Combustion and Flame 186 (2017) 1–16

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Development of a two-part n-heptane oxidation mechanism for two stage combustion process in internal combustion engines

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ARTICLE INFO

Article history:
Received 27 January 2017
Revised 21 July 2017
Accepted 26 July 2017

Keywords:
n-Heptane mechanism
Two-part mechanism
Ignition delay time
Low temperature combustion
Diesel engine

ABSTRACT

This paper presents an attempt to build a very reduced kinetics mechanism of n-heptane to simulate the two stage ignition process in terms of ignition delay time and in-cylinder pressure profiles over the whole range of engine operations. Starting from the previous 26 reactions and 25 species mechanism, two reduced schemes have been developed, one with 18 reactions and 19 species and the other with 13 reactions and 14 species. The reduction step shows that when the reactions describing the first stage are reduced as in the 18-step model, the accuracy is poor. The second 13-step model, where the reaction path describing the low temperature period has been kept, is more reliable when the window of engine operations is restricted. From this reduction step, a two-part reaction mechanism linked with a temperature criterion has been developed, while maintaining a wide range of engine operating conditions. This mechanism includes a low temperature reaction group and a high temperature reaction group, linked with a transition temperature correlation. Ignition delay times calculated with the two-part model are compared to those from the detailed mechanism. In addition, the comparison of the Indicated Mean Effective Pressure (IMEP) with the results of the previous 26-step mechanism has been done. The results obtained with the present model are in good agreement with the 26-step one. Moreover, this model has a very short computational time and thus could be used in CFD simulations as well as single zone or multi-zone engine models, and also model-based design.

1. Introduction

Modern internal combustion engines must meet increasingly drastic emissions regulations for exhaust pollutants such as particulate matter (PM), nitrogen oxides (NOx), unburned hydrocarbons, soot and carbon monoxide. In addition, with the necessity to reduce the impact of CO_2 emissions on global warming, engines must achieve the lowest level of this greenhouse effect gas. Over the past two decades, research has been heading toward new combustion modes for internal combustion engines that can simultaneously reduce exhaust emissions, CO_2 emissions and improve thermal efficiency. The most prominent alternative combustion mode is low temperature combustion (LTC) which is an alternative emerging engine technology [1]. Over the last 20 years, various names have been assigned to this combustion process such as: ATAC, CAI, PREDIC, PCCI, UNIBUS, HCCI [2–8]; a complete overview of these combustion modes is given in reference [1]. The Homogeneous Charge Compression Ignition (HCCI) engines have been given significant research efforts to understand the fundamental mechanisms of this combustion mode in the last decades [9–13]. The use of highly diluted premixed air–fuel charge in HCCI allows for low emissions of nitrogen oxides (NOx), soot and particulate matter. In HCCI combustion mode the heat release rate (HRR) is governed by chemical kinetics, [14–16] leading to significantly higher pressure rise rate in comparison with SI and Diesel engines. Consequently, in HCCI mode the engine operation is very noisy [1,17–18], one of the primary constraints governing the maximum power output limit.

For HCCI engine applications and especially Diesel fuelled engines, fuels with lower octane ratings such as n-heptane, diesel or dimethyl ether (DME) are preferred. This category of fuel displays a two stage ignition behavior [19–21]. The heat release rate occurs in two stages, respectively a low temperature period followed by a high temperature period. In addition, alkanes such as n-heptane are more conductive to LTC than branched alkanes, as for example iso-octane. The simulation of LTC combustion requires an accurate description of chemical reaction kinetics. In recent years, several reduced mechanisms have been published in the literature [22–27] to model the two stage mode for different fuel types. The main goal of these reduced mechanisms is to minimize the central processing unit (CPU) time when the chemical reactions mechanism is

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http://dx.doi.org/10.1016/j.combustflame.2017.07.031
0010-2180/

coupled with CFD, to simulate the engine cycle during HCCI process. For engine applications, a very reduced mechanism including a minimal number of variables is very attractive for CFD simulations and for model-based control, especially if the number of species is lower than ten. Currently, the available reduced mechanisms in the literature contain more than 20 species. Beside these type of mechanisms, some reduced ad-hoc models have been proposed in the literature to describe the basic chemical interactions [26,28–29]. The knowledge of the major ignition steps is used to define a set of global reactions, commonly based on species classes instead of real species. For this type of kinetics model, the challenge is to select accurate descriptions of species classes and global reactions.

The present study was motivated by the need to reach an n-heptane scheme including a number of species lower than 10. Therefore the main objective has been targeted on further mechanism reduction instead of building a global mechanism. In a previous study, a 26 reactions and 25 species mechanism [25] for n-heptane has been derived from two detailed mechanisms developed by Lawrence Livermore National Laboratory (LLNL) [30–31] and by Chalmers University [32]. This 26-step mechanism has been developed with the aim of reproducing the same trends as the detailed mechanism for the entire range of engine operations. It has been validated in terms of ignition delay times, two stage process, pressure profiles and the histories of the off-gas species (CO, CO_2, H_2O, etc.). This scheme has been implemented in a CFD code to simulate engine cycle at varying operating conditions with an acceptable computational time [12]. Additionally, it has also been integrated in a stochastic reactor model including a micromixing time model to describe HCCI process [33] with reduced computational time, in comparison with previous CFD code simulations.

Among the reduced mechanisms published in the literature, Peters et al. [26] derived by algebraic manipulations on a skeletal mechanism of 56 reactions and 38 species a chemical kinetic mechanism for n-heptane with 30 reactions and 27 species. This 30-step model is dedicated to the description of first and second stage ignition, thereby the transition period is not taken into account. Starting from this 30-step model and using steady state approximations, the authors derive a subset of four different reactions for each regime. Müller et al. [27] published a global model based on a 4-step with adjusted rate coefficients at high pressure. This model based on activation energy arguments was postulated and has been validated for a pressure equal to 40 bar at varying equivalence ratio. The results of this 4-step model show an ignition delay time close to the full kinetics mechanism, with a maximum error of less than 20% in the region around 850 K. Keck and Hu [28] developed a 14-step global kinetic model based largely on suggestions by Benson [29]. This global model has been based on a branched chain mechanism to correlate the data measured on a constant volume combustion bomb. The objective of Keck and Hu study was to explore the explosion limits for fuel–air mixtures compressed by an expanding laminar flame front.

Instead of developing an ad-hoc global mechanism like in the above mentioned papers, the approach for this study was to explore if further systematic mechanism reduction is possible to reach a minimum species number. This is a prerequisite for engine applications, considering the wide range of temperature, pressure and gas composition existing in internal combustion engines, linked to operating conditions (inlet pressure and temperature, dilution by EGR...) and engine geometry. Starting from the previous 26 reduced reaction mechanism, a first attempt to derive a very reduced model with lower species number, based on two reduced kinetics models with rate constants adjusted for a few reactions, has failed due to the large window of engine operating conditions. From the observations on the relevant processes of two stage combustion, a two-part mechanism linked to a temperature criterion has been developed in a second phase of this study.

The following section of this paper is dedicated to the different attempts to build a very reduced mechanism as close as possible in terms of ignition delay times and in-cylinder pressure to the detailed mechanism developed by Lawrence Livermore National Laboratory [30–31] (LLNL) and the 26-step model [25]. Section 3 is dedicated respectively to the development of the two-part mechanism, and to the comparison of ignition delay times and IMEP between the two-part mechanism, the detailed mechanism and the 26-step reduced scheme. Finally, the conclusions are presented in Section 4.

2. Reduction

2.1. General considerations

Figure 1 shows the definition of the main ignition delay time during a compression and expansion stroke cycle. This delay time is the time between the start of compression and the time τ_2 when the H_2O_2 decomposition occurs and OH concentration increases rapidly, leading to the in-cylinder pressure rise. This figure also shows the delay time of the first stage ignition τ_1 when the formation of hydroperoxide H_2O_2 occurs. The phasing is defined as: $\tau = \tau_2 - \tau_1$.

In this paper, the simulations have been done at variable volume, using Senkin application of Chemkin code [34], for the different reduction phases of this section. The variable volume calculations reproduce the compression and expansion strokes, thereby assuming a homogeneous zero dimensional adiabatic model of the internal combustion engine. In Section 3, simulations were carried out with a previous code designed for investigations on HCCI processes [33] based on a stochastic reactor model. In all cases where EGR is taken into account, the EGR composition has been fixed equal to: CO_2 (12%), H_2O (2%), N_2 (83.5%), O_2 (2.5%).

In addition, the mechanism reduction was associated with a sensitivity analysis to temperature with Senkin application at variable volume simulations. In order to reduce the dispersion in magnitude of the different coefficients and perform easier comparisons between different sensitivity coefficients, the sensitivity coefficients have been averaged over time, and normalized by the maximum value of the averaged coefficients.

2.2. 18-Step reaction mechanism

The 26-step mechanism is presented in Table 1 [25]; the objective here is to test first if it is possible to perform further reduction, while maintaining the same accuracy as the 26-step to describe the two stage ignition, with an error lower than 5% in terms of ignition delay times and Indicated Mean Effective Pressure (IMEP) over a large range of engine operations (see Table 2). In this mechanism, the pathways of n-heptane oxidation described by Curran et al. [35] have been kept as shown in Table 3. In the 26-step model the lean mixtures are modeled by seven reactions (numbered 14, 15, 17, 20, 21, 24 and 25 in Table 1), in order to reproduce the HCCI mode features. Besides, as presented in Table 3, the chemistry for low temperature regime (below 1000 K) is described by the whole degenerated chain branching pathways summarized as follows:

$RH + O_2 \rightarrow R + HO_2$ (Initiation)

$R + O_2 \longleftrightarrow RO_2$ (First O_2 addition)

$RO_2 \rightarrow QOOH$ (Internal H abstraction)

$QOOH + O_2 \longleftrightarrow O_2QOOH$ (Second O_2 addition)