Thrust-Chamber Technology for Oxygen Difluoride/Diborane Propellants

R. W. Riebling and W. B. Powell
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

Nomenclature

A^*	=	nozzle throat area, ft^2
C_p	=	heat capacity, Btu/lbm/°F
d_f	=	fuel orifice diameter, in.
h_g	=	gas side film coefficient, Btu/in.^{2} sec/°F
$I_{sp_{vac}}$	=	vacuum specific impulse, sec
K	=	reaction rate constant, sec^{-1}
P_c	=	chamber stagnation pressure, psia
q/A	=	heat flux per unit area Btu/in.^{2} sec
r	=	mixture ratio (O/F), dimensionless
T_{gr}, T_w	=	gas recovery and wall temperatures, °F
V	=	velocity, fps
v_f	=	fuel injection velocity, fps
ϵ	=	thrust chamber expansion area ratio
ϵ_c	=	thrust chamber contraction area ratio
η_{c*}	=	characteristic velocity efficiency, %
$\eta_{I_{sp}}$	=	specific impulse efficiency, %
ρ	=	density, lb/ft^3

Introduction

Analyses of high-launch-energy unmanned outer-planetary orbiter missions through 1970–1985 indicate that payloads probably will be severely constrained by the capabilities of economical launch vehicles, such as Titan/Centaur/Burner II. One way to increase the payload is to use high-energy propellants in the spacecraft propulsion system. System studies have led to the choice of oxygen difluoride (OF_2) and diborane (B_2H_6) as a promising candidate propellant combination because of 1) the potentially high $I_{sp_{vac}}$ (~400 sec at an expansion area ratio ϵ of 60) at a relatively low chamber pressure P_c of about 100 psia, and 2) a relatively broad common liquidus range (105°F with a maximum vapor pressure of 100 psia). Low P_c is important because liquid chemical propulsion systems required by unmanned missions envisioned for the next decade or so will burn relatively small quantities of propellant (1000—3000 lbm) at relatively low thrust levels (300–1000 lbf). Both of these constraints dictate a pressure-fed (low P_c) propulsion system rather than a pumped (high P_c) system.

Such a propulsion system (Table 1 and Fig. 1) is now under development at JPL, and it is being designed to be capable of operating anywhere between the solar orbits of Venus and Pluto. This survey article covers one aspect of this program: thrust chamber technology for the OF_2/B_2H_6 propellants. Advanced development of three types of pressure-fed chambers is under way: 1) a film-cooled or mixture-ratio-stratified chamber made of an advanced carbonaceous or graphitic material, or possibly a metallic material; 2) a regeneratively cooled metallic thrust chamber; and 3) a heat-pipe-cooled metallic thrust chamber. A preliminary, subscale technology program in support of the first type was described earlier.[1] The second is the subject of recently initiated contractual

Robert W. Riebling holds a B.S. (1960) and an M.S. (1961) in Chemical Engineering from the Polytechnic Institute of Brooklyn and a Certificate in Propulsion and Power Conversion Systems from the University of California at Los Angeles, Calif. He is presently Supervisor of Combustion Devices Development in the JPL Liquid Propulsion Section. In this capacity, he is responsible for both in-house and contracted research and advanced development in the areas of Earth- and space-storable bipropellant and monopropellant thrust chambers, injectors, and materials. Earlier, Mr. Riebling was a member of the Mariner Venus 67 propulsion flight team, a propulsion consultant to the Voyager Project, and the JPL Resident Engineer for Surveyor vernier-propulsion at Thiokol-RMD. He has conducted independent research and published widely in the fields of orifice hydraulics and injection element characterization. He lectures on injector design at UCLA and is a registered Professional Mechanical Engineer in California. He is a Member of the AIAA.

Walter B. Powell received an A.B. in Mechanical Engineering from Stanford University in 1937 and an M.S. in Aeronautical Engineering from the California Institute of Technology in 1940. He was employed by the Douglas Aircraft Company at El Segundo, Calif., for about one year. In September 1941, he started work at Caltech's GALCIT Project No. 1, later to become known as the Jet Propulsion Laboratory, in Pasadena, Calif. There, over the course of nearly thirty years, he has conducted research and development programs spanning the full range of solid and liquid propellant rocket motor technology, from the earliest JATO rockets to the present-day space-storable liquid propulsion systems. Mr. Powell was the first manager of JPL's test station at Edwards, Calif. He is now widely acclaimed for his achievements as Program Manager of the JANNAF Performance Standardization Working Group. A member of the Technical Staff, in the JPL Liquid Propulsion Section, he is a registered Professional Mechanical Engineer in California. He is an Associate Fellow of the AIAA.

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Table 1 Characteristics of helium-pressurized, OF_2/B_2H_6 propulsion system for outer planet missions

Characteristic	Value
Thrust, lbf	1000
Chamber pressure, psia	100
Estimated delivered $I_{sp_{vac}}$, lbf-sec/lbm	400
Mixture ratio (O/F)	3
Thrust vector control method	2-axis gimbal
Expansion area ratio	60
Fuel flow rate, lbm/sec	0.625
Oxidizer flow rate, lbm/sec	1.875
Nominal propellant tank pressure, psia	240
Number of starts	6–20
Thermal control	Passive (if possible)
Temperature limits, °R	$250 \begin{Bmatrix} +30 \\ -40 \end{Bmatrix}$
Lifetime in space, yr	10

effort. The heat pipe concept is discussed in detail in another paper.[2] It is planned to select the most promising thrust chamber concept for final development to flight-prototype status. We shall review here the technology effort in the key areas of heat transfer, propellant flow characteristics, solids deposition, vacuum ignition behavior, delivered vacuum performance, and materials development. Other areas in which further effort appears justified will be identified.

Engine Duty Cycles

Presently envisioned engine duty cycle requirements for two typical orbiter missions—one to Mars, the other to Jupiter—are shown in Table 2. In both cases, the engine will be shut down for long periods between burns, but there are no apparent throttling or pulsing requirements. The critical engine events are fixed-thrust (1000-lbf) long-duration firings—about 500 sec for the Jupiter mission, and about 1000 sec for the Mars mission. The use of integrating accelerometers to monitor and control the velocity increments is planned, so precise engine startup and shutdown transients are not absolutely necessary. However, because of the minimum allowable quantities of propellant residuals, it will be necessary to hold propellant flowrates close to the design values, so that the maximum allowable increase in thrust chamber throat area is ~5%. This requirement will be difficult to meet with the present state-of-the-art.

The longest firing durations demonstrated to date[3] have been 80 and 370 sec with FLOX*/B_2H_6 propellants. The injector and chamber concepts and materials used were shown earlier[4] to be capable of 1000-sec firings with the FLOX/monomethylhydrazine (MMH) propellant combination and were thought to be capable of extension to OF_2 or FLOX/B_2H_6 propellants. The multiple-element, radial-pattern, self-impinging doublet injectors were made of nickel. They produced a flow that was stratified into a core region (containing 70-wt % of the total propellant flow at a mixture ratio r of 3.85) and a peripheral barrier zone (containing 30-wt % of the propellants at an average r of 0.5). The purpose was to lower the driving-gas temperature for heat transfer and the concentrations of oxidizing chemical species in the vicinity of the walls. The specific injector design employed (the result of numerous optimization experiments) was chosen to maximize combustion efficiency, minimize heat flux to the walls, and minimize solids deposition. Injectors of this general type are illustrated in Refs. 1, 3, and 4.

Table 2 Typical 1000-lbf OF_2/B_2H_6 engine duty cycles (burn times in secs)

Parameter	Mars orbiter	Jupiter orbiter
1st trajectory correction	22	22
2nd trajectory correction	22	22
Orbit insertion	1000	488
Orbit trim	22	22
Orbit plane change	...	520
Total	1066	1074

* A low-cost substitute for OF_2, which has been shown[3] to adequately simulate it with respect to performance and heat transfer, it is a mixture of 70-wt % F_2 and 30-wt % O_2.

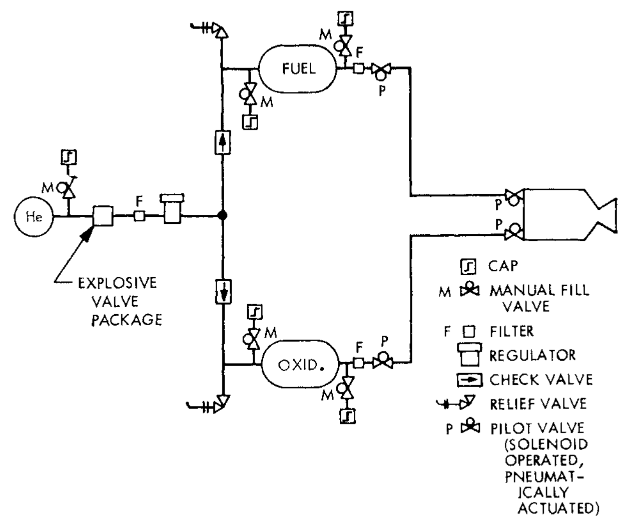


Fig. 1 Schematic representation OF_2/B_2H_6 propulsion system.

The chambers (Fig. 2) consisted of a carbon-phenolic ablative liner and an AXF-AS† synthetic graphite throat insert, backed up by a silica-phenolic ablative insulator. Carbonaceous and graphitic materials of these general types had been successfully demonstrated[4] in long-duration FLOX/MMH firings, and the configuration and specific materials of Fig. 2 were, like the injector, chosen after a series of shorter duration optimization firings.

The long-duration firings, conducted at a chamber pressure P_c of ~100 psia and an over-all r (core and barrier zone combined) of 1.95, yielded combustion efficiencies (η_{c^*}) of about 93% based on theoretical shifting values at the core r (3.85). The tests were made at ground level with a low-ϵ expansion nozzle, but the flow rates corresponded to approximately 1000 lbf of thrust in space vacuum. The injectors suffered no damage, but two serious problems emerged which, unless solved, could affect successful spacecraft propulsion opera-

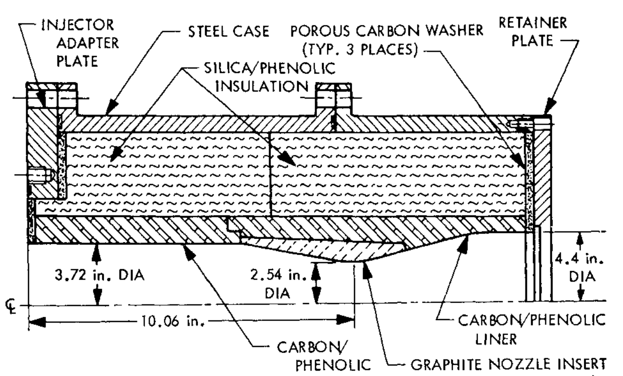


Fig. 2 Schematic cross section of chamber assembly used in 370-sec firing with 70-30 FLOX/B_2H_6.[3]

† A product of Poco Graphite Inc., 1200 Jupiter Road, Garland, Texas.

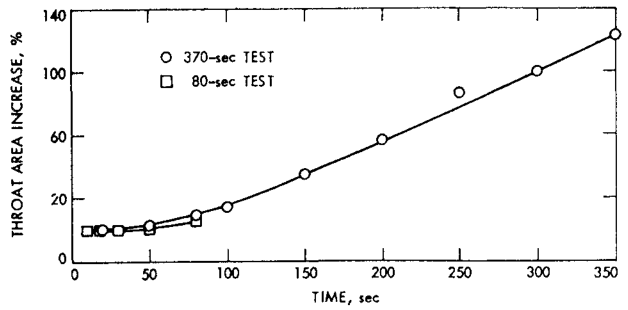


Fig. 3 Variation of nozzle throat area in 80-sec and 370-sec duration firings with FLOX/B_2H_6 propellants.[3]

tions: 1) excessive throat erosion; A^* was 5% larger after the 80-sec test, and 124% larger (with a different, but identical, chamber) after 370 sec, which is clearly unacceptable, (Fig. 3), and 2) copious deposits of boron-containing solids on the injector face and the interior surfaces of the chamber and nozzle. Because of the potential orifice blockage effects of such deposits, a post-fire gas purge of the injector will be required unless this problem is resolved, and this would increase the weight and complexity of the propulsion system.

The mechanism of throat erosion with carbonaceous materials is presently only imperfectly understood. Mechanical erosion may contribute and would be enhanced by the particulate nature of the synthetic graphites used to date. (Pyrolytic graphite has been used recently in the fabrication of chamber liners, but these have not yet been evaluated experimentally with OF_2/B_2H_6). Chemical attack is also a strong possibility. Chemical reaction between graphite and the boron-rich barrier gases is theoretically possible, based on thermodynamic equilibrium calculations. On the other hand, if the intended barrier protection were progressively destroyed, as by the encroachment of solid deposits over the barrier spray orifices, the wall would be exposed to the oxidizer-rich core gases, and chemical attack—of a different nature—would again result. In either case, the rates of such reactions could be accelerated (an undesirable effect) by the large surface areas of graphite exposed to the combustion gases as a result of using the pressed-powder grades of synthetic graphite. The higher wall temperatures resulting from barrier zone destruction would also accelerate oxidative chemical erosion.

These two problem areas are currently being subjected to vigorous attack. Gas-liquid injectors have yielded encouragingly low amounts of deposits compared to the liquid-liquid types. Several types of liquid-liquid injectors[5,6] have similarly shown great promise in short-duration tests. Advanced materials, specifically chosen to circumvent the chemical attack problem, are being test-fired with OF_2/B_2H_6 at JPL.

A satisfactory long-duration firing capability has yet to be demonstrated with barrier-cooled carbonaceous or graphite-lined thrust chambers. Partly for this reason, work was recently begun on the alternative heat pipe[2] and regenerative concepts, both of which are expected to operate at wall temperatures low enough to permit the use of metals, such as nickel, as materials of construction.

While throttling and pulsing operations are not immediately required, some analytical and experimental work has been done in anticipation of possible future requirements.[5] The results indicate that throttling or pulsing operations with OF_2/B_2H_6 lie within the capabilities of the present state-of-the-art technology. Adding such operational modes to some future space-storable propulsion system, if required, should be relatively straightforward, provided, of course, that other operational problems, such as solids deposition, can be reduced to a noninterfering level.

Demonstrated Performance and Heat-Transfer Characteristics

Although firings of the OF_2/B_2H_6 propellant combination were first conducted under IR&D funding by Thiokol-RMD in 1960, no performance data from those tests are available. Under NASA contracts in 1962 and 1963, Thiokol-RMD conducted test programs that culminated in tests of 2000-lbf thrust motors at the Arnold Engineering Development Center altitude test facility. The maximum $I_{sp_{vac}}$ achieved was 383 lbf-sec/lbm at $\epsilon = 40$ with $P_c \cong 148$ psia and $r = 3.22$.[7-9]

Rocketdyne first fired the OF_2/B_2H_6 propellants during an in-house study in 1966. Work was followed under three NASA contracts: NAS7-304[3] involved design and testing of a boundary-controlled thrust chamber made of graphite; under NASw-1229,[10] gaseous B_2H_6 and liquid OF_2 were burned in a hardware configuration designed to give maximum performance without regard to heat transfer; and under NAS7-741,[11] performance was evaluated at $\epsilon = 60$ using two different injectors, each incorporating a different means of reducing the heat flux to the chamber and nozzle. Work is currently underway at Rocketdyne on two more contracts: NAS7-767 to continue development of a film- or boundary-cooled thrust chamber; and NAS7-765 to develop a regeneratively cooled chamber. All of this work has been, and is, at the 1000-lbf thrust level.

The Aerojet-General Corporation has fired FLOX/B_2H_6 under two contracts: NAS7-713,[5] to develop a micro-orifice "platelet" injector and a compatible thrust chamber, and NAS7-659[12] to establish a boundary environment to control the chamber wall heat flux and erosion. Contract NAS7-697, currently underway, is to develop a heat-pipe-cooled thrust chamber for eventual use with OF_2/B_2H_6.[2]

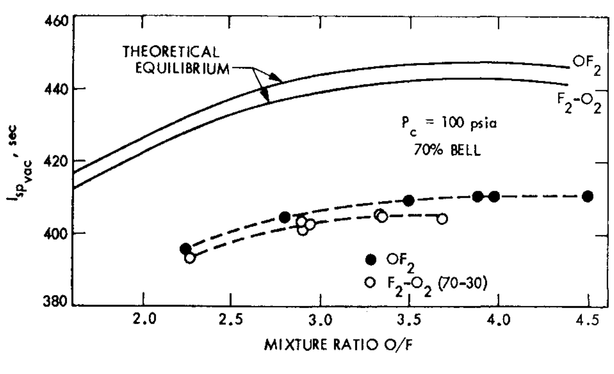


Fig. 4 Delivered vacuum performance of OF_2/B_2H_6 and FLOX/B_2H_6 with uniform mixture ratio distribution.[10]

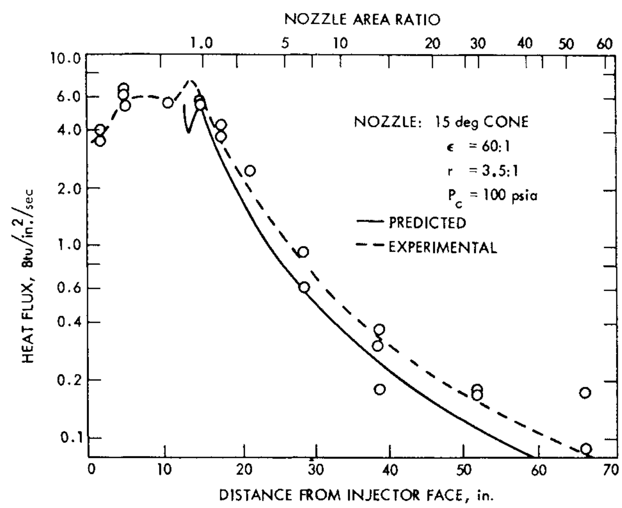


Fig. 5 Heat flux profile in OF_2/B_2H_6 firings with uniform mixture ratio distribution.[10]

Maximum Performance

The work of Ref. 10 demonstrated the maximum performance potential of the OF_2/B_2H_6 propellants. A vacuum specific impulse of 412 lbf-sec/lbm was achieved at $r = 4.0$ with $\epsilon = 60$ and $P_c = 100$ psia (Fig. 4). Comparative tests showed that a 15° conical nozzle was very slightly superior to a "bell" nozzle (1 lbf-sec/lbm), and OF_2 gave about 1.5% higher performance than did a FLOX simulant. These results were obtained with a gas-liquid triplet injector designed to give uniform mixture ratio distribution and maximum performance. The triplet elements near the chamber wall were rotated to avoid direct impingement of oxidizer fans on the wall, but no concessions were made to reduce chamber wall heat flux at the possible expense of performance. Typical heat flux measured during these performance tests is shown in Fig. 5.

Performance with Reduced Heat Flux

In the work of Ref. 11, tests were conducted to determine the performance that could be attained using some of the fuel to establish a lower heat-flux, fuel-rich boundary region to protect the chamber wall. The results, using both film coolant and a stratified mixture ratio distribution with a low-r layer next to the chamber wall, showed that both methods are effective in reducing q/A at the expense of a decrease in performance. Liquid film coolant keeps the injection end of the chamber at a low temperature, and if sufficient coolant is used, an appreciable heat flux reduction can be realized down past the nozzle region, to $\epsilon \simeq 5$. Stratified mixture ratio distribution seems to protect the chamber and the nozzle to $\epsilon = 20$ or more. For a given reduction in peak q/A, higher performance can be obtained with stratified flow than with film coolant; although the stratified flow will have a higher heat flux at the injector end of the chamber, it will maintain its over-all advantage far into the expansion region of the nozzle. Thus, with boundary control, nozzle throat heat flux can be reduced to 4 or 5 Btu/in.^{2}-sec with a delivered I_{sp} of 380–390 lbf-sec/lbm. This represents a performance penalty of only 5–8% for a peak throat heat flux reduction of 40–50%, as seen in Fig. 6.[11] Performance (normalized to an over-all r of 3.0) vs throat heat flux is shown for each of four test configurations. Except for one point, there is a consistent relationship between over-all I_{sp} and throat heat flux. The seemingly ambiguous point on Fig. 6 corresponds to injection of what was apparently an insufficient film coolant; so that mixing of the film and core flows could have resulted in a high-temperature boundary flow by the time the combined flow had progressed as far as the throat.

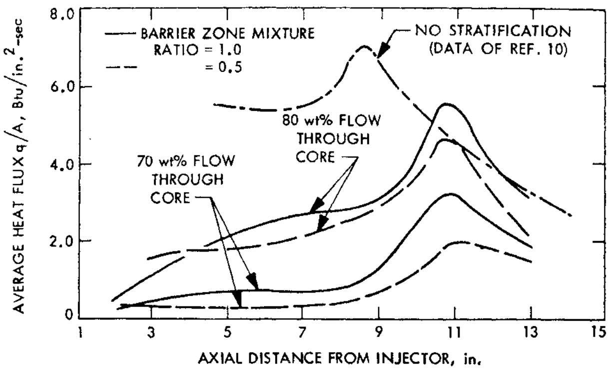


Fig. 7 Chamber heat flux comparison for four stratified injectors with $FLOX/B_2H_6$ propellants.[11]

The optimum form of boundary protection will depend on such factors as allowable heat flux and performance decrement levels, thrust chamber cooling concepts, and materials compatibility. Although for certain applications additional data would have to be obtained over a broader range of the parameters involved, a basic performance capability and its relationship to heat transfer have been established. It might also be possible to combine liquid film and stratified boundary-layer mixture ratio protection.

Combustion Chamber Heat Flux and Cooling Configurations

For the stratified flow technique, 20–30% of the total propellant flow is injected close to and roughly parallel to the chamber wall at a r of 0.5–1.0, to form the cool stratum or "barrier zone." Chamber and nozzle heat flux can often be reduced by this technique (Fig. 7).[11] For the liquid film technique, the coolant is supposed to remain on and cool the chamber wall at least as far as the start of the nozzle convergence, and this has been demonstrated with the N_2O_4/MMH propellant system.[13] With the OF_2/B_2H_6 propellant system, however, the combination of high core-gas heat transfer to the film and low B_2H_6 heat capacity result in complete evaporation of the liquid film by the time it has flowed only a short distance,[3] as discussed later. The vapor then mixes with adjacent combustion gases to form a low-r low-temperature stratum near the wall. Thus, for the OF_2/B_2H_6 combination, there is little difference between the two techniques, and liquid film cooling in the conventional sense is not possible. Typical q/A distributions obtained by using various amounts of B_2H_6 as a film coolant are shown in Fig. 8[11]; the

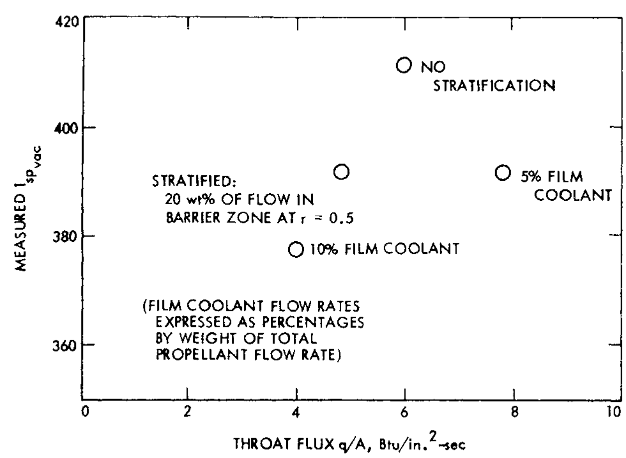


Fig. 6 Performance of OF_2/B_2H_6 vs heat flux for four-boundary control schemes; P_c = 100 psia, r = 3; ϵ = 60; 15° cone.

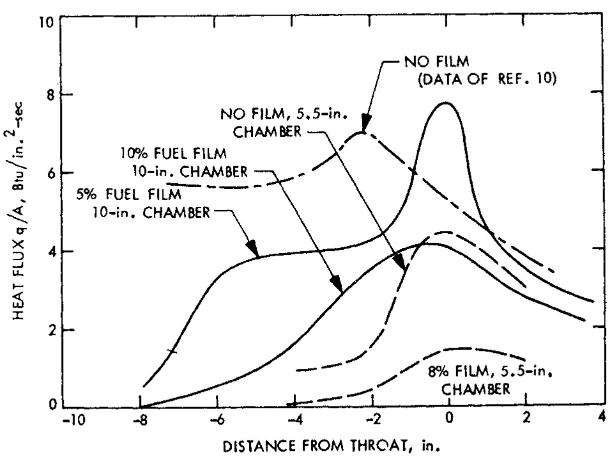


Fig. 8 Chamber heat flux comparison for injectors with liquid B_2H_6 film cooling.[11]

throat value decreases as the amount of film coolant is increased and as the distance to the throat from the point of film coolant injection is decreased.

The use of boundary control together with refractory materials leads to radiation-cooled or passively-cooled thrust chamber concepts. In the former, the wall reaches a temperature slightly lower than the gas recovery temperature T_{gr}, the net convective heat flux from the gas to the wall being lost by radiation from the external surface of the chamber. Such a chamber concept is being pursued by Rocketdyne; control will be maintained via an initially liquid B_2H_6 film, and chamber construction will be of synthetic graphite or a refractory metal. A passively-cooled chamber, on the other hand, is insulated, so that there is little or no heat loss to the outside; as a result, the wall comes into equilibrium at the full T_{gr} (except for the effect of radiation from the inside surface of the nozzle exit cone). Aside from this, the two concepts are quite similar, and available boundary-flow heat-transfer information is applicable to both. Passively-cooled OF_2/B_2H_6 thrust chambers are being evaluated at JPL.[1]

In regenerative cooling systems, the conductive metals that can be used to separate the coolant from the combustion gases generally have a much lower working temperature (1000–1500°F) than the refractory materials used for radiation- or passively-cooled chambers. At these lower T_w's, the heat flux may be nearly as high as the cold-wall values cited earlier. Thus, materials of limited high-temperature strength are in contact with extremely high-temperature combustion gases on one side and with coolant fluids having limited heat capacity and heat-transfer characteristics on the other side. Some reduction in heat flux can again be achieved by boundary-flow control. Regeneratively cooled thrust chambers are being developed by Rocketdyne.

The heat-pipe version of the regeneratively cooled thrust chamber now under development by Aerojet could ultimately avoid the necessity for stratification, with its resultant performance losses, by using the heat-pipe principle to distribute the chamber wall heat flux, so that the coolant encounters only a uniform average wall temperature, with a consequent leveling of heat flux peaks.[2] Aside from this engine, however, all engine concepts currently under development require some barrier protection.

The creation of fuel-rich stratified barrier zones has been studied extensively, and the results of parametric variations affecting heat transfer and chemical compatibility have already been reported.[3,12] Information on boundary control via a liquid B_2H_6 film has become available only recently, and so will be treated here at somewhat greater length.

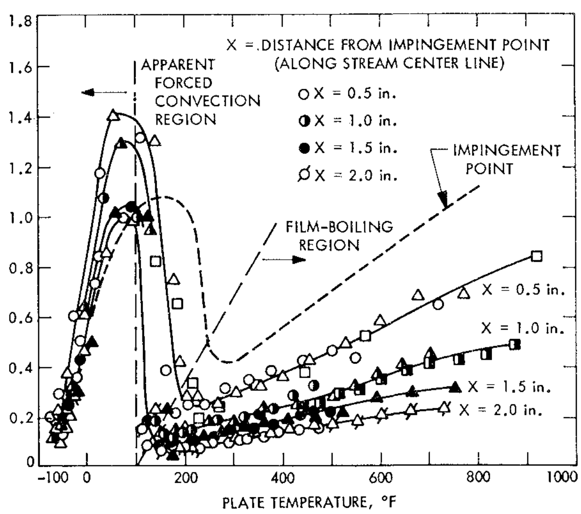


Fig. 9 Variation in diborane film cooling characteristics as determined in heated plate studies.[12]

Heat Flux Reduction via Film Cooling

Film cooling by B_2H_6 has been applied in two ways.[3] Initially, many small streams of coolant were directed at the chamber wall at an angle of ~30°. These streams were deflected by the wall and spread out to form individual films which coalesced at the edges. Cold-flow experiments revealed that this method left small triangular unprotected areas upstream of the point where the sheets from the streams coalesced. Lateral momentum at the point of coalescence caused coolant to pile up and create thick ridges in the coalesced film; these were felt to be susceptible to shear-stripping by the accelerating combustion gases. Furthermore, test-firings indicated that creation of a B_2H_6 film from many individual streams impinging on the wall at a shallow angle was relatively inefficient. It has since been found that B_2H_6 coolant can be introduced with improved efficiency as a continuous film with a tangential, as well as an axial, velocity component, from a thin annular slot whose outside boundary coincides with the inside wall of the thrust chamber. Swirl injection has, therefore, become more or less the standard approach for film cooling, and adequate design criteria are available.[3,13]

Once laid down on the chamber wall by either method, the film coolant is heated from both sides. Very soon it is heated to its vaporization temperature, which will be somewhat lower than the normal saturation temperature corresponding to P_c, as a result of the hot gases flowing across the surface of the film. From then on, the liquid film evaporates at approximately constant temperature until it is completely consumed and forms a vapor layer into which the combustion gases gradually mix by turbulent diffusion. Analytical studies and correlation of experimental data[3] have now established the following knowledge with respect to the transfer of heat to thin B_2H_6 films under thrust chamber conditions:

1) Several times as much heat is usually transferred into the liquid film from the hot gas side as can be transferred from the chamber wall side.

2) The heat-transfer rates from the chamber wall to the fluid film range up to ~1 Btu/in.²-sec. The maximum heat-transfer coefficient of ~0.01 Btu/in.²-sec °F (nucleate boiling) decreases to less than 0.0005 Btu/in.²-sec °F in the film boiling regime, i.e., $T_w > 250$°F and pressures near 100 psia.

3) The heat-transfer coefficient between the combustion gas and the liquid film surface is higher than the corresponding solid-surface heat-transfer coefficient by a factor of 2–4. This is presumed to be due to a rippling of the surface of the fluid film by moving combustion gases. Under these conditions, q/A may be as high as 5 Btu/in.²-sec.

4) Liquid B_2H_6 film lengths of only $\frac{1}{2}$–1 in. are to be expected under typical operating conditions.

Propellant Coolant and Flow Characteristics

Film Coolant Properties of Diborane

After the B_2H_6 film coolant has been vaporized, its stagnation temperature increases as it progresses down the cham-

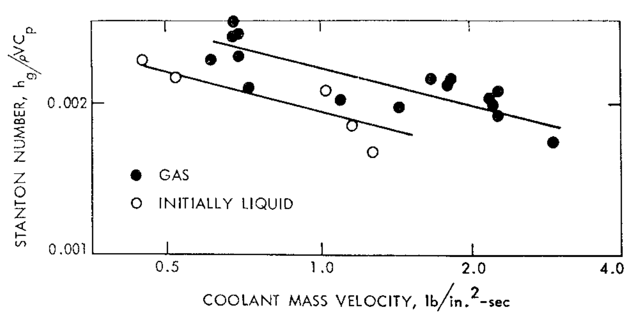


Fig. 10 Stanton number correlation of B_2H_6 heat-transfer data.

ber and nozzle, since the rate of transfer of heat and energy from the core gas to the vapor film is higher than the rate of transfer of heat from the vapor film to the wall. However, q/A and T_{gr} are both much reduced compared to the conditions which would exist were the wall to be in direct contact with an unmodified core flow.

In a series of tests simulating heat transfer from a hot chamber wall to B_2H_6 film coolant,[12] a cold fuel stream was impinged on a preheated plate at an angle of 20°. Heat flux was determined from the rate of cooling of the plate at several locations downstream (Fig. 9). The B_2H_6 stream was injected at −70°F into a test chamber maintained at 100 psia (T_{sat} = −32.5°F), so that there was very little liquid subcooling. The velocity of the stream was ~150 fps, and the initial T_w's were as high as 900°F. At T_w's above 200°F, the heat-transfer characteristics correspond to what would be expected in the film-boiling regime, with heat-transfer coefficients of 0.0004–0.0010 Btu/in.²-sec°F. The steeply rising curves on the left-hand side of Fig. 9 (T_w's from −70°F up to about +30°F) seem at first to suggest classical nucleate boiling. However, more detailed analysis shows that this result could be expected from forced convection flow of liquid B_2H_6; classical nucleate boiling should produce much steeper slopes. The q/A levels in Fig. 9, from 0.10 to 1.4 Btu/in.²-sec, are entirely consistent with the values used in an analytical model to correlate data obtained from tests of film-cooled thrust chambers.[3]

Regenerative Coolant Properties of Diborane

In regeneratively cooled thrust chambers the coolant may experience heat-transfer regimes ranging from forced convection to forced convection with nucleate boiling, to film boiling, and to vapor-phase forced convection. Recent studies[14] have indicated that B_2H_6, when used as a regenerative coolant, is required to vaporize. Some exploratory experimental work on heat transfer to gaseous B_2H_6 and on heat transfer in the region of transition from liquid to gaseous B_2H_6 has been done recently.[14] Tests were conducted using a preheated copper block of large mass with a cylindrical passage (d = 0.081 in., L/d = 85) through its center. In some tests, gaseous B_2H_6 was supplied from an upstream heat exchanger at temperatures from 50° to 300°F, and the test passage was initially heated to temperatures from 200° to 600°F. In other tests, liquid B_2H_6 was supplied at −150° to −200°F. The upper line on Fig. 10 (through the solid data points) correlates heat transfer to gaseous B_2H_6; the lower line (open data points) represents averaged data in the regime in which the fluid entered as a liquid and emerged as vapor. Figure 11 shows that the data obtained for heat transfer to gaseous B_2H_6 conforms to a widely used heat-transfer correlation equation. Since there are no experimental data on thermal conductivity of B_2H_6, a calculated value was used in reducing the data to the form of Fig. 11; other properties can be obtained from the literature.[15]

The liquid-to-vapor data of Fig. 10 show that vaporization can be accomplished in a passage of L/d = 85 at reasonable wall temperatures and mass velocities, and the other data indicate that B_2H_6 vapor can absorb up to 4 Btu/in.²-sec with a coolant side wall temperature of less than 800°F at a coolant passage mass velocity of 3.5 lbm/in.²-sec. These values appear compatible with practical regeneratively cooled thrust-chamber designs, where the throat heat flux can be reduced to 4 Btu/in.²-sec by using a moderate amount of mixture ratio stratification, and with heat-pipe-cooled thrusters, where the heat-flux transformation properties of the heat pipe can be used to reduce the heat flux to the coolant to a uniform average value on the order of 1–2 Btu/in.²-sec.

Oxygen Difluoride as a Regenerative Coolant

Analytical studies of both regenerative and heat-pipe-cooled OF_2/B_2H_6 thrust chambers have indicated the desirability of using OF_2 as well as B_2H_6 as a coolant.[2,14] Heat-transfer data for OF_2 have been obtained using apparatus similar to that used for the B_2H_6 data previously discussed, and are presently being reduced and correlated. In the meantime, heat transfer to similar fluids, such as oxygen and nitrogen, has been measured in the liquid forced convection, nucleate boiling, and gaseous forced convection regimes, and the correlations developed for these fluids are presumed to be applicable for predicting the heat-transfer characteristics of OF_2. Typical heat-transfer correlations are given in Refs. 16 and 17. The physical properties of OF_2 that may be needed to correlate heat-transfer data, and for other design purposes, are tabulated in Ref. 15.

Diborane Stoppages

Two apparently different types of flow stoppage in small passages have been experienced with B_2H_6. One type is thought to result from the deposition of decaborane ($B_{10}H_{14}$) on surfaces colder than 211°F (its freezing point). For $T_w >$ 600°F, higher boranes, having even higher freezing points, may be formed. Flow stoppages of this nature can be avoided by assuring that B_2H_6 is not exposed to $T_w >$ 600°F, or that B_2H_6 previously heated above this temperature is not subsequently exposed to $T_w <$ 211°F. It is not regarded as a major problem of engine development.

A second type of flow stoppage has been encountered in B_2H_6 flowing as a liquid through small orifices or tubes. The mechanism has not yet been explained, although localized buildup of frozen B_2H_6 near regions in which cavitation occurs has been advanced as a possibility, because in one instance no obstruction could be found after system warmup. This type of flow stoppage was experienced in the feed system of the copper-rod heat-transfer apparatus described previously. With the upstream fluid at −150°F and at 150 psia pressure, gradual plugging occurred in the feed line (which contained a flow metering orifice and/or a short length of $\frac{1}{8}$-in. tubing between lengths of $\frac{1}{4}$-in. tubing). When the upstream pressure was decreased to 100 psia, however, no plugging was encountered. The same stoppage was observed when ethane was used to simulate B_2H_6. Similar time-dependent plugging of B_2H_6 injector orifices and internal feeder passages has been observed in JPL test-firings of micro-orifice injectors.

Other experiments conducted at JPL were unable to reproduce this kind of blockage in a B_2H_6 cold-flow system. Specifically, liquid B_2H_6 at −200°F was flowed through a cavitating venturi (to control its flow rate), and then through a plate containing several sharp-edged holes, each 0.020 in. in diam, with a pressure drop of ~70 psi. The B_2H_6 was discharged into a refrigerated and pressurized receiver, so the back pressure on the system could be adjusted by controlled venting of the receiver. At constant flow rate, there was no change in orifice plate pressure drop during tests in which back-pressure was held constant at various levels for periods

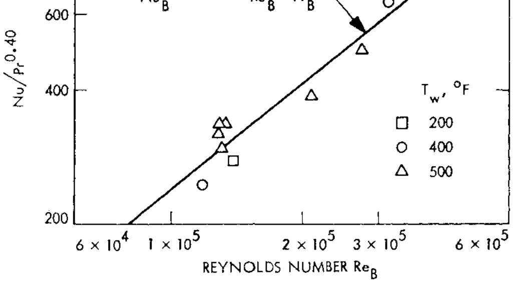


Fig. 11 Nusselt number correlation of B_2H_6 heat-transfer data.

of up to 60 sec, which indicated the absence of flow blockage under these conditions. Additional information must be generated in this area before development of flight prototype models can proceed with confidence.

A true freezing flow stoppage can occur if the FLOX mixture is used as a simulant for OF_2 in tests with B_2H_6. Here the oxidizer is more than 100°F colder than the freezing point of B_2H_6. Actual freezing of B_2H_6 can occur if the injector passages are cooled to below −265°F, either by heat exchange with the FLOX oxidizer or during prestart chilldown of the equipment.[5] This appears to be primarily a test stand and development program problem, encountered as a result of attempting to save money by using the less expensive FLOX as a simulant for OF_2; in some instances the thermal control problems introduced by the use of this oxidizer simulant may overshadow the difficult-enough problems of working with OF_2 and B_2H_6.

Most of the information essential to the heat-transfer design of 1000 lbf OF_2/B_2H_6 engines of any type is now on hand.

Vacuum Ignition

Vacuum ignition characteristics of both OF_2 and FLOX with diborane with 100-lbf-thrust engines at simulated altitudes in excess of 250,000 ft were determined.[18,19] One- and nine-element unlike doublet injectors and hard-seat, in-line solenoid valves were used in most of the tests. The primary variables investigated were propellant lead/lag, chamber pressure (100 and 20 psia), and propellant and hardware temperatures. Instrumentation included optical propellant entry and ignition detectors and high-response, flush-mounted piezoelectric pressure transducers in the thrust chamber and in each propellant manifold. The results exposed no serious vacuum ignition problems with either oxidizer. Smooth ignition of OF_2/B_2H_6 is dependent upon nearly simultaneous liquid injection of fuel and oxidizer. Fuel leads of longer than a few milliseconds produced significant pressure disturbances in the oxidizer manifold. On the other hand, OF_2 leads of longer than a few milliseconds frequently resulted in chamber pressure spikes. No chamber pressure spikes were observed with FLOX leads, even under conditions which closely duplicated the OF_2 tests which produced spikes; this difference suggests that the problem may be associated with oxidizer vaporization rates.

Propellant and engine temperatures did not appear to influence ignition times either. Wide temperature ranges were investigated: from −170 to −320°F for the OF_2, from −250 to −320°F for the FLOX, from −100 to −250°F for the diborane, and initial engine temperatures from +70 to −250°F. Although temperature did not affect ignition time, the character of manifold filling was strongly dependent on injector temperature and propellant temperature (vapor pressure). As expected, warmer temperatures produced "softer" manifold fills, as evidenced by the manifold pressure histories.

In common with other liquid propellant systems, ignition times were shortened by rapid filling of injector manifolds. To accomplish this, rapid valve response, low system pressure drops, high propellant flow rates, and minimum passage volumes are, of course, required.

Ignition generally occurred in a low-density, low-temperature propellant vapor flow which preceded the bulk liquid flow. The "pilot flame" thus produced is apparently beneficial in providing a smooth transition to steady combustion with full-flow liquid or two-phase injection. Establishment of the pilot flame was aided by a minute gaseous preflow through the hard valve seats during the few milliseconds between the application of current and the start of poppet

Table 3 OF_2 (or FLOX)/B_2H_6 deposits morphology

Injector[a]	Oxidizer propellants	ϵ_c	Tests, (duration, each)	O/F	P_c, psia	Principal constituent[b]	Reference
Self-impinging doublets							
a) Edgewise core impingement, barrier zone	FLOX	2.14	13 (7 sec)	3–4	100	B_2O_3	3
b) Same as above	FLOX	5.0	4 (7 sec)	3–4	100	B_2O_3	3
c) Same as above	FLOX	5.0	1 (3 sec)	2.4	100	B	[d]
d) Maximum core fan spacing, barrier zone	FLOX	5.0	1 (3 sec)	2.2	100	B	[d]
e) Maximum core fan spacing, boundary-layer coolant jets	FLOX	8.0	1 (1.5 sec)	Not reported	57	B	12
f) Edgewise core impingement, barrier zone	F_2	2.14	3 (2 sec)	3.8–4.0	100	None	20
O-F-O triplets							
g) Barrier zone	FLOX	1.5	1 (5 sec)	2.3	105	B	12
h) No film cooling or barrier zone	FLOX[c]	2.1	12 (~2 sec)	2.9–4.5	100	None	10
Micro-orifices							
i) Showerhead, barrier zone	FLOX	1.5	3 (1 sec)	2.0–8.0	100	Slight B	5
j) Self-impinging doublet, barrier zone	FLOX	1.5	1 (2 sec)	15	100	Slight, not measured	5
Unlike doublets							
k) Sheets, exposed, elements	OF_2	6	1 (1.5 sec)	2.1	100	Heavy B	[d]
l) Sheets, buried, vented elements	OF_2	6	1 (3 sec)	2.1	100	None	[d]

[a] Test letters correspond to figure parts of Fig. 12.
[b] 80-wt % or more, as determined by chemical analysis.
[c] Gaseous B_2H_6 used here; liquid B_2H_6 in all other cases.
[d] Unpublished JPL work.

transfer. Ignition delays were somewhat shorter with FLOX than with OF_2. Since the dominant ignition mechanism appears to be gas-phase propellant reactions, the shorter delays with FLOX may be attributed to its higher vapor pressure and the fluorine-enriched vapor which results from vaporization of the mixed oxidizer. Solid combustion residues were found in the thrust chamber following each test.

During some tests, high-pressure peaks occurred in the oxidizer manifold and occasionally caused delayed ignition due to momentary interruption of the oxidizer flow. Some of these perturbations were attributed to fuel entering the oxidizer manifold. But in one case, a spike occurred when OF_2 only (no fuel at all) entered a chamber containing accumulated boron-rich deposits from previous firings. Thus, in addition to the other deleterious effects of deposits enumerated below, they may also bring about hard starts at altitude. Several instances of post-ignition "pops" in the thrust chamber and oxidizer manifold were observed, but popping was too infrequent to allow analysis of the mechanisms involved.

Additional vacuum ignition testing is required to verify the validity of these guidelines over a wider spectrum of hardware configurations. In particular, testing with a wider variety of flight-type valves is desirable to further investigate the role of the gaseous preflow/pilot flame ignition mechanism and its relation to valve sealing and opening characteristics.

Solids Deposition Problem

One of the more serious and least understood problems is that of solids deposition, sometimes on combustion chamber walls and in the divergent portions of nozzles, but most frequently on the injector face where it can lead to several undesirable consequences. Propellant flowrates may be reduced; jets may be misdirected, enhancing the possibility of localized burn-through; and, fuel-rich barrier protection may be progressively destroyed as solids deposit over the barrier orifices. Indeed, this latter phenomenon is suspected of being a primary cause of excessive throat erosion in the long-duration tests discussed earlier. In all of these cases, post-firing injector purges to aid in dislodging the deposits may be required, and this could materially increase the propulsion system complexity.

Solids deposition has emerged as a major problem area in most of the OF_2 or $FLOX/B_2H_6$ experimental programs conducted to date. Because these programs were conducted essentially concurrently, and because a deposition problem was not fully anticipated at their outset, the results are largely empirical and unrelated. No methodical studies have yet been made. Only a few combinations of injector element type, chamber geometry, and operating conditions have been found to yield deposit-free combustion, even for firings of very short duration.

This situation may be appreciated with the aid of Table 3 and Fig. 12. Self-impinging doublet jets (most frequently evaluated to date) and triplet jets have given varying amounts of deposits with both propellants injected in the liquid state. Changing from edgewise core fan impingement, Fig. 12c, to maximum core fan spacing, Fig. 12d, had little apparent effect. Interestingly, a certain configuration of unlike impinging liquid sheets, Fig. 12l, has so far produced virtually no deposits, and for gaseous fuel/liquid oxidizer injection, triplet elements, Fig. 12h, have likewise given virtually deposit-free operation. Micro-orifice injectors, Figs. 12i and j, have produced only slight boron deposits, but have shown signs of internal flow blockage in the fuel side.

Combustion with F_2 as the oxidizer resulted in deposit-free operation in one isolated case (Fig. 12f). There are no discernible effects of over-all r or P_c over the relatively narrow ranges of these variables investigated, and no apparent first-order influence of the chamber contraction ratio ϵ_c from 1.5 to 8.0. Most of the injectors evaluated have had peripheral boundary-layer cooling or barrier protection.

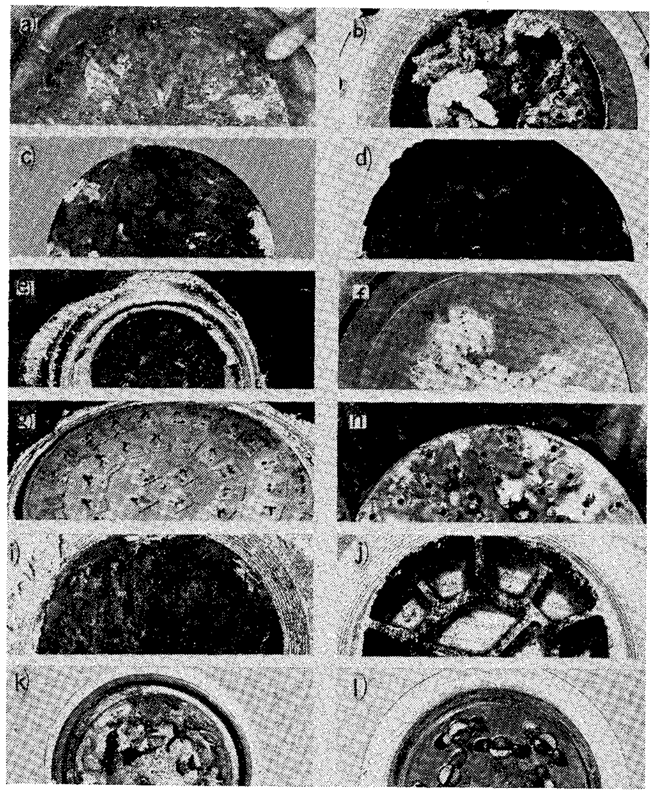


Fig. 12 Comparison of typical post-test appearance of OF_2 and $FLOX/B_2H_6$ injectors (identified in Table 3; photographs not to scale) (photographs a, b, f, and h, courtesy of Rocketdyne; e, g, i, and j, courtesy of Aerojet Liquid Rocket Co.; all others, JPL).

No clear trend in the chemical composition of the deposits is evident from the published results. In the work carried out by Rocketdyne, B_2O_3 was the predominant constituent, but in all other programs, including that of Refs. 18 and 19, elemental boron was the major component of the deposits. Furthermore, the influence of the motor shutdown sequence on the quantity and chemical identity of the deposits has not been reliably established. It has been suggested[3] that solids deposition may be a time-dependent phenomenon in certain specific instances, but insufficient data exist to permit the generalization of this contention.

There are two probable primary sources of particulate, elemental boron: the combustion process itself, and the pyrolysis of B_2H_6. As shown in Table 4, boron can be formed in appreciable quantities as a natural product of OF_2/B_2H_6 combustion at $O/F \leq 1.5$. For $1.45 \leq O/F \leq 1.10$, the boron thus formed can exist in the liquid state at combustion temperatures. Neglecting pressure effects, this liquid boron may be estimated to solidify below about 4, 150°F. Since injector face temperatures are usually considerably cooler than this, it would seem to be theoretically possible for the liquid boron naturally present to solidify on the injector. With $O/F <$ 0.5, considerable solid-phase boron can be produced by the

Table 4 Approximate concentration and state of boron in combustion products of $OF_2/B_2/H_6$[a]

O/F	T_c, °F	Mole % B	State
2.0	5390	0	...
1.5	4670	7.0	Vapor
1.45	4600	8.4	Incipient liquid
1.1	4150	19.0	Incipient solid
1.0	3990	22.0	Solid
0.5	3040	35.0	Solid

[a] Calculated for −135° F liquid B_2H_6 and −229° F liquid OF_2 at P_c = 100 psia, assuming one-dimensional shifting equilibrium in the chamber.

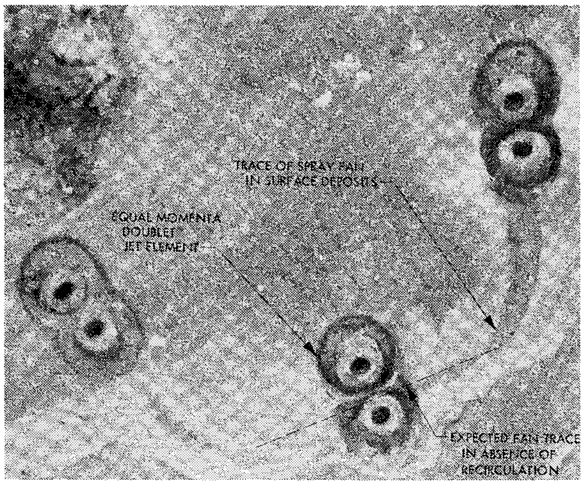


Fig. 13 Evidence of gas recirculation across face of 200-lbf OF_2/B_2H_6 self-impinging doublet jet injector.

combustion process. The adhesive qualities of the solid material in the combustion environment are not known.

Elemental boron can also be formed by the pyrolysis of diborane. At low temperatures, this reaction proceeds relatively slowly via a complex route of intermediate steps. But at high temperatures, shock-tube studies[21] have shown that the pyrolysis proceeds essentially according to an irreversible over-all reaction. Thus,

$$B_2H_6 \rightarrow 3H_2 + 2B \tag{1}$$

at a rate governed by

$$-d[B_2H_6]/dt = K[B_2H_6] \tag{2}$$

where

$$\log_{10}K = 10.32 - 5690T^{-1} \tag{3}$$

with $K = \sec^{-1}$ and $T = °K$.

Thus, even at such moderate flame temperatures as 3040°F, corresponding to $r \simeq 0.5$, the pyrolysis rate constant K is about 2.5×10^7; the reaction proceeds almost instantaneously to completion.

Thus, the diborane fuel and its combustion are a potentially rich source of elemental boron and a possible source of oxides such as B_2O_3. Predominantly boron-containing deposits would probably be favored by fuel-rich conditions, since these conditions enhance boron generation by both the combustion and pyrolysis processes. On the other hand, oxidizer-rich conditions would be expected to favor B_2O_3 formation. Indications of gradations in deposits composition, with a partial

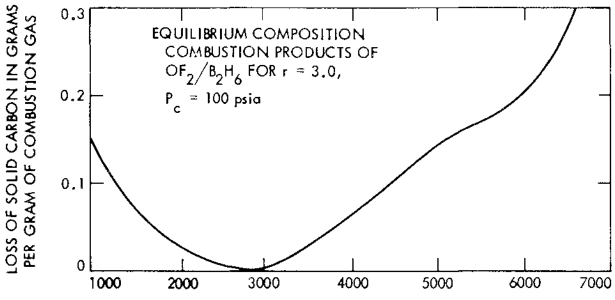


Fig. 14 Predicted loss of carbon (or graphite) from thrust chamber wall in boron-rich combustion environment, assuming chemical equilibrium is attained.

correlation with position relative to fuel- and oxidizer-rich regions, have been reported.[3]

Whether formed by combustion or pyrolysis, elemental boron would be expected primarily in regions away from the injector face, where the steady flame front is releasing the energy necessary to drive both kinds of process. Back-diffusion, gas recirculation, and possible liquid splashback from impinging jet backspray are therefore suspected as prime mechanisms for the physical transport of boron from the zones in which it is generated to those in which it can solidify or otherwise settle out. To this end, it has been suggested[3] that low ϵ_c's, with their attendant high chamber gas velocities, ought to minimize the extent of recirculatory flow and the attendant stagnant zones which could, respectively, transport and deposit solid products. However, the presence of deposits in chambers of relatively low ϵ_c and the absence of deposits in chambers of high ϵ_c (Table 3), present counterexamples to this simple explanation.

Figure 13 reveals clearcut indications of the presence of nonaxial gas flows which appear to vary in magnitude and direction across the injector face. Frequently, regions which exhibit such evidence of strong transverse flows show a remarkably light degree of deposition; they may be effectively swept clean. Conversely, regions that appear to be more nearly quiescent often display inordinately heavy solid deposits. This suggests that deposition may depend on local recirculation patterns, the effects of which are probably accentuated at high contraction area ratios.

This argument can be reinforced by examination of photographs such as those of Figs. 12k and 12l, which show the post-test appearance of two-200-lbf impinging-sheet liquid propellant injectors (the injectors are described in Refs. 1 and 6). The element design and arrangement, injection velocities, flow rates, r, P_c, and η_{c*} (97%) were exactly the same in both cases, with one exception. The injector of Fig. 12k had exposed elements (see Fig. 5, Ref. 1); whereas that of Fig. 12l had its elements buried and vented within the face. Thus, the product gas stream resulting from the reactive backspray that this element produced was channeled out of each of the vent slots shown in Fig. 12l. The areas swept by these gas streams, either singly or in reinforcing combination, are remarkably free of deposits, even though the ϵ_c employed was relatively large (6:1). The only difference between the injectors of Figs. 12k and 12l was the local gas recirculation pattern. A similar effect is probably achieved for a different reason in the liquid-gas-liquid triplet elements that also operated without deposition (Table 3). Here, the so-called "mixing region" of the central gas jets (which characteristically is a divergent cone with about a 50° included angle) may provide sufficient overlapping axial outflow regions to effectively block any back-diffusion or recirculatory transport of deposits.

Perhaps the most serious implication of the problem is the fact that it could extend to all candidate OF_2/B_2H_6 thrust chamber concepts for this class of missions, if liquid-liquid self-impinging doublet jet elements continue to be used. All concepts—regeneratively, boundary-, heat-pipe-, and passively-cooled—depend on either film or stratified mixture ratio cooling to reduce adiabatic wall temperatures and provide a compatible chemical environment at the walls. Solids deposition cannot be permitted to destroy this protection.

Fortunately, preliminary analyses[2,14] indicate that two of these candidates—the regeneratively and the heat-pipe-cooled engines—will provide one or both propellants to the injector in the vapor phase, as a result of phase changes in the cooling passages. Deposit-free operation has already been demonstrated[10] for this case. Similarly, at least two kinds of injectors promise freedom from serious deposit problems for the other two candidates which will require liquid-liquid injection, and other approaches may also prove feasible once the underlying processes are better understood. The several instances of deposit-free operation are encouraging and indicate that a methodical, analytical and experimental attack on the problem should yield a workable solution.

Advanced Materials for Thrust Chambers

Lightweight carbonaceous or graphitic materials are being considered for passively-cooled thrust chambers and for boundary-cooled chambers, where the wall temperatures can exceed the melting points of the common metals. Nickel, columbium, or tantalum alloys may be used for regeneratively or heat-pipe-cooled chambers, or possibly for boundary-cooled chambers with copious fuel film cooling, where wall temperatures are suppressed by means of active cooling. The supporting development being conducted under JPL technical management is primarily in the area of the carbonaceous materials. Before it was shown[3] that copper, beryllium, and Be/Cu alloys are not practical for OF_2/B_2H_6 boundary-cooled chambers, the high-temperature properties of these materials were determined in some detail, and the results are reported.[22]

Carbon-Based Materials

ATJ graphite was successfully used as a chamber and liner material with FLOX/MMH propellants as early as 1964.[3] Throat erosion was kept within tolerable limits by the use of a low-r peripheral combustion zone, which functioned as a protective "barrier" by reducing the concentrations of such reactive species as water and oxygen in proximity to the graphite walls. However, this scheme proved less successful with FLOX/B_2H_6, as described earlier. The mechanism for this unacceptably high erosion rate has not yet been conclusively established. The graphite may have been attacked by boron-containing species in the fuel-rich barrier gases, or the progressive buildup of solid deposits on the injector may have gradually destroyed the barrier protection, permitting oxidation of the graphite by the high-r core gases.

Chemical equilibrium calculations indicate the possibility of graphite erosion as a result of boron carbide (B_4C) formation; the results of such a calculation for the combustion species resulting from OF_2/B_2H_6 burned at $r = 3.0$ and $P_c = 100$ psia are shown as a function of wall temperature in Fig. 14. Although zero erosion is indicated at $T_w \cong 3000°R$, the possibility of appreciable chemical attack under equilibrium conditions at other temperatures must be conceded. Unfortunately, kinetic rate data are unavailable for this class of reactions, and the speed with which the equilibrium conditions are attained remains unknown.

If the reaction rates are rapid, however, a reaction between the boron-rich barrier and a graphitic wall to form B_4C is a distinct possibility. To counter this, chamber liners have been made of B_4C‡—the end product of such a reaction—to minimize the chance of this reaction occurring. The chambers are hot-pressed to rough dimensions from pure B_4C powder and then ground to their final dimensions. The resultant parts are pure recrystallized B_4C and contain no binders. Although B_4C will not melt below 4450°F, oxidation begins at about 2015°F, and effective barrier protection is still required. Boron-carbide liners are now being evaluated with OF_2/B_2H_6 propellants at the 200-lbf thrust level, but due to their inherent brittleness and the complexities of their manufacture, a more resilient, more readily fabricable material may prove desirable.

If reaction rates are relatively slow and adequate barrier protection can be provided by the injector, carbonaceous or graphitic materials should still prove entirely satisfactory. The standard grades of synthetic graphite, such as ATJ and various kinds of POCO graphite, have been and are being

‡ A product of Gallard-Schlesinger Chemical Mfg. Corp., Atomergic Chemetals Division, Carle Place, New York.

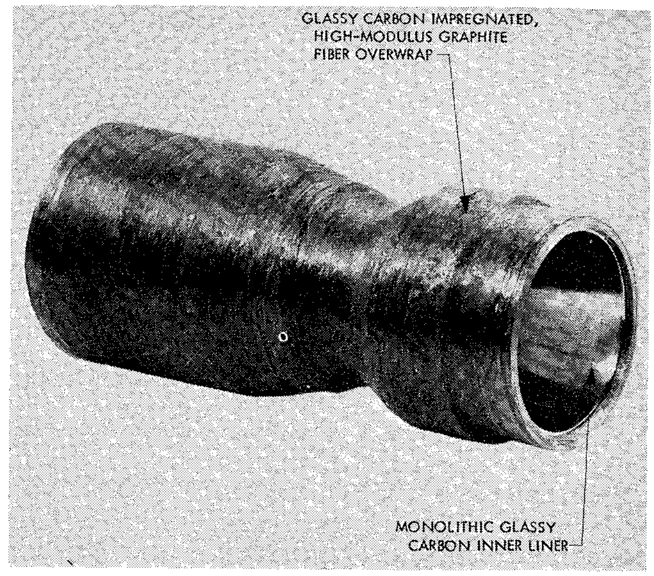
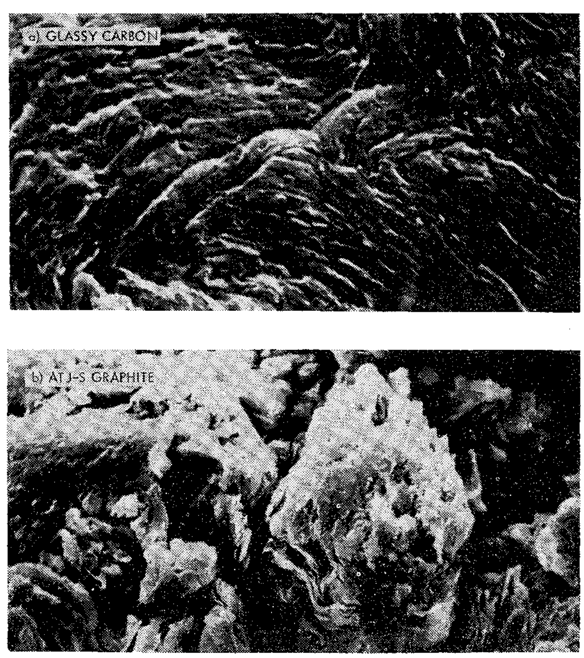


Fig. 15 Glassy carbon thrust chamber liner for 200-lbf OF_2/B_2H_6 rocket motors; photograph courtesy of Lockheed Research Laboratories, Palo Alto, Calif.

evaluated for boundary- and passively-cooled applications. A relatively new material, known as "glassy carbon,"§ has thermal properties similar to those of the synthetic graphite grades, but exhibits superior strength and a much reduced surface area. Reinforced-composite thrust chamber liners have been made from this material, and are presently being evaluated with the OF_2/B_2H_6 propellants. The typical liner shown in Fig. 15 represents the first rendering of this novel material into the shape of a de Laval nozzle.

Glassy carbon has a tensile strength approximately three times that of the best synthetic graphite grades, and a compressive strength about six times that of graphite. More



a)

b)

Fig. 16 Scanning electron microscope photographs of the surfaces of a) glassy carbon and b) ATJ-S synthetic graphite after sublimation at 3000°C (~10,000X magnification); photograph courtesy of McDonnell Douglas Corp., Santa Monica, Calif.

§ A product of Lockheed Palo Alto Research Laboratory, Palo Alto, Calif.

significantly, it has a typica surface area of only about 4×10^{-4} m^2/g, ¶ compared to 10.47–0.87 m^2/g for ATJ graphite.[23] Therefore, chemical erosion rates should be correspondingly reduced. Comparative surface areas are illustrated in Fig. 16.

Glassy carbon is a monolitic, nongraphitic form of carbon produced by the thermal degradation of an organic polymer. The resin is molded to shape and then pyrolyzed to the glass-like condition. Liners are produced to net dimensions by incorporating a uniform shrinkage factor into the mold design; $\frac{1}{8}$-in.-thick walls are now possible. The monolithic liners are then overwrapped with a 2-ply, polyacrylonitrile-based, high-modulus graphite fiber (Fig. 15) in a wet-winding process, whereby infiltration with a furfuryl alcohol based resin is accomplished. Subsequent pyrolysis results in a hard external shell of graphite-fiber-reinforced glassy carbon, which acts as the principal structural member. The composite liner is then machined to its final external dimensions.

Concluding Remarks

A number of basic, existing capabilities of OF_2/B_2H_6 thrust chambers, including delivered vacuum performance compatible with the requirements of propulsion systems for envisioned unmanned planetary missions, have been demonstrated. The interrelationships between that performance and both chamber heat flux and boundary-layer control schemes have been established in sufficient depth to permit intelligent design tradeoffs. Throttling and pulsing capabilities, though not immediately required, appear to be readily obtainable. Combustion instability has not emerged as a major problem and has rarely been encountered. Smooth, rapid vacuum ignition of OF_2/B_2H_6 has been repeatedly demonstrated, and design criteria have been established to minimize start transient overpressures and ignition delays.

The heat-transfer properties of B_2H_6 have been determined in sufficient detail to permit intelligent design for either film or regeneratively cooled applications. Several new, advanced nonmetallic chamber materials, such as boron carbide and glassy carbon, have been developed to the point where it is now possible to render them into monolithic chamber/nozzle liners. These offer improved potential for high-temperature erosion resistance in the OF_2/B_2H_6 combustion environment.

The foremost problem area is the deposition of boron-containing solids on the face of the injector, which can compromise both restart capability and the boundary protection required to assure minimal throat erosion, by clogging injection orifices. However, several injector types are now available which are not seriously subject to this disadvantage. Orifice plugging via internal deposition of B_2H_6 freezing or decomposition products at restrictions in flow areas has also been identified, but may be easier to design around.

Flight prototype engine development that is just now getting under way with programs for boundary-, regeneratively, and heat-pipe-cooled rocket engines, can draw upon this broad technology base, which enhances the chance of success in meeting the goal of demonstrating a high-performance, long-firing-duration, 1000-lbf-thrust OF_2/B_2H_6 spacecraft rocket engine.

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¶ As determined by BET analysis with Krypton.[24]