

# A global model for the NO released in vegetation fires

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## Résumé:

*Les feux de végétation sont une source majeure d'émissions de CO, CO<sub>2</sub>, NO<sub>x</sub>, composées organiques volatiles et particules dans l'atmosphère. Pour décrire l'impact de ces feux sur l'environnement et modéliser leurs émissions, il est nécessaire de comprendre les processus impliqués dans la combustion de la végétation. De même, l'analyse de la cinétique des réactions de combustion dans la phase gazeuse est décisive pour la modélisation du comportement des feux de végétation car la vitesse et la quantité d'énergie libérée par la végétation sont dérivées de sa chimie fondamentale et de sa combustion. Dans ce travail, une approche numérique a été utilisée pour étudier les mécanismes de formation du NO dans les feux de végétation au niveau de la source, étant donné le rôle joué par NO sur la formation de l'ozone troposphérique. Les mécanismes réactionnels les plus importants impliqués dans la chimie du NO ont été identifiés en effectuant une analyse des voies réactionnelles et une analyse de sensibilité avec le mécanisme cinétique détaillé GDF-kin<sup>®</sup> 3.0. Un mécanisme de cinétique global à deux étapes a été proposé pour modéliser la conversion de l'azote volatile présent dans la végétation en NO, en considérant que l'azote constitutif de la végétation est entièrement libéré sous forme de NH<sub>3</sub>. Les paramètres des équations de vitesses de réaction de ce modèle ont été déterminés dans des conditions de réacteur parfaitement agité correspondantes aux feux de végétation à l'aide du code PSR de CHEMKIN-II et du mécanisme cinétique détaillé GDF-kin<sup>®</sup> 3.0.*

## Abstract:

*Vegetation fires are a major emission source of CO, CO<sub>2</sub>, NO<sub>x</sub>, volatile organic compounds and particulates to the atmosphere. To describe the impact of these fires on the environment and to model their pollutant emissions, it is necessary to understand the processes involved in the combustion of vegetation. Likewise, the analysis of combustion kinetics in the gas-phase is decisive for modeling vegetation fires behavior given that the rate and amount of energy released from the fuel are derived from the fundamental chemistry of the fuel and its combustion. In this work, a numerical approach has been used to study the mechanisms of NO formation in vegetation fires at the source level, given that NO plays an important role on the formation of ground-level ozone. The major reaction mechanisms involved in NO chemistry have been identified using reactions path analysis and sensitivity analysis with a detailed kinetic mechanism (GDF-kin<sup>®</sup> 3.0). Moreover, a two-step global kinetic mechanism has been proposed herein to account for the conversion of volatile fuel-bound nitrogen to NO, considering that the volatile fraction of fuel-bound nitrogen is released as NH<sub>3</sub>. Data from simulations using the PSR code from CHEMKIN-II package with the detailed kinetic mechanism GDF-kin<sup>®</sup> 3.0 have been used to formulate reaction rate expressions of the global model under vegetation fires conditions.*

**Keywords:** NO emissions, fuel-N, gas-phase reaction kinetics

## 1 Introduction

Vegetation fires are a major emission source of CO, CO<sub>2</sub>, NO<sub>x</sub>, volatile organic compounds and particles to the atmosphere. These pollutants can form, in turn, secondary pollutants with implications at local/regional scale or at global scale, as NO<sub>x</sub> which are major contributors to ground-level ozone [1]. To describe the impact of vegetation fires on the environment, especially on the atmosphere, and to model their pollutants emissions, it is necessary to understand the processes involved in the combustion of vegetation. NO<sub>x</sub> are mainly produced on the flaming combustion stage and NO appears to be prevailing over NO<sub>2</sub> as observed in

field experiments [2]. Several mechanisms can lead to the NO formation. These mechanisms imply either the fixation of the molecular nitrogen contained in the air (i.e. thermal, prompt, N<sub>2</sub>O and NNH pathways) or the oxidation of organic nitrogen chemically bound in vegetation (i.e. fuel-N pathway). In the combustion of vegetation, the main path for NO formation is the fuel-N route [3]. This mechanism is more complex than the other NO formation paths and even though the overall mechanism is fairly well established, details are still under investigation especially for heterogeneous mixtures due to the sensitization effects between species, such as carbon oxides and hydrocarbons to nitrogen oxides [4]. This is the case of the gases released from the thermal degradation of vegetation which form a mixture containing a great variety of chemical species (i.e. CO<sub>2</sub>, CO, CH<sub>4</sub>, etc.) [5]. Indeed the complexity of the combustion processes involving the degradation gases of vegetation relies on their composition and the wide range of conditions occurring in vegetation fires.

The aim of this work is to improve the current knowledge on the combustion processes responsible for the NO emissions of vegetation fires at the source level. Thus, we have developed a two-step global oxidation scheme to account for the NO emissions. The major reaction mechanisms involved in NO chemistry have been identified using reactions path analysis and sensitivity analysis with a detailed kinetic mechanism (GDF-kin<sup>®</sup> 3.0). The kinetic parameters of the global model have been determined using numerical data obtained with GDF-kin<sup>®</sup> 3.0 in a perfectly-stirred reactor environment.

## 2 Materials and Methods

### 2.1 Degradation gases of vegetation

When vegetation is exposed to a thermal source, during the degradation the parent fuel-N is released as volatile-N and char-N. To our knowledge, there are no studies on the literature concerning the composition of the degradation gases of vegetation quantifying the volatile fraction of fuel-N. However, Leroy and co-workers [6] carried out a detailed study of the oxidation of a CH<sub>4</sub>/CO/CO<sub>2</sub> gases mixture representative of the thermal degradation of *Pinus pinaster* needles, (a widespread species characteristic of the forests in the Mediterranean Basin often used in fire tests). So, we considered the CH<sub>4</sub>/CO/CO<sub>2</sub> gaseous mixture proposed by Leroy and co-workers but doped with the corresponding volatile-N fraction released from the thermal degradation of the pine needles. For this, we assumed that volatile-N was only composed by NH<sub>3</sub> because although the nitrogen species (NH<sub>3</sub>, HCN) initially follow different oxidation paths, the steps that determine the selectivity towards NO and N<sub>2</sub> are the same [7]. Then, we considered that the volatile-N fraction corresponded to 80% of the amount of fuel bound nitrogen [8], which was obtained from an elementary analysis of a sample of *Pinus pinaster* needles. The resulting mixture composition for the degradation gases of *Pinus pinaster* needles was: 0.23 % of NH<sub>3</sub>, 30.43 % of CO, 50.98% of CO<sub>2</sub> and 18.36% of CH<sub>4</sub> (mole fractions). This mixture has been used as the inlet mixture composition to run the simulations.

### 2.2 Numerical approach

The calculations have been carried out with the PSR code from CHEMKIN-II package [9] which provides predictions of the steady-state temperature and species composition in a perfectly stirred reactor (PSR). In a PSR the rate of conversion from reactants to products is kinetically-controlled and not mixing-controlled. So, combustion is uniquely characterized by the residence time, the inlet mixture composition and temperature.

The global model formulation has been derived from the full reaction mechanism GDF-kin<sup>®</sup> 3.0 [10] through sensitivity analysis and reaction paths analysis of PSR calculations. GDF-Kin<sup>®</sup> 3.0 was developed for the oxidation of natural gas, and consists of 883 reactions and 121 species. Moreover, it takes into account the major and the minor alkanes presents in the natural gas, covering most of the C1-C6 hydrocarbons, and the chemistry of nitrogen oxides [11]. Even though GDF-Kin<sup>®</sup> 3.0 has not been specifically developed for the combustion processes of vegetation; it has proven its performance for different test environments (e.g. shock tubes and jet-stirred reactors, premixed flames) and in various conditions [10]. Regarding the calibration of the reaction rate expressions of the global model, a regression analysis has been performed whereby the global parameters have been adjusted to match both the main species (i.e. NO and NH<sub>3</sub>) concentration profiles given by the global model and the detailed mechanism in function of temperature. For this, the NO global model was implemented in conjunction with a five-step global mechanism [12] to model the combustion of the CH<sub>4</sub>/CO/CO<sub>2</sub> present in the degradation gases of vegetation. This mechanism was developed for the conditions encountered in vegetation fires and it was calibrated by using the experimental

data obtained in a perfectly-stirred reactor [6].

Simulations for the sensitivity analysis, reaction path analysis and the calibration of the model have been performed at atmospheric pressure and at a constant residence time of 1.3 s [13], for temperatures ranging between 773 K and 1273 K (step 50 K). Since NO formation is favored at fuel-lean conditions [4,14], the equivalence ratio has been fixed at 0.6. Moreover, the global model has been validated under stoichiometric conditions.

### 3 Results and analysis

#### 3.1 Reaction pathways analysis and sensibility analysis

Figure 1 presents the reactions paths diagram of the principal reactions involved in the NO chemistry in the conditions of this study which has been obtained from the results of both the reaction pathways analysis and the sensitivity analysis. As shown in figure 1, the oxidation of NH<sub>3</sub> leads to two main products, NO and N<sub>2</sub>. NH<sub>3</sub> is converted to NH<sub>2</sub> mainly by hydrogen abstraction through the reaction NH<sub>3</sub> + OH ↔ NH<sub>2</sub> + H<sub>2</sub>O. NH<sub>2</sub> is then partly recycled back to NH<sub>3</sub>, essentially by reacting with the hydroperoxyl radical: NH<sub>2</sub> + HO<sub>2</sub> ↔ NH<sub>3</sub> + O<sub>2</sub>. The subsequent reactions of NH<sub>2</sub> largely determine the formation of either NO or N<sub>2</sub>, once NO is produced, since formation of N<sub>2</sub> occurs mostly through the reaction of NH<sub>2</sub> with NO.

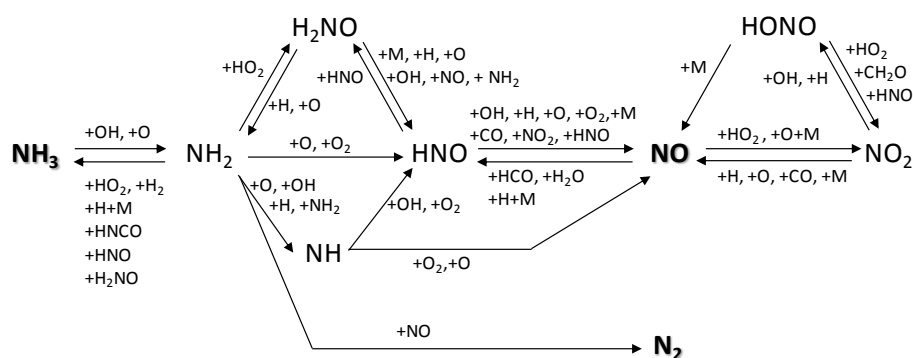


FIG. 1 – Reactions path diagram for the NO chemistry.

NO formation occurs essentially through the oxidation of nitroxyl: HNO + O<sub>2</sub> ↔ NO + HO<sub>2</sub>, by following the sequence NH<sub>3</sub> → NH<sub>2</sub>(→H<sub>2</sub>NO) → HNO → NO (figure 1). Thus nitroxyl can be formed directly by NH<sub>2</sub> or via H<sub>2</sub>NO species. The reaction pathway involving H<sub>2</sub>NO has been identified as being important only in the presence of high CO<sub>2</sub> concentrations [4], which is the case of this study. Once NO is formed, some NO to NO<sub>2</sub> interconversion occurs by the reaction of NO with the hydroperoxyl radical (NO + HO<sub>2</sub> ↔ NO<sub>2</sub> + OH). However, part of the NO<sub>2</sub> is converted back to NO. For temperatures lower than 1023 K, NO<sub>2</sub> reacts with CO to form NO and CO<sub>2</sub> (figure 2a). It worth noting that in this range of temperatures the oxidation of CO is not efficient. For temperatures higher than 1023 K, when the NO production is more efficient, NO<sub>2</sub> is almost entirely converted back to NO by reacting with the H/O radicals (figure 2a).

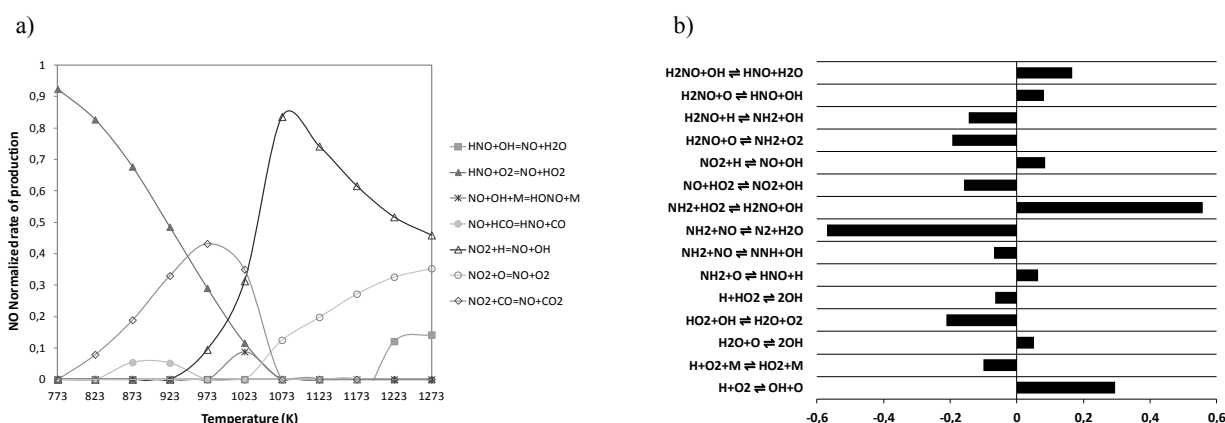


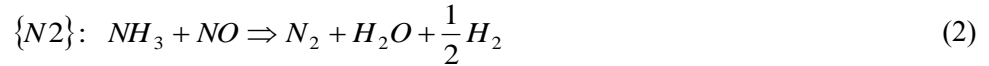
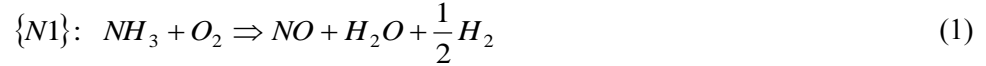
FIG. 2 – a) Normalized rates of production of NO. b) PSR code outputs for NO sensitivity analysis at 1073 K.

NO is also removed to form  $N_2$  by reaction with amidogen and to form HNO by reacting with HCO at high temperatures. As  $NO_2$ , HNO is almost entirely converted back to NO.

These results are in agreement with the sensitivity analysis (figure 2b), which show how the NO chemistry strongly depends on reactions involving  $NH_2$ . Sensitivity analysis also shows how the composition of the radical pool plays an important role on the NO chemistry. The reaction  $H + O_2 \leftrightarrow O + OH$  limits the size of the O/H radical pool and favors the OH radical.

### 3.2 NO global kinetic model

To model NO chemistry in the conditions of this study, it has been considered the formulation proposed by Mitchell and Tarbell [15]:



This reaction scheme represents fairly well the NO chemistry in relation with the reactions path analysis and the sensitivity analysis results. To determine the rate of  $NH_3$  oxidation reaction (equation (1)) the classical steady-state assumption was used to relate the OH radical to the main components, since the most important reaction on the consumption of ammonia in the conditions of this study is that with the OH radical. Consequently the concentration of OH was supposed to be proportional to the square root of the product of  $O_2$  and  $H_2$  concentrations. Concerning the reaction of NO consumption (equation (2)), it was assumed that its reaction rate was first order in  $NH_3$  and NO.

The reaction rate expressions of the global model obtained from the calibration with the detailed mechanism GDF-kin<sup>®</sup> 3.0 are given by equations (3) and (4), where  $\dot{\omega}$  is expressed in  $\text{mol}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$ , T is the temperature (K) and R the universal constant of gases ( $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ):

$$\dot{\omega}_{\{N1\}} = 3.22 \times 10^{12} T^2 [NH_3]^{1.00} [H_2]^{0.50} [O_2]^{0.50} \exp\left[-\frac{62000}{RT}\right] \quad (3)$$

$$\dot{\omega}_{\{N2\}} = 7.03 \times 10^{19} T^{-1.3} [NH_3]^{1.00} [NO]^{1.00} \exp\left[-\frac{37000}{RT}\right] \quad (4)$$

Figure 3 shows the comparison between the calculated  $NH_3$  and NO concentrations (mole fraction) as a function of the temperature using the global reaction mechanism, and the reference detailed chemistry at fuel-lean conditions.

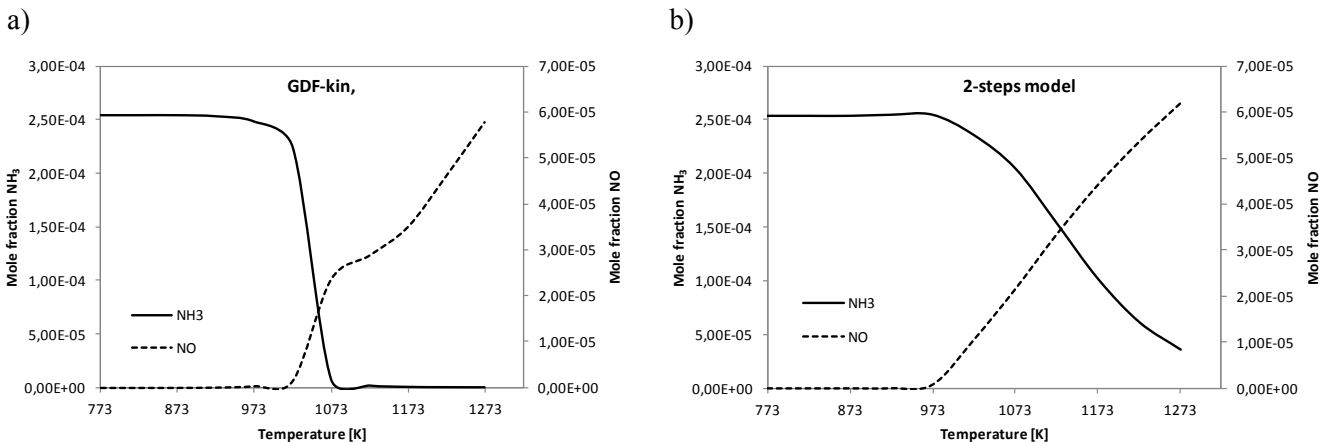


FIG. 3 – Comparison between the NO and  $NH_3$  mole fractions concentrations obtained with the detailed mechanism GDF-Kin<sup>®</sup> 3.0 and the global model developed in the present work as a function of the temperature at fuel-lean conditions.

As it can be seen on this figure, the NO concentration profile is properly predicted with the global model.

The difference between the overall production of NO obtained with the global and the detailed model is 7.4 %. Regarding NH<sub>3</sub>, there is also a good agreement in general terms between the predicted concentration profile by the global model and the detailed mechanism. However, the oxidation of NH<sub>3</sub> as a function of the temperature is sharper when predicted by the detailed mechanism GDF-kin<sup>®</sup> 3.0 than when predicted by the global model. As a result the global model is not able to predict the entire consumption of NH<sub>3</sub>. The relative error in the prediction of the global consumption of NH<sub>3</sub> by the global model in comparison with the detailed mechanisms is 14.1 %. Figure 4 presents the results concerning the validation of the model under stoichiometric conditions. These results exhibit the same tendency than that at fuel-lean conditions, showing a fairly good agreement between the predicted mole fraction of NO by the global model and the detailed mechanism. However, the global model overestimates the production of NO at low temperatures. So, the difference between the global NO production estimates by both models is 11.7 %. Concerning the global consumption of NH<sub>3</sub> at stoichiometric conditions, the difference between the predictions of both models is 9.6 %. Thus, according to these results, the reaction paths responsible for the NH<sub>3</sub> consumption and the NO formation at stoichiometric conditions are essentially the same than at fuel-lean conditions (figure 1). Consequently, the two-step global model is also applicable at stoichiometric conditions.

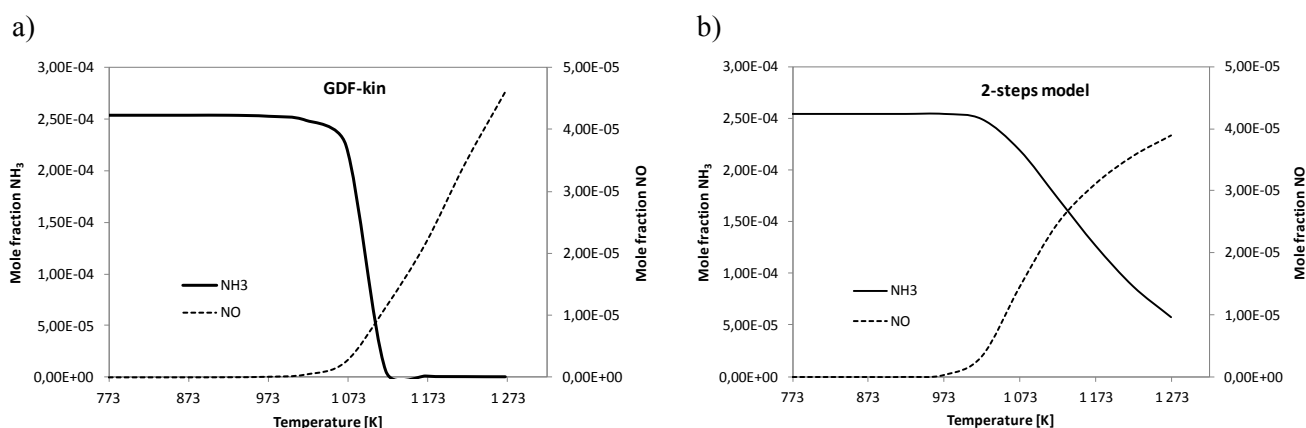


FIG. 4 – Comparison between the NO and NH<sub>3</sub> mole fractions concentrations obtained with the detailed mechanism GDF-Kin<sup>®</sup> 3.0 and the global model developed in the present work as a function of the temperature at stoichiometric conditions.

To our knowledge, there are no experimental data in the literature concerning the NO formation in PSR devices for CH<sub>4</sub>/CO/CO<sub>2</sub>/NH<sub>3</sub> gases mixtures in the conditions of this study. However, and in order to backup at least in the order of magnitude the present results with experimental data, we have compared the results of this work in terms of the percentage conversion of NH<sub>3</sub> to NO with the results Mendiara and Glarborg [4], even if the conditions of this work are different from the ones used with the two-step global model.

Mendiara and Glarborg [4] studied the NH<sub>3</sub> chemistry in the oxy-fuel combustion of methane. Experiments were performed in a flow reactor at temperatures ranging between 973 K and 1773 K, at different fuel equivalence ratios (0.13 to 1.55) and for CH<sub>4</sub>/NH<sub>3</sub> mixtures highly diluted in CO<sub>2</sub> or N<sub>2</sub>. For CH<sub>4</sub>/NH<sub>3</sub> mixtures diluted in N<sub>2</sub> the conversion of NH<sub>3</sub> to form NO varied between 47% at fuel-lean conditions to 38% at stoichiometric conditions. For CH<sub>4</sub>/NH<sub>3</sub> mixtures diluted in CO<sub>2</sub> these values were 27% and 19% respectively. The results of this work show that conversion factors of NH<sub>3</sub> to NO strongly depend on the presence of CO<sub>2</sub> in the mixture. Indeed, as stated by Mendiara and Glarborg [4], CO<sub>2</sub> inhibits the NO formation under stoichiometric and fuel-lean conditions.

The corresponding values of percentage conversion of NH<sub>3</sub> to NO in the present study varied between 28.5% at fuel-lean conditions and 19.8% at stoichiometric conditions. These results are in accordance with the values found by Mendiara and Glarborg [4] in the presence of CO<sub>2</sub>. Thus, the general tendencies observed in these experimental datasets and the results obtained with the two-step global model are in agreement.

## 4 Conclusions

NO emissions from the combustion of vegetation at the source level have been studied numerically, considering that the volatile fraction of fuel-N released due to the thermal degradation of vegetation

is  $\text{NH}_3$ . The main chemical pathways involved in the NO formation and their occurrence have been established for fuel-lean conditions by the reactions path analysis and the sensitivity analysis. In these conditions NO is mainly produced through the sequence  $\text{NH}_3 \rightarrow \text{H}_2\text{NO} \rightarrow \text{NH}_2 \rightarrow \text{HNO} \rightarrow \text{NO} (\leftrightarrow \text{NO}_2)$ . The reaction paths responsible for the NO formation at stoichiometric conditions are essentially the same than at fuel-lean conditions.

A two-step global kinetic model has been proposed for the oxidation of ammonia. The obtained mechanism succeeds in predicting the NO formation with relatively high accuracy in comparison with the numerical values obtained with the detailed kinetic mechanism GDF-Kin<sup>®</sup> 3.0, at fuel-lean and stoichiometric conditions. Moreover, the predicted conversion factors of  $\text{NH}_3$  to NO by using the two-step global model are in accordance with the values found in the literature.

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