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SOLID GAS GENERATORS FOR CHEMICAL LASERS

By

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ABSTRACT

DIRECTORATE FOR RESEARCH & INFORMATION
AND DEVELOPMENT (DASD-PA)
DEPARTMENT OF DEFENSE

Solid gas generator formulations which produce H_2 , D_2 and a mixture of F_2 and NF_3 have been developed for HF/DF chemical lasers. NF_4BF_4 has been chosen as the oxidizer candidate for the F_2/NF_3 solid gas generator. A continuous reactor for the photolytic production of NF_4BF_4 was designed and assembled. A production rate of 5g in one hour of pure NF_4BF_4 has been achieved. The F_2/NF_3 solid gas generator formulation $NF_4BF_4/KF/Sn$ was selected for further evaluation. Burning rates of the order of .08 cm/sec and yields of approximately 34 wt% available fluorine have been realized. Pressed pellets exhibited excellent mechanical and safety characteristics. A mixture of $LiAlD_4$ and ND_4Cl has been selected, characterized and test fired at the 1500g level at a burning rate of 0.064 cm/sec. A point design concept for a F_2/NF_3 fuel system has been developed incorporating existing laser and gas generator technology.

INTRODUCTION

The objective of this program was to evaluate feasibility and practicality of solid gas generators for Navy high energy lasers. Solid gas generators are desirable because of potential handling, storage, logistic and safety advantages. A DF chemical laser requires fluorine and deuterium for the formation of excited DF. Gaseous fluorine and deuterium are conventionally stored in pressure cylinders or in cryogenic form. Because of the well-known drawbacks of both methods, efforts were initiated at the Naval Surface Weapons Center to develop the technology suitable for storage of fluorine and deuterium in a solid matrix at ambient temperatures. Since hydrogen can be bonded or absorbed reversibly with both metals and nonmetals, a great number of chemical compounds exist which may be considered as potential storage systems. On the other hand, fluorine forms extremely stable compounds with the elements thus limiting the number of promising solid fluorine storage systems.

DISCUSSION

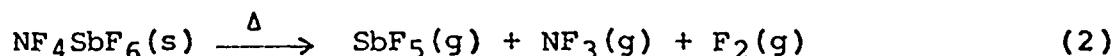
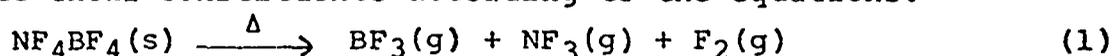
Solid F_2/NF_3 Gas Generators: For the storage and generation of fluorine NF_4^+ salts have emerged as the prime oxidizer candidates. The Naval Surface Weapons Center has screened a large

This effort was sponsored by the Navy High Energy Laser Project Office (PM-22/PM-455),
Naval Sea Systems Command.

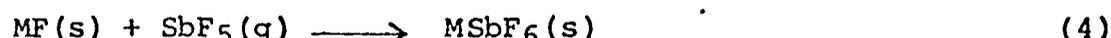
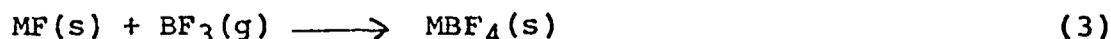
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number of formulations using these relatively new fluorine compounds. Based on both thermochemical calculations and experimentally observed fluorine yields, reaction temperatures, combustion gas compositions, safety tests, burning rates and storability a family of promising formulations has been selected for further evaluation.

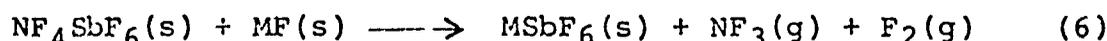
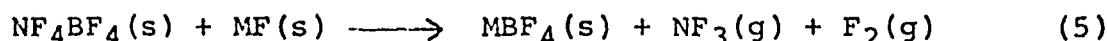
The basic concept used to generate F₂/NF₃ for Navy high energy laser applications is the thermal decomposition of NF₄⁺ salts such as NF₄BF₄ and NF₄SbF₆ (1), (2), (3). At elevated temperatures (>200°C) these fluorine rich compounds decompose into their constituents according to the equations:



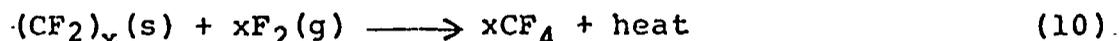
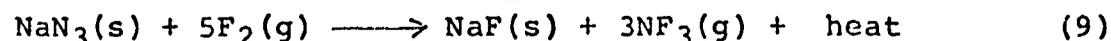
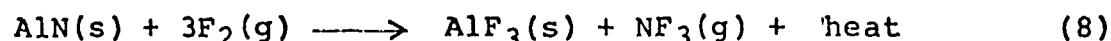
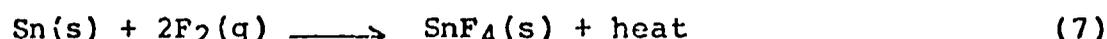
Since existing HF/DF chemical lasers are greatly affected by high molecular weight gaseous species such as BF₃ and SbF₅, alkali metal fluorides are mixed with the oxidizer salts to retain BF₃ and SbF₅ as a solid reaction product (equations 3 and 4).



The alkali metal fluoride (or complexing agent) serves two purposes: (a) retains gaseous contaminants that are deleterious to the operation of a chemical laser in a solid "clinker" residue and (b) provides additional heat to help drive the desired reaction by the formation of a complex metal fluoride salt. The overall reaction can then be written.



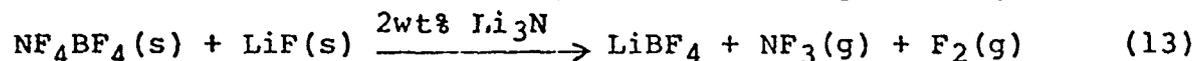
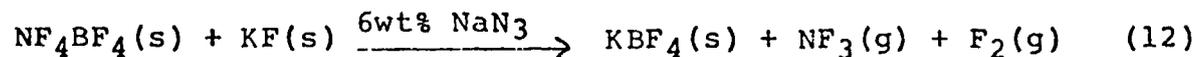
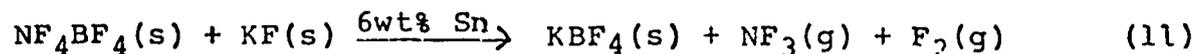
The above reactions are endothermic and require additional heat for a self-sustaining reaction, therefore, a fuel is added which reacts with a portion of the available fluorine producing heat and fluorinated reaction products. Metals, metal nitrides, azides and fluorinated hydrocarbons have been used with some success. A few examples are given below.



Fuels producing nonvolatile metal fluorides and/or NF₃ are extremely attractive since high molecular weight gaseous fluorine compounds, whose fluorine content is unavailable for laser use, produce a gaseous effluent exhibiting low γ values imparting

a high unfavorable systems impact on the chemical laser.

NF_4BF_4 has been chosen as the oxidizer candidate for the storage and generation of fluorine because of its high fluorine yield upon reaction with suitable fuels and the ease of removal of the undesirable combustion product BF_3 . The following formulations have been studied.



Formulating and Testing: Since NF_4BF_4 is extremely sensitive to moisture, all operations were conducted in a nitrogen atmosphere dry box. Combustion tests, strand burning rate determinations, Taliani and 30 day storage tests were carried out in the appropriate apparatuses purged with dry helium.

Sample formulations were mixed in Teflon containers and tested for sensitivity with respect to impact, sliding friction and electrostatic discharge. The $\text{NF}_4\text{BF}_4/\text{KF}/\text{Sn}$ formulation evaluated experimentally gave the following results:

Impact	:	125 mm (5kg wt)
Sliding Friction	:	1000 lbs (8 ft/sec)-no fire
Electrostatic Discharge:		0.275 joules (5kv)

This formulation exhibited an autoignition temperature of 230°C using differential thermal analysis (DTA) (Figure 1). A small rise in the base line below this temperature was attributed to slight impurities in the sample.

Ignition and combustion studies were conducted in a high pressure window bomb. A hot wire nichrome wire was used as an ignitor. Chamber pressures prior to and after combustion were recorded with the aid of a Bourdon gauge. Burn times were visually observed and recorded with a stop watch. Due to the relatively slow burning rates and ignition lag times observed no real advantage was thought to be gained using more sophisticated timing devices. The formulation $\text{NF}_4\text{BF}_4/\text{LiF}/\text{Li}_3\text{N}$ exhibited a rather slow burning rate (~ 0.02 cm/sec) essentially independent of chamber pressure. In contrast the formulations $\text{NF}_4\text{BF}_4/\text{KF}/\text{NaN}_3$ and $\text{NF}_4\text{BF}_4/\text{KF}/\text{Sn}$ ignited readily and produced substantially higher burning rates (Figure 2).

Fluorine yields and gas analysis samples were obtained using a modified Parr calorimeter bomb passivated with molecular fluorine prior to use. Due to small sample sizes (1.0 gram) and the difficulties encountered in handling gaseous fluorine compounds, experimental error was considerable, but a quick comparison could be made between competing formulations.

Test results are shown in Table I.

Table I
Fluorine Yield and Gas Analysis of Selected
F₂/NF₃ SGG Formulations

Formulation	Yield (wt% F)	Gas Analysis (M%)			Density (g/cc)
		F ₂	NF ₃	N ₂	
NF ₄ BF ₄ /LiF/Li ₃ N	44	31.0	59.6	9.4	2.14
NF ₄ BF ₄ /KF/NaN ₃	36	31.7	46.1	22.2	2.23
NF ₄ BF ₄ /KF/Sn	34	42.0	53.4	4.5	2.20

Promising formulations were subjected to standard storage tests used to evaluate solid rocket propellants. A typical Taliani test at 110°C is shown in Figure 3. A gassing rate less than 1.0 mm/min is considered acceptable. A more in depth study of the storability of NF₄BF₄ formulation was conducted over a 30 day period. Sample grains (1 gram) were stored under helium at 71°C in passivated stainless steel vessels fixed with a Bourdon pressure gauge. Pressure increases were recorded daily. After 30 days pressed pellets showed a weight loss of approximately one percent. Subsequent gas analysis identified the gas as NF₃. After storage pellets were difficult to ignite and the burning rate decreased considerably. These results can be rationalized by assuming a slow reaction between oxidizer and fuel or oxidizer and complexing agent. Storage problems of this nature require further investigation before a solid F₂/NF₃ gas generator incorporating NF₄BF₄/MF/fuel can be accepted for shipboard applications.

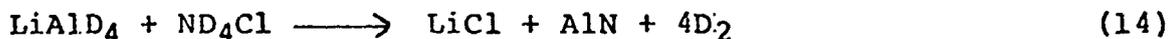
NF₄BF₄ Synthesis: Because of the attractiveness of NF₄BF₄ as an oxidizer its availability at a reasonable cost must be demonstrated. Two methods have been pursued by workers in this field to synthesize NF₄BF₄. The first approach is a one-step synthesis involving the photolytic reaction of the constituents BF₃, NF₃ and F₂ at -196°C (4). Material obtained from this reaction is better than 99% pure but had a low production rate of 3g/hr. The second approach is a multi-step metathetical process in liquid HF starting with NF₄SbF₆ (5), (6). This method produces a product of lower purity but at a production rate of greater than 100g/hr. An effort has been initiated at the Naval Surface Weapons Center to improve the yield of the photolytic process so that it becomes suitable for large scale production of NF₄BF₄ at a reasonable cost. Several batch type UV reactors have been assembled and evaluated. Some of the parameters examined were: effects of reactant composition, pressure, exposure time, light intensity, exposed surface area

of condensed reactants, temperature, effect of adding O_2 to the reactant mixture and the composition of the reactor materials. Based on these data, a reactor has been designed for continuous operation (Figure 4). It consists of a UV lamp surrounded by a liquid nitrogen cooled container which is scraped continuously by three rotating blades. The UV lamp is cooled by a fluorocarbon liquid.

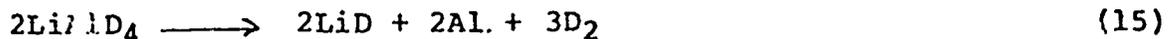
The maximum production rate achieved thus far was 4.9g of NF_4BF_4 in a one hour run. The yield appears to be proportional to the intensity of the UV lamp in the fluorine absorption region. Generally, a 1:1:1 molar ratio of $BF_3:NF_3:F_2$ has been used and changing the ratio to 2:1:1 did not improve the production rate. The amount of product obtained in a run appears to be dependent on the total amount of reactants condensed rather than on the radiation time, and product appears to form predominantly during the condensation period. Consistent with this are indications that unreacted BF_3 after being scraped from the cold surface recondenses in such a fashion that it is either not in the radiation zone or is not in adequate contact with the other reactants. At the present time insufficient data has been collected to select the optimum reactor design. It is hopeful that photolytic NF_4BF_4 will be available at a cost that is acceptable to the Navy's high energy laser program.

Solid H_2/D_2 Gas Generators: For the storage and generation of deuterium the metal hydride/ammonium salt systems have emerged as the prime candidates (7). These systems provide a volume storage capability comparable with liquid hydrogen and release hydrogen upon initiation of a chemical reaction between the metal hydrides and the ammonium salts. A particular mixture of $LiAlH_4/NH_4Cl$ or $LiAlD_4/ND_4Cl$ has been selected for the development of prototype hydrogen and deuterium gas generators. Pertinent data on formulation safety, storability, yield, burning rate, reaction temperature, flow rates, physical properties & gas composition have been generated. A practical gas generator incorporating a pelletized bed concept has been designed, built and tested. Due to the relatively slow burning rates of acceptable solid hydrogen/deuterium gas generator formulations, a pelletized bed system was selected for scale-up over the conventional single grain design. Test generators with pelletized beds have been manufactured and tested.

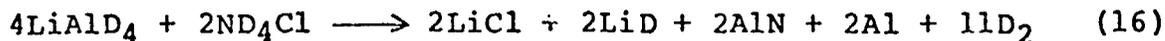
The basic formulation makes use of the exothermic reaction between $LiAlD_4$ and ND_4Cl according to the equation:



In practice this reaction does not reach completion due to an extremely high flame temperature removing volatile ND_4Cl from the reaction site. Excess $LiAlD_4$ reduces the flame temperature by decomposing endothermically according to the equation:



The overall reaction can be written:



The above reaction proceeds at a controlled rate and temperature yielding the desired products. The formulation selected for scale-up and testing in a prototype gas generator is as follows:

LiAlD₄ 53.4 wt%
 ND₄Cl 36.6 wt%
 Fe₂O₃ 5.0 wt%
 Kraton binder 5.0 wt%

Ferric oxide and kraton are added as burning rate modifier and binder respectively.

Pressed pellets exhibit excellent mechanical and safety characteristics (Table II and III). They can be handled in the dry box without fear of cracking chipping or dusting. At lower binder concentrations grain integrity declined accompanied by an increase in sensitivity. At higher binder concentrations gas purity (% D₂) decreases drastically due to an increase in the HD and H₂ concentrations.

Table II

Mechanical Properties of D₂ Grades

T ^o F	σ _m	ε _m	E _p
-65	1349	No	No
77	635	4.23	19400
165	340	3.38	13000

Table III

Safety Characteristics of D₂ SGG Formulation
2LiAlD₄/ND₄Cl/Fe₂O₃/Kraton

Impact 125mm (5kg wt)
 Sliding Friction 180 lbs (8ft/sec)
 Electrostatic Discharge 0.275 joules (5 kv)

Gas analyses were obtained on one gram samples. Pellets were ignited in a closed bomb and the gaseous products were analyzed in the mass spectrometer. Results are in good agreement with those calculated assuming random scrambling of the D₂ and H₂ molecules to produce HD (Table IV).

Table IV

Gas Analysis of the Gaseous Combustion Products
From the D₂ SGG Formulation
2LiAlD₄/ND₄Cl/5% Fe₂O₃/5% Kraton

Gas	Predicted M%	Observed M%
D ₂	85	82.6
HD	14	14.8
H ₂	1	2.6

The investigation of the burning rate as a function of chamber pressure showed a decrease in burning rate with increasing pressure (Figure 5). The burning rate plateaued at 5wt% Fe₂O₃. Ferric oxide provides additional heat to the system via a thermite reaction but also obviously acts as a catalyst

Figure 6 shows a prototype D₂ gas generator used for testing at NSWC. Pellets are ignited inside and outside as well to achieve a constant mass flow rate. Tests were conducted at the 150 and 1500 gram levels with pellets 0.5" in diameter and 0.25" long. Chamber pressures were regulated by means of critical flow nozzles operating between 500 and 1500 psi. Burn times were on the order of six seconds producing exhaust temperatures between 230 and 430°C. Pressure/time profiles were obtained as the first test data point and appear to meet requirements for scale-up.

F₂/NF₃ Feed System Concept: To provide guidance for the development of a solid F₂/NF₃ gas generator and to couple experimental results with existing laser technology work was initiated in developing a point design concept for a F₂/NF₃ fuel system. The design consists of a number of gas generating cartridges each containing a pelletized charge of the F₂/NF₃ formulation, a manifold assembly to carry the evolved gas, a storage tank and a mass-flow regulating system. The charge in the gas generating cartridges is pelletized since the burning rates which have been demonstrated require the large surface area of a pellet bed to produce the required mass flow rate. In operation the system is precharged to a desired pressure. During laser firing and depletion of the gas supply in the manifold assembly and storage

tank a cartridge is ignited when the system pressure drops to a value just above the minimum operating pressure. Since the system volume has been chosen to store one SGG cartridge's quantity of gas plus the "precharge" gas, the final pressure after a cartridge is fired will be no higher than the initial pressure and will probably be lower. If a longer laser shot time is necessary, another SGG will ignite when the pressure drops, and so forth. This system concept does not present a final, optimized design. It does however offer some illustration of how the F_2/NF_3 formulation could be used in a real system.

CONCLUSIONS

A solid F_2/NF_3 gas generator formulation using NF_4BF_4 as the oxidizing agent has been developed. A burning rate of .08 cm/sec and a yield of 34wt% available fluorine has been achieved. Pressed pellets exhibit excellent mechanical properties without the aid of binders. Initial storage tests indicate a relatively short shelf life due to slow reaction of oxidizer with fuel or complexing agent. Further efforts are required to demonstrate the feasibility of a high yield F_2/NF_3 solid gas generator with adequate safety and storage-life characteristics.

Critical yield parameters for the photolytic synthesis of NF_4BF_4 have been studied. The results show that yield and production rate rely heavily on the exposed surface area and light intensity of the UV lamp in the fluorine absorption region. Additional work is needed in developing a reliable and practical reactor for the photolytic production of NF_4BF_4 .

A deuterium gas generator charged with a pelletized solid reactant of 1500 g total weight has been developed. The generator delivered D_2 gas over a period of six seconds. Scalability appears feasible.

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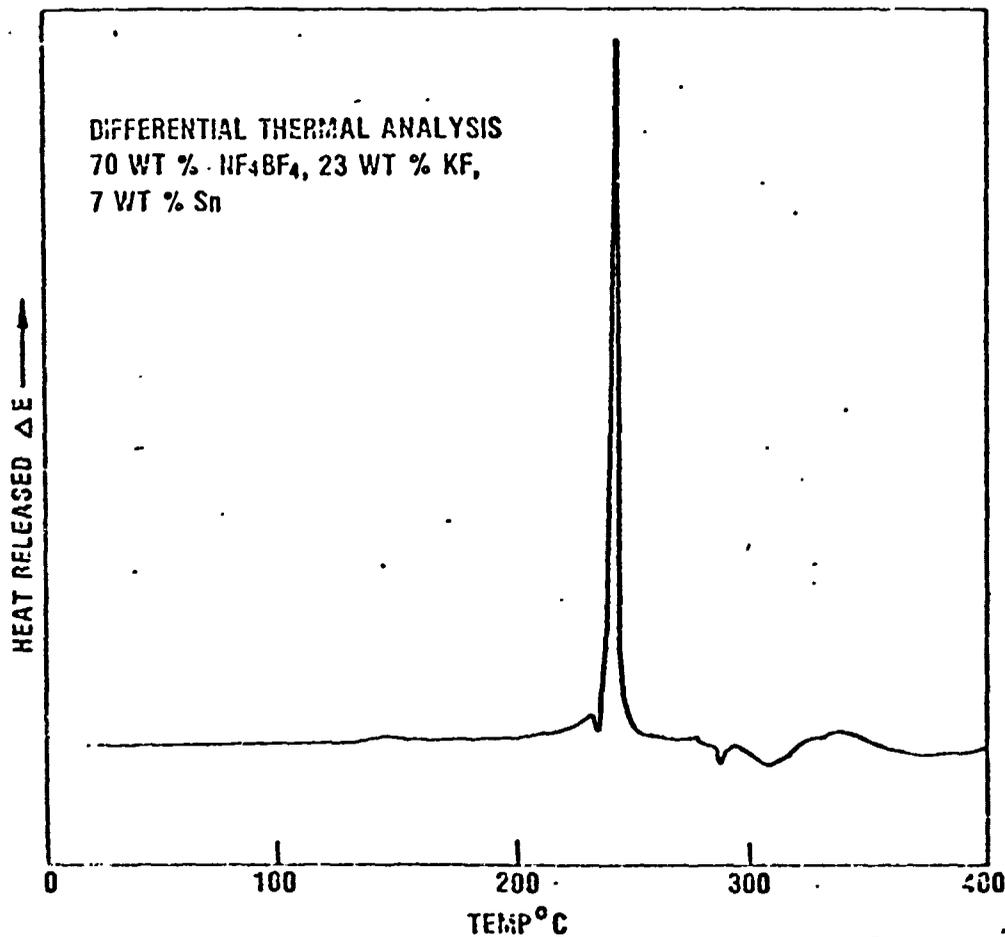


Figure 1

Differential Thermal Analysis $\text{NF}_4\text{BF}_4/\text{KF}/\text{Sn}$

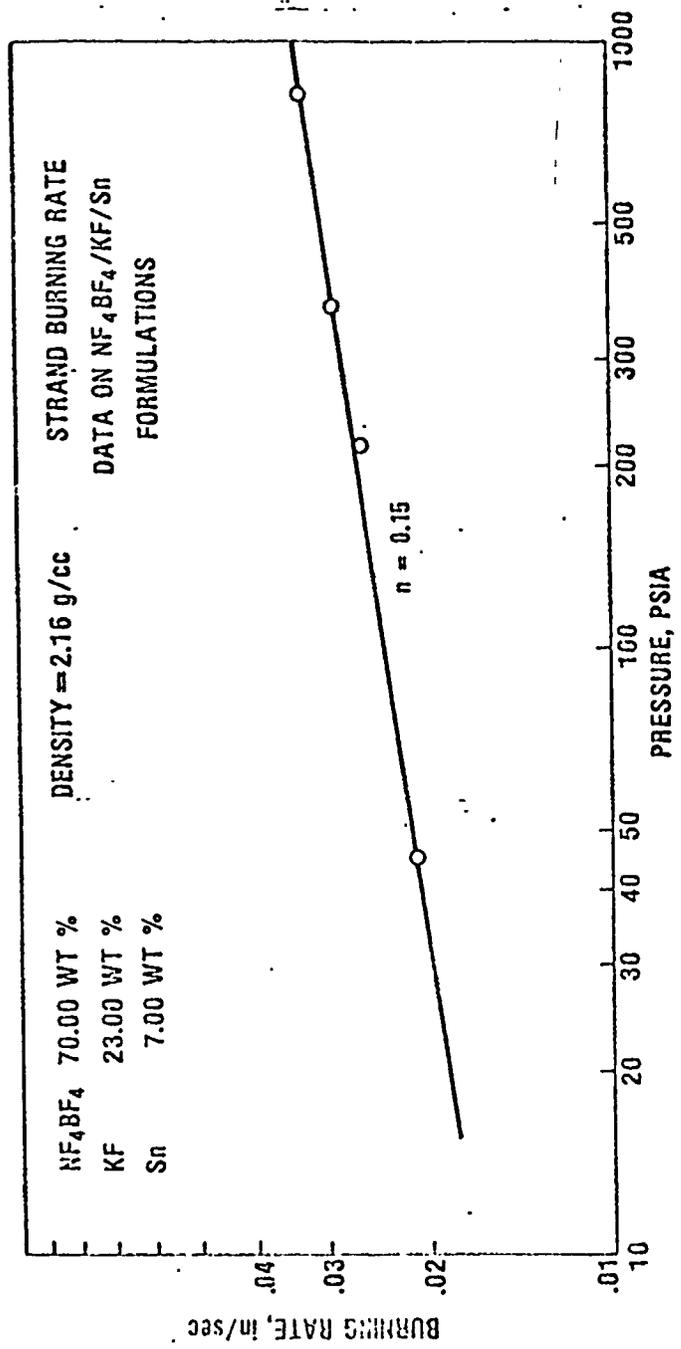


Figure 2

Burning Rate as Function of Pressure NF₄BF₄/KF/Sn

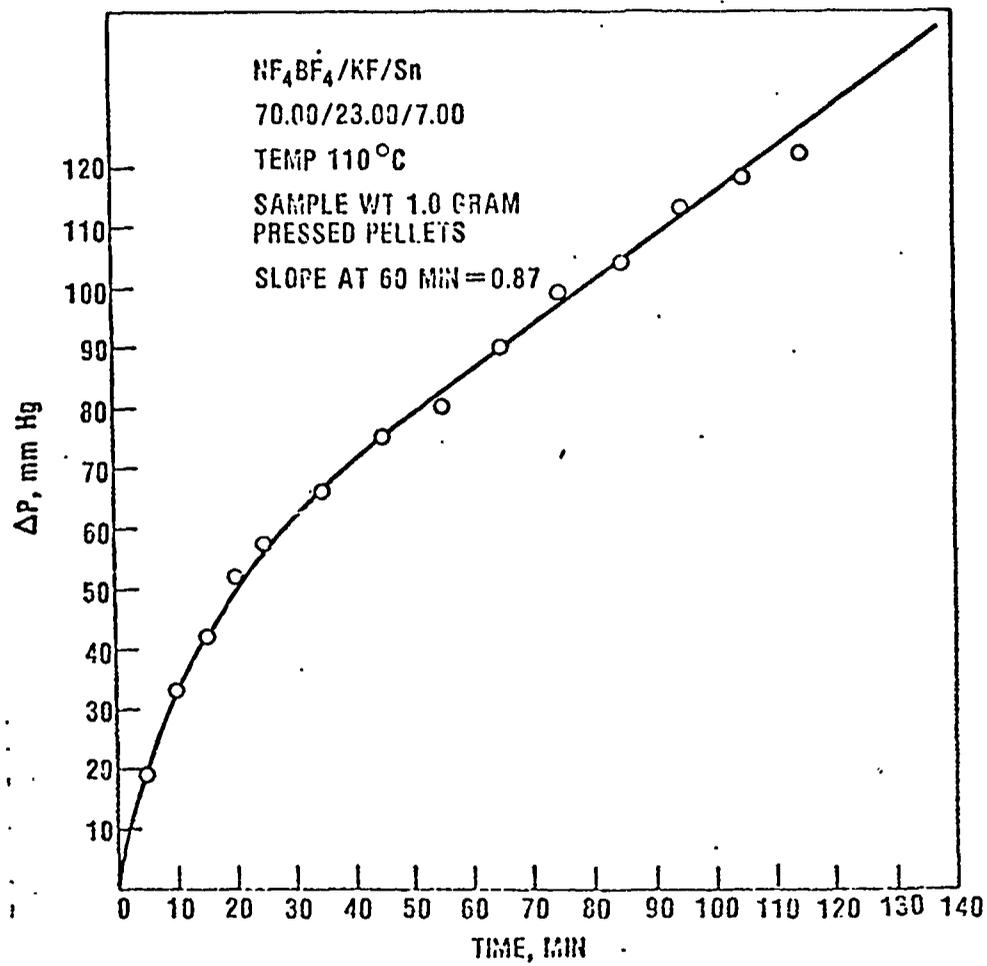


Figure 3
Taliani Test Data

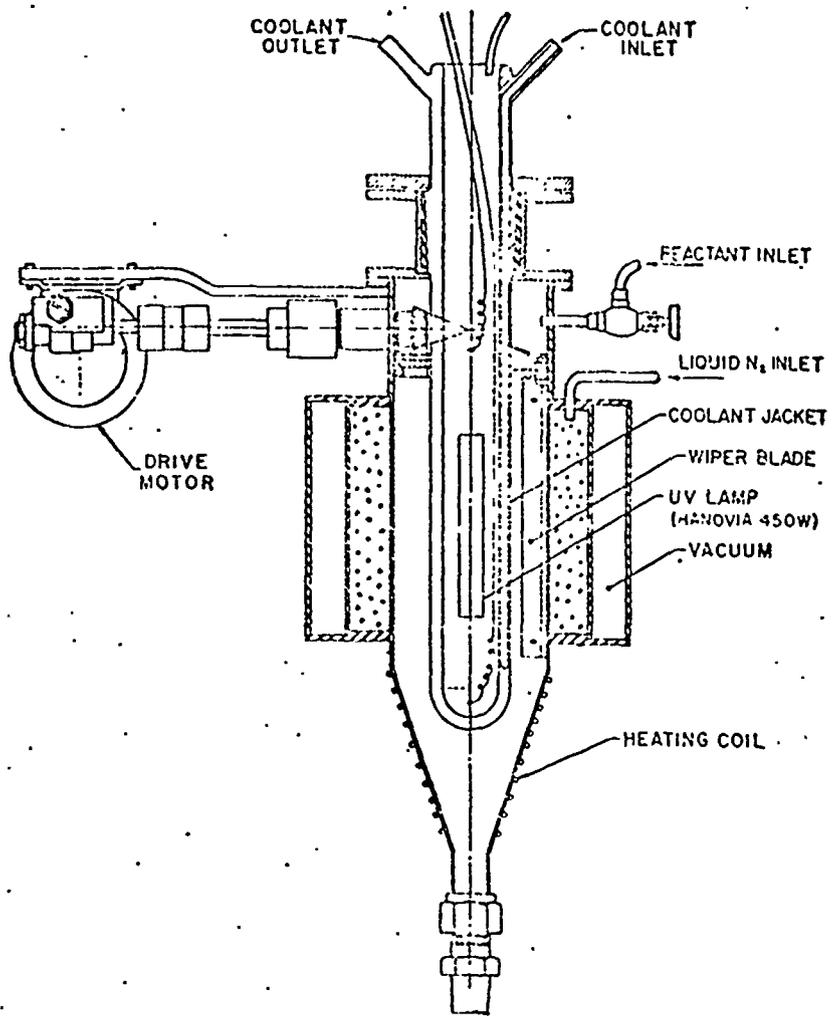


Figure 4

NF₄BF₄ Photolytic Synthesis Apparatus

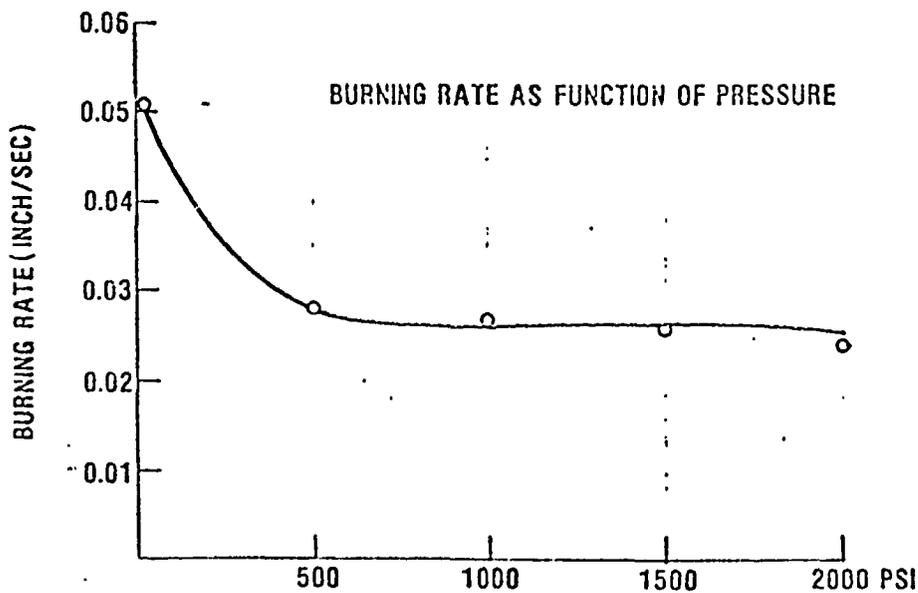
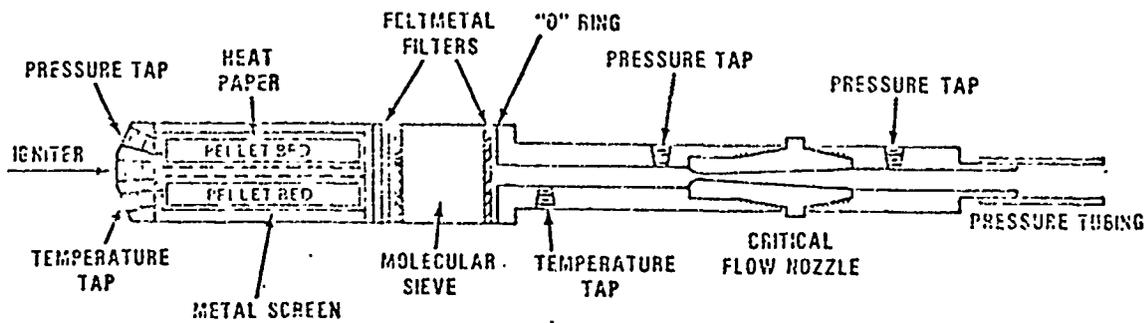


Figure 5

Burning Rate as a Function of Pressure 2LiAlD₄/ND₄Cl



(GRAIN CONFIGURATION: PELLET (0.49" DIA/0.25" LENGTH))

Figure 6

Multi-Grain D₂ Solid Gas Generator