On Diffusive Supersonic Combustion

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ABSTRACT

Simple analytical methods are presented for the analysis of chemical kinetic effects in supersonic combustion.

Three different regions are shown to occur in supersonic diffusive combustion.

The first region is close to the injector exit, where the flow may be considered frozen for the main reacting species and where the radical concentration is being built up. This is the ignition delay region. A simplified kinetic scheme of the H_2–air reaction is deduced for this region. The linear differential equation giving the H concentration has been discussed and integrated in a representative case. In terms of this solution the limits of the ignition region may be determined.

Far from the injector exit the flow is close to chemical equilibrium. The reaction region is very thin, so that convection effects may be neglected. Then the governing equations reduce to ordinary differential equations, that may be integrated by using an integral method. In this way, deviations from equilibrium may be determined in terms of the reaction kinetics.

An extension of the integral method, developed for the analysis of the near-equilibrium region is proposed for the study of the transition region.

1. INTRODUCTION

Hypersonic air breathing propulsion rests on the possibility of rapidly mixing and burning some types of fuels in a supersonic air stream.

The oncoming free stream of air cannot be decelerated to subsonic velocities, because this would give rise to temperatures so high that a large

percentage of the mixture going out of the combustor would be dissociated, with the corresponding losses in efficiency.

Therefore mixing as well as combustion should be so rapid as to take place during the small residence times available to the air stream when going through the combustion chamber. Hence, highly reactive fuels such as hydrogen and perhaps methane should be used. In addition the air stream must be decelerated to increase the static temperature and reaction rates.

In order to avoid the appearance of shock waves the heat release should be smoothly distributed. This may be accomplished with less difficulty if the heat release is diffusion controlled.

The mixing problem has been analysed by a number of investigators using the conservation equations in differential form[1] or in integral form[2]. The fluid-dynamic mixing problem may be uncoupled from the chemical kinetics problem if one of the assumptions of chemical equilibrium or frozen flow is made.

Of course the complete conservation equations including the chemical kinetic terms may be solved using high speed computers. Because of the large number of parameters involved in the computation, and in order to assess the influence of each parameter, the computing effort is similarly large.

In this paper the emphasis is on simple analytical techniques for the evaluation of chemical kinetic effects.

First, chemical kinetic effects may be fairly simply considered when the flow is nearly frozen. This is the situation close to the injector exit. The ignition delay length, marking the beginning of the heat release zone, may be evaluated using this analysis.

Second, the deviations from chemical equilibrium due to chemical kinetic effects will be evaluated for the near-equilibrium situation. This is the case, far from the injector or in large combustors.

Finally a possible extension of the near-equilibrium treatment to cover in an approximate way the intermediate cases will be considered.
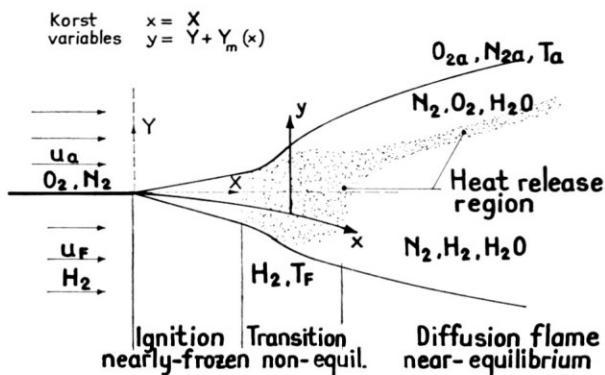

FIG. 1

Although the analysis given above may be used in connection with more complex mixing situations, for presentation of the method, only the mixing of two parallel streams of hydrogen and air will be considered. In addition, the simple Korst et al. model[3] of the conservation equation will be used in the analysis.

Although the mixing model to be used may have an important effect on the fluid-dynamic result, the influence on the chemical kinetics aspects of the problem is not so large.

Figure 1 shows schematically the three different regions that are to be analysed.

SYMBOLS

h_s total enthalpy
D mass flux of atomic oxygen across the boundary layer given by eqn. (17)
M given by eqn. (18)
U mean velocity $= (u_a + u_p)/2$
u, v velocity components along the Korst co-ordinates
w_i mass rate of production of the ith species per unit volume
x, y intrinsic co-ordinates of Korst, *see* Fig. 1
Y_i mass fraction of the species i.
ε turbulent diffusivity
ξ, η similarity variables, *see* eqn. (4)
ξ_1 given by eqn. (16)
ρ density

Suffixes
a air stream conditions
F conditions at the fuel stream

2. CONSERVATION EQUATIONS

The conservation equations for the two-dimensional case are as follow:
Conservation of species:

$$\rho u \frac{\partial Y_i}{\partial x} + \rho v \frac{\partial Y_i}{\partial y} = \frac{\partial}{\partial y}\left(\rho \varepsilon \frac{\partial Y_i}{\partial y}\right) + w_i$$
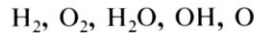
Momentum:

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial}{\partial y}\left(\rho \varepsilon \frac{\partial u}{\partial y}\right)$$
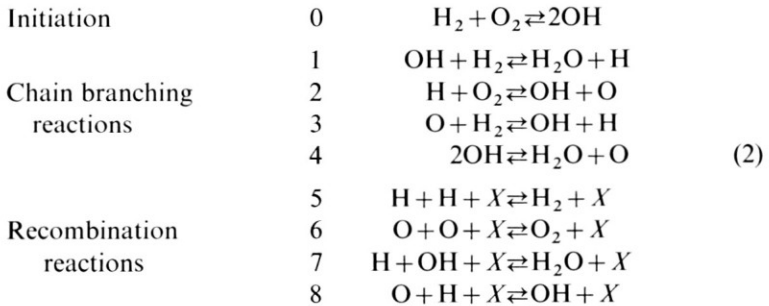
(1)

where ε is the turbulent eddy diffusivity.

The Crocco integral will be used instead of the energy equation.

In addition to nitrogen (mass fraction Y_N) the following species are considered[2]:

$$H_2, \ O_2, \ H_2O, \ OH, \ O$$

that may react according to the following kinetic scheme: (X represents any species)

Initiation	0	$H_2 + O_2 \rightleftarrows 2OH$
	1	$OH + H_2 \rightleftarrows H_2O + H$
Chain branching	2	$H + O_2 \rightleftarrows OH + O$
reactions	3	$O + H_2 \rightleftarrows OH + H$
	4	$2OH \rightleftarrows H_2O + O$
	5	$H + H + X \rightleftarrows H_2 + X$
Recombination	6	$O + O + X \rightleftarrows O_2 + X$
reactions	7	$H + OH + X \rightleftarrows H_2O + X$
	8	$O + H + X \rightleftarrows OH + X$

(2)

All these reactions should be taken into account for the evaluation of the mass production rate w_i of each of the species i. For example, the contribution of the forward reaction 1 to the H_2O production is

$$w_{H_2O} = 18 \left(\frac{\rho}{17} Y_{OH} \right) \left(\frac{\rho}{2} Y_{H_2} \right) K_1$$

The rate constants of the forward (K_j) and reverse (K_{-j}) reactions of the form

$$K_j = k_j \exp\left(\frac{-E_j}{RT} \right)$$

are given in Table 1. The temperature is in $^\circ K$.

The rate constants are given in $(mol/cc)^{-1} \ sec^{-1}$ for second-order reactions, and in $(mol/cc)^{-2} \ sec^{-1}$ for third-order reactions.

For simplicity, in the following, the Korst model[3] of the above equations will be used.

Continuity of species: $\qquad U \dfrac{\partial Y_i}{\partial x} = \varepsilon(x) \dfrac{\partial^2 Y_i}{\partial y^2} + \dfrac{w_i}{\rho}$

(3)

Momentum: $\qquad\qquad\quad U \dfrac{\partial u}{\partial x} = \varepsilon(x) \dfrac{\partial^2 u}{\partial y^2}$

where U is a mean velocity $U = (u_F + u_a)/2$.

The equations are assumed to hold in an intrinsic co-ordinate system to be determined afterwards by means of the integral momentum equation. The eddy diffusivity is assumed to be a function only of x.

TABLE 1

j	$\dfrac{k_j}{k_{-j}}$	$\dfrac{E_j}{E_{-j}}$ cal/mol °K
0	10^{11} 2×10^{13}	7×10^1 6×10^5
1	3×10^{11} $1 \cdot 2 \times 10^{15}$	6×10^3 2×10^1
2	3×10^{11} $2 \cdot 7 \times 10^{13}$	$1 \cdot 8 \times 10^1$ $3 \cdot 3 \times 10^1$
3	3×10^{11} $1 \cdot 3 \times 10^{11}$	8×10^3 6×10^3
4	3×10^{11} $3 \cdot 12 \times 10^{15}$	6×10^3 $2 \cdot 49 \times 10^1$
5	10^{16} $2 \cdot 3 \times 10^{17} (1000/T)^{1/2}$	0 $1 \cdot 1 \times 10^5$
6	10^{15} $10^{18} (1000/T)^{1/2}$	0 $1 \cdot 3 \times 10^5$
7	10^{17} $3 \times 10^{22} T^{-1}$	0 $1 \cdot 1 \times 10^5$
8	10^{16} $10^{17} (1000/T)^{1/2}$	0 $1 \cdot 1 \times 10^5$

For the analysis of these equations the following variables will be used. They are the similarity variables in both the frozen flow or the equilibrium flow case.

$$\xi = x \qquad \eta = \frac{y}{f(x)}$$

where $f(x)$ is given by

$$f(x) = 2\sqrt{\left[\int \frac{\varepsilon}{U} \, d\xi\right]}$$

In terms of these variables the governing equations become

$$\frac{\partial^2 Y_i}{\partial \eta^2} + 2\eta \frac{\partial Y_i}{\partial \eta} = \left[\frac{4}{\varepsilon}\int \frac{\varepsilon}{U} \, d\xi\right]\left[U \frac{\partial Y_i}{\partial \xi} - \frac{w_i}{\rho}\right]$$

$$\frac{\partial^2 u}{\partial \eta^2} + 2 \frac{\partial u}{\partial \eta} = 4 \frac{U}{\varepsilon}\left[\int \frac{\varepsilon}{U} \, du\right]\frac{\partial u}{\partial \xi}$$

(4)

With the boundary conditions:

$$\eta = -\infty \qquad u = u_F \qquad Y_i = 0 \qquad (i \ne H_2)$$

$$\eta = \infty \qquad u = u_a \qquad Y_i = 0 \qquad (i \ne O_2, N_2)$$

The following integral may be deduced from the above equations

$$u = \tfrac{1}{2}(u_F + u_a) + \tfrac{1}{2}(u_a - u_F)\,\mathrm{erf}\,\eta \tag{5}$$

$$h_s = \tfrac{1}{2}(h_{sF} + h_{sa}) + \tfrac{1}{2}(h_{sa} - h_{sF})\,\mathrm{erf}\,\eta \tag{6}$$

$$\left.\begin{aligned}
Y_{H_2} + \tfrac{2}{18}Y_{H_2O} + \tfrac{1}{17}Y_{OH} + Y_H &= \tfrac{1}{2}(1 - \mathrm{erf}\,\eta) \\
Y_{O_2} + \tfrac{16}{18}Y_{H_2O} + \tfrac{16}{17}Y_{OH} + Y_O &= \tfrac{1}{2}Y_{O_{2a}}(1 + \mathrm{erf}\,\eta) \\
Y_{N_2} &= \tfrac{1}{2}Y_{N_{2a}}(1 + \mathrm{erf}\,\eta)
\end{aligned}\right\} \tag{7}$$

The above relations (5) to (7) give the solution to the problem if, in addition, the frozen flow assumption ($Y_H = Y_{OH} = Y_O = Y_{H_2O} = 0$), or the equilibrium flow assumption ($w_i = 0$ for four of the species) is used.

3. THE IGNITION DELAY REGION

Close to the injector exit the mixing and convection terms are, for the main reacting species H_2 and O_2, much more important than the chemical production.

In addition, there is no appreciable heat release in this region, and the concentration of the other reacting species is small.

Then, the H_2 and O_2 concentrations are given by the frozen flow solution

$$\begin{aligned}
Y_{H_2} &= \tfrac{1}{2}(1 - \mathrm{erf}\,\eta) \\
Y_{O_2} &= \tfrac{1}{2}Y_{O_{2a}}(1 + \mathrm{erf}\,\eta)
\end{aligned} \tag{8}$$

and the temperature may be determined in terms of the total enthalpy using Crocco relation.

Chemical kinetic scheme in the ignition delay region

The temperature of the air stream should be of the order of $1200°K$. Lower temperatures would give rise to large ignition delays. If the air static temperature at the injector exit was much larger the final combustion temperature would be too high, and the products would leave the combustor with a large percentage of dissociated species. The hydrogen stream static temperature would be lower.

For these temperatures, the chemical kinetic scheme is reduced to an initiating reaction:

0 $\qquad\qquad H_2 + O_2 \rightarrow 2OH$

and the following chain branching reactions

1 $\qquad\qquad OH + H_2 \rightarrow H_2O + H$

2 $\qquad\qquad H + O_2 \rightarrow OH + O$

3 $\qquad\qquad O + H_2 \rightarrow OH + H$
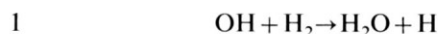
The initiating reaction may become unimportant if there is an appreciable amount of radicals H, OH or O initially present either in the air or fuel stream or in the injector boundary layers.

The forward reaction constants of 1 and 3 are much higher than that of reaction 2.

In addition the concentrations of O, H, OH and H_2O are initially small so that the backward reaction may be neglected. Hence in most of the ignition delay region:

(a) Any OH initially present or produced by the initiation reaction 0, will be immediately converted by means of the fast reaction 1 into H_2O and H.

(b) Similarly, any amount of O initially present will be converted by means of reaction 3 into OH and H; while the OH thus produced will be transformed immediately into H_2O and H by means of reaction 1.

(c) Whenever the reaction $H + O_2 \rightleftarrows OH + O$ takes place, the OH and O thus produced will be immediately converted into H and H_2O by means of reaction 1 and 3.

As a consequence, we may use as initial conditions: two atoms of H and one mol of H_2O exist instead of each initial atom of O. Similarly one mol of H and H_2O should be considered instead of each mol of OH.

Also the initiation reaction 0 together with the chain branching reactions may be reduced to the overall reaction

4 $\qquad\qquad 3H_2 + O_2 \rightleftarrows 2H_2O + 2H$

with the overall rate of reaction

$$w_H = \frac{w_{H_2O}}{18} = \frac{K_0}{32\rho^2} Y_{H_2} Y_{O_2} + \frac{K_2}{16\rho^2} Y_H Y_{O_2} \qquad (9)$$

Ignition delay in the pre-mixed case

As an example, and in order to compare with the existing theories, the ignition delay region will be analysed when diffusion is neglected (or in the pre-mixed case).

The conservation equation for atomic hydrogen may be written

$$U \frac{dY_H}{dx} = \frac{K_0}{32} \rho Y_{H_2} Y_{O_2} + \frac{K_2}{16} \rho Y_{O_2} Y_H \tag{10}$$

where K_0, K_2, ρ, Y_{H_2} and Y_{O_2} may be considered constant.
    As initial condition we may write

$$x = 0, \quad Y_H = (Y_H)_i$$

where
$$(Y_H)_i = (Y_H)_0 + \frac{(Y_O)_0}{16} + \frac{(Y_{OH})_0}{17}$$

the subscript 0 indicates here the original concentrations of the radicals, transformed into atomic hydrogen by the fast reactions 1 and 3.
    By integrating eqn. (10) we obtain

$$Y_H = \left((Y_H)_i + \frac{K_0}{2K_2} Y_{H_2} \right) \exp \left[\left(\frac{K_2 Y_{O_2}}{16U} \right) x \right] - \frac{K_0}{2K_2} Y_{H_2} \tag{11}$$

and the result obtained in ref. (4) using the complete kinetic scheme is recovered and generalised.
    The relative influence of the initiation reaction 0 or initial radical concentration may be evaluated easily.
    According to the above simplified scheme the difference in molar concentration of atomic hydrogen and water is kept constant through the ignition delay region.
    The Y_O and Y_{OH} mass fractions are determined in this region by the relations

$$K_2 Y_H Y_{O_2} = K_3 Y_O Y_{H_2} = \tfrac{32}{17} Y_{OH} Y_{H_2} \tag{12}$$

There are many criteria to define the end of the ignition delay. One could use as a criterion that the backward reaction 1 should be of the same order as the forward reaction 2. Afterwards the amount of OH and O radicals would grow rapidly until a partial equilibrium would be attained. This equilibrium concentration would change slowly because of the recombination reactions responsible for the heat release.
    The critical $(Y_H)_c$ mass fraction would then be

$$(Y_H)_c \sim \frac{1}{4} \frac{K_2}{K_{-1}} Y_{O_2} \sim 10^{-2} \exp \left(\frac{1000}{T} \right) \tag{13}$$

In terms of $(Y_H)_c$ the ignition delay is given by

$$\frac{L}{U} = \frac{16}{K_2 \rho Y_{O_2}} \ln \left(\frac{(Y_H)_c}{(Y_H)_i + (K_0/2K_2) Y_{H_2}} \right) \simeq \frac{\exp(-9000/T)}{p} \tag{14}$$

Diffusion effects in the ignition delay region

Diffusion of radicals as well as diffusion of the main reacting species should be considered in the analysis of the ignition delay region.

In this region the mass fractions of H_2 and O_2 are given by relation (1) because the flow may be considered frozen for these species.

If we neglect the effect on the turbulent diffusivity of the injector boundary layers, $\varepsilon(x) = \alpha x$. And if, in addition, we use the overall rate of reaction (9) for the production of H we get the following equation for Y_H

$$\frac{\partial^2 Y_H}{\partial \eta^2} + 2\eta \frac{\partial Y_H}{\partial \eta} = \frac{2\xi}{U}\left[U \frac{\partial Y_H}{\partial \xi} - \frac{K_0}{32}\rho Y_{H_2} Y_{O_2} - \frac{K_2}{16}\rho Y_{O_2} Y_H \right] \tag{15}$$

This equation is linear in Y_H, and the influence of non-homogeneous initial or boundary conditions and the non-homogeneous initiation reaction terms $K_0 \rho Y_{H_2} Y_{O_2}$ may be studied in turn.

We consider in the following the effect of the introduction in the mixing region of O atoms coming from the injector boundary layer. These O atoms immediately cause the appearance, because of the chain branching reactions 1 and 3, of a double amount of H radicals.

So that the equation to be solved is

$$\frac{\partial^2 Y_H}{\partial \eta^2} + 2\eta \frac{\partial Y_H}{\partial \eta} = 2\xi_1 \left[\frac{\partial Y_H}{\partial \xi_1} - f(\eta) Y_H \right] \tag{16}$$

where $f(\eta)$ is given by

$$\frac{K_2}{16}\rho Y_{O_2} Y_H = \left(\frac{K_2}{16}\rho Y_{O_2} \right)_a f(\eta)$$

and

$$\xi_1 = \xi \frac{\left(\frac{1}{16}K_2 \rho Y_{O_2} \right)_a}{U}$$

As initial condition for eqn. (16) we may write that

$$32 \int_{-\infty}^{\infty} \rho Y_H u \, dy = \int_{0}^{\infty} \rho Y_0 u \, dy = D \tag{17}$$

The first integral in (17) is the mass of H at the origin, $\xi_1 = 0$, of the mixing layer. It is proportional to the mass of O atoms, D, at the end of the injector boundary layer, which is given by the second integral.

If we assume that the thickness of the boundary layer is small compared to the ignition delay length, we may write the initial H concentration for the mixing region as a Dirac δ function of y.

Then if the production terms $f(\eta) Y_H$ were neglected, Y_H would be given by

$$Y_H = \frac{M}{\xi_1} \exp(-\eta^2) \tag{18}$$

where M which may be deduced by taking (18) into (17) is given by

$$M = \frac{D}{32} \left(\frac{K_2 \rho Y_{O_2}}{16} \right)_a \frac{\beta}{u_a \rho_a \sqrt{(2\alpha U)}}$$

and β is of order unity. Hence for small ξ, Y_H should be given by (18).

Equation (16) with the initial condition (18) may be integrated easily if $f(\eta)$ is assumed to be constant, for example, equal to unity. The solution is

$$Y_H = \frac{M \exp(\xi_1 - \eta^2)}{\xi_1} \tag{19}$$

Equation (16) will be numerically integrated for other distributions of $f(\eta)$ and the results will be published later.

By following the approach of ref. (5), the maximum atom concentration in the injector boundary layer as well as the value of D has been calculated, and the results are given in Fig. 2.
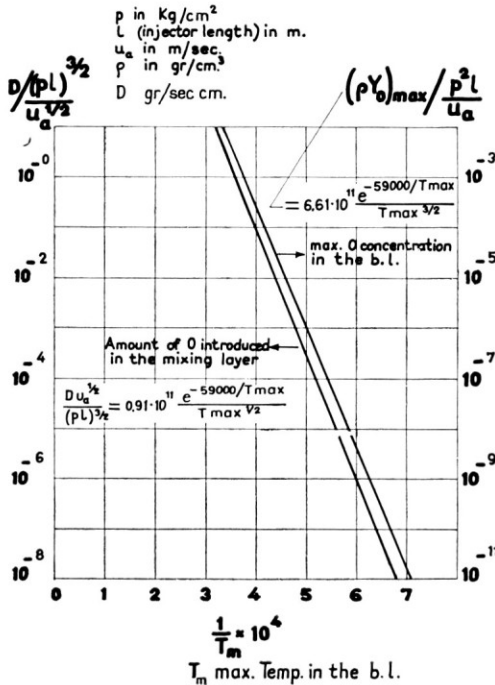

FIG. 2

4. NEAR-EQUILIBRIUM REGION

Far from the injector exit the thickness of the reaction region becomes thin compared with the mixing layer thickness.

Outside the reaction region the mass fractions and temperatures are given by the equilibrium flow values. Molecular hydrogen and oxygen co-exist only in the thin non-equilibrium region.

Because of the large changes in the gradients of temperature and concentrations across the reaction region, convection effects may be neglected compared with diffusion effects[6, 7].

Then, the species conservation equations reduce to

$$\frac{1}{\rho}\frac{\partial}{\partial y}(\rho\varepsilon)\frac{\partial Y_i}{\partial y} = -\frac{w_i}{\rho} \tag{20}$$

These equations may be solved as ordinary differential equations, where ε plays the role of a parameter.

An integral, approximated, method has been given in ref. (8) that reduces eqns. (20) to a system of algebraic equations.

5. THE TRANSITION REGION

The integral method of ref. (5) is presently being extended to analyse the transition region. In this method the right-hand side of eqn. (4) is approximated by an exponential of the form

$$A_i(\xi)\exp\left\{-\alpha_i(\xi)[\eta-\eta_i(\xi)]^2\right\}$$
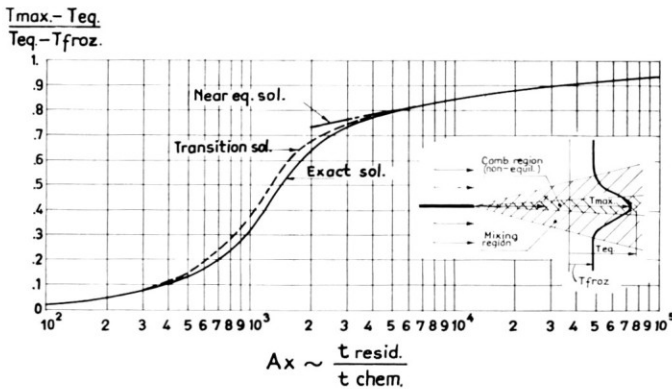

FIG. 3

x

the resulting equation is first integrated with respect to η. The boundary conditions provide additional relations for the determination of the parameters. Then, the chemical production terms are evaluated using the complete kinetic scheme and the Y_i given by the solution of the approximate conservation equation mentioned before.

A system of ordinary differential equations is obtained for A_i, α_i and η_i may be integrated numerically without difficulty.

In Fig. 3 the near-equilibrium solution, the intermediate solution, and the exact solution are given for the laminar mixing of two reacting gases which obey simple Arrhenius kinetics. The exact solution is given in ref. (6).

Further numerical results for the hydrogen–air reaction will soon be published.

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