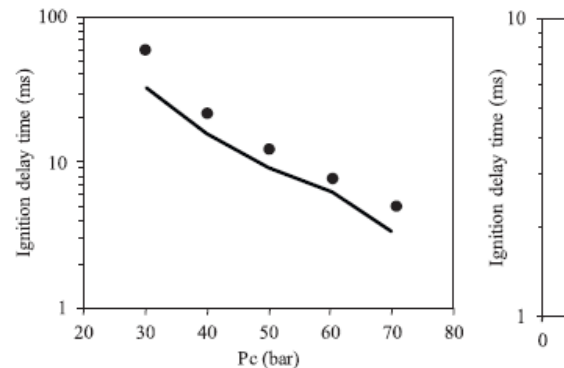
^cDNV GL Oil & Gas, P.O. Box 2029, 9704 CA Groningen, the Netherlands

^dDepartment of Chemistry and Center for Advanced Scientific Computing and Modeling, University of North Texas, 1155 Union Circle #305070, Denton, Texas 76203-5017, United States

*Corresponding author. E-mail: h.levinsky@azc.rug.nl



(b) pure $\text{NH}_3, T_c = 1140$ K



(c) 5% DME, $T_c = 900$ K

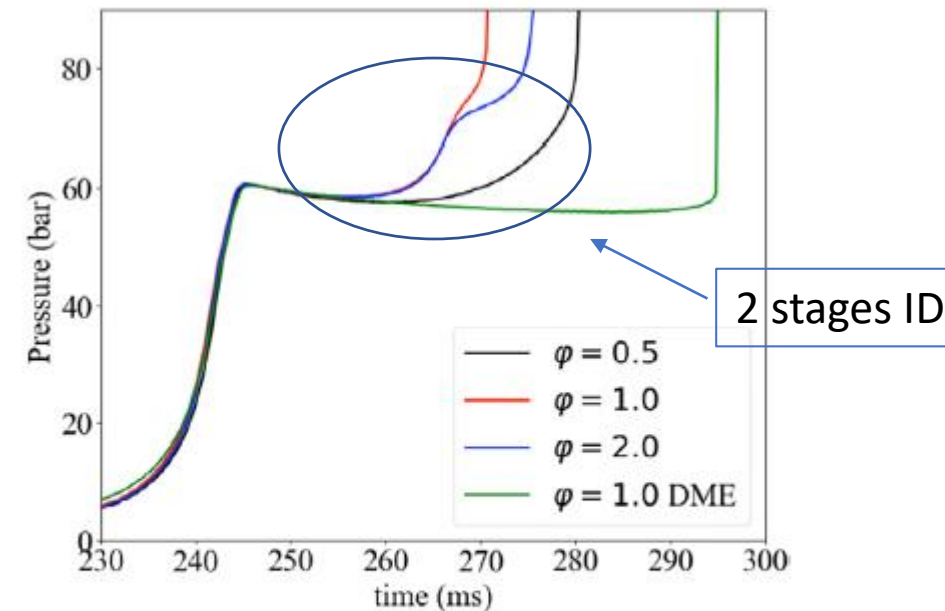


Fig. 2. Measured pressure traces of NH_3 with 2% DME at $T_c = 950$ K and $P_c = 60$ bar. Two-stage ignition is shown at $\phi = 1.0$ and 2.0, slow, pre-ignition pressure rise at $\phi = 0.5$. The curve for DME at $\phi = 1.0$ and 625 K represents “normal” ignition.

First-stage heat release due to reactions of nitrogen containing species, but initiated by **early heat release and OH formation from DME oxidation**

□ Impact of ammonia on n-heptane ID

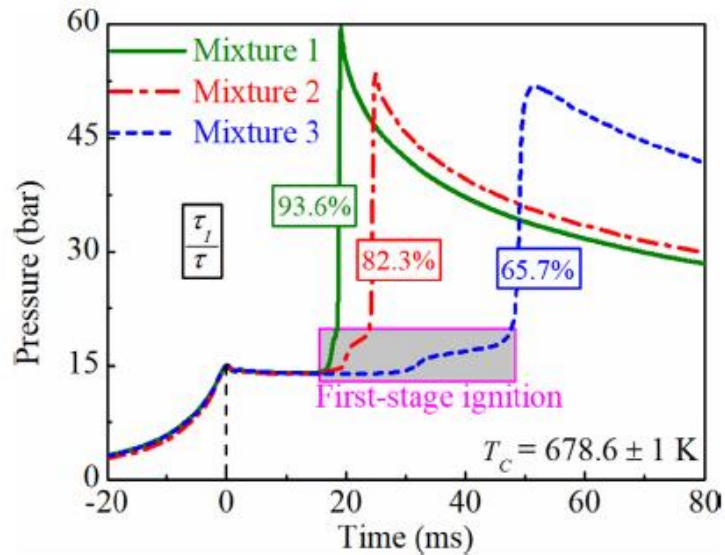
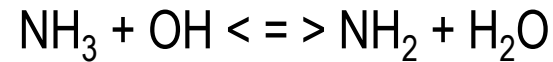
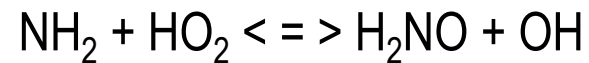


Fig. 4. Comparison of the experimental autoignition pressure curves of n-heptane/NH₃ blending fuels with NH₃ fractions of 0% (mixture 1), 20% (mixture 2), and 40% (mixture 3).



- the largest negative sensitivity at 20% and 40% NH₃ blends (as expected).
- This reaction consumes a lot of radicals and lowers the rate of the low- T reaction of n-heptane, thus greatly delaying the first-stage ignition



- The only positive sensitivity reaction of the NH₃ subset
- consumption HO₂ radical, production of active OH radical
- promoting the autoignition of NH₃ /n-heptane blend.

Combustion and Flame 217 (2020) 4–11



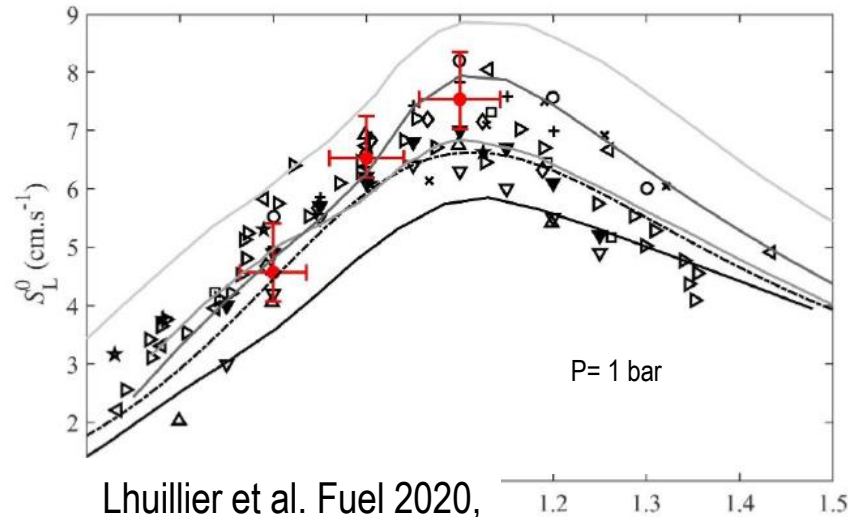
The effect of ammonia addition on the low-temperature autoignition of n-heptane: An experimental and modeling study

Liang Yu, Wei Zhou, Yuan Feng, Wenyu Wang, Jizhen Zhu, Yong Qian, Xingcai Lu*

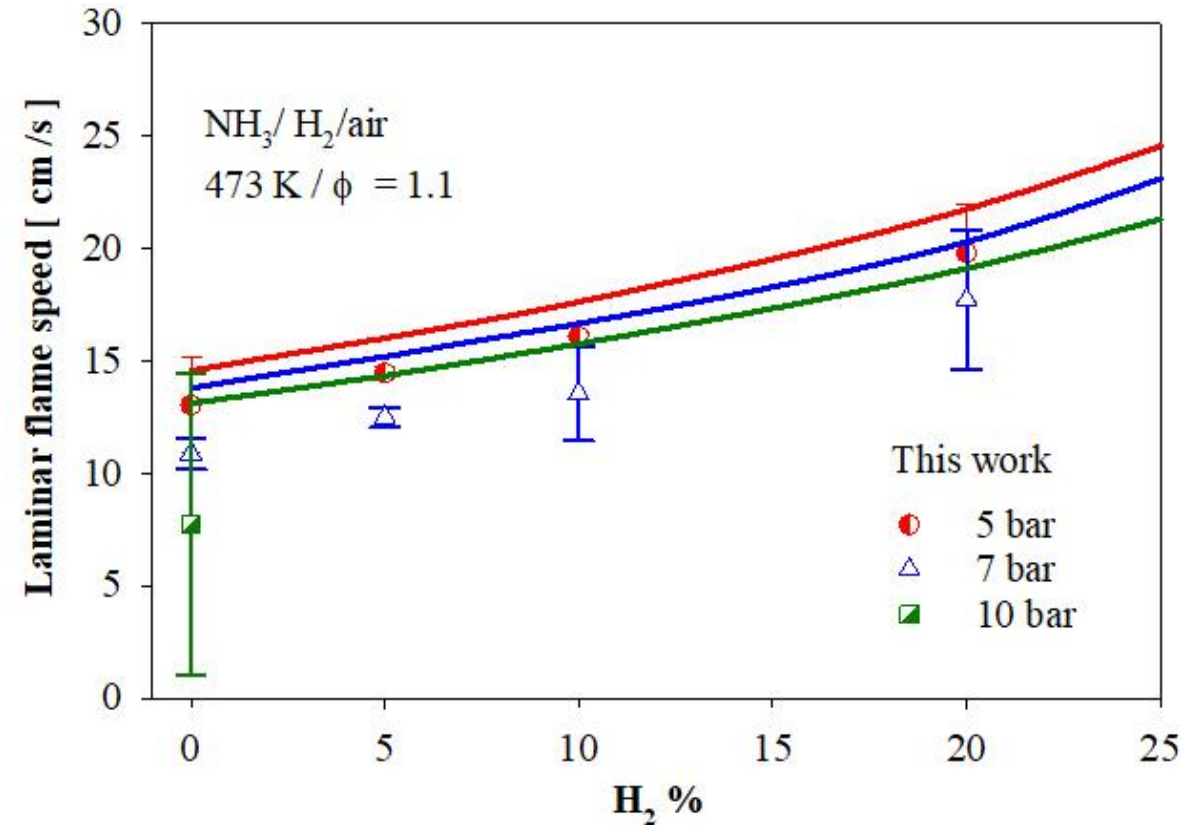
School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

First kinetics mechanism

□ For ammonia only



Lhuillier et al. Fuel 2020,
 UORLEANS/VUB PHD thesis 2020
 Shrestha et al., PROC12021
 BTu PhD thesis 2021



- Laminar flame speed of NH_3/H_2 blend decreases as pressure increase.
- As in 1 bar case increase of H_2 fraction in fuel blend increases the flame speed.
- At higher pressure above 3 bar model overpredicts the flame speed for some points.
- Increase in flame speed with H_2 addition is due to radical promoting effect of H_2 chemistry.

□ In mixture ('done' with H₂ and CH₄) but

□ interactions of NH₃ with practical hydrocarbon fuels, such as gasoline, diesel, or surrogate fuels, never reported

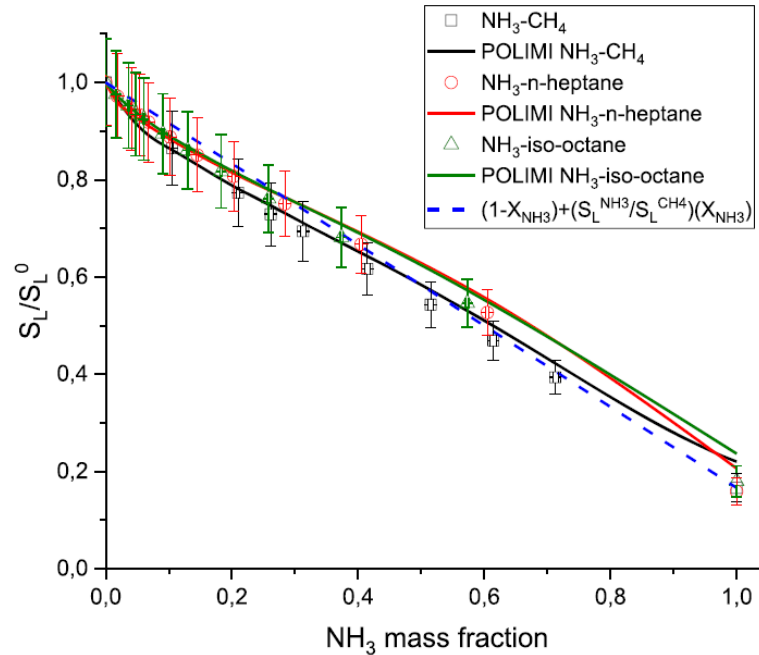


Figure 5. Experimental (symbols) and simulated (lines) stoichiometric S_L versus NH_3 mass fraction at 338 K and 1 atm, normalized by S_L of pure fuel/air mixtures (S_L^0). Black squares, CH_4/NH_3 -air mixtures; red circles, n -heptane/ NH_3 -air mixtures; and green triangles, iso-octane/ NH_3 -air mixtures. The value of S_L for pure NH_3 is from ref 63.

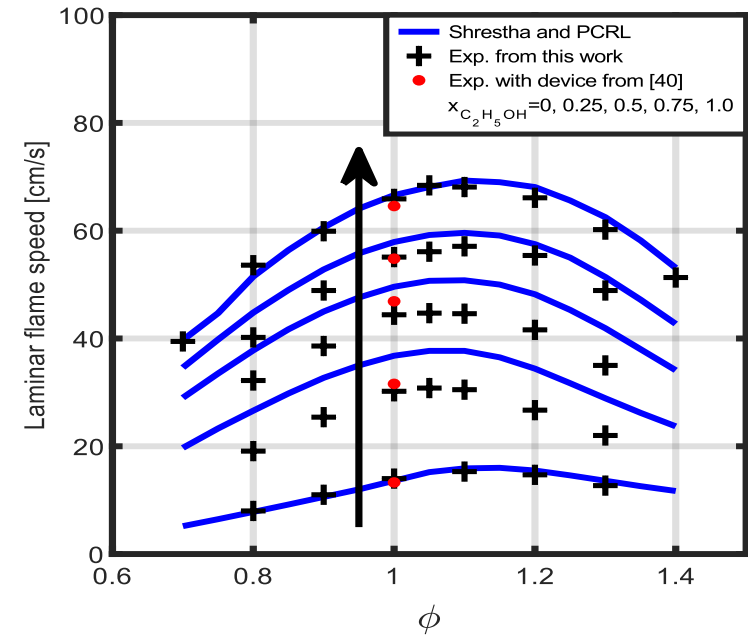
Comparative Effect of Ammonia Addition on the Laminar Burning Velocities of Methane, n-Heptane, and Iso-octane

November 2020 · Energy & Fuels XXXX(XXX) · [Follow journal](#)

DOI: [10.1021/acs.energyfuels.0c03424](https://doi.org/10.1021/acs.energyfuels.0c03424)

Lab: Alexander A. Konnov's Lab

Marco Lubrano Lavadera · Xinlu Han · Alexander A. Konnov



Comparison of the laminar flame speed of different ammonia/ethanol blends from the kinetics simulation with Shrestha and PCRL merged mechanism (continuous line) and experimental data (+symbol) at 423K and 1 bar: bottom to top $X_{\text{C}_2\text{H}_5\text{OH}}=0, 0.25, 0.5, 0.75, 1.0$

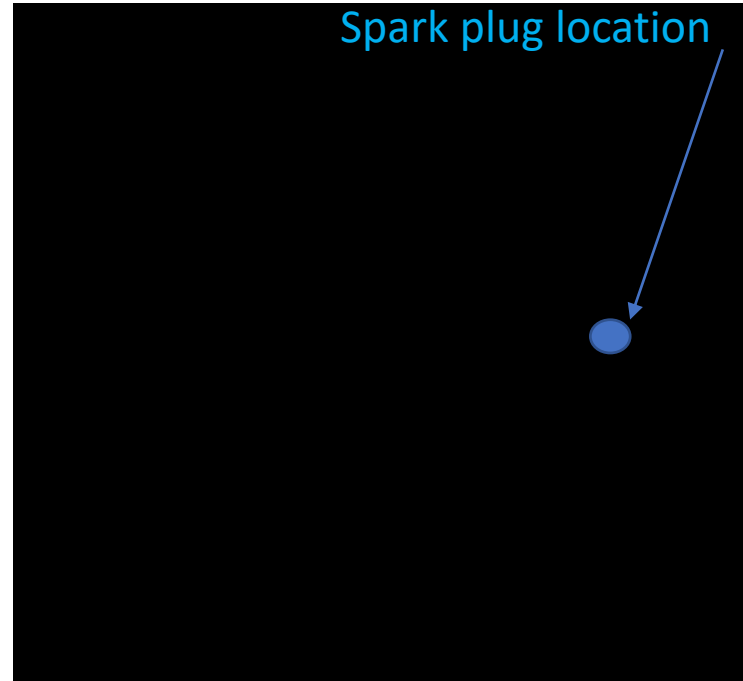
FIRST VISUALISATION OF AMMONIA FLAME PROPAGATION IN ICE

Engine Type	Current PSA EP6DT	Spark assisted Diesel engine
Displacement Volume V_{cyl}	400 cm ³	500 cm ³
Compression Ratio	10.5	16
Valves	4	4
Tumble ratio	2.4	
Swirl ratio		1.1

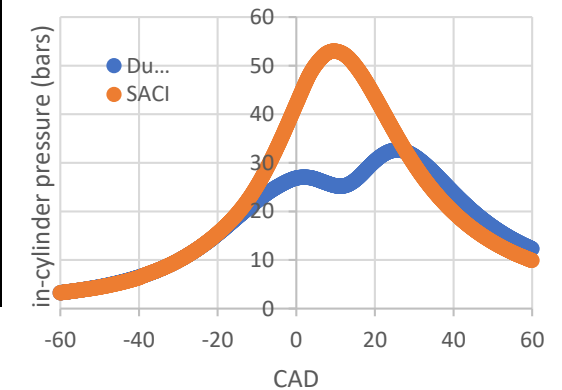
- Engine speed : 1000 rpm,
- Intake pressure = 0.9 bar
- Tintake = 35°C, Spark timing : -40 CAD

3 images/CAD, during 67 CAD

-40 CAD to 27 CAD ATDC



FULLY PREMIXED PROPAGATION



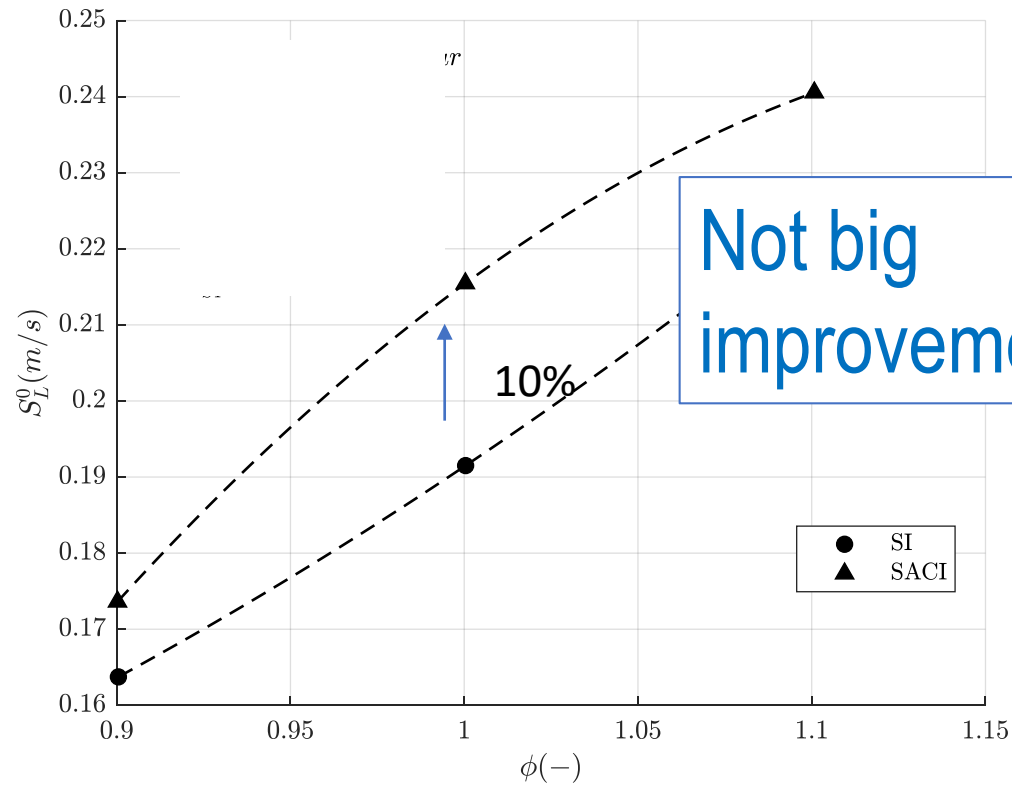
ER NH₃ = 0.9

IMEP = 6.7 b

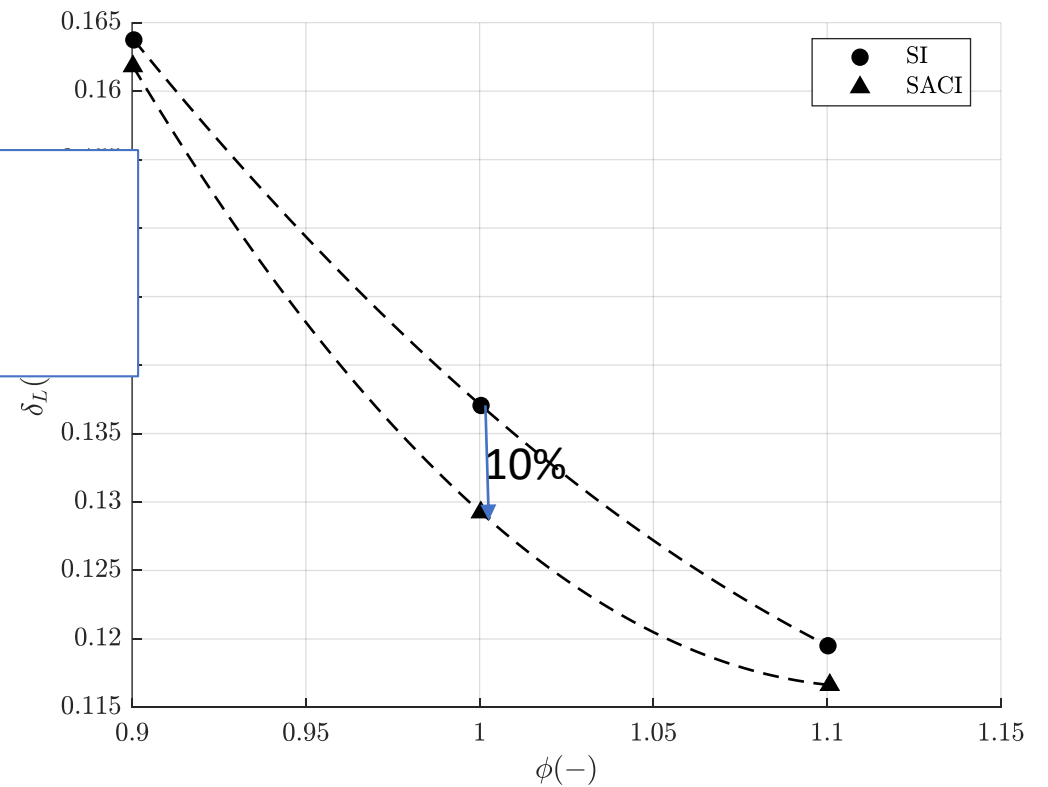
PREMIXED TURBULENT FLAMES

Example SI engine to Spark ignited Diesel engine

	SI	SAD
P (SIT)	8 b	12 b
T (SIT)	640K	698 K
U'(SIT)	2.5 m/s	1.5 m/s
Lt (mm)	1.5 mm	0.8 mm



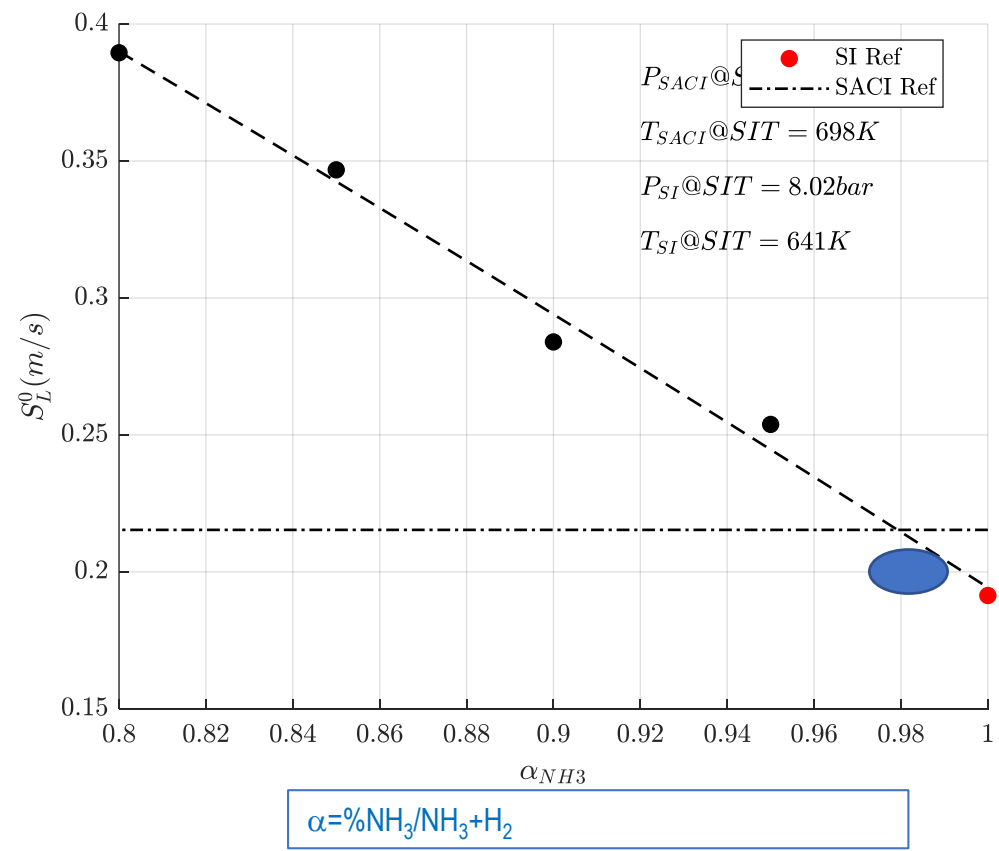
Not big improvement



PREMIXED TURBULENT FLAMES

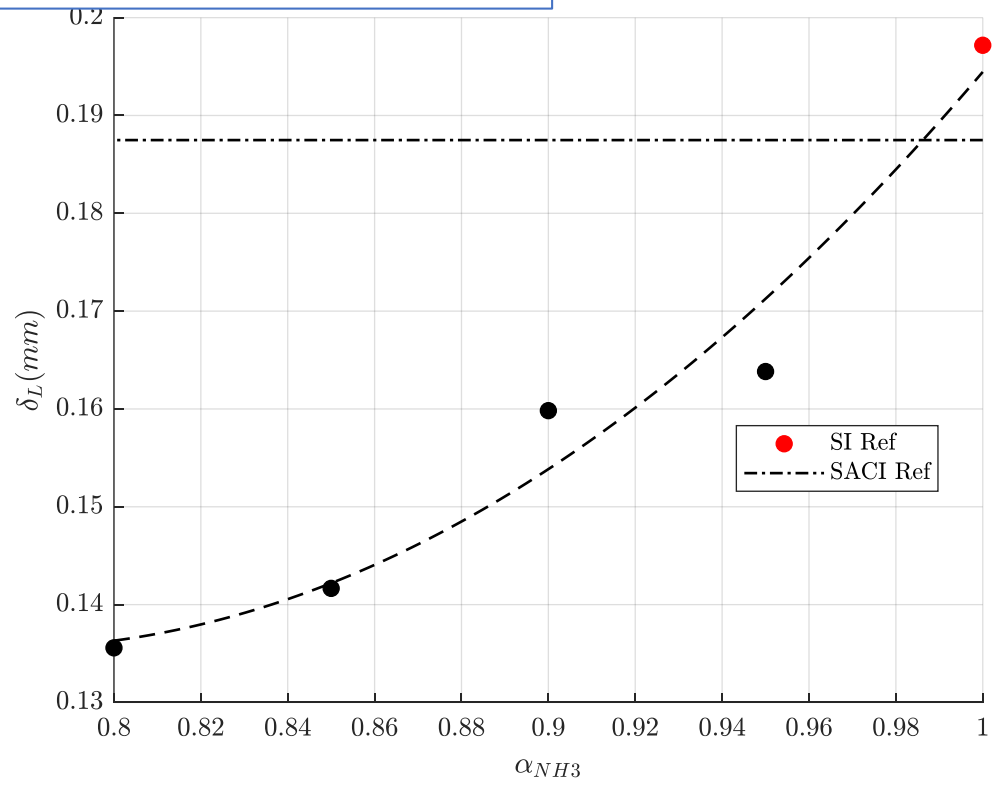
SI to SACI :

	SI	SACI
P (SIT)	8 b	12 b
T (SIT)	640K	698 k



$\alpha = \%NH_3 / (NH_3 + H_2)$

Less than H₂ !!

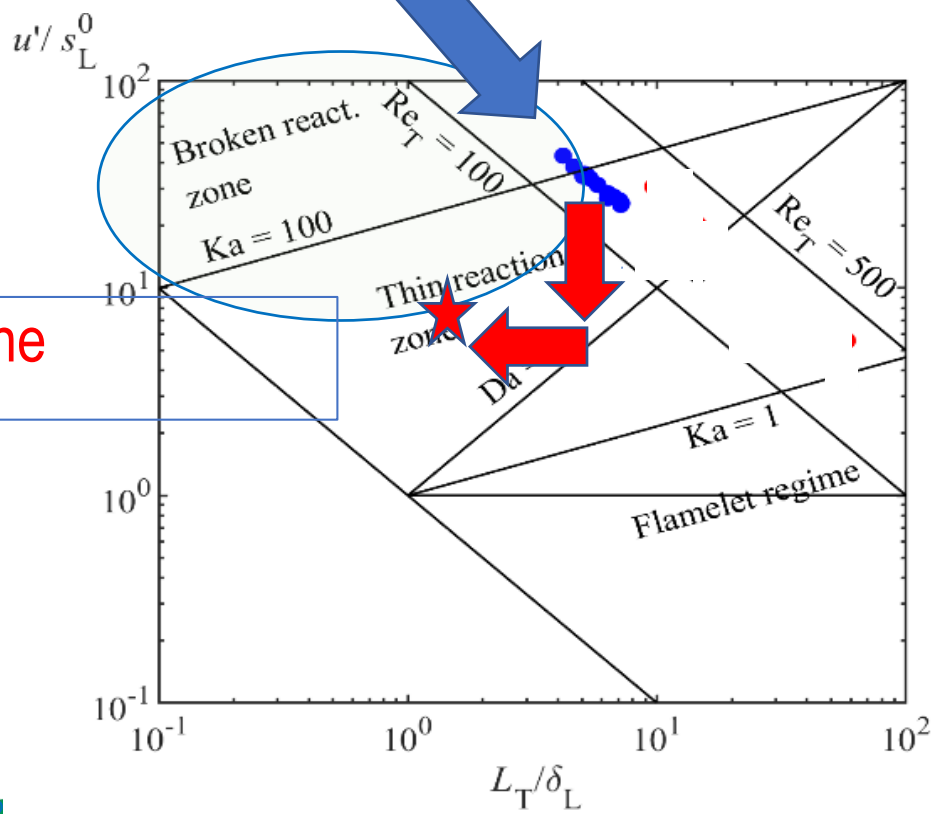


PREMIXED TURBULENT FLAMES

- What flow field ?
- What engine design for NH₃ Combustion ?

SI engine

SA D engine

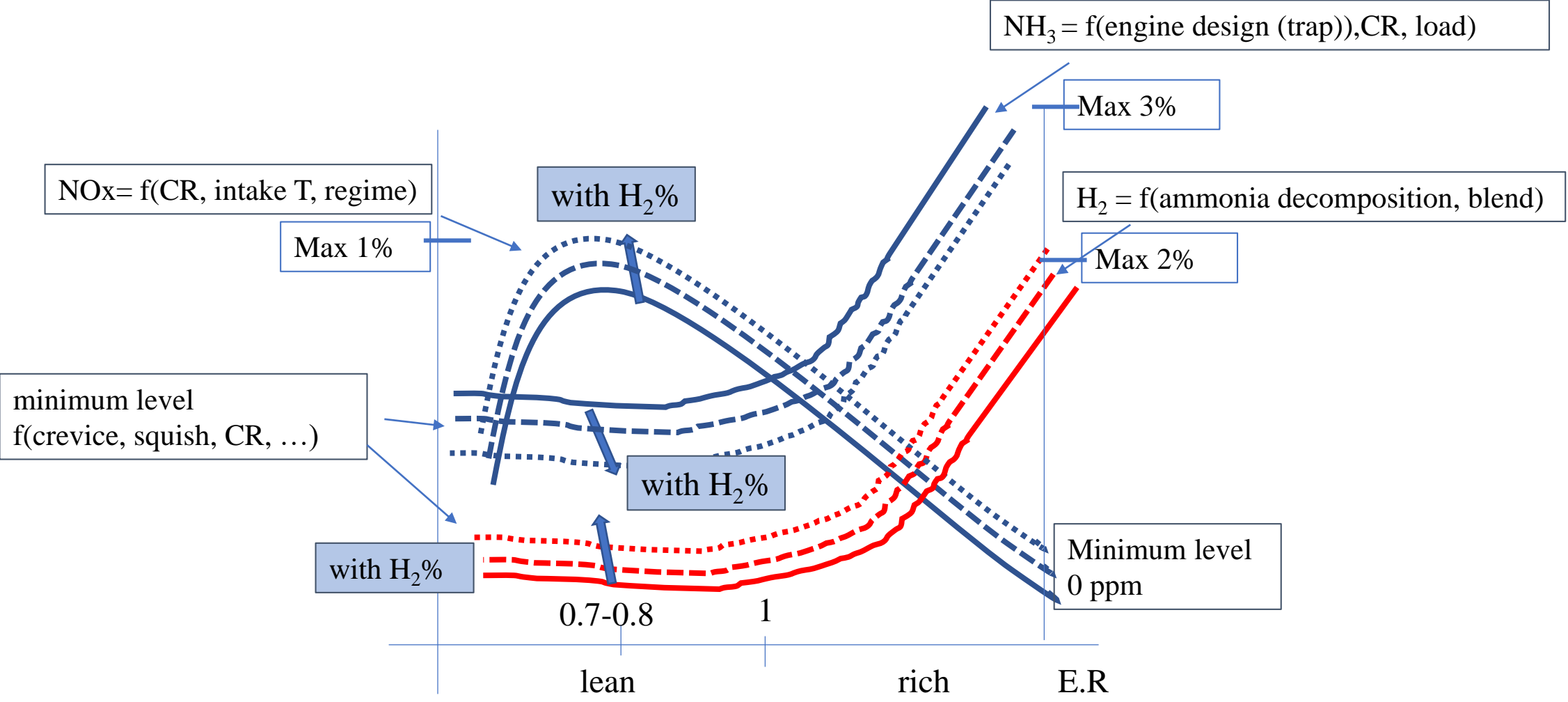


	SI	SACI
P (SIT)	8 b	12 b
T (SIT)	640K	698 K
U'(SIT)*	2.5 m/s	1.5 m/s
L _T (mm)*	1.5 mm	0.8 mm



NH₃/10%H₂, ER=1, u'=0.65 m/s

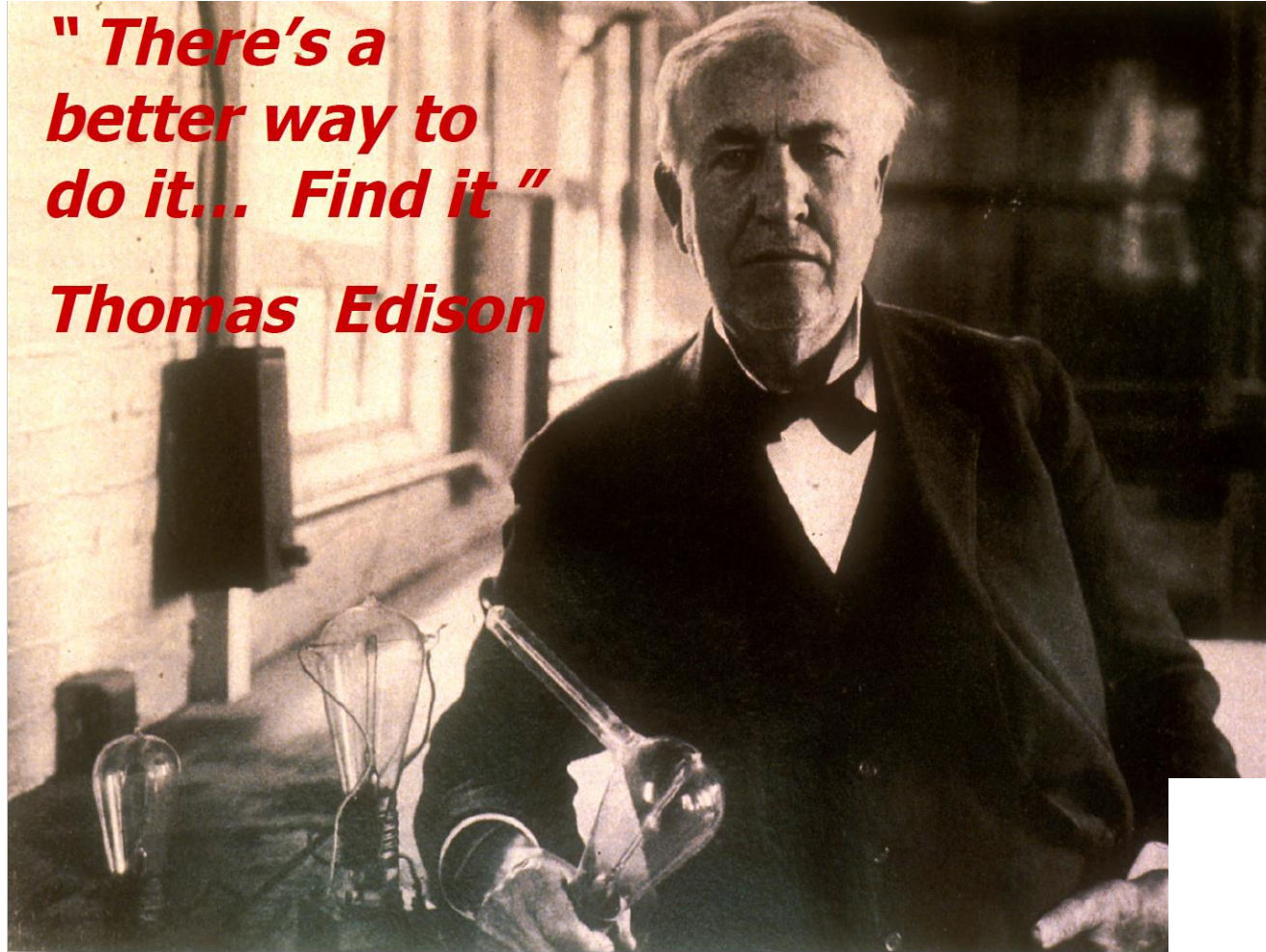
POLLUTANT EMISSIONS : TENDENCIES



CONCLUSION : AMMONIA IN ICE

" There's a better way to do it... Find it "

Thomas Edison



Good luck
and
HAVE FUN



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