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Foreword

This first issue of *The Iranian Journal of Chemical Engineering (IJChE)*, as a forum for dissemination of chemical engineering knowledge at national and international levels, is going into a timely press and circulation, as two developments in recent years have enhanced the need for the Journal. First, restructuring Iran´s higher education system through establishment of an integrated Ministry of Science, Research and Technology with significant growth in research funding; and second, the unprecedented boom in the petrochemical, gas and oil process industries, which demand further chemical engineering research.

This publication belongs to *The Iranian Association of Chemical Engineering (IAChE)*, which has been very active in organizing scientific events including annual national conferences and publishing a number of other journals. *IAChE* has been successful in facilitating communications among chemical engineers of Iran, both in academia and in the industries.

Chemical engineering is a vigorous and dynamic discipline, where in addition to the traditional core of the field, many new interdisciplinary areas have evolved in recent decades. It is expected that this journal could be an appropriate forum for publication of research findings in all of these areas.

It is my pleasure to welcome all readers of the first issue of this new journal. I would also like to thank our distinguished contributors, Board of Editors and reviewers, who made this publication a reality. I would also like to appreciate the co-operations and support of the Deputy Minister for Research of the Ministry of Science, Research and Technology. We hope that with continued support and contributions of Iranian and international researchers, this journal can receive proper recognition in the scientific community.

Jafar Towfighi
Editor-in-chief

Investigation of Pollutant Generation by Simulation of Premixed Gaseous Combustion Using Aspen Plus

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ABSTRACT

The mechanism of air pollutant generation during combustion of gaseous fuels is simulated with ASPEN Plus process simulator release 9.1 -3 (1994). Based on the concept of minimization of total Gibbs free energy of the system, adiabatic flame temperatures for several stoichiometric fuel/air mixtures are calculated. Analysis of combustion products including air pollutants with concentrations as low as 1 ppb is carried out and compared with previous works. Sensitivity analysis to study the effect of changing reaction temperature and fuel/air ratio on pollutant concentrations are also carried out and the results are discussed. Detailed tables and various graphical resul ts are presented, demonstrating the powerful capabilities of ASPEN Plus in combustion modeling and air pollution studies.

Keywords: *Air Pollution, Combustion Simulation, Premixed Flames, Gaseous Combustion, Pollutants Generation, ASPEN Plus*

Introduction

Modern process simulators are powerful and helpful tools to study and imitate chemical reactions, analyse product streams and optimize process parameters without using expensive equipment, laboratory materials and precise measuring instruments.

Many researchers believe that with continuing rapid progress in computer modeling, we may eventually reach the state of being able to predict the performance of turbulent multi -reaction systems without recourse to costly exprimentation [1]. ASPEN, PRO -II, PROvision, HYSIM, PROCEDE, ASCEND and SPEED -UP are some known simulation packages used in a wide variety of chemical engineering applications. Most of them are sequential oriented, are menu-driven and are used to study the steady state operations. The last two are equation-oriented and capable of dynamic simulation, which includes analysis of transient and time-dependent precesses.

In this work, ASPEN Plus release 9.1 -3 was employed to simulate the combustion reactions of pre-mixed gaseous mixtures and to investiga te the mechanism of air pollution generation. This process simulator, which was developed at Massachusetts Institute of Technology, U.S.A., incorporates up-to-date databanks for pure component properties based on the American Institute of Chemical Engineer ing DIPPR Tables [2], including 59 combustion product components and radicals for temperatures up to 6000K.

Thermodynamics of Multireaction Equilibria

The equilibrium state in a multi-reaction system depends on the number of independent chemical reactions involved, and with each reaction, there is a separate equilibrium constant. Calculation of all equilibrium constants requires details of all selected and specified independent reactions. But, this method of calculation of all equilibrium constants is very complicated and does not lend itself to standardization so as to allow a general program to be included in the simulator.

The alternative criterion of the equilibrum state is based on the fact that at equilibrium, the total Gibbs free energy of the system has its minimum value. The Gibbs reactor chosen for this modeling is based on the minimization of the total Gibbs free energy of the system. According to this method, for equilibrium calculation for a set of chemical reactions, the reactants with initial amounts and conditions and only the product components are specified. Details of the reactions involved, stoichiometry, and equilibrium coustants are not necessary for calculation of the product species concentrations. The total Gibbs free energy of a single phase system at specified T and P is a function of the Gibbs free energy of all its constituents:

$$(G)_{P,T} = G(n_1, n_2, n_3, ..., n_i) \qquad (1)$$

The values of n_i should be calculated by minimizing the energy function and regarding the problem constraints. The standard solution to this type of nonlinear optimization problems is obtained using Lagrange's Undetermined Multipliers, λ_k [3].

The material balance for k elements in i species is:

$$\sum_i n_i a_{ik} - A_k = 0 \qquad (2)$$

$$\sum_i y_i - 1 = 0 \qquad (3)$$

The energy function G is modified as an objective function F:

$$F = G + \sum_k \lambda_k (\sum_i n_i a_{ik} - A)_k \qquad (4)$$

At high flame temperatures when fugacity coefficients may be assumed unity, the objective function is at its optimum when:

$$\left(\frac{\partial F}{\partial n_i} \right)_{T, P, n_j} = \sum n_i a_{ik} - A_k = 0 \qquad (5)$$

knowing that the total heat of reaction is given by:

$$\Delta H = \Delta H_R + \Delta H_{298} + \Delta H_P \qquad (6)$$

while, ΔH_R and ΔH_P are reactants and products enthalpy changes, respectively. This equation can be used for calculation of the adiabatic flame temperatures, assuming negligible heat losses. The above set of nonlinear equations may be solved by a suitable numerical technique such as matrix inversion or Gauss-Seidel iteration, which are incorporated in most process simulators. The final solution yields n_i, the concentrations of all species, including the pollutants present in the combustion products.

Modeling Procedure

Fig.1 shows the flow diagram for the pre-mixed combustion flames. Separate streams of fuel and air flow into an ideal mixer, which povides perfect mixing. The mixture stream then enters the virtual reactor and after equilibrium reactions, leaves as combustion products. ASPEN Plus incorporates several types of reactors for different applications, namely, Stoichiometric, Equilibrium, Yield, Plug Flow, Batch and Gibbs reactors. In case of a multi-reaction system, such as combustion of a hydrocarbon fuel/air mixture, which involves numerous dissociating, recombination and elementary reactions, the Gibbs reactor is prefered for obvious reasons.
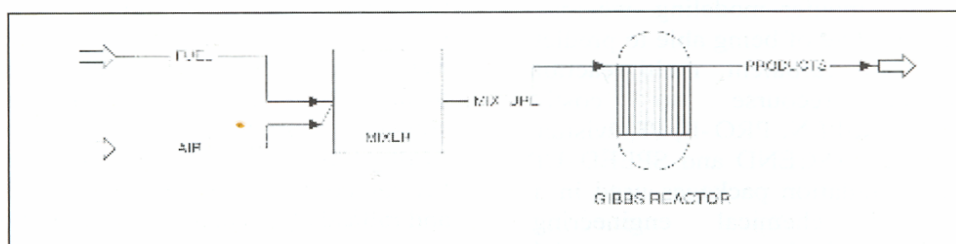

**Figure 1.** Flow diagram of premixed gaseous combustion modeling

Several fuels, namely methane (CH_4), ethane (C_2H_6), propane (C_3H_8), LPG (Liquefied Pertoleum Gas, a typical mixture of 60% n-C_4H_{10} and 40% C_3H_8) and hydrogen (H_2) are studied in this work. From many species present in combustion products, twenty four components that are found and detected in most hydrocarbon combustion reactions, including those responsible for air pollution, are specified and included in the simulation model. These species in their usual relative concentration order are: N_2, H_2O, CO_2, CO, O_2, H_2, OH, NO, H, O, HO_2, NO_2, N_2O, HNO, N, HN, CHO, HCN, CH_2O, CN, CH_3, C_2H_4 and SO_x.

Fuel/air mixtures in stoichiometric proportions, as shown in Table (1), at an initial temperature of 300 K and pressure of 1 atm are assumed to be completely mixed and reacted to the equilibrium condition. Reactor pressure is kept constant at 1 atmosphere. Reactor temperature is specified with a tolerance of 1 K in each run. Selecting the ideal gas option (SYSOP 0) for PVT calculations, which is satisfactory enough for elevated temperatures, concentrations of various species in the product stream, and the heat duty of the reactor were calculated. When the reactor temperature was given a value below the mixture flame temperature the heat duty of the reactor was calculated to be negative, which means some heat must be added to the reactor from an external source to maintain the reaction at the flame temperature. On the contrary, when the reactor temperature was set higher than the corresponding flame temperature, the reactor heat duty was positive which indicates how much heat is allowed to be extracted from the reactor before it cools down to the flame temperature. So, an adiabatic reactor with a heat duty of zero represents a self sustained reaction at the flame temperature of the mixture. This is the criterion for the calculation of the adiabatic flame temperature in this work.

Table 1. Stream flow rates for stoichiometric fuel/air mixtures, kmol/s

Fuel	Fuel flow rate	Oxygen flow rate	Nitrogen flow rate
CH_4	100	200	752.4
C_2H_6	100	350	1316.7
C_3H_8	100	500	1881
LPG	60 n-C_4H_{10} 40 C_3H_8	590	2219.6
H_2	100	50	188.1
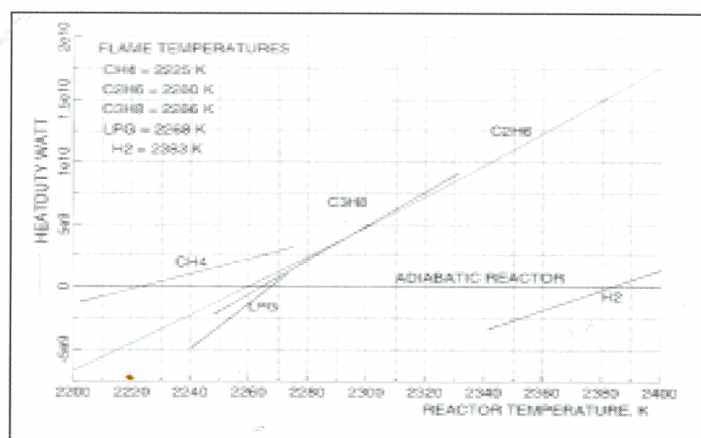
Figure 2. Adiabatic flame temperature for stoichiometric mixtures

Results and Discussion

By using a sensitivity analysis tool provided in ASPEN Plus, the reactor temperature was varied over a narrow range close to the reported flame temperature for each fuel and the adiabatic performance of the reactor corresponding to the adiabatic flame temperature was calculated precisely. Fig.2 gives a summary of results for the determination of flame temperatures. The heat duty of the reactor is plotted as a function of reactor temperature for different fuel/air mixtures at stoichiometric ratios.

Table (2) shows the analysis of combustion products for different fuels. A stoichiometric fuel/air mixture is considered to react to equilibrium at the appropriate flame temperature. The major product species N_2, H_2O, CO_2 and CO are expressed in mole fractions; the next six species O_2, H_2, OH, NO, H and O in ppm, and the following seven components HO_2, NO_2, N_2O, HNO, N, HN and CHO in ppb. Other species may be present in the combustion products at mixing ratios less than 1 ppb.

Reported methane flame temperatures are 2210 K[4], 2222 K[5], 2232 K[6] compared to 2225 K that is found in this work. Combustion product concentrations have been calculated using different number of species [7]. One of the early works for computer modeling of flame temperature and product composition calculation is by Gordon and McBride [8]. A recent simulation of pre-mixed gaseous flames is by Hamidi and Farshchi [9], which could produce safisfactory flame temperatures and combustion product concentrations for several fuels. Some of these results are summarized in Table (3). It should be mentioned that the accuracy of pollutants concentrations as well as calculated flame temperatures strongly depends on the number of product species chosen and included in a simulation. The accuracy of thermochemical data as well as different solution techniques also play a role. Slight differences between results arise mainly because only the first ten important species present in the product stream had been considered in those works.

Table 2. Analysis of combustion products for several fuels Stoichiometric fuel/air ratio at specified flame temperatures, mole fractions, ppm and ppb

| Product Species	CH$_4$ 2225 K	C$_2$H$_6$ 2260 K	C$_3$H$_8$ 2266K	LPG 2268 K	H$_2$ 2383 K
N$_2$	0.70864	0.71715	0.72082	0.72214	0.64434
H$_2$O	0.18336	0.15831	0.14836	0.14479	0.32351
CO$_2$	0.08536	0.09745	0.10266	0.10453	-
CO	0.00896	0.01166	0.01250	0.01279	-
O$_2$	4553 ppm	5541 ppm	5511 ppm	5909 ppm	4754 ppm
H$_2$	3615 "	3488 "	3313 "	3248 "	15330 "
OH	2924 "	3266 "	3277 "	3278 "	7009 "
NO	1980 "	2372 "	2468 "	2503 "	2678 "
H	393 "	466 "	470 "	471 "	1827 "
O	215 "	293 "	312 "	319 "	548 "
HO$_2$	880 ppb	1050 ppb	1073 ppb	1080 ppb	1882 ppb
NO$_2$	330 "	415 "	438 "	446 "	370 "
N$_2$O	94 "	113 "	117 "	119 "	120 "
HNO	51 "	60 "	60 "	61 "	143 "
N	14 "	21 "	23 "	23 "	75 "
HN	<1 "	1 "	1 "	1 "	6 "
CHO	<1 "	1 "	1 "	1 "	-
HCN	<1 "	<1 "	<1 "	<1 "	-
CH$_2$O	<1 "	<1 "	<1 "	<1 "	-
CN	<1 "	<1 "	<1 "	<1 "	-
CH	<1 "	<1 "	<1 "	<1 "	-
C$_2$H$_4$	-	-	<1 "	<1 "	
C$_3$H$_6$	-	-	<1 "	<1 "	

Table 3. Analysis of combustion products and pollutants from other sources Stoichiometric fuel/air mixtures at specified flame temperature, mole fractions

Product Species	CH_4		C_2H_6	C_3H_8	
	2207 K [9]	2222 K [5]	2240 K [9]	2247 K [9]	2219 K [7]
N_2	0.7087	0.709	0.7178	0.7210	0.7341
H_2O	0.1834	0.18	0.1585	0.1484	0.1423
CO_2	0.0854	0.085	0.0976	0.1028	0.1004
CO	0.0089	0.009	0.0115	0.0124	0.0099
O_2	0.0045	0.004	0.0055	0.0058	0.0048
H_2	0.0036	0.004	0.0035	0.0033	0.0032
OH	0.0028	0.003	0.0032	0.0032	0.0027
NO	0.0020	0.002	0.0024	0.0025	0.0020
H	0.0004	0.0004	0.0005	0.0005	0.0035
O	0.0002	0.0002	0.0003	0.0003	0.0020
HO_2	-	-	-	-	$<10^{-5}$
NO_2	-	-	-	-	-
N_2O	-	-	-	-	$<10^{-5}$
HNO	-	-	-	-	-
N	-	-	-	-	$<10^{-5}$
CH_3	-	-	-	-	$<10^{-5}$
CHO	-	-	-	-	$<10^{-5}$
CH_2O	-	-	-	-	$<10^{-5}$
C_2H_4	-	-	-	-	$<10^{-5}$
C_3H_6	-	-	-	-	$<10^{-5}$
C_2H_5	-	-	-	-	$<10^{-5}$

The effect of changing the reaction temperature on the concentration of product species and pollutants was also studied as a temperature sensitivity analysis. The results for stoichiometric methane/air and propane/air mixtures in the temperature range of 1000-4000 K are shown in Figures 3 to 7. Similar patterns for product concentration changes are observed for the other hydrocarbon fuels.
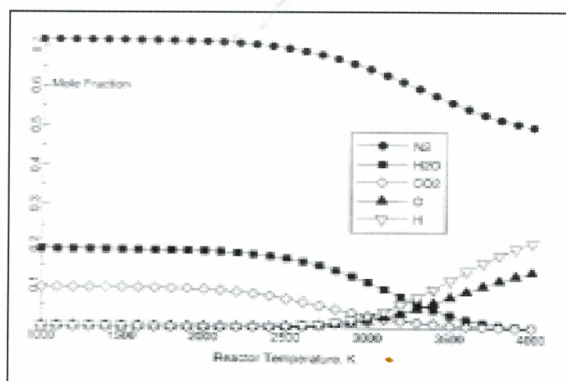
Figure 3. Concentration Variations with Temperature in CH4 Flame
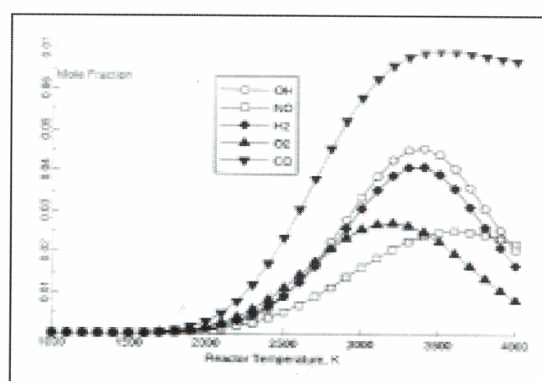
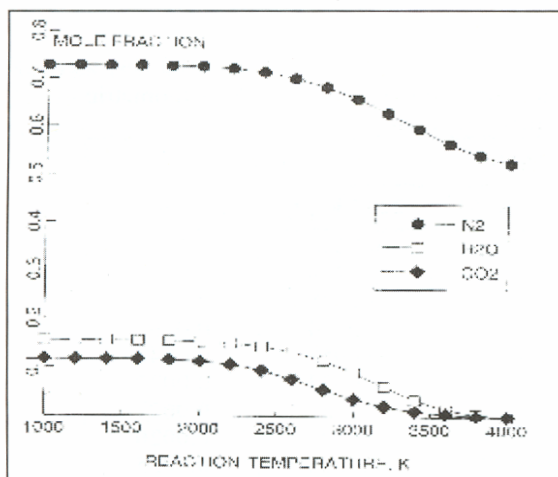**Figure 4.** Concentration Variations with Temperature in CH4 Flame

Figure 5. Concentration profiles for N2,H2O and CO2 as a function of temperature in Propane flame

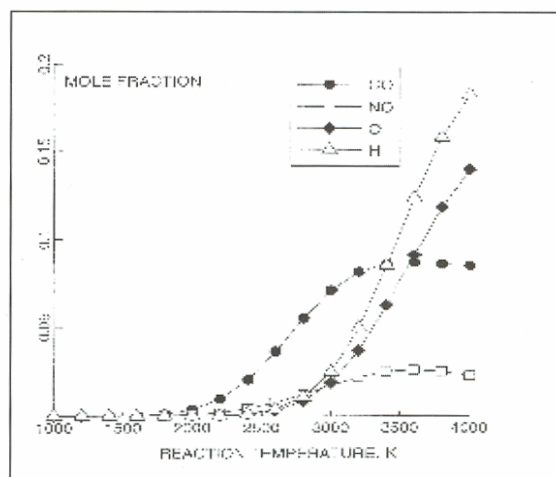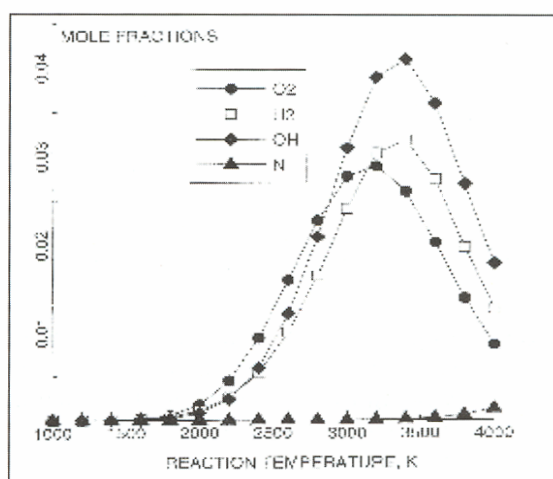**Figure 6.** Concentration profiles for CO, NO,O and H as a function of temperature in Propane flame

Figure 7. Concentration profiles for O2,H2,OH and N as a function of temperature in Propane flame

It is interesting to notice that complete combustion indicated by stoichiometric concentrations of H_2O and CO_2 is predicted at low temperatures, even at less than 1000 K, Fig.3. This is a slow combustion process which requires a long time to attain equilibrium. At elevated temperatures, most stable molecules dissociate above 3500 K into H, O and N atoms. CO concentration increases with temperature up to 3500 K, then remains almost constant. The presence of NO and other oxides of nitrogen also becomes significant with increasing temperature, Fig.4. Although these extremely high reactor temperatures are not of practical significance, but

they provide an indication of the trend of concentration changes.

Another sensitivity analysis was carried out to study the effect of varying fuel/air mixture when the equivalence ratio (Φ, mole fraction of fuel in the mixture divided by the mole fraction of fuel in the stoichiometric mixture) is varied from 0 to 3. The reactor temperature was set constant at the flame temperature. The results for methane/air and propane/air mixtures are shown in Figures 8 to 12. When the fuel concentration corresponds to the stoichiometric ratio ($\Phi = 1$), optimum combustion occurs. On the lean side ($\Phi < 1$), oxidizing species are present at excess concentratios and OH radicals are found at

maximum concentration near the lower limit of flammability ($\Phi = 0.55$), Figures 9 and 12. On the fuel rich side ($\Phi > 1$), cocentrations of CO and H_2 as well as most HC compounds increase progressively, which indicates incomplete and polluting combustion. Similar behaviour was observed when other hydrocarbon fuels were examined. It should be mentioned that flame temperature is maximum when $\Phi = 1$, and drops when Φ changes in both directions.
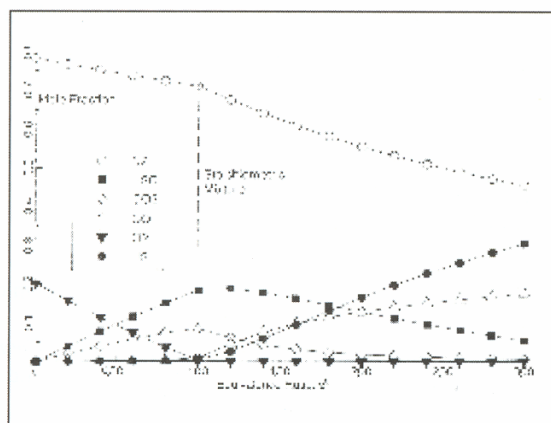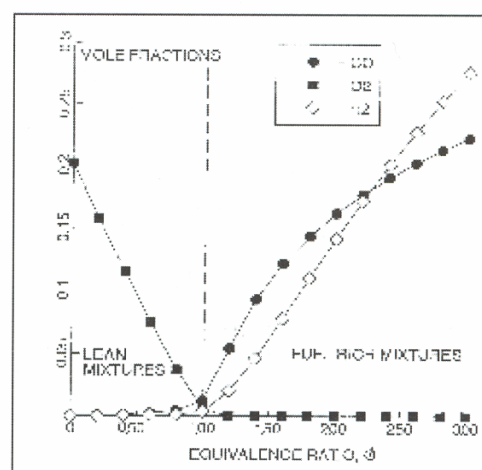

Figure 8. Concentration Variations with Temperature in CH_4 Flame
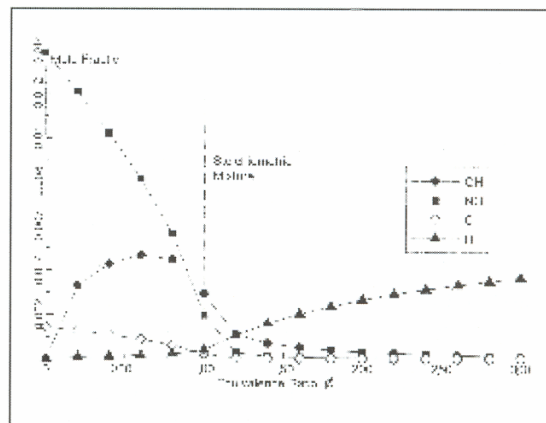
Figure 9. Concentration Variations with Fuel Ratio in CH4 Flame
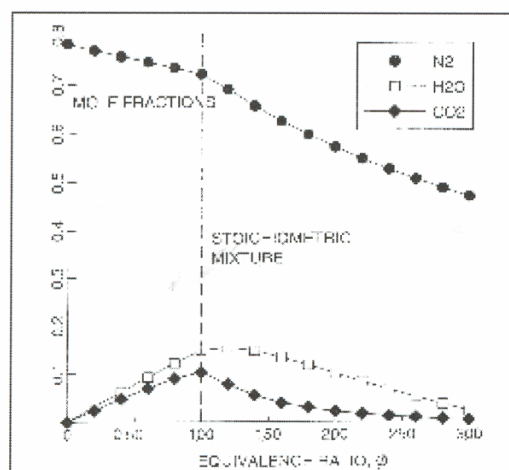
Figure 10. Concentration profiles for N2, H2O and CO2 as a function of equivalence ratio in F ropane flame

Figure 11. Concentration profiles for CO, O2 and H2 as a function of equivalence ratio in Propane flame
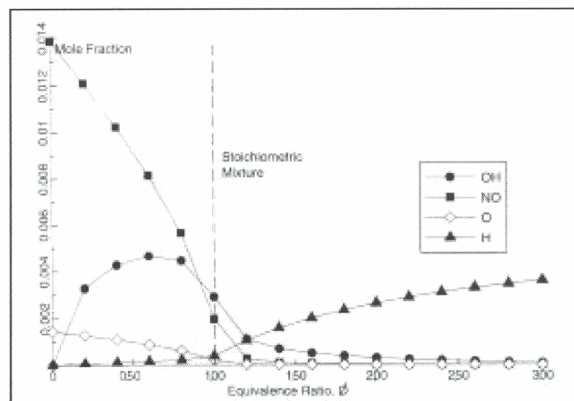
Figure 12. Concentration profiles for NO, OH, O and H
as a function of equivalence ratio in Propane flame

Conclusion

ASPEN Plus process simulator showed to be a powerful tool for combustion modeling and air pollution studies. Based on the minimization of the total Gibbs free energy of the reacting system, adiabatic flame temperatures for several fuel/air mixtures were calculated precisely. Combustion products included over twenty species with concentrations as low as 1 ppb. The heat duty of non-adiabatic reactions were determined and the results were compared with recognized works.

Sensitivity analysis capability provided in the package enables one to study the effect of changing the reactor temperature or fuel/air ratio on the product stream composition [10,11,12]. Choosing different number of product species results in different levels of accuracy of the calculated parameters. Graphical representation and the theoretical interpretation of the conditions for pollutants generation are other examined potentials.

Regarding the increasing importance of air pollution research and its deep interrelation with combustion modeling and simulation, this work shows some typical procedure and solved examples by ASPEN Plus for practical purposes.

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