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COMPARISON BETWEEN CHEMICAL KINETICS AND CHEMICAL EQUILIBRIUM APPROACHES FOR NO AND CO FORMATIONS ON SPARK IGNITION ENGINE CONDITIONS

Alessandro J.T.B. de Lima
Waldyr L.R. Gallo
UNICAMP, Mendeleyev St. 200, Campinas-Brazil
ajtblima19@fem.unicamp.br
gallo@fem.unicamp.br

Abstract. *A series of theoretical analyses of pollutant formation in combustion processes has been undertaken in a computer program for a closed, isometric and isothermal system. The objective was to study and develop pollutant formation models in Spark-Ignited Engines for a 12-chemical species case. Three similar cases, each considering different chemical species and reactions, were firstly studied to evaluate the composition of the gases, based on chemical equilibrium. Next, the same systems were analyzed on a chemical kinetics methodological approach. The goal was to compare the differences between species concentration and reaction times for different thermodynamic states similarly found in spark ignited engines. Based on the calculated reaction times, situations where chemical kinetics is more coherent than chemical equilibrium are presented. The nonequilibrium effects are analyzed for Nitric Oxide (NO) and Carbon Monoxide (CO), showing how far from equilibrium state they are, depending on the process. Results indicated that NO and CO molar fractions reached proximity to chemical equilibrium for temperatures higher than 2400K at similar engine conditions.*

Keywords: *Spark Ignition Engines, Chemical Kinetics, Chemical Equilibrium, Nitric Oxide, Carbon Monoxide*

1. INTRODUCTION

Since the 1950s, the world has given greater importance to pollutant emission from combustion processes and their control in the automotive industry. The necessity of better knowledge of the formation of regulated pollutants in a spark ignited engine cycle collaborates to a better capacity of automobiles to emit pollutants under the emission limits. Two of the main pollutants yielded on engines are nitric oxide (NO) and carbon monoxide (CO), which cause serious changes in the atmosphere and damage to human health and to the environment of the planet.

In order to predict gas composition during and after combustion process, there are two basic approaches to deal with this problem: chemical equilibrium is a first option capable of calculating the composition of gases rapidly, although it provides different concentrations during combustion and expansion strokes than found in experimental setup in an engine test (Spadaccini and Chinitz, 1972). Chemical kinetics, on the other hand, requires more computational effort to predict the gas composition, but it follows the phenomenon more coherently, providing results more similar to engine experiments.

A considerable number of chemical kinetic models are presented in the literature (Patterson and Henein, 1972; Annand, 1974; Benson *et al.*, 1975; Miller and Bowman, 1989). Although they can predict well enough the formation of pollutants in Spark Ignited (SI) Engines, it is not easy to compare the results of a new-generated model with the traditional models presented by most sources. It is required several other routines, which predict heat transfer, blowby, thermodynamic properties and others, just to compare pollutant results. There is no comparison basis for an intermediate model, between simple and most robust cases.

Therefore, a series of simple models was developed and will be presented in this work, which covers this gap described above. By focusing on some regulated ICE pollutants, three chemical models with different reactions predict NO and CO formations (Newhall, 1969; Zel'dovich *et al.*, 1947), based on considerations presented by Way (1976), by chemical equilibrium and chemical kinetics approaches. The text indicates the chemical reactions used on each model and the rate constants for all chemical reactions. A range of temperatures usually found in spark ignited engines during combustion and expansion processes was applied to the model and the obtained results were described in terms of NO and CO molar fractions, besides their reaction times. Finally, a comparison between chemical equilibrium and chemical kinetics approaches is presented, indicating which approach must be used on different phases of the engine cycle.

2. MATHEMATICAL MODELS AND ASSUMPTIONS

Three chemical models were undertaken in order to calculate the final gas composition by considering chemical reactions. The models considered an isothermal and closed thermodynamic system, where a certain amount of mass of gases reacted under the chemical reactions previously defined. Both chemical equilibrium and chemical kinetics assumptions were applied on this model and comparisons between the results of these two approaches were made. The difference between each one of the models are the quantity of chemical species and chemical reactions considered, as well as the initial gas composition. While chemical equilibrium indicates the final composition after the chemical reactions finished, chemical kinetics considers the rate of reaction of each species during time, approaching the chemical equilibrium state after a specific time of reaction.

The considered thermodynamic conditions try to reproduce conditions on combustion and expansion strokes in spark ignited engines. The range of temperatures varied from 1800 to 2500K, while the volume varied from $25cm^3$, $250cm^3$ or $2500cm^3$.

2.1 Chemical Equilibrium

3 different models were developed with different objectives for the chemical equilibrium approach. First model considered nitric oxide (NO) formation in a closed system with simplified air ($0.79N_2 + 0.21O_2$) under the thermodynamic conditions described earlier, with 5 chemical species (O, O_2, N, N_2, NO). Second model considered carbon dioxide (CO) formation in a closed system with a mixture of CO, CO_2, H_2 and H_2O representing combustion products of anhydrous ethanol (C_2H_6O) under stoichiometric conditions and 8 chemical species ($CO, CO_2, H, H_2, H_2O, OH, O, O_2$). The last model merged both conditions of the previous models, considering NO and CO formations in the same system with a mixture of gases ($Ar + CO_2 + H_2O + N_2$) from a simplified combustion of anhydrous ethanol under stoichiometric and thermodynamic conditions and 12 chemical species ($Ar, CO, CO_2, H, H_2, H_2O, OH, O, O_2, N, N_2, NO$).

The methodology to solve this problem by chemical equilibrium was similar to the one presented by Way (1976) and Gallo (1990), with exception that a mixture of gases was provided as initial condition to the problem. The method of convergence used on the model was the secant method. The conservation of each species (C, H, O, N, Ar) and some chemical reactions were considered to solve these problems. To the final model, the reversible chemical reactions considered were:

$$N_2 + O_2 \longleftrightarrow 2NO \tag{1}$$

$$2H_2O + O_2 \longleftrightarrow 4OH \tag{2}$$

$$2CO + O_2 \longleftrightarrow 2CO_2 \tag{3}$$

$$2H_2 + O_2 \longleftrightarrow 2H_2O \tag{4}$$

$$N_2 \longleftrightarrow 2N \tag{5}$$

$$H_2 \longleftrightarrow 2H \tag{6}$$

$$O_2 \longleftrightarrow 2O \tag{7}$$

The first model considered Eq. (1, 5, 7), while the second model considered Eq. (2, 3, 4, 6, 7). The equilibrium constant associated with each chemical reaction may be calculated by:

$$K_n = K_p \left(\frac{R_u T}{P_o V}\right)^{\Delta n_{eq}} = n_{i,e}^{(\nu''_{i,s} - \nu'_{i,s})} \tag{8}$$

2.2 Chemical Kinetics

The chemical kinetics approach was applied to the same three models described on the chemical equilibrium section. The chemical reactions were simulated with the aim of reaching the chemical equilibrium state. The reaction times to reach chemical equilibrium were then obtained and used later to be compared with spark ignited engine reaction times, which may indicate a possible equilibrium tendency. Such as the chemical equilibrium models, each of the kinetic models considered different number of chemical reactions. The final model considered 26 elementary chemical reactions (forward and backward), which are presented now:

$$OH + H \longleftrightarrow H_2 + O \tag{9}$$

$$OH + O \longleftrightarrow O_2 + H \tag{10}$$

$$OH + H_2 \longleftrightarrow H_2O + H \tag{11}$$

$$OH + OH \longleftrightarrow H_2O + O \tag{12}$$

$$CO_2 + H \longleftrightarrow CO + OH \tag{13}$$

$$H + OH + M \longleftrightarrow H_2O + M \tag{14}$$

$$2H + M \longleftrightarrow H_2 + M \tag{15}$$

$$2O + M \longleftrightarrow O_2 + M \tag{16}$$

$$CO + O + M \longleftrightarrow CO_2 + M \tag{17}$$

$$CO + O_2 \longleftrightarrow CO_2 + O \tag{18}$$

$$O_2 + N \longleftrightarrow NO + O \tag{19}$$

$$NO + N \longleftrightarrow N_2 + O \tag{20}$$

$$OH + N \longleftrightarrow NO + H \tag{21}$$

First model considered Eq. (16, 19, 20), while the second model considered Eq. (9, 10, 11, 12, 13, 14, 15, 16). Each chemical species had its rate of reaction calculated by the law of mass-reaction (Eq. 22):

$$\frac{dC_i}{dt} = \sum_{k=1}^{R=26} (\nu_{i,k}^{''} - \nu_{i,k}^{'}) k_{f/b,k} \prod_{j=1}^{N} C_j^{\nu_{j,k}^{'}} \tag{22}$$

The system of ordinary differential equations obtained by Eq. (22) is solved by the combination of the implicit trapezoidal method and Newton-Raphson method. This combination of methods was used instead of a explicit traditional Runge-Kutta because they calculate faster, allowing the use of time-steps of 10^{-4}s instead of 10^{-8}s required for the Runge-Kutta to avoid stability issues (Kee *et al.*, 2005). The forward rate constant $k_{f,k}$ is obtained by the modified Arrhenius equation 23, with the constants obtained by several other authors.

$$k_{f,k} = A \left(\frac{A}{298} \right)^{b_k} \exp^{\left(-\frac{E_{a,k}}{R_u T} \right)} \tag{23}$$

The backward rate constant $k_{b,k}$ is obtained by the relation between chemical kinetics and chemical equilibrium (Eq. 24):

$$\frac{k_{f,k}}{k_{b,k}} = K_{c,k} = K_{p,k} \left(\frac{R_u T}{P_o} \right)^{\Delta n_k} \tag{24}$$

Table 1 shows the Arrhenius expression used for each chemical reaction, as well as their respective references:

Table 1. Reaction Rate Constant Parameters

Reaction	A $(m^3/kmol.s)$	b	E_a $(kJ/kmol)$	Reference
$OH + H \longleftrightarrow H_2 + O$	4.3E7	2.8	16.21E3	(Tsang and Hampson, 1986)
$OH + O \longleftrightarrow O_2 + H$	2.61E10	-0.5	0.25E3	(Tsang and Hampson, 1986)
$OH + H_2 \longleftrightarrow H_2O + H$	9.31E8	1.6	13.8E3	(Baulch *et al.*, 1992)
$OH + OH \longleftrightarrow H_2O + O$	9.95E8	1.14	0.42E3	(Baulch *et al.*, 1992)
$CO_2 + H \longleftrightarrow CO + OH$	2.26E7	1.55	-3.34E3	(Lissianski *et al.*, 1995)
$OH + H + M \longleftrightarrow H_2O + M$	2.49E11	-2	0	(Baulch *et al.*, 1992)
$2H + M \longleftrightarrow H_2 + M$	2.19E9	-1	0	(Baulch *et al.*, 1992)
$2O + M \longleftrightarrow O_2 + M$	1.89E7	0	-7.48E3	(Tsang and Hampson, 1986)
$CO + O + M \longleftrightarrow CO_2 + M$	6.67E8	0	12.55E3	(Tsang and Hampson, 1986)
$CO + O_2 \longleftrightarrow CO_2 + O$	2.53E9	1	200E3	(Tsang and Hampson, 1986)
$N + O_2 \longleftrightarrow NO + O$	2.69E9	1	27.19E3	(Baulch *et al.*, 1992)
$N + NO \longleftrightarrow N_2 + O$	4.28E10	0	6.57E3	(Baulch *et al.*, 1992)
$N + OH \longleftrightarrow NO + H$	2.83E10	0	0	(Baulch *et al.*, 1992)

3. RESULTS OF THE MODELS

This section presents the obtained results for the three models previously commented. First, results from the 5-species model for NO formation are presented with comparisons between the chemical equilibrium and chemical kinetics models. Then, some results from the 8-species model for CO formation are detailed. Finally the 12-species model results, with nitric oxide and carbon monoxide formations, are indicated.

The results from the chemical equilibrium models were firstly compared to the online gas-mixture chemical equilibrium program developed by the Dandy research group (CSU, 2017). Diverse comparisons between the developed chemical equilibrium models and the reference results were made and the maximum discrepancy found was close to 1% in stable species (CO, NO, H_2O, etc.).

3.1 Nitric oxide simplified model

Figure 1 shows the equilibrium molar fraction of nitric oxide formed in the first simulation for both chemical equilibrium and kinetics models. The amount of 1x10^6 kmol of simplified air was considered in an isothermal and isometric closed system, where the temperatures and volumes varied and their influence on the model was checked. The kinetic result of NO was compared with the equilibrium value to check if the kinetic model is capable of converging to the chemical equilibrium state, with a specific number of chemical reactions and rate constants. First, the figure indicates that the different volumes/pressures on the system did not change significantly the formation of nitric oxide. A difference is perceptible at high temperatures, higher than 2400K. Second, even considering dry air in the model, the final molar fraction of NO in each case is lower than 2.5%, which indicates that at combustion processes a lower molar fraction would be found, since there are other chemical species and fuel, what would collaborate to a lower NO formation. It is also notable from Fig. 1 that both models converged to similar results of nitric oxide formation on the whole temperature range and at three different volumes. The maximum relative error found between the molar fractions of NO by equilibrium and kinetic results was around 0.49% at 2450K and $2500cm^3$.

Figure 2 presents the equilibrium reaction times calculated by the chemical kinetic model at different temperatures and volumes. The plot indicates that considerably high reaction times are required for the model to achieve chemical equilibrium at temperatures close to 1800K. At higher pressures (lower volumes), the calculations indicate lower reaction times required for the system to achieve equilibrium. Elevating temperature causes the reaction times to reduce and achieve lower orders of magnitude. The greatest reduction of reaction time occurs for $25cm^3$, where the reaction time calculated for 1800K is approximately 4138 greater than the time for 2500K. The lowest reaction time found was at 2500K and $25cm^3$, where it take the system almost 0.1s to achieve equilibrium. This value is more than 10 times greater than a usual engine cycle time, which indicates that this model would not achieve equilibrium in a common SI engine.

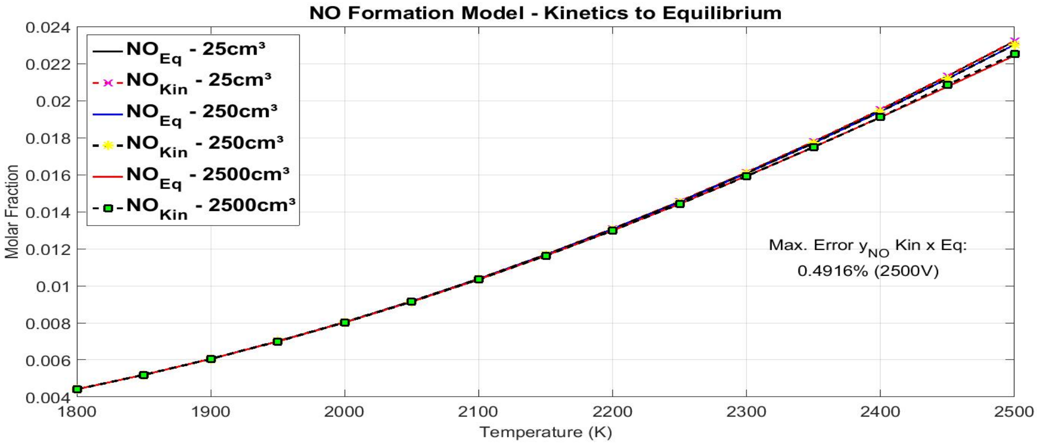

Figure 1. Chemical equilibrium versus chemical kinetics NO formation equilibrium values between 1800 and 2500K

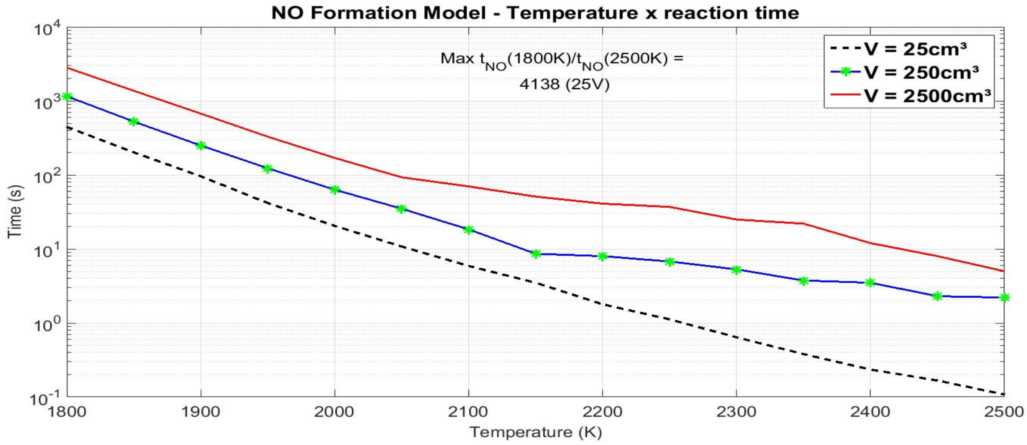

Figure 2. Chemical kinetics NO formation versus equilibrium reaction times between 1800 and 2500K

3.2 Carbon monoxide simplified model

On this section, the results focus on the carbon monoxide simplified model. Such as the nitric oxide model, this model considers 1x10^{-6} kmol of mixture (with molar fractions of $0.1CO + 0.5CO_2 + 0.1H_2 + 0.3H_2O$) at the same thermodynamic conditions previously commented. Figure 3 presents the same idea of Figure 1, but for the CO reaction mechanism. Little effect was noticed by the application of different pressures and volumes in the model for CO formation at temperatures lower than 2100K. Higher temperatures than that at the volume of $2500cm^3$ indicate a considerable increase of CO formation, reaching 23% of molar fraction of the system at 2500K. This indicates that lower pressures at high temperatures collaborate to CO formation and CO_2 reduction. The maximum difference found between the CO molar fraction obtained by the kinetic model when compared to the equilibrium model was of 0.0077% at 2300K and $2500cm^3$.

Figure 4 shows the equilibrium reaction times for the thermodynamic conditions of the CO system. The reaction times required for this system to reach equilibrium at 1800K are considerably lower than the times for the NO simplified model, though the reductions of reaction time with the temperature increase are lower than the ones found on the NO case. The reaction time order of magnitude for CO is lower than the NO's. Despite of this situation, the behavior of the plot is similar to Fig. 2. The greatest reduction of reaction time found was at $250cm^3$, where the carbon monoxide reaction time at 2500K is 31.61 times lower than at 1800K. Still, in most of these situations, the model did not achieve a equilibrium time comparable with engine cycle times; only at $25cm^3$ and 2400K the model approach 0.01s.

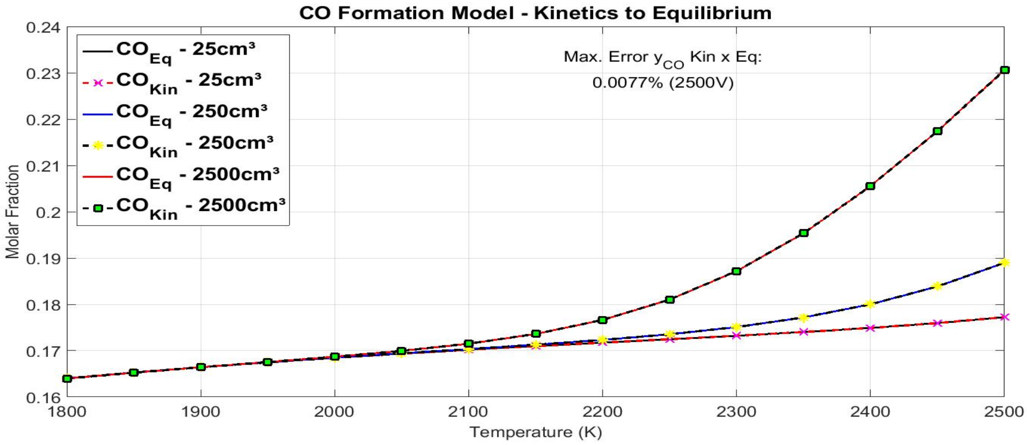

Figure 3. Chemical equilibrium versus chemical kinetics CO equilibrium values between 1800 and 2500K

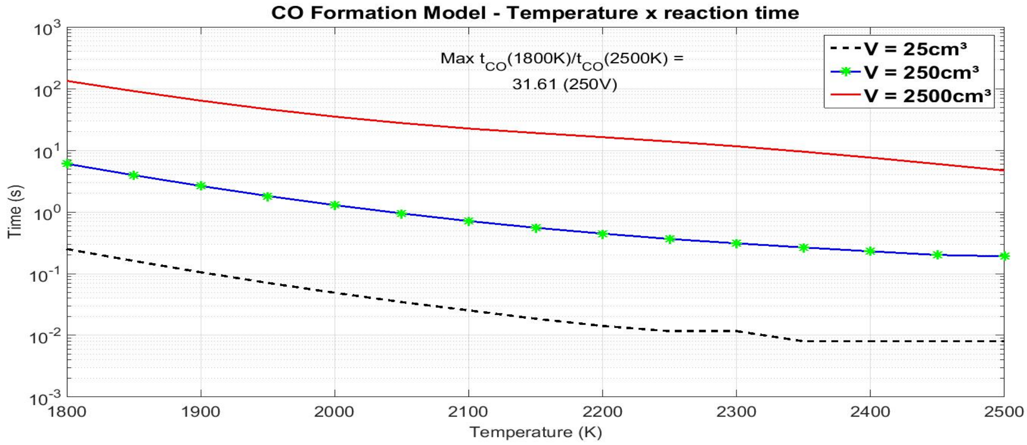

Figure 4. Chemical kinetics CO formation versus equilibrium reaction times between 1800 and 2500K

3.3 Nitric oxide and carbon monoxide combustion model

The final model puts together the nitric oxide and carbon monoxide reaction mechanisms, with an addition of Eq. (17, 18, 21), which are chemical reactions to represent an expansion of CO formation mechanism, besides the extended Zel'dovich NO reaction mechanism. $1\text{x}10^{-6}$ kmol of a mixture of gases simulating combustion products from an SI engine was used as the initial composition in the model. The initial molar fraction was $0.0081Ar + 0.1212CO_2 + 0.1944H_2O + 0.6763N_2$, attempting to represent a stoichiometric gas composition of a combustion process. Figure 5 presents the comparison between the obtained equilibrium molar fractions for NO by chemical equilibrium and chemical kinetic models. Good agreement is found between the equilibrium and kinetic curves at all temperatures and three different volumes. The greatest error found between equilibrium and kinetics was 3.85% at 1800K and $2500cm^3$. This value may be justified by the higher complexity of the model, which produces greater numerical errors and the uncertainty of rate constants on specific temperatures, etc.; in most cases, these differences were lower than 1%. The figure also shows a great difference between the NO molar fractions when the temperature is increased. The maximum nitric oxide molar fraction is 8000ppm, found at 2500K and $2500cm^3$, which indicates an increase of the volume (reduction of pressure) in the system collaborated to higher NO concentrations. The orders of magnitude found for the three cases were the same, which indicates that pressure affects NO formation, but not as significantly as on CO formation at Fig. 3.

Figure 6 describes the same analysis as 5 for carbon monoxide. Good agreement was also found between the chemical equilibrium and chemical kinetics results. The temperature increase elevates CO molar fractions, especially at higher volumes, such as commented earlier on the CO simplified analysis. A maximum error of 7.43% was found between the two models, at 1800K and $2500cm^3$. The values found for CO molar fraction is an order of magnitude greater than NO values. The model indicates that almost 5% of the final gas composition is carbon monoxide, at 2500K and $2500cm^3$; this result indicates the same behavior found at CO simplified analysis that at higher volumes and tempearatures, a higher amount of CO is yielded by the chemical system.

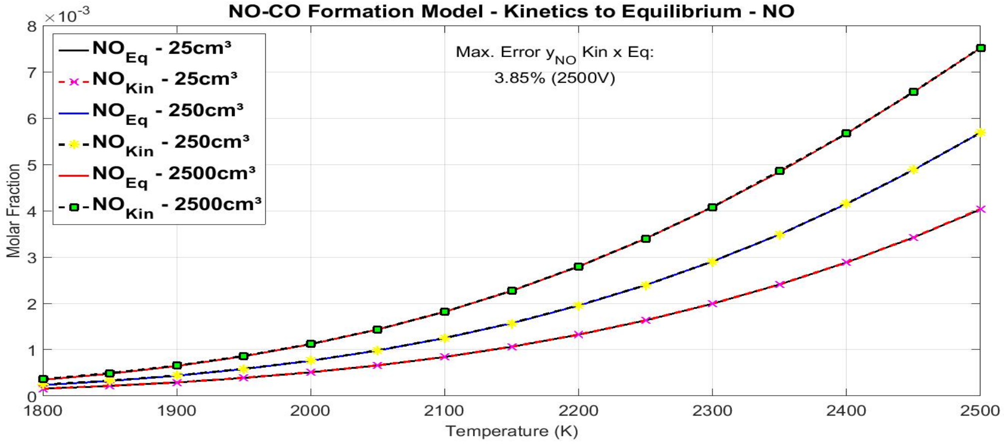

Figure 5. Chemical equilibrium versus chemical kinetics NO formation equilibrium values between 1800 and 2500K

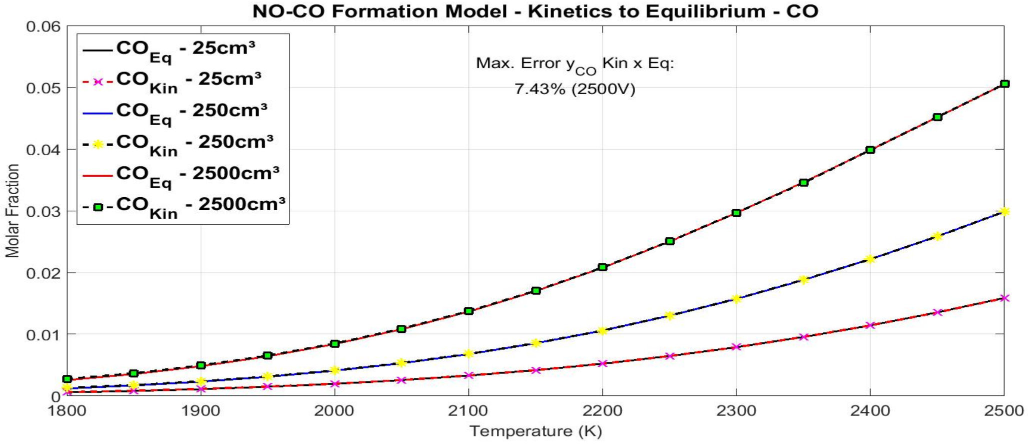

Figure 6. Chemical equilibrium versus chemical kinetics CO formation equilibrium values between 1800 and 2500K

Figure 7 shows the relation between the reaction times required for nitric oxide to achieve chemical equilibrium on the mixed reaction mechanism and temperature. The objective was to obtain a qualitative reaction time scale for this mechanism and compare it with usual engine cycle times of common automobiles. It indicates that lower reaction times are required on this model to NO reach equilibrium, when compared to 2. Two orders of magnitude reduction is found for this compound, from 10^3 to 10^1s at $2500cm^3$ and from 10^2 to 10^{-1}s at $25cm^3$. The effect of pressure increase (volume reduction) collaborates to yield nitric oxide faster, approaching lower reaction times. Still, this reduction on the reaction times is not enough to indicate that at engine thermodynamic conditions the reaction mechanism achieve chemical equilibrium, since the values found are higher than 10^{-3}s, which is a representative value of an engine cycle. Additionally, the engine does not stay at the same temperature for this duration; the average temperature during the cycle is much lower than these temperatures simulated here, which is another point that indicates that chemical kinetics is required to predict coherently pollutant formation. Finally, the maximum ratio of reaction times for NO mechanism calculated was close to 2246 times, which indicates a reduction of almost 50% when compared to NO simplified mechanism.

Figure 8 shows the reaction time results for carbon monoxide. The CO reaction times increased on this mechanism when compared to CO simplified analysis. At $2500cm^3$ the CO reaction time required to reach equilibrium is almost 1100s while at the simplified analysis the same conditions indicated an order of magnitude lower. Despite of this result, the tendency of chemical equilibrium for carbon monoxide is still higher than nitric oxide case, especially at lower temperatures. The closest condition simulated for the model showed that the required CO reaction time is lower than 10^{-2}s, which is still higher than a general engine cycle time. Therefore, CO mechanism still does not reach chemical equilibrium at engine conditions. The maximum ratio of reaction times found for CO mechanism was 519.75 at $250cm^3$.

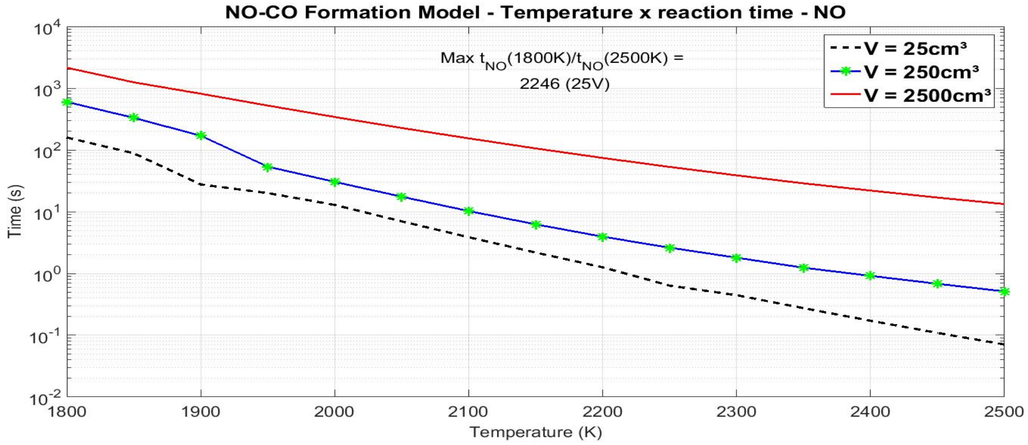

Figure 7. Chemical kinetics NO formation versus equilibrium reaction times between 1800 and 2500K

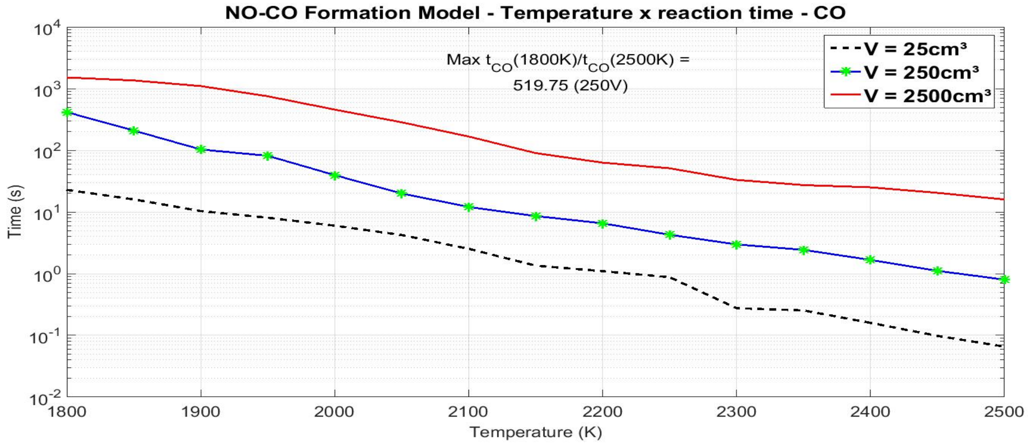

Figure 8. Chemical kinetics CO formation versus equilibrium reaction times between 1800 and 2500K

4. CONCLUSIONS

This work aimed to present a gradual development of chemical kinetic models for regulated pollutants on spark-ignited engines and its comparison with chemical equilibrium. Each one of the models presented conditions where they were capable of converging to chemical equilibrium, with an error greater than 1% only in specific conditions on the most complex model. This comparison allowed the calculation of reaction times of both nitric oxide and carbon monoxide mechanisms, which provides a quantification of the required time to reach equilibrium. Their values indicate if a possible assumption of chemical equilibrium under the conditions simulated is coherent or not. At temperatures close to 2500K and low volumes ($\approx 25cm^3$) the mechanism approximate to chemical equilibrium, although an ordinary SI engine does not provide neither enough time nor steady similar conditions to reach this specific state. Therefore, a chemical kinetics model must be applied during the combustion and expansion strokes of an engine simulation in order to predict coherently the formation of NO and CO.

The simplified models provided enough robustness to the analysis since it allowed possible comparisons between the most complex chemical model with them. The effectiveness of each rate constant, besides the refinement of the numerical methods applied on the models and the reaction times required for each species to reach equilibrium was only possible because of these simplified model. The idea of comparing a chemical kinetic model with analytic results obtained by chemical equilibrium corroborates the kinetic model, since it indicates that it is capable of producing coherent results and therefore is capable of predicting the formation of such pollutants on an SI engine simulation, for example.

The final chemical kinetics model was capable of calculating values on the same order of magnitude on chemical equilibrium conditions without requiring great computational resources to calculate the rates of reaction times higher than found on engine cycles. The implicit trapezoidal method, together with Newton-Raphson, provided low computational times, being faster and more stable than explicit numerical methods like Runge-Kutta for example, which presents problems of step-size when dealing with stiff EDO systems such as found on chemical kinetic calculations Kee *et al.* (2005).

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