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FINAL REPORT

SOLID ROCKET COMBUSTION SIMULATOR TECHNOLOGY
(Using the Hybrid Rocket for Simulation)

by

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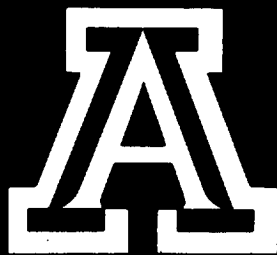
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This paper reexamines the hybrid rocket in light of several important unanswered questions regarding its performance. The well-known heat transfer limited burning rate equation is quoted, and its limitations are pointed out. Several inconsistencies in the burning rate determination through fuel depolymerization are explicitly discussed. The resolution appears to be through the postulate of (surface) oxidative degradation of the fuel. Experiments are initiated to study the fuel degradation in mixtures of nitrogen/oxygen in the 99.9%/0.1% to 98%/2% range. The overall hybrid combustion behavior is studied in a 2"-diameter rocket motor, where a PMMA tube is used as the fuel. The novel results of this study include detailed, real-time infrared video images of the combustion zone. Space- and time-averaged images give a broad indication of the temperature reached in the gases. A brief outline is shown of future work, which will specifically concentrate on the exploration of the role of the oxidizer transport to the fuel surface, and the role of the unburned fuel that is reported to escape below the classical time-averaged boundary-layer flame.

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CHAPTER 1:

HYBRIDS REVISITED

Abstract

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role of the oxidizer transport to the fuel surface,
and the role of the unburned fuel that is
reported to escape below the classical time-
averaged boundary-layer flame.

Nomenclature

a, b	Coefficients of the regression rate
B	Mass transfer number; coefficient of reaction
C_f	Local skin-friction coefficient
C_p	Mean specific heat
C_H	Stanton number
D	Depolymerization energy
E	Activation energy
h	Enthalpy
k	Heat conductivity
M	Molecular weight
Re	Reynolds number

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ical Engineering; Associate Fellow AIAA.
**Graduate Research Assistant.

u	Velocity component parallel to wall
v	Velocity component normal to wall
x	Spatial coordinate parallel to wall
y	Spatial coordinate normal to wall
θ	Reduced activation energy
μ	Viscosity
ρ	Density
ϵ	Emissivity
α	Absorptivity
τ	Shear stress
σ	Stefan-Boltzmann constant

Subscripts

e	Free stream flow
o	Without blowing
0	Solid phase
ox	Oxygen
s	Stagnation state
TD	Degradation
w	Condition at wall
∞	Free stream

Introduction

A controllable, flexible, and safe propulsion
system is needed for space missions. As
compared with solid and liquid rockets, the
hybrid rocket has become a very important
candidate for use as a propulsion system. The
hybrid rocket is potentially important because it
has the promise of combining many of the
advantages of both liquid and solid rockets.
The configuration of the hybrid rocket engine is
basically similar to that of a solid rocket, except
that the former uses solid fuels instead of solid
propellants. Also, in the hybrid rocket, the
oxidizer is stored in the tank in liquid form.

Solid rocket boosters have failed cata-
strophically in 1985 and 1986 during launches
of the Titan and STS-Challenger. The failures
were caused by defects in case bonding and a
leak in the combustion chamber wall,
respectively.[1] In the hybrid propulsion system,
the combustion chamber contains only the solid
fuel, while the liquid oxidizer is stored in a
tank and injected through a feed system into a

combustion channel inside the solid fuel. The hybrid rocket does not rely at all on case bonding.

In solid rockets, a small leak in the chamber wall results in the immediate ignition (followed by self-sustained combustion) of all propellant surfaces along which the leakage gases flow. The same situation in hybrids would cause an extremely fuel-rich flow, with hardly any widening of the leakage flow path, because hybrid combustion occurs along well oxidizer-ventilated surfaces only. Therefore, the hybrid is much safer than solids. Because of the volatility and flammability of liquid fuel (such as liquid hydrogen) in the liquid rocket, it is not hard to imagine how much more dangerous the liquid rockets are than the hybrids would be.

The controllability (including restart) of the propulsion system is very important for space missions. In the solid rocket, it is almost impossible to stop or restart the combustion after the ignition of the rocket. Since the oxidizer and fuel are not cured together in the hybrid rocket as in the solid rocket, where the oxidizer is stored in a tank, we may control the combustion of the hybrid rocket by controlling the flow of the oxidizer. Also, we may achieve stop and restart of the hybrid rocket. It is well known that achievement of controllability of the liquid rocket is gained at a great loss of simplicity in liquid rocket systems. Consequently, the comprehensive property of controllability, flexibility, and safety makes hybrid rockets a very important, promising propulsion system for use in future space missions.

Selection, formulation, and processing of *fuel alone* are far simpler tasks than the same for solid propellant binders, where the interactions with various solid ingredients (oxidizer particles) must be considered. In addition, the fuel requirements are relaxed for the hybrid; this means that many variations are possible. All of these ultimately translate into *cost savings*. Since the oxidizer is a very well studied and abundantly available liquid/gaseous component (contrasted with specially prepared solids like AP), the cost comparisons have shown a dramatic *factor of 30* improvement compared to state-of-the-art solid propellants.[1] A completely different stimulus for the study of hybrids is provided by studies of future space missions that intend to use local in-situ resources (ISRU). Efforts are underway to manufacture/extract oxygen at extraterrestrial sites. The *utilization* of this oxygen in the simplest form, a gas generator, is likely to be a simple hybrid device. Another stimulus has recently come from the applicability of a hybrid motor as a test bed for materials testing; materials compatibility, high-temperature stability, nozzle survivability, liner/insulation performance, etc., can all be tested with a hybrid as a gas generator. Wide variations in gas temperature, composition, and oxidizer/fuel are possible; also, wide variations in pressures and flow rates are easily achieved without the inconveniences/dangers of instability, extinction, or costly propellant tailoring programs (that will be necessary if we were to rely on solid propellant rockets for these purposes).

These advantages of controllability, safety, reliability, wide-tolerance fuels, cost, and potential instability-free combustion have not gone unrecognized. Programs to exploit these advantages are underway.[2-5] It is apparent that solving many of the remaining problems can quickly result in easy acceptability of the hybrids. Attempts at building operational hybrids, without really understanding their fundamentals, can lead to unfortunate setbacks,[6] besides casting needless doubts on the fundamental technological feasibility itself. Many of these types of unnecessary negative images will dissolve away in a well-planned program that clearly identifies specific deficiencies in our understanding of hybrids. One possible matrix that identifies the specifics in one, albeit important, aspect of hybrids (namely, the fuel burning rate or, more generally, combustion) is shown in Table 1. It is seen that simple theories based upon gas-phase heat transfer limited combustion can explain the experimentally observed performance at low flow rates and high pressures (see, for example, Marxman and Gilbert[7] and Marxman[8]), but fail at higher flow rates and lower pressures.[9,10] Invoking slow gas-phase chemical kinetics[8,11] can explain the pressure dependence, but is hardly the final resolution since unrealistic numerical values are needed for this process. Similarly, thermal degradation of the fuel polymer in an inert atmosphere (not the hybrid environment) can be treated in detail and can be shown to match experimental data trends and numerical values as long as the experiments are conducted in an inert atmosphere (hot plate, for example).[12] Earlier skepticism[13,14] concerning the applicability of these low heating rate data (from hot plate pyrolysis studies) to high heating rate environments in hybrids was allayed through

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Table 1. Hybrid theories.

Theories Based Upon	Can Explain	Cannot Explain
• Gas-phase heat transfer $r \propto (\rho U)^{0.8}$	Burning rate at • low flow rates • high pressures	Burning rate at • high flow rates • low pressures • pressure dependence
• Gas-phase kinetic postulates $\dot{m}''' \propto [F] [O] P^n K_1 e^{-E/RT}$	Burning rate at low pressures (with unreasonable constants)	Burning rate at low pressures (with known constants)
• Condensed-phase (fuel) thermal degradation $dN/dt = -NBe^{-E/RT}$	Pyrolysis rate in inert atmospheres	Pyrolysis in reactive atmospheres
• Oxidative degradation of fuel $dN/dt = -[O]NB_1 e^{-E/RT}$	• Fuel burning rate in · reactive atmospheres • Pressure sensitivity	• "Saturation" effect • Unburned fuel
• [?]	• Full hybrid range • Scale-up rules • Transients	[?]

systematic *use* of the fundamental data in accurate mathematical formulations rather than in simple-minded "extrapolations." Introduction of oxidative degradation as a pyrolysis augmentation mechanism at the fuel surface not only explained the possible burning rate phenomenon but also accounted for the pressure sensitivity at high flow rates.[12] Despite its "consistency checks," a quantitative theory including oxidative degradation has not yet been developed. Many recent studies (see, for example, Korting et al.[15]) have added valuable experimental data to the hybrid literature, but have not developed the complete picture. For example, one self-consistent theory should be able to explain the fuel pyrolysis behavior in both inert and reactive environments, explain the burning rate behavior at low and high flow rates and low and high pressures, and *predict* verifiable scaling rules, besides accurately predicting the combustion efficiency (unburned fuel fraction). We should not have to resort to different theories, or mechanisms, to explain different facets of the same phenomenon.

After identifying the various facets of the hybrid rocket, the "big picture" is shown in Fig. 1. The most important unanswered question is, "What is the rate of oxidizer transport to the fuel surface at various values of pressure and flow rates?" Also important is the question of

time-averaged flame temperature in the boundary layer at various pressures and flow rates. These will be input to a comprehensive theory of hybrid operation and will be verified quantitatively through experiments on static rockets of several scales.

In 1963, Marxman and Gilbert[7] proposed a heat transfer limited model for the hybrid rocket combustion (Fig. 2). In the heat transfer controlling model, the mass transfer number of Spalding[16], B [B = $(\rho v)_w/(\rho_e u_e) \cdot 1/2 \, C_f$], is a very important parameter which represents the effect of mass addition on the velocity profile, the Stanton coefficient, and the boundary thickness in the boundary layer. It is very hard to determine this important number in Marxman and Gilbert's model.

In the heat transfer model, the diffuse process is considered as the key process that will control the hybrid combustion. However, it has long been recognized that, in certain situations, the kinetics of gas-phase, heterogeneous, or solid-phase reaction may influence or even control the burning rate.[7,17] The experimental results, particularly those of Smoot and Price,[9,10] have delineated the conditions under which the diffuse-limited model (heat transfer limited model) becomes inadequate. Much work has been done on the importance of
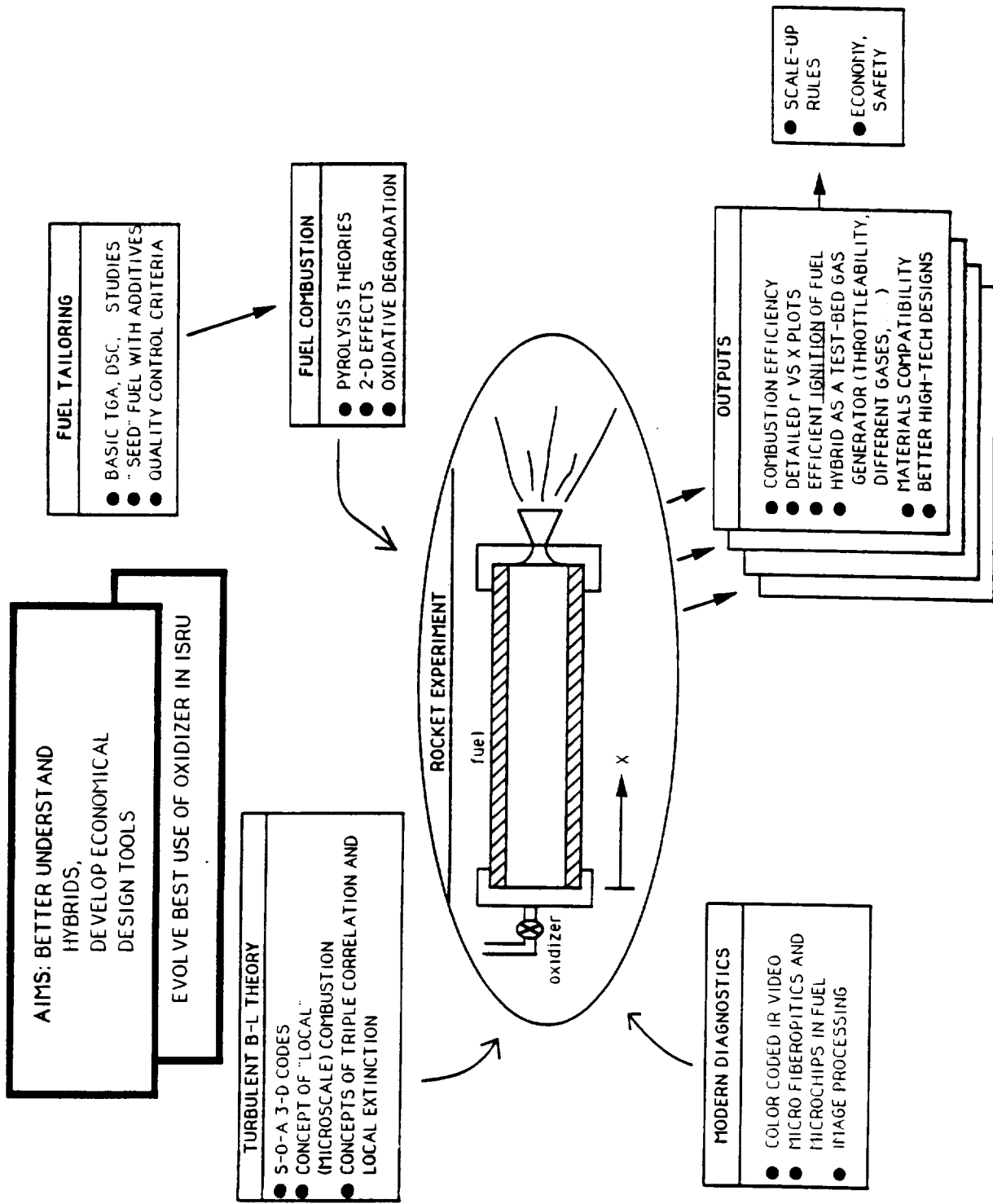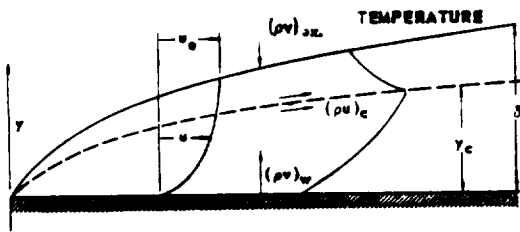
AIMS: BETTER UNDERSTAND HYBRIDS, DEVELOP ECONOMICAL DESIGN TOOLS

EVOLVE BEST USE OF OXIDIZER IN ISRU

FUEL TAILORING
- BASIC TGA, DSC, STUDIES
- "SEED" FUEL WITH ADDITIVES
- QUALITY CONTROL CRITERIA

FUEL COMBUSTION
- PYROLYSIS THEORIES
- 2-D EFFECTS
- OXIDATIVE DEGRADATION

TURBULENT B-L THEORY
- S-O-A 3-D CODES
- CONCEPT OF "LOCAL" (MICROSCALE) COMBUSTION
- CONCEPTS OF TRIPLE CORRELATION AND LOCAL EXTINCTION

ROCKET EXPERIMENT

fuel

oxidizer

x

MODERN DIAGNOSTICS
- COLOR CODED IR VIDEO
- MICRO FIBEROPITICS AND MICROCHIPS IN FUEL
- IMAGE PROCESSING

OUTPUTS
- COMBUSTION EFFICIENCY
- DETAILED r VS x PLOTS
- EFFICIENT IGNITION OF FUEL
- HYBRID AS A TEST-BED GAS GENERATOR (THROTTLEABILITY, DIFFERENT GASES,)
- MATERIALS COMPATIBILITY
- BETTER HIGH-TECH DESIGNS

- SCALE-UP RULES
- ECONOMY, SAFETY

Fig. 1 Hybrid rocket research plan.

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Fig. 2 Boundary layer combustion model.

the role of the kinetic of the gas-phase reaction, surface reaction, and the solid fuel degrada -tion.[12,18,19]

What we want to do is to explore the role of the oxidizer transport to the fuel surface and the role of the unburned fuel that is thought to escape below the classical time-averaged boundary layer flame in order to obtain detailed distributions of the concentration and temperature in the boundary layer. We also want to find a better way of explaining the pressure dependence of the regression rate so the predicted regression rate can be compared with experimental results. This will then enable the design of a better hybrid propulsion system.

At present, we are working on an experimental hybrid rocket that consists of two plexiglass tubes. The inner one is used as the fuel tube, and the outer tube as a holder which fixes the inner tube and takes the pressure. The gaseous oxidizer is fed into the combustion channel of the inner tube from the head of the rocket. The fuel tube can be various polymeric fuels; for the time being, we just use PMMA as the fuel tube because it is easy to make comparisons with the extensive early data.

In order to understand the effect of the existence of oxidizer near the solid surface on the degradation of the solid fuel, we begin a TGA experiment using the mixture of nitrogen/oxygen in the range 99.9%/0.1% to 98%/2%. As pointed out by Marxman and Gilbert,[7] the flame zone is the temperature discontinuity. In this paper, we intend to investigate the temperature distribution inside the boundary layer under different pressures using an advanced real-time infrared camera. These images are easily computer processed for high-lighting zones.

In light of all the limitations of the present work, the worthwhile contributions are thought to be as follows: the experimental investigation

of the degradation of the PMMA under small concentrations of oxidizer, which is helpful for grasping the key process in the hybrid combustion, and the use of a real-time infrared camera for understanding the transportation process in the boundary layer.

Hybrid Combustion Theory

The heat transfer limited model, based on an idealized turbulent boundary layer combustion, was presented by Marxman and Gilbert[7] in 1963. It is assumed that combustion occurs in a relatively thin flame zone within the boundary layer above the sublimating surface (Fig. 2). Because of the reaction in the boundary layer flame zone and the mass addition from the solid surface, the flow is easily transferred from laminar flow to turbulent flow. Therefore, the hybrid boundary layer was treated as turbulent over the entire length.

By assuming that the hybrid regression rate is controlled by the heat transfer from the flame to the fuel surface, it is shown that

$$\rho_f \dot{r} = (\rho v)_w = \dot{Q}_w / \Delta H , \qquad (1)$$

where ρ_f is the density of solid fuel, $\dot{r}$ is the linear regression rate of the fuel surface, $(\rho v)_w$ is the gas phase mass flux of fuel at the fuel surface, $\dot{Q}_w$ is heat transfer per unit area to the wall, and ΔH is the effective heat of gasification of the solid fuel; and

$$\dot{Q}_w = \frac{h}{C_p} \frac{\partial h}{\partial y}\bigg|_w = C_{H0} \frac{C_H}{C_{H0}} \rho_c U_c (h_{cs} - h_{wg}), \qquad (2)$$

where C_{H0} is the Stanton number in the absence of blowing, U_c is the axial mass flux at the combustion layer, h_{cs} is the stagnation enthalpy at the flame, and h_{wg} is enthalpy at the wall in the gas phase.

The reduction in heat transfer to the wall caused by blowing is accounted for by the ratio C_H / C_{H0}. The relation between C_H / C_{H0} and the mass transfer number B is as follows:

$$C_H / C_{H0} = \begin{cases} 1.2 B^{-0.7} & 5 < B < 95 \\ \\ \ln(1.0 + B)/B & B < 5 \end{cases} \qquad (3)$$

Let $L_e = P_r = 1$. Reynold's analogy then holds across the entire boundary and is expressed by the equation

$$-\frac{\dot{Q}}{\partial h_s/\partial y} = \frac{\tau}{\partial U/\partial y} \cdot \tag{4}$$

where $\dot{Q}$ is heat flux and τ is shear stress. Therefore, the relation between the Stanton number and the friction coefficient, consistent with the combustion, is obtained as

$$C_H = \frac{1}{2} C_f(\rho_e U_e^2/\rho_c U_c^2) \cdot \tag{5}$$

Marxman then postulated that the friction coefficient in the hybrid combustion is approximately the same as that for an ordinary boundary layer with equivalent blowing. Therefore,

$$C_{f_0} = 2cRe_x^{-0.2} \, Pr^{-2/3} \tag{6}$$

and for $Pr = 1.0$

$$C_{H0} = cRe_x^{-0.2} \left[\frac{\rho_e}{\rho_c}\right] \left[\frac{U_e}{U_c}\right]^2 \tag{7}$$

where c is a function of mainstream Mach number, which is about 0.03 for the low Mach numbers expected in the hybrid.

Combining equations (2) through (7), the closed form for the regression rate is obtained as follows:

$$\dot{r} = \frac{cGRe_x^{-0.2}}{\rho_f} \frac{C_H}{C_{H0}} \frac{U_e}{U_c} \frac{h_{cs} - h_{wg}}{\Delta H}$$

$$+ \frac{\sigma\epsilon_w(\epsilon g T_c^4 - \alpha g T_w^4)}{\rho_f \Delta H} \cdot \tag{8}$$

The last term on the right-hand side is the result for consideration of radiation heat transfer in the boundary layer.

The regression rate expression reflects the fact that convective and conductive heat transfer to the surface is governed by the aerodynamics of the turbulent boundary layer. It is shown that the regression rate is proportional to $G^{0.8}$ and is also a function of the position along the tube, but not of pressure. From the measured result,[9] it is not hard to see that the model works well in the low specific

mass flux region but cannot match the experimental result at high mass flux.

Ramohalli and Stickler[12] proposed a pressure sensitive model for the hybrid combustion. In this model, it is thought that the solid fuel will be depolymerized into small fragments instead of monomers. So, the concept of fragment size vaporizing (FSV) arises. The determination of FSV as shown by Ramohalli[20] is

$$FSV = \frac{32.8}{M} P^{-0.2615} \exp(3.67 \times 10^{-3} \, T_w) \cdot \tag{9}$$

He postulated that the regression rate is governed by the surface degradation. The reaction subsurface thermal depolymerization is supplemented by surface depolymerization by active species. These active species may be unburned oxidizer that was transported to the surface through bulk turbulent eddy transport across the classical time-averaged "flame sheet." The pressure enters the control function through its effect on the concentration of the active species near the surface.

Based on the energy and backbone conservation equations,

$$\frac{d}{dx}\left[k\,\frac{dT}{dx}\right] + \rho c\dot{r}\,\frac{dT}{dx} = D\rho N B_{TD}\, \exp(-E_{TD}/RT) \tag{10}$$

when $x = 0$, $T = T_w$; when $x = \infty$, $T = T_0$

$$-\frac{dN}{dt} = N B_{TD}\, \exp(-E_{TD}/RT) \tag{11}$$

when $x = 0$, $N = N_w$; when $x = \infty$, $N = 1.0$,

the regression rate for the hybrid combustion for the large activation energy fuel is obtained as follows:

$$\dot{r} = \left[\frac{k}{\rho c} B_{TD} \exp(-E_{TD}/RT_w)\Big/[(T_w - T_0)/T_w]\right.$$

$$\cdot \frac{E_{TD}}{RT_w}\left[\left[\frac{D}{c(T_w - T_0)} + 1\right]\right. \tag{12}$$

$$\left.\left.\cdot \log \frac{FSV}{FSV - 1} - \frac{D}{c(T_w - T_0)FSV}\right]\right]^{1/2} \cdot$$

From this expression, the pressure dependence of the regression rate is easily seen through the pressure dependence of FSV.

In this pressure sensitive model there is no region of hybrid combustion that can be considered fully pressure independent. The dependence relationship of the reduced regression rate, $\tilde{r}$ ($\tilde{r} = \dot{r}/r_\infty \cdot G_\infty^n/G^n \{\rho_n(Pr_f/P_\infty)/\ln[(Pr_f)/P]\}^{1/2}$) and reduced mass flow rate $\tilde{G} = G/G_0 \cdot P_\infty/P_{ox}$ is shown by Ramohalli and Stickler[12] (their fig. 6). It is shown that $\tilde{r}$ is constant in the conventional pressure-independent region and that P is linear in the conventional full-pressure region and decreases with the reduced mass flux G.

For the comparisons of the heat transfer limited model and the pressure sensitive model, we calculated the dependence of $\tilde{r}$ on T_w (Fig. 3). From these results, it is seen that there is serious inconsistency between the two methods, which leaves us a lot of opportunity to develop and perfect the hybrid combustion theory. It is challenging to study the depolymerization of the solid fuel under small concentrations of active species.
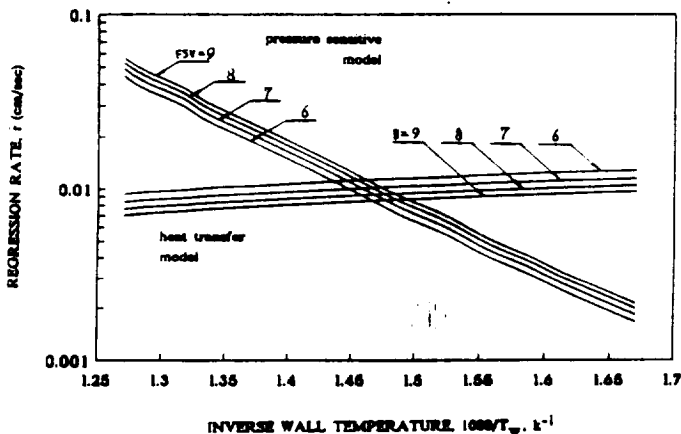
Fig. 3 Comparison of the heat transfer and pressure sensitive models.

Experimental Apparatus

A hybrid experimental rocket is designed to investigate the ballistic characteristics of a hybrid rocket. Two tubes are employed as the burning tube and the case of the rocket. For easy comparison with previous work on hybrid combustion, we use PMMA plastic as the burning tube and as the case, although there is no reason for limiting the fuel type. The inner

diameter of the burning tube is 2 inches and its thickness is 0.25 inch. The outer diameter of the outer tube is 3 inches, with a thickness of 0.25 inch. The length of the test portion is 12 inches. The oxidizer is a mixture of nitrogen and oxygen, the ratio of which can be easily changed. The oxidizer is supplied from the head of the rocket. The nozzle is composed of two parts: a graphite throat and a metal case. The nozzle is specially designed for a wide range of chamber pressures.

In order to study the boundary layer in detail, an adequately thick boundary layer is desired. In our design of the hybrid rocket, the thickness of the turbulent flow is about 10 mm for the wide variations of working conditions. A schematic of the rocket is shown in Fig. 4. In this rocket, a wide range of specific mass flux is achieved through the adjustment of the throat diameter of the nozzle. The range of the mass flux is 0.01 lb/sec·in^2 to 0.4 lb/sec·in^2. The corresponding pressure is 20 to 70 psi. The throat diameter may be adjusted if a wider range of pressure is needed.
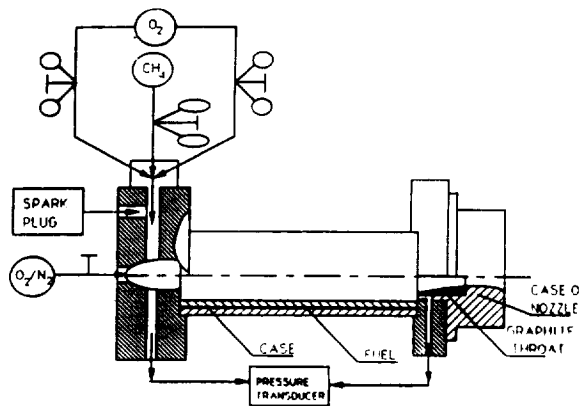

Fig. 4 Schematic of the experimental rocket.

Procedure and Measurement System

Once the apparatus was actually constructed, the main experimental procedure was to make sure everything was connected and tight. The outside of the burned tube was coated with silicon grease so that it would not bond with the larger tube, as happened before. Also, some coating is needed for the nozzle throat in order to prevent erosive damage.

When the oxidizer flows over the solid surface, the oxidizer will diffuse through the boundary layer and the vapor of solid fuel after

sublimation will diffuse toward the oxidizer free stream, also. There is a combustion zone in the boundary layer. Temperature discontinuity was assumed by Marxman and Gilbert.[7] Here, we use an infrared camera to measure the temperature distribution in the boundary layer. We also use two pressure transducers, which are mounted on the head and aft to investigate the history of the pressure during the rocket firing. The measurement system is shown in Fig. 5.
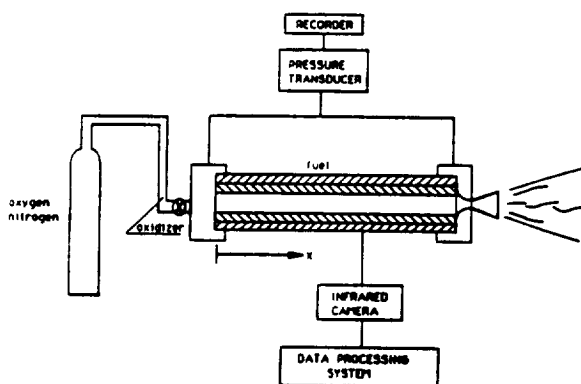

Fig. 5   The measurement system.

Results and Discussion

It is thought that the chemical kinetic rate of degradation of the fuel PMMA in the presence of small concentrations of oxidizer species may hold the key to a complete understanding of hybrid combustion. The experiments were initiated to study this degradation in the mixture of nitrogen/oxygen in the range of 99.9%/0.1% to 98%/2%. The temperature in the experimental sample of PMMA was kept at 600 to 700°K, which is the temperature in the rocket firing. At the present time, only two experimental results are available which cannot be explained convincingly.

As the preliminary study for the mechanism of the hybrid combustion, it was necessary to investigate the species concentration and temperature distribution. An advanced infrared camera was used to measure the temperature under different chamber pressures, which could be changed from 20 to 70 psi. Due to the difficulty of transparency of the PMMA to infrared waves, the results were not satisfactory. Hopefully, we may obtain more successful results after more trials.

At the time of this writing (April 1990), the following sub-tasks have been accomplished:

1. The motor has been designed and built.

2. Cold flow tests have been completed.

3. Initial runs have been made.

4. Infrared pictures have been taken.

5. PMMA degradation tests have been made.

Summary and Future Work

Based on the experimental investigation of the hybrid rocket, we can make the following conclusions:

1. The experimental system can achieve wide working conditions of pressure, specific mass flux, and oxidizer and fuel composition.

2. The time-averaged temperature in the boundary layer is independent of the mean oxidizer flow rate and the operational pressure (Table 2).

3. The observations tend to support the view that in hybrid combustion the surface reaction (in the small concentration of oxidizer) is important to the regression rate of the solid fuel.

4. A convincing mechanism of the full hybrid operation has not been developed yet.

Future work includes the investigation of the distribution of the small concentration of oxidizer near the solid surface and the investigation of the transport of the oxidizer in the boundary layer in order to determine the effect of the oxidizer on the pyrolysis of the solid fuel. Through these investigations we will hopefully get a clear understanding of the mechanism of the hybrid combustion and be able to propose a better design of the hybrid rocket.

Table 2. Boundary layer mechanics.

Heat Transfer	Species Transport	
	Oxidizer	Fuel
• To fuel surface from combustion zone • Convection • Radiation • During transients • Ignition • Instability?	• To combustion zone from free stream • To fuel surface across time-averaged "flame" zone	• To combustion zone from surface • Unburned and escape below time-averaged "flame" zone

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CHAPTER 2:

POLYMER COMBUSTION IN THE HYBRID ROCKET

Abstract

This paper presents the highlights from a detailed theoretical and experimental research program aimed at obtaining a better understanding of hybrid rockets. The well-known heat-transfer-limited burning rate equation is quoted, and its limitations are pointed out. The fuel was carefully studied for its oxidative degradation characteristic in a thermogravimetric analyzer, recognizing fully that these low-heating-rate studies may not be directly extrapolated to the hybrid regimes. It is found that the small concentration of oxygen is very important to the fuel pyrolysis process. Also, preliminary rocket firing experiments were conducted in a small-scale (5 cm diameter, 30-60 cm long) transparent motor, using state-of-the-art fuel systems in a stream of oxidizer.

Nomenclature

a, b	Constant and coefficient, respectively, in Eq. (2)
C_H	Stanton number
D	Mass diffusion coefficient
E	Activation energy
G	Specific mass flow rate
h	Enthalpy
K	Heat conductivity
m	Mass of polymer
Re	Reynolds number
T	Temperature
u	Velocity component parallel to wall
v	Velocity component normal to wall
x	Spatial coordinate parallel to wall
y	Spatial coordinate normal to wall
μ	Viscosity
ρ	Density
ϵ	Emissivity

α	Absorptivity
σ	Stefan-Boltzmann constant

Subscripts

e	Free stream flow
g	Gas phase
o	Without blowing
f	Solid phase
ox	Oxygen
s	Stagnation state, solid state
TD	Degradation
w	Condition at wall
∞	Free stream

1. Introduction

Combustion in the hybrid rocket provides a unique opportunity to study several details of polymer pyrolysis, surface reactions, vaporization, boundary-layer mixing, gas-phase chemical reactions, heat transfer, and the ultimate generation of thrust. Since the injected gas flow rate can be externally controlled, the rate of combustion and, as a consequence, the pyrolysis rate can be controlled, too. The fuel can be tailored to suit our needs in several ways; addition of small quantities of metal, catalysts, and even oxidizers can significantly alter the chemistry and energetics. Thus, we see that, even if the hybrid rocket is not used in flight, its simple geometry and flexibility provide an excellent test bed in which to study a variety of combustion reactions. In addition to the thorough study of fuel pyrolysis, one can also attempt to match the products from any other fuel/oxidizer combination, thereby simulating the desired gas streams. Such streams provide a valuable source for testing materials under realistic flow conditions. Since self-sustaining combustion can occur only beyond a (fairly high) percentage of oxidizer in the fuel mixer, we have the added advantage of *safety* in tests that do not exceed such oxidizer percentages.

With the promise of all of these advantages, one would expect that the hybrid rocket would be a well-studied, well-established technology today. Unfortunately, this is not the case, yet (1991). While the reasons are complex and varied, the remarkable potentials of the hybrid continue to go unrealized. Many of the fundamental pieces of information needed to build hybrids with confidence are not available. One of the less-understood mechanisms concerns combustion in the turbulent boundary layer over a vaporizing solid. Initial studies treated the problem as heat-transfer-rate limited and obtained fairly accurate trends of the burning rate variation with oxidizer flow rates; the limitations became clear at high flow rates and low pressures. Ascribing these experimentally observed inconsistencies to slower vapor-phase chemical kinetic effects at the lower pressures seemed to qualitatively explain the phenomena, but only with the use of unrealistic values of numerical constants for the fundamental reaction rates. Subsequent efforts have explored a

number of somewhat ad hoc theories that appear to be fairly successful in explaining observed effects in isolated instances. A comprehensive theoretical understanding of the big picture, however, has remained elusive. Any theory that cannot bring coherence to the component processes of polymer pyrolysis, surface chemistry, vapor-phase chemical kinetics, turbulent macrotransport, and micromixing of reactants can be regarded as incomplete, at best, and will be open to skepticism. Also, scale-up and commitment to important programs will undoubtedly be regarded as premature.

In this effort, an attempt has been made to look at the big picture from the start (Ramohalli and Yi 1990). The fundamental equations governing the polymer fuel pyrolysis and regression are analytically solved, including the nonlinear Arrhenius degradation rate term. The solution, quoted from an earlier work, is used in conjunction with a simplified model of vapor-phase combustion that recognizes that the micromixing of the fuel and oxidizer is imperative for chemical reactions to occur. In addition, consideration is given to several other necessary conditions that must be met for combustion to take place; these include the attainment of a mixture strength within the flammability limits, availability of a sufficiently strong ignition source with the (necessary) intermittent turbulent zone, the nonattainment of a strong thermal gradient (due to flame stretch) that could extinguish the local flame(lets) due to heat loss, and the maintenance of these necessary conditions long enough for the chemical reactions to be completed in the combustion zone. These can be quantitatively expressed as

$$ Y = \frac{\overline{[F][OX][T]}}{\sqrt{[F]^2}\sqrt{[OX]^2}\sqrt{[T]^2}} \geq C , $$

where [F], [OX], and [T] are instantaneous values of concentrations of fuel, oxidizer, and temperature. Complex as these conditions are, they are still not sufficient to completely describe the combustion, since a significant fraction (as much as 20%) of the fuel can escape unburned below the classical time-averaged "flame" in the boundary layer. It is particularly important to recognize that this loss can occur in an otherwise acceptable operation; this phenomenon appears to have been first recognized by the French (ONERA), who also corrected this through a turbulent ante chamber that ensured mixing and complete combustion, albeit with increased mechanical complexity. A better understanding of the basics can avoid these additions.

In pursuit of the big picture, our work is divided into four major groups. Fundamental work on small samples of the fuel has generated important data on the possible oxidative degradation. Detailed thermochemical calculations have provided insight into the mechanisms of boundary-layer heat transfer. Modeling of the turbulent combustion through micromixing is shedding some light on the importance of a triple correlation coefficient. And, experiments on a small-scale (5 cm diameter, 30–60 cm long) transparent motor have yielded data on mass-averaged burning rates. Initial results confirm the importance of examining the full combustion scenario rather than simplistic treatments of the component processes. It is hoped that these results, and novel interpretation, will provide motivation for further studies.

2. Plan of the Research

As was discussed by Ramohalli and Yi (1990), study of the regression process of the solid fuel under a small concentration of oxygen is the key to increasing the understanding of the whole hybrid combustion process. Schulte et al. (1987) measured the concentration of oxygen near the solid surface in the real combustion process and found that it was not equal to zero. As pointed out by Ramohalli and Yi, it is a good postulation to think that this small concentration of oxygen will act as a catalyzer in the pyrolysis process.

The heat-transfer-limited model based on the idealized turbulent boundary combustion was presented by Marxman and Gilbert (1963). It is assumed that the combustion occurs in a relatively thin flame zone within the boundary layer above the sublimating surface. The boundary layer was treated as turbulent over the entire length. By considering the heat balance between the gas and solid phases, the regression rate of the solid fuel was obtained as follows:

$$\dot{r} = \frac{CGRe_x^{0.2}}{\rho_f} \frac{C_H}{C_{Ho}} \frac{U_e}{U_c} \frac{h_{cs} - h_{wg}}{\Delta H} + \frac{\sigma(\epsilon_{wg}T_c^4 - \alpha_g T_w^4)}{\rho_f \Delta H} . \tag{1}$$

It is shown that the regression rate is proportional to $G^{0.8}$ and is a function of the position along the tube, but not of the pressure. It can explain the experimental dependence of the regression rate $\dot{r}$ on specific mass flow rate G for the low-G region (Smoot and Price 1965a, 1965b).

By considering the microbehavior of the polymer, Ramohalli and Stickler (1971) proposed the novice concept of fragment size vaporizing (FSV). From the heat and backbone conservation equations, the dependence of the regression rate on the wall temperature and pressure and on the physical and chemical properties of solid polymer was exploited.

The above-mentioned representative modules can explain some aspects of the hybrid combustion behavior, but they cannot comprehensively explain all the aspects of the hybrid combustion phenomenon. The inconsistency can be seen in Fig. 1.

In our theoretical study, we began with the pyrolysis of the fuel based on the basic TGA experimental observations. By considering both the energy and the mass (species) conservation between gaseous and solid phases, the set of PDE's have been built to describe the combustion process. We are not unaware of the difficulties involved in solving the PDE's.

As the basic main step of the experimental research, the experimental hybrid rocket has been built. Different hybrid rocket firings are being prepared for the different flow rates, gas compositions, and working chamber pressures. In the beginning, the PMMA plastic tubes will be employed as the fuel tubes.
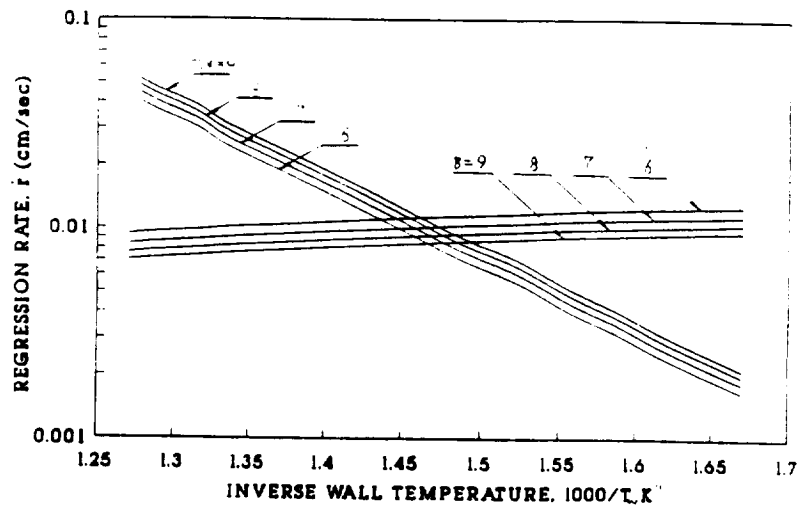
Fig. 1. Comparison of the heat transfer and pressure sensitive models.

3. The Experimental Results

3.1 *TGA Experiment*. The TGA experimental setup was designed and assembled by Yi Zhao, Chemical Engineering Department, The University of Arizona. The system mainly consists of the furnace, reactor, gas-fed system, temperature control system, and temperature and mass recording systems.

In order to get a stabilized temperature, the furnace was preheated for about 1-2 hrs. The certified gas flowed through the reactor for 2-3 hrs to make sure the ambient gas condition in the reactor was exactly the gas employed for each experiment run. The PMMA plastic samples were shaped in a cube 0.380 cm × 0.286 cm × 0.286 cm. The flow rate of the certified gas was 500 cc/min.

In the PMMA TGA experiment, the samples were held in a metal net suspended in the air of the reactor. The reactor was kept at the desired stabilized temperature. The certified gas mixture of O_2 and N_2 was cycled from the top of the reactor to the bottom. Eight PMMA pyrolysis experiments have been implemented for different gas and temperature conditions. The results are shown in Fig. 2.

For the test period with a stabilized temperature, the rate of volatilization of PMMA is a linear function of the volatilization. The variation trend is in good agreement with the experimental results given by Madorsky (1964). The rate of the pyrolysis in the former case is much higher than that in the later due to the existence of oxygen in the former. The regression results show

$$\frac{d(m_0 - m)}{m_0 dt} = b - a \frac{m_0 - m}{m_0} . \tag{2}$$

The regression results for the different experimental conditions are given in Tables 1 and 2. It is found that:
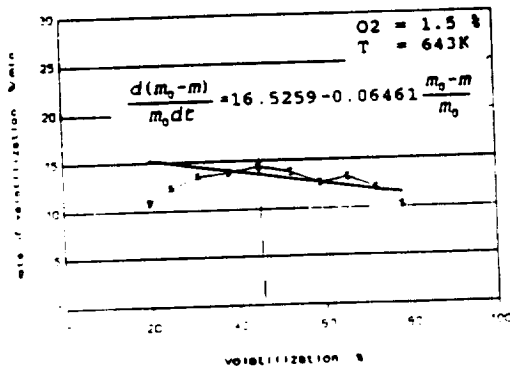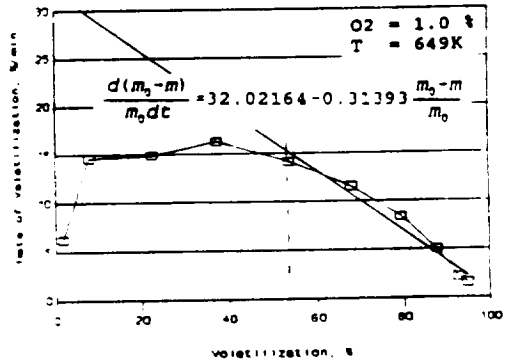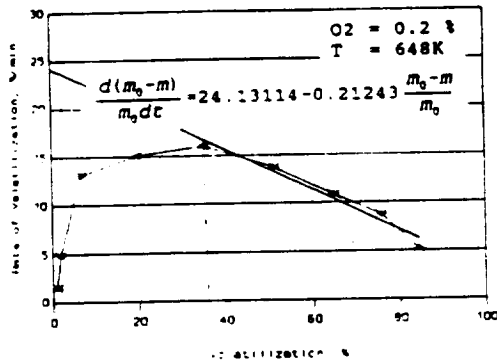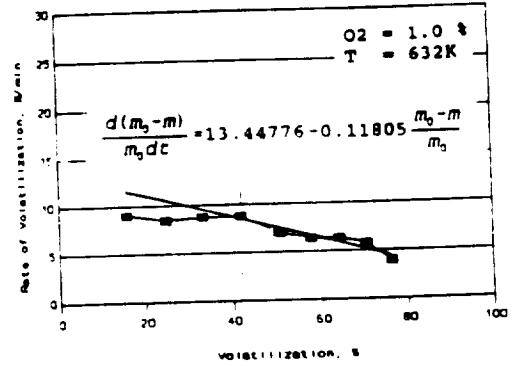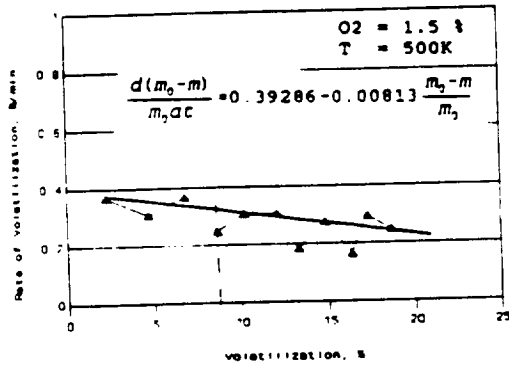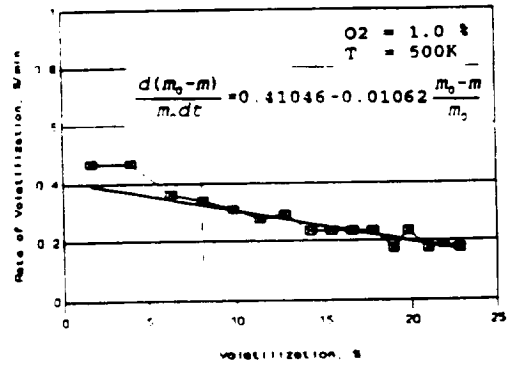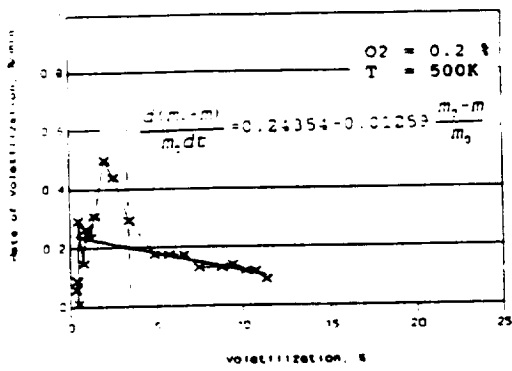
Fig. 2. PMMA TGA results.

Table 1. Regression results for constant b in Eq. (2).

Conc. O$_2$	Temperature			
	500	632	643	648
0.2%	0.24354			24.13114
1.0%	0.41046	13.44716		32.0216
1.5%	0.39286		16.5259	

Table 2. Regression results for coefficient a in Eq. (2).

Conc. O$_2$	Temperature			
	500	632	643	648
0.2%	0.01259			0.21243
1.0%	0.01062	0.11805		0.31393
1.5%	0.00813		0.06461	

a. The constant b increases as the concentration of oxygen increases. It increases greatly with an incease in temperature.

b. The coefficient a decreases with an increase in the concentration of oyxgen, but increases greatly with an increase in temperature.

From the above, we can see that the temperature is the dominating factor for the PMMA pyrolysis process and that the concentration of oxygen is very important. Therefore, the concentration of oxygen is important to the whole hybrid combustion process.

3.2 *Surface Microstructure Observations.* A scanning electron microscope was employed to analyze the surface structure of the tested sample residuals. Figures 3-5 are surface scanning photographs of PMMA samples tested under different conditions. The samples were tested at 0.2%, 1.0%, and 1.5% oxygen concentration conditions. The temperature for all the experiments was the same, 500 K.

Comparison of Figs. 3-5 shows that the size of the voids, or the roughness of the surface, of the residual sample increases greatly with an increase in the concentration of oxygen in the ambient gas. It is further evidence that the small concentration of oxygen near the solid surface is very important to the pyrolysis process of the PMMA fuel, and thus to the whole combustion process.

3.3 *Interpretation of Data.* It is clear from the small-sample data that the general degradation pattern and rate behavior are consistent with those in the classic work of Madorsky (1964). The variation with temperature is consistent with an Arrhenius rate fit. The activation energies and pre-exponentials are being carefully derived at the present time.
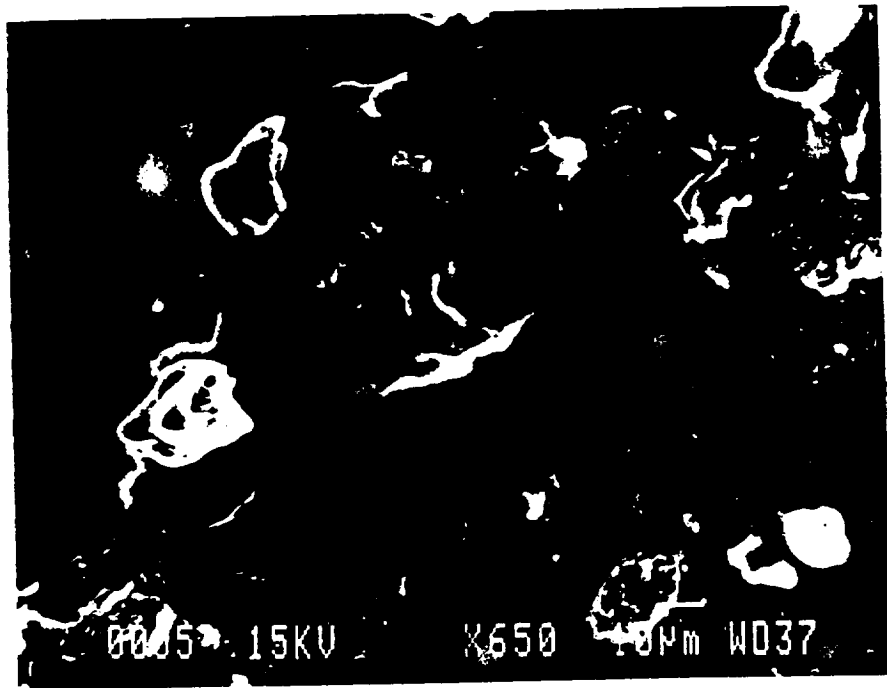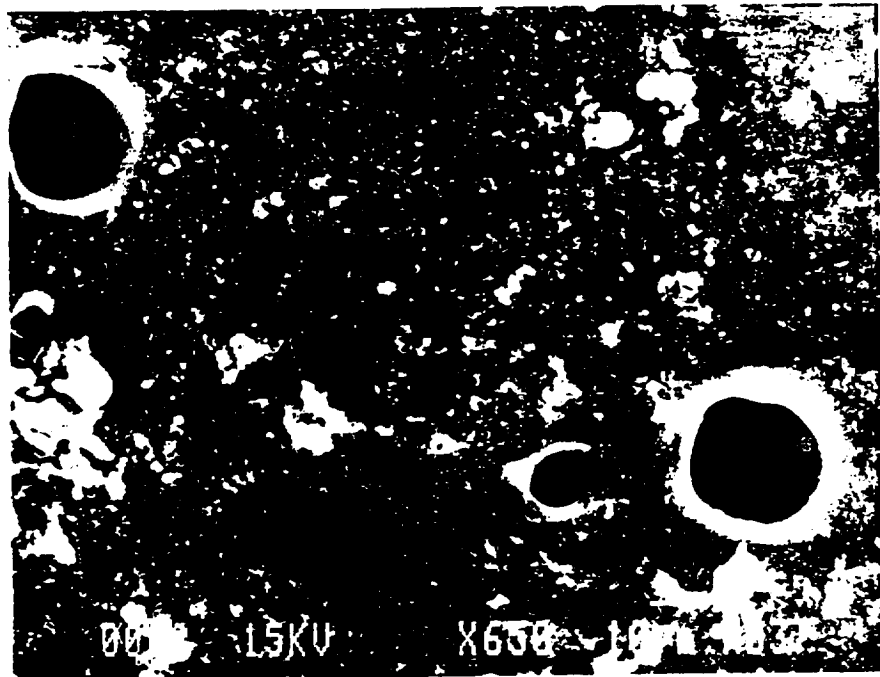
Fig. 3. The SEM for sample tested in $O_2 = 0.2\%$.

Fig. 4. The SEM for sample tested in $O_2 = 1.0\%$.

Fig. 5. The SEM for sample tested in $O_2 = 1.5\%$.

The variation with the oxidizer concentration (i.e., oxygen partial pressure in the mixture with nitrogen) is interesting. The rate increases, but saturates very quickly. That is, the presence of oxygen seems to (catalytically?) enhance the depolymerization rate of the fuel, but only to a certain extent. This is understandable in terms of a simple gas-solid interaction collision model, where the molecules of oxygen have only limited access to the surface layer of the fuel. More work is underway to precisely delineate the mechanism and to determine the optimum concentration.

3.4 *Hybrid Combustion Theory.* The theoretical model at this time is as follows:

$$\frac{d}{dy}\left[K \frac{dT}{dy}\right] + \rho C \dot{r} \frac{dT}{dy} = \rho_s B_s \exp(-E_s/RT_s) \tag{3}$$

$$\frac{d}{dy}\left[D \frac{d\rho_{ox}}{dy}\right] + v \frac{d\rho_{ox}}{dy} = \rho_{ox}\rho_f B_g \exp(-E_g/RT_g) \tag{4}$$

$$\frac{d}{dy}\left[D \frac{d\rho_f}{dy}\right] + v \frac{d\rho_f}{dy} = \rho_{ox}\rho_f B_g \exp(-E_g/RT_g) \tag{5}$$

$$\left.\begin{array}{ll}
\rho_{ox}|_{y=0} \to 0, & \rho_{ox}|_{y\to\infty} = 1, \\[6pt]
\rho_f|_{y=0} = 1, & \rho_f|_{y\to\infty} = 1, \\[6pt]
T|_{y=0} = T_s, & T|_{y\to\infty} = T_\infty,
\end{array}\right\} \tag{6}$$

where ρ_{ox} and ρ_f are the normalized densities of gaseous oxidizer and fuel in the gas phase, and v is the velocity component in the vertical direction.

We fully understand that there is still a lot of work to be done, especially in the solution of the PDE's, before we have a complete understanding of the whole hybrid combustion process. The motivation for our presenting such preliminary work is just to point out the working direction of our research.

3.5 *New Ideas.* It is instructive to consider possibilities for control of the burning rate through other techniques, in addition to the oxidizer flow rate. The data above clearly suggest that the presence of powerful oxidizers in the vicinity of the fuel surface can enhance the pyrolysis rate and, consequently, the overall fuel burning rate. In the conventional hybrid geometry, the presence of oxodizer(s) at the fuel surface is pretty much at the mercy of turbulent (unmixed, unburned) transport across the classical time-averaged flame sheet in the boundary layer. What if we actually incorporate a small fraction of oxidizer (AP, AN, etc.) in the fuel? Also, if we are interested in simulating hot exhaust gases of specific composition and temperatures, we could introduce additives in the fuel formulation. All of these ideas are being pursued at The University of Arizona at the present time.

3.6 *Hybrid Rocket Experiments.* The schematic of the experimental rocket is shown in Fig. 6. Two tubes are employed as the burning tube and the rocket case. For easy comparison, we use PMMA plastic as the burning tube and rocket case. There is no reason to limit the fuel type. The outer diameter of the outer tube is 3 inches. The length of the effective test portion is 12 inches. The maximum specific mass flow rate of the system is about 0.4 lbm/sec in^2. The working chamber pressure can be adjusted in the region of 20 to 80 psi. Extensive preliminary testing has demonstrated the reliability of the whole system. Figure 7 shows the working rocket.

4. Future Work

Future work includes a detailed study of the theoretical model and the solution of the corresponding set of PDE's. Also, the extensive rocket firing and unambiguous TGA data will be another main aspect of research. The experimental study will be used as the background for building the theoretical model. These can be summarized as in Fig. 8.

5. Summary

This interim summary of a well-planned activity in hybrid combustion should give a glimpse of the big picture. The various component processes that comprise the hybrid rocket operation are systematically examined. The fundamental aim is to bring coherence to the field, which continues to suffer from inconsistencies. Fuel depolymerization and pyrolysis studies are conducted in a TGA apparatus with specific provision for varying the oxygen concentrations; the values of the concentration employed experimentally are those that are expected in turbulent boundary-layer transport and those that have been actually measured in several experiments at different
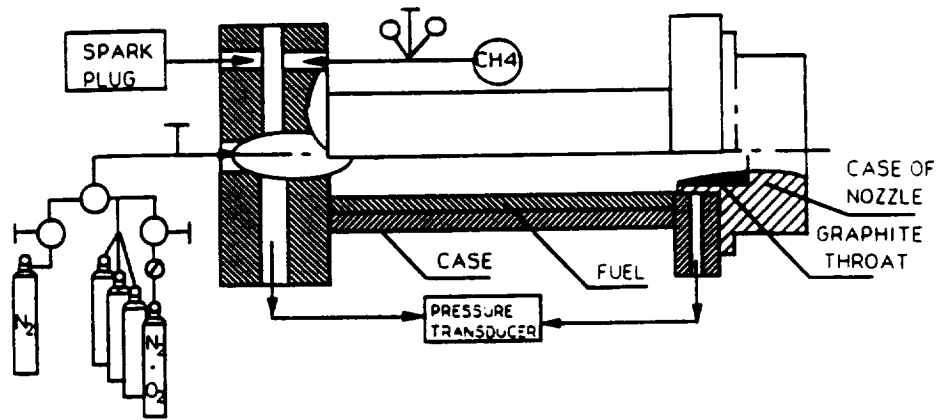
Fig. 6. Schematic drawing of experimental hybrid rocket.
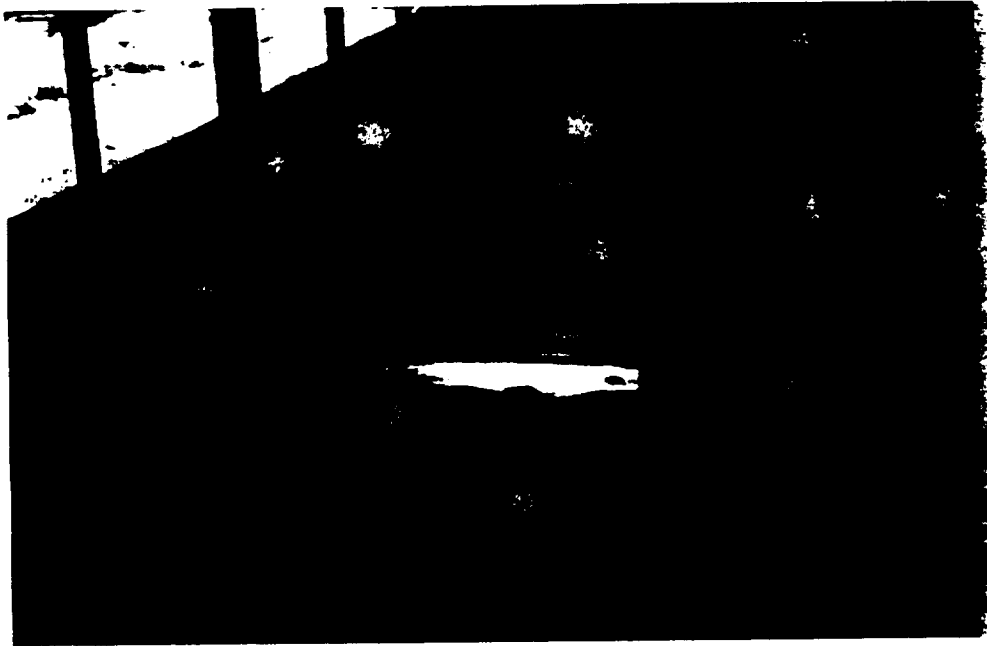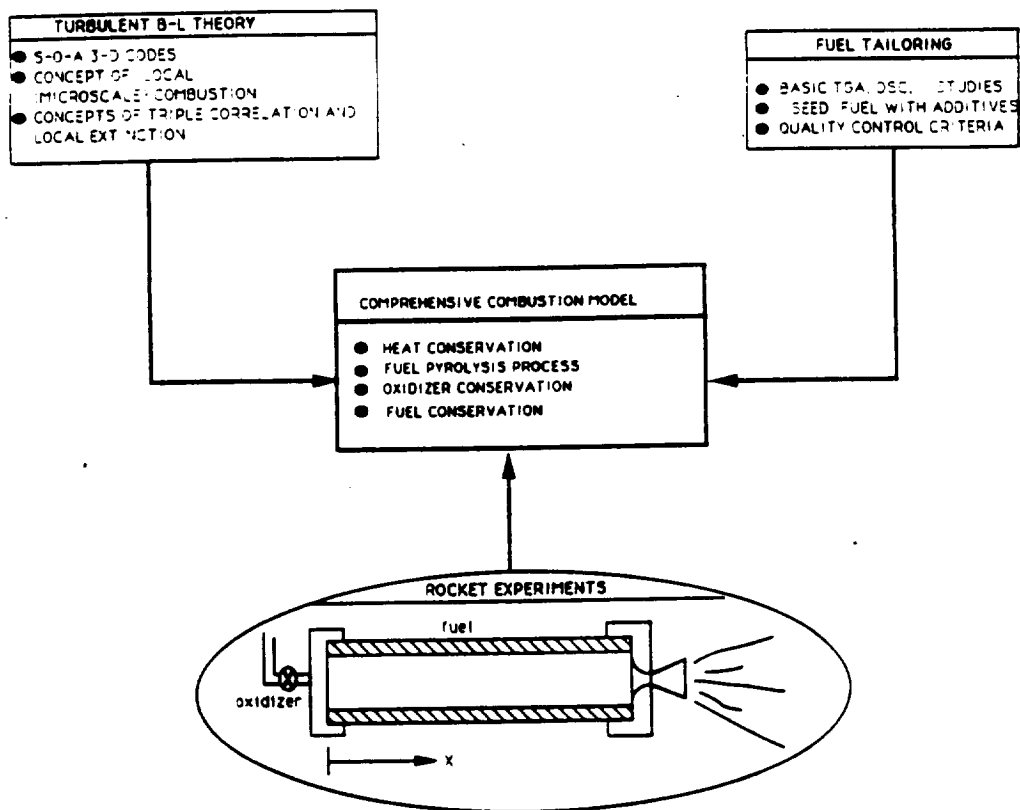

Fig. 7. The working hybrid rocket.

Fig. 8. The future hybrid research plan.

laboratories around the world. Turbulent boundary-layer transport and micromixing are interpreted in terms of a triple correlation function that accounts for molecular mixing, attainment of sufficiently strong mixture ratio within the flammability limits (for the fuel oxidizer combination on hand), maintenance of this mixture ratio at the requisite temperature for a sufficiently long time for ignition to occur, and the non-occurrence of a steep temperature gradient (due to flame stretch in the turbulent field) that could extinguish the flame(let) due to heat loss.

In addition to these "component" studies, actual rocket firings have been conducted in rockets varying in size from 5 cm I.D. to 9 cm I.D. and varying in length from 30 cm to 60 cm. At the time of this reporting, all of the large-scale tests have been conducted with polymethylmethacrylate (plexiglas) as the fuel and enriched air as the oxidizer. This choice resulted from considerations of past historical data available for ready checks, safety, economy, and flexibility, in addition to the transparent nature of the case, which allows for easy visualization. Other fuel/oxidizer combinations are being pursued at the present time.

The single most important conclusion that can be reached is that these developments in hybrid combustion are sufficiently promising to provide motivation for further developments and applications.

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CHAPTER 3:

WASTE MANAGEMENT OF 'SOLID' PROPELLANTS: THE HYBRID SOLUTION

Abstract

Increasing global concerns about the impact of propellant waste products have prompted a detailed look at the very basics of propellant ingredients and their missions. The ecological costs of cleanup and disposal are somewhat uncertain at the present time, but a popular model is used in assessing quantitative impact on the environment. The hybrid system is next considered using the same model. It is shown that the hybrid system offers orders-of-magnitude advantages in the costs of waste management, especially when recycling of unspent ingredients is included. Experimental data are presented to show the typical fractions of "waste" in hybrids and indicate that the hybrids system offers considerable advantages with a small penalty in performance. Some modern diagnostics are introduced to quickly assess the environmental impact.

1. Introduction

Waste management in general, and of solid propellants/explosives in particular, will continue to grow in seriousness and importance in the future. With increased awareness of the environmental impact of human activities, it is only natural that the issue of the "more sensitive" materials be addressed at the earliest. Since many of these materials are being used for various strategic and important applications (for example, construction, safe demolition of old structures. etc.), it is not a practical solution to suggest that we abandon their use simply for environmental considerations. On the other hand, it is precisely their extensive application in society that prompts one to explore ways to render their use environmentally acceptable.

Serious consideration of this topic at the present time should not be misinterpreted to imply that safety/environmental aspects have been ignored in the past. There are numerous examples of the propellants/explosives community scientifically developing acceptable substitutes for traditional chemicals that were placed on the toxic list after tests by health officials and environmentalists. A ready example is the much used anti-oxidant phenvbetanaphthalamine. which has been replaced by a more benign chemical in recent years.

Waste management of propellants/explosives has several important aspects: formulation, testing, flight experiments, residue disposal, and air pollution are some obvious ones. Assessing the true impact of these in a quantitative manner is a challenge. We need valid and proven techniques for properly accounting for all of the factors involved. It would be nice, indeed, if an unambiguous single number could be associated with the problem. Such a number could be the inverse figure-of-merit (FoM) of the propellant/explosive. Similar problems in other fields that involve a large number of variables, which must be coherently interpreted for an assessment of the overall impact, have been treated recently. Almost 1000 parameters were carefully integrated into the evolution of a single FoM in space missions (Ramohalli and Kirsch 1989, Ramohalli et al. 1992, Preiss 1991). The limitations of such an FoM are appreciated; nevertheless, it provides a first step in evaluating complex problems. A similar FoM that reflects the environmental impact of waste from explosives/propellants is currently being developed at The University of Arizona.

This paper takes a somewhat unorthodox approach to the waste-management problem. Instead of presenting results from a study of the details of solid propellants, the approach taken here is to ask the fundamental question concerning the availability of *alternative propellant technologies* that may have a far smaller impact on the environment while retaining most of the proven good features, such as specific impulse, density, and readiness. One such technology, the hybrid rocket, has been studied extensively. With the fuel and the oxidizer being separate, the cost, safety, shelf-life, and controllability/throttlability have all been shown to be substantially better than in the solid propellant rocket (Ramohalli and Yi 1990). A detailed study of the performance clearly indicates that comparable performance can indeed be obtained while enjoying the other good features mentioned (Ramohalli et al. 1991). The natural question that arises, during these environmentally sensitive times, concerns the hybrid characteristic associated with waste management.

Theoretical and experimental results are presented to show that waste management is at least one order of magnitude easier in the hybrid, compared to the solid propellant rocket motor. Chemical equilibrium calculations are performed using a well-known code. The product concentrations are computed for a state-of-the-art solid propellant motor and a comparable hybrid. The toxins, grouped under hydrogen chloride, oxides of nitrogen, metal-containing species, and the cyanide family, are quantitatively compared in the two cases. To have a meaningful basis of comparison, these numbers are then normalized by the delivered specific impulse.

Next, 25 hybrid motors of varying fuel composition are formulated and fired in a static test stand. The diagnostics include infrared pictures of the plume, measurement of the wasted fuel, and the delivered thrust. The results confirm the beneficial effects of the hybrid rocket.

Brief mention is made of the increasing difficulty of disposing of solid-propellant wastes. One figure is quoted for the current costs of such disposal in a specific case. On the other hand, the

wasted material in the hybrid is merely the fuel, which is (under most circumstances) no more difficult to dispose of than other rubber products, such as tires. This is not to suggest that used-tire disposal is a solved problem at the present time! We are merely stating the fact that tire disposal is far simpler than disposing of propellants/explosives. The oxidizer (liquid) is not wasted and can be reused.

It is concluded that the hybrid rocket technology, which has already been recognized for its potentials in safety, costs of manufacture, controllability, storage, transportation, etc., also possesses significant advantages over its solid propellant counterpart in waste management.

2. The Hybrid System

As is well known, solid propellants contain both the fuel and the oxidizer, well mixed. When the "mixture" is at the molecular level, the propellants belong to the class of homogeneous or double-base propellants. When the particle sizes are far larger than molecular (0.1-500 μm), the propellants belong to "mixed" or composite systems. Thus, these propellants possess the potential for hazardous explosions or, at least, self-sustained combustion. In addition, once formulated, separation of the oxidizer from the fuel is not easy. It is also important to note that many of the solid "oxidizers" (for example, AP) currently used can also act as propellants, in that they are capable of self-sustained combustion, so even if the oxidizer can be separated from the fuel, it is not clear that the hazards are eliminated. *Wastes from such operations include those during manufacture, storage, end-use, and unintended disposal.* Thus, disposal of many of the solvents, ingredients, unused propellants, and product stream must be considered.

The hybrid is characterized by separate storage of the oxidizer and the fuel. In the direct hybrid, the fuel is typically a solid polymer, which may have special particulate ingredients, and the oxidizer is a liquid, which is fed into the chamber and supports combustion in the gaseous state. It is apparent that this system is easier to handle in terms of waste management. For acceptability by the propellant/rocketry community, however, these statements must be quantified and be supported by engineering analyses of the demanded performance parameters. This section considers two analyses of the typical hybrid. One is an attempt to match the solid propellant performance as closely as possible, even to the extent of product species and temperature, and the other is to simply present performance of small-scale hybrids from a fundamental point of view.

2.1. Solid Rocket Combustion Simulators

Over 100 combinations of solid fuel and liquid oxidizers were considered in a detailed calculation of the performance. Thermodynamic performance was calculated using CET86, the

NASA Lewis program. The formulation that yields results close to that of a state-of-the-art solid propellant motor (namely the shuttle SRB) is designated formula (b) and has epoxy-cured HydroxylTerminatedPolyButadiene (HTPB) as the matrix, with aluminum and ammonium chloride. The performance with oxygen as the oxidizer is compared in Figures 1-3, showing that the match is better than 97% in terms of specific impulse, principal products, and temperature. These data demonstrate that it *is* possible to match the performance of state-of-the-art solids.

Now we must consider the "waste" management. For this purpose, the normal operation is considered first. That is, we catalog the emissions. For this purpose, the toxins are grouped as chlorine-containing compounds, cyanides, and the oxides of nitrogen. Formulations shown in Table 1 are used in computing the toxins shown in Figures 5-8; these should be complemented by the data presented in Figure 4 on the delivered specific impulses. In fact, it is instructive to normalize the toxin concentrations by the delivered specific impulse to have a meaningful basis of comparison. This has been done in Figures 7 and 8.

2.2. Waste Generated in Hybrid Operations

Unconsumed reactants/ingredients must be considered waste in the usual sense. This will be the fuel in the hybrid. (The liquid oxidizer can be reused and will not be a waste.) The fraction of the unburned fuel has been observed to be dependent upon the length-to-diameter ratio of the grain. The experimentally measured values are shown in Figure 9. The raw data are shown in Figure 10. It should be repeated that small-scale hybrid motors (6 cm diameter and lengths varying from 20 cm to 45 cm) have been fired 25 times with the clear polymethylmethacrylate fuel grain, 7 times with the HTPB with 27% aluminum, and 7 times with HTPB with 5% aluminum. The results on remnant fuel are very consistent and show far greater dependency on the L/D than on the fuel type.

Ultimately, these waste numbers must be translated to the common base of *cost*. For the purposes of this paper, we have used the current numbers for disposal of inert-binder solid propellants at a well-known facility. We are paying $60/lb (approximately $130/kg) for the disposal of aluminized HTPB/AP propellants. It is our understanding that the propellants are destroyed through detonation, thus assuring no long-term hazardous effects. The main point for the purposes of this paper is that we now have a reference figure for the cost of disposal of propellants. ·

On the other hand, the disposal of unburned waste hybrid fuel is handled in the general class of *sensitive* material, as opposed to *hazardous* material. The Office of Risk Management (formerly the Office of Safety) at The University of Arizona estimates $8/lb. This is typical, and not exclusive to this particular facility. We now have a basis for a comparative study of hybrids versus solids in terms of waste disposal. The hybrid rocket uses 23% solids and 77% liquid (oxidizer), so the
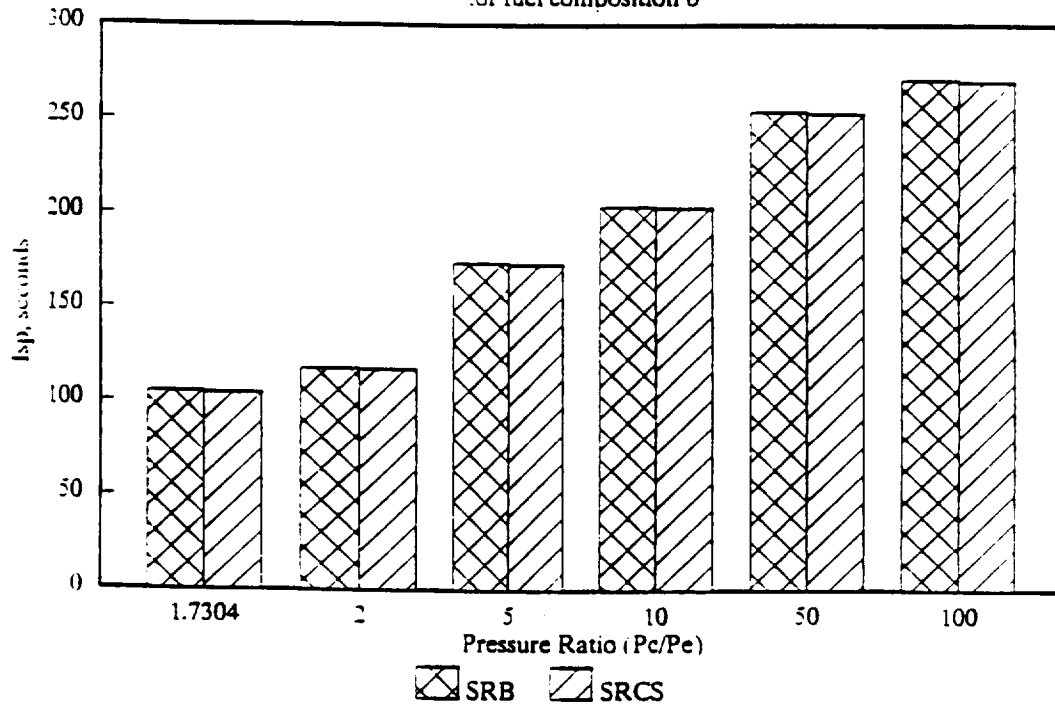
SPECIFIC IMPULSE
for fuel composition b

Figure 1. Specific impulse of SRB and hybrid fuel (b).

GAS TEMPERATURES
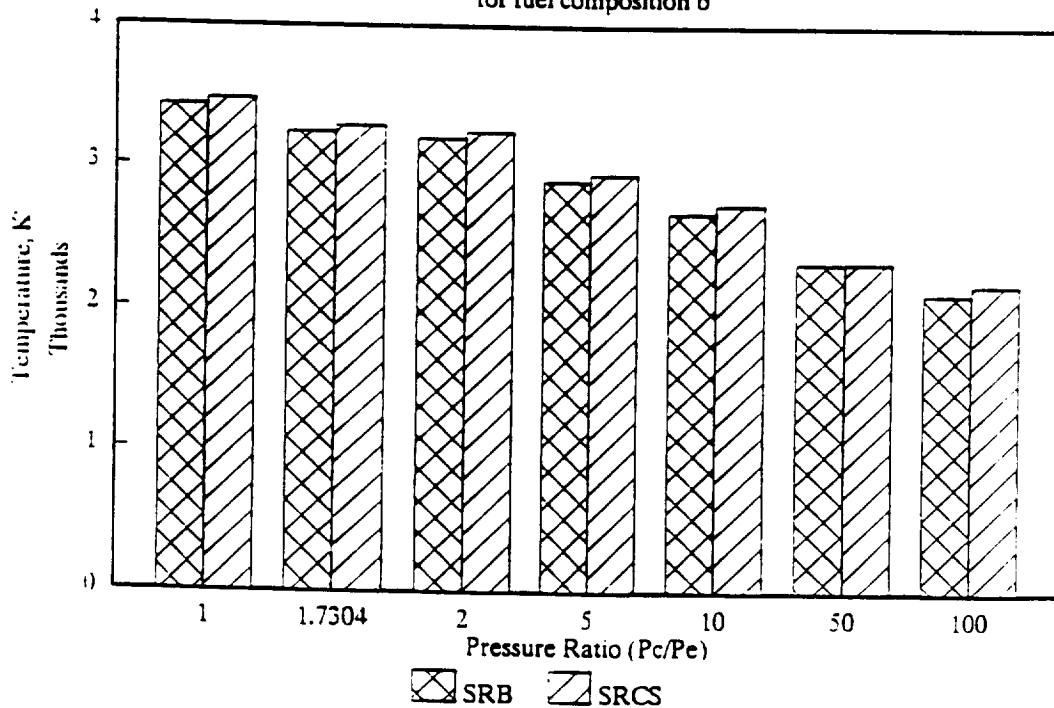for fuel composition b

Figure 2. Chamber combustion temperature of SRB and hybrid fuel (b).

COMBUSTION PRODUCTS
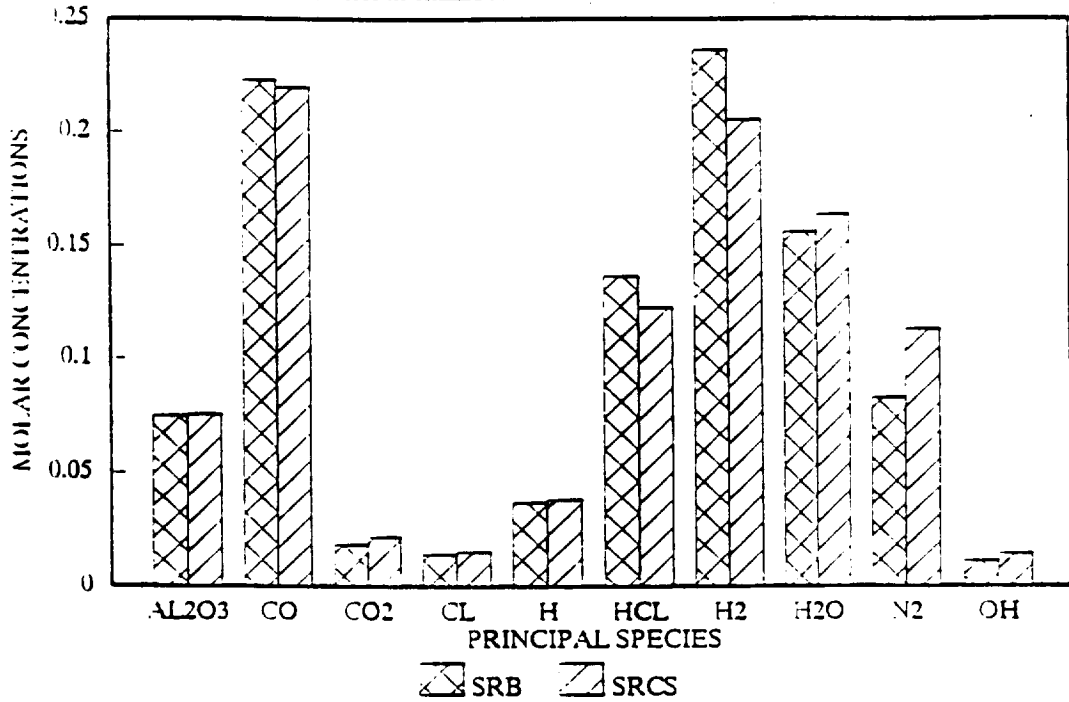
Species in chamber at 600 psia for fuel composition b

Figure 3. Combustion products of SRB and hybrid fuel (b).

Table 1. Propellant ingredients of SRB and hybrid rockets.

NAME	HTPB	Al	NH$_4$ClO$_4$	N$_2$O$_4$	Mg	Zr	O$_2$
SRB	14%	16%	70%				
HP-121	21%			38.6%			40.4%
HP-122	28.7%			52.9%			18.4%
HP-123	24.3%			44.7%			31%
HP-124	18.6%	10.0%					71.4%
HP-125	17.5%	9.5%					73.0%
HP-126	16.6%	8.9%					74.5%
HP-127	15.8%	8.5%					75.7%
HP-128	15.0%	8.1%					76.9%
HP-129	15.1%				7.4%		77.5%
HP-130	13.7%	3.7%				12.5%	70.1%
HP-131	15%	4.0%				13.7%	67.3%

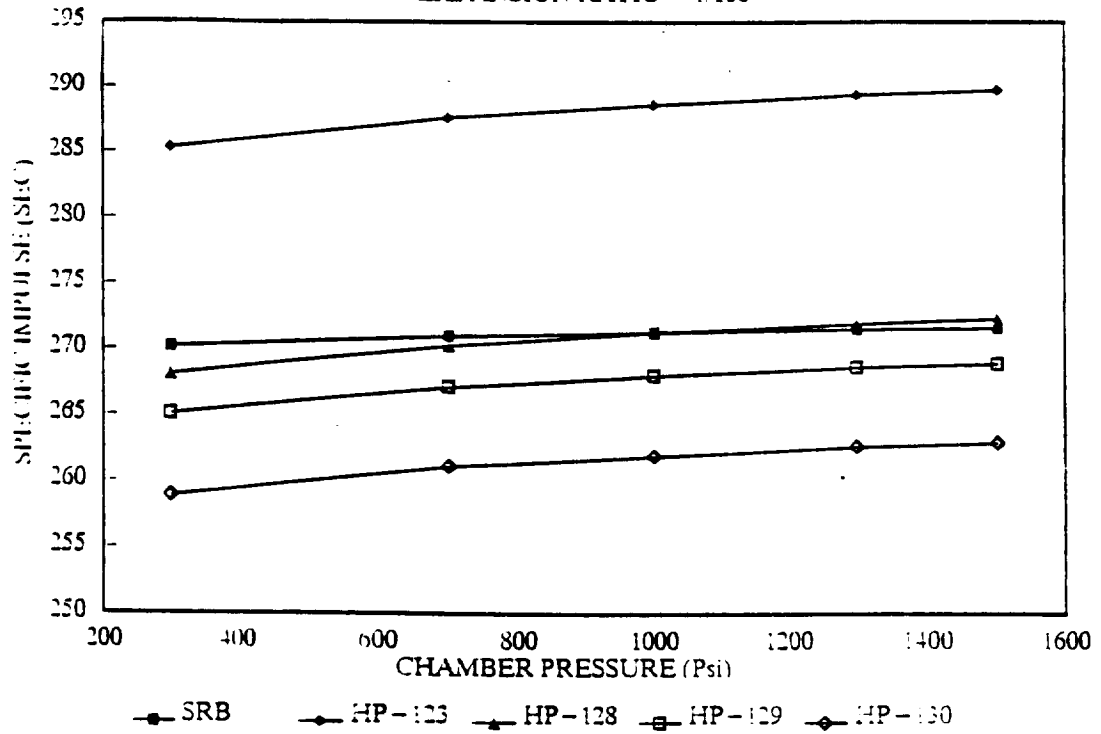SPECIFIC IMPULSE OF SRB AND HYBRID PROPELLANTS
EXPANSION RATIO = 1/100

Figure 4. Specific impulse of SRB and hybrid propellants.

TOXIN MASS FRACTION OF SRB AND HYBRID PROPELLANTS
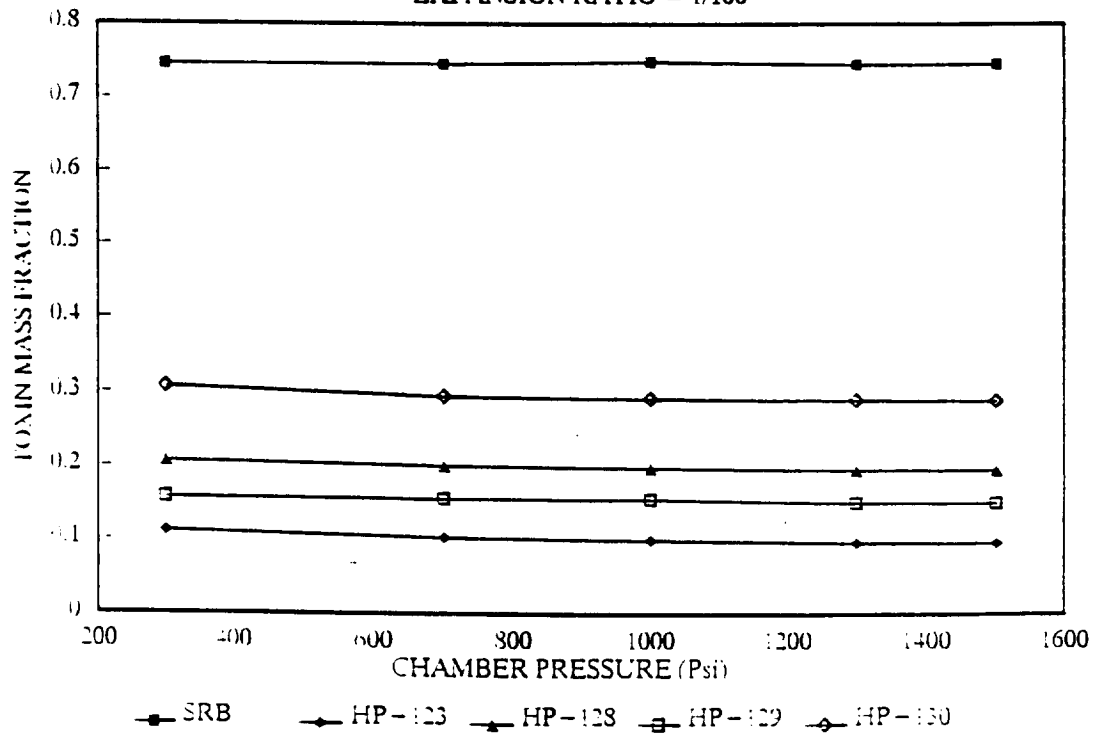EXPANSION RATIO = 1/100

Figure 5. Toxin mass fraction of SRB and hybrid propellants.

SPECIFIC IMPULSE OF HTPB/Al/O2 HYBRID PROPELLANTS
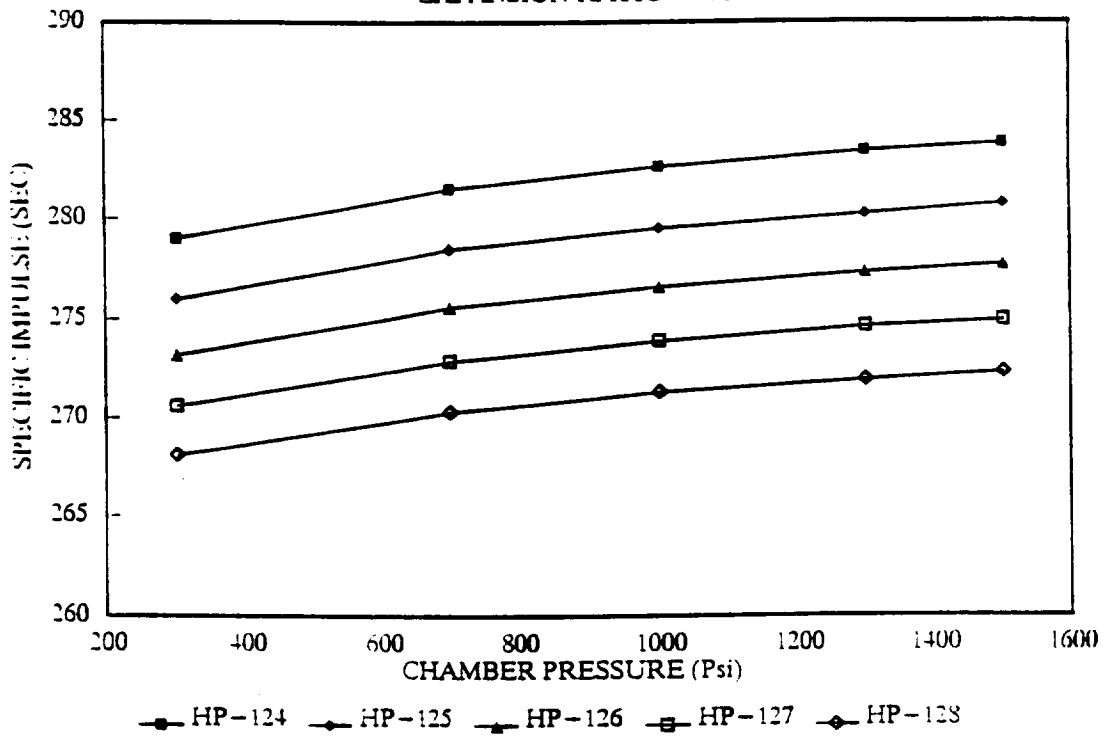EXPANSION RATIO = 1/100

Figure 6. Specific impulse of HTPB/Al/O$_2$ hybrid propellants.

TOXIN MASS FRACTION PER ISP OF HTPB/Al/O2 HYBRID PROPELLANTS
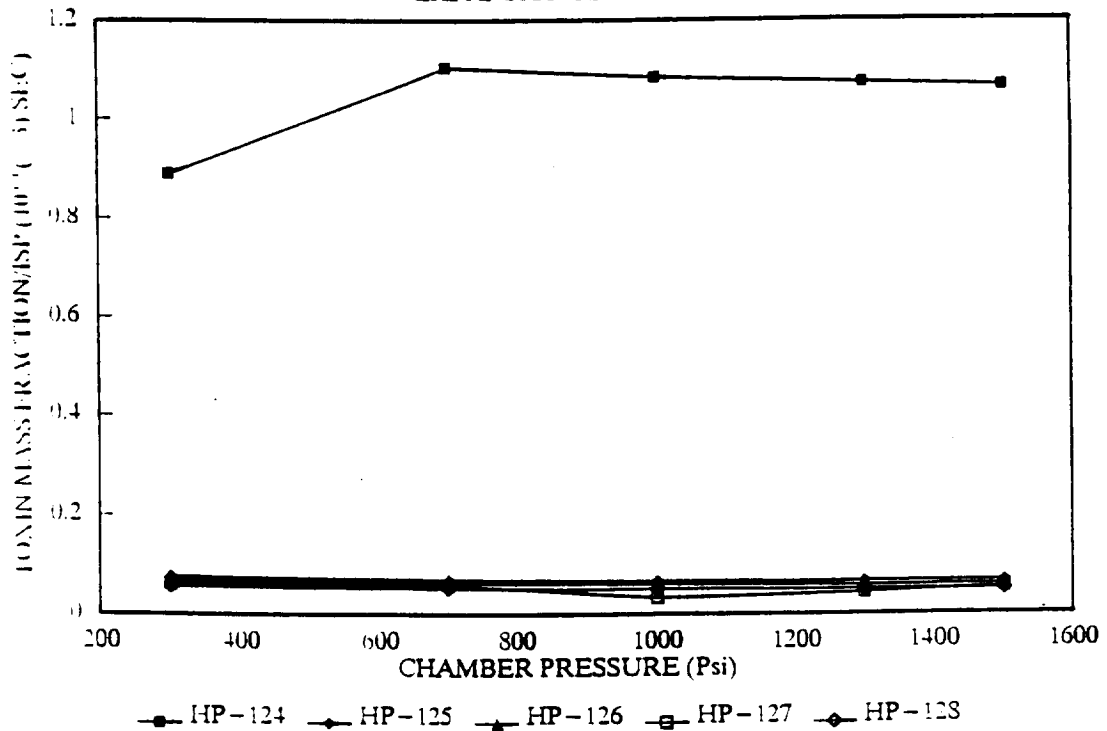EXPANSION RATIO = 1/100

Figure 7. Specific toxin mass fraction of HTPB/Al/O$_2$ hybrid propellants.

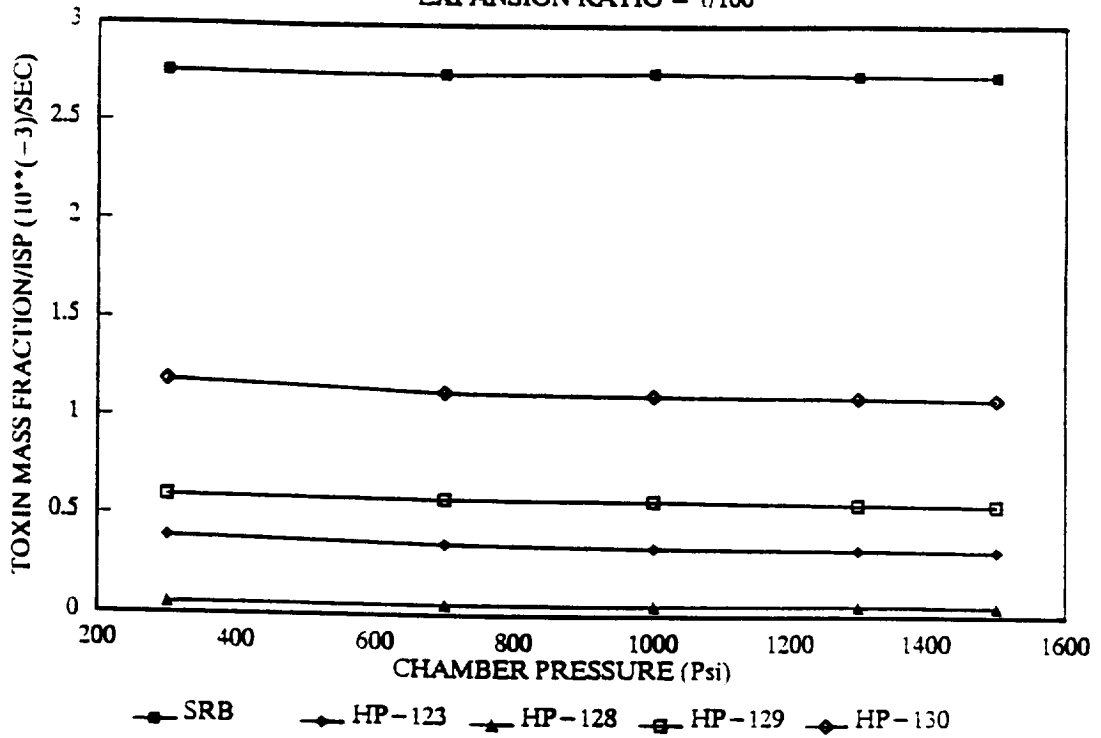TOXIN MASS FRACTION PER SPECIFIC IMPULSE
EXPANSION RATIO = 1/100

Figure 8. Specific toxin mass fraction of SRB and hybrid propellants.
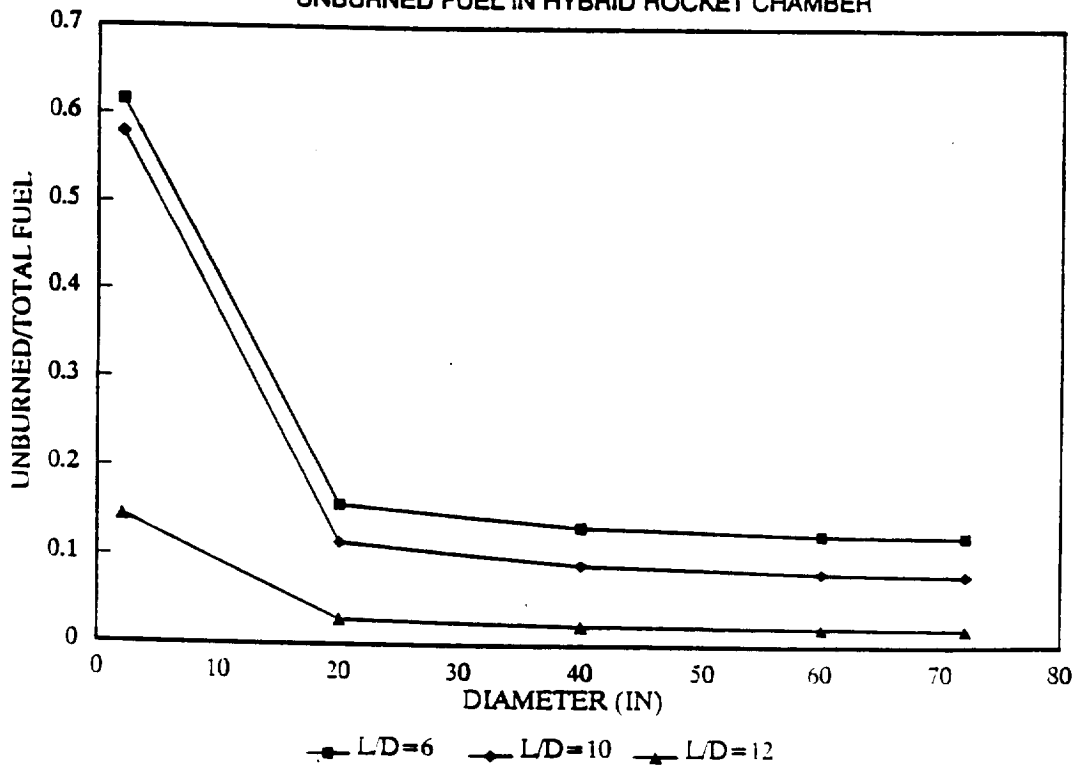
UNBURNED FUEL IN HYBRID ROCKET CHAMBER

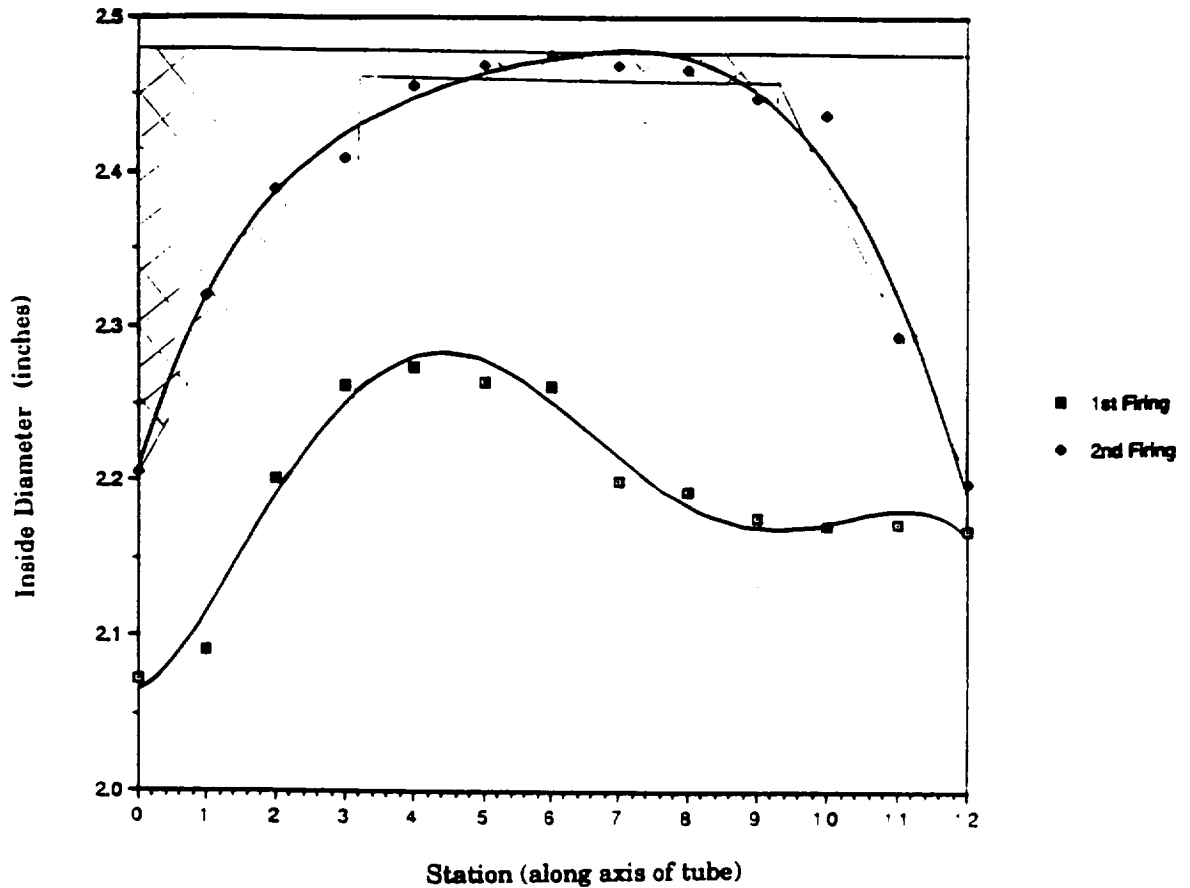Figure 9. Unburned fuel in hybrid rocket chamber.

Figure 10. Typical burned hybrid grain shape.

$8/lb for solids has to be modified to account for the proper waste number. The ratio is now obvious. The cost of disposal of the hybrid waste is 0.03, or 3%, of the cost of disposal of comparable solids on a performance basis. This does not take into account the differences in the typical wasted material in firing a solid versus a hybrid. Indications are that there is a smaller fraction of unspent fuel in the hybrid, compared to the unspent propellant in the solid, further strengthening the argument for the hybrid.

3. Diagnostics

One of the important aspects of waste management is the detection of toxins and wastes. It would be good to have a real-time-accurate diagnostic system to continuously monitor the emissions and waste. It is simply not practical to instrument the plume with hundreds of chemical sensors, or thermocouples, to monitor the local concentrations. Fortunately, a modern system is available to continuously monitor the plume and, indeed, the overall system.

The infrared radiometer used is the Inframetrics Model 600L. The spectral bandpasses are 8-12 μm, 3-5 μm, or 2-12 μm. The horizontal resolution at 50% slit contrast for the 8-12 μm bandpass

is 2.4 mRad, 148 IFOVs per line (256 pixels per line). The horizontal resolution for the 3-5 μm range is mRad, 100 IFOVs per line (256 pixels per line).

A camera, scanner, monitor, and VCR are used to take video-cassette recordings (VHS) of the hybrid. The setup used in videotaping the plume's activity is shown in Figure 11. The camera is set approximately 4 ft from the plume. The IR camera has a scanning rate of 8 kHz horizontal, 60 Hz vertical. The output rate is 15,750 Hz horizontal and 60 Hz vertical. The plume firings are recorded and used later for analysis in finding the composition and temperature profile. The temperature range for the 8-12 μm spectral bandpass is 0° to 1000°C and the typical minimal detectable temperature difference is 0.1°C. An infrared picture of the plume is shown in Figure 12.

4. Summary

This paper has made a first start on a problem that is bound to be of growing concern worldwide. Waste management of propellants and explosives will come under the same scrutiny as many other commerical products. It is shown that unconventional approaches to propulsion may introduce orders-of-magnitude cost savings in waste disposal. The hybrid rocket is compared on a meaningful basis with the solid. In addition to the proven good features of safety, controllability, and low cost, it is seen that hybrid-waste disposal is also much easier.

In an end-to-end life-cycle cost analysis, the costs of waste management will become important. It is hoped that the initial results presented here will provide a stimulus for further studies of the hybrid rocket.
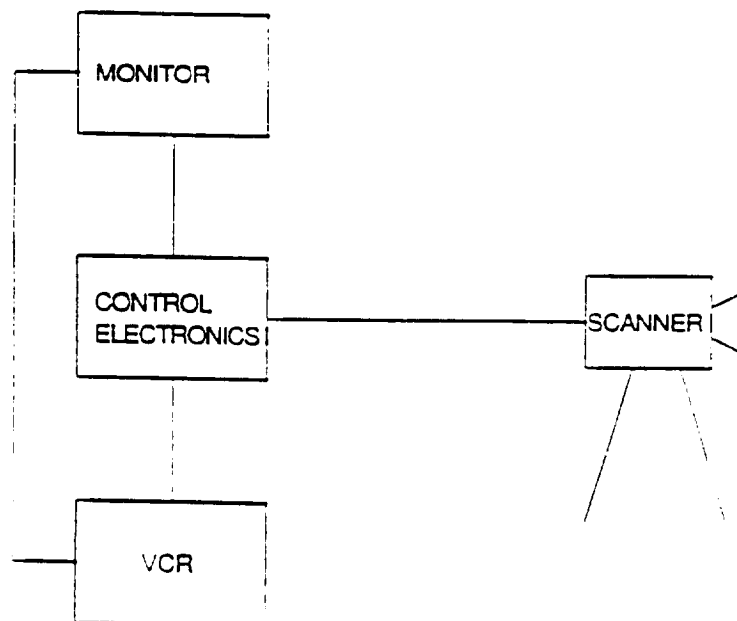
Figure 11. Setup used in video-taping hybrid rocket's plume.
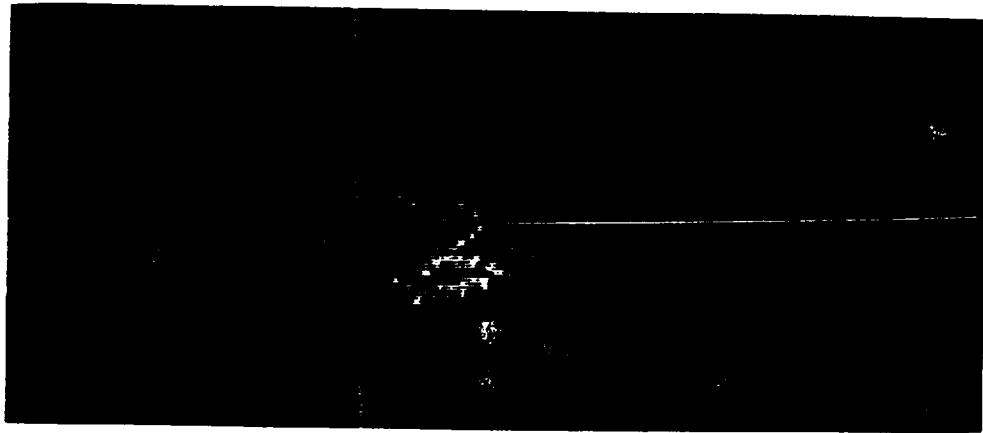
Figure 12.   Infrared picture of hybrid rocket plume.

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CHAPTER 4:

HYBRIDS FOR HEAVY-LIFT PROPULSION: UNSOLVED PROBLEMS

Abstract

This paper examines the basic unsolved problems of hybrid rockets, with the specific intention of facilitating solutions that could enable the attainment of the full potentials of the hybrid as a heavy-lift propulsion system. After a brief enumeration of the remarkable advantages of safety, cost-effectiveness, stop-restart capability, and simplicity of the manufacturing process, two major hurdles to deployment are discussed: one is developmental (no one has yet fired a truly "large-scale" hybrid motor; limited data are available for such systems) and the other is technical. There are several basic issues that are not clearly understood at present. The remainder of this paper focuses on these technical issues.

A comprehensive turbulent hybrid combustion model is presented. After a brief development of the fundamental equations, the burning rate of the solid fuel is shown to depend upon the (small) concentration of oxidizer species that reach the fuel surface, even across the classical time-averaged flame in the boundary layer. The temperature profile is explicitly related to the fuel/oxidizer combination and to the oxidizer flow rate. Results from a carefully conducted set of experiments are presented. A specially formulated fuel containing aluminum in a hydrocarbon binder, with some special ingredients, is fired in a 2.5"-diameter motor at various pressures. Modern diagnostic systems are used. One is an infrared video-imaging camera, whose output is digitally processed to reveal thermograms of the hot gases. Another novel system involves the identification of species by FT-IR (Fourier trans-form infrared spectrometer) of the exhaust plume. The species' constitution is related, through a theory, to the combustion efficiency. Through this well-knit program of theory, experiment, and modern diagnostics, it is found that several fundamental details of the operation of a hybrid rocket can be related to basic transport and chemical kinetic phenomena. The paper concludes with a summary of the principal findings that could have implications to large-scale hybrid rocket development.

Introduction

Our plans for space missions and operations are contingent upon transportation to space; this access to space has frequently been tacitly assumed to either exist or be available when necessary. Practically all of the space missions so far have relied upon solid or liquid propellant rockets. Another rocket system exists, but lack of development has hindered its application. This "third" system, namely the hybrid rocket, uses solid fuel and liquid oxidizer, or, in the inverse hybrid, solid oxidizer and liquid fuel. This simple separation of fuel and oxidizer introduces remarkable advantages in safety, reliability, affordability, and environmental compatibility, besides being controllable. Estimates have shown that the cost of a hybrid can be one-thirtieth (1/30) of that of a comparable solid propellant rocket.[1] Of course, the cost should not simply be the acquisition cost, we must evaluate the overall life-cycle cost of the full end-to-end system. This should include the cost of waste disposal, environmental impact, and (expected) hazard mitigation. The shelf-life is also an important factor. In a recent study, it was shown that the cost of environmental impact during processing, end use (firing), and disposal of waste is likely to be one order of magnitude less than that for comparable solid propellant rockets.[2] In another recent study of earth-to-orbit propulsion, it was recommended that hybrids be given serious consideration as strap-on boosters for lower stages.[3] Other

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studies indicate that larger thrusts are also possible from single engines.[4,5]

Considering all of these advantages, it is instructive to investigate why the hybrid has not yet made it to the mainstream. The reasons are several and complex, varying from purely technical to rather vague. Lack of commitment to its development during the time when intensive developments were made in large solid and liquid rockets is one reason. With the more recent recognition of its remarkable potential, hybrids have been studied seriously in the last few years.

The purpose of this paper is to clearly delineate the specific unsolved problems that must be studied before the hybrid can compete with solids and liquids. By its very nature, which involves boundary-layer combustion of mixing fuel and oxidizer, it is easy for some unburned fuel to escape below the classical time-averaged flame zone (see Figure 1 below). This loss represents a loss in performance, both in the specific impulse and the volumetric efficiency of the system. Variations on the simple geometry have included cartwheel fuel grains, post-chamber turbulators, and fuel modification through additives. While these have improved the combustion efficiency in test cases, the optimum solution has not yet been implemented in operational (flight) motors.

Since pressure sensitivity was not observed in initial motor tests, it was assumed that hybrids are immune to pressure-coupled instabilities, which, along with other varieties of instabilities, are also prevalent in solids and in some liquids. Simple heat-transfer limited theories also confirmed this absence of pressure sensitivity. Subsequent experimental data have shown pressure sensitivity at high flow rates of the oxidizer and/or low pressures in the chamber. A number of theories attributed this pressure sensitivity to (slow) vapor phase chemical kinetics, with minor variations in the way transport, mixing, and combustion were treated.[6-9] A detailed examination of the fuel, from subsurface preheating through conversion to products in the vapor phase, revealed that the pressure sensitivity may simply be the proverbial tip of the iceberg;[10] many existing concepts of fuel pyrolysis, vaporization, mixing, and combustion had to be revised in light of these findings. The fact that combustion instability had "never" been observed in hybrid tests did not help the advancement of these theoretical developments. Lately, instability has been reported in several hybrid rockets care-

fully instrumented with appropriate transducers in strategic locations.[11] Whether it is simply a feed problem in the oxidizer injection, or a more involved problem, is being debated. Ignition is another poorly understood phenomenon in hybrids.

The fundamental point is that these basic problems must be understood and solved before operating hybrids can become a reality. Proceeding with short-term solutions and an incomplete understanding will only invite trouble downstream. Many problems with the much more developed solid rockets have been traced to a lack of understanding of the fundamentals (see, for example, *Aviation Week & Space Technology*, June and November 1982[12,13]). Considering the fragile status of the fledgling hybrid system for heavy lift, it will be most unfortunate if temporary fixes do not prevent major disasters later; hybrids could needlessly suffer significant setbacks if the applications outpace solutions to basic problems.

The propulsion system's performance is defined by both the specific impulse and propellant mass-fraction. The specific impulse level achievable in the HTPB/LOX (liquid oxygen) hybrid is expected to closely approach that of an equivalent liquid rocket engine (same chamber/exit pressure condition). However, the liquid system probably has a design-point propellant mass fraction and a propellant utilization efficiency advantage over on equivalent hybrid unit. The theoretical results show that a hybrid rocket can reach a performance level higher than that of a solid rocket.[2] However, solids provide a higher propellant mass fraction and good propellant utilization. The advantages of safety, reliability, environmental compatibility, and operability have made the hybrid a potential candidate for future space propulsion.

As pointed by the National (USA) Space Propulsion Synergy Group,[14] two as yet unsolved and somewhat unique hybrid rocket performance-degrading problems (which normally would be addressed in any further development efforts) are (1) the relatively lower overall combustion efficiencies achieved to date and (2) the problem of non-full combustion of the solid fuel. The combustion inefficiency reduces the specific impulse, thus significantly penalizing the attainable hybrid performance level. The combustion efficiency problem has already drawn attention from hybrid researchers. Marxman and Gilbert[15] suggested that combustion efficiency could be improved

2

by disrupting the core flow at the end of the grain and forcing the unused oxidizer to mix rapidly with the fuel-rich products in the boundary layer. This has been done experimentally, and the performance increased by as much as 30%, a level claimed to be near the theoretical limit.

Even though there has been wide agreement on the hybrid combustion model for a long time, few of the papers on hybrids deal directly with the details of combustion inside the turbulent boundary layer. Most of the papers concentrate on the internal ballistics and the solid fuel regression dependence on the oxidizer flow rate and chamber pressure.

The representative hybrid combustion models are the heat-transfer-limited model and the pressure-sensitive model. These models can explain some aspects of the regression rate dependence, even though there are obvious inconsistencies between them. However, they supply no details regarding the completeness of the combustion inside the rocket. It is believed that the basic and detailed chemical reactions and mixing process inside the turbulent flow should be considered together with the solid fuel thermal degradation process in order to clear up model inconsistencies and to provide guidance for improvement of combustion efficiency.

In this paper, a theory of turbulent reacting flow will be introduced and developed. The turbulent reactive flows are normally simplified as diffusion-controlled flow or chemical kinetically controlled flow, depending on the typical first Damköhler number, which is defined as the ratio of chemical reaction time to diffusion time. An obvious example of the turbulent diffusion flame is the oxidizer (or fuel) jet. Almost all of the current turbulent diffusion flame research deals mainly with the diffusion flame between a gaseous oxidizer and a gaseous fuel.

A comprehensive turbulent hybrid combustion model is proposed in this paper. The model synthesizes the turbulent mixing and chemical reaction processes with the solid fuel degradation process. At this time, the numerical results are not available, as verification of this new comprehensive hybrid combustion model is still in progress. However, a carefully conducted set of experiments are presented. A specially formulated fuel containing aluminum in a hydrocarbon binder, with some special ingredients, is fired in a 2.5"-diameter motor at various pressures. Modern diagnostic systems

are used. One is an infrared video-imaging camera, whose output is digitally processed to reveal thermograms of the hot gases. Another novel system involves the identification of species by FT-IR of the exhaust plume. The species' constitution is related, through a theory, to the combustion efficiency.

Comprehensive Turbulent Hybrid Rocket Combustion Model

The general picture of hybrid propellant rocket combustion is similar to that of a turbulent diffusion flame, where the flame zone is established within the turbulent boundary layer (Figure 1). In the classical hybrid rocket, fuel is in a solid state (like solid propellant in a solid rocket) and the oxidizer is in a liquid or gaseous state and is fed into the rocket chamber by high pressure or a pump. The fuel enters the boundary layer as result of sublimation or degradation (pyrolysis), while the oxidizer is fed into the boundary layer from the main stream. Combustion will occur when a suitable mixture ratio of fuel and oxidizer has been reached. There is a small concentration of unburned oxidizer, which passes across the classical combustion zone to the solid fuel surface; also, some unburned fuel escapes through the nozzle.[7,16,17]
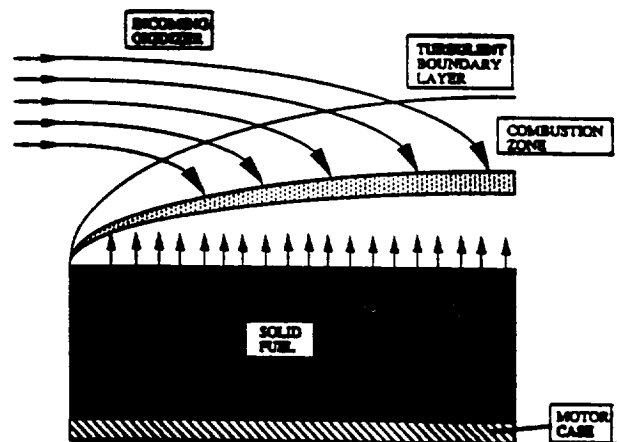
Fig. 1. General model of hybrid combustion.

Marxman and Gilbert[15] proposed a heat-transfer-limited model based on the idealized turbulent boundary layer combustion. They suggested that the entire combustion process is controlled by the heat transfer from the gas phase to the solid phase. From the heat balance equation, the solid fuel regression rate (or burning rate) is obtained as

$$\dot{r} = 0.036 \ \frac{G^{0.8}}{\rho_f} \left[\frac{\mu}{x}\right]^{0.2} B^{0.23} \ . \tag{1}$$

3

where G is the specific mass flow rate; B is the mass addition number defined as

$$B = \frac{(\rho V)_s}{(\rho_e U_e)\frac{C_f}{2}} ;$$ (2)

C_f is the skin friction coefficient; X is the axial coordinate along the tube beginning at the leading edge; and ρ is the density of the solid fuel. This heat-transfer-limited model reflects the fact that convective and conductive heat transfers to the solid surface are governed by the aerodynamics of the turbulent boundary layer. The regression rate is proportional to $G^{0.8}$, but does not depend on pressure. To some extent, it can explain the dependence of the specific mass flow rate on the regression rate.[9] Also, it shows the variation of the regression rate along the fuel tube.[15] However, the dependence of the regression rate on pressure cannot be explained by this model.

Kumar [Ramohalli] and Stickler[10] proposed a pressure-sensitive model of hybrid combustion. They proposed that the solid fuel is depolymerized into small fragments, instead of monomers, thereby theorizing the concept of fragment size vaporizing (FSV). FSV is determined by[18]

$$FSV = \frac{32.8}{M} P^{-0.2615} \exp\left[\frac{3.67 T_w}{1000}\right].$$ (3)

where M is the molecular weight of the monomer, P is the pressure in the gas field, and T_w is the wall temperature. It is assumed that the regression rate is governed by the surface degradation. Based on the solid phase energy equation and the fragment size equation, the regression rate has already been obtained. The pressure dependency of the regression rate is reflected in the pressure dependency of FSV and the concentration of the oxidizer at the surface (wall).

As pointed out in Reference 19, there is inconsistency between these two models. Neither of these models can satisfactorily explain the regression dependence of both the flow rate, G, and chamber pressure. There is not much discussion on the detailed combustion inside the turbulent boundary layer nor enough guidance to improve the overall combustion efficiency.

In order to fully understand the hybrid combustion mechanism, so that the key to improving its combustion efficiency can be

found, the detailed combustion and transportation process inside a turbulent boundary should be addressed comprehensively. It is not sufficient, nor is it accurate, to consider only the gas phase effect or only the solid phase contribution. It is postulated here that the oxidizer-catalyzed surface degradation process is important to solid fuel pyrolysis, while the small concentration of oxidizer is the result of chemical reactions and transportation processes inside the turbulent boundary layer. In the following turbulent hybrid rocket combustion model, the turbulent reactive flow and the solid fuel degradation will discussed separately.

For simplicity, the solid fuel is considered as a center-perforated tube and the incoming oxidizer is fed in a uniform gas flow (Figure 2). In the gas field, the uniform oxidizer flow travels along the fuel tube and diffuses toward the solid fuel surface. The solid fuel will evaporate to a gaseous fuel vapor after receiving heat from the combustion zone. Because of the chemical reactions and mass addition from the side wall, the flow transfers very easily from laminar to turbulent. The combustion will occur only when the oxidizer and fuel vapor are well mixed. The mixing process is the controlling process for combustion.
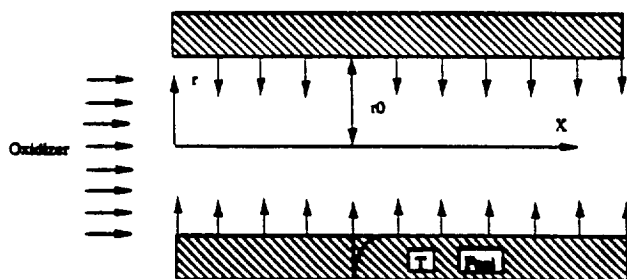
Fig. 2. Comprehensive turbulent hybrid combustion model.

The Navier-Stokes equations, including chemical reactions, species conservation, and variable-property effects, are used as the basic equations to describe turbulent reacting flows. Bilger[20] has given the Favre-averaged equations in axisymmetric boundary-layer form for continuity, species, momentum, energy, turbulence kinetic energy, and concentration fluctuations. Second-order closure of these equations is obtained by the usual device of modeling the turbulent fluxes and higher order correlations in terms of the computed variables. An important hypothesis is that it is the Favre-averaged turbulent fluxes and correlations that are to be modeled, and that this should be done in terms of Favre-averaged variables. The closure used

here is the $k\epsilon$ model of Launder et al.,[21] which is one that appears to work well for axisymmetric jet flows. The equations are:

$$\frac{\partial}{\partial x}(\overline{\rho}\widetilde{u}) + \frac{1}{r}\frac{\partial}{\partial r}(r\overline{\rho}\widetilde{v}) = 0 \tag{4}$$

$$\overline{\rho}\widetilde{u}\frac{\partial\widetilde{u}}{\partial x} + \overline{\rho}\widetilde{v}\frac{\partial\widetilde{u}}{\partial r} = \frac{1}{r}\frac{\partial}{\partial r}\left[r\mu_t\frac{\partial\widetilde{u}}{\partial r}\right] - \frac{dP}{dx} . \tag{5}$$

where the tilde represents Favre-averaging and the overbar, conventional time-averaging. The reasons for Favre-averaging are that (1) it will keep the governing equations in simple forms and (2) the measurements of velocity and composition yield average values that are close to the Favre-averaged values. Normally, the energy equation and the species conservation equation will be included to close the equations. It will be very difficult to deal with the chemical reaction rate term, even for the simplest one-step irreversible chemical reaction. Many researchers[20,22,23] have already shown that the complexity related to the chemical reaction rate can be avoided in the diffusion flame for the case of fast chemistry. If we further make the usual assumption of unity Lewis number and equal diffusivities for species, the species concentration Y_i, enthalpy h_i, and temperature T are functions of the mixture fraction ξ only. The mixture fraction can be defined as

$$\xi = \frac{\beta - \beta_1}{\beta_1} , \tag{6}$$

where "1" stands for the incoming flow and β is a conserved scalar defined as $\beta = Y_F - rY_{ox}$ (Y for mass fraction) for a one-step irreversible reaction.

$$[F] + r[OX] \rightarrow (1 + r)[P],$$
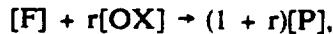
(by weight), that is, 1 kg of fuel reacts with r kg of oxygen and produces $1 + r$ kg of product.

The two principal models for fast chemistry are the flame sheet model and the shifting equilibrium model. In the flame sheet model, the combustion zone is an ideal surface with zero thickness. There will not be any oxidizer on the fuel side nor fuel on the oxidizer side. In the shifting equilibrium model, the chemical reactions will occur anywhere, as long as the temperature is high enough and there is enough oxidizer and fuel. In the hybrid rocket combustion case, there is evidence of a small concentration of oxygen near the solid fuel surface, which is contradictory to the flame sheet assumption. Therefore, the equilibrium model is employed in our comprehensive hybrid combustion model. The species concentration, the enthalpy, and the combustion temperature in the gas field can be determined by the local oxidizer and fuel mixture ratio using any combustion program, such as the well-known CET-86 computer code. The average values of these quantities are of interest and can be obtained by weighing the function $Q(\xi)$ by the probability density function $P(\xi)$, that is,

$$\widetilde{Y}_i = \int_0^1 \widetilde{P}(\xi)\widetilde{Y}_i(\xi)d(\xi) \tag{7}$$

$$\overline{T} = \overline{\rho}\int_0^1 \frac{T(\xi)}{\rho(\xi)}\widetilde{P}(\xi)d(\xi) . \tag{8}$$

$$\frac{1}{\overline{\rho}} = \int_0^1 \frac{1}{\rho(\xi)}\widetilde{P}(\xi)d(\xi) . \tag{9}$$

where the temperature is a conventional time average because the measured temperature from the thermocouple is close to this averaged value.

In order to close the governing equations, equations for the turbulent kinetic energy, k, and the Favre-averaging turbulence dissipation, ϵ, should be included:

$$\mu_t = C_\mu\overline{\rho}\frac{k^2}{\epsilon} \tag{10}$$

$$\overline{\rho}\widetilde{u}\frac{\partial\xi}{\partial x} + \overline{\rho}\widetilde{v}\frac{\partial\xi}{\partial r} = \frac{1}{r}\frac{\partial}{\partial r}\left\{r\left[\frac{\mu_t}{\sigma_\xi}\right]\frac{\partial\xi}{\partial r}\right\} \tag{11}$$

$$\overline{\rho}\widetilde{u}\frac{\partial k}{\partial x} + \overline{\rho}\widetilde{v}\frac{\partial k}{\partial r} = \frac{1}{r}\frac{\partial}{\partial r}\left\{r\left[\frac{\mu_t}{\sigma_k}\right]\frac{\partial k}{\partial r}\right\}$$
$$+ \mu_t\left[\frac{\partial\widetilde{u}}{\partial r}\right]^2 - \overline{\rho}\epsilon \tag{12}$$

$$\overline{\rho}\widetilde{u}\frac{\partial\epsilon}{\partial x} + \overline{\rho}\widetilde{v}\frac{\partial\epsilon}{\partial r} = \frac{1}{r}\frac{\partial}{\partial r}\left\{r\left[\frac{\mu_t}{\sigma_\epsilon}\right]\frac{\partial\epsilon}{\partial r}\right\}$$
$$+ C_{\epsilon 1}\frac{\epsilon}{k}\mu_t\left[\frac{\partial\widetilde{u}}{\partial r}\right]^2 - C_{\epsilon 2}\frac{\overline{\rho}\epsilon^2}{k} . \tag{13}$$

5

The boundary conditions will be:

at $x = 0$, $\quad \tilde{u} = u_\infty$, $\quad \tilde{v} = 0$,

$$\tilde{T} = T_\infty, \quad \tilde{\xi} = -1 \tag{14}$$

at $r = r_0(x)$, $\tilde{u} = 0$, $\overline{\rho}\tilde{v} = \rho_s \dot{r}$,

$$\tilde{T} = T_w, \quad \frac{\partial \tilde{\xi}}{\partial r} = 0. \tag{15}$$

The interaction between turbulent flow and combustion can be seen from the governing equations. The combustion products are a function of fuel fraction $\tilde{\xi}$, while $\tilde{\xi}$ is a function of $\overline{\rho}$, but $\overline{\rho}$ is determined by the combustion products. This fluid-chemistry coupling relationship can be reflected by iteration in numerical calculations. For a given trial $\overline{\rho}$, find $\tilde{\xi}$, combustion products Y_i, and combustion temperature $\overline{T}$. The local density $\overline{\rho}$ of the combustion products can be determined from Y_i and T for a given pressure field. If the trial value and calculated value of $\overline{\rho}$ are not the same, iteration is necessary until an acceptable difference between them is reached.

The governing equation for the solid fuel regression will be the thermal degradation equation. There are many solutions of thermal degradation.[10,24,25] Here, we adopt the pressure-sensitive model developed by Kumar and Stickler:[10]

$$k \, \frac{1}{r} \frac{d}{dr}\left[r \, \frac{dT}{dr}\right] + \rho c \dot{r} \, \frac{dT}{dr} = D\rho N B_{TD}$$

$$\times \exp\left[-\frac{E_{TD}}{RT}\right] \tag{16}$$

$$-\frac{dN}{dt} = N B_{TD} \exp\left[-\frac{E_{TD}}{RT}\right] \tag{17}$$

with boundary conditions

at $r = r_0(x)$, $\quad T = T_w$, $\quad N = N_w$

at $r = \infty$, $\quad T = T_0$, $\quad N = 1$,

and the energy balance equation at the fuel surface,

$$-k \, \frac{dT}{dr} = \dot{r}\rho c(T_w - T_0) + \frac{D\rho\dot{r}}{FSV}, \tag{18}$$

where N is the fraction number of back-bond bonds, FSV stands for fragment size vaporizing,

and D is energy needed for complete depolymerization.

As mentioned before, there is a small concentration (less than 2%) of unburned oxidizer passing across the "combustion zone" to the solid surface. Ramohalli et al.[26] conducted TGA experiments for PMMA under small concentrations ranging from 0.2% to 1.5%. They found that the small concentration of oxidizer, which acts as a "catalyst," plays a very important role in the PMMA pyrolysis process. It is realized that the oxidizer near the solid surface will, to some extent, control the pyrolysis rate of solid fuel. So, T_w, N_w, and FSV will be determined by the material properties, but will still be functions of surface conditions, such as the oxygen concentration. In the comprehensive model above, the turbulent flow and the solid fuel pyrolysis process are incorporated through the burning rate $\dot{r}$ and the surface conditions.

Experimental Investigations

Our purpose at this stage is to develop two categories of new hybrid rockets. The first group of hybrid fuels are used to simulate the advanced solid rocket's performance, combustion temperature, throat erosion effect, and even its combustion products. This hybrid rocket can be used as a test bed to improve our understanding of the solid rockets in order to introduce higher cost effectiveness through better predictability and elimination of known deficiencies. It is a challenge to simulate the entire combustion of the solid rocket without reducing the safety, controllablity, restartability, and flexibility of the hybrid rocket. The SRB (solid rocket booster) is used as the target for this simulation technique. As has been shown from calculations,[26] there is a 99.7% match between the specific impulse per propellant mass of the new hybrid rocket and that of the SRB and a 99.5% match between the chamber combustion temperature of the hybrid and that of the SRB. There is also a 97.0% match between the molar concentration of the hybrid combustion products and that of the SRB. The chemical reaction constant for the water-gas chemical process ($C_{(s)}$ + $H_2O \rightarrow CO + H_2$), related to the throat erosion process of the hybrid, is almost identical to that in the SRB. (We are aware that these hybrids are not the best ones with regard to environmental pollution because of the existence of hydrogen chloride.)

Experiments with the second group of hybrid fuels focused on the environmental

6

issues. Theoretical results show that waste management is at least one order of magnitude easier with the hybrid, compared to the solid rocket motor.[2] Chemical equilibrium calculations were performed using the CET-86 code. The product concentrations were computed for the SRB and a comparable hybrid. The toxins, grouped under hydrogen chloride, oxides of nitrogen, metal-containing species, and the cyanide family, were quantitatively compared in the two cases.

The hybrid fuels of Group I were manufactured in the Space Technologies Laboratory II at The University of Arizona. The solid part of the hybrid rocket is composed of HTPB as resin, aluminum particles, and ammonium chloride particles. The aluminum particle is 15 μm and can be used directly in the manufacturing of the fuel. The as-received ammonium chloride particle is very coarse (about 300 micrometers), and even had agglomerates, so pretreatment was necessary.

In order to decrease its viscosity, HTPB is heated to 160°F for 30 minutes before any particles are added into the batch of Baker-Perkins planetary mixer. The ammonium chloride particles are added to the batch at two separate times, 30 minutes apart. After all the aluminum particles and ammonium chloride particles are put into batch, the fuel is mixed under vacuum for three hours.

The well-mixed fuel is then cast into the rocket mold, which has already been placed in the transparent vacuum unit. After many trials, it was found that the fuel should be kept in the vacuum unit for at least 12 hours after being cast into the mold in order to eliminate bubbles in the fuel. Even though bubbles will not cause any serious explosion problems, as in the solid rocket, the existence of bubbles will affect the uniformity and fuel density. The cast fuel is cured in an oven at 110°F for 3 days.

It is very important to notice that, although the new fuel can simulate an (AP)-containing solid rocket, its manufacture is conducted in an ordinary industrial mixer without any expensive explosion-proof processing equipment or automated facilities. The manufacturing process is depicted in Figure 3.

The newly made hybrid rockets were tested in the AME Rocket Testing Lab at The University of Arizona. The schematic structure of the experimental hybrid rocket is shown in Figure 4. Different oxidizer mixtures (90/10 and 60/40 of oxygen/nitrogen) have also been tried to verify the wide combustibility of the new fuel. Experiments have been done for four different oxidizer mass flow rates (0.005 to 0.020 lbm/sec/in^2), four different working chamber pressures (30 psi to 60 psi), and two different aluminum concentrations of the solid fuel (5% and 27%). The results are very encouraging; ignitions have been quick and uniform and no abnormal combustion phenomena have been observed in these firings.

The advanced infrared camera and Fourier transform-infrared spectrometer (FT-IR) have also been employed to monitor the combustion process. We will obtain combustion product compositions from the IR image in the near future.

Figure 5 shows the experimentally determined regression rate as a function of axial position for four specific flow rates. It is shown that the regression rates of our fuels are about five time as high as the PMMA's. The variance curve of the PMMA regression rate is shaped like a "horse saddle." The burning rates of fuels are scattered widely, because the burned fuels are not as hard as the PMMA and it is very difficult to accurately measure the fuel ports. The minimum regression rate occurs at about the mid-point of the fuel tube, that is, $(X/L)_{r-min} = 0.5$. It is not even close to the predicted value:[15]

$$\left[\frac{X}{L}\right]_{r-min} = \left[\frac{2.8R_e^{0.2}}{L/D}\right]^{1.25} = 5.55 . \qquad (19)$$

Summary and Future Work

The proposed Turbulent Hybrid Rocket Model is the first one to consider the detailed turbulent chemical reactions and the solid fuel pyrolysis. In this model, the distribution of the combustion products can be calculated for the entire rocket combustion chamber, which can then be used as a guide to improve the overall combustion efficiency. The regression dependence on the flow aerodynamics can be reflected in the interaction between the solid fuel and the turbulent flow. We hope to clear up the inconsistencies between the current models by using the proposed comprehensive model. The hybrid rocket manufacturing process is safe, simple, and reliable. The fuel tubes have demonstrated good combustion properties, and the experimental results have shed some light on the internal ballistics of hybrid rockets. However, extensive experiments must still be

```
┌─────────────────┐                ┌─────────────────┐
│  PRETREATMENT   │                │    ADD REST     │
│   OF NH4CL      │                │   OF NH4CL      │
└─────────────────┘                └─────────────────┘
         │                                  │
         ▼                                  ▼
┌─────────────────┐  ┌─────────────────────┐  ┌─────────────────┐
│ PREHEAT OF BATCH│  │ ADD HALF OF NH4CL AND│  │ MIX UNDER VACUUM│
│ FOR 30 MIN. AT 160F│→│ AL THEN MIX FOR 30 MIN│→│  FO R 150 MIN.  │
└─────────────────┘  └─────────────────────┘  └─────────────────┘
                                                        │
                                                        ▼
                     ┌─────────────────┐  ┌─────────────────┐
                     │ CAST FUEL KEPT IN│←─│ CAST IN VACUUM  │
                     │ VACUUM FOR 12 HRS│  │    CHAMBER      │
                     └─────────────────┘  └─────────────────┘
                              │
                              ▼
                     ┌─────────────────┐
                     │ FUEL CURES AT   │
                     │ 110F FOR 3 DAYS │
                     └─────────────────┘
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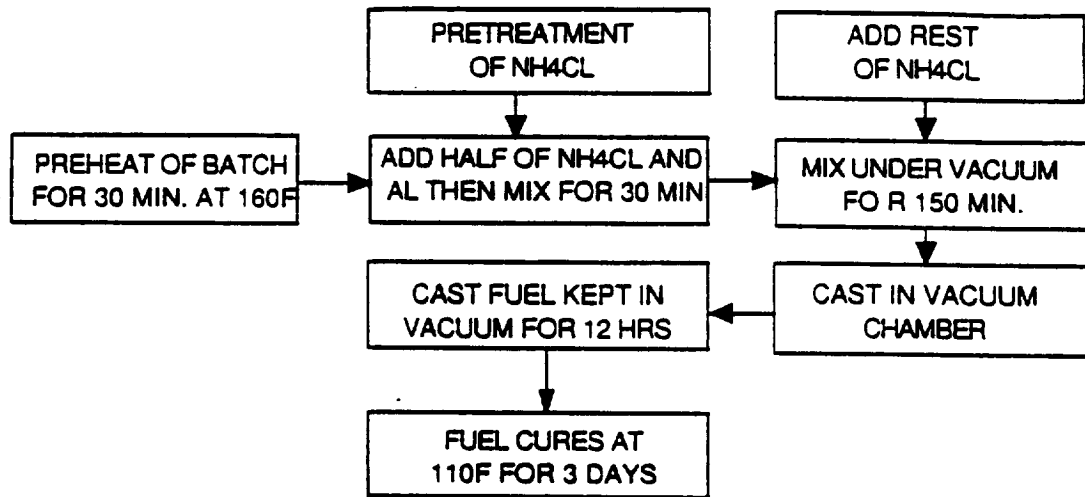
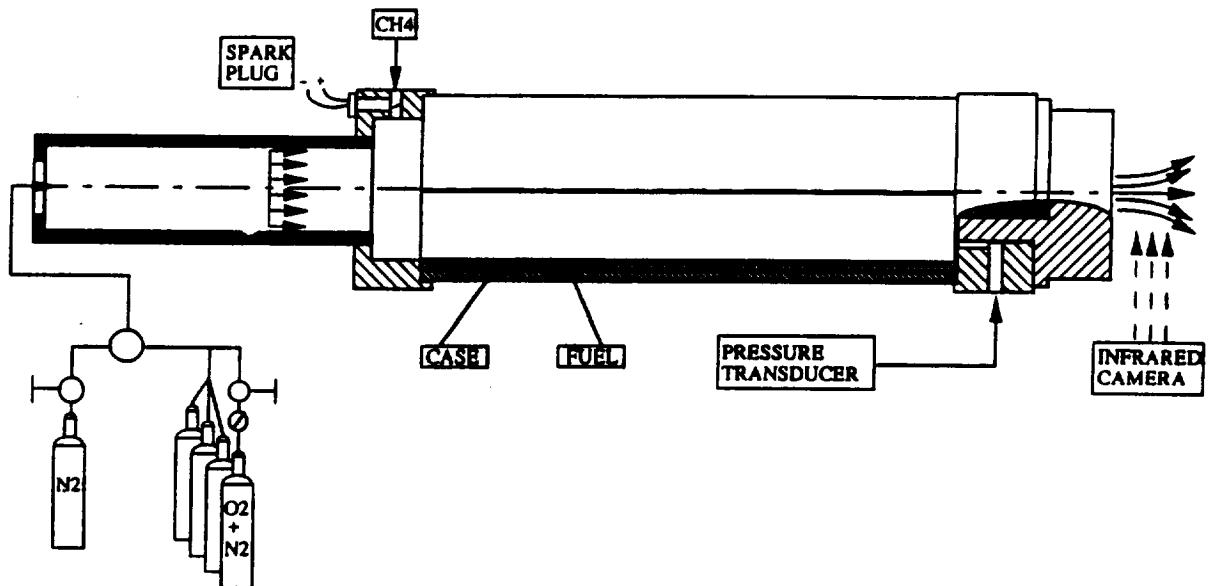Fig. 3. Flow chart of the fuel manufacturing process.

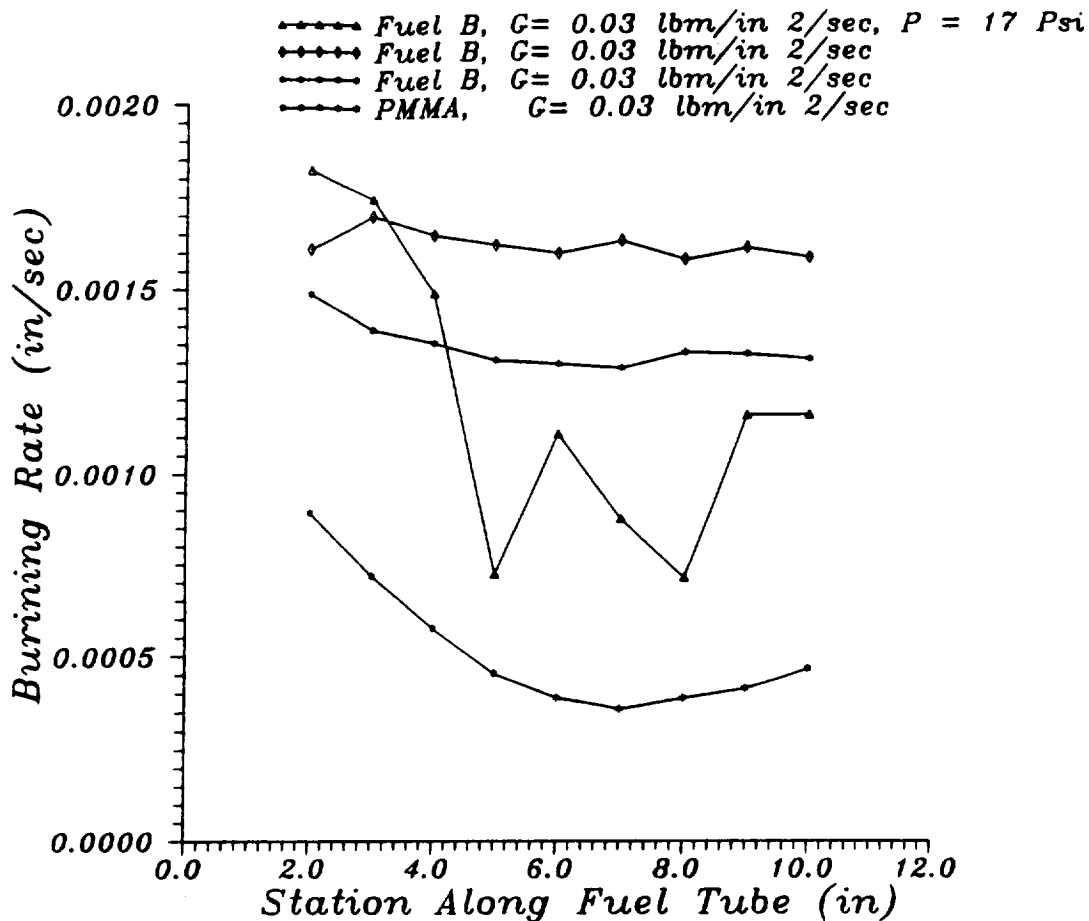Fig. 4. Schematic of the experimental hybrid rocket.

Fig. 5. Regression rate variation along fuel tube.

done to verify the proposed model. so that the hybrids can enter the mainstream of heavy-lift vehicles.

Acknowledgments

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CHAPTER 5:

HYBRID COMBUSTION WITH METALLIZED FUELS

Abstract

The two main unsolved, but somewhat unique, technical performance-degrading problems of hybrid rockets are the low overall combustion efficiencies and the incomplete combustion of the solid fuel.[1] It is shown that the low regression rate is the intrinsic reason for these two problems. Through an understanding of the oxidation kinetics of solid fuel with and without metallic ions, it is concluded that even a small concentration of metallic ions will significantly increase the regression rate of the solid fuel.

The fundamental degradation behavior of a typical hybrid fuel (HTPB) is examined with TGA (thermogravimetric analysis). TGA results show that high surface temperatures will increase the degradation rate. Fuels manufactured in the Space Technologies and Propulsion Laboratory at The University of Arizona have been tested in a laboratory-scale experimental hybrid rocket. As compared with the "baseline" behavior of HTPB fuel regression rates, a small amount of metal powder added to the fuel will significantly increase the regression rate. About 5% improvement of the fuel regression rate is observed with only 1% (by weight) of additional metal. At higher concentrations, an upper limit of regression rate improvement will be reached. For Cu^{2+}, this limit seems to be near 10%. A cleaner exhaust, indicating better combustion efficiency, was observed with these fuels. Small-amplitude "irregular" combustion was observed in some rocket tests.

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‡ Professor, Department of Aerospace and Mechanical Engineering, and Co-Director, NASA Space Engineering Research Center.

Introduction

The recent resurgence of interest in hybrid rockets appears to be more serious and, hopefully, more permanent than in the past. It has been well known for some time that hybrid rockets can offer the advantages of cost effectiveness, controllability, non-catastrophic failure modes, stop-restart ability, and more benign exhaust.[2] Considering all of these advantages,[3,4] it is instructive to investigate why the hybrid has not yet made it to the mainstream. The reasons are several and complex, varying from purely technical to rather vague. Lack of commitment to its development during the time when intensive developments were made in large solid and liquid rockets is one reason. Although the fundamental processes in the hybrid rocket appear to be simple, many of the details have not been well understood. This deficiency in our understanding may introduce problems in the application of hybrid technology to launch systems.

The low regression rate of the solid fuel is the basic problem which degrades the overall performance of the hybrid rocket. In classical hybrid rocket combustion, the oxidizer is in the liquid or gaseous state, while the fuel is in a solid state. The oxidizer, stored in a tank in liquid form, is fed to the combustion chamber either by turbopump or stored high-pressure inert gas. When the solid fuel is heated, it will evaporate. Fuel vapor must then mix and react with the gaseous oxidizer from the main stream. Some fuel and oxidizer escape through the nozzle without reacting. This loss can greatly penalize the overall hybrid rocket combustion efficiency. Certainly, increasing the fuel regression rate will enhance the mixing, thus improving the combustion efficiency. Moreover, as indicated by the Space Propulsion Synergy Group,[1] the low regression rate introduces a greater port area requirement. The low packing density in the rocket chamber will contribute to a low impulse density.

From the preceding, it is clear that increasing the fuel regression rate is one of the keys to greater hybrid rocket combustion efficiency. More importantly, it is a key to helping hybrid rocketry enter the mainstream of propulsion systems. The regression rate increase of the solid fuel can be achieved either by fluid mechanical or chemical methods. In the former, the emphasis is on the improvement of the mixing process between the oxidizer and the fuel vapor. Also, this will help more oxidizer to be delivered to the fuel surface. As discussed by Ramohalli and Yi[3] and later in this paper, a small concentration of oxidizer will improve the hybrid fuel degradation rate. In general, this adds more complexity to the propulsion system. One chemical method consists of adding some catalyst(s) to improve the degradation process of the solid fuel. An investigation of this chemical method is presented in this paper.

The detailed degradation (pyrolysis) behavior of a typical fuel type (HTPB) is examined by TGA. It is found that the fuel degrades almost instantly at a certain high temperature (about 400°C). In our TGA experiments, the samples are placed in a small oxygen concentration atmosphere, so the temperature corresponding to the maximum degradation rate is lower than in Brazier and Schwartz's experiments.[5] The overall degradation behavior of the fuels is similar to each other. The 400°C is close to the reported solid fuel surface temperature. This indicates that raising the solid fuel surface to a higher temperature will greatly enhance the regression rate.

Based on the kinetics analysis,[6] the main effect of the metallic ions on the polymer degradation is to reduce the activation energy and to react with the oxygen, or to form some complex compounds. Small concentrations of different metal ions (Cu^{2+}, Cr^{2+}, Co^{3+}, Fe^{3+}, Al^{3+}) can catalyze the degradation significantly. In the current investigation, different metal ions have been added to the fuel to catalyze the degradation process. These hybrid fuels have been tested in a laboratory-scale experimental hybrid rocket.

It should be noted that the authors are aware of the current emphasis on non-metallized fuels in hybrid rocket research.[7] However, the purpose of this project is to find some very effective catalyst(s) to significantly increase the regression rate of the solid fuel, without sacrificing operational simplicity or negatively impacting the environment.

Theoretical Considerations

HTPB Degradation Kinetics

We are aware of the limitations of low-heating-rate TGA studies and of the prevailing thoughts on the very applicability of these to solid rocket combustion environments. But these TGA studies do provide valuable insight into some very basic degradation mechanisms that are relevant to hybrids. Figure 1 is one in a series of TGA experiments for HTPB samples under small concentrations of oxygen (1.0% O_2, bal. N_2). It is apparent that the maximum rate of weight loss occurs at 400°C, which is the typical surface temperature of the HTPB fuel (600-700 K). It is pointed out by Stivala et al.[8] that the degradation process of polybutadiene can be divided into two stages. During the first stage, the fuel degrades by about 10% of the original mass. The major products of the first stage are butadiene and the dimer 4-vinylcyclohene (VC), plus minor amounts of other unidentified hydrocarbons. Most of the fuel degrades in the second stage. At the start of the second stage, significant butadiene is still observed, but the VC content is very low. At the maximum rate of the second stage, there is little butadiene or VC, but there is a complex mixture of many hydrocarbons. From the preceding, one can see that depolymerization is the primary process during the first stage of degradation. Figure 2 shows the TGA experiment results of Brazier and Schwartz[5] for polybutadiene polymer in an inert N_2 atmosphere with a heating rate of 100°C/min. Our TGA experiments are conducted at a much higher heating rate, which is closer to the hybrid rocket combustion environment.

Comparing our experimental results with the results of Brazier and Schwartz,[5] it can be concluded that the small concentration of oxygen helped the fuel to reach the maximum degradation rate at a relatively lower temperature.

Oxidative Degradation of Metal Fuel

The effect of copper on the degradation of rubber was studied by Miller[9] in 1865 from the point of view of an aging process. In 1942, Chovin[10] reported the effect of copper on the oxidation of rubber with his kinetic measurements. Villain[11] then showed that most copper compounds possessed the same catalytic activity.

The mechanism of the gas-phase metal-catalyzed oxidation has been well established. The catalytic activity of the metallic compound has been connected with its conductivity.[12,13] In general, the p-type conductors, such as cupric oxide, are considered to be good catalysts, while the n-type conductors, such as zinc oxide, are poor catalysts.

Generally, the kinetic results are more reproducible for the liquid phase than for the solid phase due to the homogeneity of the medium. Therefore, the kinetic results obtained in the liquid phase have been frequently employed as guidelines for the study of the mechanism in the solid phase oxidation.

**TGA EXPERIMENT - 2   BASELINE
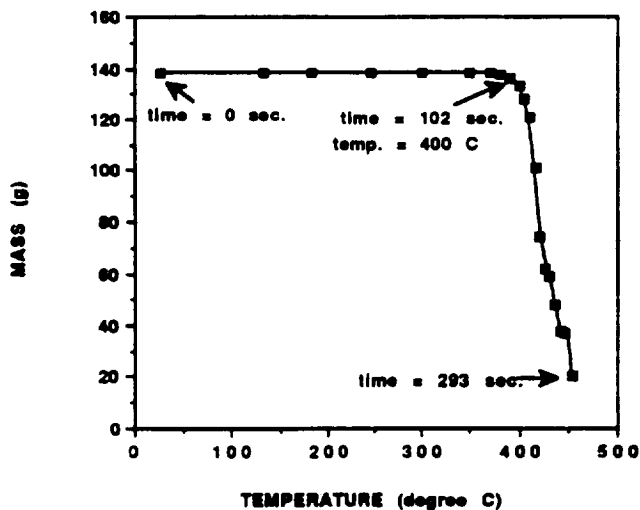HTPB FUEL MASS vs. TEMPERATURE**

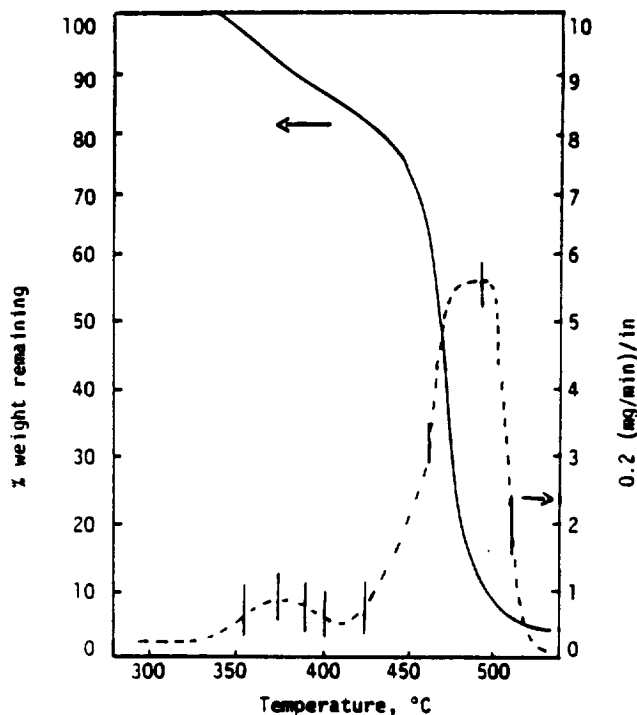Fig. 1.   HTPB TGA results in O_2-containing
atmosphere.

Fig. 2.   HTPB TGA result in inert atmosphere.[5]

The primary reaction is the chain formation of the hydroperoxide, in which the catalyst both starts and stops the reaction chain. The subsequent reaction is the unimolecular decomposition of the hydroperoxide via a "heavy-metal catalyst-hydroperoxide" complex to give the ketone.

The equations proposed by Robertson and Waters[14] on the reaction between hydroperoxide and metallic ions have formed the basis for many later kinetic studies:

$$M^{n+} + ROOH \rightarrow M^{(n+1)+} + RO \cdot + OH^- \qquad (1)$$

$$M^{(n+1)+} + ROOH \rightarrow ROO \cdot + H^+ + M^{n+} \qquad (2)$$
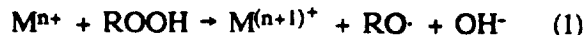
where M stands for metallic iron and ROOH for the radical of the polymer. The sum of these two equations gives the same products as in bimolecular thermal decomposition:

$$2ROOH \rightarrow RO \cdot + RO_2 \cdot + H_2O . \qquad (3)$$

It has been shown that the metallic ions affect the rate of initiation and the rate of propagation. Kochi and Rust[15] reported that the metallic ions could affect the rate of termination if the metallic ions come from a complex with the R· radicals.

During the early stage of autoxidation, it has been suggested that the metallic ions might oxidize the hydrocarbon directly. Uri[7] suggested three possibilities: (1) reduction of activation of traces of hydroperoxide already present in the system; (2) direct reaction of a metal ion with oxygen; and (3) complex formation of metal compounds with oxygen and subsequent formation of an $H_2O \cdot$ radical.

It was pointed out by Lee et al.[16] that, as in the case of the gas-phase oxidation of hydrocarbons, not all metals possess the same catalytic activities in a given medium. In general, for a polybutadiene polymer, according to the induction time, Co^{2+} and Mn^{2+} ions were the strongest. The reactivities could be arranged as follows: $Co^{2+} = Mn^{2+} > Cu^{2+} > Fe^{3+} > Pb^{2+} > Ce^{4+}$. The rates followed a slightly different order: $Co^{2+} > Fe^{3+} > Cu^{2+} > Mn^{2+} > Pb^{2+} > Ce^{4+}$.

Hybrid Rocket Combustion

Early in the 1960's, a series of experiments by Smoot and Price[17-19] showed that, for a given pressure, after a critical oxygen flow rate, the regression rate of the butyl rubber and polyurethane will not increase much with the increase of the oxidizer flux. For HTPB fuel, a similar result is obtained in the current experiments. It is postulated here that, in the lower oxidizer range, the regression rate of the fuel solely depends on heat transfer from the gas field to the fuel surface. The heat transfer process depends on the temperature inside the "combustion zone" and the thermal conductivity

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of the solid fuel. The addition of metal powder in small concentrations will not significantly affect the temperature in the combustion zone, and thus will increase the regression rate of the fuel only slightly. But after the critical oxidizer flux, the fuel degradation will be the controlling process for the regression rate. The metallic ions will catalyze the degradation process, thereby increasing the overall regression rate.

Experimental Investigations

Fuel Manufacturing

All hybrid fuels used in the experiments were manufactured at the Space Technologies and Propulsion Laboratory at The University of Arizona. We have a Baker Perkins APV planetary mixer that meets industry standards. The fuel is made of hydroxyl-terminated polybutadiene (HTPB) as resin. To make the fuel opaque, a small amount of carbon black is added. This is done in order to increase the radiative heat transfer from the rocket chamber to the fuel surface. This combination of HTPB and carbon black is considered to be the "baseline" fuel in the following experiment matrix. The fuel is then thoroughly mixed. This is a vacuum process, which will guarantee air bubbles are removed from the fuel, which results in a fuel with consistent density and uniformity. After the fuel is completely mixed, a certain amount of Isonate (isocyanate) is added as a curing agent.

The fuel is then cast into a rocket mold. The rocket mold consists of a plastic 2.5-inch OD tube placed between two end plates. The

tube is 0.25 inch in thickness and is from 12 to 36 inches in length. A 0.5 to 2.0 inch steel rod, coated with a dry lubricant release agent to prevent the fuel from sticking, is placed in the center of the mold. The combustion port is made by the removal of this steel rod after curing. The cast fuel takes about 12 hours to cure. The fuel is then cut into several segments, each with a length/diameter ratio of 10, which are measured both in inside diameter and length and finally weighed.

Test Motor Apparatus

A schematic structure of the experimental hybrid rocket is shown in Figure 3. The fuel is placed in the front part of a steel casing, 12-24 inches in length and 3 inches in outer diameter. The oxidizer is a mixture of oxygen and nitrogen, the ratio of which can be easily changed. The oxidizer is supplied to the head of the rocket, where it passes through a long flow straightener tube before entering the test section. Methane is also supplied at the head of the rocket for the purpose of initiating combustion in the rocket in conjunction with a continuous-firing spark plug. The nozzle is composed of two parts, a graphite throat and a metal case. Through the adjustment of the tank pressure, a specific mass flux range of 0.01-0.15 lb/in^2s is achieved. The working chamber pressure can be adjusted in the range of 40-300 psia.

Firing Procedure and Data Acquisition

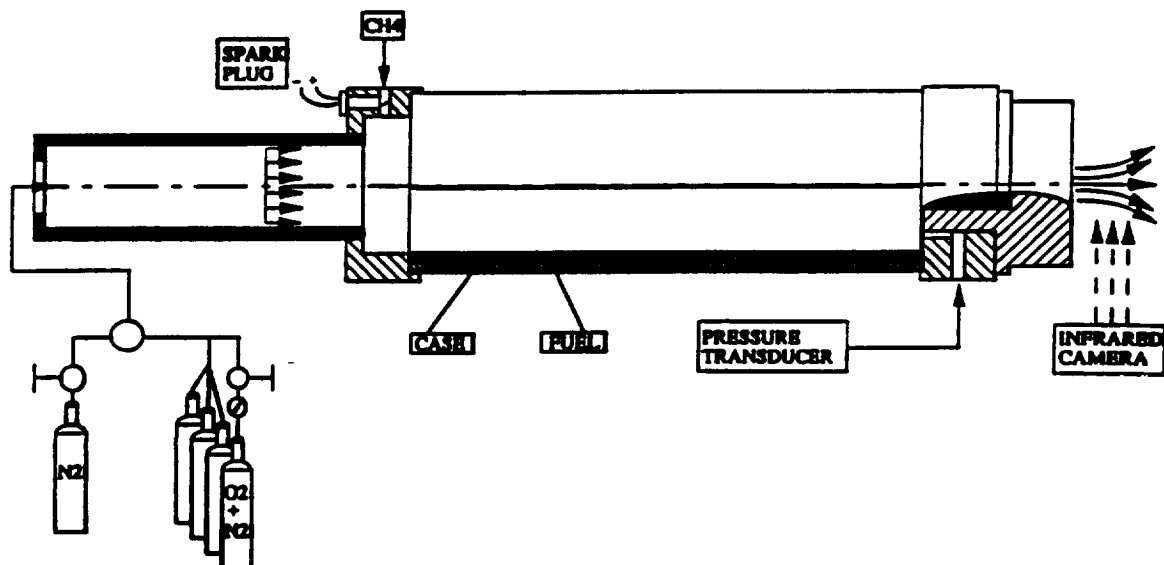After the fuel has been loaded and sealed into the test section, the rocket is ready to be

Fig. 3. A schematic of the experimental hybrid rocket.

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fired. The hybrid rocket motor firings are also done at The University of Arizona in the Space Technologies and Propulsion Laboratory. After an initial nitrogen purge, the oxidizer is turned on through a central control panel. The methane and spark plug are also activated at this time to initiate combustion. After the fuel has ignited, the methane flow and the spark plug are turned off. When the prescribed burn time is completed, the oxidizer is turned off and the system is again purged with nitrogen.

The data analysis consists of measuring initial and final port diameters and lengths, and initial and final masses. A pressure transducer is used to acquire the chamber pressure and a video camera is used to record the entire firing process. An infrared camera, a Fourier transform-infrared spectrometer (FT-IR), gas-chromatography, and a scanning electron microscope (SEM) have been used for analysis purposes, but were not reported on here.

Experimental Test Matrix

The experimental test matrix was set up to evaluate the effectiveness of adding metallic ion catalysts to the "baseline" fuel in an effort to increase the burning rate. Initially, it was imperative to obtain a solid baseline curve of the fuel burning rate versus oxidizer flux. The "baseline" information will help us to identify the heat transfer-controlled zone and the degradation-controlled zone for the hybrid combustion. This was accomplished by a total of 10 rocket firings over an oxidizer flux range of 0.05-0.5 lbm/in^{2}sec. The firings mentioned above and discussed later were conducted at approximately the same chamber pressure (about 70 psig) by adjusting the nozzle diameter. The metallic ion catalysts that were chosen were aluminum oxide, Al_2O_3, cupric oxide, CuO, cobalt oxide, Co_3O_4, and copper chromite, $2CuO \cdot Cr_2O_3$. These catalysts were added in the amount of 1% of the total fuel mass. These fuels were fired in the oxidizer flux range from 0.01 to 0.15 lbm/in^{2}sec. Because of its positive effect on the regression rate, additional tests were performed on the catalyst CuO to determine the influence of metal ion concentration on regression rate. The concentrations chosen here are 1, 3, 5, 8, and 13%.

TGA experiments were also conducted. The main purposes of the experiments were (1) to observe the detailed degradation behavior of HTPB with different kinds of catalysts, and (2) to see the effect of oxygen on the HTPB degradation properties. The TGA experimental setup was designed and assembled in the

Chemical Engineering Department at The University of Arizona. The system mainly consists of a furnace, reactor, gas-fed system, temperature control system, and temperature and mass recording systems.

In order to get a stabilized temperature, the furnace was preheated for about 1-2 hrs. The certified gas flowed through the reactor for 2-3 hrs to make sure the ambient gas condition in the reactor was exactly the gas employed for each experiment run. The HTPB fuel samples were shaped in a cube about 0.25" × 0.35" × 0.15". The flow rate of the certified gas was 100 cc/min.

In the HTPB TGA experiments, the samples were held in a metal net suspended in the air of the reactor. The reactor was kept at the desired temperature. The certified gas mixture of O_2 and N_2 was cycled from the top of the reactor to the bottom. Six degradation experiments of HTPB with three different compositions were conducted. Figures 4 and 5 are the TGA results for HTPB fuel with additives of pyrogallic acid and calcium compound, respectively.

Irregular Combustion

The irregular combustion phenomenon is one of the important issues for hybrid rockets. There has been much discussion on this topic. We have conducted about 70 hybrid rocket firings in the Space Technologies and Propulsion Laboratory. A variety of fuels including PMMA, PBAN, and HTPB have been used in those firings. Different fuel loading positions, i.e., upstream and downstream, have been tried. "Irregular" combustion cases were observed only in couple of rocket firings, when the fuel is loaded upstream. A graphic video record is available.

Results and Discussion

In Figures 1, 4, and 5, different TGA results for three different catalysts in the HTPB fuel are shown. It is clear that the HTPB degradation can be divided into two stages. In the first stage, the fuel degrades very slowly. In the second stage, the fuel degrades very quickly once it reachs a high temperature. From this observation, we can propose that, in hybrid combustion, keeping fuel surface temperature above this cutoff temperature will improve the degradation rate greatly. It also can be seen that the cutoff temperature corresponding to the maximum regression rate is lower in the presence of oxygen. It is clear that the small concentration of oxygen near the fuel
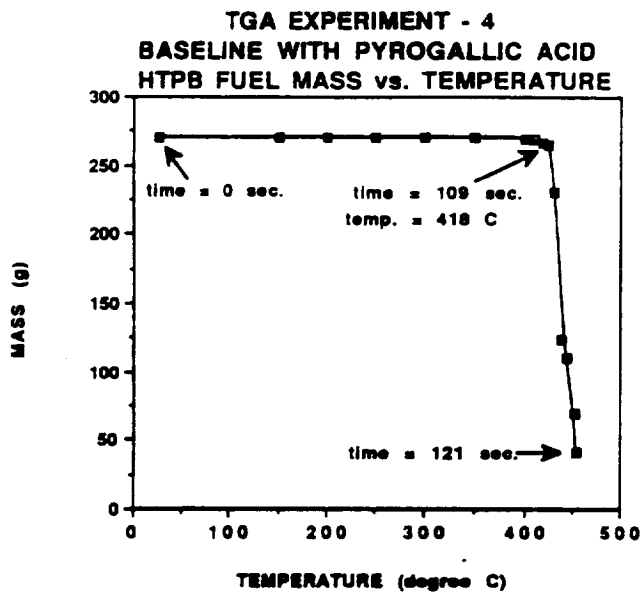
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TGA EXPERIMENT - 4
BASELINE WITH PYROGALLIC ACID
HTPB FUEL MASS vs. TEMPERATURE

time = 0 sec.

time = 109 sec.
temp. = 418 C

time = 121 sec.

Fig. 4. HTPB/pyrogallic acid fuel TGA result.

TGA EXPERIMENT - 5
BASELINE WITH A CALCIUM COMPOUND
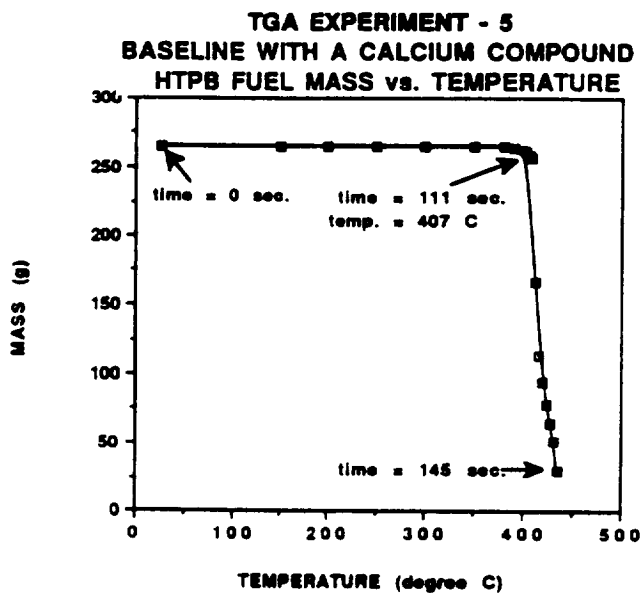### HTPB FUEL MASS vs. TEMPERATURE

time = 0 sec.

time = 111 sec.
temp. = 407 C

time = 145 sec.

Fig. 5. HTPB/calcium compound fuel TGA result.

surface is very important to the fuel degradation process. The additives of pyrogallic acid and the calcium compound will not improve the pyrolysis properties of HTPB fuel.

The results of the combustion experiments are summarized in Figures 6 and 7. There are two conclusions that can be drawn from these. First of all, the metallic ions affect the HTPB degradation only in the degradation-controlled regime. Second, there is a significant difference in the catalytic effects among all the catalysts
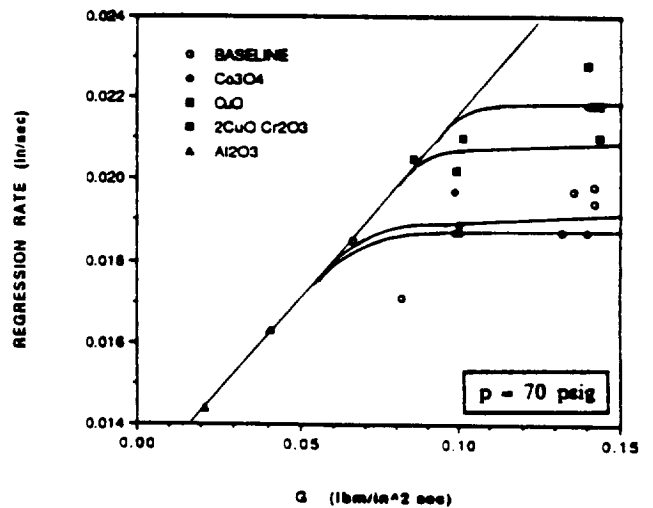
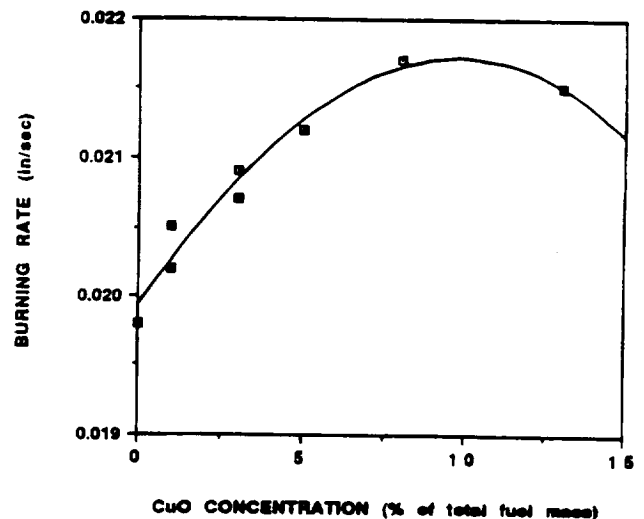Fig. 6. The effect of metallic ions on HTPB pyrolysis.

Fig. 7. The effect of CuO concentration on HTPB pyrolysis.

tested so far. Of the four metal-containing compounds tested as catalysts, the cupric oxide and copper chromite showed the best improvement in regression rate (Figure 6). It was decided that the cupric oxide would undergo more testing to determine the dependence of regression rate on metal ion concentration. Copper chromite was identified as a candidate for later testing.

The results of the testing using cupric oxide are shown in Figure 7. The concentrations tested were 1, 3, 5, 8, and 13% of the total fuel weight. It can be seen that the burning rate does increase with increasing metal concentration, reaching an apparent limit near a metal concentration of around 10%. This limit

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corresponded to an approximately 10% improvement in the regression rate. It should be noted that a 5% increase was observed with only a 1% addition of the metal compound.

Summary

The following conclusions can be drawn from the experimental investigations and the theoretical discussion:

1. The TGA results of HTPB under inert and active environments indicate that a small concentration of oxygen is very important to the hybrid fuel degradation properties.

2. Using metallic ions to catalyze the hybrid rocket fuel is an effective test case. The small amount of catalyst will not sacrifice the benign plume advantage of the hybrid rockets.

3. The metallic ions are only effective in the degradation-controlled regime. There are significant differences in the catalytic effects among different metallic ions. Copper ions are very effective.

Future investigations will focus on quantifying the effects of the metal additives on the exhaust products, as well as the identification of other possible catalysts. Copper chromite remains to be investigated as a candidate. It is also desired to investigate the low-amplitude combustion irregularities that were observed. This investigation should focus on the interactions of additives with other potential causes of instability.

The tests presented here will need to be followed with more tests in order to obtain a sufficient data base for a statistical analysis of the results. It is important that the behavior of hybrid fuel combustion at high oxidizer flux be further defined. In this region, slow regression rates are a limiting factor. This is where metal ion catalysis can have the greatest effect. Since the majority of flight motors will operate at high oxidizer fluxes, this method has the potential to offer operational performance improvement without sacrificing simplicity.

Acknowledgments

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