

THE PENNSYLVANIA STATE UNIVERSITY
ENERGY AND GEO-ENVIRONMENTAL ENGINEERING
MATHEMATICAL METHODS FOR ENERGY SYSTEMS
PROF. DEREK ELSWORTH

Simulation of H₂-O₂ Constant Volume Combustion using Comsol Multiphysics™

Peter Perez

May 1st, 2007

1. Introduction

Traditional analysis of thermodynamics and efficiency of internal combustion engines is performed applying a mass and energy balance throughout the engine cycle according to the first law of thermodynamics [1]. Comprehensive analyses of idealized internal combustion engines are found in the literature, and these studies have served as the basis for further optimization of current engine technologies [2-5]. However, practical systems are far from the thermal efficiencies predicted by the first law due, among other factors, to the non-ideality and irreversibilities of real engine processes [6].

The main sources of irreversibilities occurring in a real diesel engine are due to the combustion reaction, the heat transfer to cylinder walls and the environment, and friction and mixing of gases through intake and exhaust valves [7,8]. Due to the irreversibilities of a system, part of the available energy, that otherwise would be used to produce work, is dissipated to create entropy. Many studies suggest that irreversibilities can be minimized by: (a) increasing combustion temperature to decrease the unrestrained character of the combustion reaction, (b) decreasing temperature differences across finite distances to reduce the heat flow and (c) decrease pressure drops and expansion across intake and exhaust valves [9-11].

The second law of thermodynamics offers a new perspective for the analysis of the performance of energy systems based on the concept of *availability*, a measure of the available energy to produce work [12,13]. Although this approach is not new [14-16], its application has been more extensive during the last 30 years [7]. A significant number of publications have been dedicated to the availability analysis of engine processes and the ways to decrease the availability destruction [17-24]. Rakopoulos and Giakoumis [25] and Caton [26] present a historical perspective and a summary of the main findings.

It is also of interest to study the entropy changes that accompany real engine processes, as the lost available work (\dot{W}_{lost}) is proportional to the rate of entropy generation (\dot{S}_{gen}) and the temperature of the environment (T_0) according to the Gouy-Stodola Theorem [27]: $\dot{W}_{lost} = T_0 \dot{S}_{gen}$. “Entropy Generation Minimization (EGM)”, “Thermodynamic Optimization” or “Finite Time Thermodynamics” are different names to describe the methods that use the second law of thermodynamics to analyze entropy generation during irreversible processes and the ways to minimize it [28-31].

In this project, the entropy generation rate will be calculated for the combustion of hydrogen in an internal combustion engine based on the formulation proposed by Hiwase et al. [32] and Daw [33] using a simple model for constant volume combustion. The ultimate goal is to develop a model to compute the lost available work as a function of engine and operational parameters. The conservation equations for mass and energy must be solved to find the mass velocity flows and temperature profiles in the combustion chamber, while the classical model proposed by Woschni [34] will be used to estimate the heat transfer coefficient and heat transfer rates to the cylinder walls.

2. Governing Equations

The governing equations for the simple model of a fuel droplet burning in a quiescent environment are presented below [32]. The droplet is surrounded by a spherically symmetric

flame in which the fuel and oxidizer react in stoichiometric proportions. The species of interest in the gas phase are fuel vapor, oxidizer and combustion products, while the liquid fuel is the only condensed phase [35]. Conservation of mass, conservation of energy and conservation of species in the gas phase are presented in Eq.1, Eq.2 and Eq.3:

Conservation of Mass:

$$\frac{\partial \rho^g}{\partial t} + \frac{1}{a} \frac{1}{r^2} \frac{\partial}{\partial r} (\rho^g r^g V_r) = 0 \quad (1)$$

Conservation of Energy:

$$\frac{\partial}{\partial t} (\rho^g C_p^g T^g) + \frac{1}{a} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho^g C_p^g T^g V_r) = \frac{1}{a^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho^g C_p^g \alpha^g \frac{\partial T^g}{\partial r} \right) + \dot{S}_E \quad (2)$$

Conservation of Species:

$$\frac{\partial}{\partial t} (\rho^g C_J) + \frac{1}{a} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho^g C_J V_r) = \frac{G}{a^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho^g D^g \frac{\partial C_J}{\partial r} \right) + \dot{S}_C \quad (3)$$

The source terms in the energy and species equations are given by:

$$\dot{S}_E = \lambda_f Da_i (\rho^g)^2 C_f C_o \exp \left(-\frac{E}{RT_i' T^g} \right) \quad (4)$$

$$\dot{S}_C = -\lambda_f Da_i (\rho^g)^2 \left(\frac{C_{p_i}^g T_i'}{Q} \right) \left(\frac{M_J}{M_f} \right) C_f C_o \exp \left(-\frac{E}{RT_i' T^g} \right) \quad (5)$$

3. Solution in Comsol Multiphysics™

The problem was setup using a simple 2D geometry and the coupled Fluid-Chemical Reactions sub-model in Comsol Multiphysics™. The following governing equations are included to solve the system:

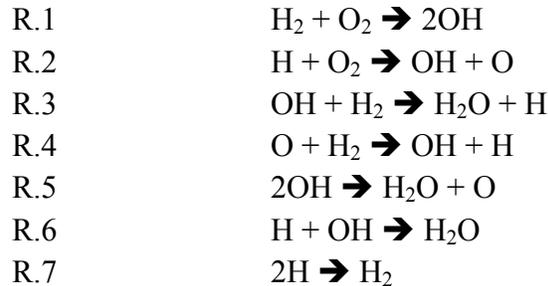
- Convection and Diffusion (Mass Conservation)
- Convection and Conduction (Energy Conservation)
- Incompressible Navier-Stokes (Momentum Conservation)

The following assumptions are considered:

- Reaction between hydrogen and oxygen occurs according to the “forward-only” 7-steps reaction model developed by the NASA Langley Research Center [36].

- Hydrogen and oxygen are fully mixed in a constant volume combustion chamber. No flows are considered before or after chemical reaction.
- Combustion is initiated by the effect of temperature, which is always above the autoignition temperature for H₂-O₂ (860K).
- Effect of pressure is not considered in the kinetic combustion model.
- Combustion chamber is thermally insulated (adiabatic combustion).

The kinetic model used to account for the production rates of the chemical species involved in the reaction is shown below:



The rate constants for the forward reactions are computed using the Arrhenius equation:

$$k_f = A \times T^B \times \exp\left(-\frac{T_a}{T}\right)$$

For which the kinetic parameters are shown below:

Table 1: Kinetic Parameters for H₂-O₂ Reactions			
Reaction	A $\left(\frac{m^3}{mol \cdot s}\right)$	B	T_a (K)
R.1	1.7×10^7	0.0	24,154.6
R.2	1.2×10^{11}	-0.91	8,309.7
R.3	2.2×10^7	0.0	2,591.6
R.4	5.1×10^{-2}	2.67	3,165.3
R.5	6.3×10^6	0.0	548.5
R.6	2.21×10^{16}	-2.0	0.0
R.7	7.3×10^{11}	-1.0	0.0

By applying the Law of Mass Action to the species participating in the elementary chemical reactions, we derived the following expressions to be included in the mass conservation equations to account for the consumption and production of species:

$$\frac{dC_{H2}}{dt} = -k_1 \cdot C_{H2} \cdot C_{O2} - k_3 \cdot C_{OH} \cdot C_{H2} + k_7 \cdot C_H \cdot C_H - k_4 \cdot C_O \cdot C_{H2}$$

$$\frac{dC_{O2}}{dt} = -k_1 \cdot C_{H2} \cdot C_{O2} - k_2 \cdot C_H \cdot C_{O2}$$

$$\frac{dC_{H2O}}{dt} = k_3 \cdot C_{OH} \cdot C_{H2} + k_5 \cdot C_{OH} \cdot C_{OH} + k_6 \cdot C_H \cdot C_{OH}$$

$$\frac{dC_{OH}}{dt} = 2k_1 \cdot C_{H2} \cdot C_{O2} + k_2 \cdot C_H \cdot C_{O2} - k_3 \cdot C_{OH} \cdot C_{H2} + k_4 \cdot C_O \cdot C_{H2} - 2k_5 \cdot C_{OH} \cdot C_{OH} - k_6 \cdot C_H \cdot C_{OH}$$

$$\frac{dC_H}{dt} = -k_2 \cdot C_H \cdot C_{O2} + k_3 \cdot C_{OH} \cdot C_{H2} + k_4 \cdot C_O \cdot C_{H2} - k_6 \cdot C_H \cdot C_{OH} - 2k_7 \cdot C_H \cdot C_H$$

$$\frac{dC_O}{dt} = k_2 \cdot C_H \cdot C_{O2} - k_4 \cdot C_O \cdot C_{H2} + k_5 \cdot C_{OH} \cdot C_{OH}$$

The solution for the constant volume combustion of hydrogen-oxygen was found using this setup. Figure 1 shows that the concentration of hydrogen and oxygen does not vary significantly with time, despite the initial temperature is well above the autoignition temperature of hydrogen. The result is somewhat contradictory because it would be expected that a “forward-only” kinetic model would lead to faster combustion rates. Validation against the known behavior of the system would allow us to compare the accuracy of the simulation using Comsol Multiphysics.

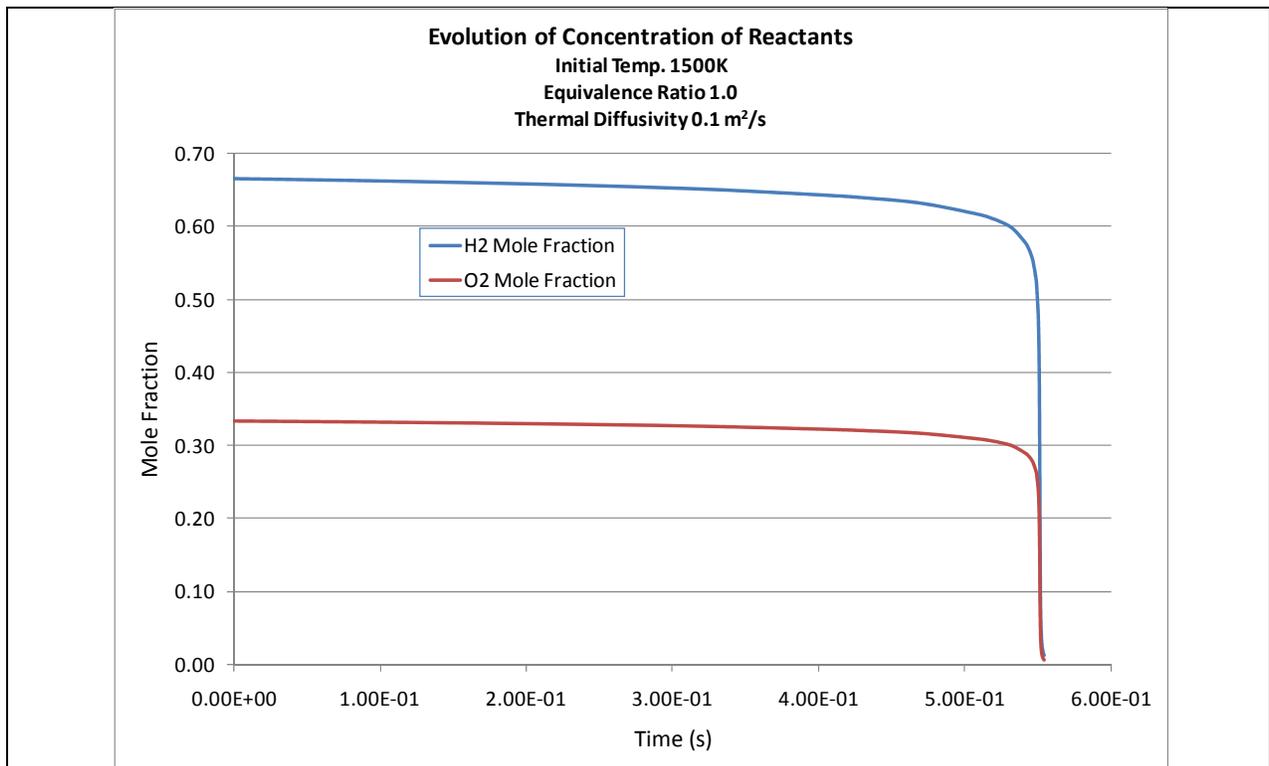


Figure 1: Evolution of Concentration of Reactants - Solution of H₂-O₂ Constant Volume Combustion using Comsol Multiphysics™

The rates of production of H₂O and OH species shown in Figure 2 behave in the same way of the rates of consumption. Production rates increase exponentially after 0.5 seconds with a sudden release of heat that increases combustion temperature to almost 4500K (Figure 3). The model gives negative values for the concentration of radicals O and H, and will not be considered.

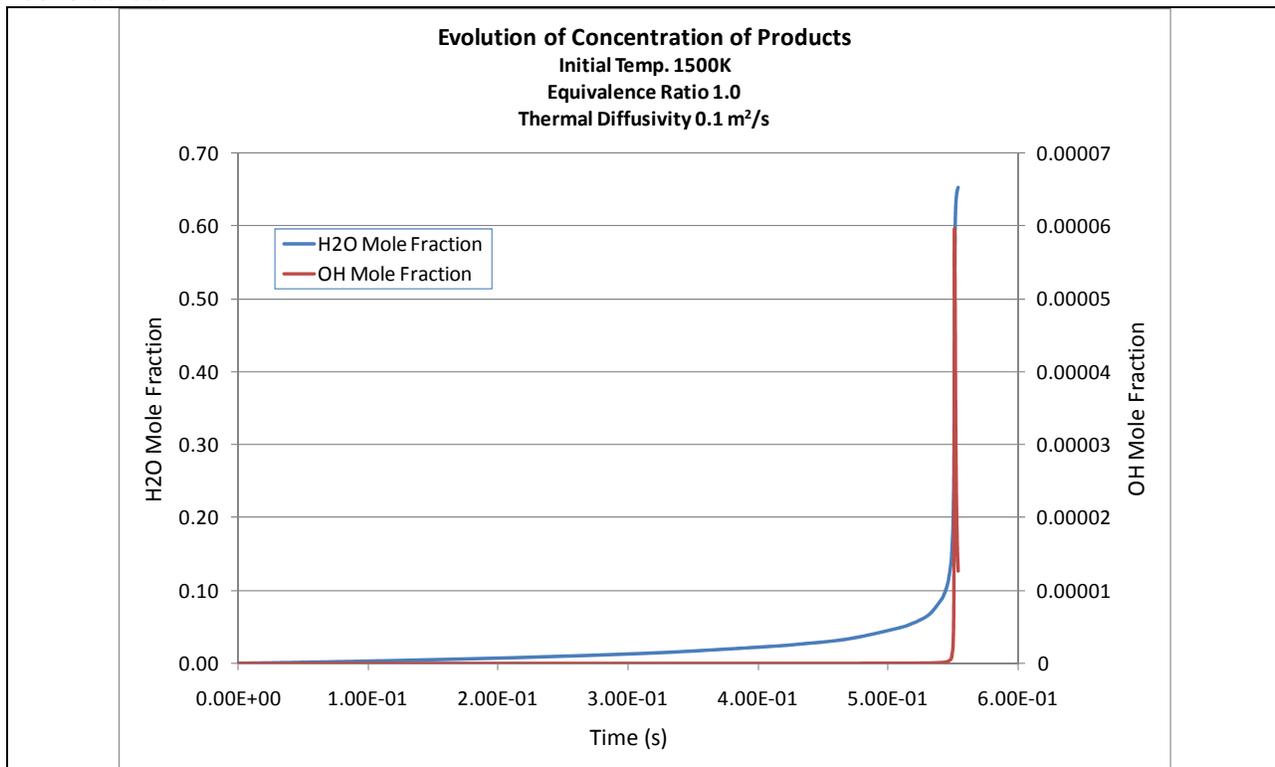
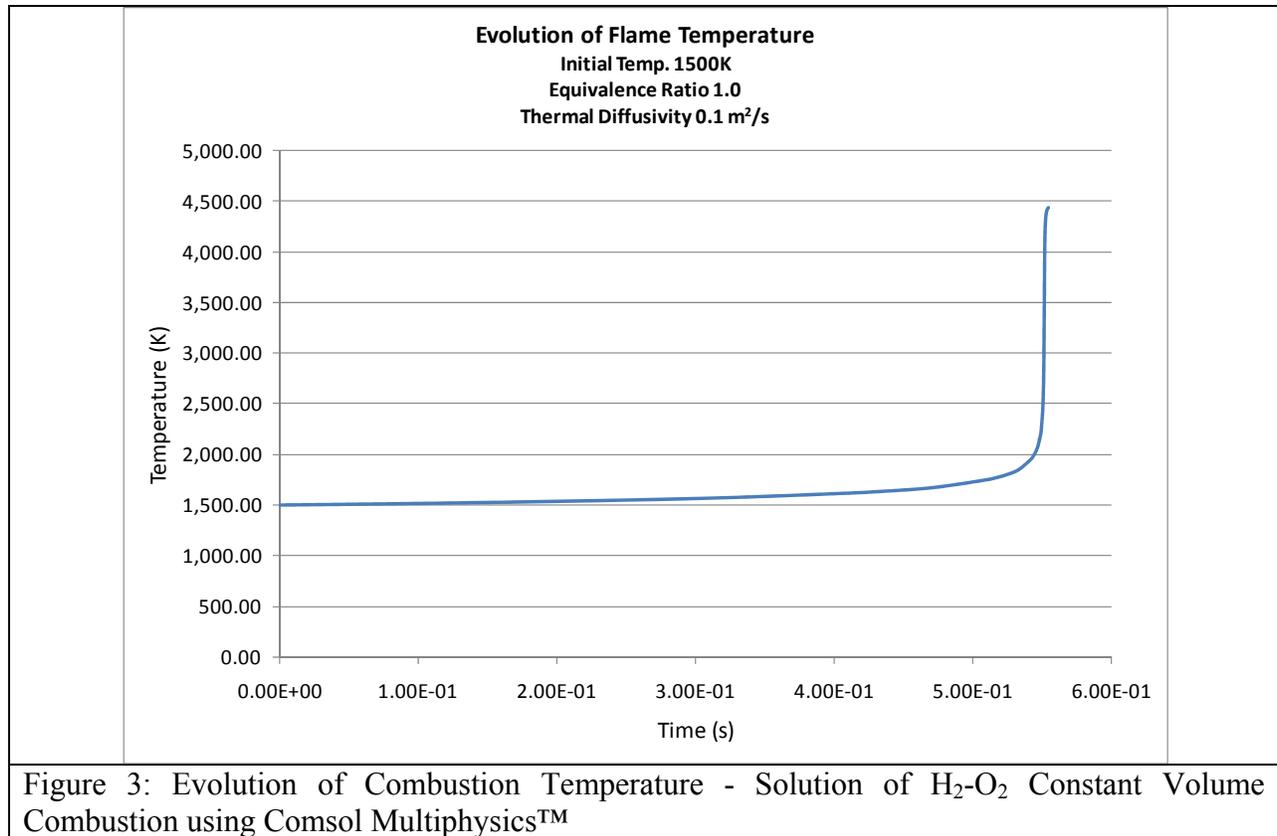


Figure 2: Evolution of Concentration of Products - Solution of H₂-O₂ Constant Volume Combustion using Comsol Multiphysics™



4. Validation

The results obtained with Comsol Multiphysics™ are compared with a simulation using the constant volume combustion module in CHEMKIN™, including a detailed kinetic mechanism for hydrogen oxidation [37]. Figure 4 shows that hydrogen is not completely consumed, but instead equilibrium is attained after 0.2 ms of reaction. The time scale also shows that hydrogen oxidation occurs at very fast rates, which is an indication that the kinetic model in Comsol Multiphysics™ does not capture the main features of the reaction.

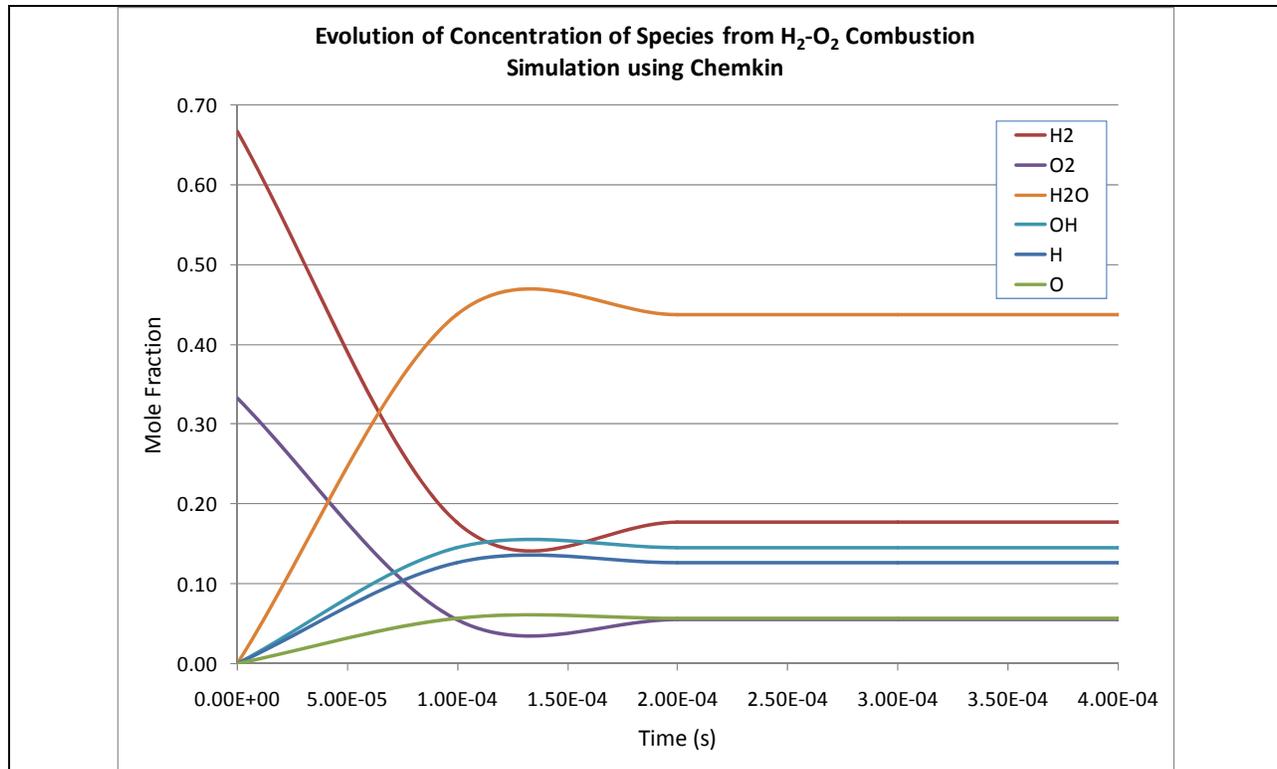


Figure 4: Constant Volume Combustion for H₂-O₂ Mixture – Simulation using CHEMKIN™
Initial temperature 1500K, Equivalence ratio 1.0

The temperature profile and adiabatic flame temperature is not significantly affected by the initial mixture temperature, as seen in Figure 5. Independently of the initial mixture temperature, final temperature is about 3350K. Concentration profiles (not shown) are not significantly affected either, which is consistent with the fact that adiabatic flame temperature strongly depends on the equivalence ratio (ϕ) [35].

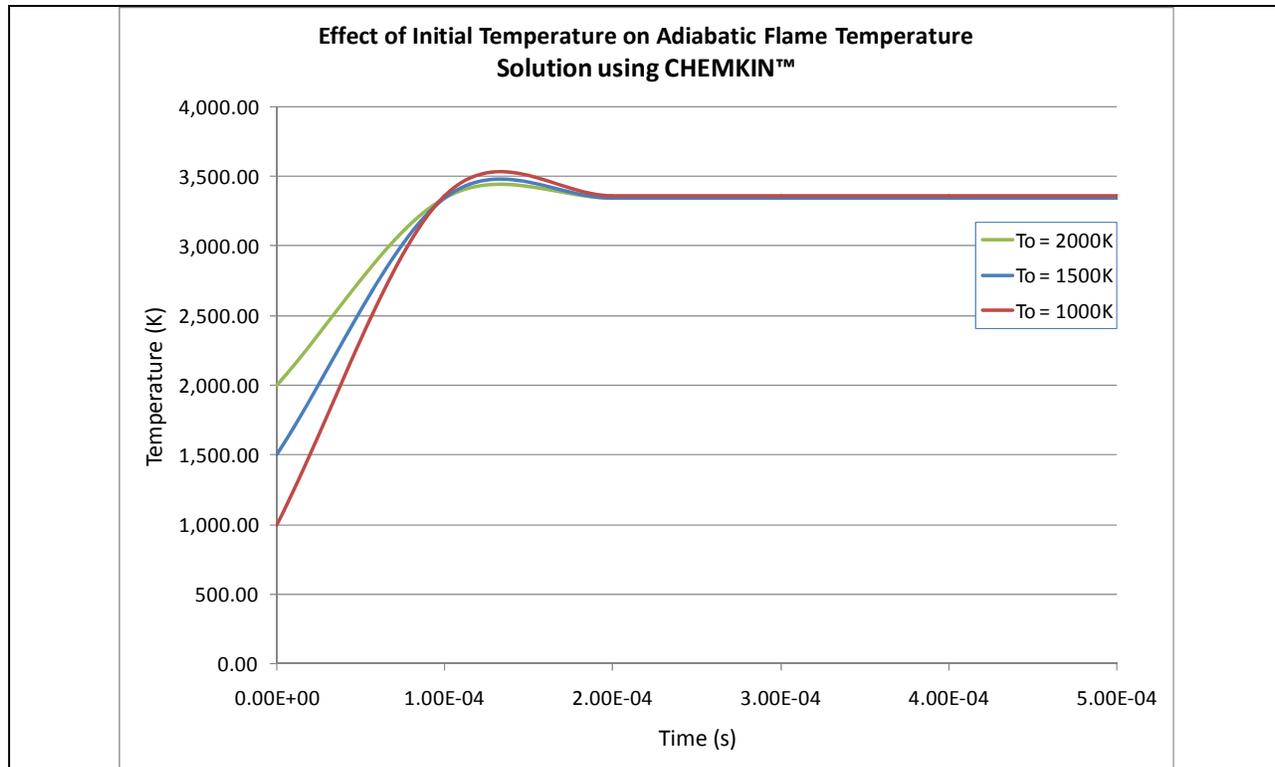


Figure 5: Effect of Initial Temperature on Adiabatic Flame Temperature of H₂-O₂ Reaction at Constant Volume – Simulation with CHEMKIN™.

5. Parametric Study

In this section we analyze the effect of initial mixture temperature (T_0), equivalence ratio (ϕ) and thermal diffusion coefficient (α) on the species concentration and temperature profiles of the H₂-O₂ constant volume combustion system. Figure 6 shows that initial mixture temperature reduces the time for consumption of hydrogen in a significant manner, although is always two orders of magnitude larger than the reaction times predicted by CHEMKIN™. As expected, reaction rates are exponentially accelerated as temperature increases. There seems to be no reaction at 1000 K, but it starts to be significant at 1500K. At 2000K, hydrogen is completely consumed after 0.012 seconds. As observed with CHEMKIN™, adiabatic flame temperature is not much affected by initial mixture temperature. This is observed in Figure 7, where the temperature profiles for 1500K and 2000K are presented. The profile at 1000K is not included because there is not reaction at this temperature.

In Figures 8 – 10 we present the effect of equivalence ratio on species concentration profiles and adiabatic flame temperature. Three cases are considered: (1) stoichiometric mixture ($\phi = 1.0$), (2) twice the stoichiometric oxygen ($\phi = 0.5$) and (3) half the stoichiometric oxygen ($\phi = 2.0$). Figure 8 shows that reaction rate increases at higher equivalence ratios (higher hydrogen mole fractions), while maximum conversion occurs at the stoichiometric equivalence ratio. The adiabatic flame temperature also exhibits the expected behavior, reaching the maximum at the stoichiometric equivalence ratio.

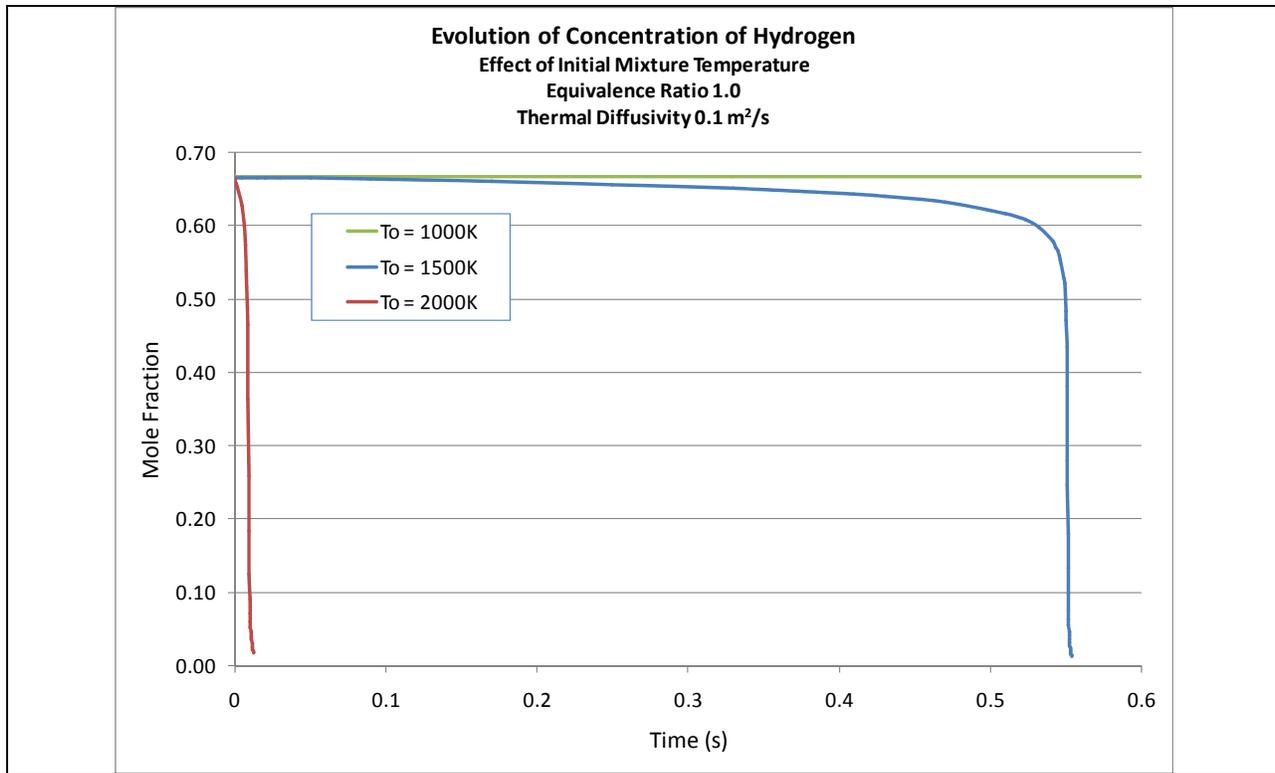


Figure 6: Effect of Initial Temperature on Evolution of H₂ Concentration

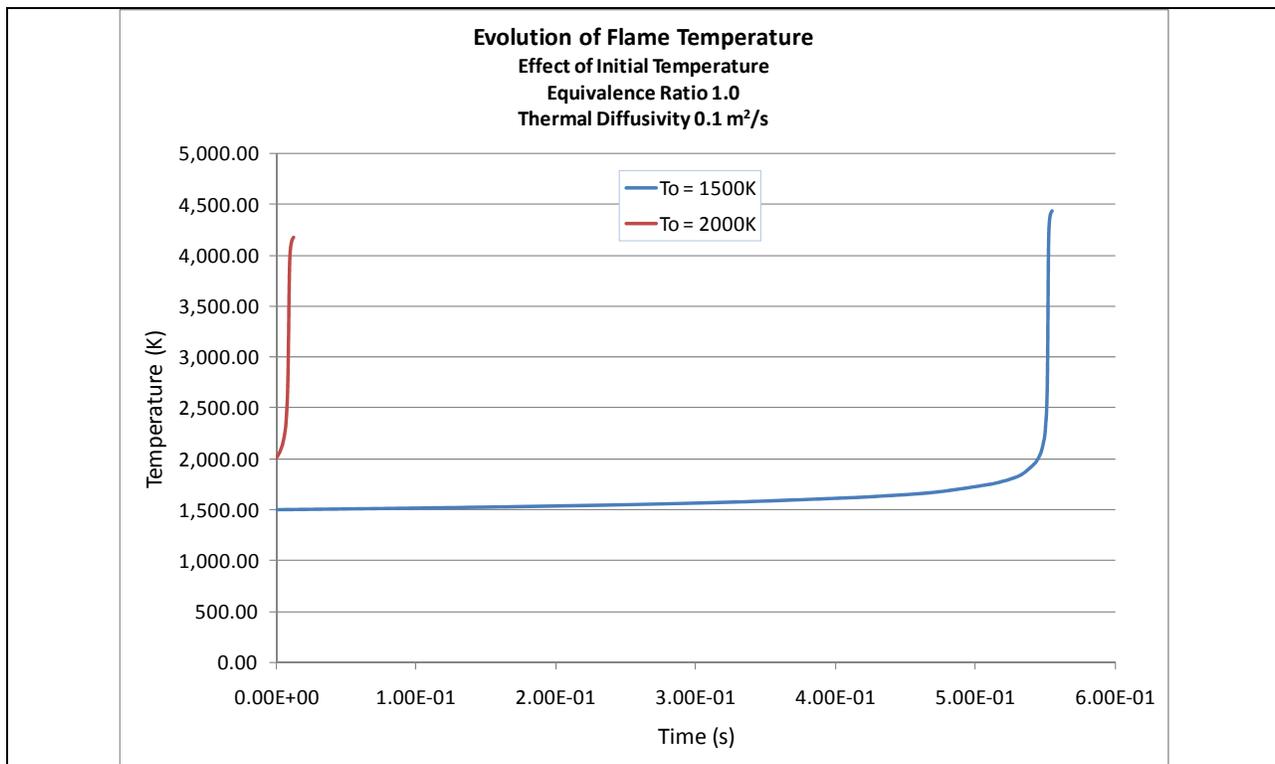


Figure 7: Effect of Initial Temperature of Evolution of Flame Temperature

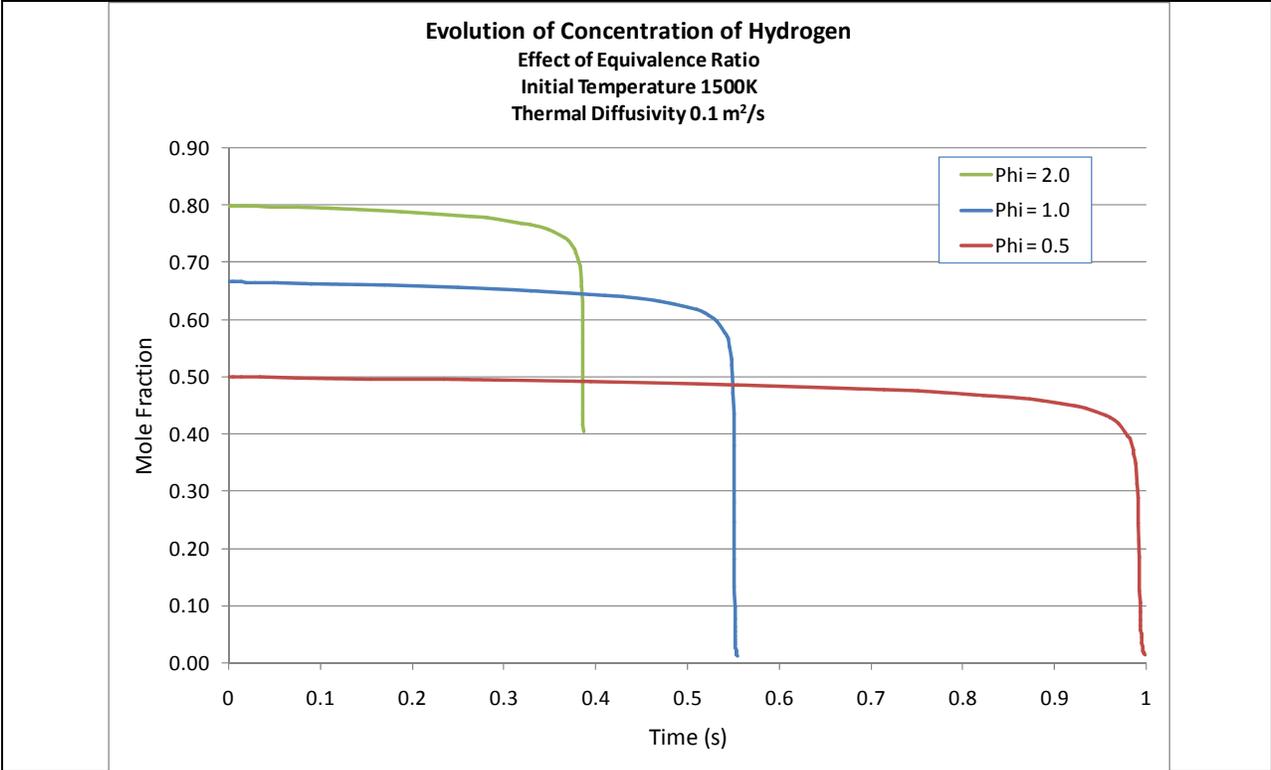


Figure 8: Effect of Equivalence Ratio on H₂ Concentration Profile

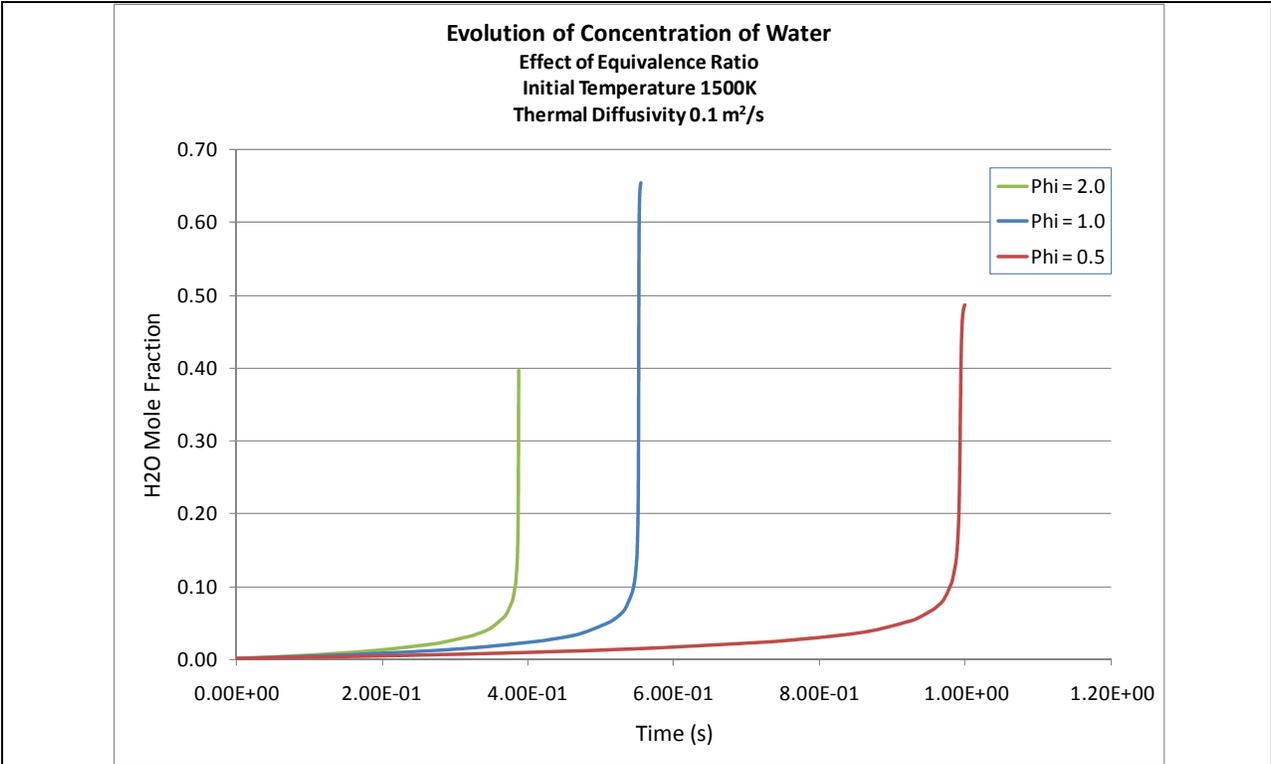


Figure 9: Effect of Equivalence Ratio on H₂O Concentration Profile

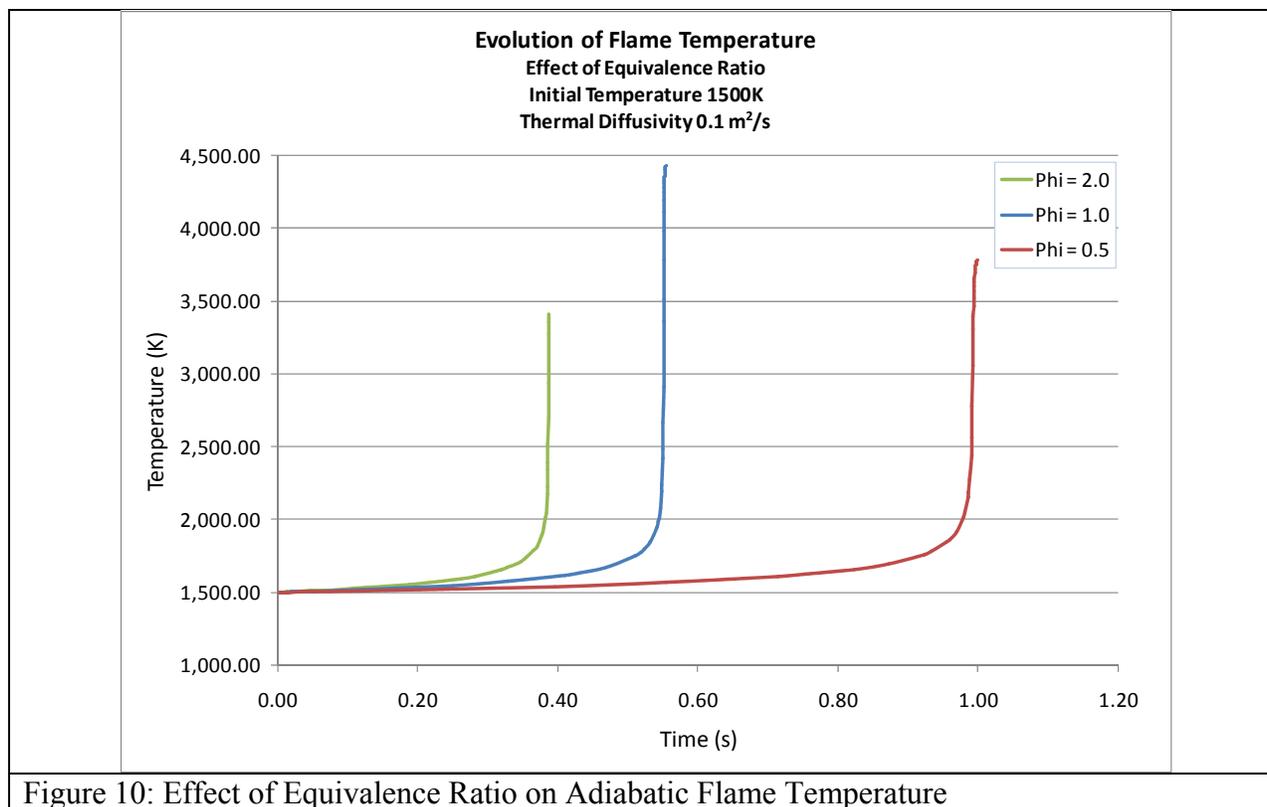


Figure 10: Effect of Equivalence Ratio on Adiabatic Flame Temperature

The effect of thermal diffusivity (α) on the results was also considered. While it was assumed that thermal diffusivity is the same for all the species, values of 0.01, 0.1 and 1.0 m²/s are considered as model parameters. In the simple reaction system considered (closed vessel, thermally insulated walls), the effect of thermal diffusivity should be negligible. This is confirmed by the results presented in Figures 11-13. The profiles for $\alpha = 0.01$ and $\alpha = 0.1$ m²/s are exactly the same in all cases, while at $\alpha = 1.0$ m²/s a change is observed, but the runs had to be stopped at 0.55 seconds due no convergence. We do not see any physical explanation to this issue, thus we assume that the problem must be in the Comsol solver. If the system was not adiabatic, one could argue that thermal energy is quickly dissipated to the surroundings and the acceleration of reaction due to heat release cannot be achieved. In the adiabatic case, the heat flux to the surroundings is explicitly forbidden.

From the experience using Comsol Multiphysics™ in this project, we want to highlight that the software is very powerful for simulation of physical processes, but the incorporation of realistic kinetic mechanisms is not straightforward unless we have the Reaction Engineering Module™. Even with the manual incorporation of the kinetic mechanism and thermodynamic data, it was not possible to predict correctly the production rates for a simple H₂-O₂ system and running times were excessively large. We regret having to spend too much time struggling with the chemistry and ending with no time to explore heat and mass transport processes in a more complex configuration, which was the initial objective of the project. Other limitation we faced is that 3D models cannot be productively developed in our Computer Lab (318 Hosler). The computers seem to be too slow for this application, even with the simplest configurations. It is our hope that this situation could be solved for the future students.

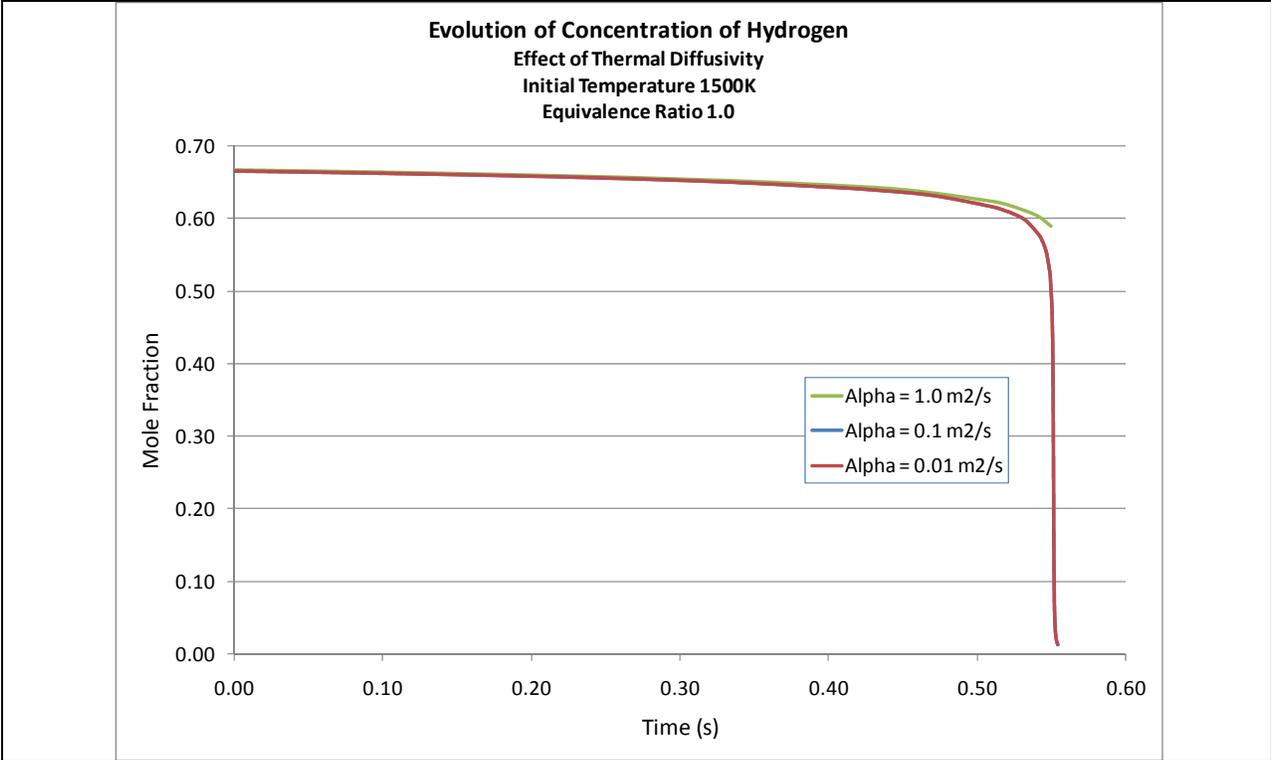


Figure 11: Effect of Thermal Diffusivity on H₂ Concentration Profile

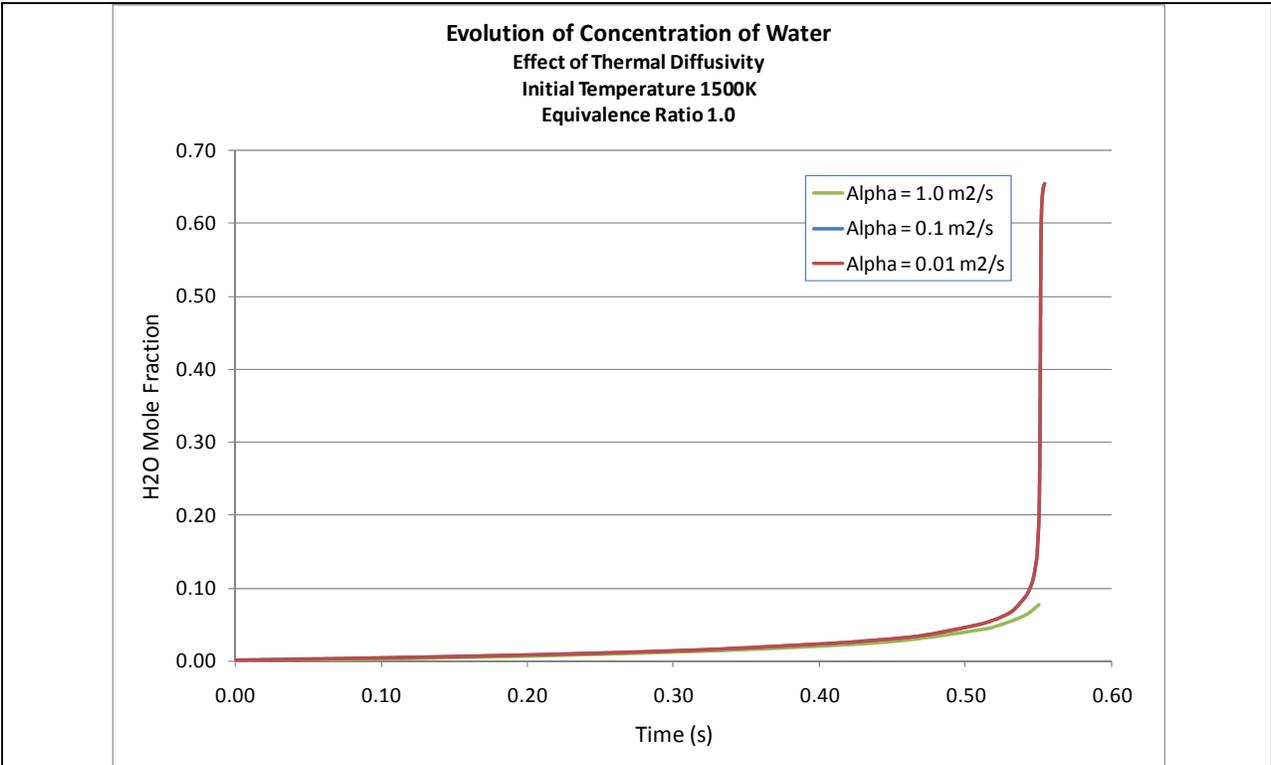
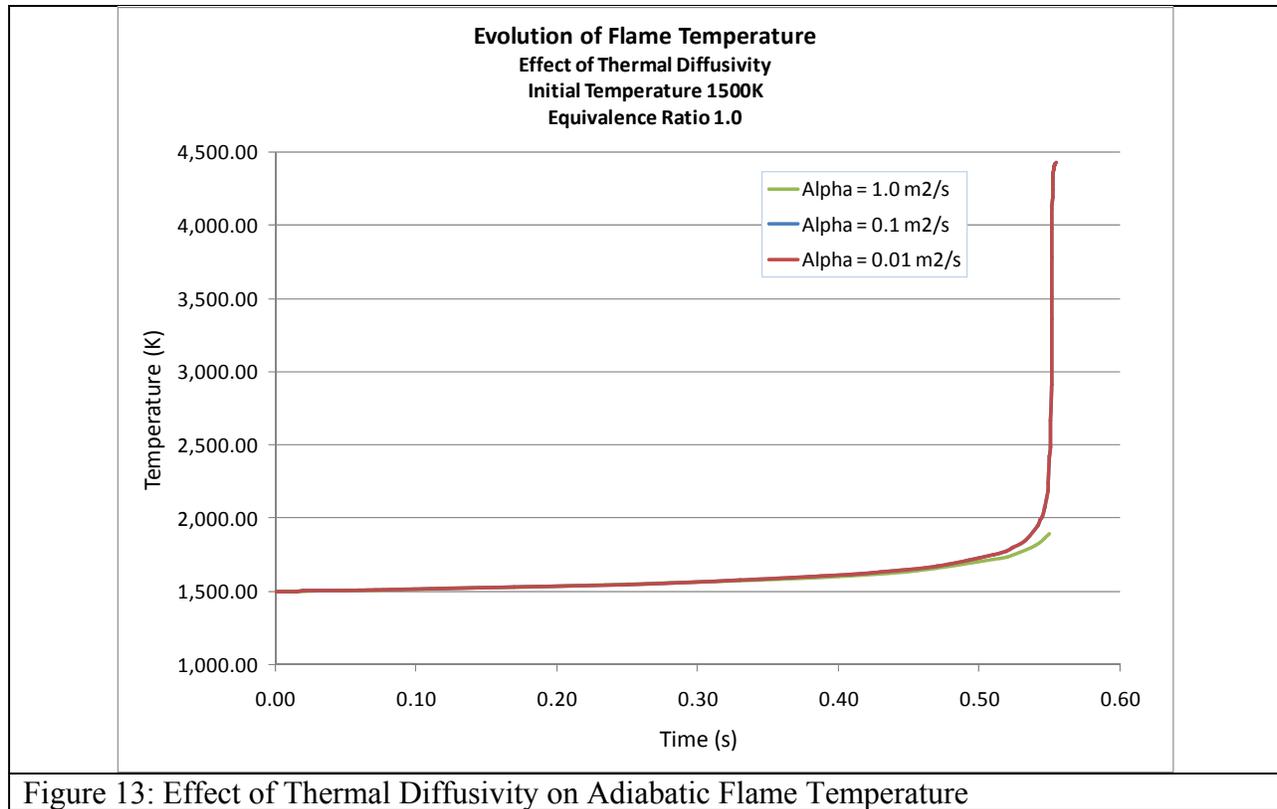


Figure 12: Effect of Thermal Diffusivity on H₂O Concentration Profile



6. Conclusions

Comsol Multiphysics™ has been used to simulate constant volume combustion of mixtures of hydrogen (H₂) and oxygen (O₂) using a 7-step forward-only kinetic mechanism. The model does not capture the features of the real system as predicted by CHEMKIN™ in terms of species profiles and adiabatic flame temperature. Species production rates are at least two orders of magnitude smaller compared to CHEMKIN™ simulation, while adiabatic temperatures are much higher due to the assumption of forward-only reactions (no equilibrium). However, the parametric study exhibits correct trends in terms of the effects of initial mixture temperature, equivalence ratio and thermal diffusivity. Further refinement of the model and higher computational capabilities are needed to reproduce experimental kinetic data, analyze heat and mass transfer in complex (open, non-adiabatic) systems and simulate the full performance 3D geometries.

Entropy generation and lost available work calculations were not considered as the model developed in Comsol™ lacks physical meaning, and processes of interest such as heat and mass transfer could not be included successfully in the model. This remains as part of future work to be considered by next students.

7. References

1. Heywood, J. B. (1988). *Internal Combustion Engine Fundamentals*. New York: McGraw-Hill.
2. Chan, S. H. (1998). Thermodynamics in a Turbocharged Direct Injection Diesel Engine. *Proceedings of the Institution of Mechanical Engineers Part D-Journal of Automobile Engineering*, 212(D1), 11-24.
3. Lapuerta, M., Armas, O., & Hernandez, J. J. (1999). Diagnosis of Di Diesel Combustion from in-Cylinder Pressure Signal by Estimation of Mean Thermodynamic Properties of the Gas. *Applied Thermal Engineering*, 19(5), 513-529.
4. Chan, S. H., & Zhu, J. (2001). Modelling of Engine in-Cylinder Thermodynamics under High Values of Ignition Retard. *International Journal of Thermal Sciences*, 40(1), 94-103.
5. Amann, C. A. (2005). Applying Thermodynamics in Search of Superior Engine Efficiency. *Journal of Engineering for Gas Turbines and Power-Transactions of the Asme*, 127(3), 670-675.
6. Hoffman, K. H., Watowich, S. J., & Berry, R. S. (1985). Optimal Paths for Thermodynamic Systems - the Ideal Diesel Cycle. *Journal of Applied Physics*, 58(6), 2125-2134.
7. Caton, J. A. (2000). On the Destruction of Availability (Exergy) Due to Combustion Processes - with Specific Application to Internal-Combustion Engines. *Energy*, 25(11), 1097-1117.
8. Chavannavar, P. S., & Caton, J. A. (2006). Destruction of Availability (Exergy) Due to Combustion Processes: A Parametric Study. *Proceedings of the Institution of Mechanical Engineers Part a-Journal of Power and Energy*, 220(A7), 655-669.
9. Aragon-Gonzalez, G., Canales-Palma, A., & Leon-Galicia, A. (2000). Maximum Irreversible Work and Efficiency in Power Cycles. *Journal of Physics D-Applied Physics*, 33(11), 1403-1409.
10. Aragon-Gonzalez, G., Canales-Palma, A., Leon-Galicia, A., & Musharrafie-Martinez, M. (2003). A Criterion to Maximize the Irreversible Efficiency in Heat Engines. *Journal of Physics D-Applied Physics*, 36(3), 280-287.
11. Zhao, Y. R., Lin, B. H., Zhang, Y., & Chen, J. C. (2006). Performance Analysis and Parametric Optimum Design of an Irreversible Diesel Heat Engine. *Energy Conversion and Management*, 47(18-19), 3383-3392.
12. Flynn, P. F., Hoag, K. L., Kamel, M. M., & Primus, R. J. (1984). A New Perspective on Diesel Engine Evaluation Based on Second Law Analysis. *SAE Technical Paper No. 840032*.
13. Primus, R. J., Hoah, K. L., Flynn, P. F., & Brands, M. C. (1984). An Appraisal of Advanced Engine Concepts Using Second Law Analysis Techniques. *Sae Technical Paper No. 841287*.
14. Moran, M. J., & Shapiro, H. N. (2000). *Fundamentals of Engineering Thermodynamics* (4th ed.). New York: Wiley.
15. Haywood, R. W. (1974). Critical Review of Theorems of Thermodynamic Availability with Concise Formulations .2. Irreversibility. *Journal of Mechanical Engineering Science*, 16(4), 258-267.

16. Haywood, R. W. (1974). Critical Review of Theorems of Thermodynamic Availability, with Concise Formulations .1. Availability. *Journal of Mechanical Engineering Science*, 16(3), 160-173.
17. Descombes, G., Maroteaux, F., & Feidt, M. (2003). Study of the Interaction between Mechanical Energy and Heat Exchanges Applied to Ic Engines. *Applied Thermal Engineering*, 23(16), 2061-2078.
18. Rakopoulos, C. D., Andritsakis, E. C., & Kyritsis, D. K. (1993). Availability Accumulation and Destruction in a Di Diesel-Engine with Special Reference to the Limited Cooled Case. *Heat Recovery Systems & Chp*, 13(3), 261-276.
19. Rakopoulos, C. D., & Giakoumis, E. G. (1997). Simulation and Exergy Analysis of Transient Diesel-Engine Operation. *Energy*, 22(9), 875-885.
20. Rakopoulos, C. D., & Giakoumis, E. G. (1997). Speed and Load Effects on the Availability Balances and Irreversibilities Production in a Multi-Cylinder Turbocharged Diesel Engine. *Applied Thermal Engineering*, 17(3), 299-313.
21. Rakopoulos, C. D., & Giakoumis, E. G. (1997). Development of Cumulative and Availability Rate Balances in a Multi-Cylinder Turbocharged Indirect Injection Diesel Engine. *Energy Conversion and Management*, 38(4), 347-369.
22. Rakopoulos, C. D., & Kyritsis, D. C. (2001). Comparative Second-Law Analysis of Internal Combustion Engine Operation for Methane, Methanol, and Dodecane Fuels. *Energy*, 26(7), 705-722.
23. Rakopoulos, C. D., & Giakoumis, E. G. (2004). Availability Analysis of a Turbocharged Diesel Engine Operating under Transient Load Conditions. *Energy*, 29(8), 1085-1104.
24. Rakopoulos, C. D., & Giakoumis, E. G. (2006). Comparative First- and Second-Law Parametric Study of Transient Diesel Engine Operation. *Energy*, 31(12), 1927-1942.
25. Rakopoulos, C. D., & Giakoumis, E. G. (2006). Second-Law Analyses Applied to Internal Combustion Engines Operation. *Progress in Energy and Combustion Science*, 32(1), 2-47.
26. Caton, J. A. (2000). A Review of Investigations Using the Second Law of Thermodynamics to Study Internal Combustion Engines. *SAE Technical Paper No. 2000-01-1081*.
27. Bejan, A. (1982). *Entropy Generation through Heat and Fluid Flow*. New York: Wiley.
28. Bejan, A. (1996). Entropy Generation Minimization: The New Thermodynamics of Finite-Size Devices and Finite-Time Processes. *Journal of Applied Physics*, 79(3), 1191-1218.
29. Orlov, V. N., & Berry, R. S. (1993). Power and Efficiency Limits for Internal-Combustion Engines Via Methods of Finite-Time Thermodynamics. *Journal of Applied Physics*, 74(7), 4317-4322.
30. Chen, L. G., Wu, C., & Sun, F. R. (1999). Finite Time Thermodynamic Optimization or Entropy Generation Minimization of Energy Systems. *Journal of Non-Equilibrium Thermodynamics*, 24(4), 327-359.
31. Durmayaz, A., Sogut, O. S., Sahin, B., & Yavuz, H. (2004). Optimization of Thermal Systems Based on Finite-Time Thermodynamics and Thermoeconomics. *Progress in Energy and Combustion Science*, 30(2), 175-217.
32. Hiwase, S. D., Datta, A., & Som, S. K. (1998). Entropy Balance and Exergy Analysis of the Process of Droplet Combustion. *Journal of Physics D-Applied Physics*, 31(13), 1601-1610.

33. Daw, C. S., Chakravarthy, K., Conklin, J. C., & Graves, R. L. (2006). Minimizing Destruction of Thermodynamic Availability in Hydrogen Combustion. *International Journal of Hydrogen Energy*, 31(6), 728-736.
34. Woschni, G. (1968). Universally Applicable Equation for Instantaneous Heat Transfer Coefficient in Internal Combustion Engine. *Sae Transactions*, 76, 176-&.
35. Turns, S. R. (2000). *An Introduction to Combustion : Concepts and Applications* (2nd ed.). Boston: McGraw-Hill.
36. Rogers, R. C., & Chinitz, W. (1983). Using a Global Hydrogen-Air Combustion Model in Turbulent Reacting Flow Calculations. *Aiaa Journal*, 21(4), 586-592.
37. O Conaire, M., Curran, H. J., Simmie, J. M., Pitz, W. J., & Westbrook, C. K. (2004). A Comprehensive Modeling Study of Hydrogen Oxidation. *International Journal of Chemical Kinetics*, 36(11), 603-622.