Liquid Fluorine No-Vent Loading Studies

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No-vent loading is a new approach for conducting load operations with high-energy propellants where release of toxic and reactive vapors must be minimized. Fluorine, oxygen difluoride, Flox, and diborane all fall into this category. Results of a two-phase experimental and analytical loading study are presented. During phase I, a simplified analytical model was formulated and feasibility of the concept was demonstrated in a 30-gal tank using liquid nitrogen as a referee propellant for liquid fluorine. Phase II included refinement of the analytical model to eliminate some of the simplifying assumptions, no-vent loading tests with liquid fluorine in a 165-gal tank, and correlation of the experimental data with the refined model. Program results showed the no-vent loading concept to be feasible. The analytical model can be used as a starting point in developing techniques for cooldown, transfer, and load and hold operations for flightweight upper stage systems.

Introduction

HIGH-ENERGY propellants are receiving increased attention for application to advanced upper stages and space propulsion systems.[1,2] Propellants under consideration include fluorine/hydrogen, oxygen difluoride/diborane, and Flox/methane. The advantages of using these propellants can be identified, but there are also practical problems associated with their use which must be considered. These problems arise primarily from the highly reactive and toxic nature of this class of propellants. For example, exposure of personnel, hardware and surroundings to the toxic and highly corrosive fluorinated oxidizer fumes must be minimized or eliminated if possible. It is therefore highly desirable to eliminate venting from the upper stage oxidizer tank during the entire mission including load, hold and launch operations. This is also true for diborane fuel which is toxic and pyrophoric.

Previous studies investigated methods of eliminating fluorine tank venting in typical F_2/H_2 upper stages for mission durations up to 90 days. The next step was to eliminate the need for fluorine tank venting during prelaunch load and hold operations. Most experience on the loading of cryogenic liquids has been obtained with systems where venting was employed, e.g., systems using liquid oxygen or liquid hydrogen. No information was found on loading cryogens without venting. As a first approach to this problem, an analytical and experimental study on no-vent loading of liquid fluorine was conducted to determine the feasibility of the no-vent loading concept, to demonstrate the concept on a reasonable scale using fluorine, and to derive an analytical model of the process for use in flightweight system studies.

The no-vent loading of a propellant is basically a nonadiabatic compression of the ullage gas. The ullage gas prior to loading can be either a mixture of noncondensable gas and propellant vapors or propellant vapor only. If a gas mixture is present, the amount of noncondensable gas must be limited to prevent tank overpressurization by gas compression during loading. In either case, the correct initial conditions must be established to circumvent tank implosion during loading.

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The approach used was to evaluate the effects of propellant loading rate and initial gas composition on the loading process only. The effects of initial two phase flow into the tank, geysering, or rapid chilling of the noncondensable gas were not evaluated since the tank and ullage gas were initially conditioned to approximately the entering liquid temperature.

For a flightweight system, loading time on the order of 15 to 20 min and maximum tank pressure of about 70 psia appear reasonable and the tests were conducted to bracket these values. No attempt was made to circumvent a negative pressure differential across the battleship test tank since an understanding of the no-vent loading process itself was desired. The study was conducted in two phases. During phase I, a simplified analytical model was formulated and feasibility of the concept was evaluated on a small scale using liquid nitrogen as a referee propellant for liquid fluorine. Phase II of the program included refinement of the analytical model to eliminate simplifying assumptions whereever possible, demonstration of the feasibility of loading liquid fluorine without venting in a 165-gal tank, and correlation of the experimental results with the refined analytical model.

Liquid Nitrogen Loading

The primary objectives of this phase of the study were to demonstrate the feasibility of the no-vent loading concept and to derive an analytical model of the process. Testing was conducted on a small scale using liquid nitrogen as the propellant. In performing this preliminary assessment, a basic understanding of no-vent loading was obtained and information on test system requirements and test procedures was acquired for later application on the tests with liquid fluorine. A simplified analytical model of the process was used to correlate the experimental data.

Analytical Model

A simplified analytical model and computer program was derived which simulates the no-vent loading process in the following steps: 1) initial conditions are specified; 2) liquid enters the tank at constant flow rate and temperature; 3) loading is terminated at either the final ullage volume or maximum pressure specified.

Two distinct fluid conditions inside the tank are considered; these are the bulk liquid and the bulk gas or ullage. The bulk gas is considered to be either pure propellant vapor (nitrogen or fluorine) or an ideal mixture of propellant vapor and a noncondensable gas (helium). The model predicts ullage pressure and temperature and volume histories of the

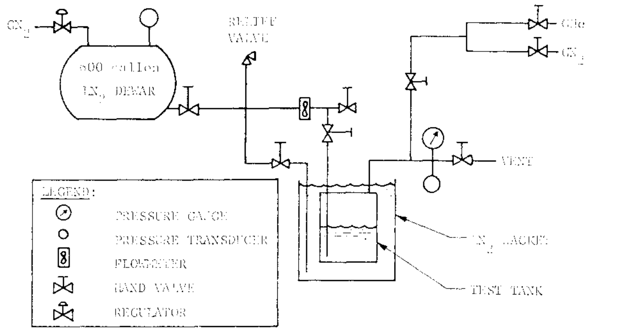

Fig. 1 Test system for liquid nitrogen no-vent loading.

bulk gas and liquid. It is characterized by the following simplifying assumptions: 1) the ullage gas is considered to behave ideally; 2) temperature and concentration gradients within the bulk gas and liquid are not considered, but differentials can exist between the bulk gas and liquid; 3) temperature of the tank wall is constant and uniform from top to bottom; 4) all gas condensed on the tank wall is added to the bulk liquid instantaneously; 5) the temperature and flow rate of the liquid entering are constant; 6) no heat transfer through tank supports or penetrating tubing is considered; 7) the tank is cylindrical with flat bottom and top.

The mass balance considers liquid entering as well as the mass transfer between the bulk gas and bulk liquid. Mass transfer between the gas and liquid occurs by condensation of propellant vapor on the walls and either vaporization or condensation at the gas-liquid interface.

An energy balance is made for each of the two fluid regions. These energy balances consider heat transfer between the bulk fluid and tank wall and between gas and liquid. Heat transfer by free convection for vertical and horizontal plates is used. Also, the Nusselt correlation[3] is employed in calculating the heat transfer through the condensing film on the wall. In addition, the energy balances consider the mass transfer occurring between gas and liquid. Liquid entering the tank is included in the energy balance for the bulk liquid. In conjunction with the energy and mass balance calculations, the model calculates ullage volume and partial pressures of the gaseous components. The mass and energy balances and heat and mass transfer mechanisms were developed previously by Fester, Pizzolato, and Page.[4] This reference should be consulted for more detail.

Simplified thermodynamic relationships are employed. The equation of state for an ideal gas is used and liquid density and vapor pressure are calculated from curve fit equations as a function of bulk liquid temperature. The saturation temperature for the condensing film on the tank walls is calculated as a function of the partial pressure. Specific heats of the pure components and heat of vaporization of the liquid are considered to be constant. The curve fit equations and constant values used apply to a pressure range of 14.7 to 200 psia and a temperature range of 130 to 200°R.

Properties of the binary gaseous mixture are calculated from the pure component properties and the corresponding mole fractions. Transport properties such as thermal conductivity and viscosity are input for the pure components and considered constant over the temperature range specified above. For the viscosity and thermal conductivity of the binary gaseous mixture, relationships derived by Wilke[5] are used. A constant diffusion coefficient is used for the binary gaseous mixture.

Tests

Liquid nitrogen was loaded into a nonvented, 30-gal cylindrical tank jacketed with liquid nitrogen as shown in Fig. 1. An initial gas mixture of helium and nitrogen was established in the tank prior to loading. The partial pressures of helium and nitrogen in the initial mixture were 4 and 12 psia, respectively. This gas mixture was selected to provide a tank pressure at or slightly above 100 psi at the end of loading. A detailed description of the test system, instrumentation and test procedure is given in Ref. 6.

Six test runs were made to evaluate the no-vent loading concept using liquid nitrogen; this included two runs each at loading rates of 1, 2, and 5 gal/min. Loading times ranged from 6 to 23 min resulting in final tank pressures between 105 and 110 psia and final ullage volumes between 5 and 8%.

Data Correlation

After completion of the test program and derivation of the analytical model, a correlation between the experimental and analytical data was made. From the six tests conducted, one test for each of the three loading rates was selected. This selection was based upon the consistency of the measured loading rates, smoothness in the pressure curves, and completeness of the data acquired. A loading start time, an approximate loading rate, and the initial conditions were determined from the recorded data for each of the three selected tests. These parameters were then used as input data to the computer program. Comparison of the calculated loading data and the test data showed that, in general, the simplified analytical model could simulate the no-vent loading process. Results for the 1 and 2 gpm loading rates are shown in Fig. 2. The correlation is quite good considering that an unsophisticated test program and a simplified model were used and no empirical adjustments were made in the analytical model. The deviations resulted from: 1) uncertainty in initial conditions; 2) variation in the manually controlled loading rates; 3) initial transients observed in the test data; 4) assuming that the wall temperature was constant.

The results obtained from this preliminary assessment with liquid nitrogen established the feasibility of loading a cryogenic liquid without venting. Good agreement was obtained between the experimental results and data calculated by the simplified analytical model. In addition, the experience gained proved useful in conducting subsequent tests with liquid fluorine. For example, the desirability of investigating loading with no helium in the tank was established. This would minimize tank pressure at the end of loading.

Liquid Fluorine Loading

Following the successful demonstration of the no-vent loading concept with liquid nitrogen in the small-scale system,

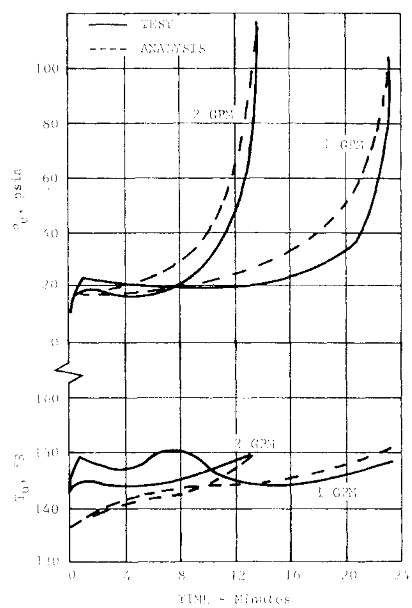

Fig. 2 Ullage pressure and temperature vs time for LN_2 loading.

feasibility demonstrations were conducted on a larger scale using liquid fluorine. The following paragraphs describe the refinements made in the analytical model, the experimental program, and the correlation obtained between the experimental and analytical results.

Analytical Model

The analytical model was refined by elimination of some of the simplifying assumptions. This refinement included: 1) incorporation of a tank geometry subroutine for either spherical tanks or cylindrical tanks with elliptical or hemispherical domes; 2) provision for calculation of tank wall temperatures, rather than assuming one constant temperature; 3) improvement of the method for calculating mass transfer at the liquid/gas interface; 4) addition of a variable flowrate subroutine.

Addition of the tank geometry subroutine allows accurate calculation of tank wall and liquid/gas interface lengths and areas as a function of ullage volume for use in the heat transfer calculations. The simplified model calculated values for a flat-ended cylinder. The new subroutine calculates the required values for either a spherical tank, or a cylindrical tank with elliptical or hemispherical domes.

Heat-transfer equations were added to the energy balance to allow calculation of tank wall temperatures. The tank wall is divided into two parts, that exposed to the ullage and that exposed to the propellant, and a temperature is calculated for each part. The added equations consider heat transfer into the wall from inside the tank and heat transfer between the tank walls and the liquid nitrogen surrounding the tank.

The method of treating mass transfer at the liquid/gas interface was changed from a calculation based on the "J-factor correlation" to the method used on the tank walls. The J-factor correlation is a form of the Chilton-Colburn analogy relating heat and mass transfer coefficients and is not amenable to use with a single component.[7] The method incorporated assumes a liquid film across which heat is transferred to the propellant. Heat transfer across the liquid film is based on free convection heat transfer for horizontal plates.[8] The net rate of heat gain or loss by the liquid film then determines the rate and direction of propellant mass transfer at the interface; this method can be used for single or multiple components.

In order to account for varying flowrates, including start and stop transients, a tabular subroutine was incorporated into the model. Sufficient values of flowrate and time to describe the flowrate variation are input to the model and the subroutine interpolates to obtain flowrate at any point in time.

Test System and Procedure

The test system, shown in Fig. 3, consisted of two 165-gal fluorine tanks with liquid nitrogen jackets that completely

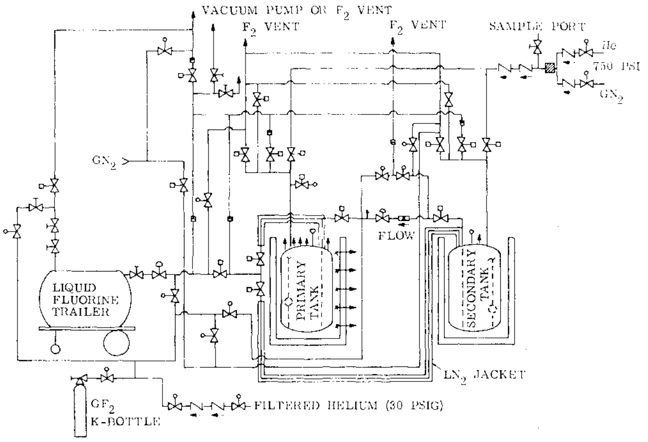

Fig. 3 System schematic, 330-gal fluorine-based propellant flow facility.

cover the tanks. Either of the 300-series stainless steel tanks could be used as a run or catch tank and each tank will hold about 2000 lb of liquid fluorine. Flowrates up to 60 lb/sec of liquid fluorine at a working pressure of 250 psig were possible through the flow section between tanks. The facility also included a pressurization and purge subsystem for supplying either helium or gaseous nitrogen, a vent/relief system, and the liquid nitrogen coolant supply. A complete description of the test system and instrumentation is presented in Ref. 9.

The procedure followed in the no-vent loading tests was as follows. The initial pressure level of helium or gaseous fluorine required in the load tank at ambient temperature to provide the desired pressure following tank cooldown was calculated from the known tank volume and average measured temperature. This pressure level (generally about 15 psia) was then established in the load tank. A minimum concentration of 99.9% by volume of either helium or gaseous fluorine was assured in the load tank by conducting multiple pressurization/vent cycles. Following loading of liquid nitrogen in the tank jacket, the ullage cooled such that a pressure of about 4 psia was established.

The loaded supply tank, containing approximately 160 gal of liquid fluorine, was then pressurized with helium to 200 psig and flow into the load tank was started. Liquid fluorine flowrate was controlled from the test console by manual setting of the supply pressure to the Domotor operator on the flow control valve. During the liquid fluorine transfer, pressures, temperatures, flowrates and propellant level were monitored. Loading was terminated when the 5% ullage level was reached.

Table 1 Initial conditions for liquid fluorine no-vent load tests

Run	Load rate, gpm	Ullage press, psia	Helium partial press, psia	Ullage temp., °R	Fluorine inlet temp., °R
1	5	4.0	NA[a]	136	146
2	10	3.4	NA	140	152
3	25	3.7	NA	NA	NA
4	25	3.8	3.8	147	150
5	25	3.8	3.8	141	150
6	10	4.1	4.1	141	153
7	10	4.0	4.0	138	NA
8	5	3.9	3.9	139	145
9	25	3.8	0	150	147

[a] Not available.

Results

Nine tests were conducted with the initial conditions shown in Table 1. Runs 1, 2, and 3 were conducted to develop techniques for establishing the initial helium charge in the load tank and to check procedures. These runs yielded qualitative rather than quantitative data. Runs 4, 5, and 6 produced useful data with helium as the initial charge. Runs 7 and 8, also with helium as the initial charge, were only partially successful. Run 9 was conducted with fluorine as the initial charge.

Results of the tests at 10- and 25-gpm loading rate with a mixture of helium and fluorine as the initial charge are shown in Fig. 4. Incomplete data was obtained at the 5-gpm loading rate; however, the temperatures and pressures were similar to those shown for 10 and 25 gpm. Results for each of the cases with helium as the initial charge were similar except that final ullage pressure and temperature decreased slightly as loading rate was decreased. This was due to the longer time available to transfer heat out of the ullage at

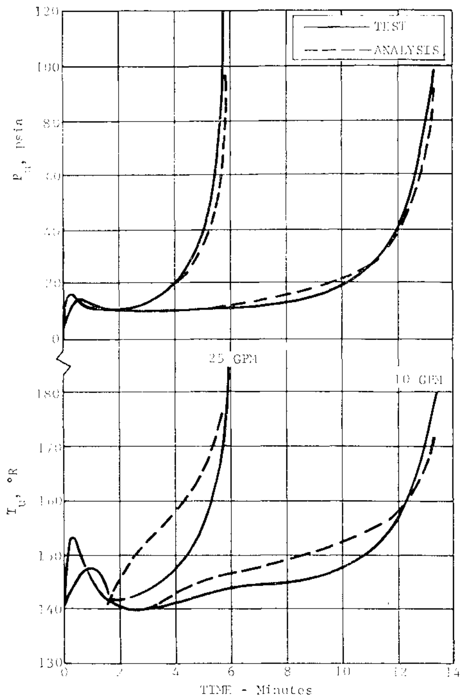

Fig. 4 Ullage pressure and temperature vs time for LF_2 loading with He initial pressurization.

lower loading rates. In general, tank pressures from 100 to 125 psia and ullage temperatures between 180 and 190°R resulted at the termination of loading when the tank was initially charged with 4 psia of helium at 140°R.

The results for the test in which fluorine was the initial charge are shown in Fig. 5. A loading rate of 25 gpm was chosen which filled the tank in about 6 min. This is probably a shorter time than would be selected for filling a flight tank. Even with this high fill rate, the tank pressure and ullage temperature only reached 14 psia and 155°R, respectively, at the end of loading. These final conditions and the pressure and temperature profiles for this test were significantly different from those obtained in the tests where the tank initially contained helium only. This difference was attributed to the difference in the amount of compression of the ullage gas. The loading test where there was no helium present indicates only a small amount of compression of the fluorine vapor. The rate of condensation on the tank walls and at the gas/liquid interface was probably sufficient to preclude significant compression. The compression in the other tests was more significant because of the presence of the noncondensable helium gas. Presumably, there is a higher loading rate at which the rate of fluorine vapor condensation would not be sufficient to preclude compression. However, this loading rate would be beyond the range of rates considered for any practical system.

A rise and fall of both pressure and temperature occurred during the first two min of loading, as shown in Fig. 4 and 5. This was attributed to the following sequence of events. At the initiation of flow, liquid fluorine entering the warm, nonjacketed line between the supply and load tanks flashed to vapor. This vapor, entering the load tank at a temperature above that of the tank, caused the pressure and temperature rise. As the transfer line cooled, vapor inflow ceased and liquid began entering the tank. Pressure and temperature in the ullage then decreased due to cooling by the tank walls and the liquid interface.

Tank wall temperature next to the ullage was measured during each run. A maximum increase of 8°F was obtained during the runs with helium in the tank. This occurred even though the tank was completely submerged in liquid nitrogen.

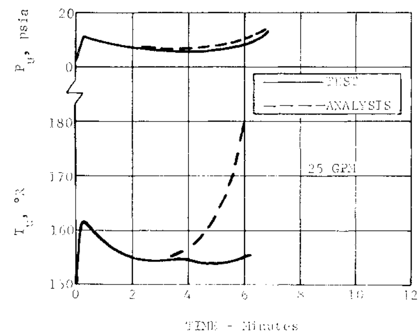

Fig. 5 Ullage pressure and temperature vs time for LF_2 loading with GF_2 initial pressurization.

Wall temperature remained unchanged during loading with only fluorine in the tank.

Data Correlation

In order to verify proper operation of the refined model, it was used to recalculate results for the preliminary liquid nitrogen load study. Comparison of the new calculations with the experimental data showed an improvement in correlation over that previously obtained. The refined analytical model was then used to correlate the liquid fluorine loading data.

As discussed previously, the pressure and temperature excursions shown in the test data at about 1 min were probably due to gaseous fluorine entering the tank ahead of the liquid fluorine. This is not considered by the model; therefore, the correlations with the model were started at 3.62 and 1.56 min into the tests for 10 and 25 gpm, respectively.

As shown by the dashed lines in Fig. 4 and 5, a good correlation was obtained except for temperature in the test that was initially charged with fluorine. In this case, the calculated temperature was too high. The deviations between the calculated and experimental data are believed to be due to the following: 1) uncertainty in initial conditions caused by gaseous fluorine entering the tank ahead of the liquid; 2) uncertainty in determination of liquid level during the tests, particularly the final level; 3) difficulty in selecting a representative method of treating condensation in the two different cases, i.e., pure condensable vapor and condensable vapor mixed with noncondensing gas.

Conclusions

From the results of both the testing and data correlation, the following conclusions can be drawn: 1) no-vent loading of liquid fluorine is feasible; 2) final ullage pressure at the end of loading can be controlled by the initial charge pressure of noncondensable gas. To attain a final tank pressure below 70 psia, the helium partial pressure in the initial gas mixture should probably be less than 2 psia at 140°R (about 7.6 psia at 530°R); 3) tank ullage pressure can be maintained at or slightly above propellant vapor pressure throughout the entire loading operation if the tank initially contains propellant vapor only; 4) the analytical model that was developed is considered to be satisfactory for use in preliminary flightweight system studies.

Application to Flightweight System

Based on this no-vent loading study, a method is proposed for loading fluorine in a flightweight system. The primary criterion, aside from not venting, is to maintain a positive pressure inside the tank to prevent implosion. The flightweight tank would include an integral tube-type heat exchanger on the tank wall. Testing conducted with the Martin Marietta fabricated Vent-Free Fluorine test fixture in the Air Force Rocket Propulsion Laboratory space chamber has demonstrated successful operation of this integral wall heat exchanger. The data is being analyzed under AFRPL Contract F04611-69-C-0033, "Vent-Free Fluorine Feed System Analysis." In addition, another heat exchanger on the fill line in close proximity to the flightweight propellant tank would be provided as part of the ground support equipment.

Prior to loading, the ambient tank would contain pure propellant vapor only at about 60 psia. The loading process would be initiated by cooldown of the flightweight tank using cold gaseous or liquid nitrogen flow through the integral heat exchanger. After the tank has been cooled, propellant loading would be initiated. Loading condition of the propellant would be such that its temperature entering the tank would be slightly greater than its atmospheric saturation temperature. Temperature of the tank and loaded liquid would be maintained slightly above the atmospheric saturation temperature during loading. This forces the ullage pressure to be slightly above one atmosphere. As loading commences, condensation of vapor prevents the ullage pressure from rising appreciably. After completion of loading, the tank would be pressurized with helium to about 15 psi above propellant vapor pressure and the integral heat exchanger would be used to maintain the tank and propellant within the desired temperature band for ground hold. The impact of accidental geysering or slug flow during the loading operation would be minimized by this approach. The ullage contains only cold propellant vapors during loading which, by proper operation of the two heat exchangers, cannot be cooled below the atmospheric saturation temperature and the problem of implosion is eliminated.

This method is also applicable for no-vent loading of Flox, oxygen difluoride, and diborane. It can be used for either loading propellants in the spacecraft prior to mating with the launch vehicle or vice versa. No-vent loading is considered to be a new approach for conducting load operations with high energy propellants at the launch complex where release of toxic and reactive vapors must be minimized.

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