Research Paper Technology

Equilibrium Composition in Combustion Products

Dr. K.Bala Showry | Principal, DRK Institute of Science and Technology.

ABSTRACT

For a combustion problem involving calculations of several species at equilibrium, it is much easier to write a computer program and calculate the concentrations, rather than to use a generalized computer program. To calculate these concentrations, one must solve a set of non-lin¬ear algebraic equations. This work describes a procedure in which the Newton-Raphson method and the successive substitution method are combined. It was found that for this type of problem, the quan¬tity of unknowns and the nature of the equations are such that, by adopting the two procedures simul¬taneously, a much faster and reliable convergence is achieved. This study also shows what possible species should be considered for these calculations.

KEYWORDS | Newton-Rap son method, Chemical equilibrium

INTRODUCTION

Chemical equilibrium is a condition when the chemical reaction, by which individual species in the burned gases react together, produce and remove each species at equal rates; hence at this condition no net change in species composition results. In most performance estimation of high temperature practical combustion processes, it is a good approximation to regard the burned gases produced by the combustion of fuel and air to be in chemical equilibrium. However, in more sophisticated combustion calculations, when the time constants of the controlling chemical reactions are short compared with time scales over which the system conditions change, then chemical reaction rates is used. Such non-equilibrium processes are controlled by the rates at which the actual chemical reactions, which convert reactants to products, occur. Often to analyze the non-equilibrium processes such as the flame propagation and the expansion process in engines, it will be just as accurate to assume these processes to be quasi-equilibrium, rather than to use the more uncertain rate constants, and overall reaction rates. Chemical equilibrium is usually described by either of two equivalent formulations, namely the equilibrium constants or the minimization of free energy. However, the two formulations reduce to the same number of iteration equations. When considering a computer program for general chemical equilibrium, there are several disadvantages in the equilibrium constant method; briefly these disadvantages are: more data and book keeping, numerical difficulties with use of components, more difficulties in testing for presence of some condensed species, and difficulties in extending the generalized method for non-ideal equations of state. On the other hand, the equilibrium constant method is simpler to adopt and formulate for a simple situation, and it was found that for most combustion problems it gives satisfactory results without elaborate and complicated computer programs.

A computer program for the calculation of complex chemical equilibrium composition was developed by NASA in the early 1960s [1]. This program is generally available and well documented and can be used for any number of species, compounds and elements in the reactants [2]. However, the program is very lengthy and some difficulties may be experienced when adapted to combustion or chemical reaction problems; for example, the internal combustion engine. For this reason it is more simple to develop a computer program to calculate a specific combustion problem and solve the necessary conservation equations for species, mass, and energy, rather than to incorporate the NASA program in a specified application problem [3].

The approach in the NASA program is to minimize explicitly the Gibbs and Helmholtz free energies of a reacting mixture at a given temperature, pressure or specific volume, subject to the constraints of element mass conservation. In the NASA program the condition for equilibrium is:

$$\sum_e v_{ei} c_i - b_e = 0 \qquad dG = 0$$

$$\mu_i + \sum_e \lambda_e v_{ei} = 0$$

Among the n possible species which are considered, gases and condensed species are treated separately. The calculations in the NASA program are more complicated because they use the Newton—Raphson method to calculate both Lagrangian multipliers and concentrations. The present study employs the first equation, which is the element balance or mass balance equation; the equilibrium constant equation is used alternative to the other two.

Meintjes and Morgan [4], developed a procedure that algebraically combines the equilibrium equations, eliminates some unknowns, and scales the simplified equations to obtain a set of simultaneous nonlinear equations that are solved with linear algebra. Their procedure combines the Gauss—Seidel and Newton methods. They claim that the Gauss—Seidel is unreliable and the Newton's method is slow.

The objective of this work is to show that by combining the Newton—Raphson method and the successive substitution method, a fast and reliable convergence is obtained to the solution of non-linear algebraic equations, which is required for the determination of composition in combustion products at equilibrium; it is also to show what possible important species should be considered for these calculations.

FORMULATION

Consider a mixture of n reacting gases in combustion products in equilibrium; and in these n species consider e chemical elements. Conservation of elements will provide e equations which relate the concentration of these n species. Also there should be $(n—e)$ sets of equations which will be related to $(n—e)$ chemical reactions in equilibrium. These $(n—e)$ equations are highly nonlinear.

The major species present in combustion products of hydrocarbon fuels at relatively high temperatures are mainly 13, which include CO2, H_2O, CO, 1-1_2, 02, N2, OH, NO, 0, H, N20, NO2, and N. These species may vary considerably with temperature, pressure, type of fuel and equivalence ratio. The main difficulties in solving the nonlinear equations and obtaining the concentration of the n species are because values of some of these molar concentrations are very small or negligible relative to others, and this causes the diagonal of the relevant matrix to be non-dominant and cause singularities. The usual method used to solve these non-linear equations is the Newton—Raphson method. This method converts the non-linear algebraic equations to iterations of linear algebraic equations which are used to solve for corrections to initial estimates of components, $n,$. The latter equations can be solved by either the Gaussian elimination, Gauss—Seidel, or matrix inversion [5].The chemical reaction equation for a fuel of molar composition $C_xH_yO_zN_w$ with air and equivalence ratio (/) can be written as:

$$C_xH_yO_Z+\frac{1}{\phi}\left(\chi+\frac{y}{4}-\frac{z}{2}\right)(O_2+3.773N_2)\rightarrow$$

$$n_{co2}CO_2+n_{H2O}H_{2O}+n_{co}CO+n_{h2}H_2+$$

If we consider the above 13 species in the products at a given temperature and pressure, we would require 13 equations to obtain the molar quantities of these species n_i. Four equations can be obtained from balance of elements C/H/N/O in the reactants and products. The other nine equations, which are highly non-linear, are obtained from equilibrium or dissociation consideration. The four element balance equations and nine equilibrium constant non-redundant reactions provide the set of 13 equations required for solution of the species concentration. The following is an example of an element balance equation for hydrogen; the other three equations are similar:

$$f(ni)=2*n_{H2O}+n_{OH}+n_H-y=0$$

The general disassociation reaction equation for jth reaction can be written as

$\sum_i a_{ij}A_i=0$ for i= 1 to n

Assuming an ideal gas, the following equations for j[th] disassociation reaction and for the unknowns n_i can be combined to form a set of (n-e) non linear algebraic equations

$$\exp\left(-\Delta G_j/RT\right)=\left(P/\left[\sum_i n_i\right]\right)y_j\prod_i n_i^{a_{ij}}$$

where, $\Delta G_j=\sum_i a_{ij}h_i-T\sum_i a_{ij}s_i$

$$y_j=\sum_i a_{ij}h_i=h_{fj}+\int_{To}^{T}C_{pi}dT\,s_i=$$

$s_i^o+\int_{To}^{T}C_{pi}\frac{dT}{T}$ for i=1 to n for species that are not ideal gas such as carbon, activity of that component is used instead of its partial pressure.

METHOD OF SOLUTION

Three methods for solution of equations leading to determination of concentrations in combustion products are considered. First the successive substitution method, second the NewtonRaphson method and third a combination of the two.

The first method is very easy to use and convergence can be achieved very rapidly, however, this method is limited only to lean mixtures, or equivalence ratios of less than 0.9. With this method provided the mixture is lean, the initial estimate of concentrations are not important, but the order in which the concentrations are calculated successively should be followed. This succession of order or flow chart is as follows:

1. Estimate a value for the concentrations n_i.
2. From carbon balance calculate concentration of CO_2.
3. From balance of hydrogen calculate concentration of H_2O.
4. From balance of nitrogen calculate concentration of N_2.
5. From balance of oxygen calculate concentration of 0_2.
6. Calculate sum of concentrations.
7. From dissociation of CO_2 calculate concentration of CO.
8. From dissociation of H_2O calculate concentration of H_2.
9. Calculations can be continued in the some manner with determination of concentrations for OH, NO, 0, H, N_20, NO_2 and N in that order.
10. Calculations are repeated from step 2 until the change in concentrations becomes very small.

The initial estimate of concentration of species to start the iteration procedure is the non-dissociated composition, with the remaining species set to a low value (say 0.1%).

The Newton—Raphson procedure usually requires inversion of an *n* **x** *n* matrix, and since the procedure is an iterative one, the matrix inversion process must be performed several times before achieving a solution. Also, as the number of species increases, the size of matrix becomes larger, hence the time taken to achieve a solution increases exponentially.

In the third method both the Newton—Raphson and the successive substitution procedures are employed simultaneously.The former procedure, because of better convergence in the rich mixture range, and the latter procedure because rapid convergence can be achieved. In this method initially concentrations of the species that are relatively large are calculated using the Newton—Raphson procedure. These species may include CO_2, H_2O, CO, H2, 02 and N_2. Once a reasonable solution is obtained then the remaining concentrations OH, NO, 0, H, N20, NO2 and N may be calculated using the successive substitution procedure. In this method, because the size of the matrix is smaller, six instead of 13, convergence is much faster, and because the concentrations of the first six species to be calculated are of the same order of magnitude, then singularities are avoided. The adaptation of the successive substitution procedure is quite satisfactory because, for the range of calculations, the values of the later seven unknowns are relatively small and have little effect on the values of the former six unknowns.

Enthalpy, entropy and equilibrium constants are calculated from the curve-fitted specific heat data in the JANAF tables [6, 7]. Surprisingly the data in these tables and its relevant curve-fitted data in the NASA program are used very widely today [8]. These data are the main source of reliable thermodynamic properties for chemical species.

Repeated calculations with the three different methods over a wide range of conditions for pressure, temperature, equivalence ratios, and initial estimates, showed that:

1. The successive substitution method gives very fast and reliable convergence, but only for equivalence ratios of less than 0.9.
2. The Newton—Raphson method with matrix of 13 x 13 was up to 500 times slower depending on what relaxation factor was used; and in certain situations convergence failed.
3. With the combined method using a matrix of 7 and 13 unknowns, very reliable convergence was achieved.
4. The combined method was up to 50 times faster than the Newton—Raphson method.
5. Once convergence is achieved and depending on what termination criterion is used, the results are exactly the same, and are independent of the numerical method employed; hence there is no need for comparison.

Results of a few typically chosen calculations are presented to show the qualitative variations and importance of the species. For the hydrocarbon the molar hydrogen carbon ratio was chosen typically as 2.

An interesting aspect of the results can be seen in the excessive rich mixture range, where the formation of carbon and other harmful radicals in premixed combustion can be studied. In Fig. 2 it can be seen that as the equivalence ratio increases above 2, concentrations of OH, CO2, and H_2O fall very rapidly and become negligible. For equivalence ratios above 3, species such as C (carbon), HCN (hydrogen cyanide), C_2H_2 (acetylene), begin to appear, while species such as CH_4 (methane), CH_3 (methyl), CN (cyano), C2N, and C_2N_2 (cyanogen), are present in much smaller quantities.

For a lower temperature of 1500 K. Here the concentrations of C and CH_4 are higher but other radicals such as HCN, H, and C2H2 decrease. For this lower temperature but a higher pressure of 50 atm, conditions which may be experienced in compression ignition engines. Here formation of CO, H2, and C are the same, but for equivalence ratio of greater than 3, concentrations of CH_4, H_2O, and CO_2 are larger. There are traces of species HCN, NH_3, and C_2H_4.

Two types of carbon appear in combustion; hard carbon and soft carbon or soot. The initial step in either case is believed to be cracking or decomposition of the fuel molecule. If the fuel impinges on a hot surface, hard carbon is formed in a surface reaction. However, soft carbon is formed in the gas phase; once a particle is borne it probably grows by reacting with carbon monoxide. Some evidence exists that detonating combustion increases the formation of soot. In gen-

eral, carbon formation increases with the C/H ratio and is greater for compact or round molecules; for example, branched chain paraffins form soot more readily than do the straight chains.

Dissociation increases with increasing temperature and decreases with increasing pressure. Thus considerable dissociation occurs in spark ignition engine during the combustion process at the temperatures and pressures usually encountered. Chemical equilibrium may be approached in the reaction zone directly behind the spark ignition flame front. On the other hand, the phenomenon of after burning leads support to the theory that equilibrium is not attained. In the compression ignition engine with its heterogenous combustion it would be difficult to separate dissociation from the condition of incomplete burning. However, the higher pressures and lower temperatures in compression ignition engines would suppress dissociation.

CONCLUSIONS

By combining the Newton—Raphson procedure and the successive substitution procedure, it was found that the concentration of species at equilibrium in combustion products can be calculated more rapidly and without difficulties with singularities. The successive substitution procedure does not converge with equivalence ratios of greater than 0.9, and the Newton—Raphson procedure alone requires up to 50 times longer computation time, and may present some problems with singularities.

The strategy involved in this work is to separate the unknown species into two groups. Concentrations of those species with high values are determined first, using the NewtonRaphson method; then the remaining species are determined with the successive substitution method. In the iteration procedure the two methods are employed alternatively until the change in values are very small. Basically this strategy can also be applied to other chemical equilibrium problems.

REFERENCES

1.F. J. Zeleznik and S. Gordon, A general IBM 704 or 7090 computer program for computation of chemical equili¬brium composition, rocket performance, detonation. NASA TN D-1454 (1962). | 2.S. Gordon and B. J. McBride, Computer program for calculation of complex chemical equilibrium composition, rocket performance, incident and reflected shocks, and Chapman Jouguet detonation. NASA SP-273 (1971). | 3.C. Olikara and A. L. Borman, A computer program for calculating properties of equilibrium combustion products with some application to IC engines. SAE paper 750468 (1975). | 4.K. Meintjes and A. P. Morgan, Performance of algorithms for calculation of equilibrium composition of a mixture of gases. Journal of Computational Physics 60, 219 (1985). | 5.B. Carnaban, H. A. Luther and J. 0. Wilkes, Applied Numerical Methods, Chapter 5. John Wiley, New York (1969). | 6.JANAF thermochemical tables. NSRDS-NB537, US National Bureau of Standards (1971). | 7.R. A. Strehlow, Fundamentals of Combustion. International Textbook (1968). | 8.J. B. Heywood, Internal Combustion Engine Fundamentals, Chapter 5. McGraw-Hill, New York