

THE MIXTURE FRACTION TO PREDICT PRODUCT SPECIES IN FIRE

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ABSTRACT

Predicting and calculating the major species products in compartment fires is of great importance since these species pose great hazard on occupants' evacuation and fire protection. To better correlate the empirical data, an approach using the mixture fraction, or mass fraction of the fuel atoms, is introduced which can be used to predict the species yield for the unsteady-state fire situation. The derivation is based on a simplified two-zone modeled compartment fire scenario. The relationships between mixture fraction and the equivalence ratio during the smoke filling period and smoke outflow period are derived and illustrated as applications of this method.

1. INTRODUCTION

The hazard of the generation of fire products in chemical reactions is a vital factor for assessing fire risk and fire protection. Compared to the thermal hazard, e.g. high temperature and heat flux of flame and smoke, the non-thermal hazard [1] can be more severe and more difficult to predict in the compartment fires.

Much experimental work has been done to study the chemical reaction process and concentration of reaction products using the parameter of equivalence ratio. It has been shown that species concentration can be reasonably correlated with the equivalence ratio in steady fires. Based on hood experimental work by Beyler [2,3] and Zukoski et al. [4,5], Tewarson [1,6] developed the basis of the equivalence ratio to correlate the species production rates in compartment fires. Gottuk and Lattimer [7] and Pitts [8,9] did more detailed work in determining and confirming the correlation with a chemical kinetics study, emphasizing the generation of carbon monoxide. All these studies were based on the average species concentration in the combustion product outflow in the steady experiments. The equivalence ratio can then be used to correlate the average concentration of the smoke layer, or the yield i.e., mass produced per mass of fuel vaporized. This method was applied to the BRI zone model by Tanaka and Yamada [10,11] who developed an algorithm for calculating the generation of species with such correlations. As this method can only be used when the reaction is at steady-state or quasi-steady state, it is not able to ideally reflect the full behavior of a fire. This limitation occurs because the equivalence ratio is varied on boundary flow rates. Its counterpart, the

mixture fraction, is a point function, and does not have the steady-state limitation. Some have tried to compensate for this limitation by invoking a global and layer equivalence ratio (GER) [5]. Zukoski et al. [5] were the first to show the limitation of the GER for the non-steady problem. They illustrated this by adding an air stream to the upper layer.

2. FORMULATION

By introducing the parameter, Z , the mass fraction (of the fuel atoms), one can simply predict the result of a reaction without considering whether it is at steady state or unsteady state. This can be done, as it will be shown, that for a general unsteady problem, the combustion reactants and product concentrations, are solely a function of Z . While Z can be directly related to the GER for the steady case, it cannot be done when unsteady. Consequently, the concentrations for a given fuel are solely dependent on Z . To illustrate it, a simplified compartment fire is considered in terms of a control volume.

As showed in Fig. 1, the control volume is chosen including the upper layer and the fire source. \dot{m}_a and \dot{m}_f are the mass flow rate of fresh air and gasified fuel coming into the compartment respectively. m is the mass in the control volume and Y_i is the mass fraction in the control volume for one kind of species, i . The mass fraction for each species i at each flow path j , is represented as $Y_{i,j}$ (the mass fraction of oxygen in the incoming fresh air is taken as 0.233).

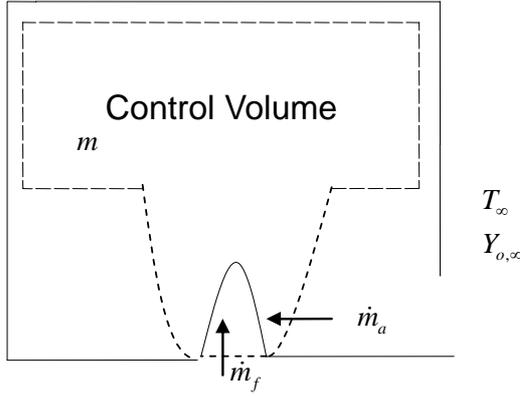


Fig. 1: Schematic of a simplified compartment fire

2.1 Conservation Equations

Consider the reaction represented as:



where r is the stoichiometric air to fuel ratio. Also consider the reaction is complete, so the products are known. The mass and species conservations for the upper layer control volume apply as follows (diffusion at the control volume boundary is ignored):

$$\left(\frac{dm}{dt}\right)_{cv} + \left(\sum_j \dot{m}_j\right)_{out} - \left(\sum_j \dot{m}_j\right)_{in} = 0 \quad (1)$$

$$\frac{d(mY_i)}{dt} + \left(\sum_j \dot{m}_j Y_i\right)_{out} - \left(\sum_j \dot{m}_j Y_{i,j}\right)_{in} = \dot{m}_{i,r} \quad (2)$$

where $\dot{m}_{i,r}$ is the production rate of species i .

Multiply Eq. (1) by Y_i and then subtract it from Eq. (2):

$$m \frac{dY_i}{dt} + \left(\sum_j \dot{m}_j (Y_i - Y_{i,j})\right)_{in} = \dot{m}_{i,r} \quad (3)$$

For i as fuel, Eq. (3) becomes:

$$m \frac{dY_f}{dt} + \dot{m}_f (Y_f - 1) + \dot{m}_a (Y_f - 0) = -\dot{m}_{f,r} \quad (4)$$

For i as oxygen, Eq. (3) becomes:

$$m \frac{dY_o}{dt} + \dot{m}_f (Y_o - 0) + \dot{m}_a (Y_o - 0.233) = -0.233r \dot{m}_{f,r} \quad (5)$$

For i as any product, Eq. (3) becomes:

$$m \frac{dY_p}{dt} + \dot{m}_f (Y_p - 0) + \dot{m}_a (Y_p - 0) = (1 + 0.233r) \dot{m}_{f,r} \quad (6)$$

Now, as in standard combustion practice, coupling variables are selected to eliminate the combustion source terms. By introducing $\beta_1 = 0.233rY_f - Y_o$, $\beta_2 = (1 + 0.233r)Y_f + Y_p$, $\beta_3 = \frac{1 + 0.233r}{0.233r}Y_o + Y_p$, and substituting β_1 , β_2 and β_3 to Eqs. (4) to (6) with some algebraic manipulation, then:

$$m \frac{d\beta_1}{dt} + \beta_1 (\dot{m}_a + \dot{m}_f) - 0.233r \dot{m}_f + 0.233 \dot{m}_a = 0 \quad (7)$$

$$m \frac{d\beta_2}{dt} + \beta_2 (\dot{m}_a + \dot{m}_f) - (0.233r + 1) \dot{m}_f = 0 \quad (8)$$

$$m \frac{d\beta_3}{dt} + \beta_3 (\dot{m}_a + \dot{m}_f) - \frac{0.233r + 1}{r} \dot{m}_a = 0 \quad (9)$$

2.2 Mixture Fraction Formulation

If Z is defined as the mixture fraction, then it satisfies:

$$\frac{d(mZ)}{dt} + \left(\sum_j \dot{m}_j Z_j\right)_{out} - \left(\sum_j \dot{m}_j Z_j\right)_{in} = 0 \quad (10)$$

as the fuel atoms are conserved. Here Z is the value in the layer, and Z_j is the value at the vent, j . Note Z_j equals Z when j is referred as an outflow vent.

As \dot{m}_f is assumed to be pure fuel, which corresponds to a mixture fraction of 1; meanwhile, the mixture fraction in the incoming air, \dot{m}_a , equals 0 as there is no fuel in it. Taking the values of 0 and 1 into Eq. (10) and incorporating with Eq.(1), we get Eq. (11):

$$m \frac{dZ}{dt} + Z(\dot{m}_f + \dot{m}_a) - \dot{m}_f = 0 \quad (11)$$

Eq. (11) is the conservation equation of mixture fraction which we will focus on. When the reaction is steady state, the differential part is zero, then:

$$Z = \frac{\phi}{r + \phi} \quad (12)$$

where ϕ is defined as the GER and $\phi = \frac{\dot{m}_f}{\dot{m}_a} r$, and r is the stoichiometric ratio of air to fuel.

In general, for one kind of fuel, $Z_i = f(t, \phi)$, i.e. Z_i is a function of t and ϕ . For the steady state, Z_i is a unique function of ϕ , only.

3. SHOWING SPECIES AS UNIQUE FUNCTION OF Z

By introducing $Z_{FO} = a_1\beta_1 + b_1$, $Z_{FP} = a_2\beta_2 + b_2$, $Z_{PO} = a_3\beta_3 + b_3$ and substituting $\beta_1, \beta_2, \beta_3$ in Eqs. (7) to (9), we obtain the equations in "Z" form:

$$m \frac{dZ_{FO}}{dt} + Z_{FO}(\dot{m}_f + \dot{m}_a) + (0.233a_1 - b_1)\dot{m}_a - (0.233ra_1 + b_1)\dot{m}_f = 0 \quad (13)$$

$$m \frac{dZ_{FP}}{dt} + Z_{FP}(\dot{m}_f + \dot{m}_a) - b_2\dot{m}_a - [(0.233r + 1)a_2 + b_2]\dot{m}_f = 0 \quad (14)$$

$$m \frac{dZ_{PO}}{dt} + Z_{PO}(\dot{m}_f + \dot{m}_a) - \left(\frac{0.233r + 1}{r} a_3 + b_3\right)\dot{m}_a - b_3\dot{m}_f = 0 \quad (15)$$

Make the equations above each be equivalent to Eq. (11). To achieve this, we need to get solutions for $a_1, b_1, a_2, b_2, a_3, b_3$.

$$a_1 = \frac{1}{0.233(1+r)}, \quad b_1 = \frac{1}{1+r}$$

$$a_2 = \frac{1}{1+0.233r}, \quad b_2 = 0$$

$$a_3 = -\frac{r}{0.233r+1}, \quad b_3 = 1$$

Therefore, Z_{FO} , Z_{FP} and Z_{PO} become respectively as follows:

$$Z_{FO} = \frac{0.233rY_f - Y_o + 0.233}{0.233(1+r)} \quad (16)$$

$$Z_{FP} = \frac{(1+0.233r)Y_f + Y_p}{1+0.233r} \quad (17)$$

$$Z_{PO} = 1 - \frac{(1+0.233r)Y_o + 0.233rY_p}{0.233(1+0.233r)} \quad (18)$$

But, Z , the mixture fraction, is not identical to Z_{FO} , Z_{FP} and Z_{PO} unless they satisfy the initial condition of the fire, i.e. $Z_{FO} = Z_{FP} = Z_{PO}$, while $Y_f = 0$, $Y_o = 0.233$, $Y_p = 0$. And it follows that Z_{FO} , Z_{FP} and Z_{PO} all show agreement with the initial condition for Z , i.e. $t = 0, Z = 0$. Thus the stoichiometric reaction species concentration can be presented in terms of Z .

Furthermore, when $\phi = 0, Z = 0$; and when $\phi \rightarrow \infty, Z = 1$. The relationship also shows agreement with the physical meaning that the limits are accordingly pure air (oxidizer) and pure fuel, respectively.

Solving Eqs. (16) to (18) above with the conditions:

$$\begin{cases} Y_f = 0, & \text{for } \phi < 1 \\ Y_f = 0, Y_o = 0, & \text{for } \phi = 1 \\ Y_o = 0, & \text{for } \phi > 1 \end{cases}$$

we can get the relationships between mass fractions of fuel, oxygen, products and mixture fraction, Z .

$$\begin{cases} Y_o = 0.233 - 0.233(1+r)Z \\ Y_f = 0 \\ Y_p = (1+0.233r)Z \end{cases} \quad \text{for } \phi \leq 1$$

$$\begin{cases} Y_o = 0 \\ Y_f = \frac{(1+r)Z - 1}{r} \\ Y_p = \frac{0.233(1-Z)(1+0.233r)}{0.233r} \end{cases} \quad \text{for } \phi \geq 1 \quad (19)$$

Fig. 2 shows the theoretical results of mass fractions of species for the case fuel of propane, i.e. $r = 15.6$.

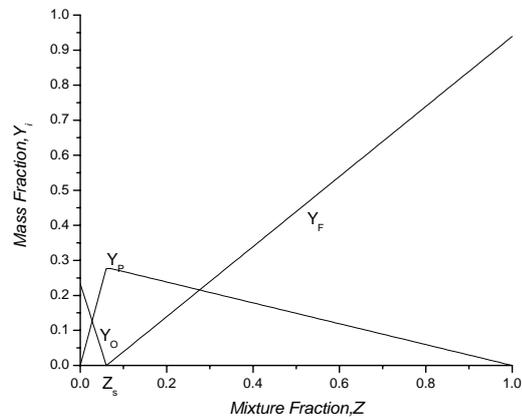


Fig. 2: Theoretical relations between mixture fraction and species concentration

Thus, we see that even for an unsteady case, each $Y_i = f(Z)$ only. And recall $\phi = f(Z, t)$ in general. Hence, ϕ is not one-to-one for Y_i in the unsteady case.

It has been shown [1-8] that a specific fuel has a unique fire relationship between species volume fraction of species and equivalence ratio, ϕ . But all of these works have been based on steady experiments. However, if ϕ is converted to Z for these data, then those resulting correlations can be used in general for prediction of unsteady compartment fire models in the zone context herein. Eq. (12) can be used to convert the results into Z format. Now a single solution of Eq. (11) in the context of a uniform smoke layer model gives Z and therefore $Y_i(Z)$ by the empirical correlations.

An example of this process was applied to the data of Beyler [2,3] for the fuel propane. This is shown in Fig. 3. We see that even for this incomplete reaction yielding CO, H₂ and excess fuel are all correlated with Z here instead of GER.

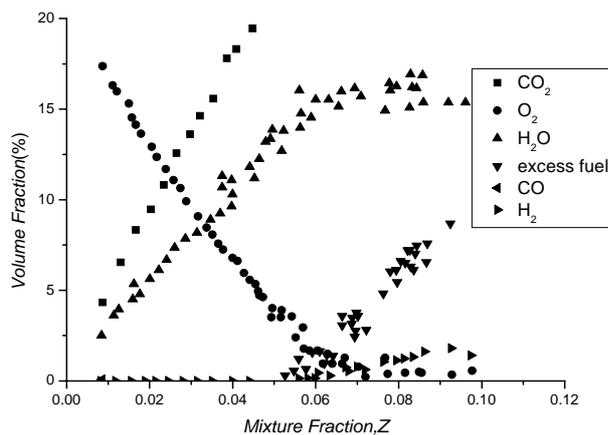


Fig. 3: Relations between mixture fraction and species concentration for propane

This example can further be compared to the complete reaction for propane by Eq. (19). Since the molecular weight of the excess fuel composition is unknown, for the purpose of comparison to the ideal complete reaction, results are converted into the form of volume fraction using the equation below:

$$\chi_i = \frac{M_{mix} Y_i}{M_i}$$

where χ_i and Y_i are volume fraction and mass fraction of a specific species, and M_i and M_{mix} are the molecular weight of the species and mixture (molecular weight of air, 29, is used for approximation). The data are compared to the ideal reaction of Eq. (19) and shown in Fig. 4. This

shows the dominant species follow the ideal complete reaction.

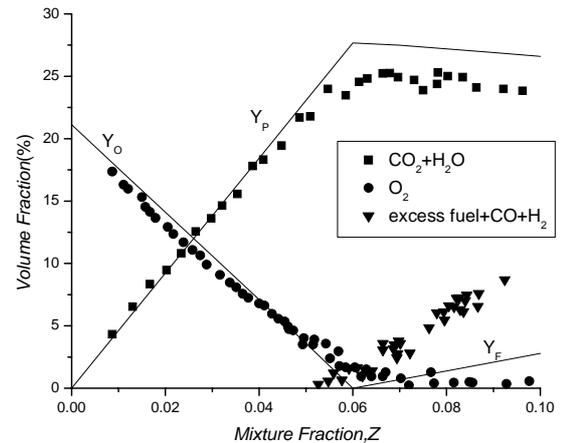


Fig. 4: Relations between mixture fraction and species concentration – comparison to an ideal complete reaction

The power of these empirical correlations is that the incomplete reaction species, e.g. CO, can be described in term of Z from experimental data as shown in Fig. 3. Since equivalence ratio is an overall property and not a local property in the system, it cannot be used as the basis for prediction in the unsteady problems. The formulation in Z follows combustion theory space is more effective than GER and can be used in unsteady applications. Consequently, we pose the hypothesis, for incomplete real reactions: Y_i is a sole function of Z for each fuel.

4. APPLICATION EXAMPLES

Existing correlations for $Y_i(\phi)$ can be converted into $Y_i(Z)$, now a combustion problem couched in term of a uniform combustion product region (as in a zone model) can solely solve for the single species Z , and obtain all Y_i . For example, Tewarson [1] gives much fuel data in term of ϕ that can be converted to Z by Eq. (12). For a compartment with vents, a fire goes through two periods: (1) filling period, and (2) outflow period. The transition of the two occurs after the smoke layer drops below the upper edge of the vent. We will illustrate the use of Z in these two periods.

4.1 Analysis for the Filling Period

For the filling period, there is no outflow from the control volume (see Fig. 1). The mass conservation equation is:

$$\frac{dm}{dt} = \dot{m}_f + \dot{m}_a \quad (20)$$

The conservation of fuel atoms gives:

$$\dot{m}_f = \frac{d(mZ)}{dt} \quad (21)$$

Here Z is the mixture fraction. Since \dot{m}_f is considered constant, thus:

$$m = \frac{\dot{m}_f t}{Z} \quad (22)$$

and

$$\frac{dm}{dt} = -\frac{\dot{m}_f t}{Z^2} \frac{dZ}{dt} + \frac{\dot{m}_f}{Z} \quad (23)$$

Eq. (20) can be written as:

$$\frac{r}{\dot{m}_a} \frac{dm}{dt} = r \frac{\dot{m}_f}{\dot{m}_a} + r \quad (24)$$

Eq. (24) can be expressed in term of ϕ and Z by using Eqs. (22) and (23):

$$-\phi \frac{t}{Z^2} \frac{dZ}{dt} + \frac{\phi}{Z} = \phi + r \quad (25)$$

or

$$-\frac{t}{Z^2} \frac{dZ}{dt} + \frac{1}{Z} = \frac{\phi + r}{\phi} \quad (26)$$

Here ϕ depends on time, as the plume entrainment rate varies with layer height. The steady solution gives Eq. (12) as expected. While it might be tempted to assume a quasi-steady fire for a given ϕ , the combustion products into the layer might be given by $Y_i(\phi)$. However, the correct result must be obtained from $Y_i(Z)$. Hence, Eq. (26) illustrate the advantage of the Z formulation, and its distinction from one in terms of ϕ . If an expression for entrainment (\dot{m}_a) were explicitly included, then Z can be found. From the empirical species correlations given in terms of Z , we can obtain all of these concentrations for all time.

4.2 Analysis for the Outflow Period

For outflow period after filling, the layer is not necessarily steady. The outflow mass term is \dot{m}_{out} .

The mass conservation equation is given for the control volume in Fig. 5 as follows:

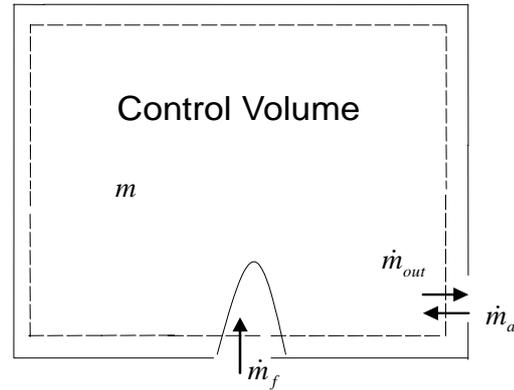


Fig. 5: Schematic of the outflow period of a compartment fire

$$\frac{dm}{dt} = \dot{m}_f + \dot{m}_a - \dot{m}_{out} \quad (27)$$

The conservation of fuel atoms is given as:

$$\dot{m}_f = \frac{d(mZ)}{dt} + Z\dot{m}_{out} \quad (28)$$

Substituting for $\frac{dm}{dt}$ from Eq. (28) gives:

$$\dot{m}_f = m \frac{dZ}{dt} + Z(\dot{m}_f + \dot{m}_a) \quad (29)$$

Eq. (29) can be expressed in term of ϕ and Z :

$$\phi = \frac{rm}{\dot{m}_a} \frac{dZ}{dt} + Z(\phi + r) \quad (30)$$

or

$$-\frac{m}{\dot{m}_f} \frac{dZ}{dt} = Z(\phi + r) - \phi \quad (31)$$

Again, the steady result of Eq. (12) follows. But now, even if ϕ is constant, Z , in general depends on time and $Y_i(Z) \neq Y_i(\phi)$.

4.3 Application of Use of Existing Data

It has been shown that Z is the preferred variable for predicting species in fire compared with the equivalence ratio. From steady experiments, the relationship between mixture fraction and equivalence ratio is given by Eq. (12) and existing correlations of experimental data for the species can be expressed in terms of Z . Already, much data for steady state experiments have been

produced by Zukoski and co-workers [4,5], Beyler [2,3], and extensively by Tewarson [1,6]. Indeed, Tewarson shows in the SFPE Handbook that data can be correlated for many fuels [1] into explicit functional forms.

For example, Tewarson [1] gives the yield of CO under ventilation controlled (VC) condition to the well-ventilated (WV) value as:

$$\frac{y_{CO,VC}}{y_{CO,WV}} = 1 + \frac{\alpha}{\exp(2.5\phi^{-\xi})} \quad (32)$$

where α and ξ are correlated to the fuel, e.g. polystyrene $\alpha = 2$, $\xi = 2.5$; PMMA $\alpha = 43$, $\xi = 3.2$. Under the steady conditions of his experiments, the mass fraction of CO produced in the product stream is:

$$Y_{CO} = y_{CO} / (1 + \frac{\phi}{r}) \quad (33)$$

from

$$(\dot{m}_f + \dot{m}_a)Y_{CO} = y_{CO}\dot{m}_f$$

Tewarson [1] reports well-ventilated results for fuels, e.g. polystyrene $y_{CO,WV} \approx 0.06$ or PMMA $y_{CO,WV} = 0.01$. Then by Eq. (12) ϕ is replaced by Z :

$$\phi = \frac{rZ}{1-Z} \quad (34)$$

Substituting into the Tewarson correlation gives the CO mass fraction as a function of Z . For any fire condition burning the same fuel, the determination of Z for the product stream (smoke layer) gives the instantaneous value of CO. This can be done for all species where $Y_i(Z)$ is known. A fire computation now only involves solving the conservation of mass, energy, and one species: Z .

5. CONCLUSIONS

The application of the mixture fraction (mass fraction of fuel atoms) is developed for a compartment zone model. This can then be used to compute unsteady results for a uniform product layer in zone models of compartment fire. From existing steady experimental correlations of species in term of equivalence ratio, it allows the prediction of species concentration for unsteady compartment fires. It is well known that the equivalence ratio is not capable of dealing with unsteady problems for computing the species concentration. It was clearly illustrated by Zukoski [4,5] who made a distinction between the global equivalence ratio and the layer

equivalence ratio. The mixture fraction, as an intensive property, circumvents this limitation while still benefiting from steady state data taken in term of the equivalence ratio that establishes the key correlations for prediction in modeling.

As a zone model is made more complex to include the mixing between the upper and lower layers, the use of the mixture fraction to model both layers needs to be examined. This has not been done yet. The current results only apply directly to a well mixed smoke layer of uniform properties with an exchange of fuel and air from the ambient.

NOMENCLATURE

Latin Symbols

a_1	variable, Eq. (13)
a_2	variable, Eq. (14)
a_3	variable, Eq. (15)
b_1	variable, Eq. (13)
b_2	variable, Eq. (14)
b_3	variable, Eq. (15)
m	mass
$\dot{m}_{i,r}$	production rate of species i
M	molecular weight
r	stoichiometric mass air to fuel ratio
t	time
T	temperature
Y	species mass fraction
Z	mixture fraction

Greek Symbols

β_1	variable, Eq. (7)
β_2	variable, Eq. (8)
β_3	variable, Eq. (9)
ϕ	equivalence ratio
χ	volume fraction

Subscripts

a	air
f	fuel
CV	control volume
i	species
in	incoming
j	flow path
mix	mixture
o	oxygen
out	outgoing
VC	ventilation controlled
WV	well-ventilated
α	parameter, Eq. (32)
ζ	parameter, Eq. (32)
∞	ambient

Superscripts

\dot{x} x per unit time (x/s)

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