NO_x Emission Prediction in Ammonia-Hydrogen Combustion via Chemical Reactor Networks

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Abstract

Climate change poses significant challenges, prompting policies for carbon neutrality by 2050. Renewable energies, particularly hydrogen as a Smart Energy Carrier (SEC), offer high efficiency and zero direct CO_2 emissions. However, its combustion creates challenges, such as increased nitrogen oxide (NO_x) emissions, necessitating innovative combustion technologies for cleaner use. Chemical Reactor Networks (CRNs) provide an effective approach for simulating detailed kinetic mechanisms with reduced computational demands. The CRN method, divides the combustor into discrete compartments that represent homogeneous flow zones, modeled as Perfectly Stirred Reactors (PSRs) or Plug Flow Reactors (PFRs). The reactors, interconnected by mass and heat exchanges, form a network designed to preserve the main characteristics of the global flow field. Data for CRNs can come from semi-empirical relationships or CFD simulations. The combined CFD-CRN method effectively predicts pollutant emissions, while statistical techniques for the compression and classification of data, like Principal Component Analysis (PCA), help automatically select features and group observations [1]. This paper focuses on investigating how CRN structures evolve under varying input conditions, particularly in ammonia-hydrogen mixtures, and examines their impact on nitrogen oxide (NO) emission predictions. Moreover, it explores the identification of a representative network that can generalize across multiple operating conditions. By integrating data-driven clustering methods with CRN modeling, this study aims to enhance the accuracy and efficiency of emission predictions in complex reacting flows.

Keywords: Ammonia combustion, Chemical Reactor Networks; Machine Learning; NO_x emissions; Principal Component Analysis

1. Introduction

The energy transition has introduced new renewable fuel candidates, such as ammonia and hydrogen. Ammonia can serve both as a hydrogen carrier and a fuel, with both options eliminating CO_2 emissions due to the absence of carbon in the fuel. However, challenges remain as technologies must be retrofitted, and these fuels may contribute to the formation of other pollutants. Ammonia is characterized by a low burning velocity and thus leads to ammonia slip due to unburned fuel and increased NO_x emissions due to the presence of nitrogen in the fuel [2] while hydrogen promotes NO_x formation due to its high reactivity [3]. Numerical tools can be employed to investigate the combustion processes of new fuels and to develop adapted designs while avoiding the need for repeated experimental campaigns or the risk of damaging materials. Computational Fluid Dynamics (CFD) is often regarded as a reliable approach for this purpose, as it allows the detailed characterization of fluid dynamics even when simplified chemical mechanisms are used. However, the computational cost of CFD simulations can increase significantly with the number of species considered, as well as with the size and characteristic time scales of the case under investigation. Chemical Reactor Networks (CRNs) provide an effective approach for simulating complex kinetic mechanisms while mitigating computational demands. This methodology, introduced by Bragg [4], partitions the combustor into discrete compartments that represent homogeneous flow zones. These zones can be modeled as Perfectly Stirred Reactors (PSRs) or Plug Flow Reactors (PFRs). The reactors are interconnected through mass and heat exchanges, thereby forming a network that preserves the essential characteristics of the overall flow field. The success of a CRN in accurately predicting outcomes for a specific test case is significantly influenced by its structural configuration, including the arrangement of reactors and their respective parameters, such as volumes, residence times, and exchanged masses. Simplified CRN structures are considerably more manageable and can converge within a matter of seconds; however, they necessitate a higher level of expertise from the user, as assumptions regarding their structural form can substantially influence the results[1]. The recent development of unsupervised clustering techniques open opportunities to automate the identification of clusters for the effective construction of simplified CRNs. In this context, the integration of data-driven methods with CRN and CFD frameworks has emerged as a powerful strategy to enhance their predictive capabilities and automate model development. Unsupervised machine learning techniques, such as clustering algorithms, can be used to identify patterns within the CFD data and assist in defining reactors, reducing the dependency on user-defined assumptions. Furthermore, data-driven approaches enable efficient feature selection and dimensionality reduction, which contribute to minimizing the computational cost while preserving essential information. This synergy between physics-based models and data-driven algorithms facilitates a more systematic and objective construction of CRNs, ultimately improving the reliability of pollutant predictions. This work aims to determine whether it is possible to develop a Chemical Reactor Network without relying on CFD simulation data as a starting point.

2. ULB furnace: NH_3-H_2 mixtures

2.1. Experimental campaign

The test case considered in this study is the ULB semi-industrial, MILD-capable furnace. The combustion chamber has a cubic shape with a 1000 mm length for each side and a 300 mm thick ceramic fibre insulation layer, resulting in 700 x 700 x 700 mm as inner dimensions. As illustrated in Figure 1, the fuel and air are injected coaxially at the bottom of the furnace. The air entering the chamber is preheated through a recuperative heat exchanger. The design of the chamber allows for the recirculation of the hot products, which is crucial for operating in a flameless regime. Additionally, four cooling tubes are located inside the combustion chamber to emulate an external thermal load, which can be adapted through the air flow rate. The ULB furnace can operate with various fuels (CH_4-H_2-NH_3) under different operating conditions (flame/flameless) at a thermal power of up to 20 kW. Two different diameters can also be used for an inner diameter of either 16 mm or 25 mm. In this paper, different ammonia-hydrogen blends are considered, from 50% NH_3-50% H_2 by volume to pure hydrogen operation. The experiments considered in the present work refer to the 16 mm inner diameter and two equivalence ratios, 0.8 and 1 [5]. The thermal power input is 15 KW, and the thermal losses change depending on the operating conditions. A summary of the conditions considered in this work is proposed in Table 1. The fuel inlet temperature remained constant

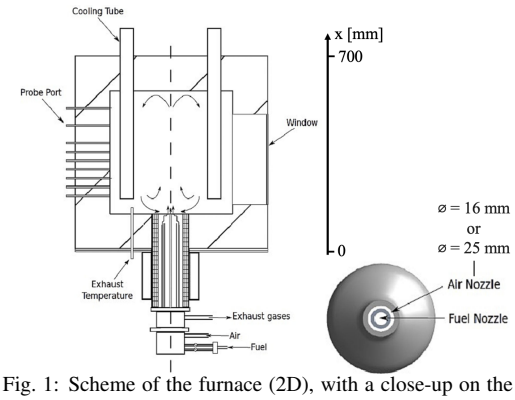

Fig. 1: Scheme of the furnace (2D), with a close-up on the air and fuel nozzles, adapted from [1]

Table 1: Operating conditions considered in the CFD, with ID = 16 mm, ϕ = 0.8 and ϕ = 1

NH_3-H_2 [vol%]	$\dot{m}_{air}$[g/s]	$\dot{m}_{fuel}$ [g/s]	$T_{air,in}$ [K]	$\dot{Q}_{loss}$ [kW]
50/50	5.77	0.511	994 / 1080	12.1 / 12.6
25/75	5.56	0.332	994 / 1057	11.6 / 12.4
10/90	5.42	0.212	985 / 1042	11.9 / 14
0/100	5.32	0.125	973 / 1025	11.2 / 11.9

at 343 K during the whole campaign. During the experiments, pollutant emissions were measured at the outlet, such as O_2,NO_x, NH_3, and N_2O for the different blends, along with the temperature profiles at one axial location and three radial positions, namely z = 100 mm, z = 150 mm, and z = 200 mm, only for the 50% NH_3/50% H_2 case, used for validating the numerical approach.

2.2. Numerical modelling

The simulations were performed using the commercial software from Ansys, Fluent 24 R1 ® [6]. Due to the symmetrical configuration of the furnace, an axisymmetric 2D mesh was considered with 45k cells, built after a grid dependency study [1]. The Reynolds-Averaged Navier-Stokes (RANS) framework was chosen with the $k-\epsilon$ turbulence model with enhanced wall treatment and the Partially Stirred Reactor combustion model. For the latter, the integral-based mixing time was retained with a C_{mix} = 0.25. The Shrestha kinetic mechanism was used, including 39 species, 267 reactions, and incorporating NO_x [7]. Radiation was considered by means of the Discrete Ordinates (DO) model, coupled with the Weighted-Sum of Gray Gases (WSGG) model for gas properties. Mass flow inlet boundary conditions were considered for both air and fuel inlets. The heat losses through the insulation wall were set by setting a negative heat flux, adapted for the axisymmetric 2D case. The convergence was ensured by following the residuals, stability of the slowest quantities of interest (such as temperature and NO_x), and checking the net heat and mass balances.

3. Chemical Reactor Network

CFD simulations of the furnace were carried out to extract the CRNs. In the context of a CRN, this flow field was segmented into distinct zones, with each zone assigned a specific reactor based on the flow topology. In this study K-means clustering algorithm [8] was used in conjunction with Principal Component Analysis (PCA)[9] to reduce the dataset dimensionality and carry out the clustering on a limited number of scalars represented by the principal components. PCA is a widely used technique to reduce the dimensionality of large datasets while retaining as much relevant information as possible. Specifically, PCA identifies a new set of variables, known as principal components (PCs), which are uncorrelated and ordered according to the amount of variance they capture from the original dataset. By projecting the data onto these PCs, it becomes possible to simplify the dataset, reduce noise, and facilitate subsequent analysis such as clustering or visualization, all while preserving the essential features of the sample. This makes PCA particularly useful when dealing with high-dimensional CFD data, where correlations among variables can obscure key patterns. The present study focuses on analyzing the performance of Chemical Reactor Networks under varying input conditions. The primary objective is to assess the feasibility of predicting the structure of a CRN in the absence of CFD data. To this end, an adapted network approach has been employed to address the investigation.

3.1. Setup of Chemical Reactor Network

To construct a CRN, CFD simulation data are needed as input for the clustering algorithm that divides the flow domain into sub-regions. To divide the domain into representative sub-regions and achieve an efficient reduction of the reactor network, the K-Means clustering algorithm was used. The input matrix X for the clustering algorithm was constructed as follows:

$$\mathbf{X} = [x_1, x_2, \ldots, x_k] \in \mathbb{R}^{n \times k} \tag{1}$$

where

- n number of cells
- k number of features

Due to the large number of variables involved, PCA was implemented to reduce the dimensionality of the data set. To determine the number of PCs we need to retain all important information, we used a scree plot. This plot graphs the eigenvalues against the corresponding PC numbers. Since the eigenvalues are ordered in decreasing order of explained variance, the scree plot will have a decreasing slope, initially with a steeper slope and then asymptotically tending to zero. The guideline is to select the number of PCs that corresponds to the "elbow" of the curve. The use of PCA improved the computational efficiency of clustering by reducing the size of the dataset and ensuring that the most relevant information was used in the clustering process. Therefore, it is crucial to select a dataset that accurately represents the flow field under study, as this will enable the construction of a more efficient reactor network. CRN simulations are very sensitive to the selection of the appropriate settings, it is necessary to determine the number of clusters into which to divide the domain, evaluate whether to use

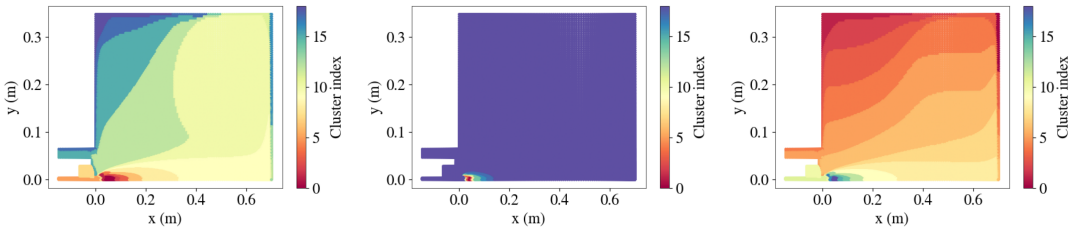

Fig. 2: Clustering obtained for (a) Dataset of temperature and species, (b) Dataset of coordinates, temperature and species, (c) Dataset of reaction kinetic rate. Application of PCA in all three datasets.

the full data set or apply PCA to reduce dimensionality, and select the appropriate kinetic mechanism to simulate combustion. The optimal configuration was selected by analyzing three key parameters by varying the number of clusters used:

- *Emissions*: This parameter evaluates the CRN's ability to reproduce the production of relevant chemical species accurately.
- *Computational Cost*: An inefficient partitioning of clusters could increase computation time without enhancing accuracy, so this factor was carefully considered.
- *Quality of Reconstruction*: This involves comparing the CRN results with the original CFD simulations regarding temperature and species domains.

3.2. Adapted Network

Once a network has been developed for a condition, an approach is required to extrapolate it to different conditions, e.g., different fuel compositions. This study raises the question of whether it is possible to obtain information about the mass exchanges between reactors using alternative methods to CFD. If successful, this approach could lead to significant savings in computational costs.

In this work, starting from a CRN designed for a starting mixture, the feasibility of adapting this network for a different mixture is examined. A starting hypothesis made in this paper posits that the existing structure of the CRN can be retained while only the inlet and outlet conditions concerning the mass flow rates of the fuel and oxidizer can be adjusted. This hypothesis holds if the change in operating conditions does not lead to a major modification of the flame structure.

In conducting our simulations, a square matrix is developed, denoted as M, with dimensions $N_R \times N_R$, where N_R represents the number of reactors in the network. Within this matrix, M_{ij} represents the mass flow rate transferring from reactor *i* to reactor *j*. It is possible to compute the total outlet mass flow rate for the *i-th* reactor as $M^i_{\text{out}} = \sum_{j=1}^{N_R} M_{ij}$. Furthermore, we can calculate the split ratio, defined as the fraction of the outlet mass flowing from reactor *i* to reactor *j* as $\alpha = M_{ij}/M^i_{\text{out}}$ resulting in a matrix that reflects these relationships. To obtain the adapted network, it is necessary to solve a linear system as:

$$(\boldsymbol{I} - \alpha^T) M_{\text{out}} = b_{\text{ext}}, \tag{2}$$

where α (split ratio) is held constant based on the previous network and is an $N_R \times N_R$ matrix, while M_{out} and b_{out} are vectors of dimension $N_R \times 1$ and correspond to the reactors and external sources of outputs and inputs respectively.

Figure 3 visually illustrates the assumptions made in this method. The elements represented by a continuous line, such as the number of reactors, the reactors themselves, and the connections, remain unchanged during the network adaptation process. This approach also keeps the mass percentages allocated to each reactor, known as the split ratio, unchanged. What gets recalculated are the masses within each reactor, which are indicated in two different colours: yellow for the original network and blue for the adapted network. These are recalculated by solving Equation 2, imposing the new inlet and outlet mass flow rates ($\mathbf{b_{ext}}$).

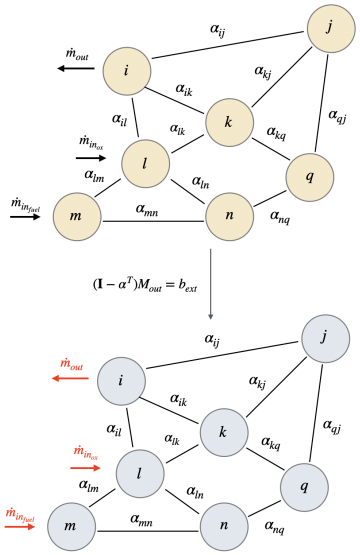

Fig. 3: Building of an Adapted CRN: from the starting CRN (top panel) only the massflows are changed, represented by the color, while split ratios (alpha) and topology of the reactors are kept fixed

4. Results

4.1. Starting CRN

Regarding the optimal settings to simulate the CRN, Figure 4 illustrates the computational cost of the simulation, which is a crucial parameter for evaluating a reduced-order model. The graph compares a comprehensive dataset that includes temperature and chemical species with a reduced dataset obtained through PCA. The benefits of processing the reduced dataset appear immediately. Additionally, the same dataset was analyzed using two different kinetic mechanisms, Stagni [10] and Galway [11]. From this analysis, it can be concluded that varying the number of clusters indicates that the reduced dataset with Stagni generally yields the best results in most cases. Several datasets were considered and compared, derived from combinations of temperature, species mole fractions, enthalpy and kinetic rates. The datasets presented in Figure 2 indicate the following observations: In case (a), the inlets, flame, and recirculation zone are clearly identifiable. Case (b) focuses solely on the flame and does not provide information about the recirculation zone. Case (c) exhibits complexity, with the presence of waves in the recirculation zone that correspond to isolated clusters, suggesting that it may not adequately represent the fluid-dynamic field. It turns out that the most representative dataset is the one obtained using the temperature and molar fractions of the species. To achieve the purpose of

Fig. 4: Computational cost graph, comparison between complete dataset and reduced dataset.

this work, an initial reactor network was constructed conventionally, using temperature and species CFD data as the input parameters. Typically, the classical method used to construct a CRN for a specific mixture necessitates the implementation of CFD simulations. This step is crucial for calculating the mass flow rates exchanged between each cell, which can then be directly applied to the mass flow rates exchanged between the reactors in the network. The chosen operating conditions for this simulation involved a mixture of 90% H_2 hydrogen and 10% NH_3, with an equivalence ratio of 0.8. Considering the scree plot, four PCs were chosen to reduce the dataset. The choice of the optimal number of clusters (k) was made comparing the emissions and outlet temperature results with the reference ones. As can be seen from Figure 5, the configuration with 19 clusters seems to be the one that best captures the data obtained from the CFD simulation, and in some cases, such as for NO, it seems to outperform it being even closer to the experimental values. Figure 6 shows through the bar

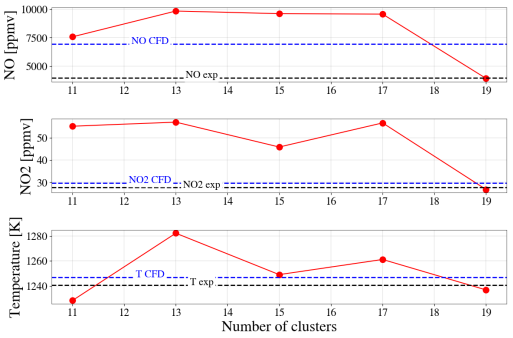

Fig. 5: Emissions and outlet temperature at varying cluster number, mixture 90% H_2 10 % NH_3.

graph the value of emissions and temperature for the case analyzed here; this shows better what was anticipated before, the CRN in this case, seems to give better predictions than the CFD. A total of 19 clusters

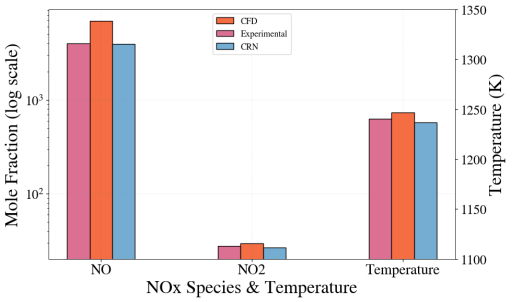

Fig. 6: Emissions and temperature extrapolated from the CRN.

were considered, and the K-means algorithm was employed to identify the clusters and the connections between them; the results are illustrated in Figure 2 (a). The network was simulated using the NetSMOKE++ software [12], selecting the Stagni kinetic mechanism for the analysis. These results show the ability of the CRN to estimate the order of magnitude of the emissions, with an error on the output temperature compared to the CFD of only 0.8136 %.

4.2. Adapted CRN

The purpose is to estimate the emissions produced by a mixture consisting of 75% H_2 and 25% NH_3 while maintaining the same network structure established in the 90% H_2 scenario. Through the assumption of recalculating the masses within each reactor, keeping the network structure, connections between reactors, and split ratios unchanged, the network for

the 75% hydrogen case was obtained. The graph below shows the result obtained for the extrapolation of the emissions and the output temperature. There are three colored bars in the figure, the orange bar represents the results obtained using the CFD simulation for the 75% H_2 and 25% NH_3 mixture, the blue bar represents the results obtained by conventionally simulating a CRN using the data extracted from the CFD (for the 75% hydrogen case) to subdivide the domain into subdomains (clusters) which will coincide with the reactors in the network; finally, the yellow bar represents the results obtained by adapting the network obtained for the 90% hydrogen case to the new mixture (75H_2, 25 NH_3).

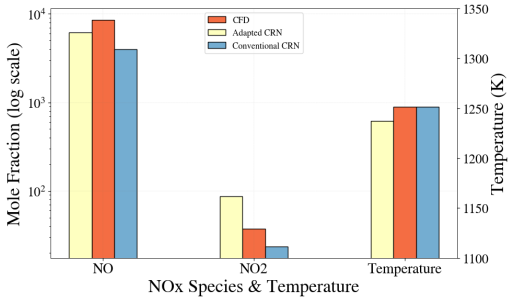

Fig. 7: Emissions and temperature extrapolated from the adapted network (from 90% H_2 10% NH_3 to 75% H_2 25% NH_3).

It is important to highlight that the CRN simulation employs a fraction of the time needed by the conventional CFD, while maintaining a comparable level of accuracy. In the table below, the values obtained in the three cases for emissions and temperature at the network outlet are shown.

Table 2: Results of NO_x emissions and temperature

Case	NO [ppm_v]	NO_2 [ppm_v]	T [K]
Adapt. CRN	6172.32	86.35	1237.46
Conv. CRN	3981.39	23.55	1251.6
CFD	8581.60	37.32	1251.5

The adapted method retains the structure of the network, but simply recalculates the flows according to the new conditions. This results in an error on NO_x, but the order of magnitude is still well captured. The error on temperature is very low (1.1%), showing that the adapted network can preserve the energy balance correctly, even if the chemistry changes. The NO_x error of the 'classical' CRN network is higher, because the setup, such as the number of clusters, may be less suitable in some cases, requiring more calibration work. This result leads us to think that by choosing the setup for a network built for a certain mixture (90 % H_2 case), in terms of emissions, it is more efficient to fit this network for another mixture (75 % H_2) than to build a new network for the new mixture with the same setup, because it may not be as efficient.

5. Conclusions

The present study assessed the feasibility of adapting an existing CRN, initially developed for a hydrogen-rich mixture (90% H_2 and 10% NH_3), to predict the emissions and temperature of a different fuel composition (75% H_2 and 25% NH_3). By maintaining the original network structure and split ratios and recalculating the inlet and outlet mass flow rates, it was possible to obtain a new adapted network without performing additional CFD simulations.
The results show that although the adapted network introduces an error in the prediction of NO_x emissions compared to the basic CFD model, it still captures the correct order of magnitude. More importantly, the error on the output temperature is remarkably low (1.12%), indicating that the energy balance is well preserved. The adapted network was obtained in a fraction of the time otherwise required for the standard CFD convergence.
These results suggest that adapting existing CRN networks based on previously validated cases may be a promising strategy to rapidly estimate the emissions and temperature profiles of new fuel blends. Integrating data-driven methods to refine split ratios or reactor parameters could further improve the accuracy of these adapted networks, paving the way for fast, flexible and reliable pollutant prediction frameworks.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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