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Fuel Mixing Effects on Propagation of Premixed Flames. I. Hydrogen+Carbon Monoxide Flames

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The combustion mechanisms in premixed flames having a mixture of hydrogen and carbon monoxide as the fuel and the stoichiometric amount of air as the oxidizer were investigated by numerical simulation to elucidate the fuel-mixing effects on the burning velocity. Hydrogen and carbon monoxide have similar physical properties and their stoichiometric flames with air are known to propagate through the same type of mechanism, governed by active species diffusion. The flames of the mixed fuel hydrogen+carbon monoxide were found here to have their heat-release rate distributions changing with conformity in shape when the fuel composition is changed. The burning velocity was found to vary almost linearly with the hydrogen content in the fuel. Furthermore, the flux of chemical energy which is carried into low-temperature regions by hydrogen atoms diffusing from the flame front was also found to be roughly proportional to the burning velocity.

Theoretical investigators of the propagation mechanism of premixed flames have proposed a few types of analytical expressions for their burning velocity.[1] These expressions are convenient for a rough estimation of the burning velocity and suggestive for understanding approximate relations between the properties of a flame and its burning velocity. However, since most of the expressions were derived under several approximations, their application to actual flames may lead to invalid results. In order to avoid such shortcomings of the analytical approaches, all the factors which may influence the burning velocity should be counted up and their contributions should be evaluated in detail.

Stoichiometric flames of hydrogen and of carbon monoxide mixed with some hydrogen-containing species follow similar propagation mechanisms.[2–4] The purpose of this paper is to analyze the chemical and physical properties of flat premixed flames with the mixed fuel hydrogen+carbon monoxide and to derive relations between these properties and the burning velocity by using computer simulation.

Simulation Model

The simulation model for flat flames was established by considering the following governing equations:

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x}(\rho v)=0, \tag{1}$$

$$\frac{\partial}{\partial t}(c_p\rho T)+\frac{\partial}{\partial x}(c_p\rho Tv)= \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+\sum_i D_i\rho\frac{\partial h_i}{\partial x}\frac{\partial \omega_i}{\partial x}-\sum_i h_i\phi_i, \tag{2}$$

$$\frac{\partial}{\partial t}(\rho\omega_i)+\frac{\partial}{\partial x}(\rho\omega_i v)=\frac{\partial}{\partial x}\left(D_i\rho\frac{\partial \omega_i}{\partial x}\right)+\phi_i, \tag{3}$$

$$p=\rho RT\sum_i\frac{\omega_i}{m_i}, \tag{4}$$

where ω_i and ϕ_i are, respectively, the mass fraction and the mass production rate of the i-th species due to reactions; other variables have their usual meanings. The boundary conditions were as follows: at the unburned side the temperature is 298 K and the gas consists of the mixed fuel and the stoichiometric amount of air, and at the burned side the gas has the adiabatic flame temperature and the corresponding equilibrium composition. The flow velocity at the unburned side is taken to agree with the burning velocity which is the eigenvalue determined by the conditions of the unburned gas.

The reaction scheme employed here consists of thirty-seven pairs of elementary reactions occurring among fourteen species and was verified previously to be applicable to the combustion of methane, carbon monoxide and hydrogen under lean and stoichiometric conditions.[5]

Results and Discussion

Burning velocities of the hydrogen+carbon monoxide flames predicted by the model are plotted in Fig. 1 as a function of the initial hydrogen content in the mixed fuel. According to the figure, when hydrogen is added by 2 mol% or more, stable combustion of carbon monoxide is promoted. The burning velocity of these mixed fuel flames varies almost linearly throughout the whole range of the initial hydrogen content, indicating that the propagation mechanisms of hydrogen and carbon monoxide flames have some aspects in common.

A hydrogen and a carbon monoxide flames have the following similarities in their chemical and physical properties in addition to those in the combustion reaction mechanisms, which will be discussed afterwards: (1) both fuels react with the same amount of oxygen in their complete combustion; (2) calorific values of both fuels are similar: 240 kJ mol^{-1} for hydrogen in lower calorific value and 280 kJ mol^{-1} for carbon monoxide; (3) the fuels and combustion products of the two flames respectively have specific heat of the same magnitude and

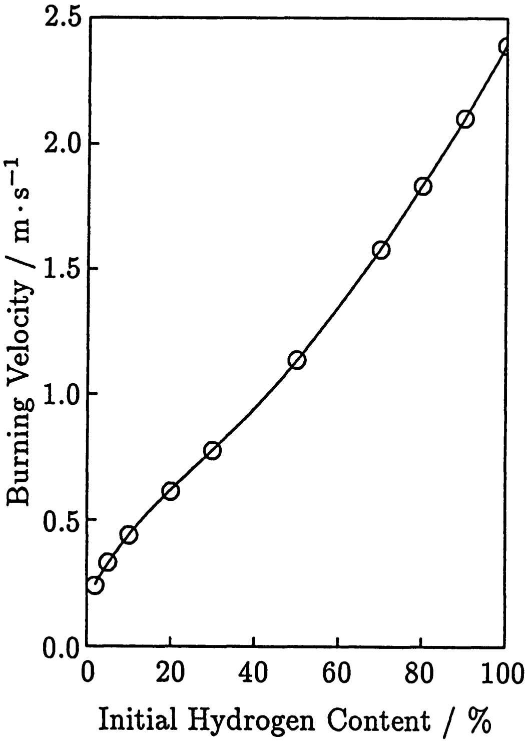

Fig. 1. Burning velocities of stoichiometric hydrogen + carbon monoxide premixed flames.

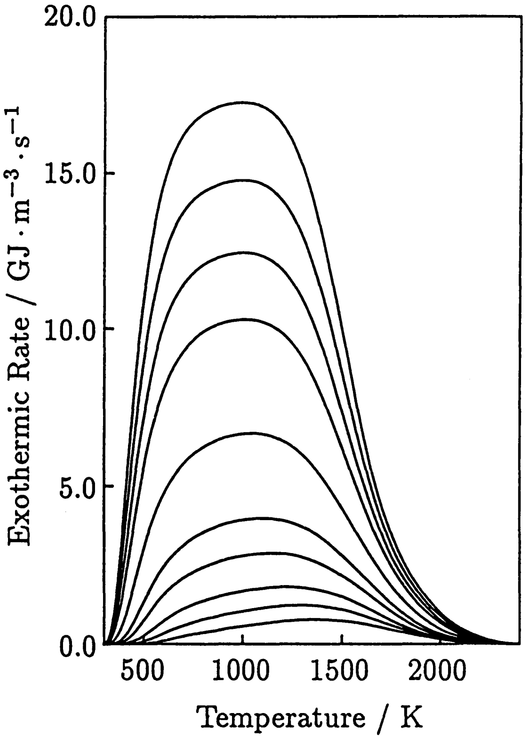

Fig. 2. Exothermic rates of hydrogen + carbon monoxide flames. The curves correspond to the flames of 100%, 90%, 80%, 70%, 50%, 30%, 20%, 10%, 5%, and 2% H_2 flames. The maximum rate decreases as the carbon monoxide content in the fuel increases.

hence the global specific heats of the two flames change similarly at any stage of their combustion. Accordingly these two flames have quite similar adiabatic flame temperature due both to (2) and (3).

The similarities in the reaction mechanisms can be inferred from the distributions of the exothermic rates, shown in Fig. 2. Strictly speaking, the temperature giving the maximum heat-release rates in the hydrogen-lean flames increases from 1050 K (50% H_2 +50% CO flame) to 1370 K (2% H_2 +98% CO flame), but it is almost fixed within a narrow range between 1000 and 1020 K in the flames containing initially more than 50% of hydrogen in the mixed fuel.

Next the mechanisms of combustion reactions in the various hydrogen+carbon monoxide flames will be discussed in detail.

As previously described,⁶⁾ in a stoichiometric hydrogen-air premixed flame under atmospheric pressure the combustion reaction proceeds according to two mechanisms depending on temperature. At low temperatures the combustion reaction mainly consists of the reactions

$$H+O_2+M \rightarrow HO_2+M, \qquad (R32)$$

$$H+HO_2 \rightarrow OH+OH \qquad (R34)$$

and

$$OH+H_2 \rightarrow H+H_2O; \qquad (R27)$$

this mechanism will be called here mechanism I. The rate of (R27) is in general about twice as large as the rates of (R32) and (R34), and hydrogen atoms, the chain carriers of these reactions, cannot self-proliferate through this mechanism alone. Their concentration increase depends, then, on diffusion from the flame front.

As the temperature rises hydroxyl radical production shifts toward the following chain branching reactions

$$H+O_2 \rightarrow OH+O \qquad (R24)$$

and

$$O+H_2 \rightarrow OH+H, \qquad (R25)$$

but hydrogen is still oxidized by reaction (R27); these three reactions constitute mechanism III. By this mechanism hydrogen atoms proliferate exponentially.

In a stoichiometric carbon monoxide flame which is modified by addition of some hydrogen-containing species such as molecular hydrogen and water vapor, the fuel is predominantly oxidized, in a wide range of temperature, through reaction⁴⁾

$$CO+OH \rightarrow CO_2+H, \qquad (R20)$$

with the hydroxyl radicals being supplied by the hydrogen-containing species. At low temperatures the combustion of carbon monoxide can thus proceed according to a mechanism similar to that of the hydrogen flame, and hence in flames containing various amounts of carbon monoxide and hydrogen the two fuels are independently oxidized by reactions (R20) and (R27), respectively. The low-temperature combustion mechanism of hydrogen+carbon monoxide, comprising mechanism I and reaction (R20), is named mechanism II.

At temperatures higher than about 1200 K the combustion of hydrogen+carbon monoxide proceeds via two mechanisms depending on the amount of hydrogen still left unreacted in this region or, in other words, depending on whether reaction (R25) can work as a hydroxyl radical source. When hydrogen is still present even in the high-temperature region the two fuels are independently oxidized by reactions (R27) and (R20); this is called mechanism IV. However, when hydrogen has been consumed within the low-temperature region, reactions (R25) and (R27) are consequently suppressed, and the oxygen atoms which would otherwise be consumed by reaction (R25) are used for the oxidation of carbon monoxide, through[4)]

$$CO + O + M \rightarrow CO_2 + M; \qquad \text{(R21)}$$

this mechanism is called mechanism V. The proportions of carbon monoxide oxidized by oxygen atoms are 14% in the 10% H_2 +90% CO flame, 19% in the 5% H_2 +95% CO flame and 26% in the 2% H_2 +98% CO flame at the positions of the maximum rate of carbon monoxide consumption.

In hydrogen-lean flames another supply of hydroxyl radicals is developed: The high-temperature decomposition of the water produced in the low-temperature region

$$O + H_2O \rightarrow OH + OH. \qquad -\text{(R26)}$$

This reaction is one of the sources of hydroxyl radicals in moist carbon monoxide flames as well.

The temperature at which reactions (R32) and (R24), the rate controlling steps of mechanisms I and III, have an equal rate or, in other words, the boundary temperature between the two mechanisms, is restricted within a narrow range between 1120 and 1180 K; the temperature range becomes narrower, from 1160 to 1180 K, if the two hydrogen-lean flames containing initially 2 and 5% of hydrogen are excluded. The variation in the boundary temperature arises from the fact that the constituents of the third body of reaction (R32) depend on the reacting gas composition (third-body species have individual reaction efficiencies).

The oxidation of hydrogen by hydroxyl radicals precedes that of carbon monoxide since the rate constant of the former reaction is much larger at temperatures above 500 K. About 45 to 70% of the initial hydrogen is oxidized to water in the region where mechanism II is predominant; the proportions of carbon monoxide oxidized to carbon dioxide, in contrast, range from 10 to 28% in the same region. Consequently the shift of the high-temperature mechanism from IV to V is sensitive to the initial hydrogen content in the mixed fuel.

Exothermicity of the reactions in the flames is ascribed as follows. At about 800 K, more than 50% of the released heat is evolved by reactions (R32) and (R27) even in the 10% H_2 +90% CO flame. Thermal energy is thus released by the same type of mechanism in the low-temperature regions of any hydrogen+carbon monoxide flames. Close to the boundary temperature between the low- and the high-temperature mechanisms, however, thermal energy is released by a wider variety of hydrogen-oxygen reactions such as reactions (R32), (R27), (R34), together with

$$OH + H + M \rightarrow H_2O + M \qquad \text{(R31)}$$

and

$$H + HO_2 \rightarrow H_2 + O_2. \qquad \text{(R33)}$$

In the flames with initial carbon monoxide content larger than 50%, the contribution of reaction (R20) rises up to 10% or more and reaches about 25% in the 10% H_2 +90% CO flame. The contribution of the oxidation of carbon monoxide with oxygen atoms, reaction (R21), to the total heat release rate also increases with increasing carbon monoxide concentration; it becomes 10% in the 30% H_2 +70% CO flame, 25% in the 10% H_2 +90% CO flame and 50% in the 2% H_2 +98% CO flame, for instance. At higher temperatures, reactions (R20) and (R21), in particular, evolve a large amount of thermal energy.

The combustible gas mixture cannot be heated in the upstream region of a premixed flame without energy supply from the flame front. The propagation, and hence the burning velocity are governed by the mode how temperature is raised in the low-temperature regions; the two propagation mechanisms, that is, the active-species diffusion mechanism and the thermal mechanism, are activated depending on the type of the supplied energies: chemical or thermal energy,[1)] respectively. The former type of energy is released into thermal energy through exothermic reactions in the low-temperature zone.

The factors governing the propagation mechanisms will be discussed on the basis of the energies which are supplied toward the low-temperature region. Chemical energy was assumed here to be carried substantially by diffusing hydrogen atoms because of their large diffusion coefficient and reactivity. In propagation theories a characteristic point dividing low- and high-temperature regions is defined as the position where the heat-increase rate due to thermal conduction equals zero; it is called the ignition point because downstream from this point thermal energy must increase only by heat liberation through reactions. This characteristic point was adopted though the fuel mixtures are not ignited, strictly speaking, just here. The temperature of the so-defined ignition point ranges from 1000 K to 1170 K, being almost constant for the flames with initial hydrogen contents larger than 30% and increasing fairly steeply as the initial hydrogen content is lowered below that value.

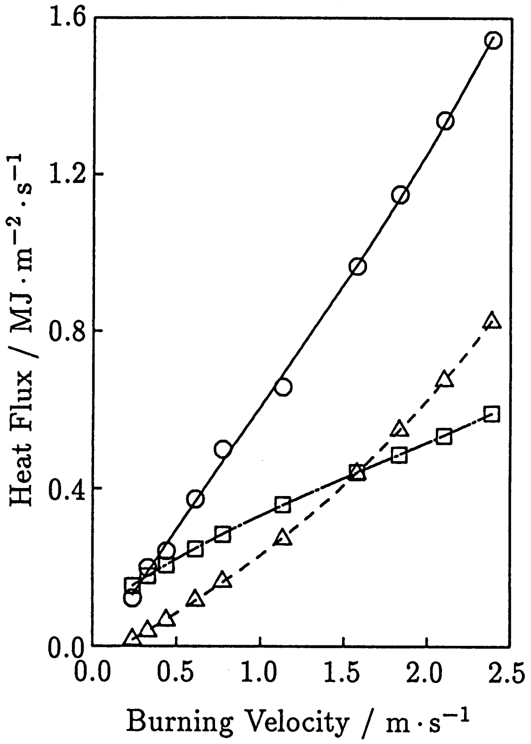

Fig. 3. Flux of thermal energy due to conduction (squares), that of the chemical energy carried by diffusing hydrogen atoms (triangles) at the ignition points, and the thermal energy release rate by exothermic reactions in the low-temperature regions (circles) of various hydrogen + carbon monoxide flames, as functions of the burning velocity.

The fluxes of thermal energy and the above-defined chemical energy at the ignition points, and the total rate of thermal energy liberation within the region upstream the ignition point are plotted against the burning velocity in Fig. 3; the two fluxes and the total heat release rate were obtained by integration of the corresponding terms of Eq. 2 from $x=0$ up to the ignition point, and therefore they designate the corresponding energies transported upstream across the ignition point.

According to Fig. 3 the total amounts of released heat in the low-temperature regions are much larger than the conductive fluxes at the ignition points except in a few hydrogen-lean flames. This comparison leads to the conclusion that propagation of most of the hydrogen+carbon monoxide flames is governed by release of heat in the upstream region due to reactions converting the chemical energy brought from the flame front by hydrogen atoms into thermal energy ; this propagation mechanism has been already pointed out for carbon monoxide flames.[2] The exothermic reactions in the low-temperature regions, reactions (R32) and (R27), the latter being activated by the hydroxyl radicals produced through the former and through (R34), are triggered by the hydrogen atoms diffusing upstream through the ignition points. The burning velocity is proportional to the amount of heat released in the low-temperature region and also is almost proportional to the chemical energy carried by hydrogen atoms diffusing upstream from high-temperature regions.

Concluding Remarks

Hydrogen and carbon monoxide have several chemical and physical similarities from the viewpoint of combustion. There are five possible reaction mechanisms in flames of hydrogen+carbon monoxide, depending on the temperature and the fuel composition; two for low temperatures and three for high temperatures. The burning velocity of these flames is simply proportional to the initial hydrogen content in the mixed fuel; this is because the reaction mechanisms do not vary with the fuel composition though addition of carbon monoxide to the fuel disturbs the smooth progression of the high-temperature hydrogen combustion mechanism. It was also found that the burning velocity of these flames has an approximately linear relation with the amount of the chemical energy carried by hydrogen atoms diffusing upstream across the ignition points and with the integrated released-heat in the low-temperature regions.

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