Northumbria University NEWCASTLE

Jaguar Land Rover

Title: Reduced syngas-based chemical kinetics mechanisms for dual fuel engine combustion applications

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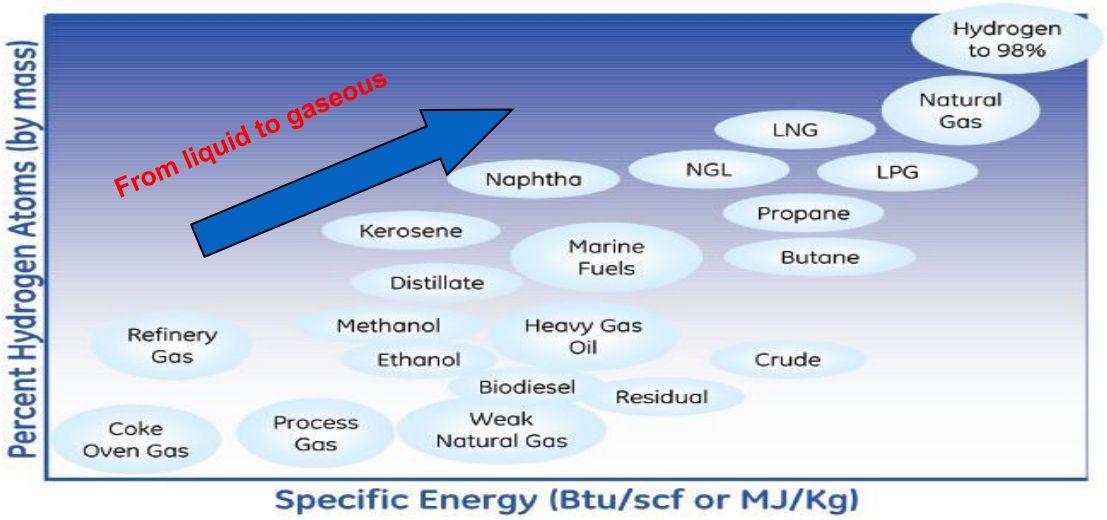
Introduction

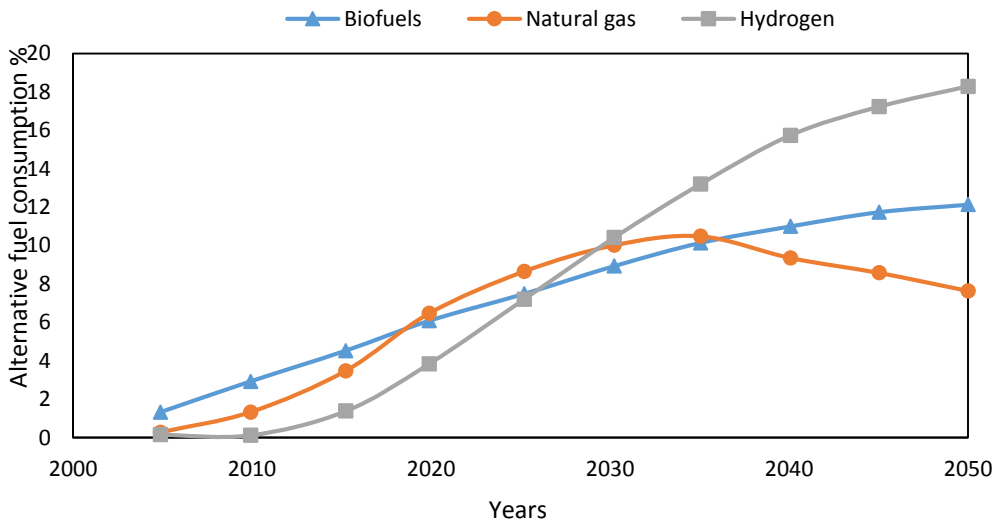
- **Shortage** of petroleum resources
- **Global** warming

→

- **Higher** thermal efficiency
- **Reduction** of CO_2



Future fuels trend [1]



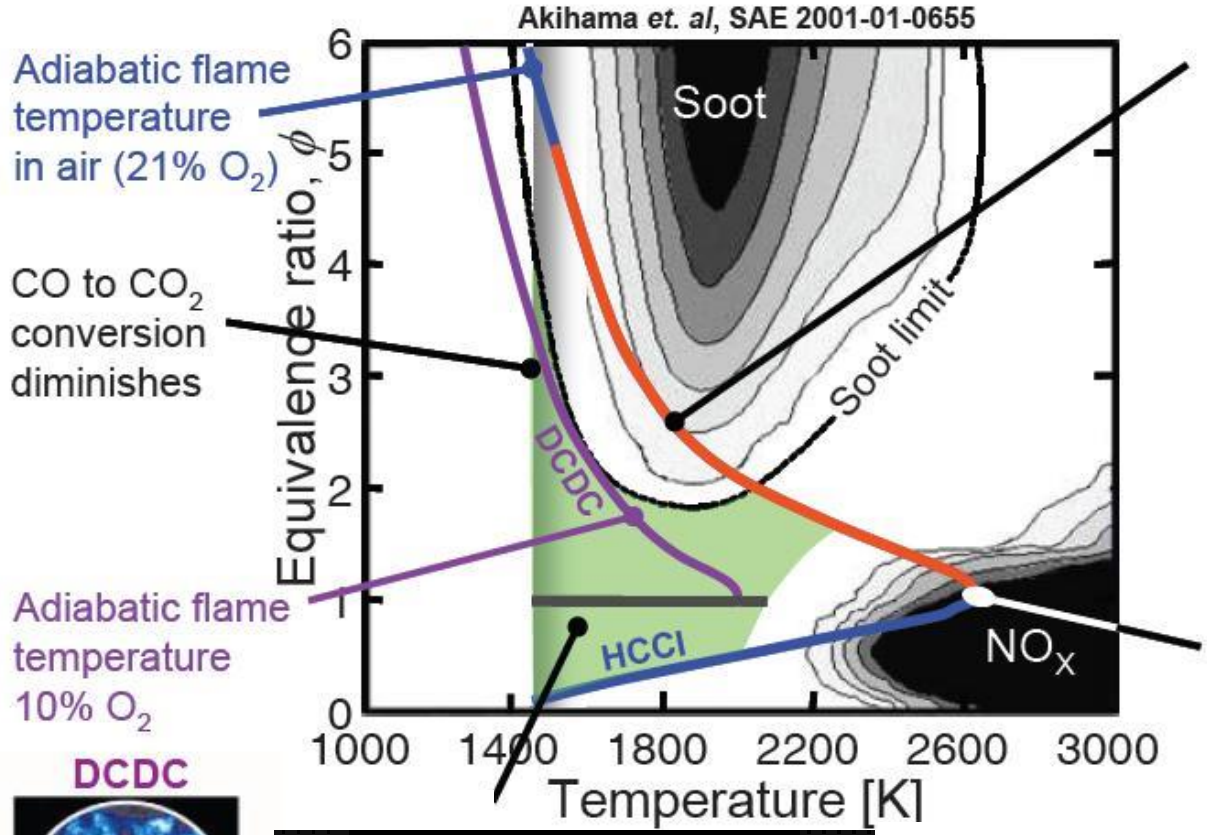
Future rate of alternative fuels consumption to the total automotive fuel consumption rate in the world [2]

Advantages of gaseous fuel

- **Variety in composition**
- **Clean exhaust → ultra low SO_x, PM and CO_2**
- **High ignition temperature → improved knock resistance**

[1]Sims, Ralph EH, Warren Mabee, Jack N. Saddler, and Michael Taylor. "An overview of second generation biofuel technologies." *Bioresource technology* 101, no. 6 (2010): 1570-1580.
[2] Adeeb Z, Glycerol delignification of poplar wood chips in aqueous medium. Energy Education Science and Technology, 2004. 13: p. 81-88.

Different engine combustion technologies



Diesel (CI) combustion

[redacted]

Spark ignition (SI) combustion

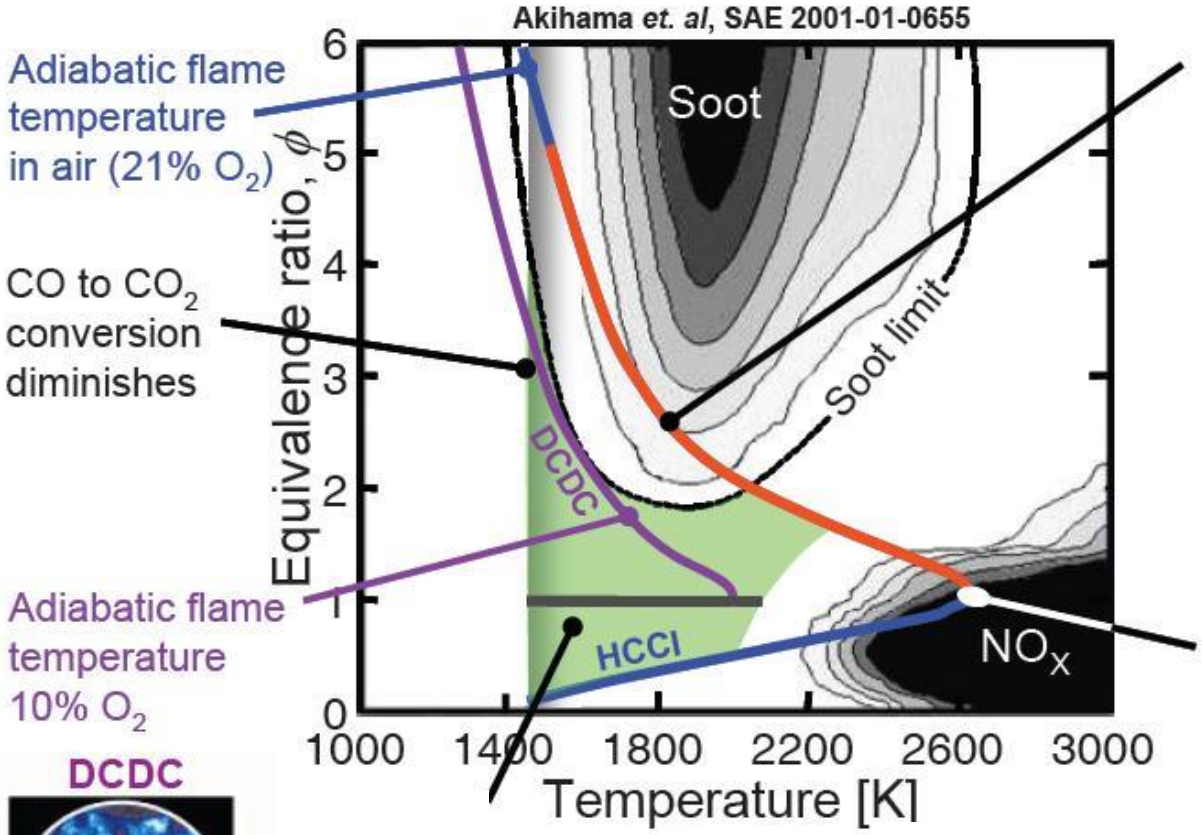
[redacted]

DCDC

[redacted]

Homogeneous Charge Compression Ignition (HCCI)

Different engine combustion technologies



Diesel (CI) combustion

- Controlled heat release (mixing)
- Controlled combustion timing
- Wide load range
- High efficiency (relative to SI)
- **NO_x and PM emissions**

DCDC

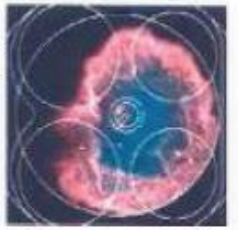
- High efficiency (high CR, n
- Low NO_x and PM emissions

- **Load range?**
- **Combustion timing?**
- **Heat release rate?**
- **Transient control?**
- **Fuel?**

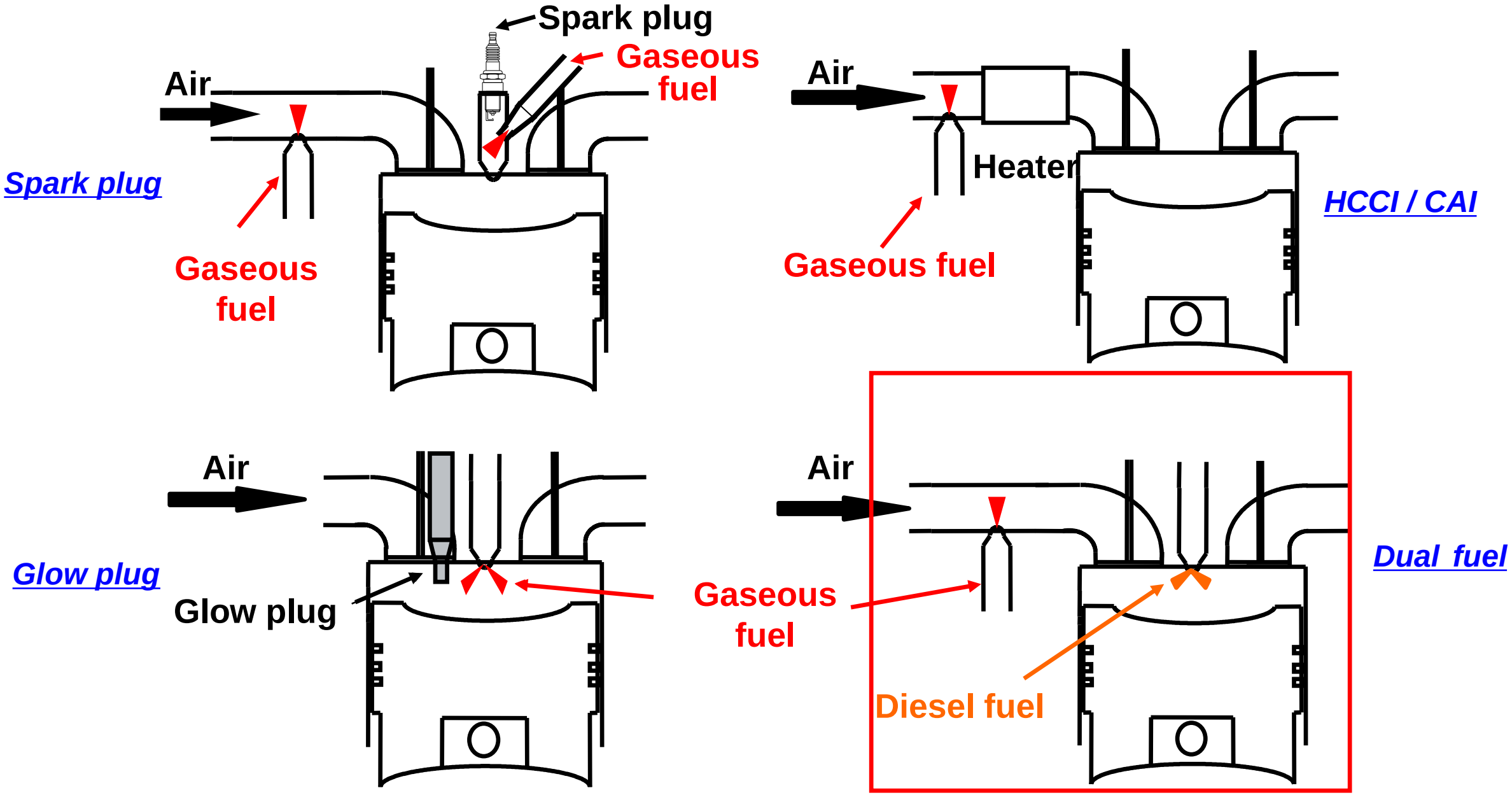
Homogeneous Charge Compression Ignition (HCCI)

Spark ignition (SI) combustion

- Controlled heat release (flame propagation)
- Controlled combustion timing
- Wide load range
- Three-way catalyst
- **Low efficiency** (relative to diesel)

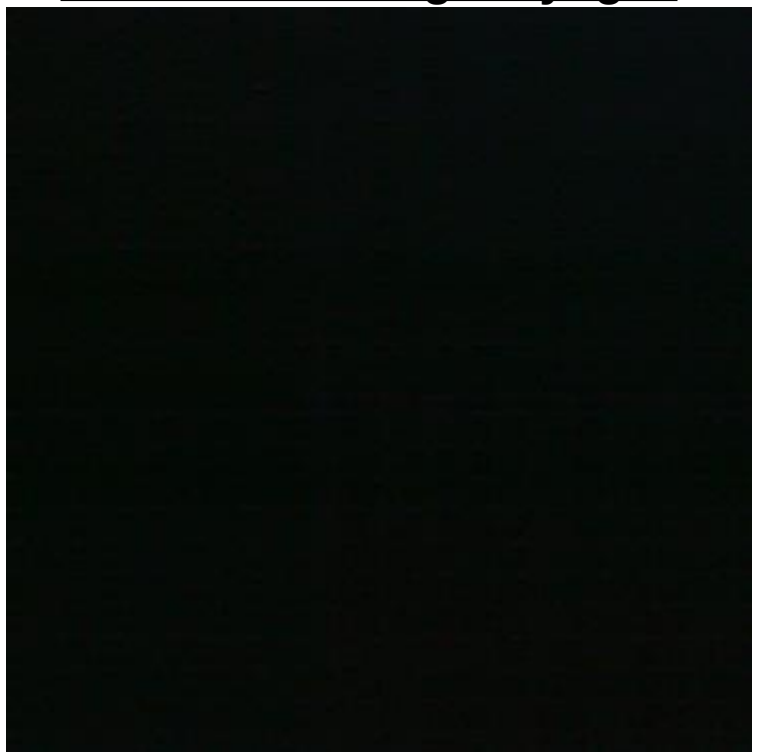


Ignition systems



Dual-fuel engine combustion

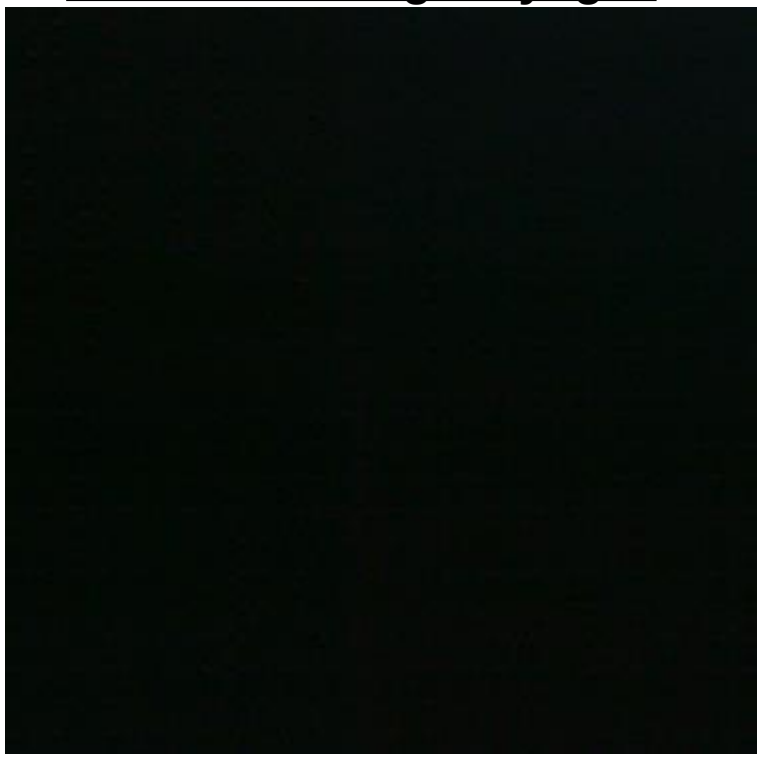
Diesel fuel 10 mg + Syngas



Conventional diesel injection [188]

High soot and NOx emissions

Diesel fuel 2 mg + Syngas

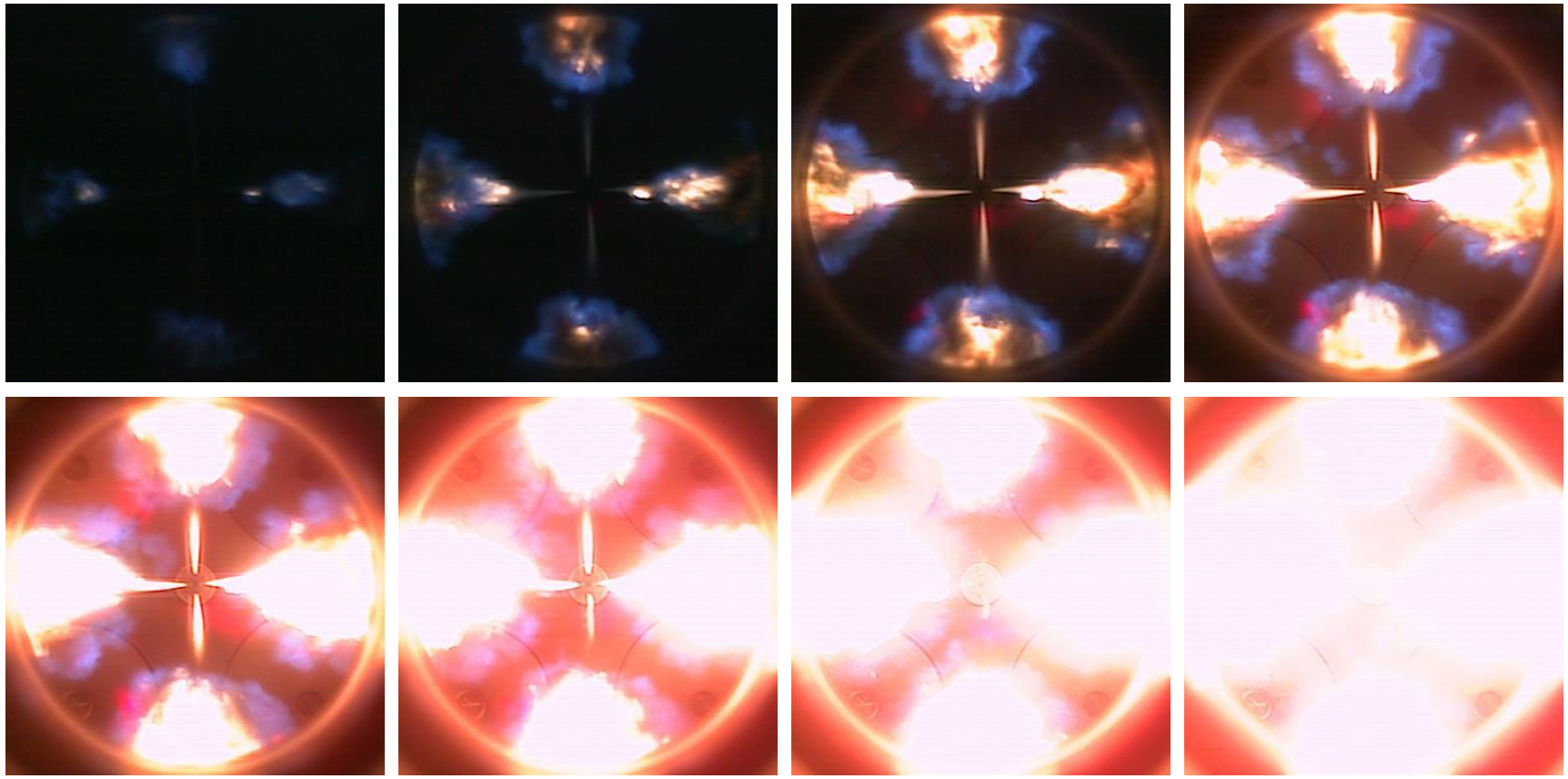


Micro-pilot diesel injection [188]

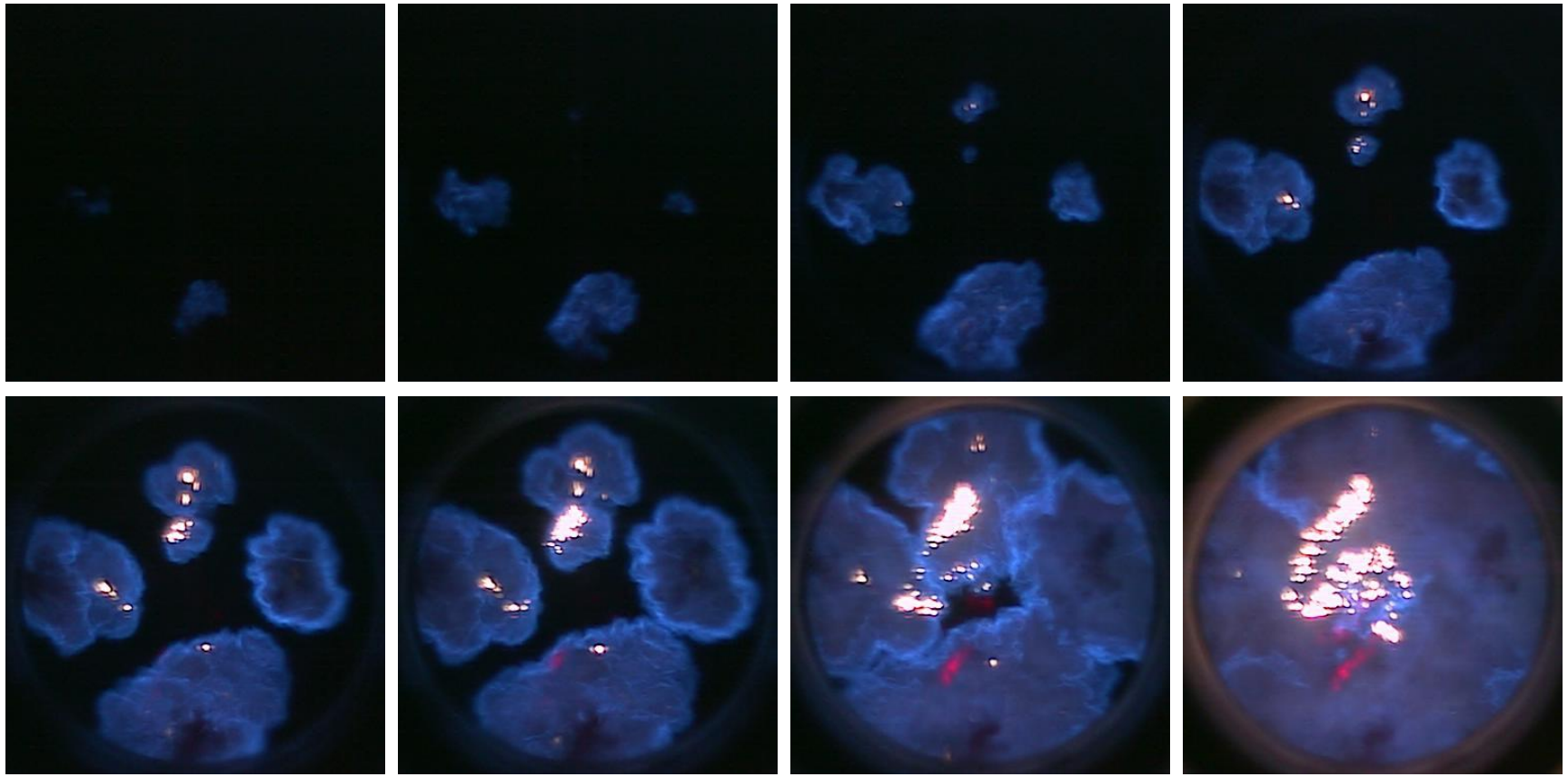
Ultra-low soot and NOx emissions

[3] Azimov Ulugbek, Eiji Tomita, Nobuyuki Kawahara, and Yuji Harada, Effect of syngas composition on combustion and exhaust emission characteristics in a pilot-ignited dual-fuel engine operated in PREMIER combustion mode. international journal of hydrogen energy, 2011. **36**(18): p. 11985-11996

Diesel fuel 10 mg + Syngas



Diesel fuel 2 mg + Syngas



Numerical analysis of the combustion process

- Chemical kinetics mechanisms that were developed during the past years were mainly focused on simulating the combustion of pure H_2 or H_2/CO syngas mixtures.
- However, simple H_2/CO mixtures **are not fully adequate** to represent real syngas fuels, since **CH_4** has a significant influence on the combustion process
- Moreover, chemical kinetics mechanisms that have been developed for the simulation of n-heptane oxidation consist of a **huge number** of species of reactions and **cannot** be implemented in multidimensional CFD simulations

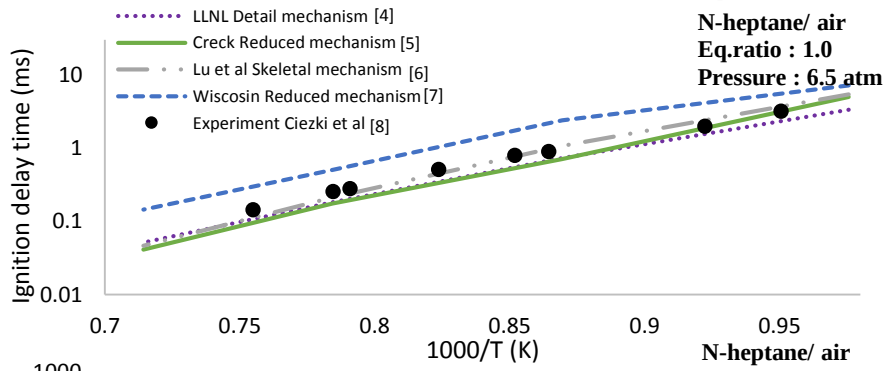
There is a need for a robust, reduced and computational efficient chemical kinetics mechanism for the simulation of multicomponent syngas combustion, syngas/n-heptane co-oxidation and NOx formation.

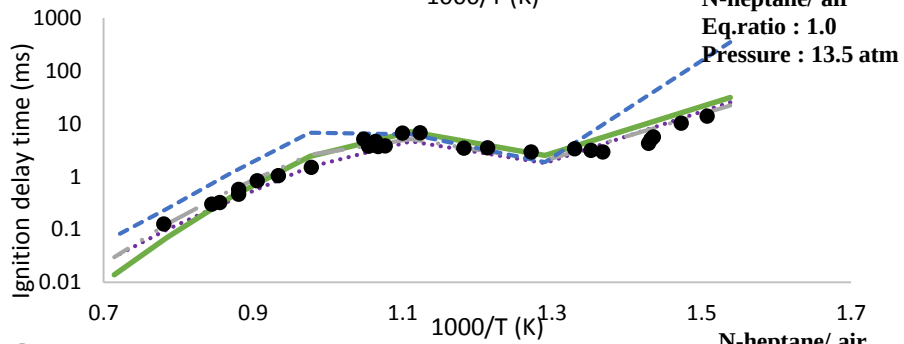
Development of a reduced chemical kinetics mechanism for n-heptane/syngas co-oxidation, syngas combustion and NOx formation

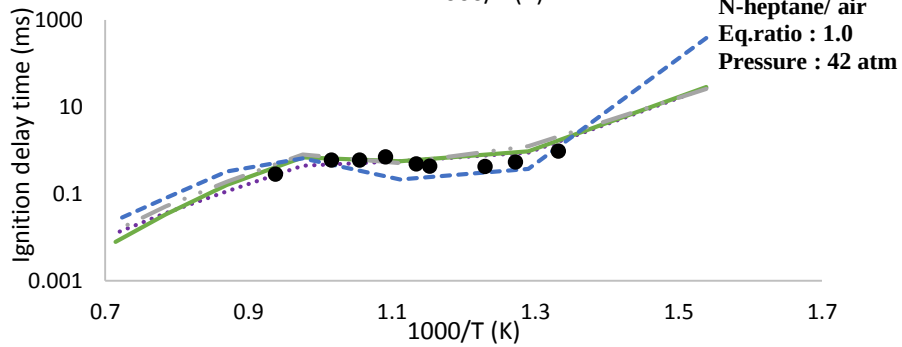
Mechanism development steps

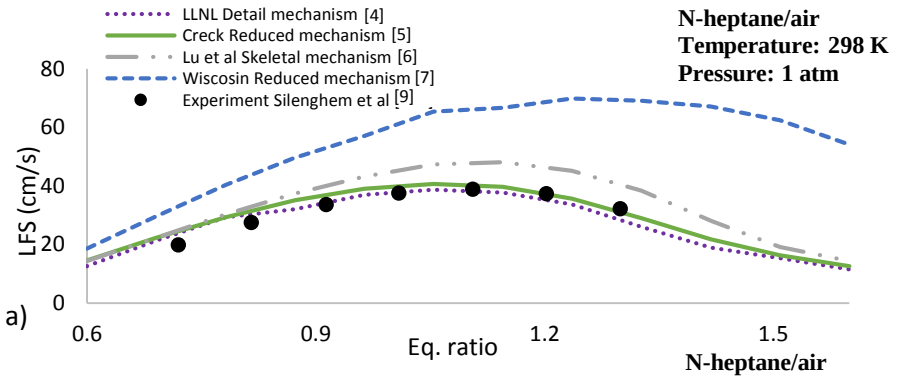
- Selection of the n-heptane mechanism
- N-heptane mechanism reduction
- Coupling between the syngas/NOx mechanism and the reduced n-heptane mechanism
- Validation of the coupled mechanism against exp. data and simulated results using other mechanisms
- Multidimensional CFD simulation

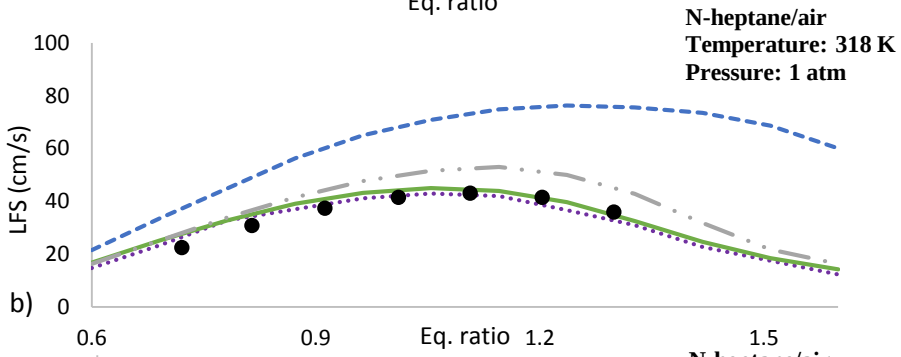
N-heptane mechanism selection

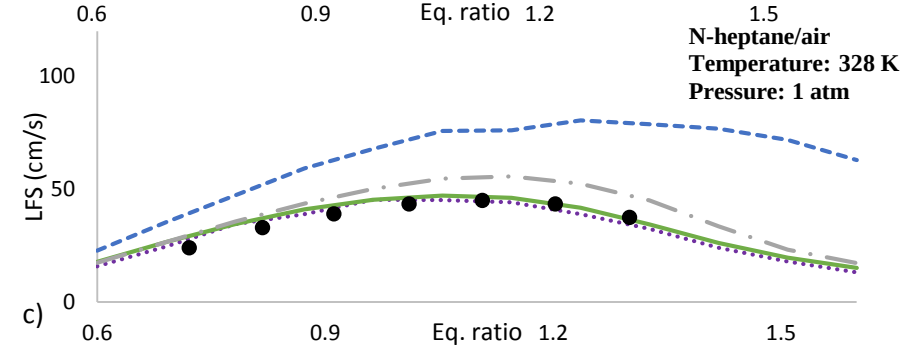












[4]Mehl Marco, William J Pitz, Charles K Westbrook, and Henry J Curran, *Kinetic modeling of gasoline surrogate components and mixtures under engine conditions.* Proceedings of the Combustion Institute, 2011. 33(1): p. 193-200.

[5] Ranzi Eliseo, Alessio Frassoldati, Alessandro Stagni, Matteo Pelucchi, Alberto Cuoci, and Tiziano Faravelli, *Reduced kinetic schemes of complex reaction systems: fossil and biomass-derived transportation fuels.* International Journal of Chemical Kinetics, 2014. 46(9): p. 512-542

[6] Lu Tianfeng and Chung K Law, *Diffusion coefficient reduction through species bundling.* Combustion and flame, 2007. 148(3): p. 117-126.

[7] Patel Amar, Song-Charng Kong, and Rolf D Reitz, *Development and validation of a reduced reaction mechanism for HCCI engine simulations*. 2004, SAE Technical Paper.

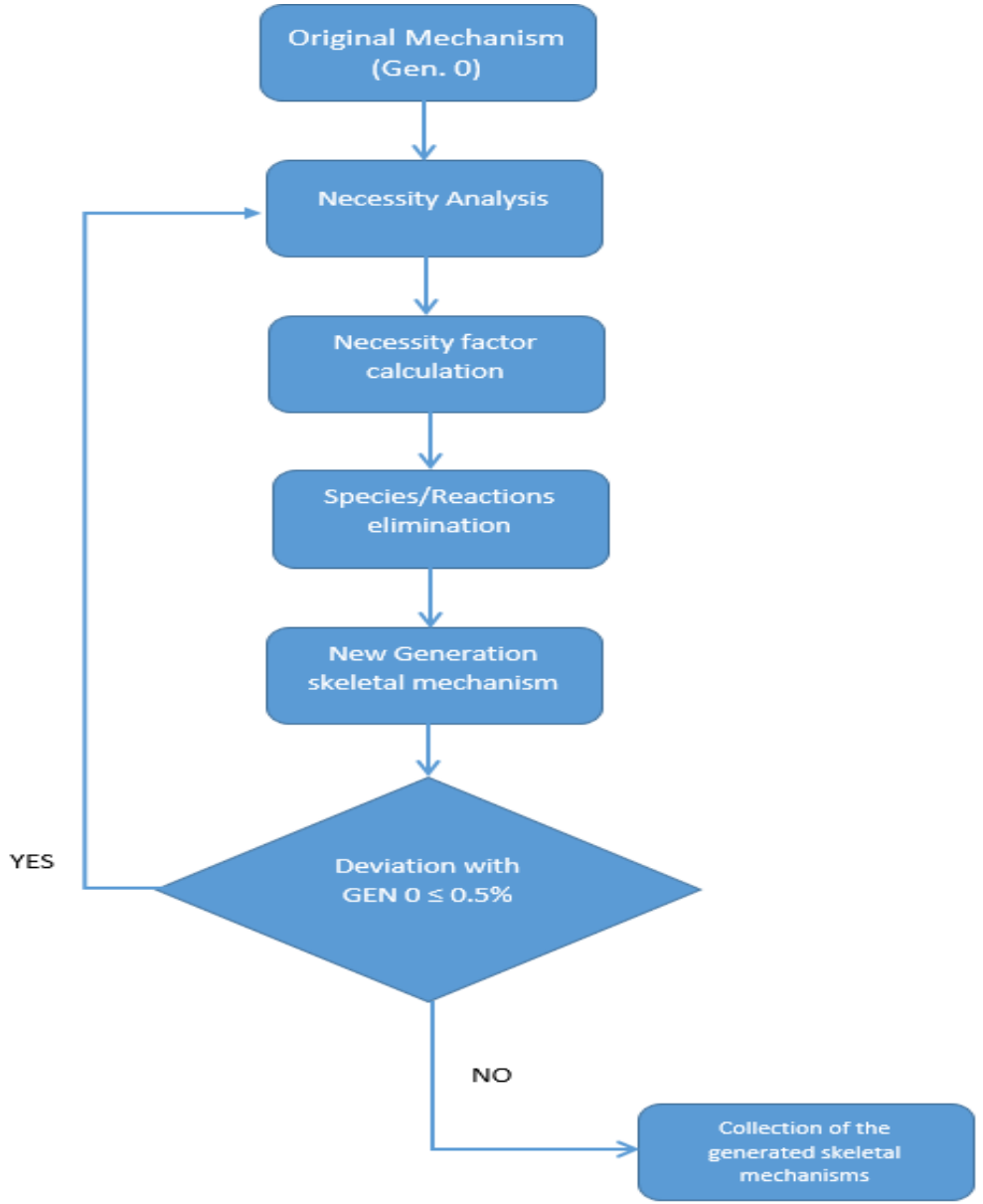
[8] Ciezki HK and G Adomeit, *Shock-tube investigation of self-ignition of n-heptane-air mixtures under engine relevant conditions.* Combustion and flame, 1993. 93(4): p. 421-433.

[9] Sileghem Louis, VA Alekseev, Jeroen Vancoillie, KM Van Geem, EJK Nilsson, Sebastian Verhelst, and AA Konnov, *Laminar burning velocity of gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene.* Fuel, 2013. 112: p. 355-365.

Mechanism reduction

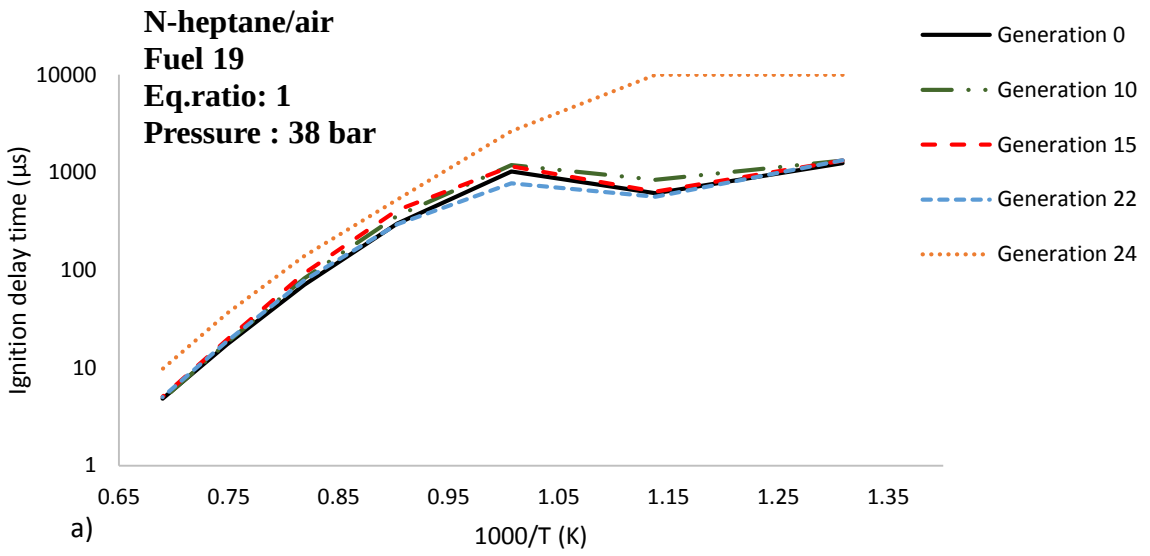
- The reduced Creck mechanism [5] was used for the reduction and coupling with the syngas/NOx mechanism developed in Part 2.
- The reduction of the n-heptane mechanism was performed by using the necessity analysis method.
- Necessity analysis is a hybrid reduction tool as it combines both flow analysis and sensitivity analysis reduction methods in order to find the reactions and species that are the most necessary for the consumption or the formation of specific targets .
- Once necessity analysis is complete, a necessity factor is calculated for each individual species in the mechanism (0<nf≤1).The closest to 1 is the most important species, while the closest to zero is the lowest important species and therefore can be eliminated from the mechanism
- The higher the necessity factor the lower is the number of reactions in the skeletal mechanism
- Two loop stopping criteria were used : a) deviation between the skeletal mechanism and the original to be lower than 0. 5% and the reactions number to be close to 300.

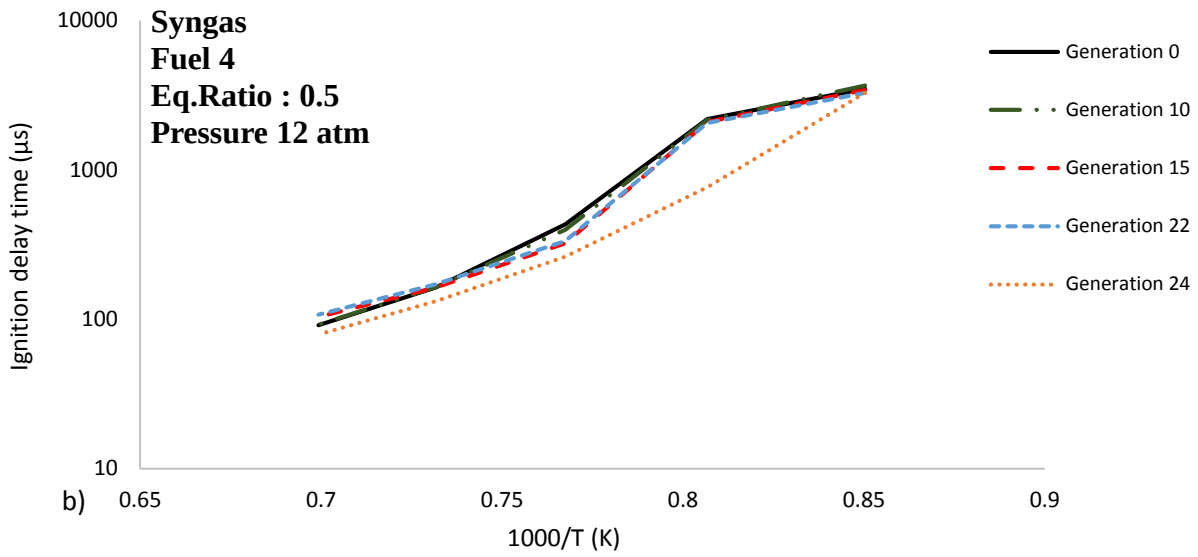
Flow chart of mechanism reduction



[5] Ranzi Eliseo, Alessio Frassoldati, Alessandro Stagni, Matteo Pelucchi, Alberto Cuoci, and Tiziano Faravelli, *Reduced kinetic schemes of complex reaction systems: fossil and biomass-derived transportation fuels.* International Journal of Chemical Kinetics, 2014. **46**(9): p. 512-542

Mechanism reduction





Overall mean error and number of reactions of each skeletal mechanism

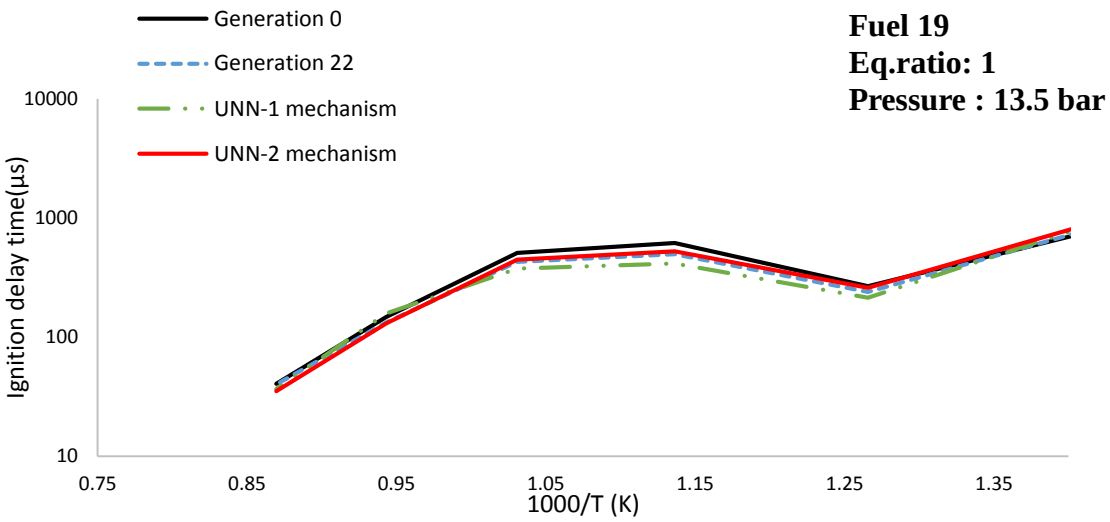
Skeletal Mechanism	Overall mean error, $\bar{\bar{\varepsilon}}$ (%)		Number of Reactions
	N-heptane	Syngas	
Generation 0 /Original Mech.[5]	-	-	1791
Generation 10	0.092	0.034	934
Generation 15	0.146	0.091	522
Generation 22	0.290	0.154	264
Generation 24	2.31	0.585	248

Generation 22 was chosen because the number of reactions lies inside the pre-set criterion (≤ 300 reactions), and, additionally, the calculated error is inside the pre-set error limit (≤ 0.5%).

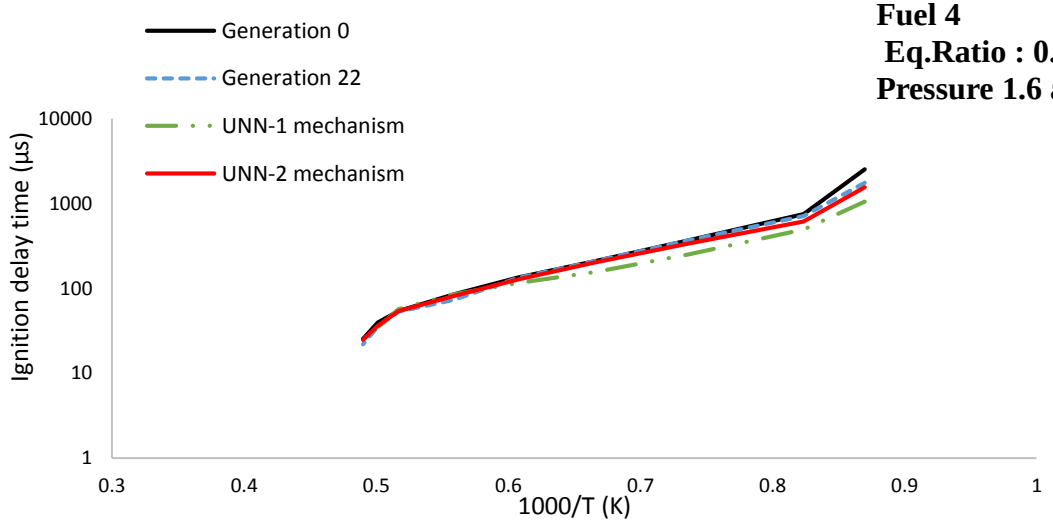
[5] Ranzi Eliseo, Alessio Frassoldati, Alessandro Stagni, Matteo Pelucchi, Alberto Cuoci, and Tiziano Faravelli, *Reduced kinetic schemes of complex reaction systems: fossil and biomass-derived transportation fuels.* International Journal of Chemical Kinetics, 2014. **46**(9): p. 512-542

Mechanisms coupling

- For syngas combustion and NOx formation, the reduced mechanism for syngas/NOx constructed in Part 2 was selected for the coupling with the 22nd Generation n-heptane skeletal mechanism.
- N-heptane skeletal mechanism includes full CH_4, H_2 and CO chemistry and therefore, no additional reactions were incorporated during the coupling. Only the rate constants were adopted from syngas/NOx mechanism. The new mechanism is called University of Northumbria at Newcastle (UNN-1) mechanism.
- According to the comparison UNN-1, is lower at NTC region for n-heptane while under-predicts the original mechanism at low temperatures for syngas.
- In order to reduce the uncertainty the rate constants of important n-heptane reactions were adjusted.
- The new final mechanism has been designed and called UNN-2



Fuel 19
Eq.ratio: 1
Pressure : 13.5 bar



Fuel 4
Eq.Ratio : 0.5
Pressure 1.6 atm

Modified n-heptane based reactions (A units cal-cm-sec-K, E units cal/mol)

Reaction	Old rate constant			New rate constant		
	A	n	E	A	n	E
$NC_7H_{16}+OH=C_7H_{15}+H_2O$	4.8E06	2.0	-2259.83	1.80E07	2.0	-2259.83
$NC_7H_{16}+HO_2=C_7H_{15}+H_2O_2$	1.76E05	2.5	14860.00	1.76E04	2.5	14860.00
$NC_7H_{15}+O_2=C_7H_{15}O_2$	2.0E11	0.0	0.0	2.0E12	0.0	0.0

UNN-2 mechanism (A units cal-cm-sec-K, E units cal/mol)

	Reactions	A	n	E
	n-Heptane Reaction EBU			
R1	$C_7H_{16}+11O_2=7CO_2+8H_2O$	0.	0.	0.
R2	$H_2+O=OH+H$	5.06E4	2.67	6287.6
R3	$H+O_2=OH+O$	3.520E16	-0.7	17061.4
R4	$H+O_2(+M)=HO_2(+M)$	4.6E12	0.4	0.0
	/LOW /1.737E19 -1.23 0.0/			
	/M/AR/0.0/ H_2/1.3/ H_2O/10.0/ CO/1.9/ CO_2/3.8/			
R5	$OH+HO_2=O_2+H_2O$	2.89E13	0.0	-496.9

Syngas reactions

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N-heptane reactions

R238	$NC_7H_{16}+CH_3CO=>CH_3CHO+NC_7H_{15}$	1.6240E06	2.0	14065
R239	$NC_7H_{16}+HCO=>CH_2O+NC_7H_{15}$	1.5160E06	2.0	12360
R240	$NC_7H_{16}+HCCO=>CH_2CO+NC_7H_{15}$	5.1360E05	2.0	5333.

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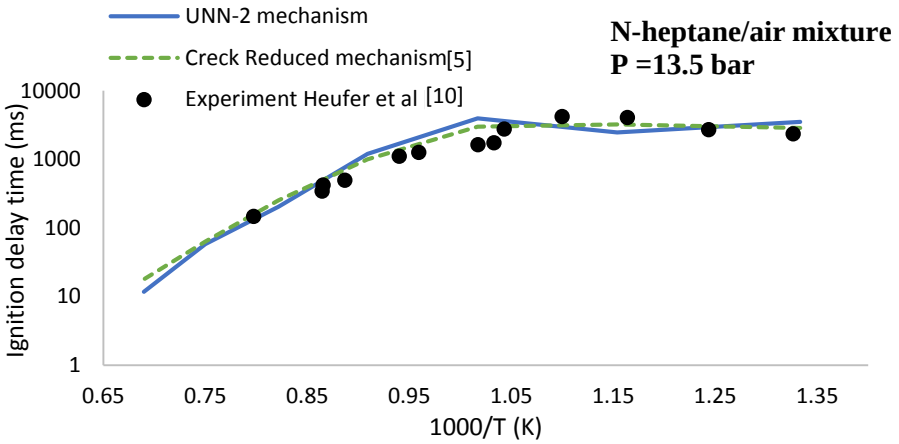
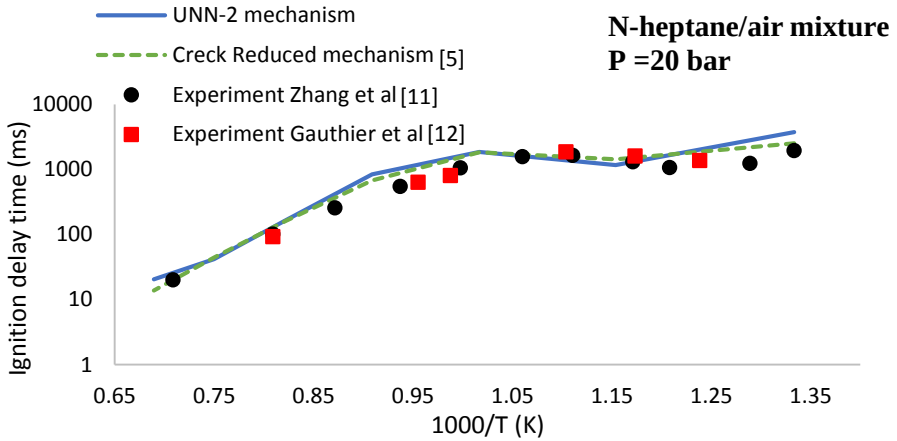
NOx reactions

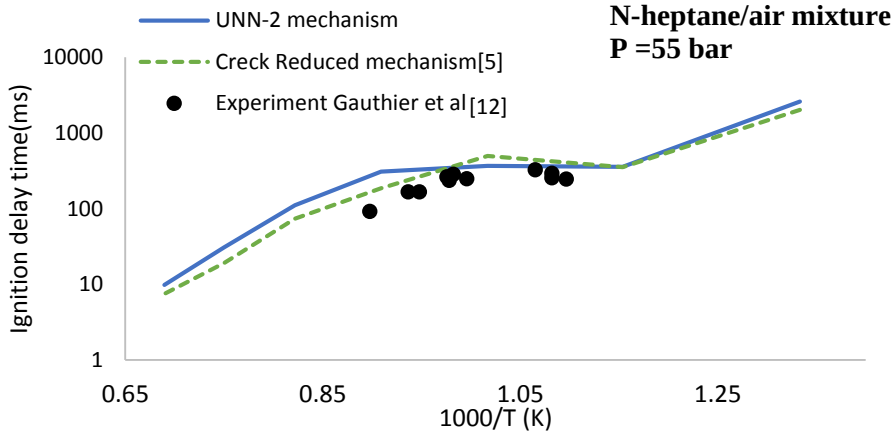
R273	$HO_2+NO=NO_2+OH$	2.11E12	0.0	-480.0
R274	$NO+O(+M)=NO_2(+M)$	1.06E20	-1.41	0.0
	/M/ H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/			
R275	$NO_2+O=NO+O_2$	3.9E12	0.0	-240.0
R276	$NO_2+H=NO+OH$	1.32E14	0.0	360.0

Validation

N-heptane oxidation







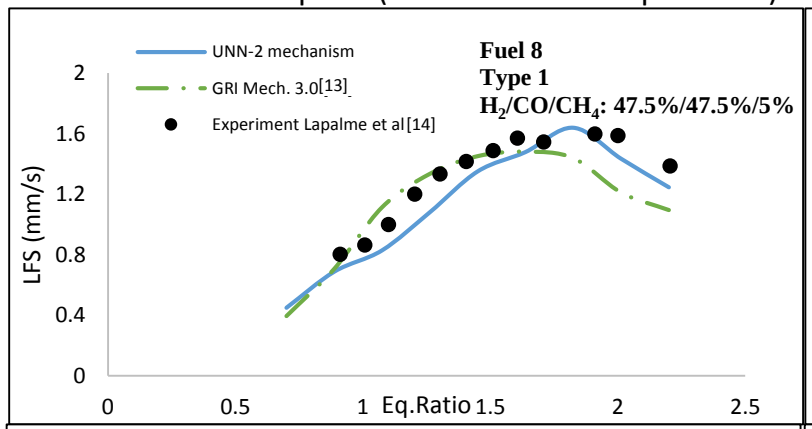
[10]Heufer KA and H Olivier, *Determination of ignition delay times of different hydrocarbons in a new high pressure shock tube.* Shock Waves, 2010. **20**(4): p. 307-316.

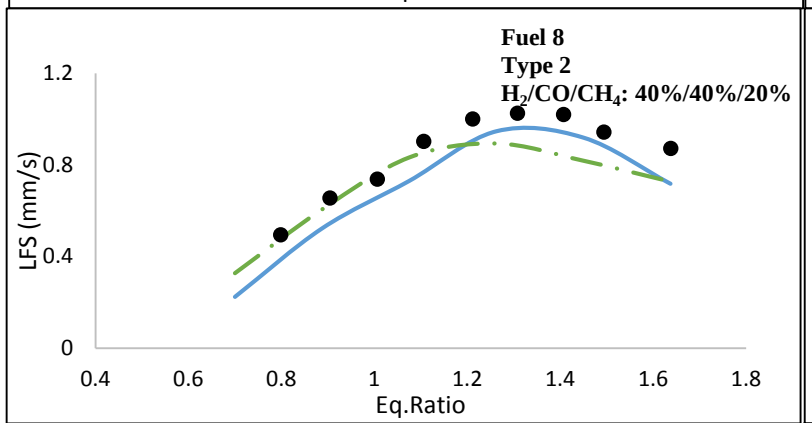
[11] Zhang Kuiwen, Colin Banyon, John Bugler, Henry J Curran, Anne Rodriguez, Olivier Herbinet, Frédérique Battin-Leclerc, Christine B'Chir, and Karl Alexander Heufer, *An updated experimental and kinetic modeling study of n-heptane oxidation.* Combustion and Flame, 2016. **172**: p. 116-135.

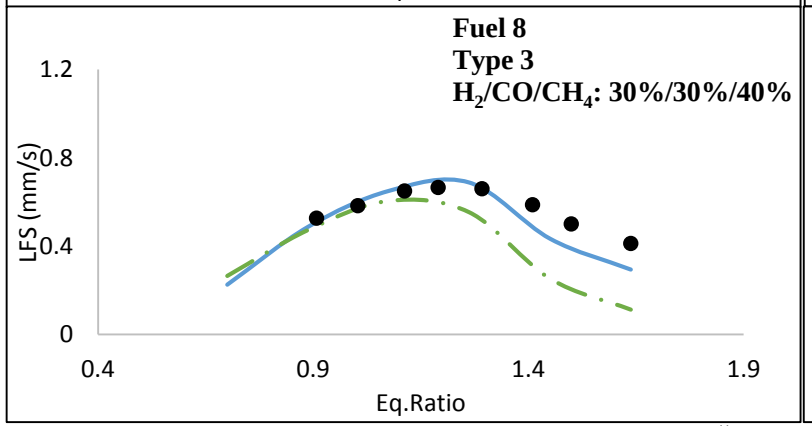
[12]Gauthier BM, DF Davidson, and RK Hanson, *Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures.* Combustion and Flame, 2004. **139**(4): p. 300-311.

Syngas combustion

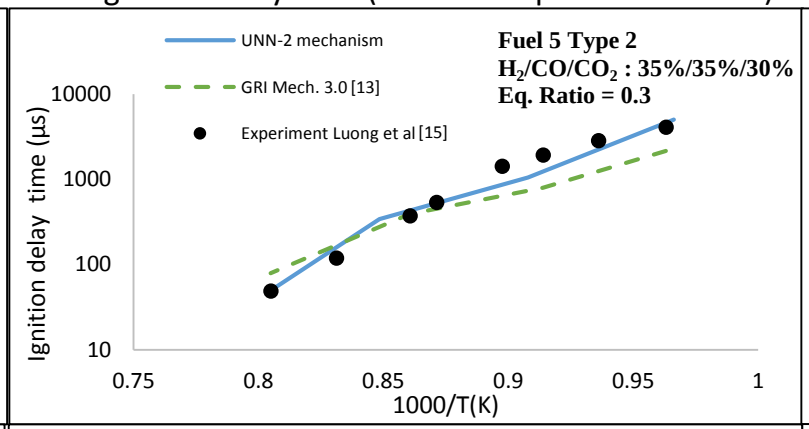
Laminar flame speed (different fuel compositions)

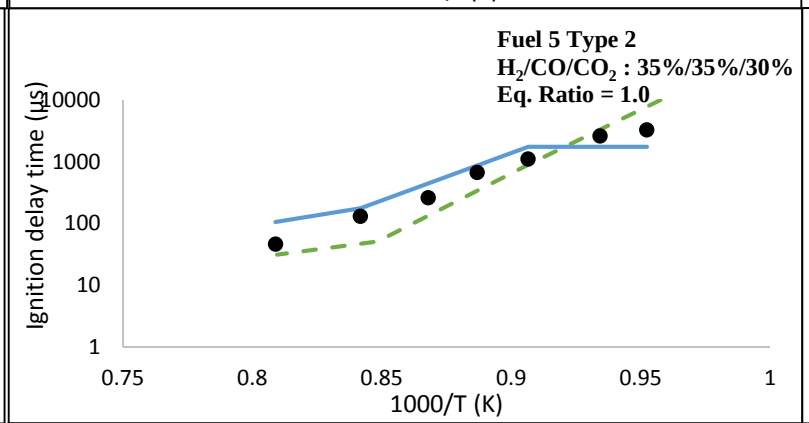


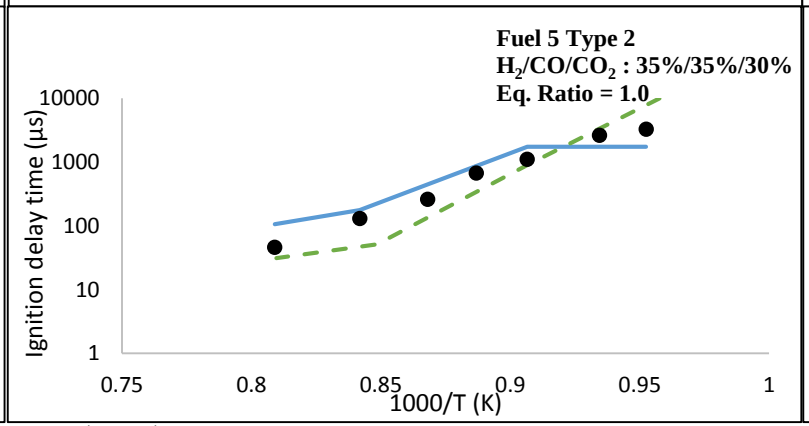




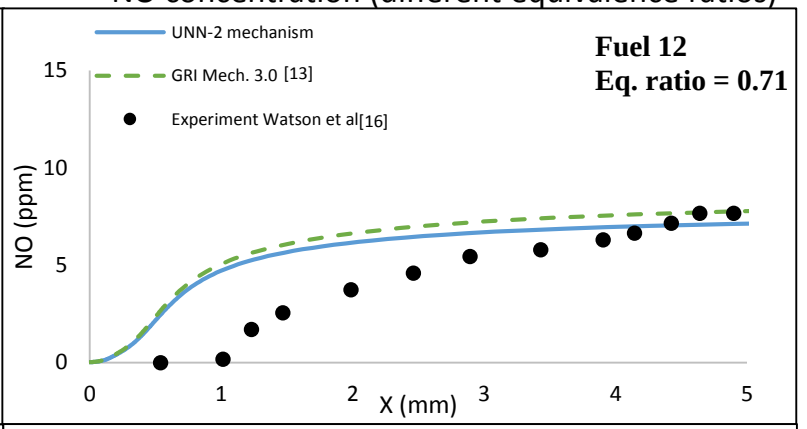
Ignition delay time (different equivalence ratios)

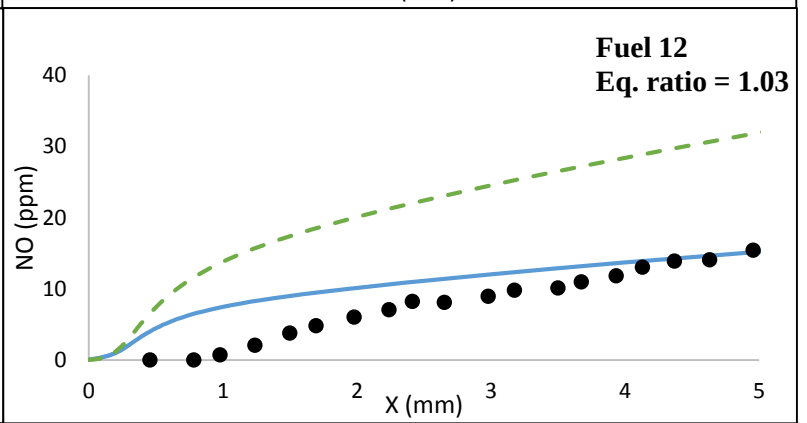


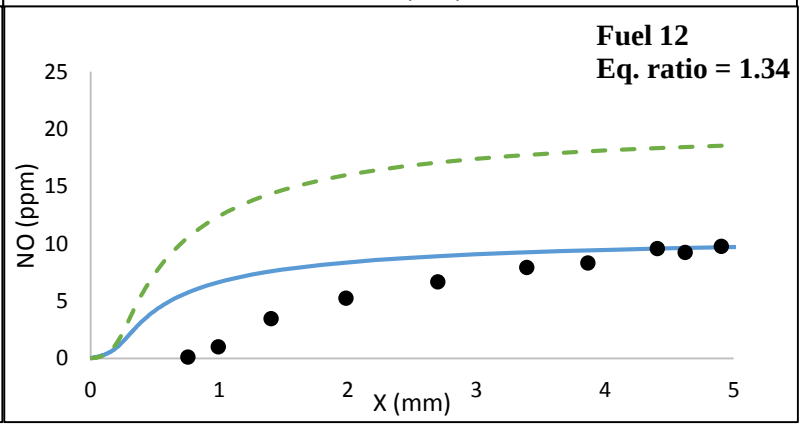




NO concentration (different equivalence ratios)







[13] Smith GP, Golden DM, Frenklach M, Moriarty NW, Eiteneer B, Goldenberg M, et al. GRI-Mech home page http://www.me. berkeley.edu/gri_mech/

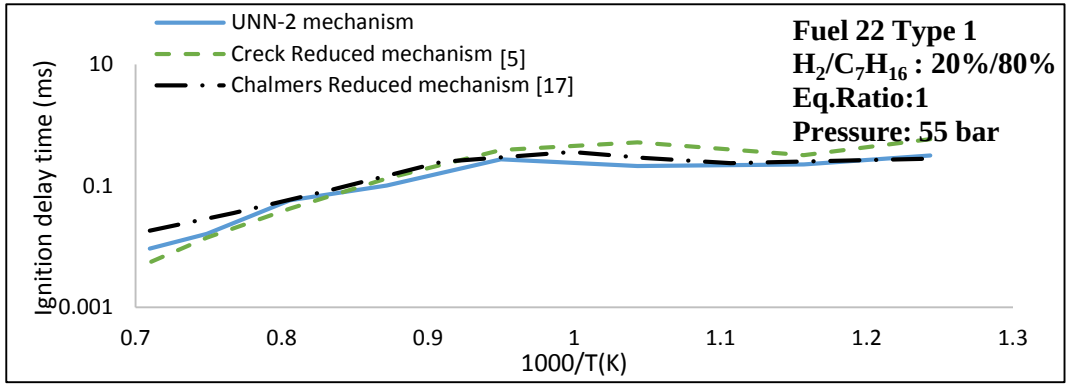
[14] Lapalme Denis and Patrice Seers, Influence of CO 2, CH 4, and initial temperature on H 2/CO laminar flame speed. International Journal of Hydrogen Energy, 2014. 39(7): p. 3477-3486

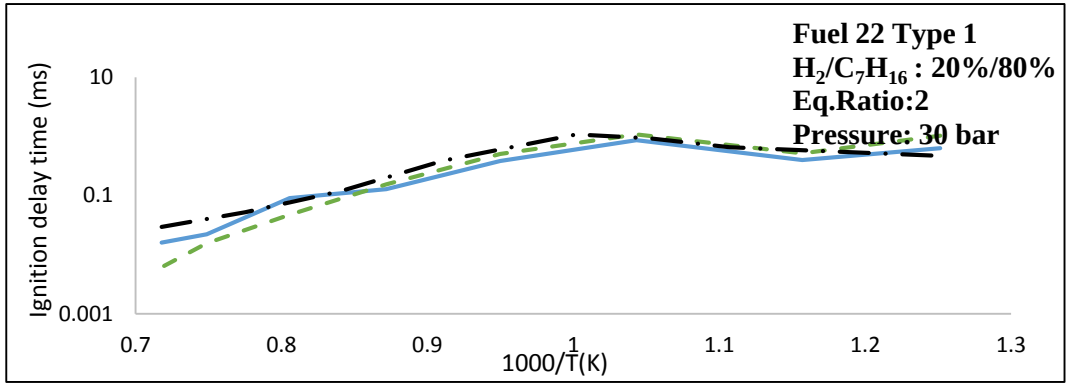
[15]Thi Luong Dinh, Yingjia Zhang, and Zuohua Huang, *Shock tube study on ignition delay of multi-component syngas mixtures–Effect of equivalence ratio.* international journal of hydrogen energy, 2014. **39**(11): p. 6034-6043.

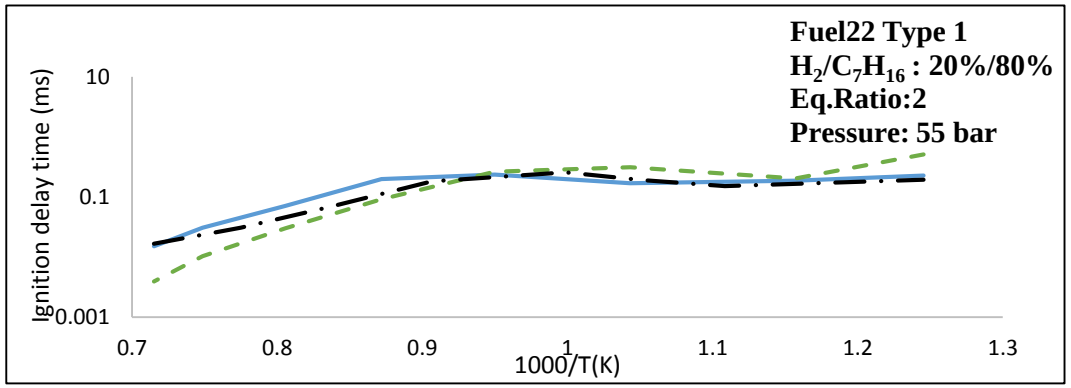
[16]Watson Graeme MG, Jeffrey D Munzar, and Jeffrey M Bergthorson, *NO formation in model syngas and biogas blends.* Fuel, 2014. **124**: p. 113-124

N-heptane/syngas co-oxidation

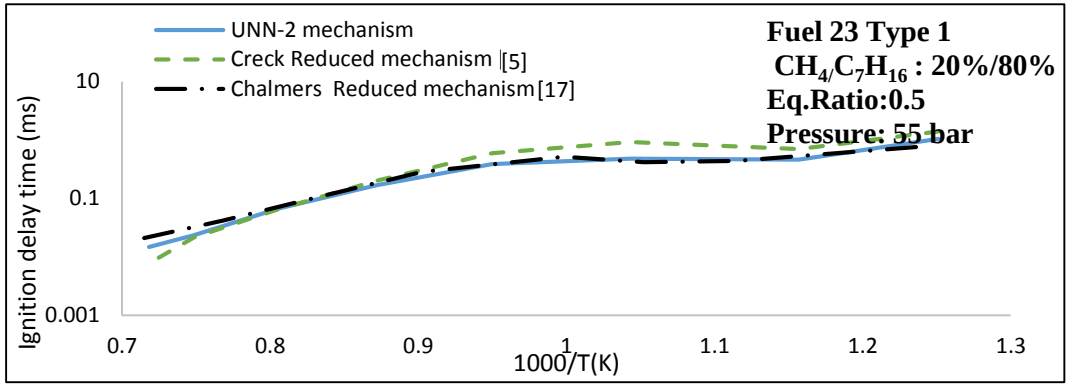
$N\text{-}C_7H_{16}/H_2$ mixture

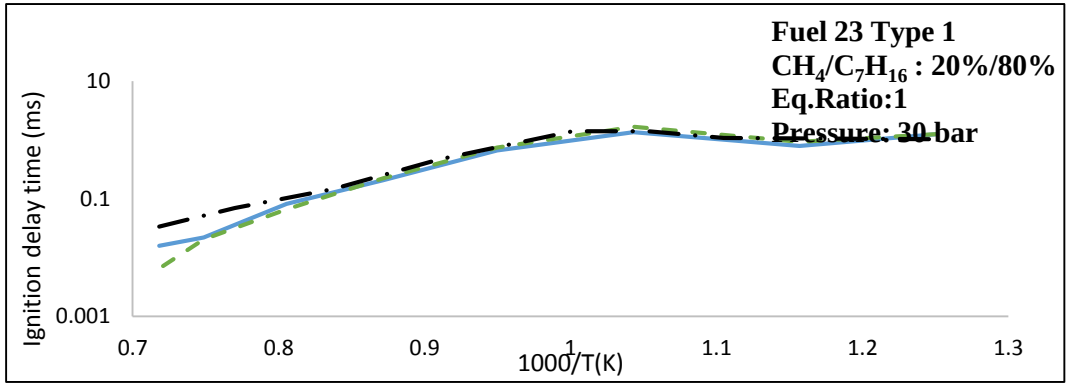


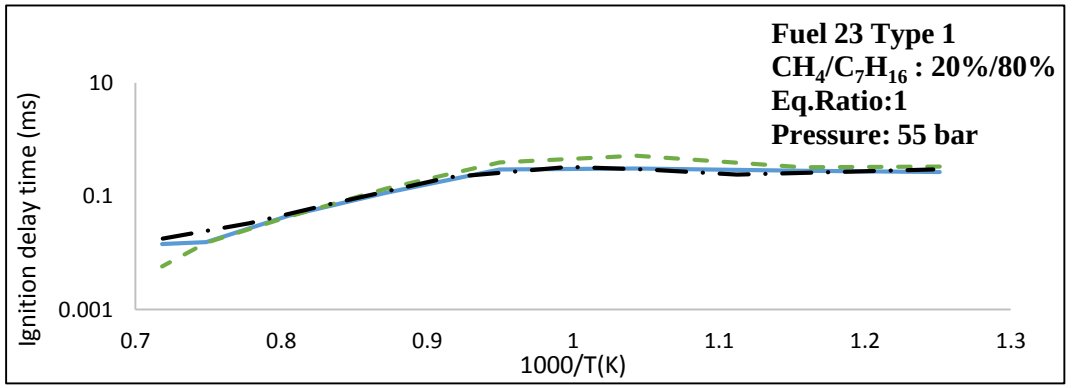




$N\text{-}C_7H_{16}/CH_4$ mixture

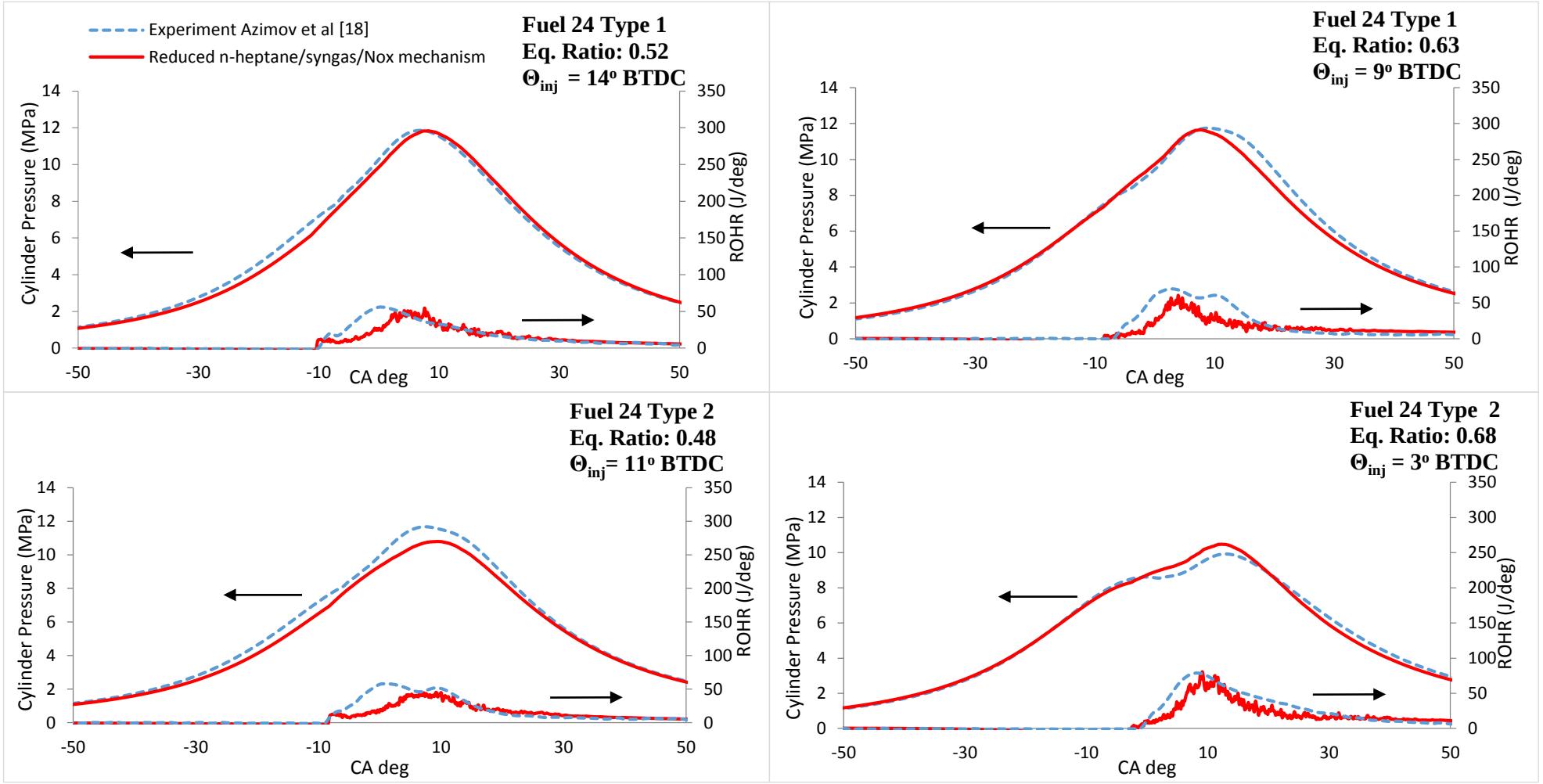






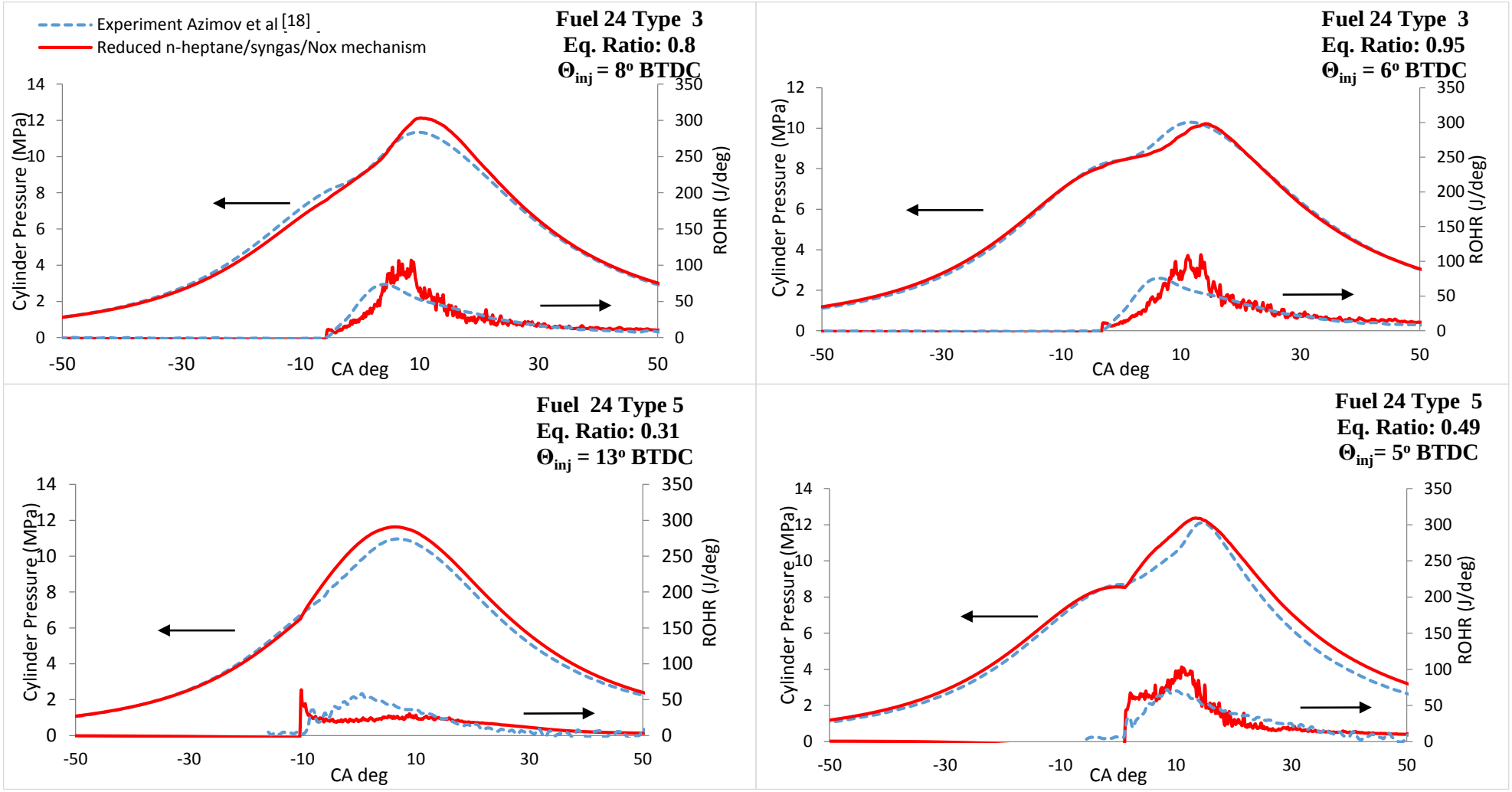
[17] CHALMERS UNIVERSITY OF TECHNOLOGY. Available from: http://www.tfd.chalmers.se/~valeri/MECH.html

CFD analysis



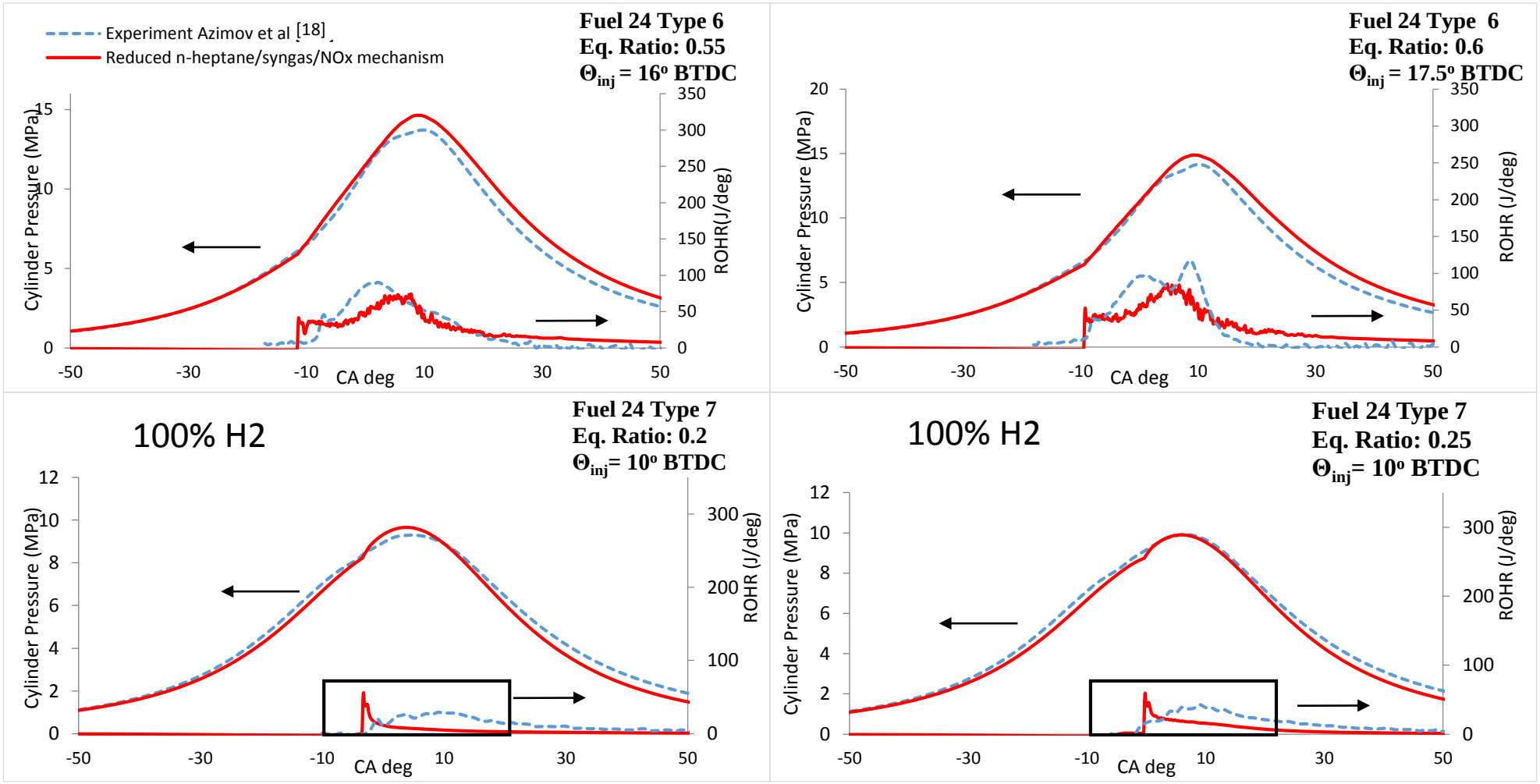
[18]Azimov Ulugbek, Eiji Tomita, Nobuyuki Kawahara, and Yuji Harada, Effect of syngas composition on combustion and exhaust emission characteristics in a pilot-ignited dual-fuel engine operated in PREMIER combustion mode. international journal of hydrogen energy, 2011. 36(18): p. 11985-11996.

CFD analysis (cont.)



[18]Azimov Ulugbek, Eiji Tomita, Nobuyuki Kawahara, and Yuji Harada, Effect of syngas composition on combustion and exhaust emission characteristics in a pilot-ignited dual-fuel engine operated in PREMIER combustion mode. international journal of hydrogen energy, 2011. 36(18): p. 11985-11996.

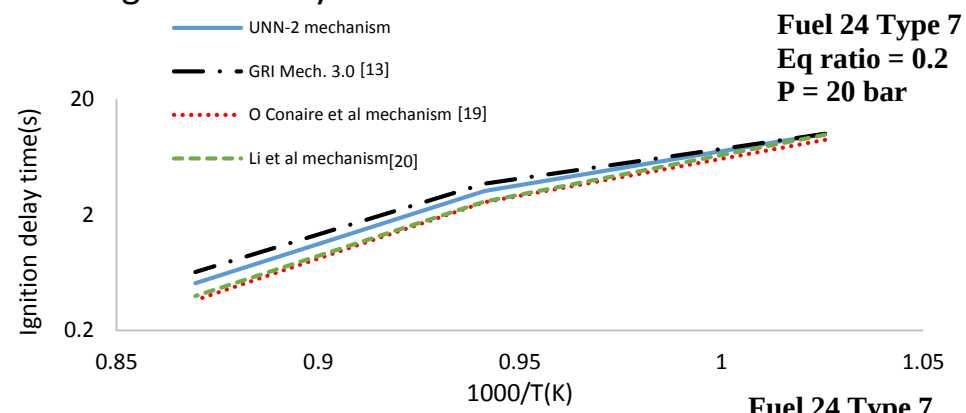
CFD analysis (cont.)

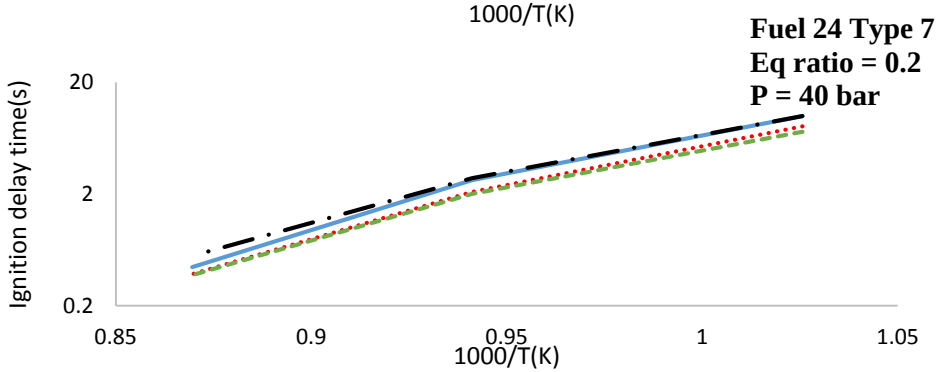


[18]Azimov Ulugbek, Eiji Tomita, Nobuyuki Kawahara, and Yuji Harada, Effect of syngas composition on combustion and exhaust emission characteristics in a pilot-ignited dual-fuel engine operated in PREMIER combustion mode. international journal of hydrogen energy, 2011. 36(18): p. 11985-11996.

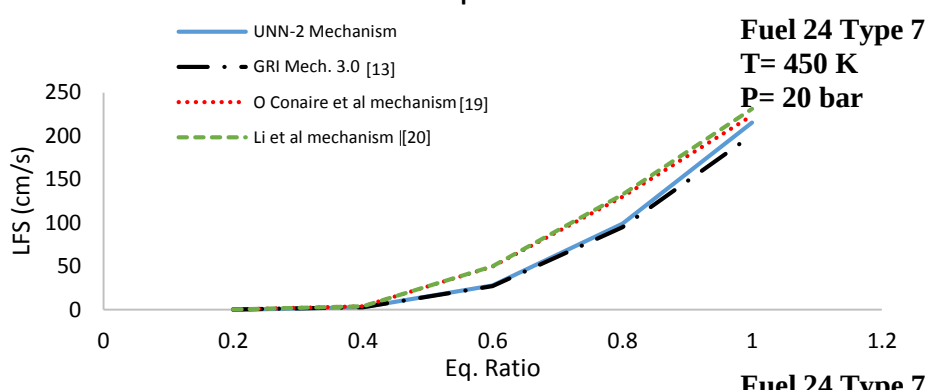
Pure hydrogen combustion

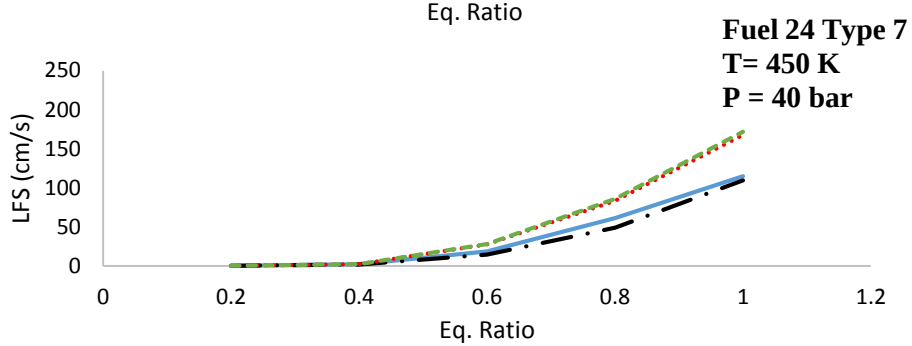
Ignition delay time





Laminar flame speed

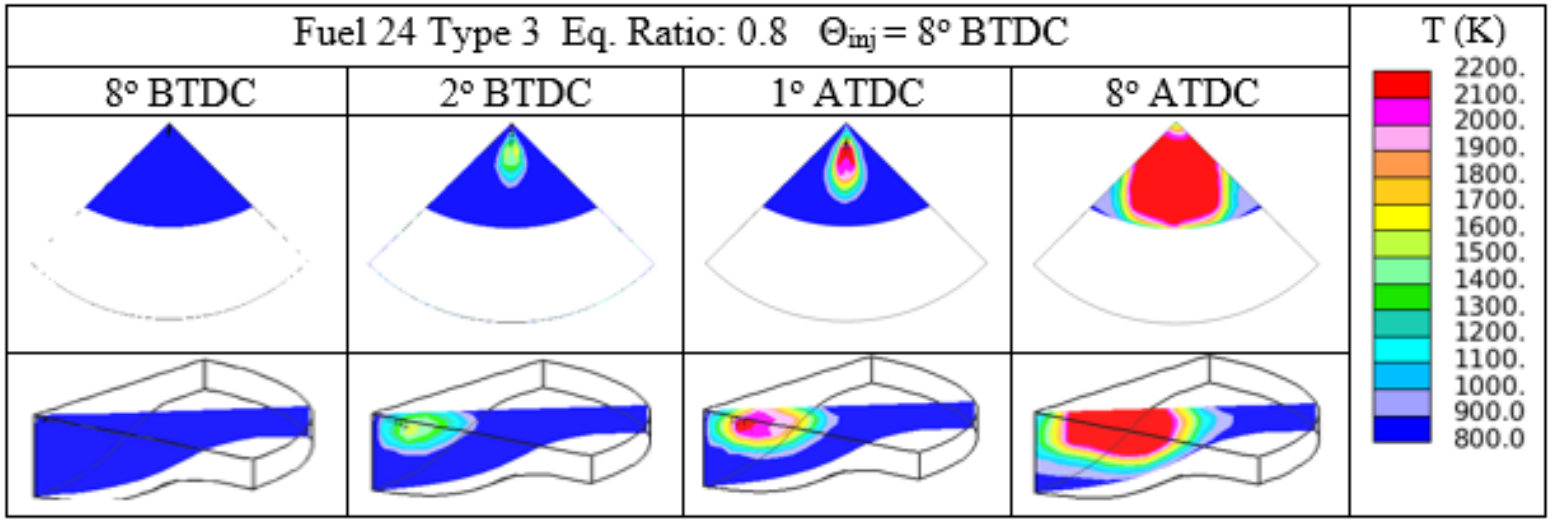


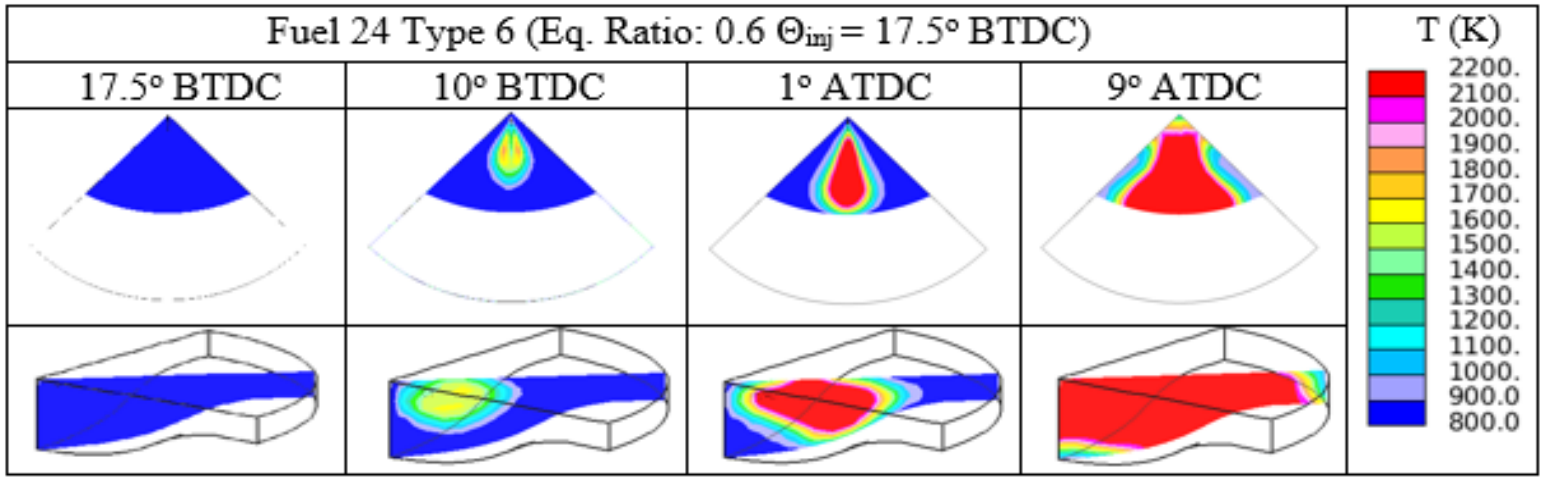


- O Connaire et al [19] and Li et al [20] mechanisms constructed for pure hydrogen combustion.
- The developed mechanism and GRI Mech. 3.0 [14] deviate especially during high temperatures and high eq.ratios .
- The deviation probably depends on the rate constants of specific hydrogen based reactions that were found to increase the reactivity of the mixture (especially rich mixtures) and control the formation of OH reactive radicals at high temperatures and pressure conditions
- Further study is required for the investigation of the specific reactions that are responsible for that deviation and the optimization of their rate constants.

[19]Ó Conaire Marcus, Henry J Curran, John M Simmie, William J Pitz, and Charles K Westbrook, *A comprehensive modeling study of hydrogen oxidation.* International journal of chemical kinetics, 2004. **36**(11): p. 603-622.
[20] Li, Juan, Zhenwei Zhao, Andrei Kazakov, and Frederick L. Dryer. "An updated comprehensive kinetic model of hydrogen combustion." International journal of chemical kinetics 36, no. 10 (2004): 566-575.

Final results - Scalars



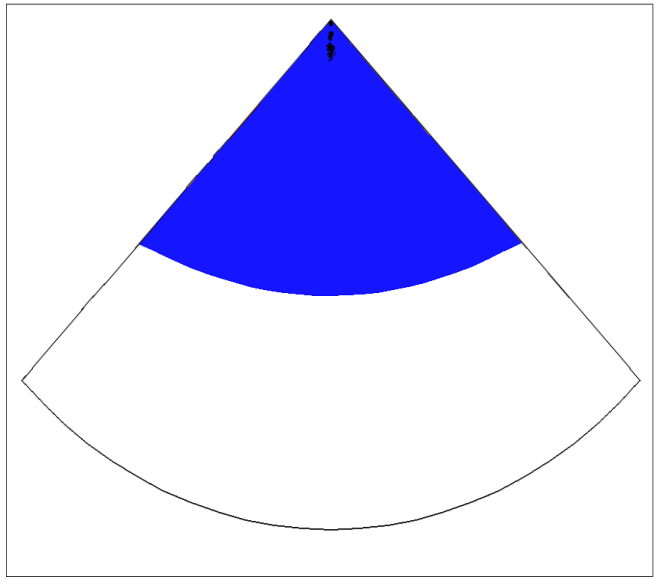


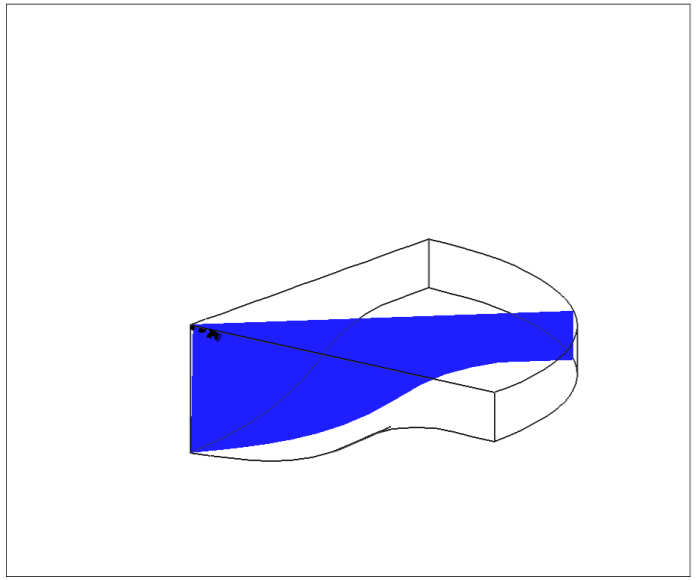
Final results (Temperature)

Top View

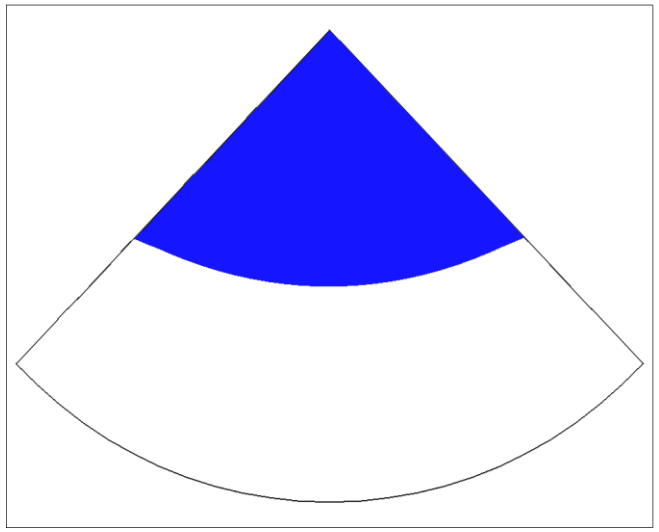
Side View

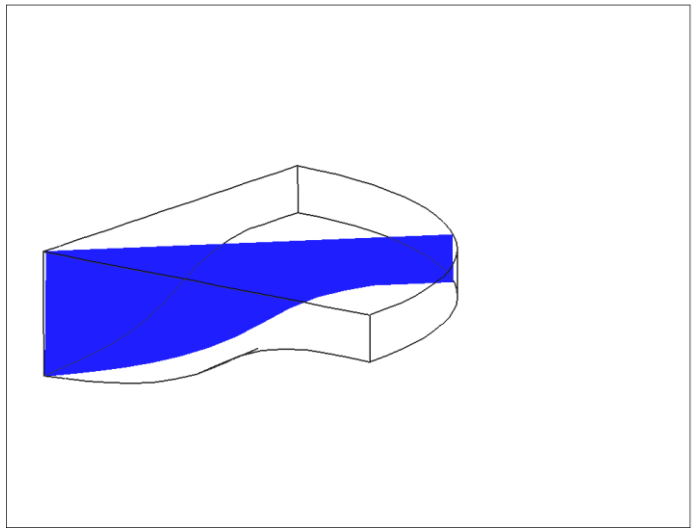
Fuel 24 Type 3
Eq. Ratio : 0.8
Θ_{inj} : 8° BTDC
N-heptane : 2mg/ cycle





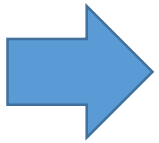
Fuel 24 Type 6
Eq. Ratio : 0.6
Θ_{inj} : 17.5° BTDC
N-heptane : 4 mg/cycle





Conclusions

	Chemical Kinetics Mechanisms	Reactions	Species
	N-heptane/syngas/NOx Mechanism		
1	**Reduced syngas/NOx/n-heptane mechanism**	**276**	**75**
2	Creck Reduced mechanism	1790	106
3	LLNL detailed mechanism	2827	654
4	Lu et al. Skeletal	842	188



- The developed mechanism contains the lowest number of reactions and species
- It includes not only multicomponent syngas reactions but also n-heptane chemistry and NOx sub mechanism
- It can be implemented in multidimensional CFD simulations with low level of complexity

Thank you for your attention.

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