Improved Chemical Mechanism of NH3/H2/Air and Adoption of Artificial Neural Network

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1 Introduction

In a recent decade, the severity of greenhouse gas emissions urged the replacement of fossil fuels with renewable energy. Ammonia, as a carbon-free fuel, has the potential to substitute fossil fuels. Liquid ammonia has a higher volumetric energy density than hydrogen or natural gas. Further, ammonia can be produced, stored, and transported on industrial scales, since ammonia has been used as fertilizer on a massive scale for over 100 years [1]. Even the production of ammonia can be carbon-neutral when renewable energy is employed. However, ammonia/air has a narrow flammability range and high auto-ignition temperature. In addition, ammonia combustion can emit NOx and unburned ammonia. The low flammability of ammonia/air mixture can be often resolved by co-combustion with hydrogen. Also, the NOx emission and ammonia slip can be prevented with a careful prediction of combustion products.

The prediction through simulation should precede the commercial use of ammonia combustion. The simulations generally solve systems of ordinary differential equations (ODEs), which are organized according to the adopted chemical mechanism. Consequently, the accuracy of the simulation is influenced by the accuracy of the chemical mechanism. There have been many researchers who proposed chemical mechanisms. Although, they validated the mechanisms with a limited number of experimental datasets. Hence, a chemical mechanism, that can be validated with universal experimental datasets, would guarantee better accuracy of the simulation. Thus, this study examined finding the chemical mechanism of NH3/H2 combustion with improved accuracy, by integrating five existing chemical mechanisms. In addition, the simulations including a detailed chemical mechanism require heavy calculation sources, especially for multidimensional simulations. One of the methods to accelerate the calculation is using an artificial neural network (ANN) instead of the ODE solver. Therefore, this study suggested an ANN that can substitute the solver.

2 Methodologies

First, a chemical mechanism was developed based on five existing chemical mechanisms. The selected mechanisms were that of Li et al. [2], Glaborg et al. [3], Okafor et al. [4], Otomo et al. [5], and GRI

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mech 3.0 [6]. A pool of the reactions from the five mechanisms was generated. Most of the reactions were from more than one of the existing mechanisms. Though a reaction was identical, the rate coefficients were different upon the referenced mechanism. Thereupon, the considerations when creating combinations of the reactions from the reaction pool were whether to include a reaction and which rate coefficients to choose for the included reaction. The combinations were randomly composed with the considerations. Each set of the combination was regarded as a chemical mechanism and tested for validation with experimental datasets. The experimental datasets were ignition delay times of diluted NH3/air and NH3/H2/air mixtures at different pressures [7, 8] and laminar flame speeds of a 1D flame of NH3/air and NH3/H2/air mixtures [9]. The combinations with small mean squared error (MSE) with experimental datasets were collected and analyzed. A combination of reactions with a small MSE could be chosen as the improved detailed kinetic mechanism.

Based on the mechanism, datasets for training the ANN were produced. The dataset was collected by time propagation of a nondimensional adiabatic and isobaric reactor, at 1 atm. Timesteps for the calculation were varied upon each initial condition and fixed during each calculation. The temperature and molar fractions at each time step and one step after became the input and output of the ANN. Since the dataset was skewed for the training of ANN, preprocessing pipelines were adopted. The preprocessing pipeline was composed of reciprocal transformation, Yeo-Johnson transformation, and standard normalization. The processed dataset was less skewed and closer to the normal distribution.

Further, several ANN structures were tested. The examined structures included five hidden layers with a ReLU activation function at each layer. The number of nodes at each hidden layer differed between 128 to 2048 at each tested structure. A structure showing maximum prediction accuracy and minimum MSE was employed. While training the model, the optimizer was Adam optimizer with MSE loss function.

3 Results and discussions

An improved chemical mechanism of NH3/H2 combustion showed better accuracy with experimental datasets than the referenced mechanisms. The improved mechanism could predict ignition delay times at different pressures and compositions within uncertainty of experiments. The predictions on NH3/H2/air mixtures were particularly improved compared to the existing mechanisms. Even the mechanism targeted on ammonia combustion could be even improved in this paper.

Further, the trained ANN attained accuracy over 98% and MSE below 10^{-5}. Fig. 1 demonstrates time propagation of temperature and the molar fractions of H2, NH3, and NO from calculation of Cantera package in python language or prediction of the ANN. The initial condition was 1300 K, equivalence ratio (ER) of 0.8, and the ratio of H2 to NH3 was 0.75. The trained ANN could not predict the time propagations at earlier timesteps. Although, the prediction of ANN became more accurate near steady states.

4 Conclusion

To minimize the emission of NOx and unburned ammonia, the products of ammonia combustion have been predicted by computational simulation. In our knowledge, the existing chemical mechanisms for NH3/H2 combustion had been validated with limited sets of experiments. Therefore, this study examined an improved chemical mechanism of NH3/H2 combustion, validated with various experimental data. Several existing mechanisms were combined, and different combinations of reactions were test for validation. An improved chemical mechanism showing lower error with experiments than

the referenced mechanisms could be found. In addition, an ANN was investigated to accelerate simulation. Temperature and molar fractions at each timestep were organized and preprocessed for ANN training. Several structures of ANN were tested to result in high accuracy on the preprocessed dataset. A structure showing the highest accuracy and the lowest error could be determined. The ANN with the structure could predict time propagation of temperature and molar fractions. The accuracy of prediction was lower at earlier transient timesteps, but the prediction became more accurate near steady state. Though, for the utilization of ANN, further enhancement of the accuracy at early time propagation remains a future work.

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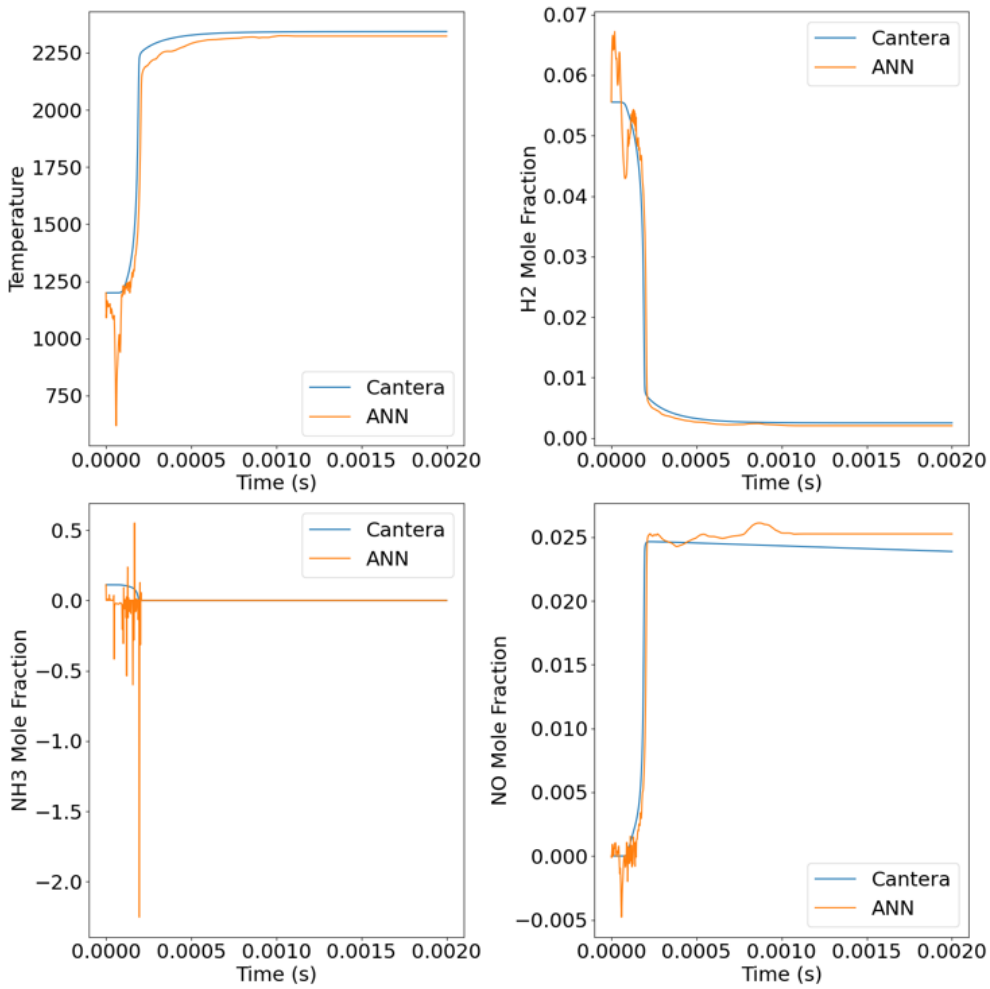

Figure 1: Comparison of calculation result using Cantera python package and the predicted result using ANN in a nondimensional adiabatic isobaric reactor with initial temperature 1300 K, ER 0.8, and the molar ratio of H2 to NH3 0.75.

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