COMPARISON OF DIFFERENT CHEMICAL KINETIC MECHANISMS OF METHANE COMBUSTION IN AN INTERNAL COMBUSTION ENGINE CONFIGURATION

by

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Three chemical kinetic mechanisms of methane combustion were tested and compared using the internal combustion engine model of Chemkin 4.02 [1]: one-step global reaction mechanism, four-step mechanism, and the standard detailed scheme GRIMECH 3.0.
This study shows good concordances, especially between the four-step and the detailed mechanisms in the prediction of temperature and main species profiles. But reduced schemes were incapables to predict pollutant emissions in an internal combustion engine. The four-step mechanism can only predict CO emissions but without good agreement.

Key words: *chemical kinetics, combustion, methane, engine*

Introduction

Detailed chemical kinetic descriptions of hydrocarbon combustion may require the tracking of hundreds of chemical species and thousands of reaction steps. For the foreseeable future, CPU time and computer memory limitations will prohibit implementation of fully detailed descriptions of combustion chemistry into computational fluid dynamics (CFD) simulations of combustion hardware.

Within CFD simulations, the number of species tracked impacts the memory usage and CPU time. As a result, it is important to minimize this number while retaining essential features of the detailed chemistry. The number of species required for simulation of combustion processes depends on the nature of the phenomenon, and the type of information desired from the simulation.

The recent development of comprehensive, validated, detailed mechanisms for combustion of large hydrocarbon is a significant step forward. Reduced chemical kinetic mechanisms that can represent important aspects of the behaviour of these detailed mechanisms using few enough scalars that they can be implemented into CFD simulations offer large potential improvement in the modelling of practical combustion devices [2].

The present research was intended to demonstrate the feasibility of the reduced reaction mechanisms in the simulation of internal combustion engines (ICE).

In this paper, three chemical kinetic mechanisms of methane combustion are compared in an ICE configuration. Methane was selected for its economic and ecological advantages. These mechanisms are: full detailed mechanisms GRIMECH 3.0, four-step reactions mechanisms, and a global one reaction mechanism.

We compared those mechanisms for temperature profiles, species profiles, and when possible, pollutant emissions for various excess air ratios.

Our results and discussion show that the four step reduced mechanism is feasible for the simulation of combustion in ICE and can replace faithfully the full detailed one but with some limitations.

Chemical reaction mechanisms for methane

Since methane is the simplest hydrocarbon fuel available; several studies have focused on methane-air flames [3]. The oxidation of methane is quite well understood and various detailed reaction mechanisms are reported in literature [4]. They can be divided into full mechanisms, skeletal mechanisms, and reduced mechanisms. The various mechanisms differ with respect to the considered species and reactions. However, considering the uncertainties and simplifications included in a turbulent flame calculation, the various mechanisms agree reasonably well [5].

In literature, several mechanisms of methane combustion exist. We can cite:
– for detailed mechanisms: Westbrook [6], Glarborg *et al.* [7], Miller and Bowman [8], and recently, Konnov [9], Huges *et al.* [10], and the standard GRIMECH [11],
– for reduced mechanisms: Westbrook and Dryer [12], Duterque *et al.* [13] (1 to 2 global reactions), Peters [14], Hutmann *et al.*, [15], and Jones and Lindstedt [16] (more than 2 global reaction), Edelman and Fortune [17], and Edelman and Harsha [18] (1 global reaction with many elementary reactions; these mechanisms are called quasi-global mechanisms).

These last mechanisms are certainly more accurate than global mechanisms but they are also numerically expansive.

All chemical models used in combustion share the same description of elementary chemical reactions, based on an Arrhenius law, leading to a rate coefficient expressed as:

$$k = AT^{\beta} e^{-\frac{E_a}{RT}} \qquad (1)$$

The values of A, E_a (or $T_a = E_a/R$) and of the temperature-dependence coefficient β are thus reaction-dependent. Based on this expression, different levels of approximation can be defined to describe the kinetics.

The three following mechanisms are investigated:

	A	β	T_a
– the global one-step reaction mechanism of Duterque [13]			
$\quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$1.50 \cdot 10^{13}$	0.0	20000
– the four-step reaction mechanism of Jones and Lindstedt [16]			
– $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	$4.40 \cdot 10^{14}$	0.0	30000
– $CH_4 + H_2O \rightarrow CO + 3H_2$	$3.00 \cdot 10^{11}$	0.0	30000
– $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	$2.50 \cdot 10^{19}$	–1.0	40000
– $CO + H_2O \leftrightarrow CO_2 + H_2$	$2.75 \cdot 10^{12}$	0.0	20000
– the standard detailed mechanism GRIMECH 3.0 (53 species, 325 reactions) [11].			

Internal combustion engine model theory

CHEMKIN is a powerful set of software tools for solving complex chemical kinetics problems. It is used to study reacting flows, such as those found in combustion, catalysis, chemical vapour deposition, and plasma etching.

CHEMKIN consists of rigorous gas-phase and gas-surface chemical kinetics in a variety of reactor models that can be used to represent the specific set of systems of interest (fig. 1).

The CHEMKIN Reactor Models allow users to simulate detailed kinetics in important industrial systems by predicting the reacting flow conditions or chemical state based on operating conditions.

Assumptions and limitations

The contents of a well mixed or stirred reactor are assumed to be nearly spatially uniform due to high diffusion rates or forced turbulent mixing. In other words, the rate of conversion of reactants to products is controlled by chemical reaction rates and not by mixing processes. Thus we consider that the reactor is "limited" by reaction kinetics. An essential element of the stirred reactor model is the assumption that the reactor is sufficiently mixed to be described well by spatially averaged or bulk properties. The major advantage of the well stirred approximation lies in the relatively small computational demands of the mathematical model. Such a model allows investigators to easily consider and analyze large, detailed chemical reaction mechanisms or complex reactor networks.

In addition to fast mixing, the modeling of homogeneous reactors requires several assumptions. First, mass transport to the reactor walls is assumed to be infinitely fast. Therefore, the relative importance of surface reactions to gas-phase reactions is determined only by the surface-to-volume ratios of each material and the relative reaction rates (rather than by transport constraints). Second, the flow through the reactor must be characterized by a nominal residence time, which can be deduced from the flow rate and the reactor volume [19].
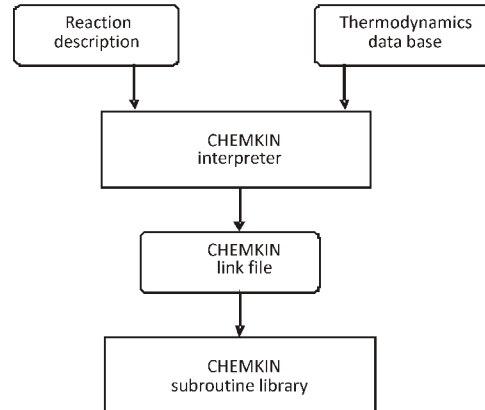

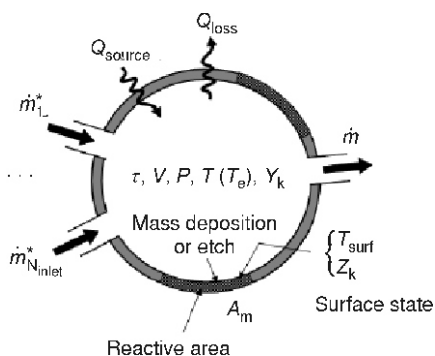**Figure 1. CHEMKIN package structure [19]**

General equations

Conservation of mass, energy, and species for a well mixed reactor or homogeneous system include net generation of chemical species within the reactor volume, and net loss of species and mass to surfaces in the reactor. Homogeneous systems include closed batch reactors, single-zone engine-cylinder models, perfectly stirred reactor approximations, well mixed (low-pressure) plasma processing reactors, for example.

Figure 2 illustrates the conceptual representation of a generic reactor chamber. A steady flow of reactants is introduced through the inlet with a given species composition and temperature. For transient systems, there may be no flow, such that the system is closed with respect to mass transfer other than surface losses or gains.

Figure 2. Schematic representation of a well mixed reactor module [19]

In our case, an ICE model simulates a combustion cylinder under auto-ignition conditions, most relevant to the study of fuel auto-ignition behaviour, engine knock, and homogeneous charge compression ignition (HCCI) engines. This model is represented by a closed homogeneous 0-D reactor (when both intake and exhaust valves are closed). This reactor has no exchange of mass or energy (adiabatic) with the exterior. So the conservation equations are reduced to:

$$\frac{dY_j}{dt} = \frac{\dot{\omega}_j W_j}{\rho}; \quad j = 1, \ldots, n_{sp} \tag{2}$$

for species conservation, and:

$$\rho C_p \frac{dT}{dt} = \frac{dP}{dt} - \sum_{j=1}^{n_{sp}} h_j \dot{\omega}_j W_j \tag{3}$$

for the energy conservation. The rate of production is $\dot{\omega}_j$ given by chemistry with eq. (1)

The displacement of the piston generates the change of the volume (fig. 3). Heywood [20] provides equations that describe the volume (to first order) as a function of time, based on engine parameters.

The engine parameters are specified by the user directly in the CHEMKIN User Interface for the ICE reactor model [19].

$$d\frac{\frac{V}{V_c}}{dt} = \Omega \left(\frac{C-1}{2}\right) \sin\theta \left[1 + \frac{\cos\theta}{\sqrt{R_p^2 - \sin^2\theta}}\right] \tag{4}$$

Figure 3. Schematic of an engine cylinder, used in the ICE model to determine the volume as a function of time

This equation allows solution of the general equations for species and energy conservation.

Inputs of the simulation are:
– chemical reaction mechanisms with Arrhenius coefficients,
– thermodynamic and transport data,
– molar fractions of reactive species (natural gas: CH_4, C_2H_6, C_3H_8, and air – O_2, N_2) for various equivalence ratios Φ, and
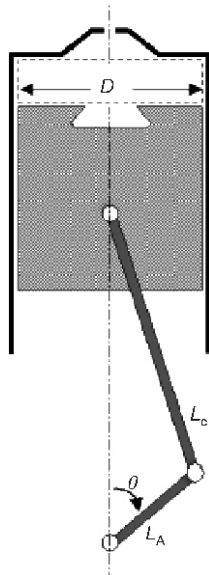– geometrical parameters of the ICE.

So we can extract information from the simulation such as:
– temperatures profiles,
– pressures profiles,
– main species profiles,
– total rate-of-production, and
– peak of temperature for various excess air ratios Φ.

Results and discussions

We simulated the combustion in a cylinder engine with the three chemical kinetic mechanisms listed below. We used various engine parameters (geometrical parameters, crank rotary speeds). An example of parameters is cited in tab. 1.

Thermodynamic and transport data used in all simulations are those proposed with GRIMECH 3.0 [11].

In this section, the consequences of the three chemical kinetic schemes for the predicted temperature and pressure profiles, species profiles and when possible pollutant emissions are compared and discussed.

Table 1. Example of test engine specifications

Parameter	Setting
Compression ratio	16.5
Cylinder clearance volume	103.3 cm^3
Engine speed	1000 rpm
Connecting rod to crank radius ratio	3.714286
Cylinder bore diameter	12.065 cm

Temperature and pressure profiles

Figure 4 shows the temperature profiles obtained with the three chemical kinetic mechanisms (Duterque, Jones and Lindstedt, and GRIMECH 3.0) for the adiabatic and stoichiometric condition ($T_{ini} = 447$ K, $P_{ini} = 1{,}07$ bar, and $\Phi = 1{,}0$).

As shown in this figure, there is some discrepancy of temperature profiles between the detailed mechanism (taken here as a reference) and the reduced ones. The combustion with reduced mechanisms occurs earlier than with the detailed mechanism. The reason of this difference in ignition delays is that the chemistry in reduced mechanisms is infinitely abrupt. In fact the species and the temperature reach their end or maximum values very quickly.

Figure 4 shows also that the one-step mechanism overpredict the combustion temperature profiles (about 200 K). This overprediction disappears when multi-step reaction kinetics is considered.

But on another hand, the peak of temperature predicted using the four-step mechanism produces good agreement with GriMech 3.0. This agreement is also shown in fig. 6 on which the peaks of temperatures for various values of excess air ratios are drawn.
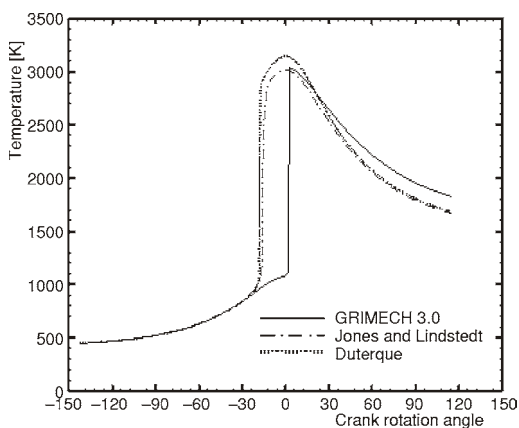
The same results are obtained for pressure (see fig. 5).

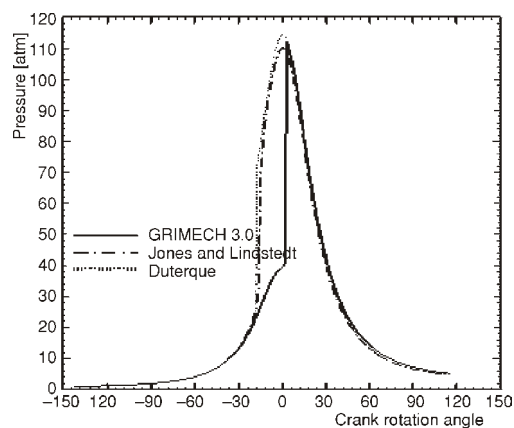**Figure 4. Comparison of temperatures profiles for equivalence ratio $\Phi = 1$**

Figure 5. Comparison of pressures profiles for equivalence ratio $\Phi = 1$

Species profiles

Figure 7 illustrates the main species profiles of CH_4, CO_2, O_2, and H_2O for the stoichiometric condition. Obviously, the one-step mechanism cannot predict the CO profiles since there are no pathways.
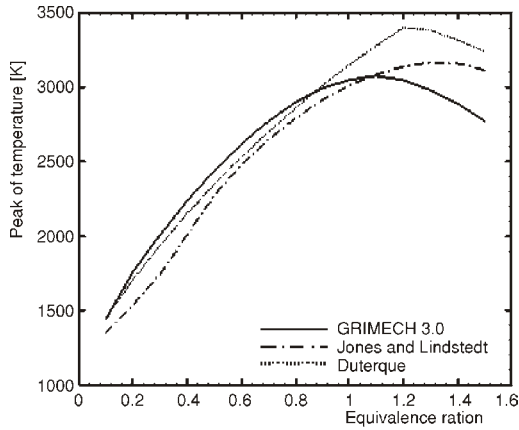
Figure 6. Comparison of peaks of temperature for various equivalence ratios Φ

Both one-step and four-step mechanisms predict earlier fuel and oxygen disappearance than predicted using the detailed mechanism.
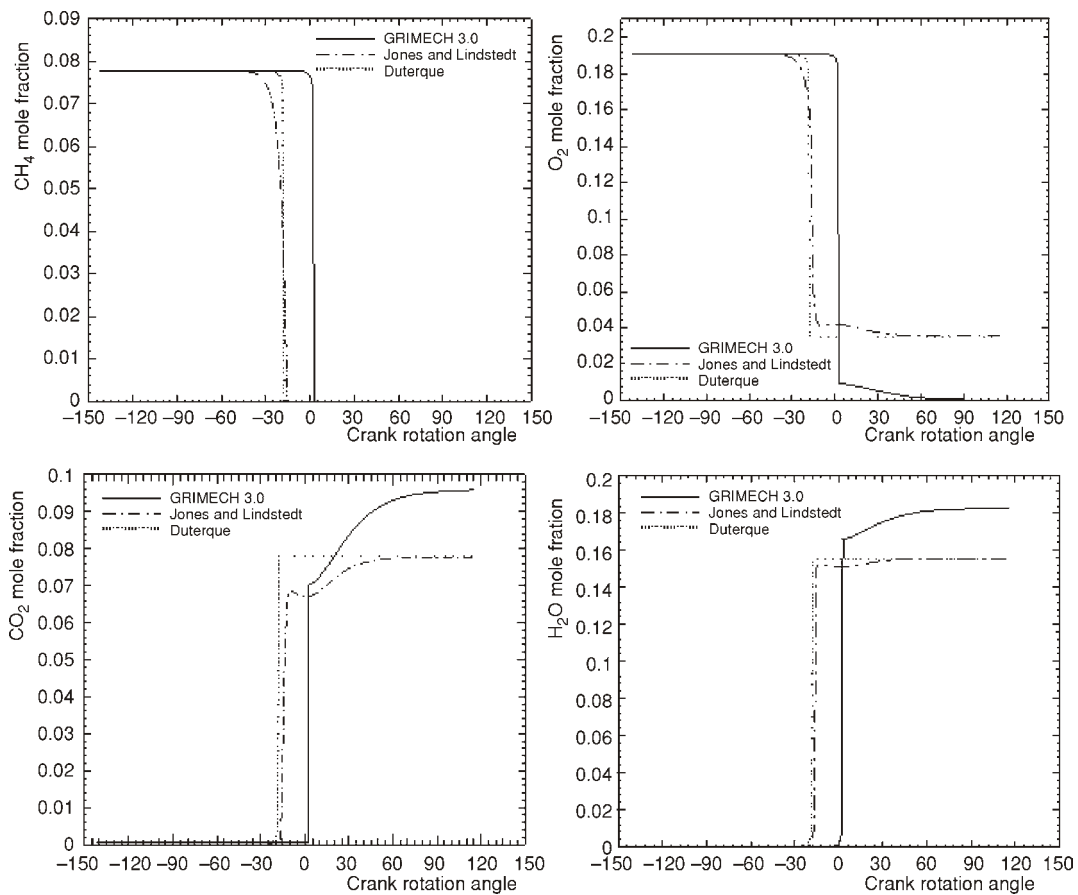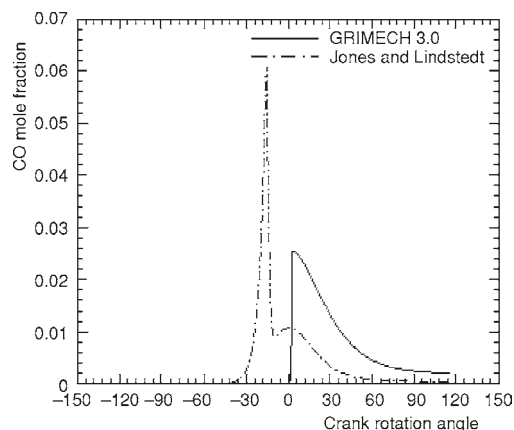

Figure 7. Comparison of main species profiles for equivalence ratio $\Phi = 1$

Figure 8. Comparison of CO emission for equivalence ratio $\Phi = 1$

For production emissions, one-step mechanism (also the four-step mechanism) dictates that CO_2 and H_2O are formed as rapidly as fuel and oxygen are consumed, since there are no alternative pathways, with a consequent larger amount of production than the detailed mechanism which requires that the fuel is pyrolysed to intermediate hydrocarbons, which are then oxidized to CO, which is then oxidized to CO_2 in a very slow reaction.

Although there is discrepancy in species profiles, the four-step mechanism have the same pace than the detailed one and produces acceptable agreement in species prediction.

Pollutant emissions

Obviously, the one-step mechanism cannot be used to predict emission of pollutants. And the four-step can only predict CO emission.

Therefore, fig. 8 compares the predicted emissions of CO using four-step and detailed mechanisms. This figure shows that the four-step mechanism overpredict CO emission in ICE. This is due to the fact that in this mechanism the totality of CH_4 is transformed into CO which has only one way to be consumed, but in the detailed mechanism CO reacts by multitude pathways.

Conclusions

Combustion within an internal combustion engine has been computed using three chemical kinetic schemes: one-step, four-step and detailed mechanisms.

The influence of these mechanisms on the temperature profiles, species profiles and pollutant emissions are compared. All comparisons were for various equivalence ratios values and engine parameters. The present object is to demonstrate the feasibility of reduced mechanisms in the simulation of combustion in engine cylinder. The results are encouraging.

As shown in the figures, all comparisons of the predicted temperature profiles, main species profiles and pollutant emissions illustrate that the four-step reduced mechanism better describes the full mechanism. Thus the full mechanism can be superseded by the four-step mechanism for engineering applications of internal combustion engine. The application of such reduced mechanism can reduce the available computational resources and cost because the number of species is reduced.

Nomenclature

A – pre-exponential factor, [molm^{3}s]
A_m – surface of the mth material in the reactor, [cm^2]
C – compression ratio of the engine, [–]
C_p – specific heat capacity at constant pressure, [Jkg^{-1}K^{-1}]
D – cylinder bore diameter, [cm]
E_a – activation energy of a chemical reaction, [Jmol^{-1}]
h_j – specific enthalpy of specie j, [Jkg^{-1}K^{-1}]
k – reaction rate coefficient, [–]
L_A – crank radius, [cm]
L_C – connecting rod length, [cm]
$\dot{m}$ – outlet mass flow rate, [kgs^{-1}]
$\dot{m}_i$ – inlet mass flow rate, [kgs^{-1}]
n_{sp} – number of species, [–]
P – pressure, [bar]
Q_{loss} – heat loss, [Js^{-1}]
Q_{source} – energy deposited into the gas from a heat source, [Js^{-1}]
R – ideal gas constant, [Jmol^{-1}K^{-1}]
R_p – ratio of the connecting rod length to the crank radius, [Jmol^{-1}K^{-1}]
T – temperature, [K]
T_a – activation temperature, [K]
T_e – electron temperature, [K]

T_{surf} – surface temperature, [K]
t – time, [s]
V – in-cylinder volume, [cm^3]
V_c – cylinder clearance volume, [cm^3]
Y_j – mass fraction of specie j, [–]
W_j – molecular weight of specie j, [kgmol^{-1}]
Z_k – site fraction of the kth species at a site, [–]

Greek letters

β – temperature exponent of the preexponential factor
Φ – equivalence ratio, [–]
θ – angular position of the crank arm, [deg]
ρ – density, [kgm^{-3}]
$\dot{\omega}_j$ – chemical production rate of specie j, [molm^{-3}s^{-1}]
Ω – speed of revolution of the crank arm, [deg s^{-1}]
τ – nominal residence time, [s]

Subscripts

j – specie

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