

N87-25888

AN ANALYSIS OF
BIPROPELLANT NEUTRALIZATION
FOR SPACECRAFT REFUELING
OPERATIONS

Abridged Version

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August 15, 1986

ABSTRACT

Refueling of satellites on orbit with storable propellants will involve venting part or all of the pressurant gas from the propellant tanks. This gas will be saturated with propellant vapor, and it may also have significant amounts of entrained fine droplets of propellant. The two most commonly used bipropellants, monomethyl hydrazine (MMH) and nitrogen tetroxide (N₂O₄), are highly reactive and toxic. This study examines various possible ways of neutralizing the vented propellants.

The amount of propellant vented in a typical refueling operation is shown to be in the range of 0.2 to 5 percent of the tank capacity. Four potential neutralization schemes are examined: chemical decomposition, chemical reaction, condensation and adsorption. Chemical decomposition to essentially inert materials is thermodynamically feasible for both MMH and N₂O₄. It would be the simplest and easiest neutralization method to implement. Chemical decomposition would require more complex control. Condensation would require a refrigeration system and a very efficient phase separator. Adsorption is likely to be much heavier.

A preliminary assessment of the four neutralization schemes is presented, along with suggested research and development plans for more detailed investigation of the problem.

Note: A more extensive report on this project has been written and will be published as a NASA JSC Internal Note.

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SUMMARY

Venting of propellants on orbiting spacecraft is an area that has not received a great deal of attention in the past. As refueling and other servicing operations become more common, however, propellant venting will be required more often. The commonly used bipropellants, monomethyl hydrazine (MMH) and nitrogen tetroxide (N2O4) are both toxic, highly reactive chemicals. If they must be vented, it would be far better to neutralize them to more innocuous species first.

The amounts of bipropellants vented during various on-orbit servicing operations are not well established. Preliminary estimates indicate that the amount of propellant vented during a typical refueling operation is likely to be about 0.2 to 5 percent of the total fuel tank capacity. Depending on the operational mode, the fuel may or may not be highly diluted with pressurant gas, helium or nitrogen. Tank leakage or deliberate propellant dumping could vent considerably more propellant.

Four potential propellant neutralization methods have been identified in the course of this study: catalytic chemical decomposition, chemical reaction, condensation and adsorption.

Catalytic decomposition is thermodynamically feasible for both MMH and N2O4. Previous experience with catalytic decomposition of hydrazine indicates a high probability of finding a suitable catalyst for MMH decomposition. With MMH, the desired reaction products (methane, nitrogen and hydrogen) are thermodynamically favored at temperatures below about 300 C. Above that temperature, however, catalytic decomposition of MMH will most likely lead to deposition of solid carbon on the catalyst, thus making it inactive. With N2O4, the desired products (nitrogen and oxygen) are thermodynamically favored from ambient temperature up to about 500 C. Previous work in development of catalysts for air pollution control, however, has never been successful in finding a decompose N2O4 to nitrogen and oxygen.

A laboratory investigation of propellant decomposition was started at JSC. Laboratory equipment was assembled to examine the products obtained when dilute streams of MMH and N2O4 are passed over catalysts. Only very limited data have been collected to date due to the limited time available during the author's summer visit.

Chemical reaction systems for neutralization of MMH and N2O4 should be feasible. It is easy to get MMH to react with an oxidizer and to get N2O4 to react with a reducing agent. The most practical system is likely to use small amounts of N2O4 to neutralize MMH and small amounts of MMH to neutralize N2O4. At the present time, however, there is very little information available on feasible mixture ratios and the effects of diluent helium or nitrogen for such systems. Operation and control of a reaction system will be considerably more complex than for simple catalytic decomposition.

Condensation and adsorption systems trap vented propellant vapors for return to earth or for later disposal in space. Condensation systems cool the vapors to low enough temperatures to condense them, then collect the droplets. Such a system would require an extremely efficient liquid-vapor phase separator, something which does not now exist. The vapor-pressure curve and very low freezing point of MMH make it a suitable candidate for a condensation system. N2O4, however, freezes at 11.2 C, at which point it still has a fairly high vapor pressure. It would be a poor candidate for a condensing system. Both MMH and N2O4 should be suitable candidates for adsorption systems, in which the propellants are adsorbed on the surface of highly porous solids. The major disadvantage to these systems is their relatively high intrinsic weight. A system capable of collecting ten pounds of propellant is likely to weigh fifty pounds.

Suggested research and development programs are outlined for each of the four potential propellant neutralization processes.

A preliminary system comparison indicates that chemical decomposition would be the simplest system to operate and control. Chemical reaction systems represent a lower development risk. Adsorption systems also have a very low development risk, but they are likely to be much heavier. Condensing systems appear to be impractical.

Conclusions and recommendations presented in this report must be considered very preliminary. The single most significant conclusion is that hard data are lacking on the feasibility of many of the candidate processes.

Note: Sections 2 through 8 are contained in the full report only, not in this abridged version.

SECTION 1

INTRODUCTION

Venting of excess liquid propellants and vapors during on-orbit refueling operations is an area that has not been studied a great deal in the past. On-orbit servicing of satellites is becoming more common, however, and on-orbit refueling is expected to become a fairly routine operation in the near future. NASA's Orbital Spacecraft Consumables Resupply Systems (OSCRS) is being developed for just this purpose.

When propellants are supplied to a satellite, the vapors present in the satellite tank must be displaced, either by venting them to space or by collecting them. In many refueling operations, there will also be pressurant gas, helium or nitrogen, present as well as propellant vapors. In addition, any venting of vapors and gases is likely to entrain significant amounts of liquid droplets or mist as well.

The most commonly used bipropellants are monomethyl hydrazine (MMH) and nitrogen tetroxide (N2O4). These are highly reactive, toxic chemicals. It is imperative that they not be spilled or vented toward astronauts or toward sensitive materials, such as optical surfaces and solar cells, on spacecraft. To accomplish refueling, then, the vented propellants must either be dispersed far from the satellite or must be treated in some manner to make them more innocuous.

1.1 ORBITAL REFUELING OPERATIONS

In a typical refueling operation, a satellite will be secured to the Shuttle Orbiter. Fuel lines will be connected by astronauts. The satellite tanks will be depressured, and possibly completely emptied, by venting to space or by venting to a catch tank on the Orbiter. Propellants will then be loaded into the satellite by pressurization or pumping from the Orbiter. If this is done with the receiving tanks kept at constant pressure, additional venting will be required as the liquids enter the tanks. If the receiving tanks are pressured by the refilling, additional venting may not be necessary.

The amount of propellant that will be vented during a refueling operation depends on many factors, some of which are very poorly defined at this time. Clearly, the size and type of tank involved will have an influence, as will the physical properties of the propellant, particularly the vapor pressure and liquid density. The

amount vented will also depend on the amount and type of pressurant gas vented in the operation. To the extent possible in this limited study, these factors are addressed in Section 2.

To place the venting problem in perspective, however, it is useful to have some idea of the possible ranges of vent flows. The studies in Section 2 generally indicate propellant venting on the order of one percent of the propellant tank capacity, with various factors pushing this from near zero to 5 percent or more. Typical refueling operations are likely to involve several thousand pounds of propellant at a time. The total to be vented, then, will be on the order of several tens of pounds of propellants along with an equal or lesser amount of pressurant.

1.2 PROPELLANT NEUTRALIZATION METHODS

There are four candidate neutralization methods considered in this study: chemical decomposition, chemical reaction, condensation and adsorption. This section describes each one briefly. More details are given in Sections 3, 4, 6, 7 and 8.

1.2.1 Decomposition

A chemical may decompose to other smaller molecules provided the overall free energy of the decomposition is negative. This criteria establishes that the process is thermodynamically feasible. Whether or not the chemical will actually decompose, assuming the decomposition is thermodynamically feasible, depends on the kinetics of the decomposition reaction. Some chemicals will decompose spontaneously at ambient temperatures; others will decompose only at higher temperatures or in the presence of an appropriate catalyst. Still others are virtually inert.

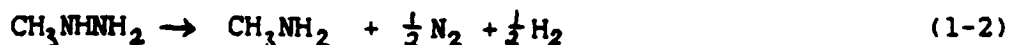
MMH can decompose in at least six ways, all of which are thermodynamically possible:



$$\Delta F^\circ = -56.8 \text{ kcal/g.mole}$$

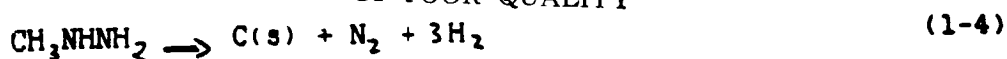


$$\Delta F^\circ = -52.4 \text{ kcal/g.mole}$$

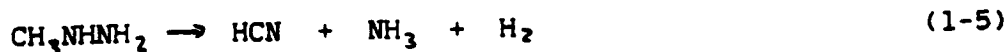


$$\Delta F^\circ = -37.0 \text{ kcal/g.mole}$$

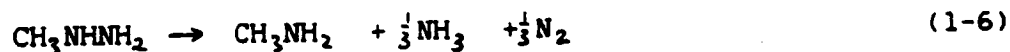
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$$\Delta F^\circ = -44.7 \text{ kcal/g.mole}$$



$$\Delta F^\circ = -18.7 \text{ kcal/g.mole}$$



$$\Delta F^\circ = -10.8 \text{ kcal/g.mole}$$

The free energies listed above are for standard conditions, one atmosphere pressure at 25 C. The free energies vary considerably with temperature; so the most thermodynamically stable products vary with temperature. Thermodynamics also favors reactions creating the largest number of product moles at lower pressures and reactions creating the fewest number of product moles at higher pressures.

N2O4 can decompose by two paths which are thermodynamically possible:



$$\Delta F^\circ = -23.4 \text{ kcal/g.mole}$$



$$\Delta F^\circ = +1.1 \text{ kcal/g.mole}$$

Even though its free energy of reaction is slightly positive, the second of these reactions takes place spontaneously, but it does not go to completion. An equilibrium mixture of N2O4 and NO2 is always present; by convention it is usually referred to simply as N2O4.

Decomposition of MMH by Equation 1-1 and N2O4 by Equation 1-7 would be the most desirable in terms of propellant neutralization. Ideally, a simple catalytic packed-bed reactor could be placed in vent lines to promote these reactions. Decomposition is examined in more detail in Sections 3 and 4.

1.2.2 Chemical Reaction

If simple chemical decomposition is not feasible, an alternative

would be chemical reaction. In this mode of operation, each propellant would be reacted with another chemical to yield innocuous products. The reactions might take place over a catalyst, or they might be simple spontaneous homogeneous reactions. MMH, a strong reducing agent, would be reacted with an oxidizing agent. N2O4, a strong oxidizer, would be reacted with a reducing agent. One obvious set of choices would be to use N2O4 in substoichiometric amounts to react with MMH, and to use MMH to react with N2O4. There are, however, other choices which should also be considered.

A chemical reaction neutralization process would obviously be more complex and require more equipment than would a simple decomposition process. In addition to the reactors themselves, there would have to be supplies of reactants and a control system to provide the right amounts when needed. Chemical reaction systems are discussed in more detail in Section 6.

1.2.3 Condensation

In a condensation system, the vent gases would be cooled to a temperature low enough to cause virtually all of the propellant to condense out of the pressurant gas. Propellant droplets, or solid particles if the temperature were low enough, would be collected by impingement devices. Collected propellants would be returned to their tanks or held in separate containers for later use or later release.

A condensation system would have the advantage of avoiding chemical reactions entirely. It would require a refrigeration system and a very efficient collection system. Condensation systems are discussed in more detail in Section 7.

1.2.4 Adsorption

An adsorption system would be similar to a condensation system in that the propellants would be trapped for later use or controlled venting. An adsorption system, however, would operate at ambient temperature. Propellant vapors and mist droplets would be adsorbed and held by suitable high-surface-area materials, such as activated carbon or silica gel. The system is simpler than a condensation system, but it may be somewhat larger since the net mass of propellant adsorbed per unit volume of sorbent is considerably less than the density of liquid or solid propellant. Adsorption systems are discussed in more detail in Section 8.

1.3 SCOPE OF THIS STUDY

The purpose of this study is to examine the bipropellant venting problem, with emphasis on methods of neutralizing MMH and N2O4. Section 2 of this report addresses the problem of estimating the amounts of propellants likely to be vented during typical operations. Sections 3 and 4 go into some detail on chemical decomposition

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processes for MMH and N2O4, respectively. Section 5 discusses the laboratory program started at JSC in 1986 to assess the feasibility of propellant decomposition. Sections 6, 7 and 8 look at the other three possible neutralization processes: chemical reaction, condensation and adsorption. Section 9 presents some preliminary comparisons among the four processes.

Conclusions and recommendations presented in this report must be considered very preliminary. The single most significant conclusion is that hard data are lacking on the feasibility of many of the candidate processes. Outlines of suggested research and development programs to provide the necessary data are presented.

SECTION 9

PRELIMINARY NEUTRALIZATION SYSTEM COMPARISON

The various possible bipropellant neutralization systems can best be compared at this time by a simple summary of the pros and cons associated with each system. Neither venting system requirements nor neutralization system designs are well enough established for a quantitative comparison at this time.

9.1 DECOMPOSITION SYSTEMS

MMH and N2O4 must be considered separately in terms of chemical decomposition processes. First consider MMH:

Pro:

In terms of chemical thermodynamics, the most stable decomposition products of MMH at temperatures up to 300 to 400 C are methane, nitrogen and hydrogen, all quite harmless. Previous experience with hydrazine decomposition leads to the expectation that suitable decomposition catalysts can be developed relatively easily. Operation and control would be quite simple; the MMH and accompanying pressurant gas, if any, would simply be vented through a packed catalyst bed. The system would be fairly light weight and compact.

Con:

Carbon deposition on the catalyst surface, resulting in catalyst poisoning, can be expected at high temperatures. Either a temperature control system on the catalyst bed or a highly selective catalyst may be required. Considerable effort may be required to obtain a catalyst which will work successfully for an extended period of time.

For N2O4:

Pro:

In terms of chemical thermodynamics, the most stable decomposition products of N2O4 at temperatures up to 1800 C are nitrogen and oxygen, both quite harmless. Operation and control would be quite simple; the MMH and accompanying pressurant gas, if any, would simply be vented through a packed catalyst bed. The system would be fairly light weight and compact.

Con:

A great deal of effort has been spent in the past searching for catalysts to decompose nitrogen oxides to nitrogen and oxygen for use in air pollution control systems. To date, no such catalyst has been found.

9.2 CHEMICAL REACTION SYSTEMS

Pro:

Both MMH and N2O4 are highly reactive. They can be reacted with each other, or with other suitable chemicals. If reacted with each other, no additional chemical supply systems would have to be carried, only the extra amounts of propellant needed for reaction. System development and design should be fairly simple. The total amount of hardware needed for the system would be quite small.

Con:

A moderately complex sensing and control system would have to be developed to feed the right amounts of reactants to the venting gases at the right times. The reaction products which would be obtained from non-stoichiometric combustion, especially in the presence of large amounts of diluent gases, are not fully established. Ignition and stable operation over a wide range of non-stoichiometric mixtures must be established.

9.3 CONDENSATION SYSTEMS

Pro:

Chemical reactions are avoided. The propellants are trapped for return to earth or for venting at a later, safer time.

Con:

A complex system is required, including a refrigeration system and an extremely efficient phase separation device. The latter is not available at this time. In the case of N2O4, freezing takes place under conditions where the vapor pressure is still fairly high. An effective condensation system for N2O4 would have to operate in the vapor-solid region, not in the vapor-liquid region.

9.4 ADSORPTION SYSTEMS

Pro:

Solid adsorption systems have been developed for many different vapors in the past. It should be fairly easy to develop systems for MMH and N2O4. Such systems are inherently simple to design, build and operate. Propellants would be captured for return to earth or for release to space at more convenient, safer times.

Con:

Adsorption systems are likely to be quite heavy compared with other alternatives. Sorbent capacities of a few tenths of a pound of propellant per pound of sorbent can be expected. The systems have fixed capacities. Once their sorption capacities are reached, any additional propellant will simply pass on through them.

SECTION 10

CONCLUSIONS

The following principal conclusions have been reached as a result of this study:

1. There has been little systematic study of the problem of on-orbit venting of storable bipropellants, either in terms of requirements for various servicing operations or in terms of methods for dealing with the propellants.
2. Preliminary estimates indicate that propellant venting during refueling operations may amount to 0.2 to 5 percent of the capacity of a propellant tank. Amounts on the order of tens of pounds of propellants may be expected.
3. Four potential processes for treating vented storable bipropellants have been identified: chemical decomposition, chemical reaction, condensation and adsorption.
4. Catalytic chemical decomposition of MMH is probably feasible. The major uncertainty in the process is carbon deposition and poisoning of the catalyst surface. This problem may be avoided by operation at relatively low temperatures (below about 300 C) or by developing a catalyst that is highly selective.
5. Catalytic decomposition of N2O4 to less innocuous materials is probably not feasible.
6. Chemical reaction systems (reacting MMH with a small amount of an oxidizer and reacting N2O4 with a small amount of a reducing agent) represent a low-risk development alternative. On-orbit operation and control, however, will be considerably more complex than for chemical decomposition.
7. Condensing systems appear to be of limited practical value. Any such system would have to incorporate an extremely efficient vapor-liquid phase separation device. A system for N2O4 is further complicated by the relatively high vapor pressure of N2O4 at its freezing point (about 2.7 psia at 11. 8 F).
8. Adsorption systems represent a low development risk alternative, but are likely to be much heavier than other systems for comparable performance.

SECTION 11

RECOMMENDATIONS

The following recommendations are made based on the conclusions reached in this study:

1. System requirement studies should be carried out to define the needs and operational limitations associated with on-orbit venting of bipropellants, both during satellite servicing and other operations.
2. Catalytic decomposition of MMH should be explored as a prime treatment method. Initial emphasis should be on catalyst screening and development to obtain a catalyst that will work effectively without becoming poisoned due to carbon deposition.
3. Catalytic decomposition of N2O4 should be explored to a limited extent only, with emphasis on determining whether the process is at all feasible.
4. Chemical reaction systems should be examined as a low-risk alternative to decomposition systems. Initial work should be aimed at determining non-stoichiometric reaction behavior of MMH and N2O4 diluted with pressurant gases.
5. If the amounts of vented propellants are expected to be very small, or if the weight penalty is tolerable, adsorption systems should be examined as a low-risk alternative to chemical treatment methods. Initial work should be aimed at identifying the best sorbents for MMH and N2O4 and determining their capacities under a variety of conditions.