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Evaluation of Kinetic Models for Autoignition of Automotive Reference Fuels in HCCI Applications

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Abstract

Clean and efficient engine research and development work needs reliable models where autoignition for automotive reference fuels are described well. These models have to include chemistry containing numbers of reactions. The predictive capability depends more on the quality of reactions describing the chemical phenomena in the mechanism than on the number of the reactions. In this work three chemical mechanisms containing 1034, 74 and 63 species for primary reference fuels (PRFs) are compared with respect to the prediction of autoignition at conditions relevant for HCCI Engines and knock in SI Engines. After validation to experimental data for iso-octane, n-heptane and mixtures of the two fuels obtained from shock tube experiments over the temperature range 700 < T < 1200K at pressures 15-60 bars, a single zone engine model is used to simulate the point of autoignition and compared against experimental results obtained from an HCCI engine in KTH labs in Stockholm. The work shows the performance of the chemical mechanisms in prediction of autoignition delay time in HCCI engines.

Key words: Autoignition, HCCI, PRF, Chemical mechanism, Short mechanism

Introduction

Homogeneous Charge Compression Ignition (HCCI) is a form of internal combustion in which well-mixed fuel and oxidizer are compressed to the point of autoignition. HCCI has characteristics of both of homogeneous charge spark ignition (SI) and stratified charge compression ignition (CI), and has the potential to combine their best properties. The fuel and oxidizer are mixed together as in SI engines but instead of an electric discharge to ignite the mixture, the pressure and temperature of the mixture are raised by compression until the entire mixture reacts simultaneously as in CI engines. The main characteristic of HCCI is the simultaneous burning of the fuel/air mixture because of ignition occurring at several places simultaneously. In recent years, a number of studies related to the HCCI combustion have been published by Aceves et al. (2005), Sjoberg et al. (2005), Sato et al. (2005), Konno and Chen (2005), Chang et al. (2004), Bengtsson et al. (2004), Epping et al. (2002), Soyhan et al. (2001), Dibble et al. (2001), Flowers et al. (2000) and Aceves et al. (2000). HCCI engines have been shown to achieve extremely low levels of nitrogen oxide emissions (NOx) without catalytic converters. The unburned hydrocarbon and carbon monoxide emissions are still high due to lower peak temperatures and must still be treated to meet automotive emission regulations as discussed in Stanglmaier and Roberts (1999), Najt and Foster (1983), Canova et al. (2007), Kim and Lee (2007), Kim and Lee (2006), Shi et al. (2006), Xingcai et al. (2005) and Kim et al. (2005).

The HCCI process essentially involves a premixed fuel/air mixture at equivalence ratios that are generally lean. Ignition leads to very rapid combustion where all heat is released approximately within 5-15 crank angle degree (CAD). In an effort to understand how mixture preparation and in-cylinder thermodynamic conditions affect the chemical kinetics, models of varying resolution provide a good basis for exploring the HCCI combustion phenomena.

A detailed investigation of the combustion processes in engines is required for the improvement of engine technology. Chemical kinetic models of the combustion process incorporated into the computational fluid dynamics models for the prediction of gas flow in the combustion chamber provide an efficient tool in terms of time and cost, for the investigation of the combustion process. During the last years detailed chemical reaction mechanisms valid for a multitude of combustion situations have been proposed. Detailed kinetic models with a large number of reactions are very complicated and consume large amounts of computational time. They are very general and validated over a wide range of different parameters.

It is therefore necessary to reduce the chemical system for use in simulations of practical combustion devices with the commercial software products. It is important to construct from the detailed reaction mechanisms, simplified reaction mechanisms that are valid for the combustion problem under consideration. The generality of the detailed mechanisms can be reduced for the specific applications by using reaction-flow and sensitivity analyses. These analyses are used to calculate a relative importance value to rank species and reactions in the detailed mechanism. Species that are less relevant for the chosen application are defined as unnecessary and removed from the detailed mechanism to generate a skeletal mechanism that is valid for the selected problem.

In this paper, three chemical mechanisms, a detailed mechanism containing **1034** species and **4238** reactions obtained from www-cmls.llnl.gov (Curran et al. 2002), a short mechanism containing **74** species and **510** reactions obtained from Chevalier (1993) and Müller (1993) and a skeletal mechanism developed from the short mechanism for conditions relevant for engine knock (**63** species and **386** reactions) given in Soyhan et al. (2002), are validated first to experimental data obtained from shock tube experiments over the temperature range $700 < T < 1200$K at pressures 15-60 bars from Fieweger et al. (2002), Davidson et al. (2002) and Gauthier et al. (2002) and then tested against experimental results obtained from an HCCI engine by Kalghatgi et al. (2002) and Andrae et al. (2002) in KTH labs in Stockholm.

Kinetic Models

Complex chemical mechanisms are increasingly used within computational models for autoignition phenomena, which is an important design tool for HCCI engine development. The evaluation of existing chemical kinetic models by relating the predictions of models to the experiments performed under engine like conditions provides a rich area for future research.

In this study, as a starting point for detailed chemistry modelling, the latest reaction mechanism from the Lawrence Livermore National Laboratory (LLNL) combustion chemistry group was used. It consists of 4238 reactions among 1034 species, most of them are reversible. The chemical interactions between n-heptane and iso-octane are only through the radical pool in the LLNL mechanism as mentioned in Curran et al. (2002).

The second mechanism for PRFs was compiled from Chevalier (1993), (C_1-C_4) and Müller (1993), (C_5-C_8) kinetics and consists of 74 species and 510 reactions. The C_5-C_8 kinetics is not a complete mechanism, meaning that it does not give a full description of all possible reaction pathways. Some minor paths are not taken into consideration. The neglected reaction paths are supposed to have a low influence on the entire combustion process. Henceforth in this paper this mechanism will be referred to as "short mechanism". The species names in the short mechanism are given in Table 1. The short mechanism is a well-developed mechanism for SI engine conditions and validated for several conditions in literature.

An automatic reduction method based on the simultaneous use of sensitivity and reaction flow analyses is applied to the short mechanism to derive a skeletal mechanism by Soyhan et al (2002) for the conditions relevant for engine knock. Predetermined parameter ranges of initial and boundary conditions is used for the reduction, for example, the initial temperature is decreased from 1200 K until no autoignition occurs to cover all possible knocking conditions. Eleven species (neoC_5H_{11}, CH, CH_2(s), CH_2OH, CH_3O_2H, C_2H, CH_2CO,

OCHCHO, CH_2CHO, C_3H_8 and C_3H_6O) are extracted from the short mechanism in construction of the skeletal mechanism. Since the short mechanism is already validated extensively and the skeletal mechanism is generated from the short mechanism for conditions relevant to engine knock, it is expected to obtain good results for conditions relevant to HCCI conditions as well. The skeletal mechanism reduced from the short mechanism containing 63 species and 386 reactions will be referred to as the "skeletal mechanism" in this paper.

The three chemical mechanisms are validated first to experimental data obtained from shock tube experiments and then tested against experimental results in an HCCI engine.

Results and Discussion

Validation against shock tube experiments

A number of calculations of shock tube experiments were performed in order to validate the short and skeletal mechanisms. The calculations were done in the range of $700 < T < 1200$K at pressures 15-60 bars, for pure iso-octane 4and n-heptane and their mixtures.

The knock characteristics of iso-octane and n-heptane are well known from different experiments. Fieweger et al (1997) carried out an extensive experimental Shock Tube investigation on autoignition of iso-octane, n-heptane and different mixtures of the two fuels.

In Figure 1, using Chemkin developed by Kee et al. (2006) and a constant volume assumption calculated first ignition limits (τ) as a function of temperature for iso-octane, n-heptane and their mixtures at pressure 40 bar and fuel equivalence ratio (ϕ) of 1.0 are compared with the experimental results of Fieweger. All mechanisms can predict the experimental data well.

Table 2 and 3 give the predicted ignition delay times calculated by all mechanisms for neat iso-octane (experimental values are taken from Davidson et al. (2005)) and n-heptane (experimental values are taken from Gauthier et al. (2004)) showing their performance over a wider pressure range. In both tables, the initial temperature in Kelvin and pressure in atmosphere are given in the first two columns. The third column has the measured ignition delay times while the 4^{th} and 6^{th} columns have the predicted ones by using the short and the skeletal mechanisms, respectively. The relative errors between the measured ignition delay times and the calculated ones by using the constant volume assumption in the Chemkin code are given in 5^{th} and 7^{th} columns.

As seen in Table 2, for iso-octane the skeletal mechanism always gives smaller relative error compared to the LLNL mechanism one. This behaviour is opposite for low temperature region in pure n-heptane cases as seen in Table 3, however for intermediate and high temperature region the short mechanism gives smaller error. The results also show that shock tube experiments are very useful to validate reaction mechanisms to be used in HCCI calculations.

Table 1. The list of all species included in the mechanism.

O_2	H	OH	O	H_2
H_2O	HO_2	H_2O_2	N_2	CH_2
CO	CO_2	HCO	CH_2O	CH_3
C_2H_4	CH_4	C_2H_6	CH_3O	CH_3O_2
CH_3OH	CH_3CHO	CH_3CO	HCCO	OCH_2CHO
CH	CH_2(s)	CH_2OH	CH_3O_2H	C_2H
CH_2CO	CH_2CHO	OCHCHO	C_3H_8	C_3H_6O
CC_8H_{17}	iC_8H_{18}	tC_4H_9	iC_4H_9	pC_4H_9
CH_2CHOO	C_3H_4-a	iC_4H_7	C_2H_5	C_3H_5-s
C_2H_3	C_3H_4-p	C_2H_2	C_3H_3	iC_4H_8
iC_3H_7	nC_3H_7	C_3H_6	C_5H_{11}-1	$C_7H_{15}O_2$-1
$C_7H_{15}O_2$-2	$C_7H_{14}OOH1$-2	$C_7H_{14}OOH2$-1	OOC_7OOH	$HOOC_7OOH$
OC_7OOH	$OC_7H_{13}O$	C_7H_{15}-1	C_7H_{15}-2	nC_7H_{16}
aC_6H_{13}	$aC_8H_{17}O_2$	aC_8H_{17}	$aC_8H_{16}OOH$-b	OOC_8OOH
$HOOC_8OOH$	OC_8OOH	$OC_8H_{15}O$	$neoC_5H_{11}$	

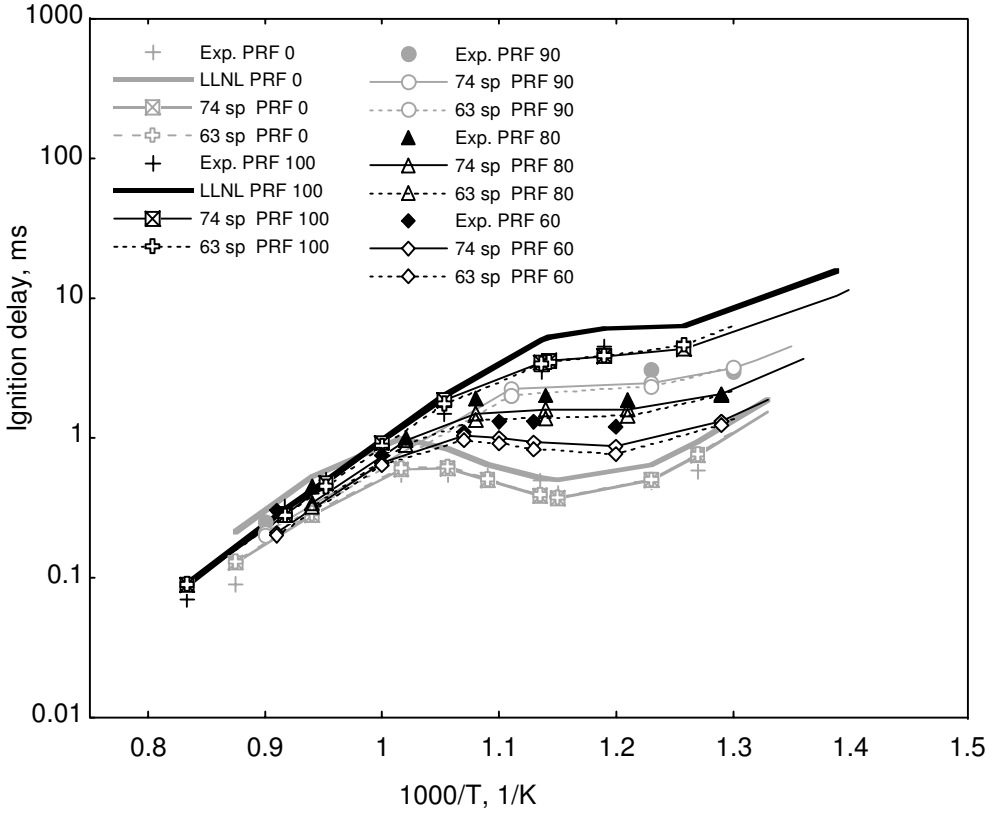

Figure 1. Model validation against shock tube ignition delay times from Fieweger et al. (1997).

Table 2. Iso-octane validation against shock tube ignition delay times.

T_5/K	p_5/atm	Experiment τ_i / μs	LLNL τ_i / μs	Rel.Err.	63 species τ_i / μs	Rel.Err.
855	56.4	1719	3118	81%	1951	13%
867	59.3	1755	2762	57%	1711	-3%
894	58.5	1193	2460	106%	1580	32%
927	55.7	1067	1897	78%	1411	32%
975	51.2	871	1070	23%	950	9%
984	18.1	1511	2562	70%	2250	49%
995	16.3	1535	2460	60%	2073	35%
1006	51.1	625	690	10%	634	1%
1015	47.8	505	650	29%	600	19%
1043	17.1	927	1291	39%	1009	9%
1077	18.4	604	804	33%	624	3%
1098	47.5	222	231	4%	219	-1%
1109	15.9	516	647	25%	501	-3%
1159	14.9	214	374	75%	330	54%

Table 3. n-heptane validation against shock tube ignition delay times.

T_5 / K	p_5 / atm	Experiment τ_i / μs	LLNL τ_i / μs	Rel.Err.	63 species τ_i / μs	Rel.Err.
806	20.0	1.38	1.17	-15%	1.08	-22%
850	19.9	1.65	1.29	-22%	1.34	-19%
906	19.8	1.84	2.30	25%	2.49	36%
909	53.9	0.25	0.36	42%	0.25	-2%
923	60.0	0.24	0.32	32%	0.22	-10%
926	60.6	0.23	0.32	38%	0.21	-10%
932	55.4	0.32	0.39	21%	0.27	-16%
985	48.6	0.36	0.70	92%	0.42	15%
1007	57.7	0.23	0.53	128%	0.29	25%
1012	18.1	0.94	2.14	127%	1.27	35%
1013	53.6	0.29	0.58	99%	0.32	9%
1023	54.2	0.26	0.54	108%	0.29	11%
1027	59.1	0.24	0.47	99%	0.25	5%
1048	16.7	0.85	1.49	75%	0.83	-3%
1057	50.0	0.19	0.45	131%	0.24	24%
1063	53.1	0.18	0.39	118%	0.21	17%
1115	52.3	0.10	0.22	117%	0.13	27%

Comparison against HCCI experiments with PRFs

After validation to experimental data for iso-octane, n-heptane and mixtures of the two fuels obtained from shock tube experiments over the temperature range 700 < T < 1200 K at pressures 15-60 bars, a single zone engine model was used to simulate the point of autoignition and compared against experimental results obtained from an HCCI engine in KTH labs in Stockholm. The full engine specifications can be found in Kalghatgi et al. (2003) and Andrae et al. (2005).

Figures 2-5 show experimental (given in Kalghatgi et al. (2003)) and calculated pressures for PRF 84 and PRF 94 in a HCCI Engine using the single zone model in Chemkin code. Using a single zone model naturally gives higher peak pressures and heat release rates compared to experiments, but still is a very useful approach for comparing the point of autoignition for different fuels.

Two intake conditions are compared; (i) high intake temperature and low intake pressure (Figures 2-3) and (ii) low intake temperature and high intake pressure (Figures 4-5).

For intake condition (i) the short and the skeletal mechanisms give slightly better prediction against the experimental data for PRF 94 and PRF 84 than the LLNL mechanism as seen in Figures 2-3.

However, for intake condition (ii) the difference between the two mechanisms and LLNL is bigger (see Figures 4-5). Moreover, at both intake conditions, the short and the skeletal mechanisms are capable of ranking the two fuels according to their autoignition quality. The detailed mechanism gives similar results as the short and skeleton mechanism for condition (i) but it is significantly less reactive for condition (ii). In addition to being overall more reactive versus temperature (see Figure 1) this could also be explained by different pressure dependence on the ignition delay, τ_i = f (T) p^{-n}, in the short and skeleton mechanism compared to the detailed.

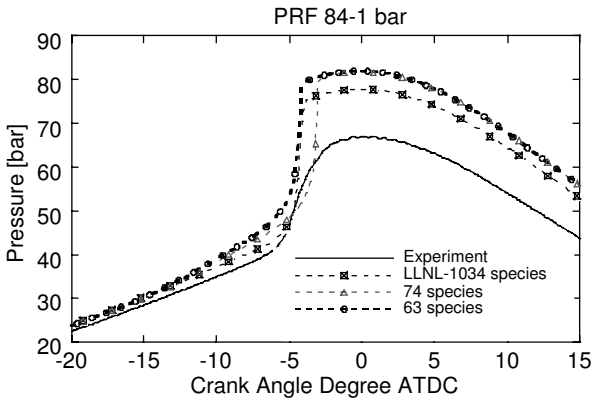

Figure 2. Experimental and calculated pressures for PRF 84 in a HCCI Engine: p_o = 1.0 bar, T_o = 393 K, ϕ = 0.2857, Engine speed = 900 rpm, ε = 16.7, V_d =1.95 dm^3. Calculations start at -99 degrees ATDC at 472 K and 1.74 bar.

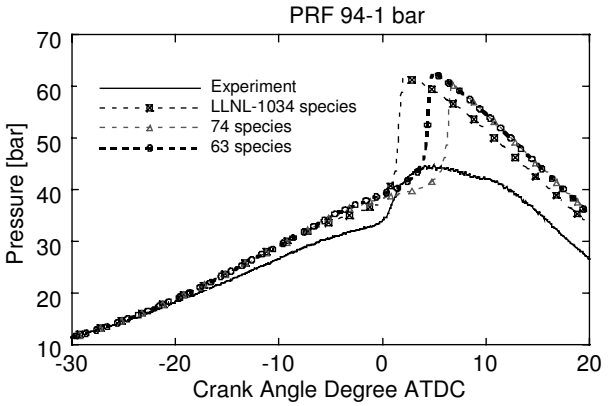

Figure 3. Experimental and calculated pressures for PRF 94 in a HCCI Engine: p_o = 1.0 bar, T_o = 393 K, ϕ = 0.2857, Engine speed = 900 rpm, ε = 16.7, V_d =1.95 dm^3. Calculations start at -99 degrees ATDC at 455 K and 1.37 bar.

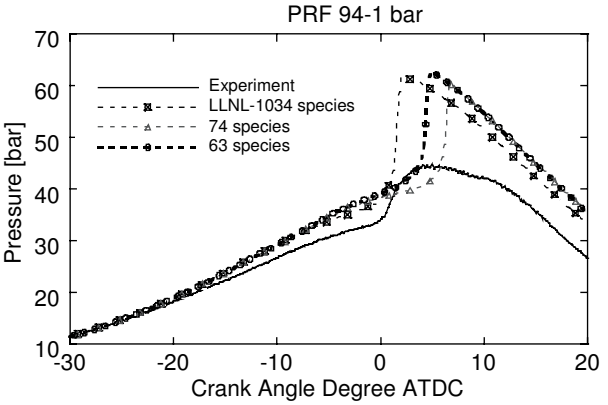

Figure 4. Experimental and calculated pressures for PRF 84 in a HCCI Engine. p_o = 2.0 bar, T_o = 313 K, ϕ = 0.25, Engine speed = 900 rpm, ε = 16.7, V_d = 1.95 dm^3. Calculations start at -99 degrees ATDC at 415 K and 3.34 bar.

Conclusions

The significant outcome of this work is to show the performance of available mechanisms in literature for predicting autoignition time in HCCI engines. In this paper, three mechanisms from literature developed for SI engine conditions are validated to experimental data for iso-octane, n-heptane and mixtures of the two fuels obtained from shock tube experiments over the temperature range 700 K < T < 1200 K at pressures 15-60 bars which corresponds to the HCCI conditions. A single zone engine model is used to simulate the point of autoignition and compared against experimental results obtained from an HCCI engine. It is shown that the short and skeletal mechanisms give good agreement in HCCI conditions and they can be used in HCCI engine simulations within the range of the validation. We hope that the results shown here are also a useful database for validation of future efforts in the field of HCCI combustion and engine development.

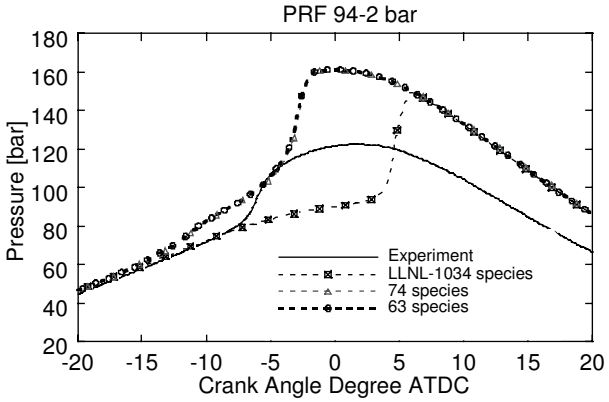

Figure 5. Experimental and calculated pressures for PRF 94 in a HCCI Engine. p_o = 2.0 bar, T_o = 313 K, ϕ = 0.25, Engine speed = 900 rpm, ε = 16.7, V_d = 1.95 dm^3. Calculations start at -99 degrees ATDC at 415 K and 3.34 bar.

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Nomenclature

Symbols

P	Pressure (atm)
T	Instantaneous cylinder gas temperature (K)
τ	First ignition limits
ϕ	Fuel equivalence ratio

Abbreviations

CAD	Crank angle degree
CI	Compression ignition
CPU	Central process unit
HCCI	Homogeneous charge compression ignition

LLNL	Lawrence Livermore National Laboratory	PRF	Primary Reference Fuel
NOx	Nitrogen oxide emissions	SI	Spark ignition

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