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Towards a 'lumped' reaction model for future 'designer' fuels

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Introduction and Motivation

While the Homogeneous Charge Compression Ignition (HCCI) process is currently one of the most promising engine processes to reduce simultaneously both NO_x and soot emissions, its applicability is hindered by its relatively limited operating range. Nowadays, however, 'designer fuels', as potentially possible to synthesize from biomass, offer unique possibilities for tailoring evaporation and auto-ignition properties almost at will, offering a means to control and expand the HCCI operation range.

For the development of such 'designer' fuels, the identification of HCCI relevant fuel properties as well as the definition of a new fuel 'index' able to describe a fuel's suitability for HCCI, is required. With this objective, within the framework of a large scale collaboration between 5 universities and more than 15 automotive companies, a large set of technical fuels covering a wide range of properties (Fig.1) is investigated, both numerically and experimentally. Starting from perfectly premixed experiments in a shock tube, followed by optical investigations on a single stroke machine and experiments on a car, respectively a heavy duty single cylinder engine, a large process chain of experiments is built up. Accompanied by numerical simulations a deeper understanding of ignition delay times and burn rates will so be achieved [1].

	1	2	3	4	5	6	7	8	9	10
	CEC-RF	n-Heptan	Naphtha 1	Naphtha 2	Kero 1	Kero 3	CCS-Fuel	Diesel 1	Diesel 2	Diesel 3
SM-Nr.			VW	Shell	07-S-001830	07-S-001903	VW	07-S-001935	07-S-001937	07-S-001908
Aromat %					25					
Naphten %			11		30	40	60			
Paraffin %		100	70	80	45	50	40	100	100	100
Clefin %			19	20		10				
Distillation										
IBP °C	220	98	80	40	153	148	157	192	199	224
5%	240		91	81	166	162	165	198	213	240
10%	245		95	90	166	163	167	202	221	246
50%	≥ 245		112	120	177	168	176	246	273	276
90%	325		139	150	247	292	192	306	310	312
95%	345-350		146	156	267	313	200	319	323	324
FBP	<370	98	165	180	283	317	215	327	330	333
CN			35	55	38	52,3	47,1	50	57	67

Figure 1: Overview of the project fuels under investigation

In HCCI engines, ignition no longer depends on an external actuator (spark or injection) but on charge conditions (p, T, EGR), mixture formation and especially on the fuel oxidation chemistry. Despite the major impact of the fuel kinetics itself, one still has to resort to reduced/global reaction mechanisms in order to simulate the complex physico-chemical interactions in practical combustion systems (3D-CRFD). The purpose of this investigation is to present a consistent approach towards such a global mechanism suitable for the complex multi-component fuels considered in the aforementioned project.

Mechanism development approaches

Although a large range of detailed reaction schemes for single- and two-component fuels are available, schemes for larger diesel fuel components ($> C_{16}$) as well as for relevant mixtures including aromatics, iso- or cyclo-paraffins are only just appearing [e.g. 2, 3, 4]. Furthermore, even after the use of any of the present reduction techniques (e.g. DRG, CSP, ILDM), the resulting skeletal or reduced mechanism typically remains too large to incorporate into most CFD simulations, in particular, if a parametric study is envisioned. [5]

As a result, empirical global reaction schemes, fitted to either experimental data or a detailed chemical model, will continue to have its applications in the future. These models, although often limited in applicability, are considerably smaller than can be achieved by the reduction of a detailed mechanism and therefore, require considerable less computation time. But more important is the possibility of these models to produce a scheme for practical fuels and fuel mixtures for which detailed mechanisms are not available. A brief survey of some characteristic models as well the underlying basic ideas can be found in the accompanying slides.

The 'lumped' reaction model

In the present work, the global n-heptane reaction mechanism of Zheng et al. [6] has been selected as starting point for the mechanism development. Its selection is based firstly, on its ability to reproduce the complex HC autoignition characteristics at low computational cost and secondly, on its simplicity and transparency offering a solid base for further improvement and extension towards non-alkanic fuels.

Reaction	$\text{Log}_{10}A^+$	E^+	$\text{Log}_{10}A^-$	E^-
1. $F + 7.5O_2 \Rightarrow 8H_2O + 7CO$	12.36	39.70		
2. $CO + 0.5O_2 \rightleftharpoons CO_2$	14.0	40.00	7.08	40.00
3. $F + 2O_2 \rightleftharpoons I_1$	$C_3^+ 20.17$	37.62	31.64	88.11
4. $I_1 \Rightarrow 2Y$	6.38	3.96		
5. $Y + 0.5F + 6.5O_2 \Rightarrow 8H_2O + 7CO$	18.00	32.67		
6. $I_1 \Rightarrow I_2$	10.45	13.86		
7. $I_2 \Rightarrow 2Y$	19.18	53.46		

Table 1: global reaction mechanism for n-heptane – Reaction Rates = $f(k_i, [X_i]^{v_i}, p^{a_i})$
Arrhenius parameters for the rate constants, units: cc, mole, s, kcal)

The model consists of 7 global reactions and 7 seven active species. Its basis structure is shown in table 1. The high temperature chemistry is embodied in the first two reactions, whereas the low and intermediate temperature phenomena are described by global reactions 3 to 5. The low temperature scheme is controlled by the interaction of the three generic species I_1 , I_2 and Y and represents the alkyl radical chemistry typical for the low temperature oxidation of alkanic fuels. Reaction rates are expressed as the product of the rate constant (Arrhenius expression), the species concentrations and for reaction 3, an additional pressure correction term.

Optimization of the 'lumped' mechanism

In order to improve and extend the models validity for n-heptane to the large range of HCCI operating conditions considered in the overall project, a genetic algorithm [8] is used to optimize the reaction rate parameters as well as the generic species heat of formation. In a first step, the parameters are optimized based on measured main ignition delay times only [7].

Results

As can be seen from figure 2, after optimization, an excellent correlation between measured and computed ignition delay times can be obtained. Except for a few points at intermediately long ignition delay times, the model shows an acceptable accuracy; with a relative error of about 10% for long and an absolute error of about 0.1ms ($\sim 1^\circ\text{CA}$) for short ignition delay times. Nevertheless, a further reduction of both the overall and local error is strived for, on the one hand by a more careful selection of the measurement points considered for optimization, on the other hand by improving the optimization algorithm settings.

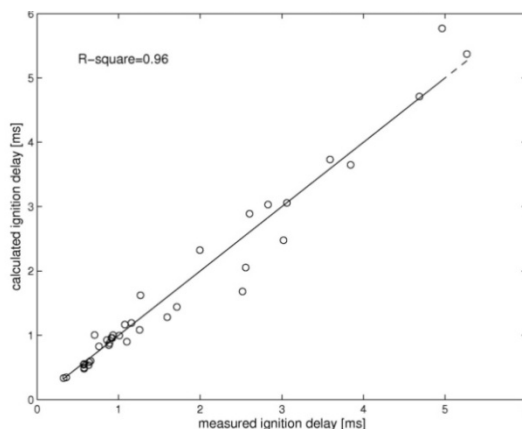


Figure 2: Correlation between measured and computed ignition delay times

As illustrated by the example in figure 3, the calibrated model is able to describe the temperature dependent influence of pressure, air fuel ratio and EGR rate on the main ignition delay times, showing the models capability to correctly account for these influences using only a limited number of reactions.

Conclusion and Outlook

The 7 step reaction mechanism of Zheng et al. has successfully been coupled with a genetic optimization algorithm and fitted to the n-heptane ignition delay data of M. Hartmann et al. [7]. The first optimization results for n-heptane and the Volkswagen CCS Diesel fuel (not presented here) indicate that the presented coupled approach can improve the predictive quality of the model and demonstrate that the Zheng model is sufficiently elaborate to emulate the influence of temperature, pressure, EGR and lambda on ignition.

In subsequent steps, the optimization algorithm will be extended to include the measured low temperature ignition delays, as well as the measured pressure traces; this, to improve the models predictive quality, both with respect to ignition timing and heat release rate. After adjustment of the stoichiometric coefficients and the species thermodynamic properties, a new set of rate parameters will be determined for each of the project fuels. Furthermore, it is currently being investigated whether modifications to the reactions itself, or the inclusion of additional reactions are necessary to model the non-alkanic project fuels.

References

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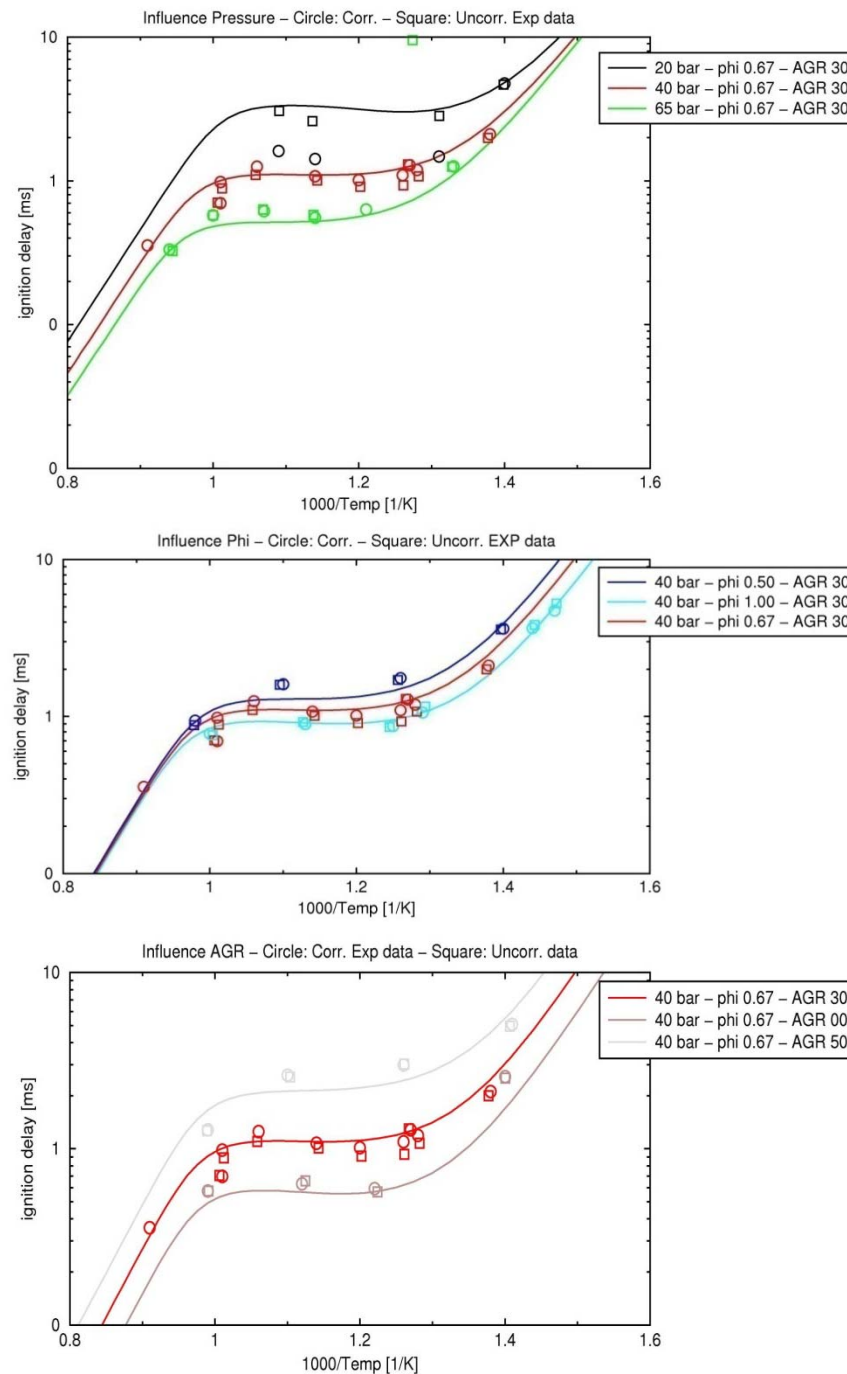


Figure 3: Comparison between measured [7] and computed ignition delay times. The uncorrected measurement values correspond to pressures slightly fluctuating around the target pressure. These values are corrected to the target pressure based on a multiple regression analysis. As can be seen, for low pressures the correction effect is significant, introducing a certain degree of uncertainty.