

APPLICATIONS OF THE GENERALIZED GLOBAL EQUIVALENCE RATIO MODEL(GGERM) FOR PREDICTING THE GENERATION RATE AND DISTRIBUTION OF PRODUCTS OF COMBUSTION IN TWO-LAYER FIRE ENVIRONMENTS

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ABSTRACT

The Generalized Global Equivalence Ratio Model (GGERM) was developed to predict the generation rates of oxygen, fuel, and other products of combustion in rooms containing fires. The GGERM extends to general transient conditions the global equivalence ratio model established during times of steady-state in experimental studies involving two-layer compartment fires. The present work uses the GGERM to predict the time-dependent upper-layer mass fractions of products of combustion (fuel, oxygen, CO, and others) in these and similar two-layer fire experiments. All predicted results are found to be plausible and, where transient data are available, predicted and measured results compare favorably.

NOMENCLATURE

$c_{H_2O,N}^{(SS)}$	constants, Eq. (A2)	$\dot{m}_{AIR}$	measured mass flow rate of air into reference-[3] facility
$c_{k,u}$	mass fraction of product k in upper layer	%EX	measured mass pyrolysis rate of hexane in reference-[3] facility
$c_{k,u}[vol]$	volume fraction of product k in upper layer	$\dot{m}_{FBK}$	mass flow rate to reactor from bulk of upper layer
$c_{k,ROUT}$	mass fraction of product k in reactor outflow	$\dot{m}_{FBK,1}$	Eq. (20)
$c_{k,ROUT}[vol]$	volume fraction of product k in reactor outflow	$\dot{m}_{FBK,3}$	Eq. (21)
$c_{k,ROUT,ST}$	$c_{k,ROUT}$ for stoichiometric combustion	$\dot{m}_{FIN}$ $[\dot{m}_{FOUT}]$	total mass flow rate into [out of] upper layer
$c_{k,ROUT}^{(SS)}$	$c_{k,ROUT}$ under steady state conditions	$(\dot{P}_F/\dot{P}_{O_2})_{ST}$	stoichiometric fuel-to-oxygen ratio
$c_{k,ROUT}^{(SS)}[vol]$	$c_{k,ROUT}[vol]$ under steady state conditions	$P_{k,FIN}$ $[P_{k,FOUT}]$	sum of rates of flow of all components of product k into [out of] upper layer
$c_{k,ROUT,ST}^{(SS)}$	$c_{k,ROUT,ST}$ under steady state conditions	$P_{k,u}$	mass of product k in lower [upper] layer
$f_k(\phi)$	Eq. (3)	$\dot{P}_{k,u}$	net rates of product k flowing to upper layer
$f_k^{(ST)}$	$f_k(\phi)$ for complete stoichiometric combustion	$P_{k,RIN}$	net mass flow rate of product k into reactor
$\dot{m}_U$	mass in upper layer	r	$(\dot{P}_F/\dot{P}_{O_2})_{ST}$
		T_U	temperature of upper layer
		$T_{U,INIT}$ $[T_{U,FINAL}]$	initial [final] temperature of upper layer
		t	time
		Γ_k	Eq. (43)
		$\Gamma_{k,o}$	Eq. (25)
		$\Gamma_{k,\bullet}$	Eq. (34)

$\lambda_{CO,N}$	constants, Eq. (A11)
$\lambda_{CO2,1}$	a constant, Eq. (A5)
$\lambda_{H2O,N}$	constants, Eq. (A8)
A	Eq. (10)
ϕ	Eq. (2)
$\phi(SS)$	value of ϕ under steady state conditions, Eq. (12)
ϕ_F	Eq. (22)
$\phi_F^{(ST)}$	value of ϕ_F under complete stoichiometric burning
$\phi_{k,ST1}$ $\phi_{k,ST2}$	constants in representation of f_k , see Eq. (A14)
ϕ_{O2}	Eq. (23)
$\phi_{O2}^{(ST)}$	value of ϕ_{O2} under complete stoichiometric burning
ω_k	mass generation rate of product k

INTRODUCTION - THE EXTENDED UPPER LAYER IN A ROOM CONTAINING A FIRE

Background

This paper presents results of applying and validating a general model, usable in two-layer zone-type compartment fire analyses, for predicting the generation rate and accumulation of combustion products throughout a multi-room facility. The model, called the Generalized Global Equivalence Ratio Model (GGERM), was presented by Cooper (1991). In this work, the GGERM is used to simulate the mass fractions of products of combustion that developed during the transient portions of the two-layer fire experiments of Morehart, Zukoski, and Kubota (1990) and Gottuck and Roby (1990). Model predictions are presented and they are compared to experimental results when available.

Consider a multi-room compartment fire and assume an upper-layer/lower-layer zone-type of description of the environment in each of the rooms. For the purpose of describing combustion processes in any room, the GGERM defines the fire and plume, which may originate in the lower layer, as part of the upper-layer zone. Also, the volumes of the fire and plume are assumed to be negligible compared to the total volume of the room. Thus, the GGERM treats all combustion processes in any room with a fire as occurring in the upper layer. The actual combustion process is modeled as if it occurs in a well-stirred reactor with a relatively rapid throughflow and a correspondingly negligible residence time.

An Overview of the GGERM

Presented here is a brief summary of the essential features of the GGERM. Let $P_{k,u}$ represent the total mass of a combustion product k in the upper layer of any room containing a fire during an arbitrary multi-room fire scenario. The goal of the GGERM is to estimate the combustion contribution to the instantaneous value of $dP_{k,u}/dt$.

Conservation of species leads to

$$dP_{k,u}/dt = \dot{P}_{k,u} \quad (1)$$

where the right-hand term represents the net rate of product of combustion k flowing to the upper layer. This term is the sum of transfers of product k to the extended upper layer from all plumes, jets, near-boundary flows, combustion zones, and other isolated or distributed sources.

The material flowing into and out of the extended upper layer generally includes various amounts of the combustion products k associated with a fuel of interest and other inert flow components. The total rates of mass inflow and outflow, $\dot{m}_{FIN}$ and $\dot{m}_{FOUT}$, and the corresponding individual rates of inflow and outflow of products k, $\dot{P}_{k,FIN}$ and $\dot{P}_{k,FOUT}$, respectively, are established from a variety of compartment fire modeling considerations. These rates are assumed to be known.

The combustion contributions to $\dot{P}_{k,u}$ are modeled by the GGERM. As depicted in Figure 1, the GGERM has two

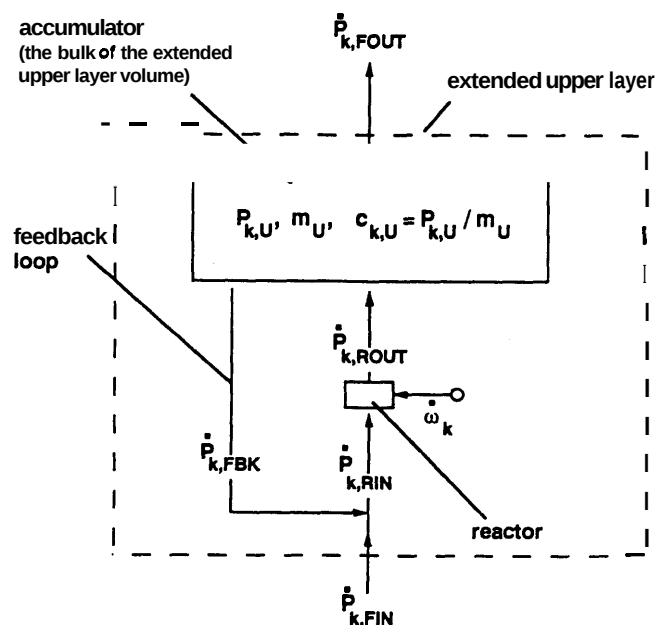


Fig. 1. The GGERM representation of combustion and flow dynamics in the extended upper-layer.

components: the accumulator, which simulates spatially-averaged properties of the generally unsteady upper layer environment; and the quasi-steady reactor, which simulates the actual combustion processes taking place there.

All of the flow into the layer is modeled as immediately "entering" the reactor where it may participate in the reaction process. The model also includes a "feedback loop" which brings flow from the bulk upper layer atmosphere into the reactor and the reaction process. A critical feature of the model is the means of evaluating the feedback mass flow rate, $\dot{m}_{FBK}$. This was presented by Cooper (1991).

The global equivalence ratio, ϕ , is defined as a normalized ratio of the rates of fuel to oxygen entering the reactor.

$$\phi = (\dot{P}_{F,RIN} / \dot{P}_{O2,RIN}) / \Gamma \quad (2)$$

where $\dot{P}_{F, \text{FIN}}$ and $\dot{P}_{O_2, \text{FIN}}$ are the mass flow rate of FUEL and O_2 , respectively, flowing into the reactor; $\dot{P}_{k, \text{FIN}}$ is defined as the mass flow rate into the reactor of these and any other products k ; and r is the known fuel-to-oxygen ratio for idealized stoichiometric combustion of a fuel of interest. Note that Eq. (2) is consistent with the ϕ definitions of all references at the end of this work.

According to the GGGERM, ω_k , the rate of generation of an arbitrary product k due to combustion, is given by

$$\omega_k / \dot{P}_{F, \text{FIN}} = f_k(\phi) \quad (3)$$

where the f_k functions for the fuel would be determined from steady state experiments of the types described in the references.

With values for ω_k , the right-hand side of Eq. (1) can be evaluated from

$$\dot{P}_{k, \text{U}} = \dot{P}_{k, \text{FIN}} - \dot{P}_{k, \text{ROUT}} + \omega_k \quad (4)$$

Then integration of Eq. (1) can proceed, leading to solutions for the $P_{k, \text{U}}$.

INITIAL VALUE PROBLEM FOR THE MASS FRACTION OF FUEL, OXYGEN, AND OTHER PRODUCTS OF COMBUSTION WHEN ALL OXYGEN INFLOW IS FROM A STANDARD ATMOSPHERE

Cooper (1991) also presents Eq. (1) in terms of $c_{k, \text{U}}$, the upper-layer mass fractions of products k .

$$c_{k, \text{U}} = P_{k, \text{U}} / m_{\text{U}} \quad (5)$$

where m_{U} is the instantaneous total mass of material in the upper layer.

Experiments reported in the references involved test configurations depicted in Figure 2. In these

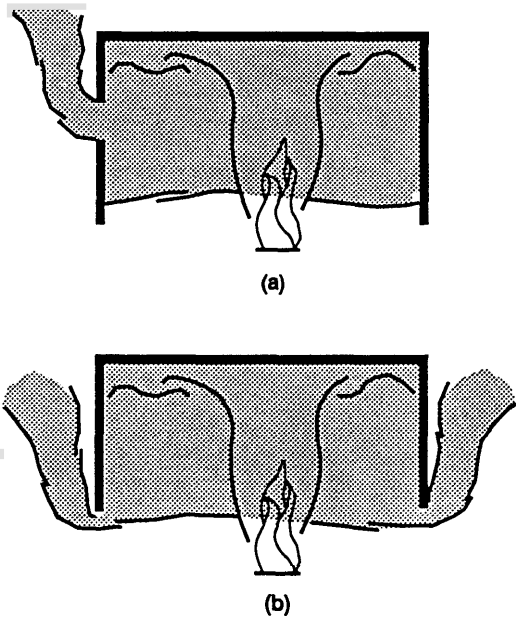


Fig. 2. The experimental configurations used in the references; (a) top, (b) bottom.

tests all components of $\dot{P}_{O_2, \text{FIN}}$ were from a standard atmosphere, i.e., with an oxygen mass fraction of 0.232.

In such scenarios it can be shown that the governing equations for $c_{F, \text{U}}$, $c_{O_2, \text{U}}$, and the other $c_{k, \text{U}}$ are

$$(m_{\text{U}} / m_{F, \text{FIN}}) dc_{F, \text{U}} / dt = \quad (6)$$

$$c_{F, \text{U}} [f_F(\phi)(m_{F, \text{BK}} / m_{F, \text{FIN}}) - 1] + 0.232r\phi^{(SS)} [1 + f_F(\phi)] / [1 + 0.232r\phi^{(SS)}]$$

$$(m_{\text{U}} / m_{F, \text{FIN}}) dc_{O_2, \text{U}} / dt = \quad (7)$$

$$c_{O_2, \text{U}} [r\phi f_{O_2}(\phi)(m_{F, \text{BK}} / m_{F, \text{FIN}}) - 1] + 0.232[1 + r\phi f_{O_2}(\phi)] / [1 + 0.232r\phi^{(SS)}]$$

$$(m_{\text{U}} / m_{F, \text{FIN}}) dc_{k, \text{U}} / dt + c_{k, \text{U}} = \quad (8)$$

$$\{c_{F, \text{U}}(m_{F, \text{BK}} / m_{F, \text{FIN}}) + 0.232\phi^{(SS)} r / [1 + 0.232r\phi^{(SS)}]\} f_k(\phi)$$

$$- \{c_{O_2, \text{U}}(m_{F, \text{BK}} / m_{F, \text{FIN}}) + 0.232 / [1 + 0.232r\phi^{(SS)}]\} r\phi f_k(\phi) \quad (9)$$

$$- \Lambda_k(t) \quad (10)$$

$$\phi = \phi^{(SS)} \{1 + (m_{F, \text{BK}} / m_{F, \text{FIN}}) c_{F, \text{U}} [1 + 1 / (0.232r\phi^{(SS)})]\} / \{1 + (m_{F, \text{BK}} / m_{F, \text{FIN}}) c_{O_2, \text{U}} \phi^{(SS)} r [1 + 1 / (0.232r\phi^{(SS)})]\} \quad (11)$$

$\phi^{(SS)}$ in Eqs. (6)-(11) is defined as the value of ϕ under virtual steady-state conditions, i.e., the value of ϕ when $m_{F, \text{BK}} = 0$ and when $\dot{P}_{F, \text{FIN}}$ and $\dot{P}_{O_2, \text{FIN}}$ are maintained at their current values.

$$\phi^{(SS)} = (\dot{P}_{F, \text{FIN}} / \dot{P}_{O_2, \text{FIN}}) / r \quad (12)$$

Define $c_{k, \text{ROUT}}^{(SS)}(\phi^{(SS)})$ as the product- k mass fraction flowing out of a GGGERM reactor under steady state conditions when the ϕ is $\phi^{(SS)}$. Then, for any product k there is a one-to-one correspondence between $c_{k, \text{ROUT}}^{(SS)}$ and f_k .

$$c_{F, \text{ROUT}}^{(SS)} = \quad (13)$$

$$0.232\phi^{(SS)} r [1 + f_F(\phi^{(SS)})] / (1 + 0.232\phi^{(SS)} r)$$

$$c_{O_2, \text{ROUT}}^{(SS)} = \quad (14)$$

$$0.232[1 + r\phi^{(SS)} f_{O_2}(\phi^{(SS)})] / (1 + 0.232r\phi^{(SS)})$$

$$c_{k, \text{ROUT}}^{(SS)} = 0.232r\phi^{(SS)} f_k(\phi^{(SS)}) / (1 + 0.232r\phi^{(SS)}) \quad (15)$$

for k other than fuel or oxygen

Solving for the f_k in the above leads to

$$f_F = [1 + 1 / (0.232r\phi^{(SS)})] c_{F, \text{ROUT}}^{(SS)}(\phi^{(SS)}) - 1 \quad (16)$$

$$f_{O_2} = c_{O_2, \text{ROUT}}^{(SS)}(\phi^{(SS)}) + [c_{O_2, \text{ROUT}}^{(SS)}(\phi^{(SS)}) - 0.232] / (0.232r\phi^{(SS)}) \quad (17)$$

$$f_k = [1 + 1 / (0.232r\phi^{(SS)})] c_{k, \text{ROUT}}^{(SS)}(\phi^{(SS)}) \quad (18)$$

for k other than fuel or oxygen

When data for the $c_{k, \text{ROUT}}^{(SS)}$ for a particular fuel are presented in reports of Figure-2-type experiments in a standard atmosphere, it is possible to determine analytic representations of these and to then construct

the f_k functions, required for use in the GGEM, by using Eqs. (16)-(18). Similarly, known f_k functions can be used to construct the $c_{k,ROUT}^{(SS)}$ by using Eqs. (13)-(15).

Eqs. (6)-(8) are completed with specification of m_{FBK}/m_{FIN} . For fire scenarios considered here, this is found from Cooper (1991) to be

$$m_{FBK}/m_{FIN} = \max(m_{FBK,1}/m_{FIN}, m_{FBK,3}/m_{FIN}) \quad (19)$$

$$m_{FBK,1}/m_{FIN} = \begin{cases} 0 & \text{if } \phi^{(SS)}/\phi_F \leq 1 \text{ or } c_{O_2,U} - c_{O_2,ROUT}^{(SS)} \leq 0; \\ [(1 - \phi_F/\phi^{(SS)})/(\phi_F/\phi^{(SS)} + 0.232r\phi_F)] \cdot \\ [(c_{O_2,U} - c_{O_2,ROUT}^{(SS)})/(0.232 - c_{O_2,ROUT}^{(SS)})] & \text{if } \phi^{(SS)}/\phi_F > 1 \text{ and } c_{O_2,U} - c_{O_2,ROUT}^{(SS)} > 0 \end{cases} \quad (20)$$

$$m_{FBK,3}/m_{FIN} = \begin{cases} 0 & \text{if } \phi_{O_2}/\phi^{(SS)} \leq 1 \\ & \text{or } c_{F,U} - c_{FUEL,ROUT}^{(SS)} \leq 0; \\ [(\phi_{O_2}/\phi^{(SS)} - 1)(0.232r\phi^{(SS)})/ \\ (1 + 0.232r\phi^{(SS)})] \cdot \\ [(c_{F,U} - c_{FUEL,ROUT}^{(SS)})/(1 - c_{FUEL,ROUT}^{(SS)})] & \text{if } \phi_{O_2}/\phi^{(SS)} > 1 \\ & \text{and } c_{F,U} - c_{FUEL,ROUT}^{(SS)} > 0 \end{cases} \quad (21)$$

where, $c_{F,ROUT}^{(SS)}$ and $c_{O_2,ROUT}^{(SS)}$ are obtained from Eqs. (13) and (14), respectively.

In the above, ϕ_F is defined as the maximum value of ϕ which leads to complete combustion of the fuel, i.e., the maximum value of ϕ where $\omega_F = -P_{F,RIN}$. Using Eq. (3)

$$\phi_F = \text{maximum root of } f_F(\phi_F) + 1 = 0 \quad (22)$$

It is assumed that $\phi_F > 0$ and is bounded.

Similarly, ϕ_{O_2} is defined as in [1] as the minimum value of ϕ which leads to complete consumption of oxygen, i.e., the minimum value of ϕ which leads to $P_{O_2,RIN} = 0$. Using Eq. (3)

$$\phi_{O_2} = \text{minimum root of } \phi_{O_2}f_{O_2}(\phi_{O_2})r + 1 = 0 \quad (23)$$

It is assumed that $\phi_{O_2} > 0$ and is bounded.

CONSTRUCTING ANALYTIC REPRESENTATIONS FOR THE PRODUCT GENERATION FUNCTIONS AND THE STEADY STATE MASS FRACTIONS FROM EXPERIMENTAL DATA

General Considerations

Application of the GGEM for a given fuel requires calculations based on analytic representations of its f_k 's and $c_{k,ROUT}^{(SS)}$'s. These would be obtained from data of steady state experiments of the kind described in the references.

When $c_{k,ROUT}^{(SS)}$ data points are provided [e.g., in Morehart, Zukoski, and Kubota (1990)], then these would

be used to construct analytic, curve-fitted representations of these functions. With Eqs. (16)-(18), these representations would be used to calculate a consistent set of the f_k 's. Similarly, if f_k data points are provided [as in Beyler (1983)], then these data points can be used to construct analytic curve-fitted representations of the f_k functions. With Eqs. (13)-(15), these latter representations would be used to calculate a consistent set of the $c_{k,ROUT}^{(SS)}$'s.

The curve-fitting task must be carried out so that the resulting $f_k(\phi)$ and $c_{k,ROUT}^{(SS)}(\phi^{(SS)})$ functions are physically and analytically well-behaved for arbitrary non-negative values of ϕ and $\phi^{(SS)}$. In particular, mutually-consistent constraints on continuity and limiting small- and large- ϕ behavior are required.

Continuity. The $f_k(\phi)$'s and $c_{k,ROUT}^{(SS)}(\phi^{(SS)})$'s are continuous functions for arbitrary non-negative values of ϕ and $\phi^{(SS)}$.

Small ϕ limit. For $0 \leq 4 \leq \phi_F$ and for $\phi \rightarrow 0$ in particular, all fuel entering the reactor is completely consumed.

$$\omega_F = -P_{F,RIN} \text{ for } 0 \leq \phi \leq \phi_F \quad (24)$$

Consistent with whatever reactor chemistry is applicable as $\phi \rightarrow 0$, the generation/consumption rate of oxygen and all products k will be directly proportional to the generation/consumption rate of fuel. The constants of proportionality are designated in terms of the characteristic product- k constants, $\Gamma_{k,0}$,

$$\lim_{\phi \rightarrow 0} \omega_k = -\Gamma_{k,0}\omega_F; \Gamma_{F,0} = 1 \quad (25)$$

$$\Gamma_{O_2,0} = -1/r \text{ for complete stoichiometric combustion at } \phi = 0 \quad (26)$$

Using Eq. (3) and (25), with $k \rightarrow O$ (i.e., k representing O_2), and Eq. (24), and then using Eq. (14) leads to

$$\lim_{\phi \rightarrow 0} f_{O_2}(\phi) = \Gamma_{O_2,0} \quad (27)$$

$$\lim_{\phi^{(SS)} \rightarrow 0} c_{O_2,ROUT}^{(SS)}(\phi^{(SS)}) = \quad (28)$$

$$0.232[1 + r\phi^{(SS)}\Gamma_{O_2,0}(1 - 0.232/\Gamma_{O_2,0}) + O(\phi^{(SS)2})]$$

Using Eq. (3) with $k \rightarrow FUEL$ and Eq. (17), and then Eq. (13) leads to

$$f_F(\phi) = -1 \text{ for } 0 \leq \phi \leq \phi_F \quad (29)$$

$$c_{F,ROUT}^{(SS)}(\phi^{(SS)}) = 0 \text{ for } 0 \leq \phi^{(SS)} \leq \phi_F \quad (30)$$

Using Eqs. (3) and (25) with k other than FUEL or O , and Eq. (24), and then using Eq. (15) leads to

For k other than FUEL or O :

$$\lim_{\phi \rightarrow 0} f_k(\phi) = \Gamma_{k,0} \quad (31)$$

$$\lim_{\phi^{(SS)} \rightarrow 0} c_{k,ROUT}^{(SS)}(\phi^{(SS)}) = 0.232r\phi^{(SS)}\Gamma_{k,0} \quad (32)$$

Large ϕ limit. For $\phi \geq \phi_{O_2} > 0$, and for $4 \rightarrow \infty$ in particular, all oxygen entering the reactor is completely consumed.

$$\omega_{O_2} = -P_{O_2, RIN} \text{ when } \phi \geq \phi_{O_2} > 0 \quad (33)$$

Consistent with whatever reactor chemistry is applicable as $\phi \rightarrow \infty$, the generation/consumption rate of oxygen and all products k will be directly proportional to the generation/consumption rate of fuel. The constants of proportionality are designated in terms of the characteristic product- k constants, Γ_k .

$$\lim_{\phi \rightarrow \infty} \omega_k = -\Gamma_k \omega_F; \Gamma_F = 1 \quad (34)$$

$$\Gamma_{O_2} = -1/r \text{ for complete stoichiometric combustion at } \phi \rightarrow \infty \quad (35)$$

Using Eq. (3), with $k \rightarrow O_2$, and Eqs. (2) and (33), and then using Eq. (14) leads to

$$f_{O_2}(\phi) = -1/(r\phi) \text{ when } \phi \geq \phi_{O_2} > 0 \quad (36)$$

$$c_{O_2, ROUT}^{(SS)}(\phi^{(SS)}) = 0 \text{ when } \phi^{(SS)} \geq \phi_{O_2} > 0 \quad (37)$$

Using Eqs. (3) and (34), with $k \rightarrow FUEL$, and Eqs. (2) and (33), and then using Eq. (13) leads to

$$\lim_{\phi \rightarrow \infty} f_F(\phi) = 1/(r\phi\Gamma_{O_2}) \text{ when } \phi \geq \phi_F > 0 \quad (38)$$

$$\lim_{\phi^{(SS)} \rightarrow \infty} c_{F, ROUT}^{(SS)}(\phi^{(SS)}) = \quad (39)$$

$$1 + (1 - \Gamma_{O_2}/0.232)[1/(r\phi^{(SS)}\Gamma_{O_2})] + O(1/\phi^{(SS)2})$$

Using Eqs. (3) and (34) with k other than FUEL or O_2 , Eq. (2) and Eq. (33), and then using Eq. (15) leads to

For k other than FUEL or O_2 :

$$\lim_{\phi \rightarrow \infty} f_k(\phi) = -\Gamma_k/(r\phi\Gamma_{O_2}) \quad (40)$$

$$\lim_{\phi^{(SS)} \rightarrow \infty} c_{k, ROUT}^{(SS)}(\phi^{(SS)}) = -\Gamma_k/(r\phi^{(SS)}\Gamma_{O_2}) \quad (41)$$

Complete Stoichiometric Combustion

When reactions only involve complete stoichiometric combustion, ϕ_F , ϕ_{O_2} , and the f_k are given by

$$\phi_F^{(ST)} = \phi_{O_2}^{(ST)} = 1 \quad (42)$$

$$f_k^{(ST)}(\phi) = \begin{cases} \Gamma_k & \text{if } 0 \leq \phi \leq 1 \\ \Gamma_k/\phi & \text{if } \phi > 1 \end{cases} \quad (43)$$

$$\Gamma_F = -1; \Gamma_{O_2} = -1/r \quad (44)$$

where the other Γ_k can be determined from the stoichiometric reaction of the particular fuel of interest. Eqs. (41)-(44) are consistent with the earlier results for "real" reactions.

The Product Generation Functions and the Steady State Mass Fractions for the Combustion of Methane Using Data of Morehart, Zukoski, and Kubota (1990)

It is assumed that the natural gas fuel used in the experiments of Morehart, Zukoski, and Kubota (1990) can be modeled as pure methane, CH_4 . That work provides $c_{k, ROUT}^{(SS)}$ data for $k = CH_4, O_2, CO, H_2O, CO_2$, and H_2 acquired during steady state combustion in the test configuration of Figure 2b. These data were acquired

over a wide range of layer temperatures, but these never exceeded 800K. $\phi^{(SS)}$ values were in the range $0 < \phi^{(SS)} < 3$. In the tests, in addition to the rate of oxygen supply to the extended upper layer through entrainment into the burner's fire plume, the gas in the upper layer collector was injected with a specified flow of air and its associated oxygen. Some of the test results and results of other natural gas tests using earlier versions of the same test configuration were presented in Zukoski et al (1989), Toner, Zukoski, and Kubota (1986), and Zukoski et al (1991).

Analytic representations for the $c_{k, ROUT}^{(SS)}$ functions which characterize the combustion of CH_4 were constructed by using these data and the above analytic constraints. The representations are presented in Eqs. (A1)-(A12) of the Appendix. Eqs. (16)-(18) were used to calculate the corresponding f_k functions. These are plotted in Figure 3. Also included in the Appendix and

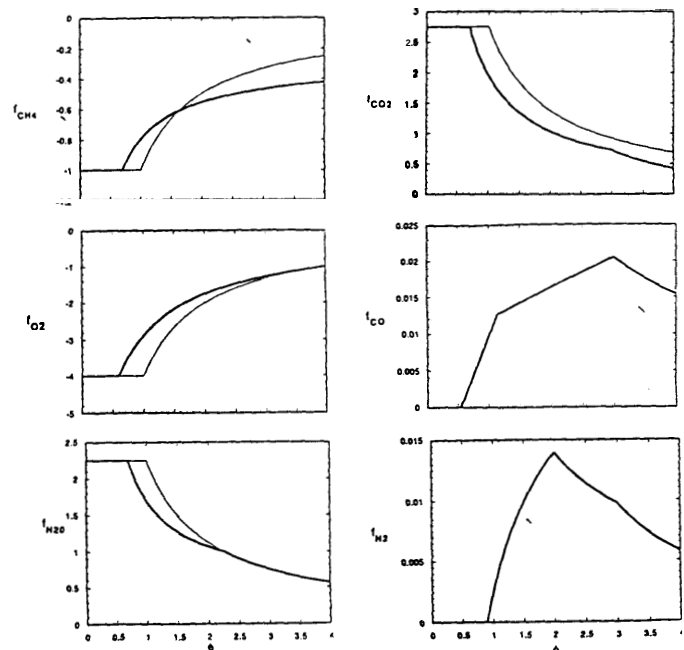


Fig. 3. Analytic representations of the f_k for the combustion of CH_4 : complete stoichiometric combustion (—), "real" combustion from data of Morehart, Zukoski, and Kubota (1990) (---).

in the latter plots are the exact results for the $c_{k, ROUT}^{(SS)}$ and the f_k , designated as $c_{k, ROUT, ST}^{(SS)}$ and $f_k^{(ST)}$, respectively, which correspond to complete stoichiometric combustion of CH_4 . (Note that the representations for the $c_{k, ROUT}^{(SS)}$ and the f_k extend beyond the $\phi^{(SS)} = 3$ limit of the experiments. For $\phi^{(SS)} \geq 3$ these can not be viewed as reliable models of real CH_4 combustion processes.) Using the $c_{k, ROUT}^{(SS)}$ equations, the GGEM will be applied below in simulations of the transient upper-layer environment of the methane combustion experiments of Morehart, Zukoski, and Kubota (1990).

It is important to point out that the data of Toner, Zukoski, and Kubota (1986) were acquired at higher layer temperatures, greater than 900K, than were the data of Morehart, Zukoski, and Kubota (1990). Regarding the generation of CH_4 , and especially O_2 , CO , and H_2O at these higher temperatures the reactions closely simulated complete stoichiometric combustion.

The data of Toner, Zukoski, and Kubota (1986) suggest that GGERM simulations at higher temperatures would be improved if the f_k 's of Eq. (3) were generally assumed to be dependent on layer temperature as well as ϕ . For now this temperature dependence is ignored. Further discussion of this will be presented toward the end of this work.

The Product Generation Functions and the Steady State Mass Fractions for the Combustion of Hexane Using Data of Beyler (1983)

Beyler (1983) provides f_k data for $k \rightarrow C_6H_{14}$, O , CO , H_2O , CO_2 , and H_2 acquired during steady state combustion of hexane, C_6H_{14} , in the test configuration of Figure 2a. $\phi^{(ss)}$ values were in the range $0 < \phi^{(ss)} < 1.8$.

Analytic representations for the f_k functions which characterize the combustion of C_6H_{14} were constructed by using these data and the above analytic constraints. The representations are presented in Eqs. (A13)-(A17) of the Appendix. These are plotted in Figure 4. Also

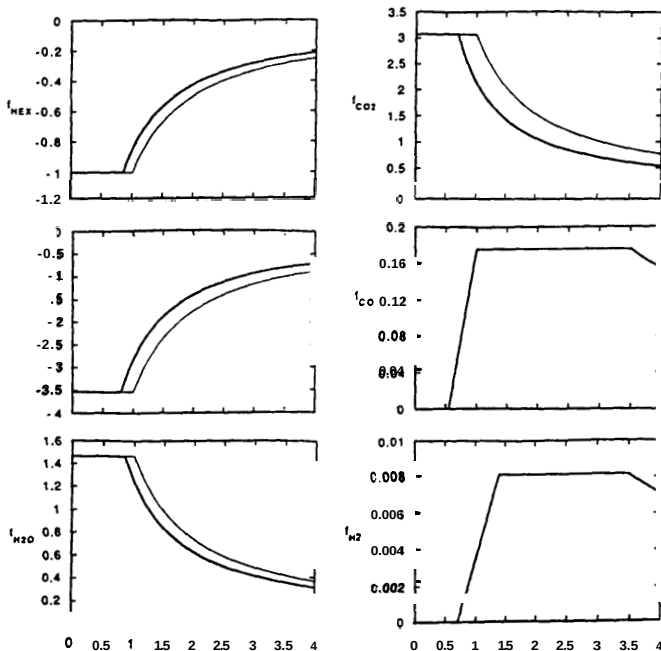


Fig. 4. Analytic representations of the f_k for the combustion of C_6H_{14} : complete stoichiometric combustion (—), "real" combustion from data of Beyler (1983) (---).

included in the Appendix and in the latter plots are the exact results for the f_k , which correspond to complete stoichiometric combustion of C_6H_{14} . (Note that the representations for the $c_k^{(ss)}$ and the f_k extend beyond the $\phi^{(ss)} = 1.8$ limit of the experiments. For $\phi^{(ss)} \geq 1.8$ these can not be viewed as reliable models of real C_6H_{14} combustion processes.) Using the f_k equations, the GGERM will be applied below in simulations of the transient upper-layer environment of hexanes combustion experiments of Gottuck and Roby (1990).

SIMULATING EXPERIMENTS OF MOREHART, ZUKOSKI, AND KUBOTA (1990) AND GOTTUCK AND ROBY (1990)

The Combustion of Methane in Figure-2b Test Configurations

Consider the 64 CH tests reported in Appendix B of Morehart, Zukoski, and Kubota (1990). The test configuration for these is depicted in Figure 2b. Except for initial test time intervals (on the order of 1 to 2 minutes), which were relatively short compared to the times to reach steady state conditions (on the order of 20 to 30 minutes), the layer interface elevation in all of these tests was constant, slightly below the bottom of the upper layer collector. In the simulations to follow it is assumed that the elevation of the layer interface, i.e., the volume of the upper layer, is constant throughout a test run. The volume is estimated to be the volume of the collector, 3.89 m^3 .

Each test was carried out with a fixed-elevation gas burner surface and with constant upper-layer supply rates of fuel and injected upper-layer air. Because of the constant-interface-elevation assumption, which implies a constant rate of air entrainment from the lower layer (i.e., the laboratory environment) to the fire plume, each test is simulated with constant values of $\dot{m}_{F,FIN}$, $\dot{P}_{F,FIN}$, and $\dot{P}_{O_2,FIN}$ where

$$\dot{m}_{F,FIN} = \dot{P}_{F,FIN} + \dot{P}_{AIR,FIN} - \dot{P}_{F,FIN} + \dot{P}_{O_2,FIN}/0.232 \quad (45)$$

and $\dot{P}_{AIR,FIN}$ is the mass rate of flow of air into the upper layer.

With the above assumptions, solutions to the GGERM Eqs. (6)-(23) have been carried out to simulate experiments of Morehart, Zukoski, and Kubota (1990). For each experiment simulated, calculations were carried out with the two different models of CH_4 combustion, viz., real combustion and complete stoichiometric combustion. In the simulations it was assumed that the initial mass fractions of products in the upper layer were the same in an ambient atmosphere, i.e., $c_{O_2,U}(t=0) = 0.232$, and all other $c_{k,U}(t=0) = 0$.

In test 1 of Morehart, Zukoski, and Kubota (1990) the initial and characteristic final temperatures of the layer were $T_{U,INIT} = 296 \text{ K}$ and $T_{U,FINAL} = 529.7 \text{ K}$, respectively. In the simulation, the upper layer temperature was assumed to be at the constant value $T_U = T_{U,INIT} + (2/3)(T_{U,FINAL} - T_{U,INIT}) = 451.8 \text{ K}$. The mass of the upper layer was computed according to a perfect gas law model with the gas constant taken to be that of a standard atmosphere. Other conditions of the test were

$$\dot{P}_{F,FIN} = 0.00135 \text{ kg/s}; \quad \dot{P}_{AIR,FIN} = 0.01030 \text{ kg/s} \quad (46)$$

In test 1, all inflowing air was from plume entrainment. Using Eq. (45) in Eq. (12), the constant simulated value of $\phi^{(ss)}$ for this experiment is found to be 2.33. The $\phi^{(ss)}$ reported by Morehart, Zukoski, and Kubota (1990) was 2.17. The difference in these two values is attributed to the fact that in the simulation the fuel was modeled as pure methane with $r = 1/4$, whereas the value in the reference is based on $r = 1/3.82$. The latter value was the result of an actual analysis of the natural gas used in the experiment.

The simulation was carried out twice, first using the real CH_4 combustion model and then using the complete stoichiometric combustion model. Simulation $c_{k,U}(t)$ results are presented in Figure 5.

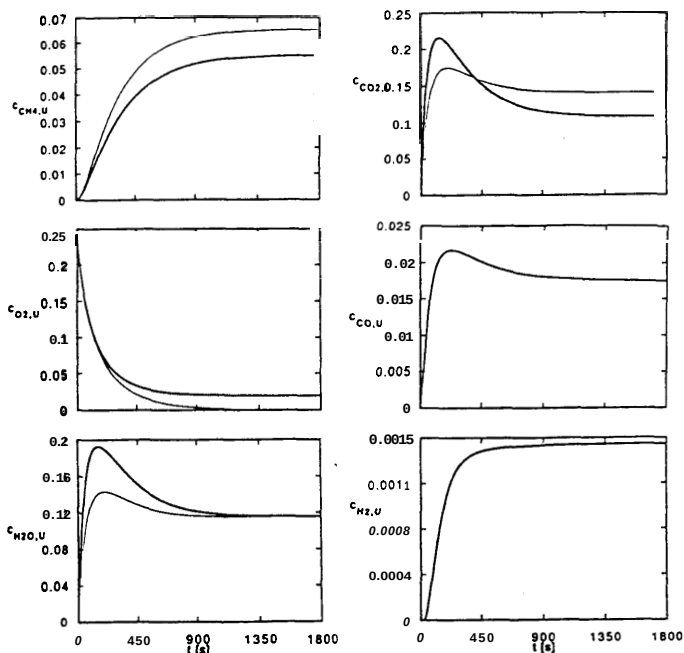


Fig. 5. Combustion of CH_4 - Results of GGGERM simulation of test 1 of Appendix B of Morehart, Zukoski, and Kubota (1990): real combustion model (—) and the complete stoichiometric combustion model (---).

As can be seen from the $c_{x,U}$ plots, the GGGERM predicts that steady state conditions are approached between 900 s and 1800 s into the experiment. This is consistent with the experimental procedure which involved steady-state gas sampling after approximately 1800 s. In Figure 5, the results for $c_{\text{CH}_4,U}$, $c_{\text{CO}_2,U}$, and $c_{\text{H}_2\text{O},U}$ offer no surprises. The GGGERM predicts that each of these mass fractions changes monotonically with time from its initial value to its steady state value. As required by the GGGERM, note that the latter steady state values are consistent with Figure 3 for $\phi = \phi^{(ss)} = 2.33$.

The plots for $c_{\text{CO}_2,U}$, $c_{\text{H}_2\text{O},U}$, and $c_{\text{CO},U}$ predict the unusual result that each of these mass fractions will reach a local maximum during the transient portion of the experiment. (It is noteworthy that for each of these products of combustion the predicted maximum is actually larger than the maximum of the steady state values for $\phi^{(ss)}$ in the range $0 \leq \phi^{(ss)} < 2.33$.) The local-maximum- $c_{x,U}$ result occurs because of the fact that during the transient portion of the experiment the upper layer environment participates in the combustion process by way of the feedback flow at times when the upper layer already contains relatively significant mass fractions of the combustion products. Thus, the products produced in the combustion process are added to the products that already exist in the layer. Instantaneously, the product concentrations of the reactor output at those times is analogous to the concentrations of the steady state upper-layer environment in a Morehart, Zukoski, and Kubota (1990) type of experiment where the laboratory atmosphere, entrained into the fire plume from the lower layer and injected directly into the upper layer, is contaminated with a non-negligible amount of the products in question. In such experiments, the steady-state upper-layer mass fractions of these products, as a function of $\phi^{(ss)}$, would exceed the

steady state mass fractions reported by Morehart, Zukoski, and Kubota (1990).

While the overall results of the above GGGERM simulation are qualitatively plausible, transient data are not now available for quantitative validation.

The Combustion of Hexanes in Figure-6 Test Configurations - One of Two Hexane Experiments of Gottuck and Roby (1990)

Consider the tests of Gottuck and Roby (1990). The experimental configuration for these are depicted in Figure 6. This is similar to the configuration of

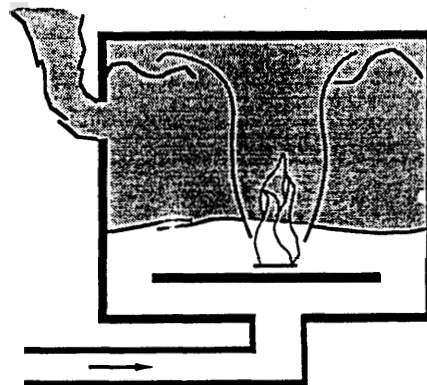


Fig. 6. Test configuration for the experiments of Gottuck and Roby (1990).

Figure 2a except for the fact that the collector is a fully enclosed space which contains the fuel source. Air supplied to the lower layer is brought in, below the elevation of the fuel source, through a duct from the outside.

The time-dependent rate of air flow through the duct is measured during the course of an experiment. This air flow is not controlled. Rather, it occurs naturally as a result of cross-duct pressure differentials generated by buoyancy forces and buoyancy-driven flows within and through the collector enclosure.

The time-dependent pyrolysis rate of the fuel is measured by a fuel-bearing load cell. A thermocouple tree measures temperatures in the enclosure as a function of time and elevation.

The GGGERM was used to simulate the larger of the two hexane-burn experiments reported by Gottuck and Roby (1990). For this experiment the thermocouple data indicate that the upper layer gases fill most of the enclosed space relatively early in the experiment. Therefore, throughout the simulation the upper-layer volume is assumed to be fixed at 1.62 m^3 , approximately ninety percent of the volume of the enclosure above the elevation of the fuel surface. The temperature history of the upper layer is taken to be the temperature measured at the elevation of thermocouple 4 of the thermocouple tree, which is approximately at the middle elevation of the assumed upper layer thickness. This temperature is assumed to be a representative value of the average layer temperature. The data from thermocouple 4 are presented in Figure 7a. According to Roby and Gottuck (1990), these data are only valid up to approximately 700 C. Other measurements indicated final peak and relatively steady temperatures of 850 C. In the simulation, the upper layer temperature was calculated according to the two-line-segment approximation of the data, which is also plotted in the figure.

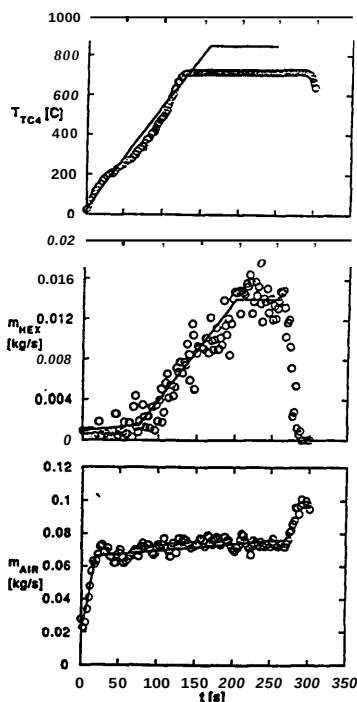


Fig. 7. Data of Gottuck and Roby (1990) and curve fits used in GGERM analysis; (a) temperature approximately at the mid-elevation of the upper layer data; (b) hexane pyrolysis rate; (c) airflow rate.

Fuel load cell data for the hexane pyrolysis rate, $\dot{m}_{\text{HEX}}$, are plotted in Figure 7b. In the simulation, the value of this, which is taken to be $\dot{P}_{\text{HEX}}$ in the analysis, was calculated according to the indicated three-line-segment approximation to this data.

Data for the duct air flow rate, $\dot{m}_{\text{AIR}}$, are plotted at the bottom of Figure 7c. This is used to approximate $\dot{P}_{\text{AIR,FIN}}$, the instantaneous air flow rate entrained into the plume and deposited into the upper layer. $\dot{P}_{\text{AIR,FIN}}$ was calculated from the indicated two-line-segment approximation to the data.

Note that the $\dot{m}_{\text{HEX}}$ and $\dot{m}_{\text{AIR}}$ approximations follow the corresponding data which indicate a step change in these value at $t = 0$.

Using Eqs. (12), $\phi^{(ss)}$ was calculated using the above-mentioned approximations for $\dot{P}_{\text{F,FIN}}$ and $\dot{P}_{\text{AIR,FIN}}$. This is plotted in Figure 8.

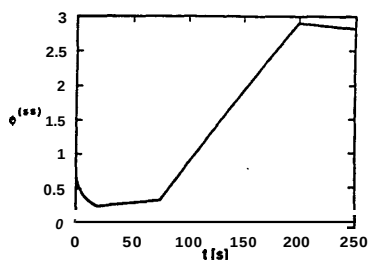


Fig. 8. $\phi^{(ss)}$ for the hexane experiment of Gottuck and Roby (1990).

The GGERM simulation of this experiment was carried out twice, first using the real C_6H_{14} combustion model and then using the complete stoichiometric combustion model. Only the real-combustion-model simulation results will be presented here.

Since experimental data was acquired for the volume fraction concentration of O_2 , CO_2 , and CO , all GGERM-computed results for the product mass fractions have been transformed into volume-fraction concentrations. The transformation was carried out with the assumption that the upper layer constituents include only: the six products of combustion, with mass fractions as computed from the GGERM; argon, with a specified mass fraction of 0.009; and nitrogen. The upper-layer volume or mole-fraction concentration of a product k will be designated here as $c_{k,u} [\text{vol}]$.

GGERM simulation results for the $c_{k,u}(t) [\text{vol}]$ are plotted in Figure 9. Included in the plots for O_2 , CO ,

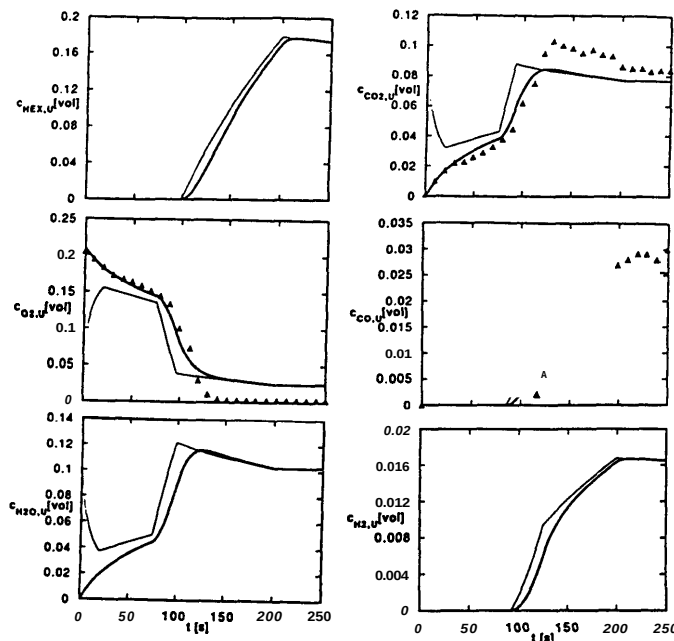


Fig. 9. Combustion of C_6H_{14} - Data and GGERM simulation of test of Gottuck and Roby (1990): data (A A A); GGERM simulation (—); and GGERM simulation with quasi-steady approximation (---).

and CO are the data for the experimentally measured volume fractions of these products. Also included are the time-dependent values of the $c_{k,ROUT}^{(ss)} [\text{vol}]$.

In Figure 8 it can be seen that the simulated step change in $\dot{m}_{\text{HEX}}$ and $\dot{m}_{\text{AIR}}$ leads to $\phi^{(ss)} \approx 0.7$ at $t = 0$. This results in initial values of $c_{k,ROUT}^{(ss)}$ which are different than the initial values of the $c_{k,u}$'s of the simulation, the latter being initialized at the concentrations of the ambient atmosphere.

To the extent that the $c_{k,ROUT}^{(ss)} [\text{vol}]$ are good approximations to the $c_{k,u} [\text{vol}]$ in the plots presented in Figure 9, the GGERM predicts that the upper layer environment is basically in a condition of quasi-steady state. As can be seen from the figures, in this particular experiment the GGERM simulation suggests that

the quasi-steady state approximation is reasonable. Nonetheless, for those products of combustion where experimental data is available for comparison, i.e., for Q , CO , and CO_2 , the transient GGERM predictions are seen to provide a superior estimate of the data than do the simple quasi-steady state predictions. To this extent, the favorable comparison between the data and the simulation results provides some validation of the GGERM.

The following additional observations and comments are offered:

1. The construction of the f_k functions for the combustion of hexane are based on the steady-state measurements of Beyler (1983). As mentioned above, the maximum of the ϕ 's in these experiments was approximately 1.8. Therefore, one's confidence in the present GGERM simulation beyond ϕ 's of 1.8, i.e., beyond approximately $t = 150$ s, should be coupled to one's confidence in the extrapolation of these f_k 's beyond 1.8. In other words, acquisition and use of new data in the high- ϕ range would lead to more confidence in high- ϕ GGERM simulations. This is of course true for CH, and other fuels as well as for hexane.
2. From approximately 150 s to the end of the test, the measured value of $c_{O_2,U}[vol]$ was 0.003, whereas the predicted value is approximately 0.03 (see Figure 9). The measured value is not consistent with Figure 8 and the c_{O_2} corresponding to the f_k of Figure 4. For example, according to Figure 8, at 150 s the value of $\phi^{(ss)} \approx 2$. According to f_{O_2} of Figure 4 and Eq. (14), this corresponds to $c_{k,ROUT}^{(ss)} \approx 0.04$. Thus, for the same ϕ , the $c_{O_2,U}$ results of the steady-state experiments of Beyler (1983), on which Figure 4 and the present hexane combustion is based, is not consistent with the present quasi-steady experimental result of Gottuck and Roby (1990). It has been determined that the discrepancy is the result of a non-negligible dependence of f_{O_2} on temperature. In particular, it is likely that for $t > 150$ s the temperature of the upper layer in the presently simulated experiment is several hundreds degrees C higher than temperatures in the experiments of Beyler (1983).

The effect of similar levels of temperature difference on the steady-state $c_{O_2,U}$ in CH₄ combustion is known from the data of Toner, Zukoski, and Kubota (1986). These were acquired at significantly higher upper-layer temperatures, as much as 200°C higher, than were those of the data of Morehart, Zukoski, and Kubota (1990). (See, e.g., Figure 4.3 of the latter work for a comparison of the high- and moderate-temperature data.) For $\phi \geq 1$, the effect on $c_{O_2,U}$ is significant and completely consistent with the effects on $c_{O_2,U}$ presently observed during the burning of hexanes. Presumably, if the hexane burn data of Beyler (1983) were acquired in a well-insulated collector with upper-layer temperatures in the 700-850 C range, the measured $c_{O_2,U}$ at $\phi \geq 1$ would be lowered from the order of a few percent to the order of a few tenths of a percent.

The expected qualitative effect of high temperature on $c_{CO_2,U}$ and τ_{mix} in the burning of hexanes can also be obtained from the cor-

responding high temperature effects in the burning of CH₄. Thus, in Figure 4.7 of Morehart, Zukoski, and Kubota (1990) for $\phi \geq 1$, the relatively high temperature of the upper layer in the experiments of Toner, Zukoski, and Kubota (1986) is seen to have resulted in $c_{CO_2,U}$ levels ten to twenty percent higher than the $c_{CO_2,U}$ levels of the relatively low-temperature experiments of Morehart, Zukoski, and Kubota (1990). A similar result is noted for $c_{CO,U}$ in Figure 4.6 of the latter work. Thus, for all three of the measured product concentrations, the high temperature effect in the hexane combustion model explains the late-time discrepancies between the present GGERM simulation and the experimental data.

It is noted that for an arbitrary fuel of interest, any significant dependence of the f_k on temperature, that may be determined in steady-state tests, could be easily incorporated into the GGERM.

The Combustion of Hexanes in Figure-6 Test Configurations - A Hypothetical Hexane Experiment

It is important to validate the GGERM with data acquired in experiments which clearly display transient behavior in the development of the upper layer environment, especially at times of relatively large values of c_{CO} . Experiments like those of Morehart, Zukoski, and Kubota (1990) would be useful in this regard. When transient data from such experiments are available they should be compared with corresponding GGERM simulations.

It would appear that experimental conditions could be chosen so that Figure-6 types of experiments would also clearly display the transient upper-layer environment of interest. As discussed earlier, the Gottuck and Roby (1990) test run simulated above was somewhat limited in this regard in that it displayed nearly-quasi-steady behavior during the interesting times of relatively high $c_{CO}[vol]$. One reason for the nearly-quasi-steady behavior was that the magnitude of $P_{F,FIN}$ resulted in relatively large induced values of $P_{N,MIN}$. From Figure 8b, the latter flow rate is seen to have a characteristic value on the order of 0.07 kg/s. For a characteristic air density of 1 kg/m³, and for the assumed 1.62 m³ upper layer volume, this corresponds to a relatively small characteristic residence time, on the order of 20 s, for flow exchange of the upper layer. (In contrast to this, the above-simulated Morehart, Zukoski, and Kubota (1990) experiment with a upper layer volume of 3.89 m³ and $P_{AIR,FIN}$ value of 0.010 kg/s has a characteristic residence time of 400 s.)

For the Gottuck and Roby (1990) test configuration it is expected that a significantly reduced fuel flow rate, leading to a corresponding reduced air flow rate, would lead to a display of the transient behavior of current interest for upper layer development. This idea was investigated by using the GGERM to simulate a hypothetical hexane-burn experiment involving values of $P_{F,FIN}$ and $P_{AIR,FIN}$ one tenth as large as the Figure 7 values used previously. All other parameters defining the experiment were assumed to be unchanged from the previous simulation. The hypothetical experiment was assumed to last 500 s, where all input parameters were assumed to be constant for the last 250 s. For O_2 , CO , and CO_2 , $c_{k,U}(t)[vol]$ results from the new simulation are plotted in Figure 10. Favorable comparisons between $c_{k,U}$ data from an actual experiment (similar to this hypothetical experiment) and $c_{k,U}$ results of its GGERM simulation would be an important validation of GGERM

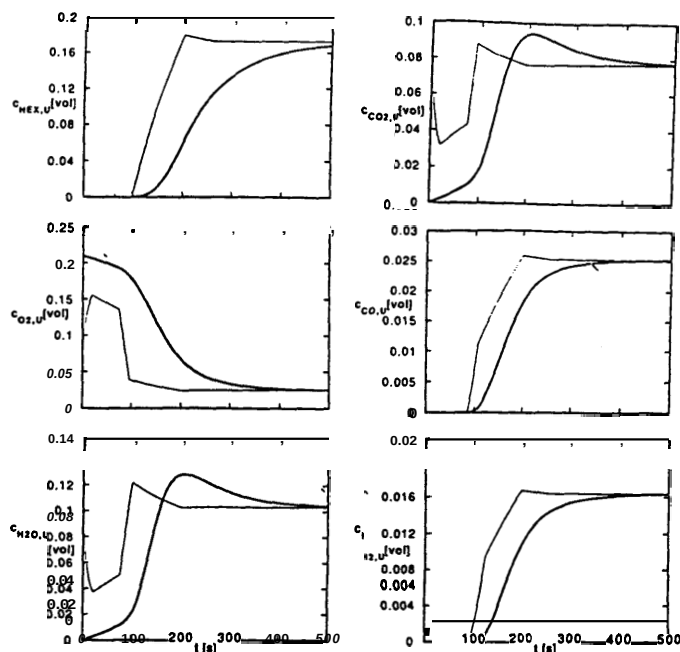


Fig. 10. Results of simulating a low-fuel-flow Gottuck and Roby (1990) test: The GGERM simulation (—) and the GGERM simulation with quasi-steady approximation (---)

capabilities.

SUMMARY AND CONCLUSIONS

The Generalized Global Equivalence Ratio Model (GGERM) was developed by Cooper (1991) to predict the generation rates of oxygen, fuel, and other products of combustion in rooms containing fires. The GGERM extends to general transient conditions the global equivalence ratio model established during times of steady-state in experimental studies involving two-layer compartment fires. The present work used the GGERM to predict upper layer mass fractions of products of combustion (fuel, oxygen, CO, and others) in these two-layer fire experiments, but during times of transient response.

Implementation of the GGERM requires knowledge of the $f_k(\phi)$ function for each product k of combustion of a fuel of interest. A f_k function predicts the steady-state generation rate of product k when the fuel burns in Figure-2-type configurations. The f_k would be constructed from data acquired in experiments of the type described in the references. Generic rules were developed for constructing the f_k from the steady-state data. The rules were then applied to data of Morehart, Zukoski, and Kubota (1990) and Beyler (1983). This resulted in prototype models (i.e., the f_k) for the steady-state combustion of methane (CH_4) and hexanes (C_6H_{14}) in Figure-2-type fire scenarios. The products of combustion considered in these latter models include O_2 , CO , H_2O , CO , H_2 , and the fuel itself.

With the characterization of methane and hexane combustion in hand, the GGERM was used to simulate transient upper-layer environments in two-layer experiments reported in Morehart, Zukoski, and Kubota (1990) (methane) and Beyler (1983) (hexanes). One of these simulations produced the unusual result of local maxima in the mass fractions of CO , H_2O , and CO . This was

explained by the action of the GGERM feedback mechanism.

All predicted results of the GGERM simulations were found to be plausible and, where transient data were available [upper-layer volume fraction of O_2 , CO , and CO for a hexanes experiment of Gottuck and Roby (1990)], predicted and measured results for the upper layer concentrations of products of combustion compared favorably. The most significant discrepancies between experiment and prediction were attributed to differences between the (relatively high) layer temperatures of the latter work and the (relatively low) layer temperatures in the steady-state f_k tests of Beyler (1983). For the most part it appears that these discrepancies could be removed with use of a data base having a more extensive layer temperature variation. Analysis of data presented in Chapter 5 of Morehart, Zukoski, and Kubota (1990) supports this contention.

A GGERM simulation of a hypothetical experiment in a Gottuck and Roby (1990) type of facility was carried out in order to identify a set of experimental conditions in that facility that would be expected to highlight the transient character of the developing upper-layer environments. Calculations suggest that a GGERM simulation which accurately predicts the experimental data from such an experiment would be an important test of the GGERM capability.

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APPENDIX: Analytic Representations of the $c_{i,ROUT}^{(SS)}$ for the Combustion of Methane (CH_4) and the f_x for the Combustion of Hexanes (C_6H_{14})

Cooper (1991) applied the curve-fitting constraints of Eqs. (23)-(43) to the steady $c_{i,ROUT}^{(SS)}$ data of Morehart, Zukoski, and Kubota (1990) for CH_4 combustion and to the f_x data of Beyler (1983) for C_6H_{14} combustion. This resulted in the the following analytic representations for fuel property functions required in the application of the GGERM.

Methane (CH_4)

CH_4 :

$$c_{CH_4,ROUT}^{(SS)} = \begin{cases} 0 & \text{if } \phi \leq 0.70 = \phi_F = \phi_{CH_4}; \\ [1 - (0.70/\phi)] / & \\ \{1 + [1/(0.037 - 0.70) - 1](0.70/\phi)\} & \\ & \text{if } \phi > 0.70 = \phi_F = \phi_{CH_4} \end{cases} \quad (A1)$$

θ :

$$c_{O_2,ROUT}^{(SS)} = \begin{cases} c_{O_2,ROUT,ST}^{(SS)} & \text{if } 0 \leq \phi \leq 0.60; \\ \{(0.232)(0.40)/[1 + (0.232)(0.60)/4]\} \cdot & \\ [(3.50 - \phi)/2.90]/(\phi/0.60)^{1/2} & \\ & \text{if } 0.60 \leq \phi \leq 3.5 = \phi_{O_2}; \\ c_{O_2,ROUT,ST}^{(SS)} = 0 & \text{if } \phi_{O_2} = 3.50 < \phi \end{cases} \quad (A2)$$

$$c_{O_2,ROUT,ST}^{(SS)} = \begin{cases} 0.232(1 - \phi)/(1 + 0.232\phi/4) & \\ & \text{if } 0 \leq \phi \leq 1; \\ 0 & \text{if } 1 < \phi \end{cases} \quad (A3)$$

CO_2 :

$$c_{CO_2,ROUT}^{(SS)} = \begin{cases} c_{CO_2,ROUT,ST}^{(SS)} & \text{if } 0 \leq \phi \leq 0.70; \\ \lambda_{CO_2,1} & \text{if } 0.70 < \phi \leq 3.00; \\ (3.00/\phi)\lambda_{CO_2,1} & \text{if } \phi > 3.00 \end{cases} \quad (A4)$$

$$\lambda_{CO_2,1} = (0.232/4)(11/4)(0.70)/[1 + (0.232)(0.70)/4] = 0.107 \dots \quad (A5)$$

$$c_{CO_2,ROUT,ST}^{(SS)} = \begin{cases} (0.232/4)(11/4)\phi/(1 + 0.232\phi/4) & \\ & \text{if } 0 \leq \phi \leq 1; \\ (0.232/4)(11/4)/(1 + 0.232\phi/4) & \\ & \text{if } 1 < \phi \end{cases} \quad (A6)$$

H_2O :

$$c_{H_2O,ROUT}^{(SS)} = \begin{cases} c_{H_2O,ROUT,ST}^{(SS)} & \text{if } 0 \leq \phi \leq 0.70; \\ \lambda_{H_2O,1}\phi - \lambda_{H_2O,2} & \text{if } 0.70 < \phi \leq 2.25; \\ c_{H_2O,ROUT,ST}^{(SS)} & \text{if } 2.25 < \phi \end{cases} \quad (A7)$$

$$\begin{aligned} \lambda_{H_2O,1} &= (c_{H_2O,2}^{(SS)} - c_{H_2O,1}^{(SS)})/(2.25 - 0.70) \\ \lambda_{H_2O,2} &= (0.70c_{H_2O,2}^{(SS)} - 2.25c_{H_2O,1}^{(SS)})/(2.25 - 0.70) \end{aligned} \quad (A8)$$

$$c_{H_2O,1}^{(SS)} = (0.232/4)(9/4)(0.70)/[1 + 0.232(0.70)/4]$$

$$c_{H_2O,2}^{(SS)} = (0.232/4)(9/4)/[1 + 0.232(2.25)/4]$$

$$c_{H_2O,ROUT,ST}^{(SS)} = (9/11)c_{CO_2,ROUT,ST}^{(SS)} \quad (A9)$$

CO :

$$c_{CO,ROUT}^{(SS)} = \begin{cases} 0 & \text{if } 0 \leq \phi < 0.55 \\ \lambda_{CO,1}\phi - \lambda_{CO,2} & \text{if } 0.55 < \phi \leq 1.15 \\ \lambda_{CO,3}\phi - \lambda_{CO,4} & \text{if } 1.15 < \phi \leq 3.00 \\ 0.0205(3.00)/\phi & \text{if } 3.00 < \phi \end{cases} \quad (A10)$$

$$\begin{aligned} a_{CO} &= 0.0127/(1.15 - 0.55); \\ \lambda_{CO,2} &= 0.55(0.0127)/(1.15 - 0.55); \\ \lambda_{CO,3} &= (0.0205 - 0.0127)/(3.00 - 1.15); \\ \lambda_{CO,4} &= [1.15(0.0205) - 3.00(0.0127)]/(3.00 - 1.15) \end{aligned} \quad (A11)$$

$$c_{H_2, \text{ROUT}}^{(ss)} = \begin{cases} 0 & \text{if } 0 \leq \phi < 0.90; \\ [0.00145/(2.00 - 0.90)]\phi & \\ - 0.90(0.00145)/(2.00 - 0.90) & \\ \quad \text{if } 0.90 \leq \phi \leq 2.00; & (A12) \\ 0.00145 & \text{if } 2.00 < \phi \leq 3.00; \\ 0.00145(3.00)/\phi & \text{if } 3.00 < \phi \end{cases}$$

Hexanes (C₆H₁₄)

$k \rightarrow \text{C}_6\text{H}_{14}, \text{O}_2, \text{H}_2\text{O}, \text{and CO}_2:$

$$f_k(\phi) = \begin{cases} \Gamma_k & \text{if } \phi \leq \phi_{k, ST1}; \\ (\Gamma_k/\phi)[1 - (1 - \phi_k)(\phi_{k, ST2} - \phi)/ & \\ \quad (\phi_{k, ST2} - \phi_{k, ST1})] & \\ \quad \text{if } \phi_{k, ST1} < \phi < \phi_{k, ST2}; & (A13) \\ \Gamma_k/\phi & \text{if } \phi \geq \phi_{k, ST2} \end{cases}$$

$$\begin{aligned} \Gamma_{\text{C}_6\text{H}_{14}} &= -1; \Gamma_{\text{O}_2} = -152/43; \Gamma_{\text{H}_2\text{O}} = 63/43; \\ \Gamma_{\text{CO}_2} &= 132/43; \end{aligned} \quad (A14)$$

$$\begin{aligned} \phi_{\text{C}_6\text{H}_{14}, ST1} &= \phi_F = 0.85; \phi_{\text{O}_2, ST1} = 0.80; \\ \phi_{\text{H}_2\text{O}, ST1} &= 0.85; \phi_{\text{CO}_2, ST1} = 0.70; & (A15) \\ \phi_{k, ST2} &= \phi_{\text{O}_2} = 10.0 \text{ for } k \rightarrow \text{C}_6\text{H}_{14}, \text{O}_2, \text{H}_2\text{O}, \text{and CO}_2 \end{aligned}$$

$$(43/84)f_{\text{CO}} = \begin{cases} 0 & \text{if } 0 \leq \phi < 0.55; \\ 0.200\phi - 0.110 & \text{if } 0.55 < \phi \leq 1.00; \\ 0.090 & \text{if } 1.00 < \phi \leq 3.50; \\ 0.090(3.50)/\phi & \text{if } 3.50 < \phi \end{cases} \quad (A16)$$

$$(43/7)f_{\text{H}_2} = \begin{cases} 0 & \text{if } 0 \leq \phi < 0.70; \\ 0.050(\phi/0.70 - 1) & \text{if } 0.70 \leq \phi \leq 1.40; \\ 0.050 & \text{if } 1.40 < \phi \leq 3.50; \\ 0.050(3.50)/\phi & \text{if } 3.50 < \phi \end{cases} \quad (A17)$$

Plots of the f_k for the Combustion of Methane and Hexanes

The f_k functions for CH₄ were computed from Eqs. (16)-(18) using the $c_{k, \text{ROUT}}^{(ss)}$ representations of Eqs. (A1)-(A12). The f_k 's for the six products are plotted in Figure 3. For C₆H₁₄, the f_k 's of Eqs. (A13)-(A17) are plotted in Figure 4.