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Ignition of Hybrid Rocket Fuels with Fuming Nitric Acid as Oxidant

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Introduction

IGNITION phenomena in hybrid combustion have received little attention and practically no work of fundamental nature has been carried out in this field. Minimum ignition delay (I.D.) coupled with smooth burning is one of the major considerations which govern the choice of a hybrid propellant system. Because start-stop operation is a potential advantage of the hybrid rocket, it is essential that the ignition of fuel with oxidizer should occur very quickly. Most of the work connected with the understanding of the combustion of hybrid propellants involves measurements of regression rates and suggestions of suitable model for hybrid combustion.[1–7] But the work on ignition delay studies, which is very important, has largely been ignored. The hypergolic hybrid propellants using solid fuel and liquid oxidizer are always preferred because the rocket motor can be stopped and restarted at will. The ignition of rocket motors using nonhypergolic hybrid propellants can be accomplished by using different techniques like hot gas, injection of hypergolic fuel or pyrogen igniters but it is difficult to restart the ignition. In order to have an insight into the combustion of hybrid propellants, it is of interest to investigate the ignition delay of these systems.

In this Note, experimental results related to ignition delay measurements of formaldehyde-type hybrid fuels are reported. The effect of different parameters like relative amounts, temperature, additives, and compactness of fuel on ignition delay has been included.

Experimental

Materials

Fuming nitric acid (specific gravity 1.5 g/cm^3) was used as an oxidizer. The hybrid fuels used in the investigation were aniline formaldehyde, o- & m-toluidine formaldehydes, and o-anisidine formaldehyde. All these fuels are hypergolic with fuming nitric acid. Aniline formaldehyde was prepared by mixing equal volumes of ice cooled purified aniline and formaldehyde solution. The mixture was stirred and temperature was not allowed to rise more than 20°C. Precipitated aniline formaldehyde was washed with distilled water and then recrystallized from benzene: o- & m-toluidine formaldehydes and o-anisidine formaldehyde were prepared in similar manner. Ammonium metavanadate, vanadium pentoxide, ammonium dichromate, potassium dichromate, and potassium permanganate were used as additives.

Measurement of Ignition Delay

Ignition delay (I.D.) of the hybrid fuels with fuming nitric acid was measured by the cup-test method.[8,9] However, the results obtained by this method will not tally exactly with the results obtained in actual rocket motor firing but will definitely give an idea about ignition delay of this hybrid propellant, because in actual rocket firing the physical factors like injection velocity, degree of atomization etc. will affect I.D. The weighed quantity of hybrid fuel in the form of powder was taken in a china dish (2″ diam) and to this was added the requisite quantity of fuming nitric acid with the help of a graduated dropping tube. The particle size of hybrid fuel was 150 μ. The experiments were done at room temperature (26 ± 2°C).

Experiments were done to find out the critical amounts of oxidizer and fuel which gave minimum ignition delay in case of each hybrid fuel. This was done by varying the quantity of fuel (0.2 g to 1.5 g) and keeping the quantity of fuming nitric acid fixed (1.0 cm^3).

Ignition delay measurements were done at 10°, 15°, 18°, 20°, and 25°C to study the effect of temperature on I.D. In case of all fuels, the O/F ratio was 1:1 except in case of aniline formaldehyde where the ratio was 1:2.

Various soluble and insoluble additives in fuming nitric acid were tried to reduce the ignition delay. The concentration of additive in acid was 4.5 g in 100 cm^3 of acid.

The effect of compactness of fuel on I.D. was investigated by measuring ignition delay of compressed fuel grains as such obtained by applying pressures of 6720, 8960, 11200, and 13440 lb on surface area 3.143 in.^{2} of the fuel. No powder was placed on the surface of the compressed grain to start ignition.

The experimental results are given in Tables 1–5.

Results and Discussion

Effect of Relative Amounts of Fuel and Oxidizer on Ignition Delay

Experiments to determine the critical relative amounts of fuel and oxidant for minimum ignition delay show (Table 1) that in case of aniline formaldehyde, o-toluidine formaldehyde, m-toluidine formaldehyde, and o-anisidine formaldehyde, the critical amounts are 0.5 g, 1.0 g, 1.0 g, and 0.30 g, respectively, the corresponding critical amount of fuming nitric acid (FNA) for each fuel is 1.0 cm^3. The minimum ignition delay values of aniline formaldehyde, o- and m-toluidine formaldehydes and o-anisidine formaldehyde, are 1.20, 0.30, 3.4, and 1.1 sec, respectively. The results of these experiments are very helpful in designing an injector.

Dependence of Ignition Delay on Temperature

Results given in Table 2 clearly show that ignition delay decreases with the increase in temperature of the system. The reason for this behavior may be attributed to the fact that reaction rates are affected by temperature. As the temperature rises, the reaction rate becomes faster which ultimately reduces

Table 1 Effect of relative amounts of fuel and oxidizer on I.D.[a]

Weight of fuel (g)	Average I.D., sec			
	Aniline formaldehyde	o-Toluidine formaldehyde	m-Toluidine formaldehyde	o-Anisidine formaldehyde
0.20	x[b]	0.50	x	1.2
0.30	x	0.40	x	1.1
0.50	1.2	0.35	4.1	2.1
1.00	1.7	0.30	3.4	2.5
1.50	1.9	0.40	3.6	...

[a] Quantity of FNA = 1.0 cm^3; temperature = 27 C.
[b] x stands for no ignition.

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Table 2 Effect of temperature on ignition delay[a]

Temperature (°C)	Average I.D., sec			
	Aniline formaldehyde	o-Toluidine formaldehyde	m-Toluidine formaldehyde	o-Anisidine formaldehyde
10	x^b	x	x	x
15	x	0.70	8.5	x
18	3.1	0.60	5.5	3.0
20	2.9	0.50	4.4	2.5
25	2.0	0.35	3.7	1.9

[a] Oxidizer/fuel ratio for aniline formaldehyde = 1:2; oxidizer/fuel ratio for other fuels = 1:1.
[b] x stands for no ignition.

Table 4 Effect of compactness of fuel on ignition delay[a]

Pressure[b] (lb)	Density of fuel (g/cm³)	Average I.D., sec
		Aniline formaldehyde
...	0.9135	1.2
6720	1.536	4.0
8960	1.962	4.1
11200	2.210	4.2
13440	2.530	6.3

[a] Surface area of the groove for reaction = 3.465 cm²; volume of FNA used = 1.0 cm³; temperature = 25°C.
[b] The pressure was applied over the fuel surface area (3.143 in.²) in each case.

the delay due to chemical factors. It is observed that the I.D. of some fuels has been reduced by 50% or more by raising the temperature from 10°C to 25°C.

Effect of Additives on Ignition Delay

Ignition catalysts have always played an important role in reducing the ignition delay of hypergolic liquid propellants and also in accomplishing the ignition of nonhypergolic bipropellants.[10–15] Certain additives have been found which reduce the ignition delay of these hybrid fuels with fuming nitric acid (Table 3). The results show that ammonium vanadate, ammonium dichromate, potassium dichromate, potassium permanganate, and vanadium pentoxide enormously reduce the ignition delay of these fuels with fuming nitric acid. The ignition delays of aniline formaldehyde, o- and m-toluidine formaldehydes, and o-anisidine formaldehyde with fuming nitric acid without additive are 1.2, 0.30, 3.4, and 1.10 sec, respectively, but in the presence of aforementioned additives, the ignition of all these fuels becomes almost instantaneous. The role of additives towards reducing the ignition delay is not very clear. The excellent role of ammonium vanadate which reduces I.D. enormously may be explained on the basis that it oxidizes the benzene ring. Ammonium vanadate is soluble in nitric acid and exists in colloidal form which has been confirmed by observing Brownian motion. Ammonium vanadate catalyses the oxidation-reduction reaction at higher temperature.[16,17] Thermochemical measurements of aniline formaldehyde —nitric acid in presence of additives reveal that these additives only accelerate the reaction rate and do not contribute towards heat of combustion. The specific impulse of the system will not be affected by these catalysts.

Dependence of Ignition Delay on the Compactness of Fuel

In actual rocket motor a grain of definite design is used and the hybrid fuels cannot be used in the form of powder as such. Efforts have been made to find the ignition delay of aniline formaldehyde in the compressed form. Different compressed grains of aniline formaldehyde using pressures of 6720, 8760, 11200, and 13440 lb have been prepared in hydraulic press and their ignition delays have been studied with fuming nitric acid (Table 4). It has been observed that the ignition delay increases as the density of the compressed grain increases. The other reason is that the diffusion rate decreases as the compactness increases. The ignition delay of aniline formaldehyde powder is 1.2 sec but the ignition delays of compressed grains are 4.0, 4.1, and 6.3 sec, respectively.

Since the ignition delay of compressed grain is quite high and is undesirable for hybrid rocket motor firing, efforts have been made to reduce the ignition delay by using ammonium vanadate catalyst. The effect of concentration of catalyst in fuming nitric acid on ignition delay of compressed grains has been investigated (Table 5). Different concentrations ranging from 0.83% to 4.15% of catalyst have been used to reduce the ignition delay from 4.0 sec to 0.10 sec which is almost instantaneous. The ignition delay has been measured by adding requisite quantity of fuming nitric acid with or without additive to a groove of known surface area of each compressed grain.

It may be reported that ignition delay slightly decreases with increase in surface area of the compressed fuel while keeping the quantity of oxidizer fixed. But this is valid only up to a certain oxidizer/fuel ratio.

Table 3 Effect of additives on ignition delay[a]

Additive	Fuels, average I.D., sec			
	Aniline formaldehyde	o-Toluidine formaldehyde	m-Toluidine formaldehyde	o-Anisidine formaldehyde
Nil	1.2	0.30	3.40	1.10
Ammonium vanadate	0.10	0.10	0.20	0.10
Ammonium dichromate	0.10	0.10	0.20	1.5
Potassium dichromate	0.50	0.10	5.8	3.5
Potassium permanganate	0.10	0.60	6.3	2.3
Vanadium pentoxide	0.10	0.10	0.2	0.1

[a] Oxidizer/fuel ratio for aniline formaldehyde = 1:2; oxidizer/fuel ratio for other fuels = 1:1; concentration of additive in FNA = 4.5 gm/100 cm³ acid; temperature = 28 C.

Table 5 Effect of concentration of additive on ignition delay[a]

Concentration of ammonium vanadate (%) in FNA	Average I.D., sec			
	Density[b] of fuel, g/cm³			
	1.536	1.962	2.210	2.530
Nil	4.0	4.1	4.2	6.3
0.83	1.1	1.3	1.9	4.8
1.66	1.0	1.3	1.8	3.5
2.49	1.2	1.8	2.0	3.5
3.32	0.10	0.4	1.0	1.2
4.15	0.10	0.4	0.8	1.0

[a] Surface area of the groove for reaction = 3.465 cm²; volume of FNA used = 1.0 cm³; temperature = 25°C.
[b] The compressed fuel grains were prepared by applying pressures 6720, 8760, 11200, and 13440 lb over the fixed surface area 3.143 in.², respectively.

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Pitch Axis Stabilization in Eccentric Orbits Using a Variable-Speed Rotor

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Introduction

A SATELLITE in a noncircular orbit stabilized by the gravitational gradient across its mass distribution undergoes planar librational motion due to the influence of the orbital motion on the attitude motion. As the eccentricity of the orbit becomes large, the amplitude of the libration increases. When the orbit eccentricity exceeds 0.355, no stable motion can exist.[1–4] This limits the use of passive gravity gradient stabilization to satellites whose orbit eccentricities are substantially less than 0.355.

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The purpose of this Note is to establish a method whereby semipassive gravity gradient stabilization can be used effectively in orbits with eccentricities significantly larger than 0.355. The method used consists of modifying the dynamical motion of the satellite by adding a small variable-speed wheel rotating about the satellite's pitch axis. The control of the wheel speed is independent of the attitude motion of the satellite, thus preserving the open-loop stabilization system and eliminating the need for attitude sensors. The speed of the wheel is dependent only on the location of the satellite in the orbit and is therefore a function only of the time since perigee passage. This technique was first considered for use in the GEOS-C satellite.[5] However, because of a decrease in the expected orbital eccentricity, it has not been implemented for that mission.

Previously, others have proposed the use of time-dependent satellite inertias for controlling satellite attitude motions.[6] However, the use of a variable-speed wheel or rotor is simpler, less expensive, and more reliable in practical applications.

Analysis

Satellite oscillations in the plane of an elliptic orbit are described by[4]

$$(1+e\cos v)(d^2\phi/dv^2)-2e\sin v(d\phi/dv)+(1/2)\delta\sin 2\phi = 2e\sin v \tag{1}$$

where e is the orbit eccentricity, $\delta = 3[(I_x - I_z)/I_y]$, ϕ is the pitch libration angle measured from the local vertical, v is the true anomaly, and I_x, I_y, I_z are the principal moments of inertia.

Consider a satellite with a variable-speed wheel rotating about the pitch axis. The moment of inertia of the rotor is defined as I_s about the spin axis, and the instantaneous speed of the wheel is Ω. The equations of motion for such a satellite in a gravitational field can be developed using the usual Lagrangian formulation. The equation for the pitch motion is

$$(1+e\cos v)(d^2\phi/dv^2)-2e\sin v(d\phi/dv)+(1/2)\delta\sin 2\phi + I_s\dot{\Omega}/I_y\omega^2(1+e\cos v)^3 = 2e\sin v \tag{2}$$

where ω is like the mean motion and is defined as $\dot{v}/(1+e\cos v)^2$ and $(\dot{\ })$ refers to differentiation with respect to time. Equation (2) will be investigated here.

Stability Regions

The criterion chosen for stable motion is that a satellite in an elliptic orbit exhibits a motion whose maximum librational amplitude is limited to less than $\pm 90.0°$. This amplitude limitation results from the more general requirement that one axis of a satellite is defined as Earth pointing and is used for such things as communication antennas and Earth observation experiments.

The stability discussed herein is restricted to the pitch motion since the roll and yaw librations are only weakly coupled to the pitch motion and are normally stable. This is particularly true when a variable-speed wheel is used. Since the wheel speed can be controlled such that there is always a momentum bias; i.e., the wheel speed would never be zero, the roll yaw plane would be gyrostabilized provided that the pitch motion were stable. This is the familiar gyrocompass stabilization concept.

The pitch axis regions of stability can be represented in a three-dimensional space in terms of ϕ, $d\phi/dv$, and v for any given eccentricity. Since a closed-form solution to Eq. (2) has not been obtained, the stable regions must be determined numerically.[3]

The stable regions can be presented stroboscopically in two dimensions (ϕ, $d\phi/dv$) by examining the trajectories at selected values of true anomaly.[7] For example, numerically obtained values of ϕ and $d\phi/dv$ can be plotted only at each perigee crossing, apogee crossing, or at any other true anomaly v of interest. If these two-dimensional figures were to be obtained for all values of v, then they could be joined together to form a tube-shaped three-dimensional surface (see Fig. 3 of Ref. 1) or stability portrait. The portrait need only be constructed for values of true anomaly from 0 to 2π radians since, after 2π