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THEORETICAL STUDIES ON HETEROGENEOUS COMBUSTION

Progress Report

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TABLE OF CONTENTS

I. Introduction

In most of the liquid-fueled chemical power plants the fuel is usually introducted into the combustor in the form of a spray jet consisting of an ensemble of droplets. The spray subsequently ignites and burns, releasing chemical energy to perform work and, at the same time, producing trace pollutants which are subsequently exhausted. Hence in order to improve the combustor performance in terms of, say, cleanliness and efficiency, understanding of the combustion characteristics of fuel spray is essential. The present program aims to study the various heterogeneous processes involved during (1) vaporization, ignition, deflagration, and extinction of single fuel droplets in the reactive environment simulating the spray interior, and (2) the vaporization, ignition, and combustion of the spray as a whole. The approach is primarily theoretical, although occasionally simple experiments have been conducted to complement the theoretical predictions. During the reporting period the following projects have been successfully completed.

II. Explosions with Chain Branching

In most theoretical combustion studies the kinetic mechanism assumed is usually that of a one-step, overall, irreversible reaction between a fuel (F) and an oxidizer (O) species leading to the formation of products as represented by

$$[F] + {}_{O}[O] \rightarrow \nu_{P}[P]$$

where ν_i is the stoichiometric coefficients. While this assumption is frequently adequate, especially when the primary mechanism for flame propagation is through heat transfer ahead of the flame, there exist many phenomena which can only be satisfactorily explained by the possibility that the reaction must have proceeded in more than one step, and that the existence of radicals must have influenced the combustion process in an essential way. One such example is the S-shaped explosion limits of the hydrogen-oxygen system, in which some of the transition limits are explained by chain branching and termination reactions.

Thus in order to gain basic understanding on the influence of such realistic kinetic mechanisms on the combustion processes, we have adopted a two-step reaction mechanisms in the simplest combustion situation of interest, to be described in the following.

The problem studied is the classical thermal explosion of a uniform, combustible mixture. That is, a combustible mixture raised to a certain temperature may explode after an induction period has elapsed. In a purely thermal explosion the heat released by the reactive mixture increases its temperature. As the temperature rises the reaction rate increases further accelerating the heat release until the rate becomes catastrophic and the system explodes. Yet another process may occur simultaneously. The reactants may produce free radicals or atoms, known as chain carriers, by means of initiation reactions. The chain carriers are multiplied through a branching reaction and are destroyed in a termination reaction. These chain reactions may proceed at an enormous rate and being accompanied by heat release may result in an explosion.

The purely thermal explosion has been extensively studied by several investigators. Explosions at higher pressures may be primarily thermal in nature; but in the low pressure explosion regime (for instance, in H_2-O_2 or CO_2-O_2 systems) chain branching is known to have a substantial influence on the explosion process. Thus in the present study we have adopted a two-step kinetic scheme represented by

$$\begin{aligned} F + R &\rightarrow nR + mA \\ R &\rightarrow rB \end{aligned}$$

where R represents a radical species and A and B are the products. The first reaction is that of chain branching, with a high activation energy and small heat release. The second is that of chain termination, with low activation energy and high heat release. The multiplication factor n designates how efficient the chain-branching step is. Thus depending on the magnitude of these kinetic parameters, the influence of the chain reactions can be assessed.

The analysis yields explicit expressions for the induction time leading to explosion. Of particular interest is the identification that for suitable values of the kinetic parameters, there exists situations under which explosion can be induced for a relatively cold mixture with the addition of only a small quantity of radicals.

This work has been accepted for publication in Combustion Science and Technology (Publication No. 10).

III. Assessment of Importance of Gas-Phase Transient Diffusion in Droplet Combustion

A frequently invoked assumption in the analyses of heterogeneous combustion systems is that of gas-phase quasi-steadiness. The assumption is based on the reasoning that because of the significant disparity between the densities of the gas and condensed phases, gas-phase transport processes occur at rates much faster than those of the condensed phase. Therefore if the ambiance is maintained steady, then the gas-phase processes can also be treated as steady, with the boundary conditions at the interface varying at a longer time scale.

Based on the above concept, it is then reasonable to expect that the quasi-steady assumption should be valid under most situations except for near or supercritical combustion when the gas-density ratio is close to or exceeds unity, or for processes which occur close to the ambiance such that the characteristic diffusion time becomes excessively long. However, earlier transient studies have shown that, even under conditions when quasi-steadiness is expected to be valid, the droplet combustion behavior is radically different from predictions of the d^2-Law, which is formulated with the quasi-steady assumption. For example, while the d^2-Law predicts that the flame diameter should decrease quadratically with time, these analyses show that it first increases and then decreases. Furthermore, these inherently transient behavior actually seem to be substantiated by experimental observations.

To resolve the above dilemma, we have recently identified an important transient gas-phase process termed fuel vapor accumulation (see Publication No. 4). That is, immediately after ignition the amount of fuel vapor present between the flame and the droplet surface is insufficient to support the flame size as required by the d^2-Law. The flame size subsequently grows by accumulating part of the vaporized fuel in the inner region instead of having them consumed at the flame. We have also demonstrated that the accumulated amount must be substantial because accumulation is at the expense of the finite droplet mass, and because volume effect dominates in spite of the low gas density.

Thus it is clear that the previous analysis has actually included two transient gas-phase processes, namely transient diffusion and fuel vapor accumulation. Therefore in order to identify the droplet gasification charateristics which are uniquely consequences of transient diffusion, and thereby assess its importance, it is necessary to suppress fuel vapor accumulation by setting the initial conditions to correspond to the d^2-Law values.

Based on the above concept, we have formulated a theory for droplet vaporization and combustion, allowing only for transient diffusion effects. Their results conclusively demonstrate that for all practical purposes transient diffusion is not an important process during heterogeneous combustion. This is a useful conclusion in that it justifies the adoption of gas-phase quasi-steadiness in theoretical modeling, which offers significant simplifications both in the analysis and also when interpreting the predictions.

The work has been submitted for publication considerations (Publication No. 11).

IV. Droplet Flame Structure with Combined Forced and Buoyant Convection

Within the realistic environment of a combustor, droplet combustion is invariably under the influence of both forced and natural (i.e. buoyant) convection. Natural convection is important because of the omnipresence of gravity, the significant temperature gradients around individual droplets, and the elevated pressure within internal combustion engines. Forced convection is important because of the droplet inertia either acquired during the injection process or when it is situated in a highly non-uniform and fluctuating flow field.

Previous studies on convection effects specialize in either forced or natural convection. Limited attempts at a unified analysis were not satisfactory in that they fail to cover the entire range of the combined convection intensity. In the present work we have identified the proper scaling law which allows the formulation of such a unified theory. Thus we have analyzed the cases of pure vaporization, ignition, flame-sheet burning, and extinction. Explicit expressions have been obtained for the vaporization and burning rates, and also the criteria governing ignition and extinction.

This work has been submitted for publication considerations (Publication No. 12).

V. Review Articles on Droplet Vaporization and Combustion

An extensive review on droplet vaporization and combustion has been prepared for Progress in Energy and Combustion Sciences (Publication No. 13). A condensed version (Publication No. 14) has been presented as one of the lead lectures at the Second International Colloquium on Drops and Bubbles, and will appear in the proceedings of the meeting. Summary of these reviews, including suggestions for further research, is given in the Appendix.

VI. Publications Resulting from Present Program

1. "Deflagration and Extinction of Fuel Droplets in a Weakly-Reactive Atmosphere," by C. K. Law, J. Chem Phys. 68, 4218 (1978).
2. "Ignition of a Combustible by a Hot Particle," by C. K. Law, AIAA J. 16, 628 (1978).
3. "Fuel Spray Vaporization in Humid Environment," by C. K. Law and M. Binark, Intl. J. Heat and Mass Transfer 22, 1009 (1979).
4. "Gas-Phase Quasi-Steadiness and Fuel Vapor Accumulation Effects in Droplet Burning," by C. K. Law, S. H. Chung, and N. Srinivasan, Combustion and Flame 38, 173 (1980).
5. "An Ignition Criterion for Droplets in Sprays," by C. K. Law and S. H. Chung, Combustion Science and Technology 22, 17 (1980).
6. "Combustion and Agglomeration of Coal-Oil Mixtures in Furnace Environments," by K. Miyasaka, C. K. Law, and C. H. Wang, Combustion Science and Technology 24, 71 (1980).
7. "A Unified Criterion for the Convective Extinction of Fuel Particles," by X. Wu, C. K. Law, and A. C. Fernandez-Pello, to appear in Combustion and Flame (1981).
8. "A Theory for the Free-Convective Burning of a Condensed Fuel Particle," by A. C. Fernandez-Pello and C. K. Law, to appear in Combustion and Flame (1982).

9. "A d^2-Law for Multicomponent Droplet Vaporization and Combustion," by C. K. Law and H. K. Law, to appear in AIAA J. (1982).

10. "Explosions with Chain Branching: Induction Period Analysis," by A. K. Sen and C. K. Law, to appear in Combustion Science and Technology (1982).

11. "Gas-Phase Transient Diffusion in Droplet Vaporization and Combustion," by M. Matalon and C. K. Law, submitted.

12. "Diffusion Flame Structure in the Mixed-Convective Stagnation-Point Flow," by A. C. Fernandez-Pello and C. K. Law, submitted.

13. "Recent Advances in Droplet Vaporization and Combustion," by C. K. Law, to appear in Progress in Energy and Combustion Science (1982).

14. "Mechanisms of Droplet Combustion," by C. K. Law, to appear in the Proceedings of the Second International Colloquium on Drops and Bubbles (1982).

APPENDIX

Summary of Review Article

The present status on understanding the mechanisms governing droplet vaporization and combustion is summarized in the following.

a. Unsteadiness during single droplet gasification has a variety of causes. The major ones are:

   i) Gas-phase unsteady diffusion, including supercritical combustion.

   ii) Droplet heating.

   iii) Fuel vapor accumulation.

   iv) Unsteadiness caused by the compositional change of multicomponent droplets.

   v) Natural and forced convection, whose intensity depends on the instantaneous droplet Reynolds and Grashof number.

   vi) Finite-rate kinetics whose effects depend on the instantaneous droplet sizes.

b. The fundamental mechanisms governing sub-critical, spherically-symmetric, single-component droplet gasification are reasonably well understood. There are two major transient processes involved, namely droplet heating which mostly influences the initial droplet regression rate, and fuel vapor accumulation which affects the flame location throughout the entire droplet lifetime. Both these processes occur on a time scale much longer than the characteristic gas-phase transport time.

c. The importance of gas-phase unsteady diffusion has not been adequately assessed. Existing analyses and concern over its apparent importance are not conclusive because the predicted unsteadiness also includes contributions from the initial conditions assumed. An unambiguous assessment should use the d^2-Law results as the initial conditions; such an analysis has not been performed. It appears likely that unsteady diffusion is unimportant for sub-critical combustion. Existing experiments results on low-pressure combustion do agree qualitatively with predictions assuming gas-phase quasi-steadiness but alowing for fuel vapor accumulation.

d. The d^2-Law totally fails to describe the flame movement. It also cannot provide quantitatively accurate estimates of either the surface regression rate or the flame temperature when dissociation is important. Its usefulness for estimation of the chemical heat release rate is also quite limited because it incorrectly equates the rate of fuel consumption at the flame with the rate of gasification at the surface.

e. Thus the minimum features that should be included in a reasonably realistic model for the sub-critical, spherically-symmetric, single-component droplet gasification are

i) Variable transport properties.
ii) Droplet heating.
iii) Fuel vapor accumulation.
iv) Dissociation at the flame.

Gas-phase quasi-steadiness can be assumed for simplicity. Such an analysis has not been performed.

f. For multicomponent droplets subject to strong convective motion, existing experimental results seem to indicate a batch-distillation like gasification mode, although theoretical predictions show the droplet composition remains non-uniform throughout its entire lifetime. The cause for such a discrepancy has not been identified. More detailed analysis and well-controlled experiments are needed to resolve this important question.

g. The phenomena of micro-explosion has potential to significantly improve charge preparation and therefore deserves further study. For miscible fuel blends the dependence of micro-explosion on the fuel composition and internal motion should be characterized. For W/O emulsions, emulsion stabiity, the optimum water droplet sizes, and the effect of pressure are the important problems requiring detailed study.

h. The fire resistant nature of W/O emulsions is intriguing and important from an application point of view. The postulate that near-equilibrium gasification exists over the fuel pool requires careful experimental investigation. With the identification of the dominant mechanism(s) responsible for this unique property, it is then possible to optimize the emulsion formulation in terms of, say, reducing the water and surfactant contents.

i. In view of the recent interest to conduct combustion experiments in the gravity-free Space Lab environment, a candidate experiment is that of the combustion and micro-explosion of multicomponent droplets. This experiment cannot be easily and perfectly conducted on earth. For example the suspension technique cannot be used because the suspension fiber can serve as heterogeneous nucleation sites to induce artificial micro-explosion. Freely-falling droplets experience forced convection and therefore internal circulation whose intensity also continuously varies because of the changes in the droplet velocity and size. Finally, the presence of natural convection also induces internal motion. Thus only in a gravity-free environment can a stationary and convection-free experiment involving an unsuspended droplet be conducted.

j. Although not specifically covered in the present review, high-pressure near-critical and supercritical combustion is a fertile area of research. The primary question to be addressed is whether the droplets can reach criticality before they have been substantially gasified. This depends on the droplet gasification rate, droplet heating rate, and the extent of elevation of the critical pressure due to dissolution of the ambient gas into the liquid. It is obvious that as the critical state is approached, the assumption of gas-phase quasi-steadiness breaks down. The ability of the droplet to maintain its spherical shape is also greatly diminished. In particular, under the supercritical state the distortion of the fuel sphere by either forced or natural convection can be so severe that it may be meaningless to assume a sphereical fuel source. In fact, study of supercritical combustion cannot be classified as droplet combustion because the droplet no longer exists.

k. Another major topic not covered in this review is the droplet motion. The drag the droplet experiences, the heat transfer to the droplet, the interfacial velocity and normal mass flux through gasification, and the internal motion are all intimately coupled. Mathematical study of these problems is further complicated by the fact that in realistic situations the droplet Reynolds number is neither large nor small. This is because while the droplets need to have sufficient inertia for penetration, the maximum Reynolds number is limited by droplet fragmentation for those fuels of interest. Therefore systematic studies assuming low, intermediate, and moderately high Reynolds number flows are all needed.