Reduction of a Detailed Kinetic Model for the Ignition of Natural Gas Mixtures at Gas Turbine Conditions

National University of Ireland, Galway
Ollscoil na hÉireann, Gaillimh

Istvan Gy. Zsely[1,2], Tibor Nagy[2], John M. Simmie[1], Henry J. Curran[1]
istvan.zsely@nuigalway.ie

[1]Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
[2]Laboratory for Chemical Kinetics, Eötvös University, Budapest, Hungary

Introduction: **Natural gas**, the primary fuel for industrial gas turbines is mostly methane (CH_4), but its composition varies depending on its origin, extraction, and transport processes. **Fuel-flexible gas turbines** are of interest to the power generation and combustion research communities. The **higher-order hydrocarbon**, *here* ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}), content of the natural gas requires the application of detailed chemical kinetic models describing the oxidation of not only methane, but also of the larger hydrocarbons. Curran and co-workers have recently developed a **detailed reaction mechanism** for the description of the oxidation of such mixtures. The size of this detailed chemical kinetic model is **far larger** (above 200 species) than can be used directly in computational fluid dynamics (CFD) calculations. **The simulation can be accelerated using reduced mechanisms**. The primary parameter of interest here is the **ignition delay time**, τ.

Mechanism reduction methods

Species elimination reduction methods allows us to keep the original species and elementary reactions in the reduced mechanisms.

- **SEM-CM method:** Simulation Error Minimization Connectivity Method[1]
- **DRGEPASA method**: combination of the **DRGEP** (Directed Relation Graph with Error Propagation)[2] and the **DRGASA** (Directed Relation Graph-Aided Sensitivity Analysis)[3] methods

Chemical model

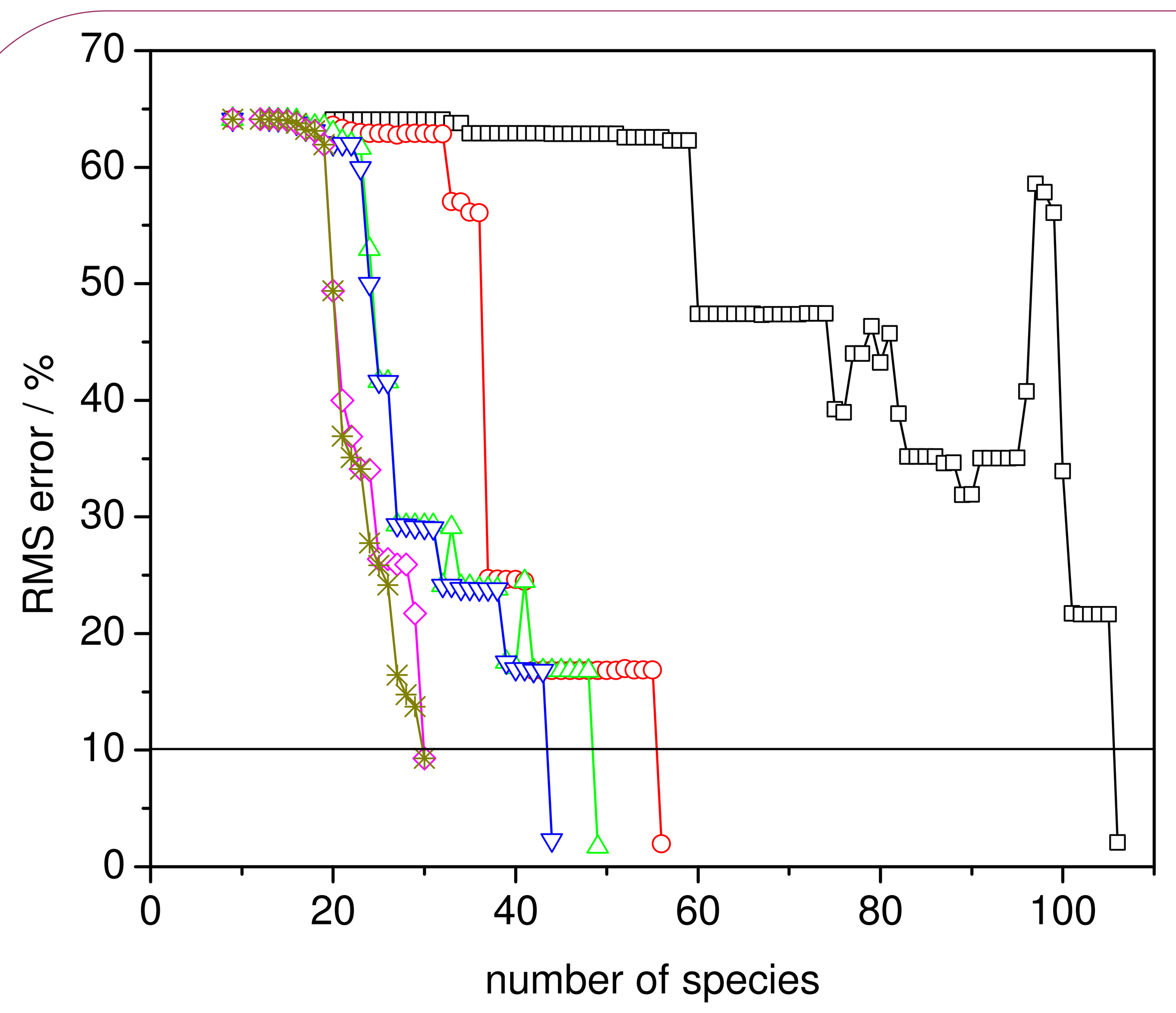
The latest version of the **C4 mechanism** that was recently developed by **Curran and co-workers[4]** was to be reduced.
This mechanism contains **230 species** up to 4 carbon atoms and 1327 reversible reactions.

Scenarios, regimes

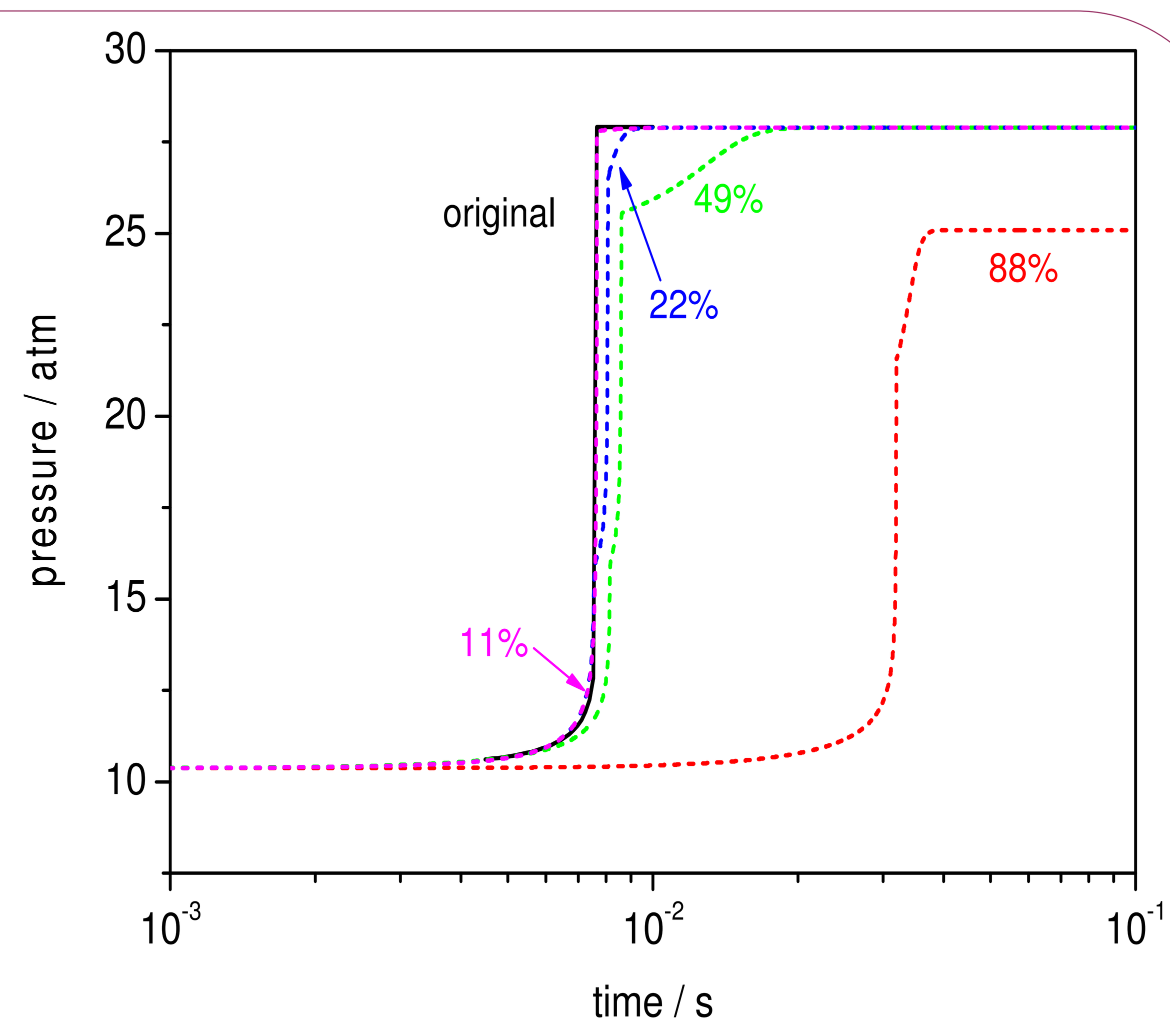
- investigated cases were same as in the **experiments of Healy et al.[5]**
- **methane/propane mixtures** (CH_4/C_3H_8 ratios of 70/30 and 90/10)
- temperatures of 713–1465 K
- pressures of 7–40 atm
- equivalence ratios of 0.5, 1.0, 2.0 and 3.0
- **altogether 174 cases**
- similar cases were grouped giving **11** different **regimes**
- **19 representative cases** (scenarios) were selected from them for mechanism reduction

Simulations

Adiabatic, **constant volume** calculations using code **TIBOX**
- part of the program package used for the mechanism reduction
- predicts same ignition delay times as CHEMKIN-PRO® (Reaction Design)



Species number of the reduced mechanisms at different depth level in the SEM-CM analysis in scenario 8. Depth level 1: □, …+4: ○, …+16: △, …+64: ▽, …+256: ◇, …+1024: ✶.



Calculated pressure profiles in scenario 2 using reduced mechanisms with different RMS error

Mechanism reduction

The error of the concentration of the major species was minimized, because this determines the error of the ignition delay time.

Reduced mechanisms were developed for:
- **each scenario**
- **most of the regimes**

Results

- Small (<35 species) and accurate (error in τ < 10%) reduced mechanisms were developed **for each selected scenario**.
- Small (<40 species) and accurate (error in τ < 10%) reduced mechanisms were developed **for seven of the regimes**.
- A **39-species reduced mechanism** was obtained which reproduces ignition delay times for all cases in regimes 1-7 with an average error of 3.9% for lean and stoichiometric mixtures containing 10% propane / 90% methane as fuel, for pressure and temperature ranges of 10–40 atm and 876–1465K.

The species list of this mechanism:
H, H_2, O, O_2, OH, H_2O, HO_2, H_2O_2, CO, CO_2, CH_2O, HCO, CH_3O, CH_3O_2H, CH_3O_2, CH_4, CH_3, C_2H_6, C_2H_5, C_2H_4, C_2H_3, C_2H_2, CH_2CHO, CH_2CO, CH_3COCH_3, CH_3COCH_2, C_3H_8, iC_3H_7, nC_3H_7, C_3H_6, C_3H_5-a, C_3H_5O, $iC_3H_7O_2$, iC_3H_7O, CH_3CHCO, C_4H_8-1, iC_4H_8, N_2, Ar

Accepted mechanisms: the calculated ignition delays deviated by less than 10% compared to the baseline, detailed mechanism calculation

regime	scenario	approx. pressure / atm	temperature / K	equivalence ratio	Initial composition in mole fraction: CH_4	C_3H_8	O_2	Ar	N_2	Required number of species in the: scenario	regime	
1	1	10	1032.6	0.5	0.0393	0.0044	0.2008	0.7555	0.0000	17	34	39
	2		1096.2	0.5						19		
2	3	20	915.5	0.5						21	21	
	4		952.9	0.5						21		
	5		1034.4	0.5						22		
3	6	30	1294	0.5						17	17	
4	7	40	876.5	0.5				0.3778	0.3778	23	23	
	8		907.4	0.5						23		
5	9	7	1318	1.0	0.0753	0.0084	0.1924	0.0000	0.7239	16	19	
6	10	24	1117	1.0						17	39	
7	11	9	918.8	1.0	0.0473	0.0203	0.1958	0.4420	0.2947	18	39	
	12		959.7	1.0						20		
	13		1244	1.0				0.0000	0.7367	19		
8	14	30	1280	1.0						18		
	15		845	1.0				0.36835	0.36835	24		
9	16	7	1291	3.0	0.1249	0.0535	0.1725	0.0000	0.6490	20		
10	17	20	779	3.0						24		
11	18	30	1144	3.0						20		
	19		787.1	3.0				0.5192	0.1298	34		

References
[1] T. Nagy, T. Turanyi, Combust. Flame 156 (2009) 417-428.
[2] P. Pepiot-Desjardins, H. Pitsch, Combust. Flame 154 (2008) 67-81.
[3] X.L. Zheng, T. Lu, C.K. Law, Proc. Combust. Inst. 31 (2007) 367-375.
[4] http://c3.nuigalway.ie/mechanisms.html
[5] D. Healy, H. J. Curran, S. Dooley, J. M. Simmie, D. M. Kalitan, E. L. Petersen, G. Bourque, Combust. Flame 155 (2008) 451-461.

Acknowledgments: Financial support from an EU Marie Curie Transfer of Knowledge grant (MKTD-CT-2004-517248) is acknowledged.

European Combustion Meeting 2009
Vienna, Austria