Chemical Pressurization of Hypergolic Liquid Propellants

Richard J. Kenny* and Paul A. Friedman†
Martin-Marietta Company, Denver, Colo.

A highly efficient method of pressurizing liquid rocket propellant tanks has been developed experimentally and demonstrated in a full-scale, flight-weight ground test article employing storable propellants. Design of the full-scale system was based on an extensive small-scale experimental program and a mathematical model computer program formulated for predicting pressurization system performance characteristics. The specific system developed for pressurizing gas generation employs solid-stream reagent injection onto the propellant surface by means of a pulse-mode pressure control system. Because of the complex nature of the quenched reaction, a method to predict the reaction mixture ratio accurately has not yet been developed and has been the primary cause for errors in the mathematical model performance predictions. Product gas composition data obtained experimentally were within 10 to 15% of predictions by well-known equilibrium methods for the same reaction mixture ratio. Such factors as injection spray pattern, reagent flow rate, and pressure have been identified as contributing to fluctuations in process characteristics, particularly when attempts are made to scale prototype system data to full-size applications. Based on the results of approximately 100 tests at pressures to 200 psig, concept feasibility was established, negligible system vibration and propellant degradation were encountered, and moderate operating temperatures and reagent consumption were experienced.

Nomenclature

A = area
C = weight fraction
c_p = heat capacity
D = diameter or characteristic length
g = gravitational constant
h = convective heat-transfer coefficient
ΔH_v = latent heat of vaporization of condensible
k = thermal conductivity
M = molecular weight
Q = heat-transfer rate
R_c = reaction condensation ratio (mass condensibles W_{cp}/ mass total products W_{tp})
R_m = reaction mixture ratio (mass oxidizer/mass fuel)
ΔT = temperature differential
W_{cp} = mass condensed products
W_f = mass fuel reacted
W_{gp} = mass gaseous products
W_o = mass oxidizer reacted
W_r = mass reagent
W_{tp} = mass total combustion products
X = mole fraction
α = free convection heat-transfer constant
β = volumetric coefficient of thermal expansion
ρ = density
μ = viscosity
$\bar{}$ = superscript indicating bulk property
i = subscript indicating constituent property

Introduction

With the advent of the Titan II storable hypergolic liquid propellants (nitrogen tetroxide and 50/50 hydrazine/unsymmetrical dimethylhydrazine mixture), considerable interest developed in the possibility of a chemical reaction inside the main propellant tank for ullage pressurization. The potential elimination of a heat exchanger and reduction in pressurant storage tank requirements results in a lower propulsion system weight, thereby improving the overall vehicle mass fraction (usable propellant weight/liftoff weight). The primary advantages of high-density pressurant storage at low pressures and moderately low pressurizing gas density have been known for some time,[1] but the feasibility of such a system installed in a flight-type propulsion system was first demonstrated this past year.

A primary consideration in the development of a chemical pressurization system is to effect the pressurization process with precise pressure control and tolerable thermal levels in the tank wall and propellant, with a minimum of propellant degradation. To achieve this objective, a three-phase program was conducted involving subscale research tests, an analytical and design study, and a full-scale system demonstration test program. The research tests were performed to develop the injection system, obtain combustion data, establish operating pressure effects, and identify full-scale system design criteria. From the results of the experimental program, the most desirable injection method was selected, a mathematical model was formulated, and a full-scale flight-weight system was developed.

Process Description

Figure 1 is a pictorial representation of the pressurization phenomenon associated with the system developed. Reactant is stored under pressure in a small tank and intermittently injected into the main propellant tank by a pressure-switch controlled pneumatic valve. Reactant flow is initiated by a propellant tank low-limit pressure switch that opens the injector valve, forcing reactant into the propellant tank by a 100- to 200-psi injector differential pressure. The reaction occurs in a concentrated area below the propellant surface because of the penetration capability of the solid-stream surface injection technique. (This method was selected for optimum performance.) The energy of the reaction is partially absorbed by the liquid propellant, providing moderate pressure rise rates in the propellant tank. Reagent injection is terminated when the propellant tank high-limit pressure switch deenergizes the normally closed injector. Experimentation established the capability of such a pulse-mode injection pressurization system to control tank pressures within ±1% at an injection frequency of 2 to 5 cps and starting with a 5% initial ullage volume.

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* Design Specialist, Advanced Technology and Development Section. Member AIAA.

† Senior Engineer, Advanced Technology and Development Section. Member AIAA.

During the research program, it became apparent that the injection technique was of primary importance in establishing pressurization process characteristics. Because of the presence of one of the reactants in a relatively infinite quiescent quantity, the nature of the injected reactant is the major factor in determining the reaction mixture ratio (mass oxidizer/mass fuel consumed), associated combustion temperature and reaction product composition, and the amount of heat transferred to the propellant as a result of subsurface combustion. A precise definition of the combustion process is required because of the need to dissipate from 45–80% of the thermal energy into the liquid propellant in order to obtain moderate operating temperatures.

The pressurization process is further complicated by the fact that the quantity of gas generated depends not only on the apparent reaction mixture ratio (R_m) but also on the condensation ratio (R_c). The quantity of injected reagent required can be expressed as follows: for the fuel tank,

$$W_o = [W_{cp}/(1 - R_c)][R_m/(R_m + 1)] \qquad (1)$$

and for the oxidizer tank,

$$W_f = [W_{cp}/(1 - R_c)][1/(R_m + 1)] \qquad (2)$$

The mass of gaseous combustion products required is readily determined by the ideal gas law with recognition of the partial pressure of propellant vapor and possible presence of an initial inert pressurant. The quantity of condensed products and the reaction mixture ratio were determined experimentally. Based on the extent of experimental investigation performed, the mixing phenomenon associated with the reaction indicated that a considerable variation in the reaction mixture ratio is possible. For the solid-stream surface injection technique, however, this ratio is always in favor of the main propellant for the nitrogen-tetroxide-50/50 hydrazine-dimazine combination (i.e., fuel-rich in the fuel tank). Consequently, a minimum quantity of injected reagent is required to pressurize a given volume.

Analysis

A mathematical model of the chemical pressurization process was developed for the IBM 7094 digital computer. The model was based on thermodynamic analysis of the experimental system, empirical relationships derived from photographic observation of the combustion phenomenon, and interpretation of ullage gas and propellant composition data. The model does not attempt to resolve specifically the combustion reaction and kinetics but uses average material and energy transfer rates as determined from test data. In the absence of reliable test data, approximations may be obtained from one of the various combustion computer programs available.[2] The solution of simultaneous mass and energy differential equations on an incremental time basis permits the prediction of transient pressurization system characteristics for either a nonvolatile or volatile propellant whose vapors may dissociate. Only the internal thermodynamics of the propellant tank with environmental influence is considered, and process gas data and reagent supply information must be furnished. Unique features of the model include 1) the solution of developed equations for either liquid or vapor phase reaction inside the main propellant tank; 2) capability for common ullage pressurization; and 3) variation in system configuration, mode of operation, and process parameters.

Comparisons of predicted reagent consumptions, injector frequency, and operating temperature histories with full-scale system test results show encouraging agreement. But because of the complex nature of the reaction process, further investigation is planned to allow performance prediction for propulsion systems with extensive variations in configuration or propellant composition.

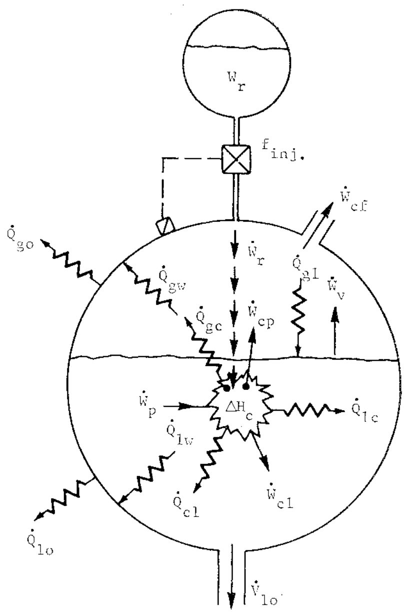

Fig. 1 Chemical pressurization process schematic.

General Logic

The mathematical model considers pressurization of a single tank, or two tanks in series with ullage gas from the primary tank used to pressurize the secondary tank. For single-tank pressurization, injection of reactant into the primary tank is controlled by either a pressure-actuated on-off valve or a constant-flow orifice. For constant-flow operation, a time increment is input, and transient conditions are calculated at the end of each interval until shutdown occurs. For cyclic or pulse (on-off) operation, high- and low-pressure values for the primary tank are inputs, and the dependent time interval is calculated for either pressure decay to the low level (injector off) or pressure increase by reaction to the high level. Pressure-sensing points may be either at tank top or bottom. The time and transient conditions are calculated at the end of each interval until shutdown occurs.

The computer program assumes homogeneous mass and energy distribution in both the liquid and gaseous phases and homogeneous temperature distribution in the tank wall adjacent to the gas and liquid. It also assumes that the ideal gas law applies to the ullage constituents. When a secondary tank is pressurized by gas crossflow from the primary tank, the entering gas is assumed to be unchanged. Subsequent conditions in the secondary tank are then computed in like manner for the primary tank.

Since the ullage gas usually consists of an inert pressurant, propellant vapor, and gaseous combustion products, the composition, average molecular weight, and bulk gas properties must be calculated at any instant. The composition of the gaseous combustion products is best determined by mass spectrometer quantitative analysis. However, good correlation has been obtained between actual data and calculated results from available combustion programs. Because of the quenching nature of the subsurface reaction, frozen product composition quenched to ambient tank conditions should be used (rather than a shifting equilibrium composition) as the product temperature is reduced from the adiabatic flame temperature to the ullage gas temperature. Condensible constituents should be considered to liquefy and remain in the liquid-phase propellant. With this information, the bulk gas properties are calculated as follows:

$$\bar{\mu} = \Sigma_i X_i \mu_i M_i^{1/2} / \Sigma_i X_i M_i^{1/2}$$

$$\bar{c}_p = \Sigma_i C_i c_{pi} \qquad \bar{k} = \Sigma_i X_i k_i \qquad \bar{\beta} = \Sigma_i X_i \beta_i$$

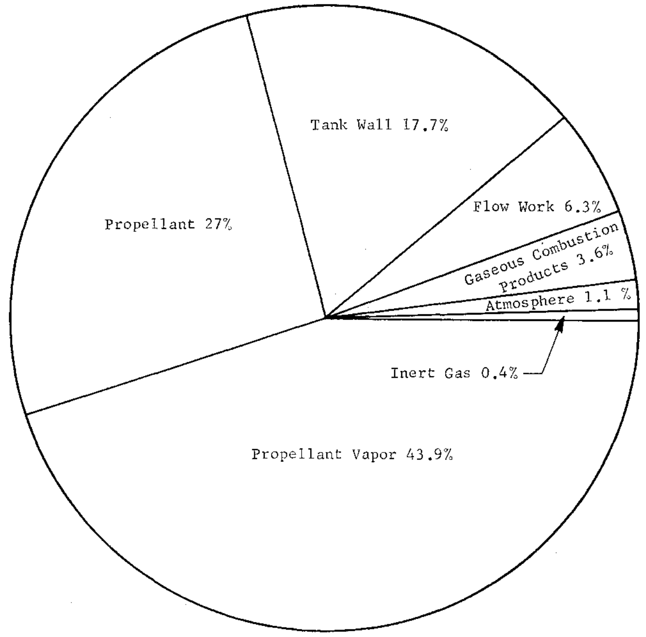

Fig. 2 Final distribution of energy released in typical reaction.

Heat Transfer

Heat transfer is considered between the gas and the adjacent wall, the tank-wall and the outside environment, the gas and the liquid, the liquid and the adjacent tank wall, and the tank wall and the outside environment. External heat transfer is calculated by $Q = hA_{\text{wall}}(T_{aw} - T_{\text{wall}})$, where T_{aw} is the adiabatic wall temperature. Both h and T_{aw} are tabular input to the program and are based on aerodynamic heating calculations for particular mission profiles, or they may reflect simple heat transfer from the ambient environment.

Calculations of internal heat transfer between the liquid and adjacent wall are based on the natural convection relationship,

$$h\,\frac{D}{k} = \frac{1}{\alpha}\left(\frac{D^3p^2g\beta\Delta T}{\mu^2}\right)^m\left(\frac{c\mu}{k}\right)^m$$

where it is assumed that $m = n = 0.25$ and $\alpha = 4$.

Because of the intermittent pressurization process, the ullage gas experiences some degree of forced convection. To account for this heat transfer from the ullage gas, α, m, and n are empirically modified to fit test data.

Combustion Theory

Convective heat transfer between the hot combustion gases in the combustion zone and the surrounding liquid is calculated by the standard relationship $Q = hA(T_f - T_l)$, where T_f is the reaction adiabatic flame temperature and T_l is the bulk liquid temperature. By relating the unit flow rate of the injected reagent to the area of the combustion zone/liquid interface (A_c), we obtain $A_c = C_a(\dot{W}_r)^{2/3}$, and for the film heat-transfer coefficient $h = C_h(\dot{W}_r)^{0.2}$, where C_h and C_a are empirically derived constants.

Simplifying, the heat transferred between the hot combustion gases and the surrounding liquid

$$Q = C_hC_a(\dot{W}_r)^{0.87}(T_f - T_l) \tag{3}$$

Total condensation of the condensible combustion products occurs in the combustion zone with a resultant enthalpy increase in the liquid:

$$Q = W_{cp}\left(\Delta H_v + \int_{T_l}^{T_f} C_{cp}\,dT\right) \tag{4}$$

where ΔH_v is the condensibles' latent heat of vaporization at T_l, and C_{cp} is the condensibles' constant pressure specific heat (vapor). The remainder of the energy liberated by the combustion reaction goes into the ullage with the gaseous combustion products. A typical energy balance for an oxidizer tank is shown in Fig. 2.

The reaction mixture ratio R_m and the ratio of condensible combustion products to total combustion products R_c are required to calculate a material balance around the combustion zone. The injected reagent flow rate is determined by the injector orifice and the pressure drop across the orifice. A material balance was performed for the reaction by comparing the amount of combustion products, based on ullage gas analyses, with the measured quantity of injected reagent. Estimation of the condensible combustion products was keyed to an oxygen balance for the fuel tank reaction and a hydrogen and nitrogen balance in the oxidizer tank.

Injection Dynamics

A study of the injection phenomenon was undertaken because the mixing technique associated with the reaction has a significant influence on the reaction mixture ratio, product composition, heat transfer to the bulk propellant, and system response. This study was aimed at establishing penetration rate and maximum depth of penetration of the injected stream into the main propellant by an analogy with a nonreacting process. The amount of penetration of the injected reagent into the main propellant is of primary significance in determining the combustion zone area and related heat transfer to the bulk liquid. In an attempt to define the primary factors influencing this phenomenon, a theoretical and experimental examination of the nonreacting solid-stream surface injection process was performed.

For the nonreacting process a finite depth of penetration can be readily determined from an energy balance when the sum of the potential and kinetic energy of the stream, diminished by the energy dissipated in frictional, inertial, and drag forces, is equal to zero. This theory was verified by test when a maximum penetration distance was noted. However, for the reacting-type process the penetration appears to be limited only by the injection duration or the physical boundary of the system. Based on the lack of correlation with theory, more extensive investigation of the penetration phenomenon with the reacting process is required to include propellant and injectant combustion rates and to identify the effects of combustion zone counterflow currents induced in the main propellant.

Experimental Program

The experimental program consisted of more than 100 subscale tests, including both single-tank and common-ullage configurations. Testing was performed in a special scale model test fixture that was 2% of the full-size system. A nominal 2½-min propellant expulsion was used, based on typical rocket vehicle mission durations. All tests were fully instrumented, and gas composition data and motion pictures of the combustion process were obtained on approximately 80 runs. During this portion of the program, the pulse mode injection system was developed and experimental data acquired for variations in injector-nozzle type, size, and location and at operating pressures of 25, 100, and 200 psig. Satisfactory system operation was achieved with injection pressurization of the initial ullage, during variable outflow and restart, and with induced random vibration. The basic test program described herein pertains to single-tank pressurization only. The common-ullage configuration was not recommended because of several special design considerations required for stable pressure control.

Test Configuration

To evaluate the effects of injection technique and acquire necessary data for full-scale system design, special 5⅓ ft^3 test tanks were fabricated from ⅝-in. wall 6061-0 aluminum helium spheres. Figure 3 shows the general equipment arrangement and the flow schematic. Each tank contained two 3-in.-diam × $\frac{3}{4}$-in. Tuf-flex camera ports for combustion photography and a 1-in.-diam Pyrex propellant outlet for visual observation of the expelled propellant. The tank outlets were contoured to prevent cavitation and dropout, and baffled to reduce vortexing and allow containment of the subsurface combustion zone. Additional ports were provided for reagent injection, overpressure protection, propellant level sensors, common ullage, instrumentation, and propellant and ullage gas sampling.

A pulse-mode pressurization system was selected and developed, based on positive shutoff, moderate operating temperatures, and precise pressure control with emphasis on system versatility. The injector was fabricated from a commercial-type chemical spraying device with a 0.0135-in.-diam orifice and was pneumatically operated. A Belleville-type pressure switch control of the four-way solenoid valve was used. This design allowed interchangeability of injector nozzles and permitted surface or subsurface reagent impingement by adjusting the length of insertion into the test tank. Reagent was supplied from a 1-in.-diam × 18-in. calibrated Pyrex reservoir pressurized to maintain a 75-psi injector differential pressure. Overpressure protection was provided by dual 2-in.-diam burst disks and a pressure switch-actuated 2-in.-diam vent and relief valve. Control console logic included automatic test sequencing, malfunction detection, and automatic corrective actions with capability for manual override. All systems were remote operated and fail-safe, with high-response isolation valves provided in the reagent supply and common ullage lines.

Test Procedure

The scope of the experimental program included an evaluation of solid-stream and 15° fan spray reagent injection with surface and subsurface impingement and a determination of common ullage feasibility. Preliminary experimentation at a 25-psig tank pressure established injector size and desirable injection methods. Subsequent tests were performed with the common ullage configuration and single-tank system at 25, 100, and 200 psig to establish operating pressure influences on the pressurization process. To determine system capability, tests were performed with a minimum 5% initial ullage pressurized by the injection system with the pressure maintained during zero, constant, and variable propellant outflow. All tests were $2\frac{1}{2}$ min long except for demonstrations simulating restart capability, when an unpressurized 10-min coast period was included.

The normal loading sequence first required filling the calibrated injectant reservoir and then pressurizing it to the desired level with nitrogen. The initial load was recorded after entrained vapor was bled from the injection system, which was then placed in a manual mode for safety. Gas sampling, instrumentation, photographic, and television equipment was then readied and a propellant sample procured. Propellants were loaded to the identical ullage (either 5 or 30%) for each test by monitored ultrasonic liquid level sensors. Prepressurization was generally accomplished by the automatic injection system; however, early tests used helium for safety. Propellant outflow was automatically initiated by the control console and manually adjusted using remote operated modulating-type propellant valves. The pressurization process maintained the tank ullage pressure within ±1% during the expulsion of 95% of the initial propellant load. A propellant low-level sensor automatically terminates injection and sequences the propellant valves closed. Final propellant sample and ullage gas sample were taken immediately after each test.

Data Acquisition

The instrumentation monitoring system employed Consolidated Electrodynamics Corporation (CEC) oscillographs and Sanborn and Bristol recorders with all systems calibrated to insure a 1% data accuracy. Pressures were measured by calibrated CEC unbonded strain-gage, bridge type transducers and were temperature compensated. Tank wall temperatures were measured by copper-constantan type T thermocouples bonded to the external surface in three locations. Shielded chromel-alumel type K thermocouples were used for measuring liquid temperatures and the ullage gas temperature profile by use of a thermocouple rake inside the tank. Propellant flow rates were obtained from Cox turbine-type flowmeters with either a Dynac digital readout or continuous Sanborn recording. The subscale test fixture was suspended on wire ropes to allow acquisition of vibration data, which were obtained by triaxial crystal-type Statham accelerometer.

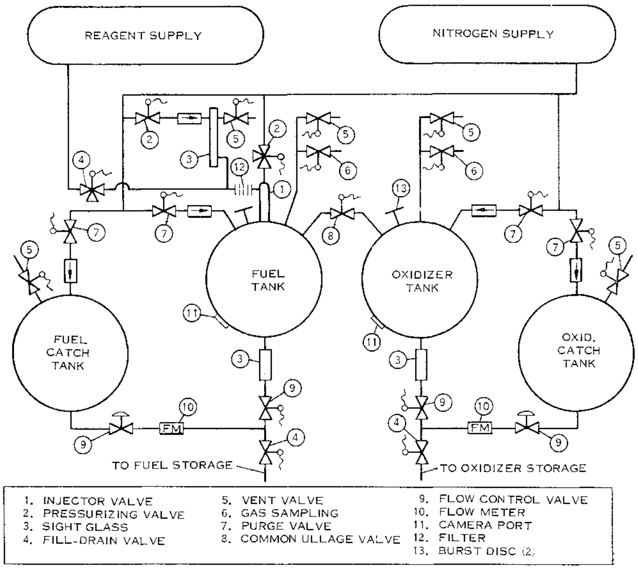

FIG. 3 CHEMICAL PRESSURIZATION TEST SYSTEM SCHEMATIC

Fig. 3 Chemical pressurization test system schematic.

In addition to photographic and television observation of the combustion process and discharged propellant, gas samples were obtained during and after each test. Approximately 120 specimens were acquired in evacuated glass bottles. Each sample was analyzed within 48 hr to an accuracy of ±200 ppm, performed on a mass spectrometer by the National Bureau of Standards at Boulder, Colo. Propellant analysis was performed by combinations of wet chemistry and thermal conductivity methods at the Martin Company Quality Control Laboratories to determine the quantity of water and other contaminants formed in addition to identifying any changes in chemical composition. Condensate obtained from the tank ullage was analyzed by mass spectroscopy, x-ray diffraction, infrared spectroscopy, and wet chemistry. A positive identification of these condensed products was not obtained because of the complex nature of the reddish brown substance; however, the primary constituents included UDMH and ammonia.

Experimental Test Results

Based on data and process information acquired during the subscale program, the feasibility of the chemical pressurization method was verified and considerable knowledge acquired for incorporation in the mathematical model used for predicting full-scale system performance. One of the most significant discoveries relating to this pressurization process was the effect of injection method on operating characteristics shown in Table 1 for the fuel tank. Each of the four injection methods produced a characteristic gaseous product composition and flame temperature as a result of the variation in apparent reaction mixture ratio. Because of the complex nature of the reaction, some empirical techniques are required for system performance prediction.

Table 1 Fuel tank injection system evaluation at 25 psig

Injection technique	ΔT gas, °F	ΔT fuel, °F	ΔT wall, °F	Reagent consumed, lb	Mixture ratio, W_o/W_f	Weight gas, lb	MW gas, $P_v = 0^a$
Surface solid	266	27	37	0.412	0.62	0.579	13.4
Surface spray	707	2	82	0.634	2.6	0.755	22.7
Subsurface solid	45	33	4	0.468	0.8	0.778	15.6
Subsurface spray	37	29	2	0.412	1.0	0.900	17.5

[a] P_v = propellant vapor pressure.

Actual flame temperatures were determined from an energy balance and supported by a qualitative comparison of combustion photographs. Variation in system operating temperatures was primarily influenced by the location of the combustion zone and the extent of reaction quenching. A similar thermal behavior was also apparent from a limited number of tests performed in the oxidizer tank, but the combustion product gas composition and reaction mixture ratio were relatively constant. Table 2 summarizes typical pressurizing gas composition for either tank as determined by mass spectrometer.

Solid-stream injection with surface impingement was selected as the optimum method for pressurizing the N_2O_4/UDMH-N_2H_4 propellant combination because of the low-molecular-weight gas obtained and desirable system operating temperature experienced. The resultant low-density pressurant is required to reduce system weight in flight applications. Subsurface injection was not considered practical for missile use because of the ±3-*g* vibration levels encountered in the longitudinal axis. With the injection method selected, an average of 0.3% by weight water is formed in the propellants with an insignificant change in composition or viscosity for a 25-psig, 150-sec test. Visual observation of the propellant during expulsion verified the absence of entrained gases or solid contaminants.

Typical data for the subscale system at a 25-psig tank pressure are shown in Fig. 4. The pressurization system exhibited stable pressure control during initial pressurization of the 5% ullage volume, rapid start transients, pressurization after a 10-min coast period, and during normal operation with an induced random horizontal vibration of $\pm\frac{1}{4}$ in. at a frequency between 1 and 3 cps. The performance of the subscale system at higher pressures is summarized in Fig. 5, with the pertinent parameters plotted.

In general, the reagent consumption is slightly higher in the oxidizer tank because of the lower operating temperatures and change in reaction characteristics. The increase in system operating temperatures at higher pressures appears to present a limitation for this injection method; however, further experimentation may alleviate excessive temperatures by subsurface injection during the first portion of propellant outflow. The temperatures are relatively moderate because of the large heat capacity of the thick-walled test vessel and small quantity of pressurant generated.

Demonstration Program

Primary objectives of the full-scale demonstration test program were 1) to demonstrate system capability in flight weight propellant tanks; 2) to accumulate sufficient data for verifying reliability, repeatability, and performance predictions; and 3) to provide design information for future system development. Demonstration of the chemical pressurization process was performed in identical fuel and oxidizer tanks at 37 psia. The tanks were 279-ft^3 capacity, chem-milled aluminum missile propellant tanks, modified slightly to accommodate the requirement of the demonstration test program. The general test procedure, data acquisition, and system configuration were identical to those used in the experimental program, except for the reagent supply and measuring system. For the demonstration tests, reagent was stored in a 0.523-ft^3 spherical steel tank suspended from a load cell. The differential reagent weight recorded provided a direct readout that showed good correlation with reagent consumption determined by an integration of the injector switch trace and known flow capacity of the injector.

Demonstration Test Results

Four tests were performed on the fuel tank and two on the oxidizer tank to achieve the program objectives. All tests were completed successfully, including one restart test with a 10-min coast period for each tank. Precise pressure control of 37 ± 0.25 psia was achieved for all tests with the experimental system injector incorporating a 0.047-in.-diam orifice tube. Reagent consumption and operating temperatures were within allowable predetermined values. No entrained gas was observed in the propellant outflow line sight glass, and there were no noticeable tank vibration or pressure surges. A sound recording made of the combustion process, however,

Table 2 Gaseous combustion product characteristics at 25 psig for various injection methods

Injection technique		Combustion products analysis, vol. %									Ullage gas molecular weight	
Fuel tank	Oxidizer tank	N_2	H_2	CH_4	NH_3	NO	CO_2	CO	H_2O	O_2	$P_v = 0^a$	P_v = actual^a
Surface solid	...	30.0	47.4	11.1	9.2	1.6	0.4	...	...	...	13.4	13.4
Surface spray	...	60.0	11.8	18.8	3.4	3.1	3.0	...	...	...	22.9	22.9
Subsurface solid	...	28.1	41.3	10.1	4.9	1.0	0.4	14.5	...	...	15.6	15.6
Subsurface solid	...	35.8	37.5	13.0	3.4	1.0	0.2	9.5	...	...	16.4	16.4
..	Surface solid	58.6	1.9	1.0	...	...	17.9	...	14.1	6.7	29.11	38.52
..	Surface spray	59.8	3.5	0.6	1.4	...	11.4	...	8.4	15.0	28.45	34.77

[a] P_v = propellant vapor pressure.

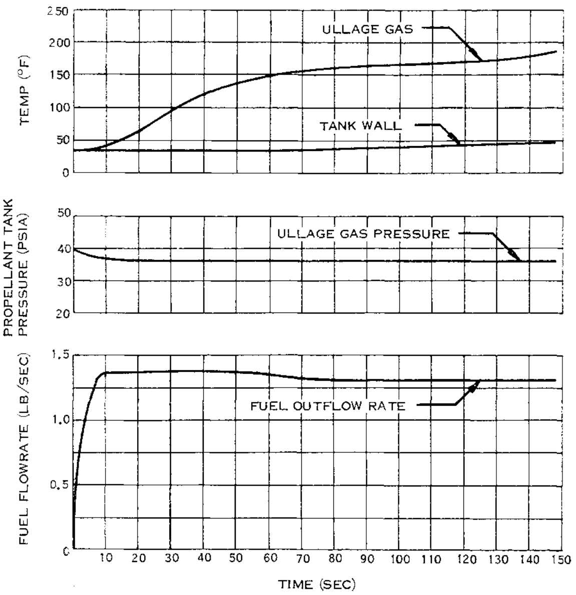

Fig. 4 Typical single-tank pressurization system performance with solid-stream surface injection.

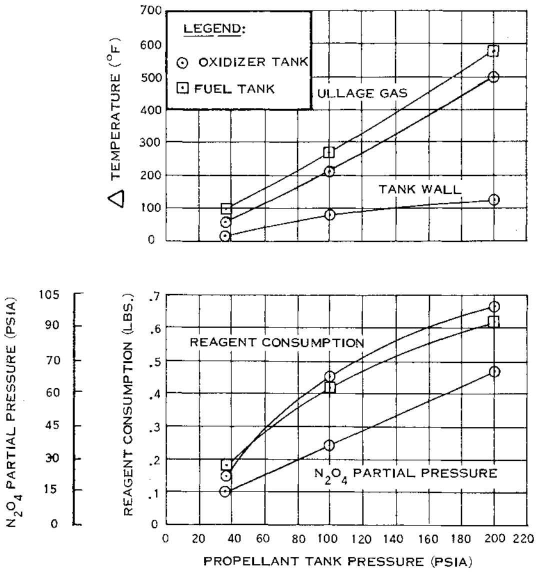

Fig. 5 Parametric test data summary.

indicated a very high rate of gas generation. The most significant observation concerning the full-scale system data was the change in reaction mixture ratio encountered from the small-scale test program. Table 3 compares the experimental and demonstration systems' performance.

A complete explanation for the change in process characteristics is not known, but the increase in injector size was probably a significant influence parameter. The gas composition was relatively unaffected and agreed with the experimental system data.

Figure 6 compares actual and predicted data for the oxidizer tank. The predicted reagent consumption was adjusted to reflect the actual variation in reaction mixture ratio. The initial injector frequency was 5 cps max with pressure controlled to within ±0.7 psia. The test was performed with helium prepressurization of the 5% initial ullage, 750-gpm propellant outflow rate, and a 2½-min test duration (except for the restart tests with a 10-min coast period). Results were similar with the fuel tank.

Design Considerations

Although a satisfactory technique has been developed for predicting the thermodynamic performance of a chemical pressurization system for the Titan II storable propellants, a considerable amount of additional investigation is needed to identify process influence parameters. Based on the extent of testing performed, empirical techniques have been developed to describe satisfactorily a good portion of the physical-chemical phenomenon. A more detailed examination of the injection and combustion process, however, will improve the accuracy for performance prediction of various full-scale system configurations.

Adiabatic Flame Temperature

The adiabatic flame temperature normally is determined by a separate IBM 7094 propellant performance program developed by NASA, since a wide variety of operating conditions can be examined in a relatively short period of time. This parameter can also be determined by a hand computation based on the heats of reaction of products and reactants, as was previously described for calculating the actual flame temperature from test data. Although the theoretical value has never been verified by a test measurement, the energy balance appears to support this method. Errors in the assumed reaction mixture ratio, needed in the mathematical model developed, will affect the amount of heat released to the system.

Reaction Mixture Ratio and Condensation Ratio

The verification or direct measurement of the reaction mixture ratio (W_o/W_F) or the condensation ratio [$W_{cp}/(W_o + W_F)$] has not been possible because of the relatively small quantities involved in the reaction and inconsistent chemical

Table 3 Reaction process mass balance comparison

Configuration	Tank pressure, psia	Mole weight, lb/lb m	Combustion product, lb gas	Water weight, lb	Total condensate, lb	Reagent weight, lb	Reaction mixture ratio, W_0/W_f	Condensation ratio, $W_{cp}/W_0 + W_F$
Experimental program (5.33-ft^3 tank)								
Fuel tank	37	15.77	0.412	0.208	0.316	0.278	0.62	0.44
Oxidizer tank	37	29.51	0.313	0.165	0.192	0.151	2.34	0.38
Demonstration program (279-ft^3 tank)								
Fuel tank	37	15.98	17.9	1.9	3.6	2.9	0.16	0.167
Oxidizer tank	37	30.5	20.8	3.27	16.54	3.3	10.32	0.443

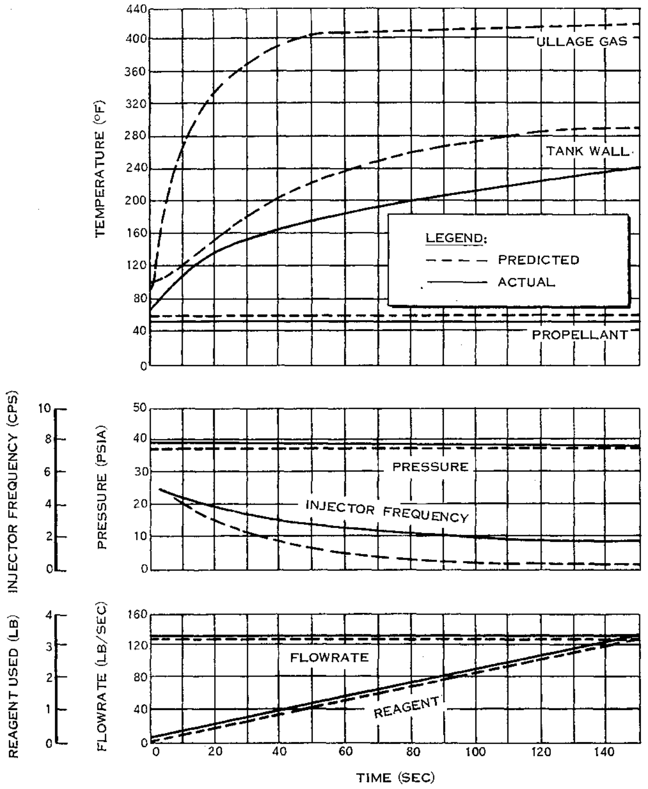

Fig. 6 279-ft^3 pressurization system performance; Aerozine 50 into N_2O_4.

determinations. Consequently, a material balance technique was utilized. This method was originally based on a knowledge of the quantity and composition of gaseous products formed and the amount of injected reagent consumed. At present, these parameters must be determined by test because of unknown influence factors. In the absence of test data, the NASA computer program is employed at the inverse equivalence ratio (stoichiometric mixture ratio/actual mixture ratio) previously established for the Titan II propellants. The quantity of condensed products is generally determined by assuming that the state of the fluid is dictated by the bulk liquid propellant temperature. The amount of condensibles for the Titan II propellants is generally less than 0.3% and is not considered an engine performance detriment. The quantity of injected reagent required must be increased to compensate for this condition. To determine maximum possible quantities of condensate formed, a material balance can be written which assumes that all available hydrogen and oxygen combine to form water. These values for the Titan II propellants are 1.1615 lb H_2O/lb fuel injected in the oxidizer tank and 0.7826 lb H_2O/lb N_2O_4 injected in the fuel tank.

Propellant Vaporization

Experimental data have shown a negligible quantity of propellant vapor in the fuel tank. Oxidizer vapors amounted to approximately 30% for a range in tank operating pressure of 25 to 200 psig. This condition apparently results from the high rate of propellant vaporization in the combustion zone. In the case of nitrogen tetroxide, the large quantity of heat required for vaporization reduces the operating temperature of the system, causing a greater quantity of reactants to be consumed. The additional propellant required for both the reaction and vaporization must be considered in assessing the pressurization system weight penalty and determining vehicle propellant load requirements. This weight penalty, however, may not be a significant disadvantage in certain cases where the propellant has a low vapor molecular weight, such as for liquid hydrogen.

Zero-Gravity Pressurization

Although no reduced gravity tests were performed, an observation of the pressurization process characteristics allows some speculation for space vehicle application. Since the heat generated by the reaction is an important factor in improving pressurization system performance by reducing the ullage gas density and consequently system weight, injection during a coast period is not recommended. Further, pressurization before a restart can be accomplished in a minimum time interval because of the exceptional gas-generating capability of this type of pressurization method. If continuous pressurization during the coast period is required, special precautions may be required to insure positive reaction control. Two situations warrant careful consideration:

1) The reaction may be affected at the tank wall or critical areas inside the propellant tank where heat damage would result.

2) The reagent may be allowed to vaporize and not react inside the tank, causing a fuel-oxidizer atmosphere that could be detonated by a liquid phase reaction.

To eliminate these two possibilities, the recommended propellant tank design would incorporate surface tension principles to establish positive propellant orientation and to insure a liquid phase reaction at all times. A nonvolatile reagent or an inert gaseous product would be desirable in this situation to improve system reliability.

Propellant Tank Pressure Control

Fundamental pressure control can be achieved by pressure-switch actuation of an electrically operated solenoid valve of low-current drain. The present state of the art limits the maximum injector frequency attainable to approximately 35 cps. By adjusting the injector orifice size and pressure control band, this pressurization method will generally exceed present modulating-type pressure control systems. Overpressure protection for a chemical-type pressurization system should include an injector isolation valve to terminate reagent supply in the event of control system or injector malfunction. Normal pressure relief devices should be incorporated in the propellant tank with sufficient flow capacity and response to accommodate a failed open injector.

Conclusions

The feasibility of applying the chemical pressurization process to missile propellant tanks has been established. Precise pressure control and moderate operating temperatures of the chemical pressurization system promote consideration of this process for a variety of applications, including missiles, rocket sleds, facility propellant supply systems, and possibly as a means of petroleum recovery. The feasibility of this pressurization method for missile applications considered propellant degradation and vibration in addition to system weight, safety, reliability, simplicity, and other operating characteristics. The exceptional capability and promise of this type of pressurization process have been established under a variety of operating conditions. In addition, the development of a suitable method of predicting chemical pressurization thermodynamic performance will extend the range of application eventually to other system configurations or propellant combinations. At present, pressurization of cryogenic propellants, high-pressure applications, and thixotropic propellant pressurization are being studied. Although considerable potential is apparent from an investigation of weight reductions achieved with this pressurization method, additional study of the reaction kinetics and process influence parameters is required before this technology can be applied to future vehicles that require high levels of performance and reliability.

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Ignition and Combustion of Aluminum in Small-Scale Liquid Rocket Engines

L. E. DEAN,* R. C. KEITH,† T. L. SUMNER,‡ AND M. V. TAYLOR§
Aerojet-General Corporation, Sacramento, Calif.

The combustion of aluminum particles was investigated in nine O_2(gas)-H_2(gas)-Al burner tests and 20 100-lbf-thrust O_2(gas)-H_2 (gas)-Al rocket-engine tests. The aluminum powder was transported to the burner or the thrust chamber by entraining it in the H_2 gas by means of a pneumatic transport system. The burner tests indicated that the ignition delay of aluminum powder clouds was dependent on the O_2-H_2 flame temperature and on the aluminum particle concentration. The 100-lbf-thrust engine tests, conducted at a nominal chamber pressure of 300 psia, yielded an experimental specific impulse of approximately 80% of the theoretical value. The major areas of performance loss, in terms of percent of theoretical specific impulse, were heat transfer and deposition, 10%; nozzle geometry and shear drag, 3%; and gas-particle flow losses, 1%. The corrected experimental I_s is about 94% of the theoretical specific impulse.

Introduction

THEORETICAL calculations have indicated that the performance of many propellant systems can be increased by metal additives. Maximum specific impulse usually occurs when the metal additive is burned stoichiometrically, and the hydrogen is utilized as a working fluid. The metal to be used as an additive should have a low molecular weight and a high heat of combustion. The O-H-Al system was chosen for the experimental work. Gaseous oxygen and hydrogen were used to minimize operational difficulties, and the aluminum was delivered to the combustor in the form of powder suspended in the H_2 gas.

Metal powder combustion was reviewed by Hartmann[1] and more recently by Markstein.[2] Friedman and Macek[3] found that, when single particles of aluminum were injected into a propane-air flame, ignition took place only when the flame temperature was above 4100°R. Since the respective melting points of aluminum and aluminum oxide are 1678° and 4172°R [Joint Army-Navy-Air Force (JANAF) data], the high ignition temperature of the aluminum was attributed to the protective effect of the inert oxide coating present on the metal particle. The coating isolated the unreacted metal from the oxidizing atmosphere, thus ignition could occur only when the oxide coating melted and allowed the oxygen to diffuse through the molten oxide and react with the metal and/or the metal to diffuse through the oxide shell to react with the oxygen atmosphere.

The earlier work of Gordon[4] also demonstrated that a temperature greater than 4200°R was required to ignite single aluminum particles. Gordon also determined that a cloud of aluminum particles would ignite and burn at a much lower flame temperature than an isolated aluminum particle. Gordon attributed the decrease in ignition temperature to the cooperative effects of the many particles heating the surrounding medium and to the conservation of radiant energy by reabsorption by neighboring particles. The same "cloud" effect was also found to occur in the ignition of boron.

Cassel and Liebman[5] found that the ignition temperature of magnesium and 50-50 magnesium-aluminum alloys decreased as the dust concentration increased. They pointed

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* Manager, Engineering Research Department, Research and Advanced Technology Division, Liquid Rocket Plant. Member AIAA.

† Manager, Physics Laboratory, Research and Advanced Technology Division, Liquid Rocket Plant.

‡ Project Engineer, Engineering Research Department, Research and Advanced Technology Division, Liquid Rocket Plant.

§Chemist, Engineering Research Department, Research and Advanced Technology Division, Liquid Rocket Plant.