Fuel 193 (2017) 294–307

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

A detailed chemical kinetics for the combustion of $H_2/CO/CH_4/CO_2$ fuel mixtures

H.C. Lee [a], A.A. Mohamad [a,*], L.Y. Jiang [a,b]

[a] Department of Mechanical and Manufacturing Engineering, The University of Calgary, Calgary, Alberta T2N 1N4, Canada
[b] Gas Turbine Laboratory, Aerospace, The National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form 29 November 2016
Accepted 15 December 2016
Available online 29 December 2016

Keywords:
Syngas/biogas combustion
Detailed mechanisms
Combustion modeling

ABSTRACT

A genetic algorithm (GA) was proposed and validated for the optimal extraction of a sub-mechanism for $H_2/CO/CH_4/CO_2$ mixtures from the detailed Aramco1.3 chemical kinetics mechanism (Metcalfe et al., 2013), which was developed for C_1–C_5 hydrocarbons and oxygenated fuels. Ninety ignition delay time data involving mixtures containing H_2, CO, CH_4, CO_2, N_2, and H_2O at wide range of experimental conditions were chosen as optimization targets to guide the GA, so that the final reduced mechanism was able to fully describe the combustion characteristics of syngas and biogas fuel mixtures. The final reduced mechanism for $H_2/CO/CH_4/CO_2$ fuel mixtures comprised of 72 species and 290 reactions (reduced from 325 species and 2067 reactions), and it was extensively validated against experimental results, such as measured ignition delay times and laminar flame speeds, over a wide range of operating conditions. The excellent agreement between the reduced mechanism and Aramco1.3 mechanism in predicting the combustion properties of $H_2/CO/CH_4/CO_2$ mixtures with maximum relative error values of only 0.9% and 2.75%, respectively for the ignition delay time and laminar flame speed results, indicates that the proposed reduced mechanism can be used for predicting the combustion characteristics of biogas and syngas fuel mixtures. Furthermore, it was observed that the reduced mechanism shows excellent agreement with the Aramco1.3 mechanism in predicting the ignition delay time of mixtures with added ethane and propane. Therefore, the proposed reduced mechanism represents the most up-to-date detailed chemical kinetics mechanism for biogas and syngas fuel mixtures, and it can also be used for predicting the combustion properties of natural gas with impurities such as ethane and propane. The reduced mechanism agreed so well with the Aramco1.3 mechanism in predicting the combustion properties of $H_2/CO/CH_4/CO_2$ mixtures, where both mechanisms performed identically in over predicting the ignition delay time for $H_2/CO/CO_2$, CO_2, $H_2/CO/CH_4$, and $H_2/CO/CH_4/CO_2/H_2O$ mixtures at several experimental conditions. These observations were also reported by Lee et al. (2015), where they proposed two new rate constants for $H + O_2(+CO_2) = HO_2(+CO_2)$ and $CH_4 + OH = CH_3 + H_2O$ to reconcile the discrepancies observed. These two new rate constants were assessed in this study by incorporating the modified rate constants into the 290Rxn mechanism (referred as 290Rxn-V1), where it was found that the modified rate constants did improve the ignition delay time predictions. However, the two proposed rate constants did not improve the predictions of the laminar flame speed for mixtures with a high CO_2 content at high equivalence ratios ($\phi > 1.2$). Therefore, optimization of the rate constants in the 290Rxn mechanism is highly recommended to further improve its agreement with experimental data for biogas and syngas fuel mixtures.

1. Introduction

There is great interest in the development of renewable and environmentally friendly fuel sources such as biogas and syngas for generating heat and electricity. Biogas and syngas are promising second-generation biofuels because they can be produced from virtually any type of renewable biomass or fossil fuel. Therefore, an up-to-date and detailed chemical kinetics mechanism to accurately predict the flame speed, ignition delay time, extinction limit, and soot formation of syngas and biogas under various mixture ratios and operating conditions is in-need. We recently published a comprehensive comparison of several notable chemical kinetics mechanisms [2], including GRI1999 [3], Li2007 [4], Davis2005

* Corresponding author.
E-mail address: mohamad@ucalgary.ca (A.A. Mohamad).

http://dx.doi.org/10.1016/j.fuel.2016.12.062
0016-2361/

[5], USC2007 [6], UCSD2014 [7], Sun2007 [8], and Aramco1.3 [1] and reported that the Aramco1.3 mechanism provided more accurate predictions of the experimental data when applied to the combustion of syngas and biogas mixtures, while the other mechanisms exhibited varying degrees of agreement with experimental data. This was not surprising, as the authors of the Aramco1.3 paper [1] updated their H/C/O sub-mechanism recently [9], and the Aramco1.3 mechanism comprises the most up-to-date rate constants. Syngas mainly comprises CO and H_2 with varying amounts of CO_2, CH_4, and H_2O [10], while biogas consists mainly of CO_2 and CH_4 with varying amounts of N_2 [11]. However, the Aramco1.3 mechanism was developed for C_1–C_5 mixtures, and therefore contains many species and reactions that are irrelevant to biogas and syngas combustion. Therefore, the main objective of this study is to find a sub-mechanism within the large detailed Aramco1.3 chemical kinetics mechanism for application to biogas/syngas combustion. This will lead to a substantially reduced number of species and reactions in the detailed sub-mechanism for biogas and syngas fuel mixtures, allowing it to be used to conduct large parametric studies on fuel mixtures, or further optimized to improve its prediction capability using significantly less computational time.

There are several systematic methodologies that can reduce a detailed mechanism, and comprehensive reviews on these methods are presented in Refs. [12–15]. The genetic algorithm (GA) method attracted our attention as it does not require any sensitivity analysis or require any knowledge of the rate constants during the reduction process, but rather it relies on eliminating reactions that are deemed unimportant for biogas and syngas combustion through a fitness function. In addition, methods such as direct path flux analysis [15] and global pathway selection [16] have been tested and used for large detailed mechanisms with up to hundreds of species, while studies [17–20] that employed the GA approach have presented the reduction of a detailed mechanism that consisted of only 338 reactions and 67 species. Therefore, one of the objectives of this study is to test this simple yet robust method for extracting a smaller sub-mechanism for biogas and syngas fuel mixtures from a large detailed mechanism such as the Aramco1.3 mechanism. The final mechanism obtained by GA is then compared to the original mechanism and published experimental data to evaluate the performance and assess the limit of the mechanism obtained in this study. Consequently, the final mechanism presented in this study is a detailed chemical kinetics mechanism that is able to mimic the performance of the Aramco1.3 mechanism in predicting the combustion properties of biogas/syngas accurately.

2. Methodology

2.1. Modeling approach

Numerical simulations were performed using the CANTERA reacting flow software package [21]. Shock tube experiments were simulated by assuming a constant volume and adiabatic conditions. The simulated ignition delay time results were computed as described in the respective publications, i.e., based on the maximum slope of the pressure profile or based on the measurement of the chemiluminescence of OH^* or CH^*. Laminar flames were simulated using the FreeFlame class included in CANTERA, which is identical to the PREMIX code [22] of CHEMKIN-II. The jet-wall stagnation flames were simulated using the premixed stagnation flame code of the CANTERA reacting flow software. The boundary conditions specified in the simulation of the jet-wall stagnation flame were taken directly from the experimental measurements, allowing a direct comparison of the measured and simulated profiles. For more information on the stagnation flames simulation methodology, refer to Ref. [23]. In all of the laminar flame speed simulations, multicomponent diffusion and Soret effects are included, as these effects have significant impact on the calculated laminar flame speed, especially for H_2/CO mixtures without any dilution at $P = 1$ atm [2]. The converged solution is obtained for a large number of grid points (approximately 400) by considering a gradient and curvature of 0.1. The standard definition of equivalence ratio (ϕ) is adopted in this work, and it is defined as follows:

$$\phi = \frac{(n_{\text{fuel}}/n_{\text{oxygen}})_{\text{act}}}{(n_{\text{fuel}}/n_{\text{oxygen}})_{\text{st}}}$$

where n represents the number of moles, and the suffixes act and st indicate actual mixture and stoichiometric mixture, respectively.

The agreement between the Aramco1.3 and the reduced mechanism obtained from GA was computed using the following objective function:

$$E_{ij} = \left| \frac{Y_{\text{Aramco},ij} - Y_{\text{reduced},ij}}{Y_{\text{Aramco},ij}} \right| \times 100\%$$

Here, E_{ij} is the absolute relative error values for the ith case. The j represents the jth data point in the ith case. The values $Y_{\text{Aramco},ij}$ and $Y_{\text{reduced},ij}$ correspond to the result for the jth data point obtained from Aramco1.3 and the reduced mechanism, respectively, in the ith case. The parameter used to compare the jet-wall stagnation flames is the reference flame speed, $S_{u,\text{ref}}$. The reference flame speed is defined as the minimum upstream velocity of the flow, prior to the temperature rise. This velocity also represents the local mass-burning rate of the flame at the inlet temperature, composition, and hydrodynamic strain rate. For brevity, only the maximum relative error values in each case ($E_{i,\max}$) and comparison between experimental data and simulated results of selected cases are plotted in this manuscript. Refer to the Supporting Information for full comparison between the experimental data and the simulated results obtained from Aramco1.3 mechanism and the reduced mechanisms.

2.2. Genetic algorithm

GA is an adaptive heuristic mathematical technique based on the ideas of evolutionary natural selection and genetics. GA works particularly well in several fields, especially if the shape of the function to optimize is not known. It finds a near optimal solution to a problem, where the optimal is defined by a criteria function (also called objective or fitness function). This sub-section only provides a conceptual representative of the algorithm and readers are referred to the work of Sikalo et al. [17] for a more detailed explanation on the algorithm.

Fig. 1 shows the genetic algorithm procedure adopted for this study and it consists of the following steps:

1. *Initialization*, where a set of initial kinetics mechanisms is generated.
2. *Evaluation*, where the performance of each mechanism is assessed and a corresponding fitness is assigned to each mechanism.
3. Genetic operators consisting of the following three processes:
   (a) *Selection*: The mechanisms are sorted based on their overall fitness, and the fittest kinetics mechanism of the current generation is retained for next generation (Elitist). The remaining new kinetics mechanisms for the next generation are chosen from the current generation based on the tournament selection.
   (b) *Crossover*: Two randomly selected mechanisms exchange information to create two new mechanisms for the next generation.