

Determination of the Equilibrium Parameters of Gaseous Detonations Using a Genetic Algorithm

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Abstract

The present work is concerned with the development of a new algorithm for determination of the equilibrium composition of gaseous detonations. The elements balance equations, and the second law of thermodynamics (i.e., the minimization of the Gibbs free energy of products), are used to determine the equilibrium composition of the detonation products. To minimize the Gibbs free energy with traditional deterministic methods one needs to solve a set of highly nonlinear equations. The numerical methods in the existing equilibrium codes suffer from several drawbacks such as the divergence possibility in some equivalent ratios, and the possibility of converging to a local relative minimum in the minimization process. To overcome these drawbacks, a genetic algorithm is presented in the present study. Converging to the global minimum of Gibbs function in all equivalent ratios, and having a reasonable CPU time are the notable aspects of the proposed algorithm.

Keywords: *Gaseous detonation, Chemical equilibrium, Genetic algorithm, Gibbs free energy*

1- Introduction

According to the second law of thermodynamics, the Gibbs free energy of combustion products attains its minimum value at the equilibrium condition. The chemical equilibrium is usually described by either of two formulations, the equilibrium constants or the minimization of the Gibbs free energy. In order to directly minimize the Gibbs free energy, one needs to solve a set of highly nonlinear algebraic equations subjected to chemical elements mass balance constraints. This set of equations is usually solved iteratively by numerical methods such as the Newton-Raphson method. The

convergency and the initial estimates of unknowns are two main challenges in traditional methods. The first computer program for the calculation of equilibrium detonation parameters (i.e., CEC) was developed at the NASA Lewis Research Center by Gordon and McBride [1]. This code uses the Newton-Raphson method to minimize the Gibbs function. The last version of this code (which is named CEA) was released in 2000. CEA is still based on the same method as CEC; of course with a more advanced non-linear solver. Among the dozens of equilibrium codes that have been developed after the first version of CEC, the

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STANJAN of Reynolds (developed at Stanford University) has been able to attract the most attention in combustion communities due to its high robustness. The minimization of the Gibbs free energy is performed by using the element potential method in STANJAN [2]. GASEQ is another equilibrium code which benefits from being highly user-friendly, though it is not as robust as CEA and STANJAN. All of these codes suffer from the possibility of converging to local relative minimums, and a rare possibility of divergency for some equivalent ratios. Recently generalized forms of STANJAN and CEA (GSTANJAN and GNASA) have been developed with some surplus constraint in addition to the mass balance constraints [3]. These constraints are needed for chemical kinetic calculations involving both the conventional local thermodynamic equilibrium (LTE) and the more general rate-controlled constrained-equilibrium RCCE assumptions. Comparison of these codes showed that GSTANJAN converges in all but one case, whereas GNASA fails to converge in almost all cases [3].

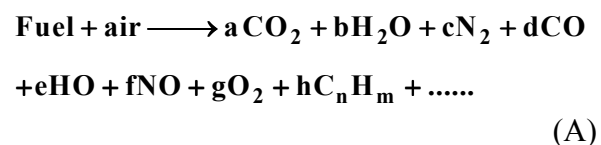
Calculations based on the Chapman-Jouguet (CJ) theory of steady state detonation have proven very successful in reproducing the experimentally determined detonation velocity and pressure in gaseous reactive mixtures. The CJ theory assumes that the flow is one dimensional, the reaction zone is infinitely thin, and the product of combustion moves with local speed of sound with respect to the detonation front. This last assumption is referred to as the CJ condition. Calculation of the detonation pressure and velocity requires the use of a chemical equilibrium code to determine the product composition with the minimum Gibbs free energy. In order to determine the equilibrium properties of detonation waves, in addition to the above mentioned challenges, the Chapman-Jouguet (CJ) condition should also be satisfied.

The minimization of a function of several

variables, subject to some constraints, is a classical optimization problem. Therefore, the determination of the equilibrium condition may be viewed as an optimization problem. Recently, researchers in different fields of science and engineering are highly attracted to one of the modern optimization methods, that is, the genetic algorithms. Among them, Brog et. al. [4], for the first time, developed a therm-chemical equilibrium code (i.e., the AMRL code) based on a genetic algorithm. Brog's main goal was the determination of the equilibrium properties of the detonation products in high explosives [4]. Despite the robustness of the new algorithm, resolving the initialization problem, and converging to the absolute global minimum, the Brog's algorithm suffers from very high CPU run time. Recently, the current authors modified the Brog's algorithm and could determine the equilibrium composition of gaseous combustion products in a reasonable CPU time [5]. The objective of the present work is to extend the modified genetic algorithm for the determination of the equilibrium parameters of detonation waves in gaseous mixtures. Although the new method is very promising, to the best of the authors knowledge, no other research on this subject has been published¹ yet.

2- The equilibrium condition of detonation products

A general chemical reaction for a hydrocarbon fuel-air mixture is shown by reaction (A):



a, b, c... are the number of moles of the

1- Recently a short un-official paper [9] is found on the internet which will be referred to in the conclusion.

products that should be determined. A simple model to predict combustion products is the thermodynamic equilibrium model. The second law of thermodynamics states that all natural processes, in isolated systems, tend to proceed in a direction that leads to an increase in the entropy of the system; this is equivalent to stating that the Gibbs free energy function of a system decreases. Therefore, in the equilibrium condition the Gibbs function of the products attains its minimum value. Therefore by minimizing the Gibbs free energy of the products, subject to the conservation of chemical elements, the equilibrium composition of the products may be determined.

Total Gibbs function of the reaction products is simply calculated by summing the Gibbs function of different species [6]:

$$G = \sum_{j=1}^N g_j n_j \quad (1)$$

where, G is the total Gibbs energy, g_j is the Gibbs energy of the j^{th} specie, n_j is the number of moles of the j^{th} specie, and N is the number of species. The Gibbs energy of the specie ' j ' is defined as:

$$g \equiv h - Ts \quad (2)$$

The conservation of chemical elements is stated as:

$$\sum_{j=1}^N a_{ij} n_j - b_i^0 = 0 \quad (i=1, \dots, l) \quad (3)$$

a_{ij} are the number of element i per mole of specie j , l is the number of chemical elements, and b_i^0 is the number of element i in the reactants. To minimize a function g , subject to a constraint f , one needs to find the zeroes of the function H that is defined as [...]:

$$H \equiv g + \lambda f \quad (4)$$

where λ is the so-called Lagrangian

multiplier. In the equilibrium problem, the function H is defined as:

$$H = g + \sum_{i=1}^l \lambda_i (a_{ij} n_j - b_i^0) \quad (5)$$

Differentiating the function, one obtains:

$$\begin{aligned} \delta H = \sum_{j=1}^N \left(g_j + \sum_{i=1}^l \lambda_i a_{ij} \right) \delta n_j \\ + \sum_{i=1}^l \left(a_{ij} n_j - b_i^0 \right) \delta \lambda_i = 0 \end{aligned} \quad (6)$$

This set of equations is highly non-linear. Most chemical equilibrium codes (e.g., CEA) solve this set of equations to find the composition of the products. However, considering the high nonlinearity of equations, very good estimates of the answers are needed to start the iteration procedure and to have a converged solution. Besides, in some cases the available algorithms converge to local minimums of the Gibbs function [4]. In the present work, based on the genetic algorithm of Brog et al., a new procedure is developed to determine the equilibrium parameters of the gaseous detonations, without encountering the mentioned problems [4].

3- The governing equations

The CJ theory assumes that the flow is one dimensional, the reaction zone is infinitely thin, and the product of combustion moves with the local speed of sound with respect to the detonation front. In a thermodynamic framework, a detonation is described simply by the conservation equations of mass, momentum, and energy, written for a finite control volume as:

- Mass conservation equation

$$\rho_1 u_1 = \rho_2 u_2 = m^0 \quad (7)$$

- Momentum conservation equation

$$P_1 + \rho_1 u_1^2 = P_2 + \rho_2 u_2^2 \quad (8)$$

- Energy conservation equation

$$h_1 + \frac{1}{2}u_1^2 + q = h_2 + \frac{1}{2}u_2^2; \quad h = e + Pv \quad (9)$$

In these equations h , u , ρ , P , q and m° are respectively enthalpy, particle velocity, density, pressure, combustion energy, and mass flow rate. The subscript 1 refers to reactants, and 2 is used for products. In the gaseous detonations the pressure of products is in the range of 10-50 bar, in which the products obey the ideal gas equation of state.

$$P = \rho e (\gamma - 1) \quad (10)$$

Combining the conservation equations, the Rayleigh line (Eq. 11) and the Hugoniot curve (Eq. 12) are derived [6].

$$\rho_1^2 u_1^2 = \frac{P_2 - P_1}{v_1 - v_2} = m^{\circ 2} \quad (11)$$

$$q - \frac{\gamma}{\gamma - 1} (P_2 v_1 - P_1 v_2) = \frac{1}{2} (P_2 - P_1) (v_1 + v_2) \quad (12)$$

CJ theory states that a steady detonation occurs when the Rayleigh line is tangent to the Hugoniot curve. The tangency point is named the CJ point. As a result, the detonation velocity attains its minimum value at this point. Therefore, in determining the CJ detonation properties, a new constraint should be satisfied, that is, the CJ condition.

4- The genetic algorithm

Genetic algorithms (GAs) are general search and optimization algorithms inspired by processes associated with the natural world. This method is based on the “survival of the

fittest” of Darwin. The method is a general one, capable of being applied to an extremely wide range of problems. A typical GA consists of the following processes [10]:

- selecting a first generation (a population of random guesses of the solution of the problem);
- a way of calculating how good or bad the individual solutions within the population are;
- a method for mixing fragments of the better solutions to form new, and on average even better solutions;
- a method of replacing better solutions (children) with old ones (parents) to produce new generations; and
- a convergency criterion to end the iteration procedure.

4.1 - Implementation of the genetic algorithm

In the present study, based on Brog’s study [4], the following genetic algorithm is utilized:

- 1- An array is made to keep the answers. The first component of this array is called the first position and other components are referred to by the number of their position.
- 2- Two random compositions for products are generated and saved in the first and second positions of the array. Each random composition contains “n” mole fractions of product species, (i.e., x_1, \dots, x_n).
- 3- Using the first and the second position a third composition is created and saved in the third position.
- 4- Using the fitness criterion, the best (fittest) composition among the first, second and third position is selected and moved to the first position, two other positions are neglected.
- 5- A new random composition is generated and saved in the second position.
- 6- Steps 2 through 5 are repeated until the convergence is achieved.

One of the most important parts of the algorithm is the relation that is used for creating new compositions from the last two selected compositions. Brog et al. used Eq. 13, in the AMRL code, to create the third composition [4].

$$\begin{cases} \mathbf{x}_1 = (\mathbf{x}_{11}, \dots, \mathbf{x}_{1N}) \\ \mathbf{x}_2 = (\mathbf{x}_{21}, \dots, \mathbf{x}_{2N}) \\ \mathbf{x}_3 = (\mathbf{g}_1 \mathbf{x}_1 + \mathbf{g}_2 \mathbf{x}_2) / (\mathbf{g}_1 + \mathbf{g}_2) \end{cases} \quad (13)$$

In Eq.13, g_1 and g_2 are the Gibbs function of x_1 and x_2 compositions, respectively.

Our numerical experiments indicate that the CPU time for creating a random composition is much more than the required time to create a third composition. Therefore, creating many new compositions by using the first and the second compositions does not affect the CPU time considerably. Using this notion, 30 new compositions are created in each iteration in the present work¹ (according to Eq. 14). This idea increases the possibility of creating worthy answers by 30 times.

$$\begin{cases} \mathbf{x}_1 = (\mathbf{x}_{11}, \dots, \mathbf{x}_{1N}) \\ \mathbf{x}_2 = (\mathbf{x}_{21}, \dots, \mathbf{x}_{2N}) \\ \mathbf{x}_{i+2} = \left(\frac{\mathbf{k} + \mathbf{i}}{\mathbf{k}}\right) \mathbf{x}_1 - \frac{\mathbf{i}}{\mathbf{k}} \mathbf{x}_2 \\ \mathbf{x}_{i+17} = \left(\frac{\mathbf{k} - \mathbf{i}}{\mathbf{k}}\right) \mathbf{x}_1 + \frac{\mathbf{i}}{\mathbf{k}} \mathbf{x}_2 \end{cases} \quad \mathbf{i} = 1 \dots 15 \quad (14)$$

In Eq.14, k is the iteration number.

1- In the AMRL code one new composition is created in each iteration.

4.2 - The convergency criterion

In a usual iteration procedure, when the difference of two consecutive values of some pre-defined parameters becomes less than a specified tiny value, the convergence is achieved. However, in a simple genetic algorithm (as the method proposed by Brog and co workers), due to the random nature of the answers, it is not possible to use such a criterion. As is observed in Figs. 1 and 2, in some iterations the answers have very sharp changes, while in others they change slowly. In the present work, convergency criterion was determined by using a statistical study. Solving hundreds of problems by the present algorithm it was empirically found that in all cases, after performing less than 3000 iterations the answers become close enough to the correct one. This point is depicted in Figs. 1 and 2. Therefore, in the present study, doing 3000 iterations is considered as the convergency criterion.

5- Determination of the CJ detonation parameters

In order to satisfy the CJ condition, the Raleigh line should be tangent to the Hugoniot curve. In the tangency point (i.e., the CJ point) detonation velocity attains its minimum value (i.e., the CJ velocity). Therefore, in the first step, the detonation velocity is built as a function of pressure. Then, the minimum value of this function is chosen as the CJ velocity. The following algorithm is employed to determine the desired parameters:

- 1- A pressure and three temperatures are estimated as CJ detonation parameters.
- 2- In the specified temperatures and pressure, the equilibrium composition of the products are determined by the genetic algorithm.
- 3- The Hugoniot equation shows an error (Eq. 15) when it is substituted by the estimated values. The Hugoniot error is defined by Eq. 15.

$$E_H \equiv q - \left(\frac{\gamma}{\gamma - 1} (P_{es} v_1 - P_1 v_{es}) - \frac{1}{2} (P_{es} - P_1) (v_1 + v_{es}) \right) \quad (15)$$

where P_{es} and v_{es} are the estimated pressure and volume.

- 4- A Hugoniot error function is made as a second order function of temperature. Then, the temperature at which the Hugoniot error is zero is determined.
- 5- Using the momentum conservation equation, the detonation velocity is calculated by Eq. 16.

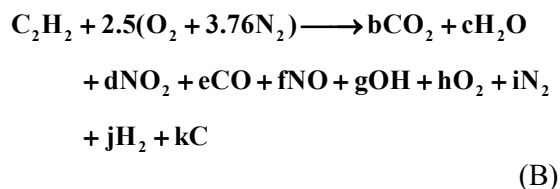
$$D^2 = \frac{P_2 + \rho_2 u_2^2 - P_1}{\rho_1} \quad (16)$$

Although the Hugoniot is satisfied by this temperature and pressure, the CJ condition has yet to be satisfied.

- 6- Steps 1 to 5 are repeated for at least three estimated pressures.
- 7- Using estimated pressures and the corresponding detonation velocities, the detonation velocity is expressed as a function of pressure. The CJ detonation velocity is determined from the minimum of the pressure-velocity function [7].

6- Results

To show the merit of the developed algorithm, two problems are considered here. The first problem contains the determination of the equilibrium composition of reaction (B) in $P=10$ atm, $T = 2000$ K.

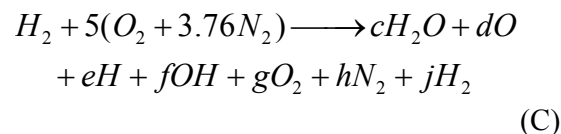


The mole fractions of CO_2 and H_2O , which are determined by the genetic algorithm, are compared with the corresponding values that are obtained using the STANJAN code (Figs. 1 and 2). The horizontal axes show the iteration number on a logarithmic scale and the vertical axes show the mole fractions of the species. The result of STANJAN is shown by solid lines .

It is seen that after about 1000 iterations, the difference becomes less than $\pm\delta\%$. Tracking the difference changes can help to probe the convergency pattern, and to develop new ideas to increase the convergency rate.

Having solved hundreds of equilibrium problems, the solution was observed to approach the correct answer after the 1000th iteration with an error value of less than $\pm\delta\%$. Therefore, in the present work, after the 1000th iteration the range of random generated compositions is confined to $x_1 \times (1 \pm \delta)$. As a result, the convergency rate increases greatly, so a considerable CPU time is saved.

To examine the validity of the presented algorithm, CJ detonation properties are calculated for two mixtures, C_2H_2 -Air and H_2 -Air. The plot of the pressure vs. detonation velocity for C_2H_2 -Air are shown in Figs. 3 and 4 for equivalence ratio (ϕ) = 0.5 & 2. The pressure-velocity diagram for H_2 -Air (reaction C) is shown in Fig. 5.



The results of the calculation by the STANJAN code for the detonation pressure and velocity for the same mixtures are also shown in the figures. It is seen that the minimum of the plot conforms precisely to the STANJAN values for the CJ detonation state. The results for the detonation temperature, pressure and velocity are also compared with the STANJAN and GASEQ values in Table 1.

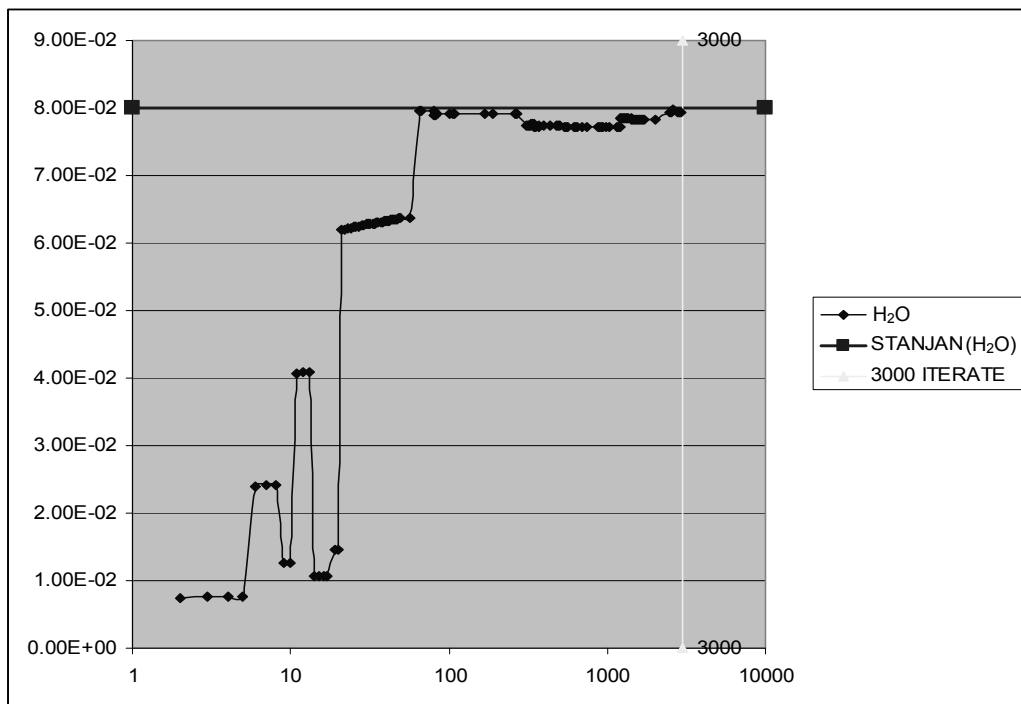


Figure 1. Present work and STANJAN results for H₂O mole fraction

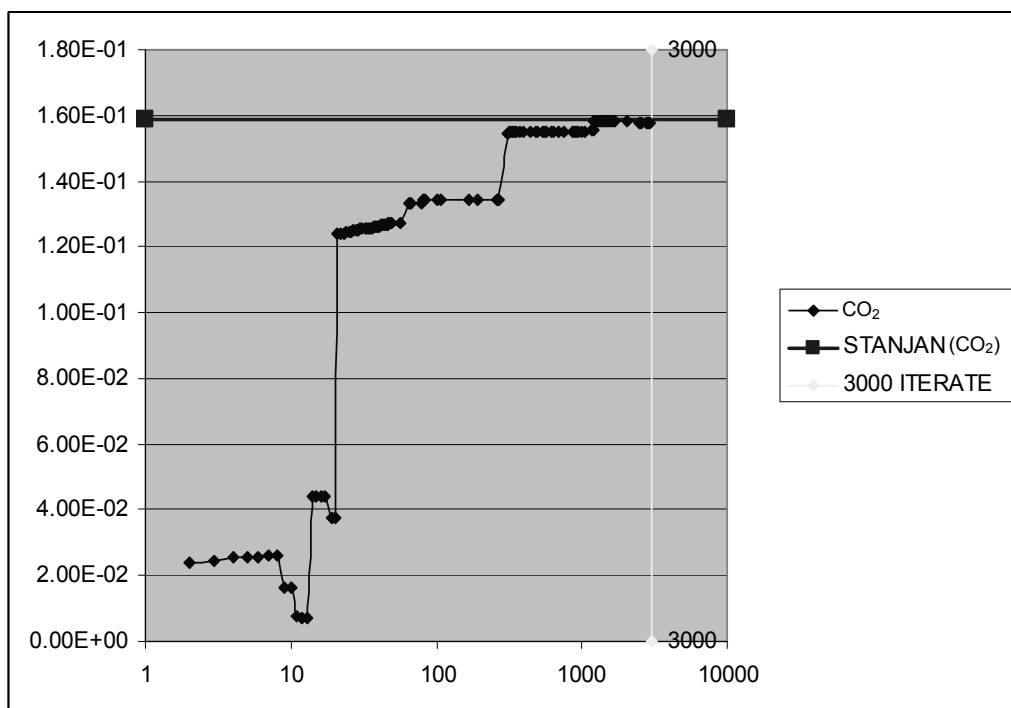


Figure 2. Present work and STANJAN results for CO₂ mole fraction

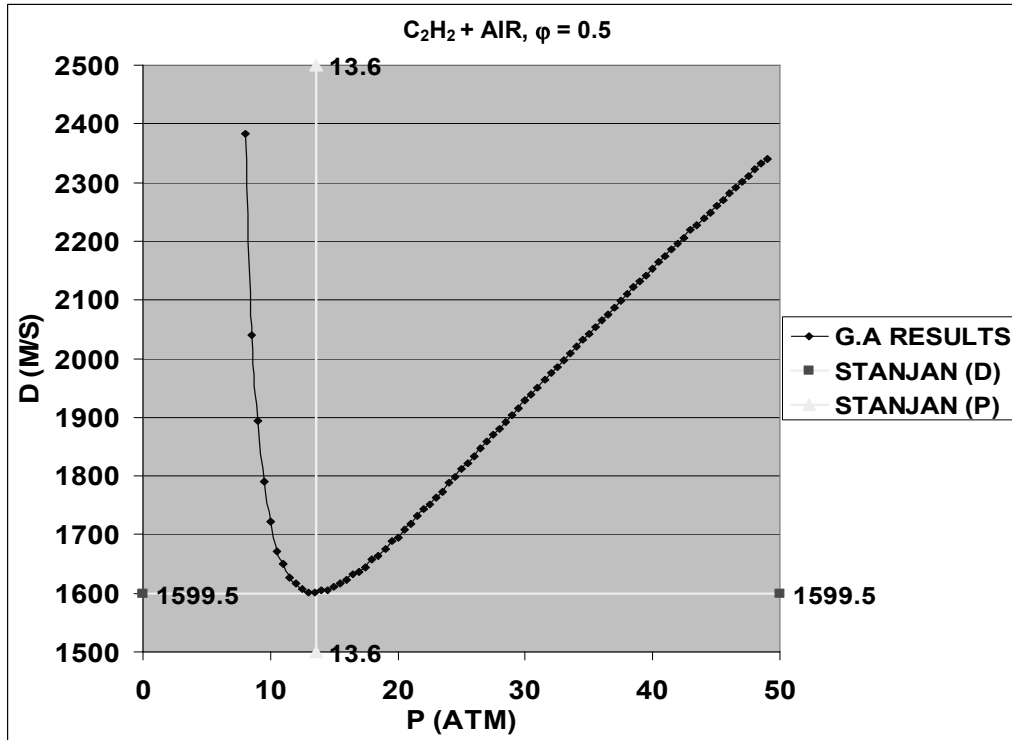


Figure 3. CJ condition for $C_2H_2 - Air$ detonation ($\phi=0.5$), compared with the STANJAN results.

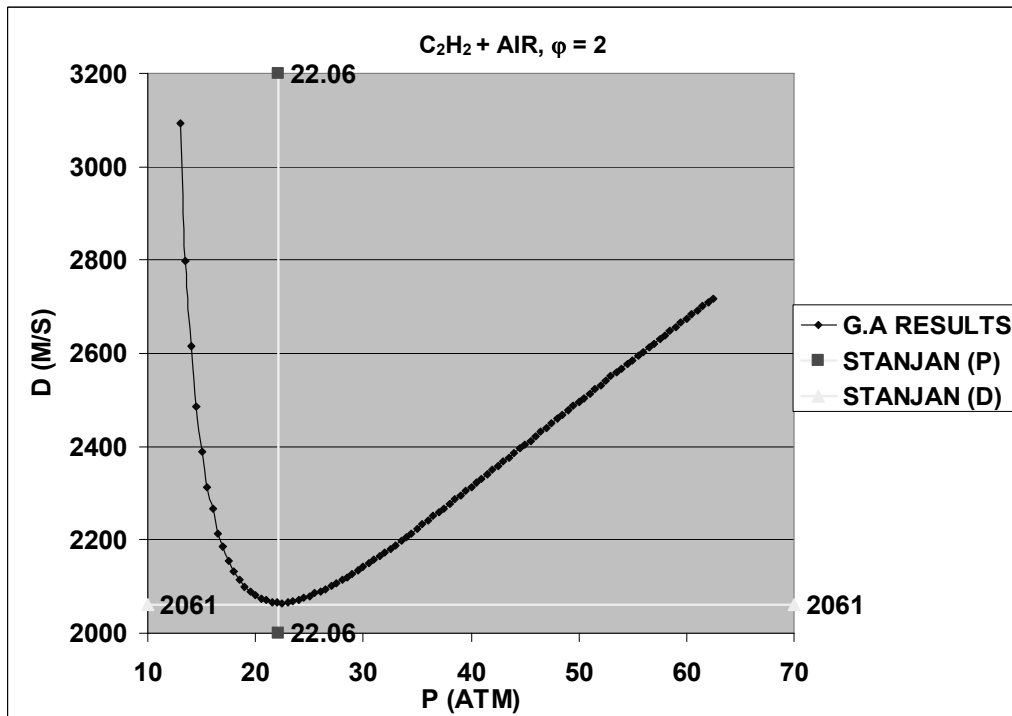


Figure 4. CJ condition for $C_2H_2 - Air$ ($\phi=2$), compared with the STANJAN results.

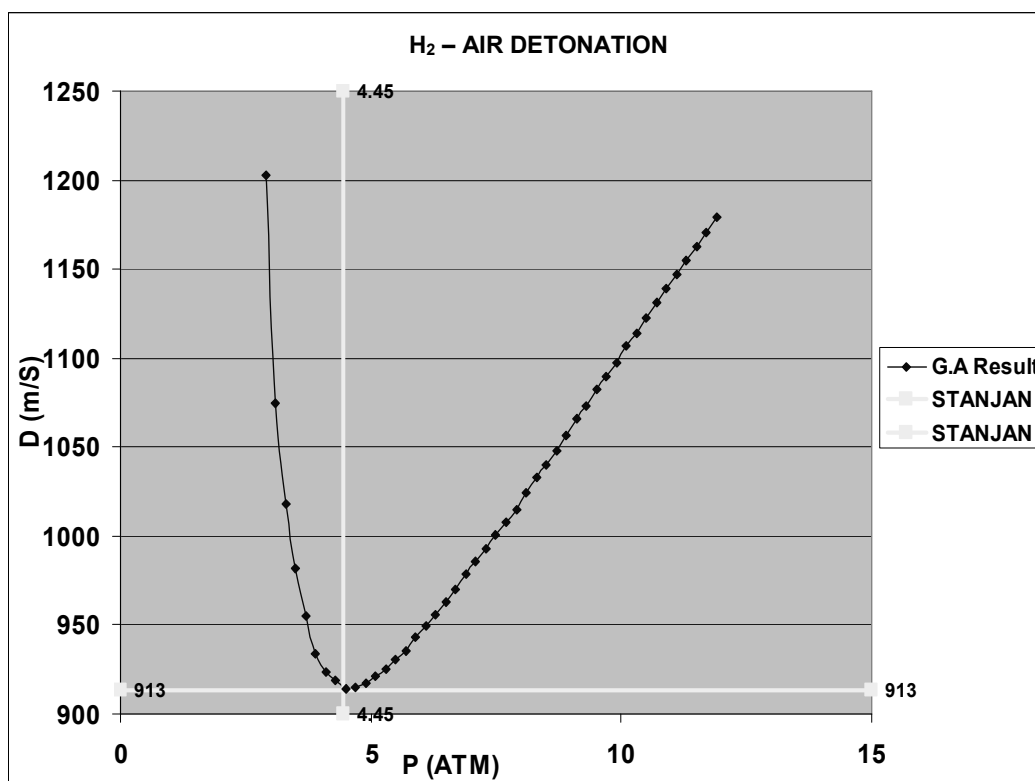


Figure 5. CJ condition for H₂ – Air,(reaction C), compared with the STANJAN results.

Table 1. Detonation temperature, pressure, velocity for C₂H₂-Air and H₂-Air mixtures, compared with the STANJAN and GASEQ results.

Reaction	Temperature, detonation velocity, pressure (STANJAN)	Temperature, detonation velocity, pressure (GASEQ)	Temperature, detonation velocity, pressure (Present work)
C ₂ H ₂ -Air ($\phi=0.5$)	2382.58 K 1599 m/s 13.6 atm	2386 K 1603 m/s 13.5 atm	2376.339 K 1587 m/s 13.5 atm
C ₂ H ₂ -Air ($\phi=2$)	3364.30 K 2061 m/s 22.06 atm	3354.8 K 2061.55 m/S 21.74 atm	3408.426 K 2088 m/s 22.2 atm
H ₂ -Air (reaction (C))	854.35 K 913.9 m/s 4.45 atm	Unable to converge	913.219 K 916.4 m/s 4.5 atm

Table (1) shows that GASEQ is not able to converge for the reaction (C). This problem is a sample of the divergence in the traditional codes. It can also be seen that the present work results are in good agreement with the STANJAN results in all cases.

7- Conclusion

In this study, a simple genetic algorithm is used for the determination of the thermo-chemical equilibrium condition in gaseous mixtures obeying the perfect gas equation of state. Using the presented algorithm, good initial estimate for the detonation parameters, which is a challenging task in traditional equilibrium calculations, is not required and the convergence to the global minimum of the Gibbs free energy function is guaranteed.

To compare the present work with a similar genetic algorithm-based study, a code similar to the AMRL code was prepared based on the specifications that Brog et al. presented in [4]. It is observed that this code needs to do many more iterations to converge to the correct answer with respect to the current work. The considerable reduction in the required iterations and the required computational CPU time in the present work are the result of new notions that are presented here. These ideas are: 1- the adaptive confining of the range of random generated compositions; 2- creating more than one new composition in each iteration; and, 3- using a new relation for creating new sets of product compositions.

In contrast to the traditional deterministic algorithms (e.g., algorithms in STANJAN and GASEQ codes), a genetic algorithm is, in fact, a probabilistic algorithm. Genetic algorithms have been extensively used in the past three decades for optimization problems in different fields of science and engineering. Due to the probabilistic nature of these algorithms, usually precise quantitative results are not expected from these algorithms. The main advantage of a genetics

algorithm is its vast and random search space which, especially with new techniques, guarantees the convergence to a global minimum [11]. The algorithm that was first proposed by Brog et al., although by itself is a primitive genetic algorithm, shall be credited as the pioneer work which brings this fascinating approach to the attention of equilibrium code developers. Unfortunately, to the best of the authors' knowledge, no official work, other than Brog's, has been published on this subject. In reference [9], which is an un-official paper, a most sophisticated GA is proposed as the initializer of an equilibrium code.

The current work started with the aim of developing a reliable algorithm for the determination of the CJ detonation properties in high explosives, where the requirement of using the real gas equation of state makes the problem much more challenging. The promising result of the first step, which is presented in this paper, encourages the authors to step forward to extend the algorithm to a general EOS. A modified approach of the GA proposed by reference [9] has been recently utilized and the initial results are quite promising. The details of the algorithm with results for a very high pressure mixture are the subject of a subsequent paper.

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