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EFFECT OF PRESSURE ON IGNITION OF HYPERGOLIC LIQUID PROPELLENTS

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13. ABSTRACT

Fluids which ignite readily at atmospheric pressure do not necessarily react at low pressures, such as in space. It is only indirectly, through the effect on rates of energy release and energy absorption, that the ignition behavior of a hypergolic liquid is influenced by ambient pressure. Therefore emphasis has been placed on the determination of how pressure affects the rates at which energy is released, absorbed, and distributed. The ignition phenomenon has been examined experimentally in a test facility, where it was possible to establish the relationship between small changes in physical environment and changes in ignition of hypergolic liquids. Ignition at low pressure was investigated with theoretical techniques, applying thermochemistry to determine amounts of energy involved, chemical kinetics to establish rates of energy release, evaporation studies to indicate rates of energy absorption, and heat transfer to clarify the distribution of energy within a propellant droplet. While the work has centered about the ignition of hydrazine-containing hypergolic liquids at low pressures, the attempt has also been made to derive generalizations which might apply to similar systems.

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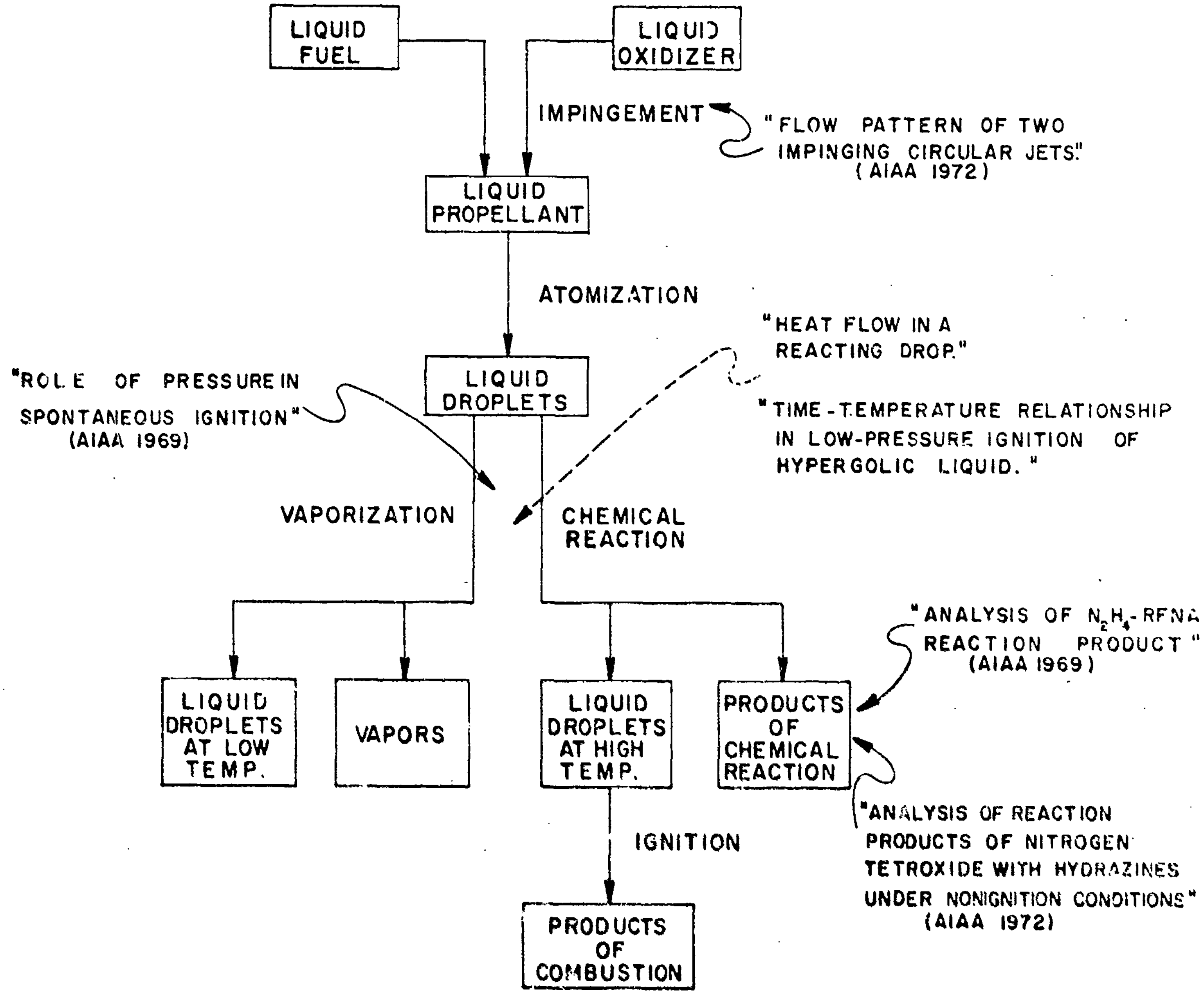
The ignition of hypergolic propellants is treated in this research effort as though it occurs as a sequence of discrete events. In each of the individual steps, as with the overall ignition process, emphasis has been placed on investigating the role of pressure. When streams of liquid fuel and liquid oxidizer impinge on each other, the two liquids mix, and the liquids then break up into small droplets of propellant. Chemical reactions occur in these droplets and, at the same time, some of the liquid vaporizes. The rate of vaporization is affected by the ambient pressure. The temperature of the droplets changes as a result of the chemical reaction and the vaporization. If the temperature of droplets becomes sufficiently high, ignition finally occurs.

Work done in investigating aspects of the inition process has led to publication of six papers. In Fig. 1 the titles of these papers are shown, together with their relationships to particular steps in the ignition process. The four published papers are as follows:

1. "Flow Pattern of Two Impinging Circular Jets" by M. A. Saad and G. J. Antonides, AIAA Journal, Vol. 10, pp. 929-931, 1972.

The pressure distribution at the interface of two impinging streams of liquid may provide information about the mechanism of ignition. Accordingly, a computer program was developed to calculate pressure distribution between two axisymmetrically positioned impinging jets. The method is based on the differential equation for the stream function, using finite difference techniques to generate numerical solutions. Pressure distribution was calculated for two jets which were equal in diameter, velocity and dynamic pressure, and also for two jets of unequal diameter.

Currently, a three-dimensional program, based on the velocity potential, is being developed to calculate pressure distribution in two equal streams which impinge at angles other than 180°.



"FLOW PATTERN OF TWO IMPINGING CIRCULAR JETS." (AIAA 1972)

"HEAT FLOW IN A REACTING DROP."

"TIME-TEMPERATURE RELATIONSHIP IN LOW-PRESSURE IGNITION OF HYPERGOLIC LIQUID."

"ROLE OF PRESSURE IN SPONTANEOUS IGNITION" (AIAA 1969)

"ANALYSIS OF N_2H_4-RFNA REACTION PRODUCT" (AIAA 1969)

"ANALYSIS OF REACTION PRODUCTS OF NITROGEN TETROXIDE WITH HYDRAZINES UNDER NONIGNITION CONDITIONS" (AIAA 1972)

FIGURE 1

2. "Analysis of N_2H_4-RFNA Reaction Product" by M. A. Saad and M. B. Detweiler, AIAA Journal, Vol. 7, pp. 1588-1592, 1969.

When streams of N_2H_4 and RFNA are injected into a low-pressure chamber, a white solid deposits on surfaces of the chamber. Yield of this solid is largest when ignition does not occur. Three analytical methods--infrared spectroscopy, chemical analysis and mass spectroscopy--were used to identify the intermediate products. It was found that hydrazinium nitrate is the major constituent of this deposit.

3. "Analysis of Reaction Products of Nitrogen Tetroxide with Hydrazines under Nonignition Conditions" by M. A. Saad, M. B. Detweiler and M. A. Sweeney, AIAA Journal, Vol. 10, pp. 1073-1078, 1972.

The chemical composition of the reaction products formed from hypergolic liquid propellants also provides information about the mechanism of ignition. The products formed with hydrazine during the reaction of nitrogen tetroxide or methylated hydrazines at low pressure were collected and analyzed by the methods of mass spectroscopy, gas chromatography, and infrared absorption spectroscopy. Products originating from both ignition and nonignition reaction were analyzed.

In a series of experiments conducted at atmospheric pressure, nonignition reaction of propellant liquids in a solvent ($CC\ell_4$) was initiated at low temperatures. Based on the analytical evidence, chemical reaction mechanisms were developed to account for the detected products.

4. "Role of Pressure in Spontaneous Ignition" by M. A. Saad and S. R. Goldwasser, AIAA Journal, Vol. 7, pp. 1574-1581, 1969.

By simulating three rate processes associated with the ignition of hydrazine and RFNA, time-temperature relationships have been calculated by means of a computer program. This program was used to compare the ignition of a gas-gas system with the ignition of an equivalent liquid-liquid system. The temperature was found to rise much more slowly in the gas-gas system than in the liquid-liquid system. It was also found, by means of this program that a tenfold reduction in pressure reduced the rate of heat generation in a gas-gas system by a factor of ten.

Also shown in Fig. 1 are the titles of two other papers, together with their associated steps in the ignition process. These are papers which have not yet been accepted for publication. They are as follows:

1. "Time-Temperature Relationships in Low-Pressure Ignition of Hypergolic Liquids" by M. A. Saad and S. R. Goldwasser. This paper was sent to the AIAA Journal in March 1973.

The attempt was made to simulate time-temperature relationships in a hypergolic liquid during the interval between mixing and ignition. A computer program was developed based on techniques used in chemical kinetics. It was assumed that decomposition and vaporization could each be described by a rate equation. Rate constants for these two processes were calculated from measured values of ignition delay time for the following propellants: N_2H_4/HNO_3, N_2H_4/N_2O_4, MMH/N_2O_4, and $UDMH/N_2O_4$. To explain the pressure dependence on ignition delay time, the activation energy associated with vaporization was treated as a function of pressure.

2. "Heat Flow in Reacting Drop" by M. A. Saad and G. J. Antonides. This paper will be submitted in July 1973.

A computer program was developed to calculate radial temperature distributions in a hypergolic liquid droplet where the surface temperature is assumed to remain constant and where the radius is diminishing due to evaporation. In a 100μ droplet of $N_2O_4 + N_2H_4$ the temperature at the center of the droplet is 7°F higher after 3 msec than at the surface. In a 50μ droplet the difference is 3°F in the same time interval.

When hypergolic liquids are mixed, various processes compete for the available energy. In particular, both chemical reactions and vaporization require some energy, although chemical reactions tend to return any energy they withdraw. However, these two processes are competitive, and the competition becomes increasingly severe as the pressure is lowered. Since vaporization of the liquid propellants seems to exert such a controlling action on the ignition process, it is useful to formulate mathematical expressions describing vaporization rate and to establish the magnitude of any associated parameters. For this reason attention is now being focused on the vaporization process with the particular goal of determining appropriate values for rate constants in rate equations, and the functional relationships between the size of liquid droplets and their vaporization rates. From these studies it may be possible to express the vaporization rate of any liquid at any pressure and temperature. This would be a step toward predicting the ignition behavior of any hypergolic liquid at any pressure. The current vaporization studies consist of theoretical work centered about measurements that had been made on this project in 1967 and 1968, in which droplets of liquid were allowed to evaporate at various pressures. To measure evaporation rates, droplets of hydrazine and RFNA were suspended in an evacuated chamber and were photographed periodically. Graphs were developed showing change in diameter of the droplets as a function of time at various pressures.

Work of an "exploratory" nature also was performed on this project. These efforts were undertaken in the belief that they would lead to significant information about low-pressure ignition of hypergolic liquids. They led to some information, but they also tended to suggest other, more promising directions to pursue in the research effort. In most cases, these other directions have been subsequently followed. Work was done in the four areas mentioned below:

1. Dynamic Ignition Tests: In a 4 ft^3 vacuum chamber equipped with micro-values and timing circuits, liquid reactants (hydrazine and RFNA; Aerozine and N_2O_4) were injected at velocities of about 40 ft per second and impinging at an angle of 90°. The total quantities used in each test amounted to about 2 grams and the proportion of reactants was chosen to correspond with the highest flame temperature that the two reactants could generate.

With the Hydrazine/RFNA system, ignition occurred at pressures as low as 10" Hg, but when the region of impingement was blocked off from the rest of the vacuum system so that the rates of heat transfer and liquid transfer were reduced while vacuum conditions were maintained constant, ignition was found to occur at pressures as low as 2-1/2" Hg.

A glass open-ended cylinder was placed vertically in the chamber so the impingement point was located just inside the upper end. Cylinders of various diameters were used, and the lowest pressure at which combustion occurred was noted. It was observed that ignition occurred at 37.3 mm Hg when a 12-inch long, 1-inch diameter cylinder was used, but that ignition did not occur below 52.5 mm Hg when a 12-inch long, 2-inch diameter cylinder was used. Ignition-delay and flame-duration time were also measured. It was noted that large quantities of a white product coated the surfaces in the test chamber whenever hypergolic reactants failed to ignite. Ignition occurred more readily when the constituents were introduced as liquids rather than as gases. Ignition occurred more readily also when these constitutents impinged on each other directly rather than when they flowed close to, but parallel with, each other. An electrically heated plate, located slightly downstream and parallel to the plane of the injection tubes, was found to increase the likelihood of ignition at low pressure.

2. <u>Static Ignition Tests</u>: Individual droplets of the two reactants (hydrazine and nitric acid) were suspended from glass filaments in a vacuum and were brought into contact with each other. Evidently, close contact between the liquid phases of the two reactants helped materially in causing ignition, and ignition could be initiated in the liquid phase. Ignition did not occur readily when only the vapor phases of the reactants interacted, but after combustion started, the process sustained itself readily whether the reactants entered as liquids or gases. The initiation of combustion in the liquid phase was recorded by high speed photography. Additional equipment was constructed. In one case, a thin stream of N_2O_4 was introduced into a sheet of Aerozine-50 and the combustion process was recorded photographically.

3. <u>Theoretical Calculations</u>: Theoretical thermochemical techniques, using a 7094 computer, have been applied in studying

hypergolic reactions. The system Hydrazine/RFNA was examined in the proportions of 55%, 60%, and 65% oxidizer. Equilibrium compositions were calculated at pressures in the range from .001 atmosphere to 1.0 atmosphere. Compositions and temperatures were calculated at adiabatic flame conditions; in addition, compositions and enthalpies were calculated at various temperatures between 3000°K and 1000°K. From these calculations, information has been obtained about the nature of the chemical species formed by the chemical reactions and the amount of energy released. By means of a computer program based on equilibrium composition, enthalpy and entropy relationships of N_2H_4/RFNA and MMH/RFNA combustion products were calculated. An H-S diagram was plotted. Four pressures were treated--1 atmosphere, 0.1 atmosphere, 0.01 atmosphere, and 0.001 atmosphere. Temperature differences at these pressures were most evident at higher temperatures.

4. <u>Electrochemistry</u>: An electrochemical cell was used to study the liquid phase reaction of N_2O_4 and Aerozine-50. The two liquids were separated by a membrane permeable to H^+ ions but not to liquid molecules. By means of electron transfer through a membrane, reaction between N_2O_4 and N_2H_4 occurs according to the equations:

$$\begin{array}{l} 2\ N_2H_{4(\ell)} \rightarrow 2\ N_2 + 8\ H^+ + 8\ e^- \\ 8\ e^- + N_2O_{4(\ell)} + 8\ H^+ \rightarrow 4\ H_2O + N_2 \\ \hline \end{array}$$

Or: $$2\ N_2H_{4(\ell)} + N_2O_{4(\ell)} \rightarrow 3\ N_{2(g)} + 4\ H_2O$$

When measured voltages were compared with calculated values, it was found that measured values were considerably less than theoretical. This is probably due to side reactions leading to products other than those ideally formed and also due to the existence of potential barriers in the chemical transformations of the liquid phase. These studies were intended to help show a correlation between emf and reaction rates of liquid phases.

The current effort is devoted to the following:

1. Developing equations and parameters describing vaporization rates of propellant liquids.
2. Determining flow patterns and pressure distributions resulting from the impingement of two liquid jets.

A laboratory test facility, useful for measuring liquid contours, has been constructed to supply data needed in the calculations of item 2 above.