

Development of a fast, robust equilibrium chemistry solver for analyses of combustion products

S. M. Aithal

Mathematics and Computer Science Division, Argonne National Laboratory
9700 S. Cass Ave., Argonne, IL 60439, USA

Phone # 630-252-3164, e-mail: aithal@mcs.anl.gov

Abstract: Chemical equilibrium calculations provide useful estimates of combustion products in a wide range of reacting flow systems. Equilibrium computations are widely used in computing finite-rate NO emissions in internal combustion engines. Equilibrium chemistry computations can also provide useful information in comparing emissions of engines with different additives such as natural gas or methanol. This paper describes a fast, robust method to compute equilibrium concentrations of combustion products by using a set of twenty species relevant to a wide range of combustible fuel-additive-air mixtures, using the equilibrium constant method. The reaction set included species such as C, C₂H₂ and HCN believed to be responsible for soot formation in rich fuel-air mixtures. An adaptation of Newton-Raphson method was used for solving the highly nonlinear system of equations describing the formation of equilibrium products in reacting fuel-additive-air mixtures. The effect of temperature, pressure, and composition for various fuel-additive-air mixtures was studied. The modified Newton-Raphson scheme was found to be a robust and fast method for computing chemical equilibrium concentrations for a wide range of operating conditions such as temperature, pressure, and composition of fuel-additive-air mixtures.

Keywords: equilibrium, dual-fuel, NO, emissions, Newton-Raphson

Nomenclature

G molar Gibbs free energy (J/mole)

k_p	equilibrium constant
P	pressure (N/m ²)
P _a	partial pressure
x_k	mole fraction of the k^{th} species

Greek Symbols

θ	crank angle
ϕ	equivalence ratio
ν	stoichiometric coefficient

Abbreviations

CAD	crank angle degrees
EGR	exhaust gas recirculation
EOC	end of combustion
PPM	parts per million
TDC	top dead center

1 Introduction

Combustion of hydrocarbons in power-generating equipment, such as gas turbines or internal combustion engines in automobiles, is a major source of air pollution. The combustion products formed from burning fuel-air mixtures contain oxides of nitrogen (NO, NO₂, and N₂O) along with CO, CO₂, and other organic compounds that are unburned hydrocarbons (UHCs) or partially burned hydrocarbons. The relative amounts of these pollutants, usually on the order of several hundred parts per million (PPM), depend on various factors including composition of the

fuel-air mixture and the operating conditions. Optimizing performance (power and efficiency), while minimizing emissions such as NO_x and soot, leads to conflicting design constraints; hence, accurate prediction of these emissions is an important consideration in the design of engines and combustors. Development of fast and robust tools for computing engine-out NO_x can aid in the design, analysis, and optimization not only of existing engines but also of newer engine designs based on a variety of fuel-additive-air mixtures (also called flexible fuel engines) [1, 2]. In these flexible fuel engines, the main fuel can be gasoline or diesel, and the additives can be natural gas (methane), hydrogen, acetylene, or alcohols (methanol or ethanol). A comparison of the emission characteristics of different fuel-additive combinations can help the design and development of such flexible-fuel engines.

Concentrations of emissions such as NO_x , CO, soot, and UHCs can be computed by using finite-rate chemistry. Finite-rate chemistry calculations require an appropriate mechanism—a set of elementary reactions and their associated reaction rate constants—to describe the soot/CO/ NO_x formation process with reasonable accuracy. Careful attention must be paid to the size of the time step and initial conditions, in order to ensure the stability and accuracy of the time-marching process. These requirements greatly increase the computational complexity and time required for solution. In order to reduce the computational complexity of full finite-rate chemistry computations, several simplifying assumptions can be made to derive rate-controlled expressions for the formation of NO and CO [3, 4]. As described in Ref. [3], the rate-controlled expression for NO formation assumes equilibrium concentrations of O, O_2 , OH, H, and N_2 computed at the local pressure and temperature in the postflame gas. Similarly, Ref. [4] computes rate-controlled CO concentrations using equilibrium concentrations of species (CO , CO_2 , O_2 , H_2O , H_2 , N_2) in the source terms. Simplified rate-controlled computations of NO as

described in Ref. [3] are widely used in quasi-dimensional engine modeling codes and are also being used for other fuel-additive air mixtures (methane-hydrogen) as described in Ref. [4]. The source terms for the rate-controlled equations for NO and CO require the equilibrium values of various combustion products. Since the engine temperature and pressure vary continuously throughout the engine cycle, temporal variation of NO (or CO) using the rate-controlled expressions requires equilibrium computations to be done often, usually every crank angle degree (CAD). Equilibrium computations performed by using look-up tables can be cumbersome and computationally expensive. Based on these considerations, a fast, robust tool for computing equilibrium concentrations of combustion products can greatly aid the design, development, and analysis of new engine operating regimes and engines fuelled by different fuel blends.

Chemical equilibrium of a closed reacting system at a given pressure and temperature can be computed by minimizing the Gibbs free energy of the system or by using the approach of equilibrium constants with a set of reactions [5]. While these two formulations are equivalent and reduce to the same number of iteration equations (see [5 and references therein]), each approach has its advantages and disadvantages. Minimization of the Gibbs free energy involves treating each species independently and does not require a set of reactions to be prescribed a priori. The details of the problem formulation and implementation using this approach are explained in [5]. For most combustion problems of interest to engineering applications, however, the equilibrium constant method is easier to formulate and implement. More important, the method can be easily coupled to computational fluid dynamics (CFD) and/or quasi-dimensional codes that compute temperature and pressure in combustors.

While the equilibrium constant method is easier to formulate and implement compared with the minimization of Gibbs free energy method, the computation of equilibrium composition of a large set of species using this method is still a daunting task. The coupled system of equations describing the formation of products is highly nonlinear and hence difficult to converge by using traditional numerical schemes such as the Newton-Raphson method. Therefore, several authors have studied equilibrium chemistry calculations using a small set of species (typically 6–13).

Rashidi [6], for example, studied a system with 13 species. Sample results were presented for hydrocarbons with an H/C ratio of 2, for a set of prescribed temperature and pressure. The numerical approach involved separating the species into two groups: species with relatively large concentrations (CO_2 , H_2O , CO , H_2 , O_2 , and N_2) and species with lower concentrations (OH , NO , O , H , N_2O , NO_2 , and N). Concentrations of those species with high values were determined first, by using the Newton-Raphson method. Following this step, the remaining species were determined with the successive substitution method. The two methods were iterated alternatively until the change in values was small. Details of the initial conditions or the total computational time were not explicitly described. Moreover, this method is likely to be unsuitable for computing the temporal variation of species concentrations in engines, however, since the initial charge consists of a fuel-air mixture with little or no CO_2 , H_2O , and H_2 (unless exhaust gas recirculation, or EGR, is used). Furthermore, for stoichiometric and rich mixtures, O_2 concentrations tend to zero at equilibrium and hence cannot be included in the list of species with large concentrations. Therefore, while the methodology presented in [6] can be used for certain types of equilibrium computations, it might not be appropriate in studying temporal variation of equilibrium products during an actual engine cycle.

Rakopoulos et al. [7] used 11 species to describe the combustion products of diesel engines. The diesel fuel was modeled as n-dodecane. The 11x11 system of nonlinear equations was reduced to a 4x4 system by algebraic manipulation. The resulting 4x4 system was solved by using the Newton-Raphson method to obtain equilibrium concentration of the products. Results for a range of temperature, pressure, and equivalence ratios were presented for n-dodecane. The main difficulty with this approach is that the procedure to reduce the 11x11 system of equations to a 4x4 system of equations can be cumbersome, especially if one is interested in studying a wide-variety of fuel-additive air mixtures, thus limiting its utility as a general-purpose design tool.

References [6-7] present sample results of the equilibrium products of hydrocarbon combustion, but neither discusses the applicability of the techniques to general fuel-additive air mixtures or in interpreting actual engine data. The work presented here, on the other hand, focuses on developing a fast, robust, general-purpose tool to compute the equilibrium products for a wide range of fuel-additive-air mixtures relevant to various engines and combustors. Specifically, the numerical tool presented can be used to compute the temporal variation of equilibrium products of an engine powered by traditional fuels such as gasoline and diesel or various fuel-additive mixtures. The tool can also be coupled to CFD codes in order to compute soot precursors in internal combustion (IC) engines [8] or equilibrium NO concentration in other combustors [9].

To accomplish these goals, we used a general set of 20 species relevant to a wide range of lean and rich combustion systems (see Table 1). Three species, namely C, HCN, and C₂H₂, believed to be important in the process of soot formation [10], were also included so as to enable the study of fuel-rich mixtures. The numerical framework developed in this work allows the user

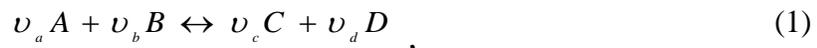
to study equilibrium composition of any fuel-additive mixture, where the fuel is of the form C_xH_y and the additive is of the form $C_{x1}H_{y1}O_{z1}$ (or $C_{x1}H_{y1}$), without any code modification. A modified Newton-Raphson scheme was used to solve the entire 20x20 system of equations using 4 element conservation equations and 16 nonlinear equations, shown in Table 2. The methodology used in this work does not require the use of hybrid solution methods as in [6] or an ad hoc reduction of the nonlinear equations as in [7], thus enhancing its utility as a design tool.

This paper is organized as follows. Section 2 discusses the set-up and solution methodology of the system of non-linear equations used in this work. Section 3 discusses verification and validation of the solver and details regarding the robustness and computational time. Section 3 discusses the applications of the numerical tool developed in this work in studying equilibrium concentrations of various fuel-additive air mixtures. Section 4 presents important conclusions and observations about this work.

2 Method of solution

The details of computing equilibrium compositions of ideal gas mixtures using the equilibrium constant method are explained in standard thermodynamic texts [11] and are briefly described below for the benefit of the reader.

Given a chemical reaction of the form



one can write the equilibrium constant k_p as follows.

$$k_p = \frac{(P_c)^{\nu_c} (P_d)^{\nu_d}}{(P_a)^{\nu_a} (P_b)^{\nu_b}} \quad (2)$$

Since the partial pressure of species A is related to the mole fraction (x_a) as

$$P_a = x_a P, \quad (3)$$

one can write the constant as

$$k_p = \frac{(x_c)^{\nu_c} (x_d)^{\nu_d}}{(x_a)^{\nu_a} (x_b)^{\nu_b}} P^{\nu_c + \nu_d - \nu_a - \nu_b} \quad (4)$$

Following the treatment in standard thermodynamic textbooks, one has

$$\ln k_p = \frac{-\Delta G^\circ(T)}{RT} \quad (5)$$

In this equation, k_p is the equilibrium reaction rate constant, R is the universal gas constant, T is the temperature, and ΔG° is the change in the Gibbs free energy computed at the temperature T . ΔG° was computed by using the procedure outline in [12].

As shown in Table 1, C_xH_y , represents the fuel (such as diesel, which is modeled as n-heptane), and $C_{x_1}H_{y_1}O_{z_1}$ represents an additive (such as CH_4 or CH_3OH). The numerical framework used in this work was set up such that the user specifies the values of x , y , x_1 , y_1 , and z_1 , so as to identify the fuel and additive. The temperature-dependent thermophysical quantities, namely, entropy and enthalpy of individual species, were computed by using CHEMKIN coefficients. For each reaction given in Table 2, the reaction rate was calculated at the prescribed temperature and pressure (P) as shown in Eq. (5). The set of 20 equations corresponding to the 20 species used in this work consisted of 4 element balance (atom conservation) equations for C, H, O, and N and 16 nonlinear equations describing the relationship between the mole-fractions of the various species and the equilibrium rate constants as described in Eq. (2) (see Table 2).

The element balance equations of C, H, O, and N can be written as follows.

$$N_c = xN_{\text{fuel}} + x_1N_{\text{additive}} + N_{CO_2} + N_{CO} + xN_{C_xH_{y-1}} + N_{HCN} + N_C + 2N_{C_2H_2}$$

$$N_h = yN_{\text{fuel}} + y_1N_{\text{additive}} + 2N_{H_2O} + N_{OH} + N_H + 2N_{H_2} + N_{HO_2} + (y-1)N_{C_xH_{y-1}} + N_{HCN} + 2N_{C_2H_2}$$

$$N_o = z_1N_{\text{additive}} + 2N_{O_2} + 2N_{CO_2} + N_{H_2O} + N_O + N_{NO} + N_{OH} + N_{N_2O} + N_{CO} + 2N_{NO_2} + 2N_{HO_2}$$

$$N_n = 2N_{N_2} + N_N + N_{NO} + 2N_{N_2O} + N_{CO} + N_{NO_2} + N_{HCN}$$

Here, N_c , N_h , N_o , and N_n are the total number of C, H, O, and N atoms, respectively, in the system under consideration. The 4 atom conservation equations shown above, along with the 16

nonlinear equations shown in Table 2, were used to obtain the concentration of each of the 20 species considered in this work. The system of 20x20 equations was solved by using an adaptation of the Newton-Raphson method.

The Newton-Raphson method is typically used to solve coupled nonlinear equations. In its most common form a system of nonlinear equations with N variables can be written as

$$\mathbf{F}(x_1, x_2, x_3, \dots, x_N) = \mathbf{0}. \quad (6)$$

The Taylor expansion of Eq. (6) can be written as

$$\mathbf{F}(\mathbf{x} + \delta\mathbf{x}) = \mathbf{F}(\mathbf{x}) + \mathbf{J} \cdot \delta\mathbf{x} + O(\delta\mathbf{x}^2), \quad (7)$$

where

$$J_{i,j} = \frac{\partial F_i}{\partial x_j}$$

Setting $\mathbf{F}(\mathbf{x} + \delta\mathbf{x}) = \mathbf{0}$, in Eq. (7) leads to

$$\mathbf{F}(\mathbf{x}) = -\mathbf{J} \cdot \delta\mathbf{x}. \quad (8)$$

Solution of Eq. (8) yields the solution vector, \mathbf{x} . However, for large systems of highly nonlinear equations, the textbook version of Newton-Raphson methods can have many convergence problems, especially for combustion systems where the Jacobian can become ill-conditioned. The main reason is that elements of the Jacobian matrix are products of reaction rate constants and partial pressures of various species. The initial mixture composition consists entirely of the fuel-additive-air mixture with other species being zero, while the equilibrium system consists of nonzero values of all species considered in the system. The species concentrations in the equilibrium mixture span 8 to 10 orders of magnitude (see Tables 3-5). Furthermore, the reaction rate constants for the set of reactions considered in Table 2 span several orders of magnitude. Figure 1 shows the variation of the reaction rate constants of reactions 1, 11, 12, and 15 shown in Table 2 for a pentane-ethanol mixture. One can see that the reaction rate constants can differ by

over 200 orders of magnitude at temperatures below 1000 K and about 100 orders of magnitude at temperatures higher than 2000 K. The large variations in the species concentrations and the reaction rate constants make the system of equations highly stiff and the Jacobian ill-conditioned. In addition to these numerical issues, another constraint is that each element of the solution vector \mathbf{x} should be greater than zero (since mole fraction of any species cannot be negative), which makes convergence of such systems extremely difficult. In order to develop a fast, robust solver for a generalized fuel-additive-air mixture, an adaptation of the textbook version of the Newton-Raphson method was formulated and tested.

In this work, the species composition vector (or solution vector comprising species equilibrium composition) \mathbf{x} consists of 20 elements corresponding to the 20 species, while the Jacobian is a 20x20 matrix. Equation (8) was solved by using the LU decomposition method, using LAPACK routines to obtain $\delta\mathbf{x}$, where $\delta\mathbf{x}$ is the “correction” used to obtain the set of values for the next iteration. The subsequent iteration (iteration $n+1$) used updated values for the solution vector \mathbf{x} ,

$$\mathbf{x}_{n+1} = \mathbf{x}_n + \alpha_n \delta\mathbf{x}, \quad (9)$$

to solve Eq. (8). Computing an approximate Jacobian based on numerical finite differences can greatly slow the computations; hence, analytical expressions for each of the elements of the Jacobian and $\mathbf{F}(\mathbf{x})$ were used. Since the set of reactions shown in Table 2 are written in a generalized form using x , y , x_1 , y_1 , and z_1 to identify the fuel and additive, the analytical forms of the Jacobian and source terms are valid for all user-defined values of x , y , x_1 , y_1 , and z_1 , thus making it a general-purpose design tool. An underrelaxation factor α was used in order to ensure the stability and convergence of the iteration procedure. The L^2 norm was computed for each iteration. If during a particular iteration, n , the L^2 norm was higher than the L^2 norm of the

previous iteration, the underrelaxation factor was reduced by 10^{-3} or ($\alpha_{n+1} = \alpha_n - 10^{-3}$). If the updated value of any specie mole-fraction was negative, it was reset to 10^{-30} . Use of the above-mentioned underrelaxation and species limiting for positivity provided the robustness to the modified Newton-Raphson scheme used in this work. The technique also ensured a rapid drop in the L^2 norm, and thus quick convergence. The iteration procedure was terminated when the L^2 norm was below a prescribed convergence criterion. All simulations studied in this work were started by setting $\alpha = 1$. For most of the cases studied in this work, the final value of α was above 0.99. Iterations for the Newton-Raphson scheme were terminated when the L^2 norm was below 10^{-25} . The use of analytical forms of the source term vector and Jacobian matrix along with optimized LAPACK routines makes the solution of the system of Eq. (8) extremely fast.

The methodology described above allows the user to test various fuel-additive combinations without any code modifications. Thus, it is a valuable design tool for analyzing rich and lean fuel-additive-air mixtures.

3 Results and Discussion

This section focuses on three aspects: verification of the Newton-Raphson solver, the computational time and robustness of the solver, and applications of this solver to compute equilibrium compositions of various fuel-additive-air mixtures. The primary application of this numerical tool is in understanding the impact of temperature, pressure, and equivalence ratio on the formation of equilibrium products of combusting mixtures. Since the equilibrium composition of the combustion products includes species such as NO, CO, C₂H₂ and HCN, this numerical tool can also be used to compare emissive products from the combustion of various fuel-additive-air mixtures.

3.1 Verification of the Newton-Raphson solver

Various fuel-additive air mixtures at various temperatures and pressures were used to rigorously test the solver. Results for pentane-methanol-air, pentane-methane-air, and rich pentane-air mixtures at a range of temperatures (2200–3200 K) and pressures (35–80 atm) are presented in Tables 3 to 5. These results demonstrate the ability of the Newton-Raphson solver to compute equilibrium concentrations of complex hydrocarbon mixtures over a range of temperatures and pressures relevant to engine operating conditions. All computations were conducted by using the constant pressure/constant temperature constraint. As seen in Tables 3 to 5, the results computed by using the Newton-Raphson solver in this work are in excellent agreement with those computed by using STANJAN [13], thus verifying the accuracy of the Newton-Raphson solver.

3.2 Computation time required for the simulation

Robustness, computational time, and wide applicability are important considerations for design and analysis tools. These issues are discussed next with reference to the new method presented.

For lean fuel-additive-air mixtures, obtaining equilibrium concentrations at a prescribed temperature and pressure typically took about 10–20 iterations, requiring a total time of less than 1 millisecond on a single-CPU 3 GHz machine. An entire sequence of 360 equilibrium calculations (conducted every CAD) for the compression/expansion stroke of a typical automotive engine cycle took about 100 milliseconds. These computations were thus about 3 orders of magnitude faster than computations conducted with STANJAN/CHEMKIN, which take on the order of 3–15 seconds for a single equilibrium calculation at a given temperature, pressure, and mixture composition.

Equilibrium calculations of rich mixtures took about 50–250 iterations, depending on temperature, pressure, and operating conditions. The time required for computing the equilibrium concentration of a rich fuel-air mixture for a single prescribed value of temperature and pressure was on the order of 5–20 milliseconds. The Newton-Raphson solver used in this work was extremely robust. Figure 2 shows the drop in residuals with iterations for a stoichiometric pentane-air mixture ($\phi=1$) and a rich pentane-air mixture ($\phi=5$) starting from an initial mixture consisting only of pentane and air (oxygen and nitrogen). The residuals drop by about 150 orders of magnitude in about 50 iterations for the stoichiometric case, whereas about 250 iterations are needed for the fuel-rich case. No numerical instability or divergence was observed for a wide range of temperatures, pressures, and mixture compositions studied in this work.

From this discussion, one can see that the adaptation of the Newton-Raphson method developed in this work is robust and computationally fast for the system of 20x20 coupled equations. Since the methodology allows the user to define the fuel and additive as inputs, the same solver can be used to study a range of fuel-additive-air mixtures and hence can be used as a reliable design tool. This work demonstrated that the Newton-Raphson method can be used to achieve good numerical stability and robustness and short computational times (on the order of milliseconds) without resorting to ad hoc reduction of the system of nonlinear equations as in [7] or using a hybrid method as in [6] for a range of fuel-additive-air mixtures, thus demonstrating the wide applicability of the method.

3.3 Applications

The numerical tool developed in this work was used to compute equilibrium products for a wide variety of hydrocarbon-air mixtures at different temperatures and pressures. The chosen hydrocarbon-air mixtures, temperatures, and pressures were representative of different fuel-

additive air mixtures used as engine fuels at different engine operating conditions. Two applications of using the equilibrium solver are described next.

3.3.1 Equilibrium concentration of fuel-rich hydrocarbon mixtures

Modern diesel engines use exhaust-gas recirculation for NO_x control. Introduction of EGR leads to reduced flame temperature and hence a reduction of NO_x . However, the combined effect of reducing charge-gas oxygen and temperatures due to EGR leads to incomplete combustion and increased particulate matter emissions. The numerical tool developed in this work was used to study important combustion products in fuel-rich (equivalence ratio >1) n-heptane-air and pentane-air mixtures. These mixtures were chosen because most theoretical computations use n-heptane as a diesel fuel surrogate [8]. Incomplete combustion of n-heptane can lead to the formation of lower hydrocarbons such as pentane. Unburned fuel (n-heptane) and partially burned fuel such as pentane lead to the formation of particulate matter in fuel-rich pockets in the combustion chamber. Figure 3 shows important species concentrations in fuel-rich pentane and n-heptane mixtures at $T = 2200 \text{ K}$ and $P = 80 \text{ atm}$. This particular temperature and pressure are representative of conditions in a diesel engine operating near full load close to top dead center (TDC). The equilibrium composition of combustion products for both pentane and n-heptane exhibit similar characteristics. As expected, there is a marked increase in CO and H_2 (almost 2 orders of magnitude) as the equivalence ratio ϕ increases above 2, with a corresponding drop in CO_2 and H_2O . Moreover, there is a marked increase in the concentration of HCN and C_2H_2 beyond an equivalence ratio of 3. C_2H_2 is believed to be a precursor in soot formation, and hence its concentration is important in understanding the effect of equivalence ratio on soot formation. Figure 4 shows the effect of temperature and pressure on the formation of C_2H_2 and HCN in

fuel-rich n-heptane air mixtures under two different operating conditions, namely, $T = 1500 \text{ K}$, $P = 35 \text{ atm}$ and $T = 2200 \text{ K}$, $P = 80 \text{ atm}$. The engine temperature and pressure are close to 1500 K and 35 atm after the beginning of the fuel injection (SOI) in a typical diesel engine, whereas $T = 2200 \text{ K}$, $P = 80 \text{ atm}$ corresponds to conditions near TDC toward the end of the fuel injection process. During the initial phase of droplet break-up and fuel combustion, the equivalence ratio in certain regions of the chamber is believed to be between 2 and 5 and hence was chosen for this study. At equivalence ratios below $\phi = 3$, formation of HCN and C_2H_2 is negligible. However, the concentration of these species increases dramatically beyond $\phi = 3$. As expected, at lower temperatures and pressures, the equilibrium concentration of C_2H_2 is higher, but it drops as the temperature and pressure increase during the compression stroke. At higher temperatures and pressures, the concentration of HCN increases as compared with its value at a lower temperature. These equilibrium computations qualitatively capture the trends reported in literature about the effect of EGR on soot formation. It is believed that combustion products in IC engines do not reach equilibrium on account of the continuously changing cylinder temperature and pressure; however, these equilibrium concentrations can provide a relative comparison between various fuel-air mixtures at various temperatures and pressure and hence can be used for design and analysis studies.

3.3.2 Effect of additives on equilibrium NO formation in dual-fuel engines

Dual-fuel engines run on a variety fuel-additive air mixtures. Dual-fuel diesel engines run using CH_4 and also other gaseous fuels such as C_2H_2 , H_2 , and CH_3OH . Experimental studies of such engines have been reported by various groups [15-17]. These dual-fuel engines have many advantages. For instance, dual-fuel diesel engines using natural gas operate on both natural gas

and diesel fuel simultaneously. The majority of the fuel burned is natural gas, whereas diesel fuel is used as a pilot to ignite the mixture. This strategy allows retention of the diesel compression ratio and the associated higher efficiency while burning cheap and clean natural gas. Dual-fuel engines can run on either liquid natural gas or compressed natural gas. Both fuels have relatively high octane numbers, which lead to performance improvements. Furthermore, engines running natural gas with diesel typically have 20% to 30% less CO₂ emissions. Dual-fuel engines can also be operated in the straight diesel mode, if need be, which greatly enhances its utility as a flexible fuel engine. Given these desirable features of dual-fuel engines, their design and optimization would benefit greatly if designers could evaluate the relative effects of the fuel-type, engine load, and speed on emissions. For instance, Lakshmanan and Nagarajan [16] report a 24% increase in NO emissions with a C₂H₂/diesel operation, and Papagiannakis et al. [15] report a reduction in NO with a CH₄/diesel operation. By studying the effect of temperature on the diesel-additive combination, some estimates of the impact of fuel-additive ratio on NO emissions can be obtained.

Figure 5 shows the effect of temperature on the equilibrium NO for various combinations of n-heptane and natural gas (CH₄). The number of moles of n-heptane and CH₄ was varied so as to maintain a constant value of enthalpy corresponding to a case of neat stoichiometric diesel operation (1 mole of n-heptane, 0 moles of CH₄). One can see that a stoichiometric n-heptane/CH₄ mixture with 0.1 moles of n-heptane and 1.457 moles of CH₄ has about a 5% lower NO concentration at conditions close to TDC (2000–2200 K) compared with neat diesel. As expected, an intermediate case with 0.5 moles of n-heptane and 0.78 moles of CH₄ results in less reduction of NO concentration. Equilibrium NO values computed at engine conditions a few crank angle degrees after EOC closely match engine-out NO predicted by reaction-rate

controlled NO models [18]. The reason is that at high temperatures and pressures existing in the engine close to TDC, the reaction kinetics responsible for NO formation approach equilibrium values. Use of equilibrium computations as shown in this section can thus provide good comparative estimates of the impact of additives on expected engine-out NO.

4 Conclusions

Chemical equilibrium calculations were conducted with a set of species relevant to a wide range of combustible fuel-additive-air mixtures using the equilibrium constant method. An adaptation of the Newton-Raphson method was developed in this work to solve the highly nonlinear, stiff system of equations describing the formation of the equilibrium products. It was shown that the solution methodology was fast and robust for a wide range of fuel-additive-air mixtures and was useful in studying the impact of temperature, pressure, and mixture composition on practical applications such as IC engines.

Acknowledgments: This work was supported by the U.S. Department of Energy under Contract DE-AC02-06CH11357.

References

1. Wallner, T., Miers, S. A., McConnell, S., "A comparison of ethanol and butanol as oxygenates using a direct-injection, spark-ignition engine," J. Eng. Gas Turbines Power 131(3) (2009).
2. Wallner, T., Frazee, R., "Study of regulated and non-regulated emissions from combustion of gasoline, alcohol fuels and their blends in a DI-SI engine," SAE paper 2010-01-1571, 2010.

3. Heywood, J. B., *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, 1988.
4. Perini, F., Paltrinieri, F., Mattarelli, E., “A quasi-dimensional combustion model for performance and emissions of SI engines running on hydrogen–methane blends,” *Int. J. of Hydrogen Energy* 35(10), 2010, 4687–4701.
5. Gordon, S. and McBride, B. I., “Computer program for calculation of complex chemical equilibrium compositions and applications,” NASA Reference Publication 1311, Oct. 1994.
6. Rashidi, M., “Calculation of equilibrium composition in combustion products,” *Chem. Eng. Technol.* 20 (1997) 571–575.
7. Rakopoulos, C. D., Hountalas, D. T., Tzanos E. I., G. N. Taklis, “A fast algorithm for calculating the composition of diesel combustion products using 11 species chemical equilibrium scheme,” *Advances in Engineering Software* 19 (1994) 109–119.
8. Som, S., “Development and validation of spray models for investigating diesel engine combustion and emissions,” Ph.D. dissertation, University of Illinois at Chicago, 2009.
9. K. Khanafer, S. M. Aithal, “Fluid-dynamic and NO_x computation in swirl burners,” *Int. J. Heat Mass Transfer* (2011), Vol. 54 (23-24) pp. 5030-5038
10. Tao, F., S. Srinivas, R. D. Reitz, D. E. Foster, “Comparison of three soot models applied to multi-dimensional diesel combustion simulations,” *JSME International Journal Series B* 48(4) (2005) 671–678.
11. Van Wylen, G. J., R. E. Sonntag, *Fundamentals of Classical Thermodynamics*, 2nd ed. John Wiley, New York, 1978
12. Kee, R. J., Rupley, F. M, Meeks E, Miller, J. A., “CHEMKIN-III: A FORTRAN chemical kinetics package for the analysis of gas-phase chemical and plasma kinetics,” Sandia technical report SAND96-8216, 1996.

13. <http://navier.engr.colostate.edu/tools/equil.html>
14. Biruduganti, M., Gupta, S., Bihari, B., McConnell, S., Sekar, R., “Air separation membranes – an alternative to EGR in large bore natural gas engines,” ASME Internal Combustion Engine 2009 spring technical conference paper ICES2009-76054, 2009.
15. Papagiannakis, R. G., Rakopoulos, C. D., Hountalas, D. T., Rakopoulos, D. C., “Emission characteristics of high speed, dual fuel, compression ignition engine operating in a wide range of natural gas/diesel fuel proportions,” Fuel 89(7) (2010) 1397–1406.
16. Lakshmanan, T., Nagarajan, G., “Experimental investigation on dual fuel operation of acetylene in a DI diesel engine,” Fuel Processing Technology 91(5) (2010) 496–503.
17. Lata, D. B., Misra, A., “Theoretical and experimental investigations on the performance of dual fuel diesel engine with hydrogen and LPG as secondary fuels,” Int. J. Hydrogen Energy 35(21) (2010) 11918 –11931.
18. Andersson, I., Eriksson, L., “A parametric model for ionization current in a four stroke SI engine”, J. Dynamic Systems, Measurement and Control, 2009, 131 (2)s. 1-11

Table 1: List of species

	Species*
1	C_xH_y (fuel)
2	$C_{x_1}H_{y_1}O_{z_1}$ (additive)
3	O_2
4	CO_2
5	H_2O
6	N_2
7	N
8	O
9	NO
10	OH
11	H
12	N_2O
13	CO
14	H_2
15	NO_2
16	HO_2
17	C
18	HCN
19	C_2H_2
20	C_xH_{y-1}

*x and y are the number of carbon and hydrogen atoms in the hydrocarbon; x_1 and y_1 , are the carbon and hydrogen atoms in the additive, while z_1 are the oxygen atoms in the additive.

Table 2: Elementary processes considered in this model

1	$\frac{1}{2}H_2 = H$	$k_1 = \frac{[H]}{[H_2]^{0.5}}\sqrt{P}$
2	$\frac{1}{2}O_2 = O$	$k_2 = \frac{[O]}{[O_2]^{0.5}}\sqrt{P}$
3	$\frac{1}{2}N_2 = N$	$k_3 = \frac{[N]}{[N_2]^{0.5}}\sqrt{P}$
4	$\frac{1}{2}H_2 + \frac{1}{2}O_2 = OH$	$k_4 = \frac{[OH]}{[H_2]^{0.5}[O]^{0.5}}$
5	$\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$	$k_5 = \frac{[NO]}{[N_2]^{0.5}[O]^{0.5}}$
6	$H_2 + \frac{1}{2}O_2 = H_2O$	$k_6 = \frac{[H_2O]}{[H_2][O_2]^{0.5}}(P)^{-0.5}$
7	$CO + \frac{1}{2}O_2 = CO_2$	$k_7 = \frac{[CO_2]}{[CO][O_2]^{0.5}}(P)^{-0.5}$
8	$NO + \frac{1}{2}O_2 = NO_2$	$k_8 = \frac{[NO_2]}{[NO][O_2]^{0.5}}(P)^{-0.5}$
9	$O_2 + \frac{1}{2}H_2 = HO_2$	$k_9 = \frac{[HO_2]}{[O_2][H_2]^{0.5}}(P)^{-0.5}$
10	$N_2 + \frac{1}{2}O_2 = N_2O$	$k_{10} = \frac{[N_2O]}{[N_2][O_2]^{0.5}}(P)^{-0.5}$
11	$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O$	$k_{11} = \frac{[CO_2]^x [H_2O]^{0.5y}}{[C_xH_y][O_2]^{x+0.25y}}(P)^{(0.25y-1)}$
12	$C_{x1}H_{y1}O_{z1} + \left(x1 + \frac{y1}{4} - \frac{z1}{2}\right)O_2 = x1CO_2 + \frac{y1}{2}H_2O$	$k_{12} = \frac{[CO_2]^{x1} [H_2O]^{0.5y1}}{[C_{x1}H_{y1}O_{z1}][O_2]^{x1+0.25y1-0.5z1}}(P)^{(0.25y1-1+0.5z1)}$

13	$C_x H_y = C_x H_{y-1} + H$	$k_{13} = \frac{[C_x H_{y-1}][H]}{[C_x H_y]} P$
14	$2C_x H_{y-1} = xC_2 H_2 + (y-x-1)H_2$	$k_{14} = \frac{[C_2 H_2]^x [H_2]^{(y-x-1)}}{[C_x H_{y-1}]^2} (P)^{(y-3)}$
15	$C_2 H_2 = 2C + H_2$	$k_{15} = \frac{[C]^2 [H_2]}{[C_2 H_2]} P^2$
16	$C_2 H_2 + N_2 = 2HCN$	$k_{16} = \frac{[HCN]^2}{[C_2 H_2][N_2]}$

Table 3: Verification of equilibrium composition of pentane-methanol mixture

Temperature (K)	3200
Pressure (atm)	35
C ₅ H ₁₂ (moles)	1
CH ₃ OH (moles)	0.1
O ₂ (moles)	8.15
N ₂ (moles)	30.644
All other species	1.0E-30

	Species	Equilibrium Mole Fraction (Current study)	STANJAN (Mole Fraction) [13]
1	C ₅ H ₁₂	1.186889E-58	0.0000E+00
2	CH ₃ OH	3.108337E-12	6.4634E-14
3	O ₂	1.790785E-02	1.7911E-02
4	CO ₂	6.401841E-02	6.4002E-02
5	H ₂ O	1.165357E-01	1.1653E-01
6	N ₂	6.902252E-01	6.9022E-01
7	N	6.506663E-06	6.5026E-06
8	O	4.830986E-03	4.8321E-03
9	NO	1.701193E-02	1.7019E-02
10	OH	1.936549E-02	1.9366E-02
11	H	5.280299E-03	5.2794E-03
12	N ₂ O	4.841432E-06	4.8389E-06
13	CO	5.227207E-02	5.2288E-02
14	H ₂	1.250074E-02	1.2501E-02
15	NO ₂	1.308406E-05	1.3075E-05
16	HO ₂	2.694174E-05	2.6933E-05

Table 4: Verification of equilibrium composition of pentane-methane-air mixture

Temperature (K)	2500
Pressure (atm)	35
C ₅ H ₁₂ (moles)	1
CH ₄ (moles)	1
O ₂ (moles)	10
N ₂ (moles)	37.6
All other species	1.0E-30

	Species	Equilibrium Mole Fraction (Current study)	STANJAN (Mole Fraction)
1	C ₅ H ₁₂	4.725217E-67	0.0
2	CH ₄	3.531725E-15	3.5264E-15
3	O ₂	3.992629E-03	3.9936E-03
4	CO ₂	1.052205E-01	1.0522E-01
5	H ₂ O	1.500578E-01	1.5006E-01
6	N ₂	7.218287E-01	7.2183E-01
7	N	4.168169E-08	4.1642E-08
8	O	1.533250E-04	1.5334E-04
9	NO	3.184135E-03	3.1852E-03
10	OH	2.748469E-03	2.7484E-03
11	H	2.063659E-04	2.0628E-04
12	N ₂ O	9.032364E-07	9.0274E-07
13	CO	1.021927E-02	1.0223E-02
14	H ₂	2.383271E-03	2.3828E-03
15	NO ₂	2.105280E-06	2.1039E-06
16	HO ₂	2.439475E-06	2.4386E-06

Table 5: Verification of equilibrium composition of rich pentane-air mixture ($\phi = 5$)

Temperature (K)	2200
Pressure (atm)	80
C ₅ H ₁₂ (moles)	5
CH ₄ (moles)	0
O ₂ (moles)	8
N ₂ (moles)	30.08
All other species	1.0E-30

	Species	Equilibrium Mole Fraction (Current study)	STANJAN (Mole Fraction)
1	C ₅ H ₁₂	4.725217E-67	0.0
2	CH ₄	3.531725E-15	3.5264E-15
3	O ₂	3.992629E-03	3.9936E-03
4	CO ₂	1.052205E-01	1.0522E-01
5	H ₂ O	1.500578E-01	1.5006E-01
6	N ₂	7.218287E-01	7.2183E-01
7	N	4.168169E-08	4.1642E-08
8	O	1.533250E-04	1.5334E-04
9	NO	3.184135E-03	3.1852E-03
10	OH	2.748469E-03	2.7484E-03
11	H	2.063659E-04	2.0628E-04
12	N ₂ O	9.032364E-07	9.0274E-07
13	CO	1.021927E-02	1.0223E-02
14	H ₂	2.383271E-03	2.3828E-03
15	NO ₂	2.105280E-06	2.1039E-06
16	HO ₂	2.439475E-06	2.4386E-06

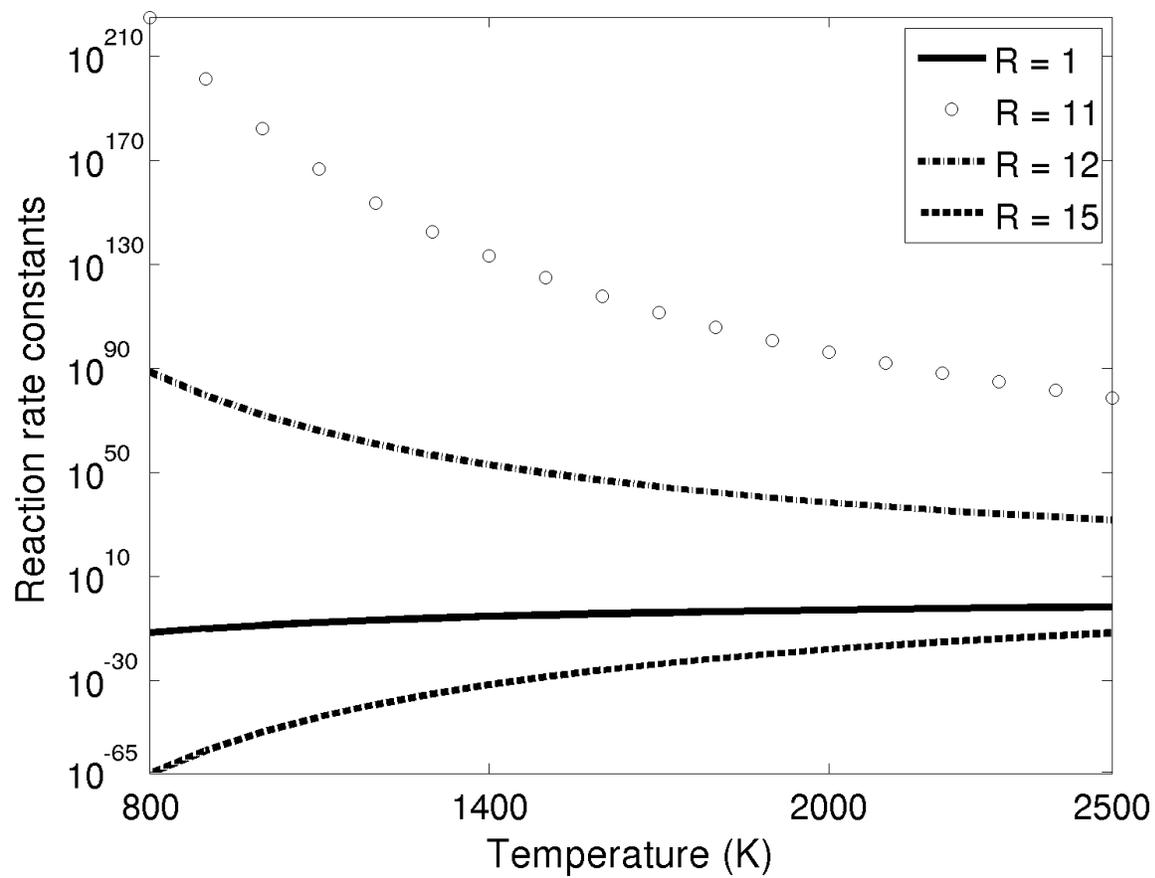


Figure 1: Variation of reaction rate constants with temperature.

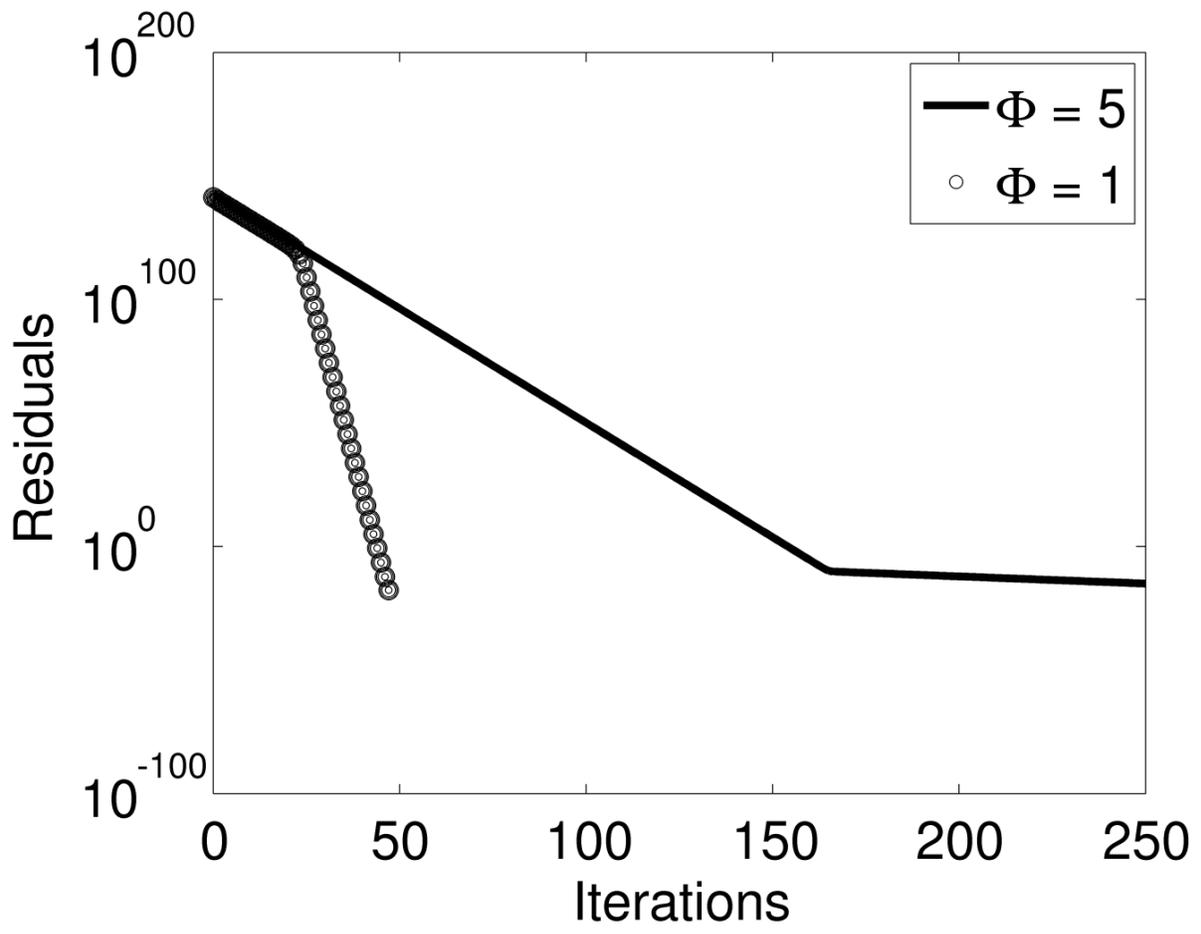
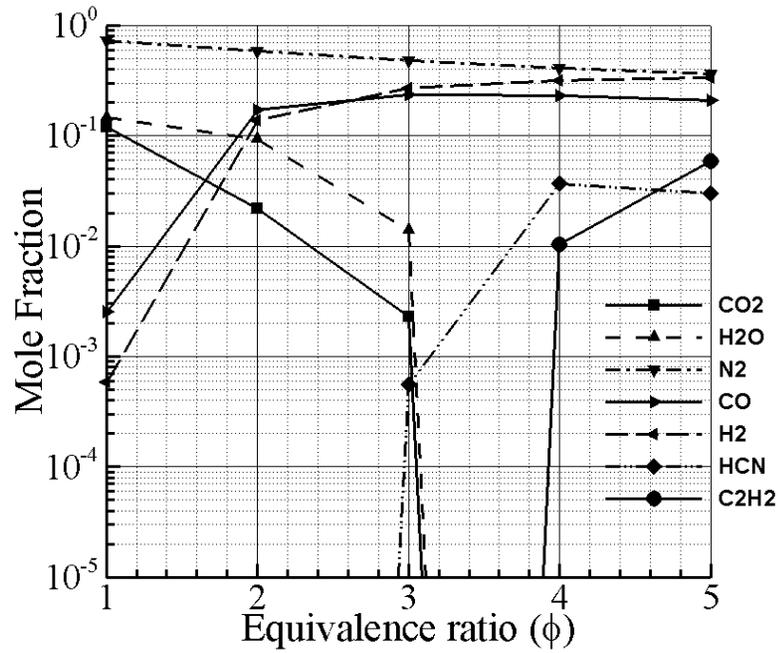
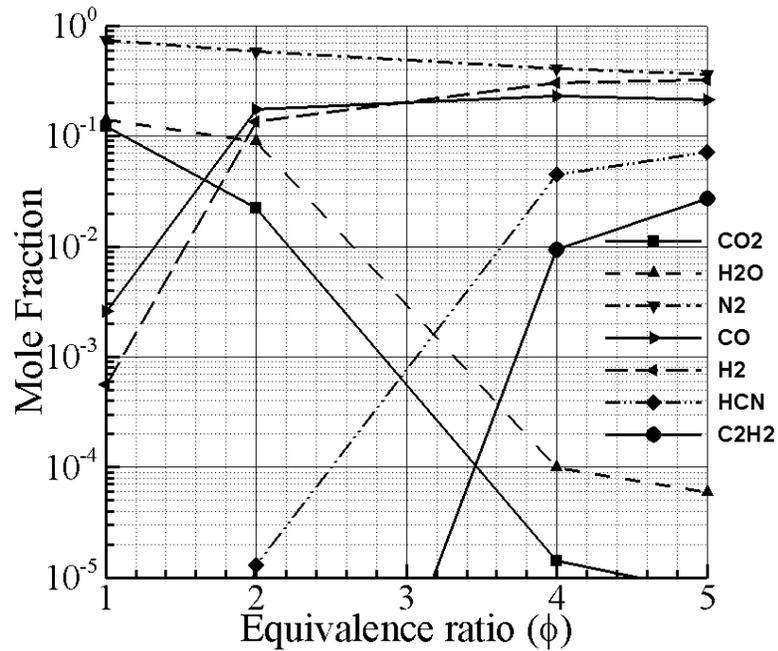


Figure 2: Variation of residuals with iterations for pentane-air mixtures.



(a)



(b)

Figure 3: Effect of equivalence ratio (ϕ) on species concentration: (a) pentane, (b) n-heptane.

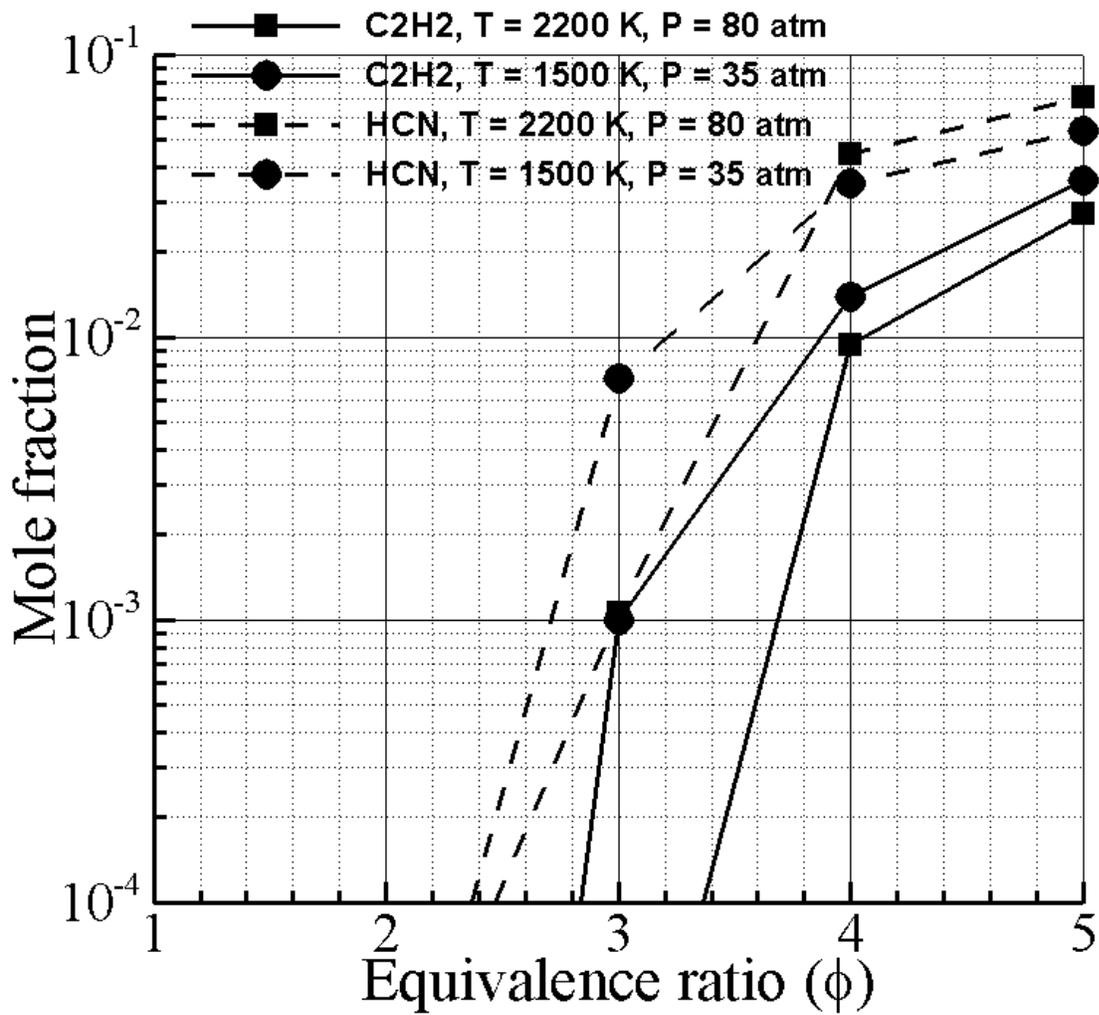


Figure 4: Effect of temperature and pressure on the formation of HCN and C₂H₂.

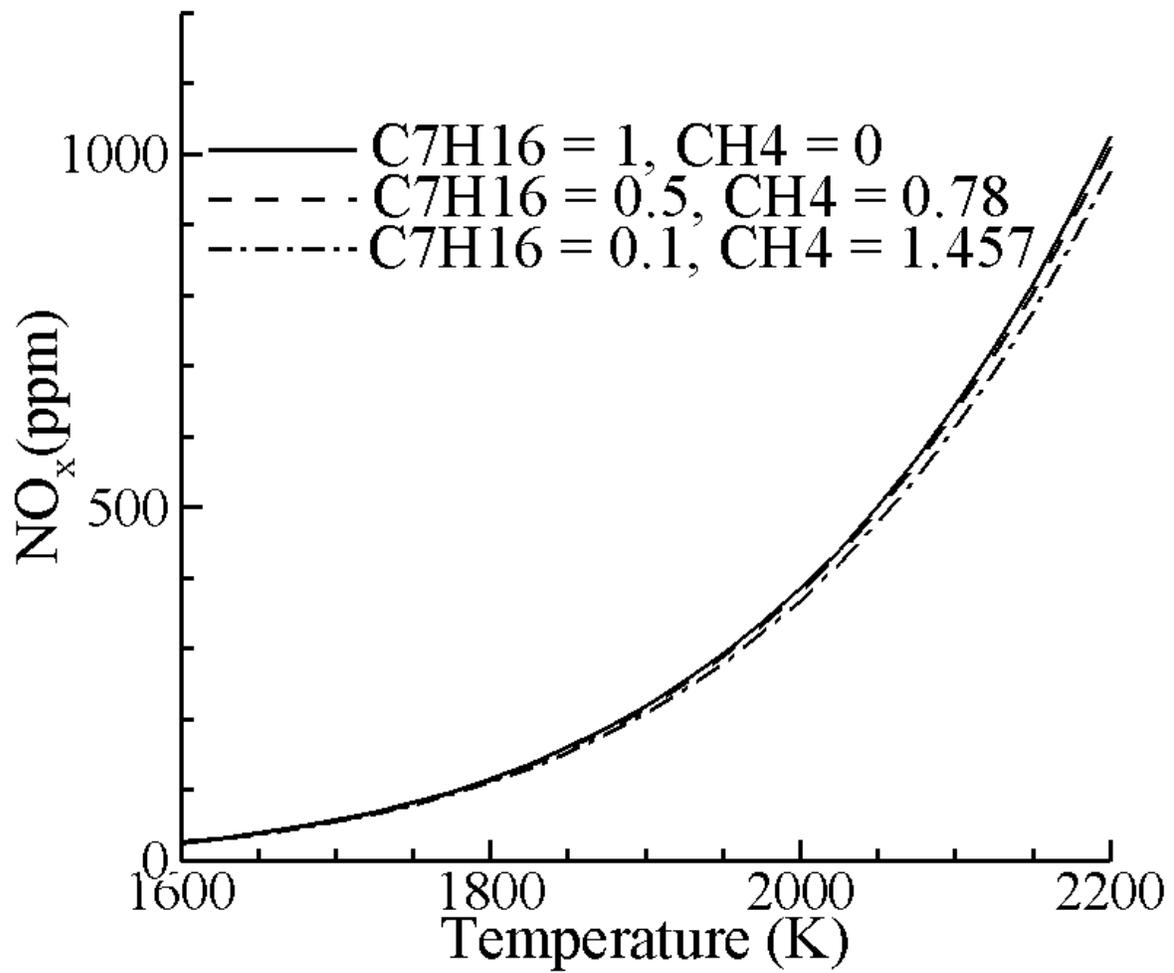


Figure 5: Variation of NO (ppm) with temperature for a natural-gas/diesel dual-fuel engine.

List of Tables

Table 1: List of species

Table 2: Elementary processes considered in this model

Table 3: Verification of equilibrium composition of pentane-methanol-air mixture

Table 4: Verification of equilibrium composition of pentane-methane-air mixture

Table 5: Verification of equilibrium composition of rich pentane-air mixture ($\phi = 5$)

List of figures:

Figure 1: Variation of reaction rate constants with temperature.

Figure 2: Variation of residuals with iterations for pentane-air mixture.

Figure 3: Effect of equivalence ratio (ϕ) on species concentration: (a) pentane, (b) n-heptane.

Figure 4: Effect of temperature and pressure on the formation of HCN and C₂H₂.

Figure 5: Variation of NO (ppm) with temperature for a natural-gas/diesel dual-fuel engine.

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.