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Automatic generation of a kinetic skeletal mechanism for methane-hydrogen blends with nitrogen chemistry

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ABSTRACT

A 48-species (with argon and helium) skeletal mechanism for methane-hydrogen blends was proposed using automated generation technique and model reduction methods. The proposed skeletal mechanism was widely validated for laminar burning velocity, ignition delay time and concentration profiles of major species using available experimental data, and good agreements are achieved. The new mechanism not only has less number of species and reactions than literature models, but also considers latest advancements in carbon, hydrogen and nitrogen chemistry. Moreover, key reactions, as well as the influence of hydrogen fraction in the fuel blend, for auto-ignition and NO formation in methane-hydrogen flames were studied through the new mechanism. It was found that crucial reactions for the ignition delay time shifts from carbon reactions to reactions of hydrogen chemistry as hydrogen fraction increases. A one dimensional burner-stabilized flame shows that hydrogen enrichment does not alter top contributing reactions for NO, but changes magnitudes and positions of peak fluxes of each reaction via temperature.

Introduction

Oil shortage and environmental pollution are becoming two serious problems in the 21st century. Policy makers and scientific community are seeking available cleaner and sustainable fuels. Due to its excellent chemical properties natural gas is considered as a promising alternative fuel and has already been successfully applied in Internal Combustion Engine (ICE) in the last two decades [1]. Natural gas engine is known to have good knock resistance, lower particulate matter (PM) emission than diesel engines [2], as well as low CO and NOx emissions in lean-burn mode [3]. However, due to its low laminar burning velocity and narrow flammability limit, natural gas engine suffers from poor lean-burn capacities, long combustion duration, and high cycle-to-cycle variations [4]. Blending hydrogen with natural gas might be a possible solution. Compared to natural gas, hydrogen has a higher laminar burning velocity [5], lower required minimum required ignition energy [6] and wider flammability limit [7], and hence improve combustion process and enhances lean-burn capacities of pure natural gas.

There are many previous studies trying to explore the possibility of applying natural gas-hydrogen blends in ICE. Huang et al. [8] experimentally showed that the brake mean effective pressure (BMEP) and the effective thermal efficiency

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increase with the increase of the hydrogen fraction in natural gas, but the combustion duration decreases correspondingly. Moreover, hydrogen addition improves the combustion stability in lean operating conditions and also extends the misfire limit [9], yet has minor effect on knocking limit at high specific loads [10]. Bhasker et al. [11] also pointed out that the 10% hydrogen addition in natural gas extends the lean limit of operation to an equivalence ratio of 0.42 as compared to 0.5 with neat CNG operation at a fixed rotational speed. Zhao et al. [12] suggested that the lean limit can be further broadened by using the high compression ratio. Deng et al. [13] investigated hydrogen fraction of 0%,30%,55% and 75% under idling condition and found that the cycle-to-cycle variation can be depressed by hydrogen addition as also concluded by Ma et al. [14] and Huang et al. [15] in other operating conditions. Furthermore, engines fueled with natural gas-hydrogen blends present much lower NOx emissions compared to pure natural gas engine [16], but the increase of hydrogen fraction might lead to much more NOx. This can be compensated by using a leaner equivalence ratio, EGR (Exhaust Gas Recirculation) [17] or retarding the ignition timing [11]. Moreover, the significant reduction of HC, CO and CO_2 [18] emissions could be achieved as the natural gas-hydrogen engine is operating on the lean condition [19]. Recently, there are some studies trying to use methane-hydrogen mixtures in compression ignition (CI) engines with pilot ignition using diesel fuel. It was found that hydrogen addition improves the rate of burning rate during partially premixed stage at low loads and reduces peak rate of heat release [20], while NOx emissions increase at all loads due to higher combustion temperature [21]. Exhaust CO_2 and particulate emissions at all engine loads are lower when methane-hydrogen mixture is used compared to diesel fuel only [22].

Some fundamental studies are available to study the laminar flame characteristics of methane-hydrogen mixtures. Basically, three combustion regimes are believed to exist depending on the hydrogen fraction in the fuel blend, namely methane-dominated combustion regime, transition regime and methane-inhibited hydrogen combustion regime. The exact boundary definition for the three regimes differs, depending on whether laminar burning velocity or auto-ignition delay time is regarded as the criterion [23,24]. Increasing the hydrogen fraction in methane-hydrogen blends was found to increase the laminar burning velocity and reduce the flame dependence on stretch [25]. The peak value of the laminar burning velocity shifts to the richer side with the increase of hydrogen fraction [24]. Significant decrease in Markstein length and critical radius of cellular instabilities is reported as more hydrogen is added to methane [26]. Petersen et al. [27] reported significant reductions in ignition delay time with methane-hydrogen blends compared to methane-only mixtures at lean flames ($\phi = 0.5$, $P = 0.5–30$ bar, $T = 1090–2001$ K). Temperature dependence of the ignition delay time is less affected by hydrogen addition. Gersen et al. [6] measured ignition delay times under stoichiometric conditions ($P = 15–70$ bar, $T = 950–1060$ K). It is interesting that the effect of hydrogen in promoting ignition increases with temperature and decreases with pressure. Huang et al. [28] also pointed out similar trend of temperature and pressure dependence. Zhang et al. [29] measured ignition delay times of methane/hydrogen/oxygen/nitrogen mixture at rich flames ($\phi = 2.0$, $P = 4$ bar, $T = 1422–1877$K). The measurements showed that the enhancement of ignition by hydrogen addition varies with temperature. The literature review concludes that hydrogen addition to methane is able to improve laminar burning velocity and also promote auto-ignition characteristics, yet the promoting effect for ignition varies with pressure and temperature.

Since numerical simulation is becoming a powerful tool for combustion studies, a reliable chemical mechanism is crucial for prediction of combustion properties, especially the formation of pollutants (NOx, CO) in ICE. With high performance computers, scientific community is already able to use skeletal or detailed chemical mechanism in ICE [30,31]. As to available mechanisms for methane-hydrogen blends, Ji et al. [5] compared the performance of different mechanisms for predicting laminar flame speed, and concluded that among Gri-mech 3.0 [32], USC 2.0 [33], Aramco 1.3 [34] and San Diego mechanism [35], Aramco 1.3 is considered as the most suitable mechanism for predicting laminar flame speed of methane-hydrogen blends. However, Aramco does not have nitrogen chemistry. It is generally accepted that Gri-mech was most widely used in recent years. It is pretty compact with 53 species and 352 reactions. The limitation is that the carbon chemistry and nitrogen chemistry are outdated, almost 20 years ago. The prompt pathway for NO is based on HCN channel instead of latest accepted NCN channel [36]. USC 2.0 consisted of 111 species and 784 reactions with nitrogen chemistry excluded. San Diego mechanism has a good performance for small hydrocarbons with only 50 species and 247 reactions. Its nitrogen sub-mechanism was proposed in 2004 and HCN channel was adopted. Recently, an updated and more compact reaction mechanism for methane was proposed by the FFCM-1 project [37], based on GRI-Mech, from which nitrogen chemistry is excluded. It has only 38 species and 278 reactions. There are also some mechanisms specifically for hydrogen combustion. Davis et al. [38] proposed a kinetic model for H_2/CO combustion, which updated 20 reactions contained in GRI-Mech 3.0 for H_2/O_2 chemistry [39]. Recently, Burke et al. [40] developed a comprehensive H_2/O_2 kinetic model for high-pressure combustion.

Literature review shows that natural gas-hydrogen blend has pretty better characteristics compared to pure natural gas, and application of this mixture in ICE is really promising. Considering good capacity of numerical simulation in predicting engine performance, a compact and reliable reaction mechanism for methane-hydrogen blends is necessary. So in the present work, a 48-speceis skeletal chemical mechanism was derived using automated generation technique and model reduction methods. The present new mechanism was validated through laminar flame speed, ignition delay and profiles of major species using available experimental data. Moreover, NO formation was analyzed using rate-of-production analysis, sensitivity analysis and reaction path analysis. Compared to literature models, the proposed new model has less number of species, update latest advancements in carbon and nitrogen chemistry, and give reasonable agreements with available experiment data.