NPS-67-84-012

NAVAL POSTGRADUATE SCHOOL

Monterey, California

FUEL PERFORMANCE EVALUATION FOR THE SOLID-FUELED RAMJET

A. GANY and D. W. NETZER

October 1984

Approved for public release; distribution unlimited.

Prepared for:

Chief of Naval Research
Arlington, VA 22217

NAVAL POSTGRADUATE SCHOOL
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NOTE: The Postdoctoral Research Associate Program (National Research Council) was funded by the Naval Postgraduate School Foundation Research Program.

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
NPS-67-84-012

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Fuel Performance Evaluation for the Solid-Fueled Ramjet

5. TYPE OF REPORT & PERIOD COVERED

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
A. Gany and D. W. Netzer

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Naval Postgraduate School
Monterey, CA 93943

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
61152N: RR000-01-10
N0001484WR41001

11. CONTROLLING OFFICE NAME AND ADDRESS
Naval Postgraduate School
Monterey, CA 93943

12. REPORT DATE
October 1984

13. NUMBER OF PAGES
35

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)
Chief of Naval Research
Arlington, VA 22217

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Solid Fuel
Ramjets

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-LF-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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Compared with hydrocarbons, some metal compounds have somewhat higher energy per unit mass, but up to about three times higher energy per unit volume.

Boron has the highest energy density (energy per unit volume) of all elements, while among all other fuel candidates only boron compounds exhibit similar potential performance.

Other possible high performance fuel candidates are boron carbide, which is the least expensive source of boron, AlB_{12} (alloy) with energy density slightly exceeding that of elemental boron, and the high borides of magnesium and silicon.

ABSTRACT

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NOMENCLATURE

A	cross-section area
f	fuel to air (mass) ratio
F	thrust
(g)	gas
g_o	standard gravity acceleration = $9.8\ m/s^2$
G	mass flux
ΔH°_f	standard enthalpy of formation
ΔH°_R	standard enthalpy of reaction
I_{sp}	specific impulse
(ℓ)	liquid state
$\dot{m}$	mass flow rate
M	molecular weight
q_R	heat of reaction
$\dot{r}$	fuel regression rate
(s)	solid state
t	time
T	temperature
TSFC	thrust specific fuel consumption
u	axial velocity
ρ	density

Subscripts

a	air; ambient conditions
e	nozzle exit
f	fuel
HC	hydrocarbon
i	combustion chamber inlet
p	fuel port
s	static-test conditions
t	nozzle throat

I. INTRODUCTION

The objective of this study was to present an overview of the potential energetic performance of chemical fuel ingredients for application in solid fuel ramjet (SFRJ) power plants or in other air augmented (air breathing) chemical propulsion devices.

The study provides a summary of existing thermochemical data [1-15], which gives basis for selection of high-energy material candidates, and compares their energetic performance to that of common hydrocarbon (HC) fuels.

Some aspects of practical use, e.g., handling, toxicity, fire hazard, and cost are also discussed.

Detailed description of the combustion phenomena was not the goal of this study. However, one should be aware of the combustion processes, as they are very important in any motor development program, and may greatly affect the overall performance of the system. Hence, a brief introduction on this subject is presented. It includes a discussion of the general combustion characteristics in the SFRJ; flame stabilization, combustor geometries, fuel regression rate, factors affecting the combustion efficiency, and problems associated with metal combustion.

The two most commonly used criteria to characterize the energetic performance of an air breathing engine are the specific impulse, I_{sp}, and the thrust specific fuel consumption, TSFC.

The specific impulse is defined as the thrust developed, F, per unit weight-flow-rate of fuel,

$$I_{sp} = \frac{F}{\dot{m}_f g_o}$$

and it is desired to be as high as possible.

The thrust specific fuel consumption, TSFC, is defined as the ratio of the fuel mass-flow-rate, $\dot{m}_f$, to the thrust developed, F,

$$\mathrm{TSFC} = \frac{\dot{m}_f}{F}$$

For TSFC, as low as possible a value is desirable.

The internal thrust developed by a jet engine during flight (where the exit nozzle is adapted to the ambient pressure) is

$$F = \dot{m}_e u_e - \dot{m}_a u_a = \dot{m}_a[(1 + f)u_e - u_a]$$

where $\dot{m}_a$ is the air mass flow rate, $f \equiv \dot{m}_f/\dot{m}_a$ is the fuel to air ratio, u_a is the velocity of air relative to the vehicle (the flight speed), and u_e is the exit gas jet velocity. The subscript e indicates nozzle exit conditions.

The type of fuel and amount of heat release affect the exit jet momentum and velocity, but have no influence on the incoming air (unless a fixed geometry system is considered in which the variation in back pressure affects air inlet operation). However, the motor performance varies with the fuel to air ratio and the flight conditions (e.g., u_a), thus the comparison between different systems and fuels is not always straight forward.

The exit jet thrust (referred to as static thrust), which is the thrust obtained in static test where the incoming air has no axial momentum (similar to turbojet static operation), is a convenient measure of combustor performance. "Static thrust" is

$$F_s = \dot{m}_a (1 + f)u_e$$

and "static specific impulse" is

$$I_{sp,s} = \frac{(1 + f)}{fg_o} u_e$$

One can show that for ramjet engines with the same amount of heat release per unit mass of air in the combustion chamber (i.e., similar "static thrust") the static specific impulse is linearly proportional to the heat release per unit mass of fuel, q_R.

$$I_{sp,\ s} \propto q_R$$

The heat release, also called "heat of combustion", is calculated in terms of the standard enthalpy change during a complete reaction with gaseous oxygen:

$$q_R = - \Delta H^{\circ}{}_R$$

Since the combustion chamber temperature in air breathing engines is relatively low compared with rocket motors (in many cases excess air is applied), chemical equilibrium considerations would usually indicate almost a "complete" (forward) reaction, and the entire (theoretical) heat of combustion is expected to be released in the combustion chamber, provided that an efficient combustion takes place.

Two-phase flow effects due to the existence of condensed particles in the exhaust jet have relatively small influence on the performance of most SFRJ systems, as the working fluid is mainly the air flowing through the system; of which at least 79% (volume), the nitrogen, remains unchanged. However, when using highly metallized fuels, typically 10 to 30% of the exhaust mass flow is condensed phase, and two-phase flow effects and incomplete combustion may become significant, as they are in aluminized solid propellant rocket motors.

It seems obvious that energetic performance of a ramjet propulsion system, as is reflected by (static) specific impulse and thrust specific fuel consumption, can naturally be characterized by the enthalpy of combustion per unit mass of fuel.

In many SFRJ systems, however, more severe constraints may be placed on the space available for the fuel than on the fuel mass. This constraint may significantly affect the system capability (e.g., range or terminal velocity). In such cases the energy release per unit volume of fuel, or the "energy density", $-\rho\Delta H^{\circ}{}_{R}$, rather than the energy per unit mass of fuel, $-\Delta H^{\circ}{}_{R}$, may be the main factor in selecting the appropriate fuel combination.

A basic discussion on the fundamentals, applications and constraints of SFRJs is given in References 16, 17.

II. SUMMARY OF COMBUSTION PHENOMENA IN SFRJ

A schematic diagram of a common-configuration-SFRJ-combustor is shown in Figure 1. Also shown in the figure are the main flow and combustion features.

The combustor is basically a hollow cylinder in which a cylindrical fuel grain, often with circular port cross-section, is placed. Incoming air flows through the fuel port. An often used cobustor geometry consists of a number of different regions and features: (1) the head end with the air inlet and rearward facing step, (2) the main combustor section where the fuel grain is placed, (3) the aft mixing chamber (downstream of the fuel grain) where reaction between fuel and air is completed due to better mixing, and (4) the exit nozzle.

Most often SFRJs employ hydrocarbon (HC) fuels, usually polymers, e.g., polybutadiene (PB), polyethylene (PE), polymethylmetacrylate (PMM - "Plexiglas"), etc. The heat feedback from the flame to the fuel causes vaporization or decomposition of the fuel. The gaseous fuel products of this process react with the air and burn in the gas phase.

In general a boundary layer flow is established along the fuel grain, downstream of flow reattachment. The free stream along the center-line is oxygen (air) rich, and the gas near the wall is fuel rich. This situation results in a diffusion flame, typically a narrow "flame sheet," within the boundary layer, relatively close to the fuel surface. Since the fuel vaporization depends on the heat transferred from the flame to the wall, boundary layer analysis predicts the following fuel regression rate dependence on the mass flux in the port, G_a

$$\dot{r} \alpha G_a^n$$

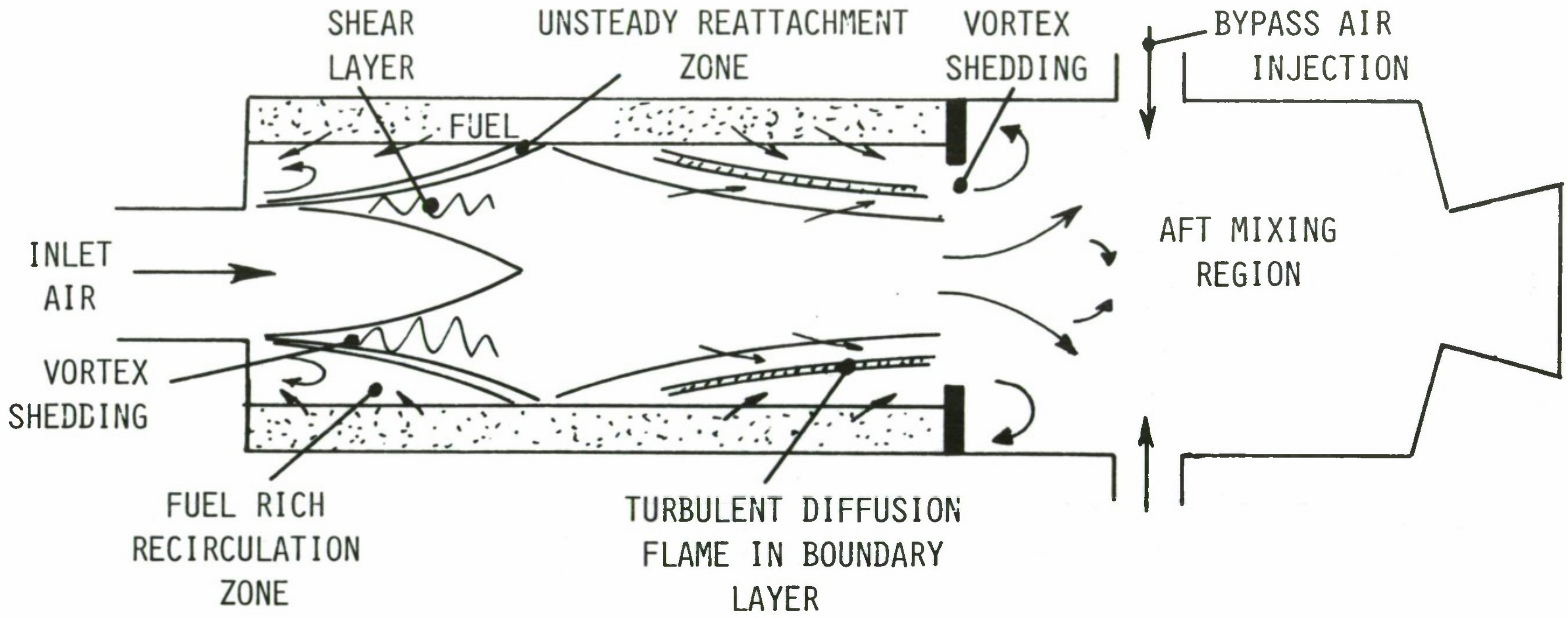

Figure 1. Schematic diagram of an SFRJ combustor showing the main geometric features and the important flow and combustion characteristics.

where $G_a=(\rho u)_{air}$, and n should be about 0.5 for laminar boundary layer and 0.8 for turbulent boundary layer.

Experimentally it has been found that the avarage regression rate has a weaker dependence on the air mass flux, and is also dependent on the pressure (especially in low pressures), and on the incoming air temperature T_a

$$\dot{r} = a\, p^k T_a^m G^n$$

where k ranges between 0.1 and 0.3, m is about 0.3, and n is 0.3 to 0.5 (see Reference 18).

One can see that the fuel mass flow rate can not be determined independently, since it is coupled with the port flow characteristics, especially the mass flux. Variation in the operating conditions (e.g., different altitude, speed, or angle of attack) and the increases in the port diameter and burning surface area which occur during combustion, will result in changes in the regression rate and fuel mass flow rate, and in deviations from the designed overall fuel to air ratio.

Some control of the fuel regression rate may be possible through the use of swirl generators in the form of controllable guide-vanes in the flow upstream of the combustor inlet. Swirl can increase the fuel regression rate.

Another often considered configuration uses bypass air. In this case the air flow is divided into two parts prior to its entering the combustor. A portion of the air flows through the fuel port and affects the fuel regression rate and the diffusion flame, while the other part is transferred directly to the aft mixing chamber. This configuration allows more ramjet fuel to be placed within the motor and can increase combustion efficiency. Use of a controllable flow division valve could also provide means for controlling the fuel regression rate and the fuel to air ratio.

The SFRJ combustor does not contain flame holders of the configuration used in conventional combustors with high speed flows. The flame stabilizing mechanism is based on sudden expansion, caused by the rearward facing step at the inlet. The separated flow forms a recirculation zone downstream of the step, which extends to the flow reattachment location. The latter generally occurs at a distance equal to 7-8 step heights.

The recirculation zone plays several important functions in the flame stabilizing mechanism: (1) it consists of a low velocity flow region, (2) it contains relatively hot gases, thus providing the heat necessary to sustain the flame, and (3) it is a fuel rich region which establishes the needed flammable mixture.

It has been found experimentally that the most important factor for flame holding is the ratio between the step height and the port diameter [16, 17]. It is usually described in the form of area ratio. (See Figure 2). Increasing the incoming air temperature increases the stable combustion limits [17].

Due to the diffusion-flame character of the combustion, complete chemical reaction and high combustion efficiency are not guaranteed. There is always a possibility that part of the fuel vapors, beneath the "flame sheet", remain unreacted and do not contribute to the energy generation within the combustor. Such a situation may result in low combustion efficiency and poor motor performance. Mixing devices (e.g., diaphragms) and especially an aft mixing chamber (see Figure 1) can provide the necessary mixing and close contact between the remaining fuel and air, and significantly increase the combustion efficiency.

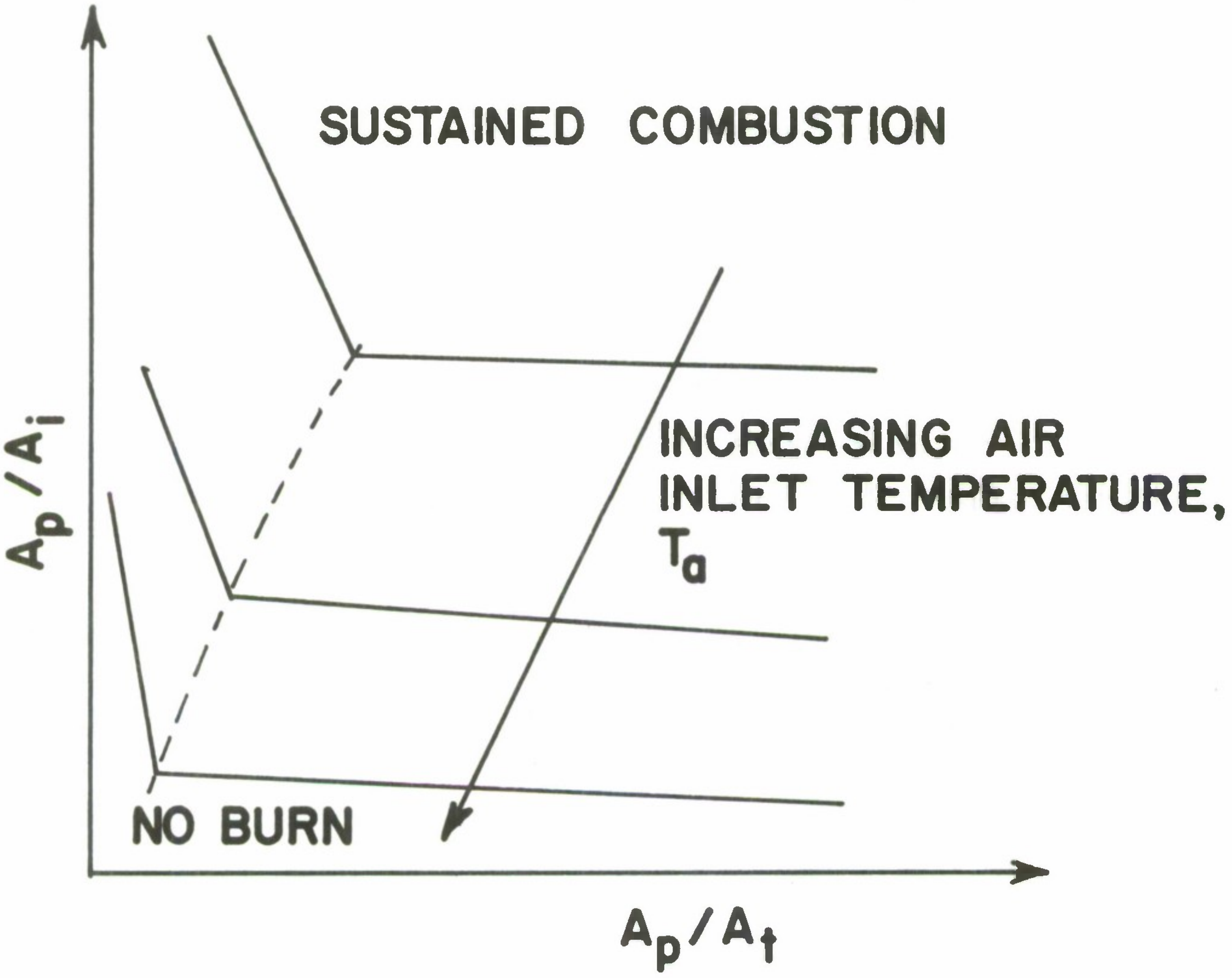

Figure 2. Flammability limit in SFRJ. Increased flame stabilization is achieved for larger step height (larger A_p/A_i), slower flow (larger A_p/A_t) and hotter incoming air (higher T_a). References 16, 17.

As will be seen later, in order to achieve high energetic performance the use of highly metallized fuels should be considered. However, metals exhibit very peculiar combustion characteristics which may result in very poor combustion efficiencies. Metals are generally incorporated into a fuel grain in the form of fine powders (typical particle size of 1 μm to 50 μm). However, they tend to accumulate at the burning surface and to form much larger agglomerates prior to their ejection to the gas stream.

Metal particles and agglomerates tend to burn individually after being heated up to their ignition temperature and exposed to an oxidizing environment. A diffusion flame in the gas phase or on the surface (depending upon the boiling temperatures of the pure metal and its oxide) is established around each particle. Several inherent problems are associated with metal particle combustion. Usually the metal is coated with an oxide layer which retards the contact and reaction between the gaseous oxygen and the underlying metal. Ignition temperature of some metals is very high, partly because of this protective oxide layer. It means that a very high surrounding temperature is required, and the heat-up period may be relatively long. Boron, in particular, ignites at a very high temperature. In the SFRJ geometry the metal is heated from the surface to the flame zone. It then passes into a region where oxidation can occur. As mentioned before, metal powders tend to form relatively large agglomerates. Hence, the combustion time of the metal particles ejected to the gas stream may be too long (typically 20-40 ms for a 100 μm diameter particle) compared with their residence time within the combustor. This results in incomplete combustion. Metal combustion also usually results in condensed phase products (oxides), which may cause two-phase flow losses. These losses should be taken into account when evaluating the system performance.

III. ENERGETIC PERFORMANCE: ELEMENTS

The heat of combustion of the elements in gaseous oxygen is generally calculated in terms of the enthalpy change (enthalpy of reaction) at standard conditions (298°K, 1 atm) per unit mass (ΔH°_R) and per unit volume ("energy density", $\rho\Delta H^\circ_R$) of the element. Note that for an exothermic reaction the enthalpy of reaction is negative.

The thermochemical data presented below was obtained from screening the available data in the open literature. (References 1 -15).

Figure 3 presents the heat of combustion of the elements in oxygen per unit mass and per unit volume. For comparison, representative values for hydrocarbon fuel (HC) of a general formula "CH_2" (e.g., polyethylene or polybutadiene) are also shown. Table 1 gives similar numerical thermochemical data for selected elements.

Figure 3 reveals that the heat of combustion of the elements (both per unit mass and per unit volume) exhibits periodic behavior with the atomic number. Hydrogen, which has the highest heat of combustion per unit mass, is the only gaseous material among all the peak energy (fuel) elements, and cannot be used in a solid fuel propulsion device, unless it is a component in a solid compound consisting of additional elements.

Interestingly, the peak values of the heat of combustion per unit mass decrease consistently from period to period by a factor of approximately 2. More accurately, starting from the first period's peak element, hydrogen, with the extremely high heat of combustion of 28.9 kcal/g, the following peak value is 55% of the first one (beryllium, 15.88 kcal/g). This "rule" holds over the first 4-5 periods and can be used to approximately correlate the peak values of each period according to

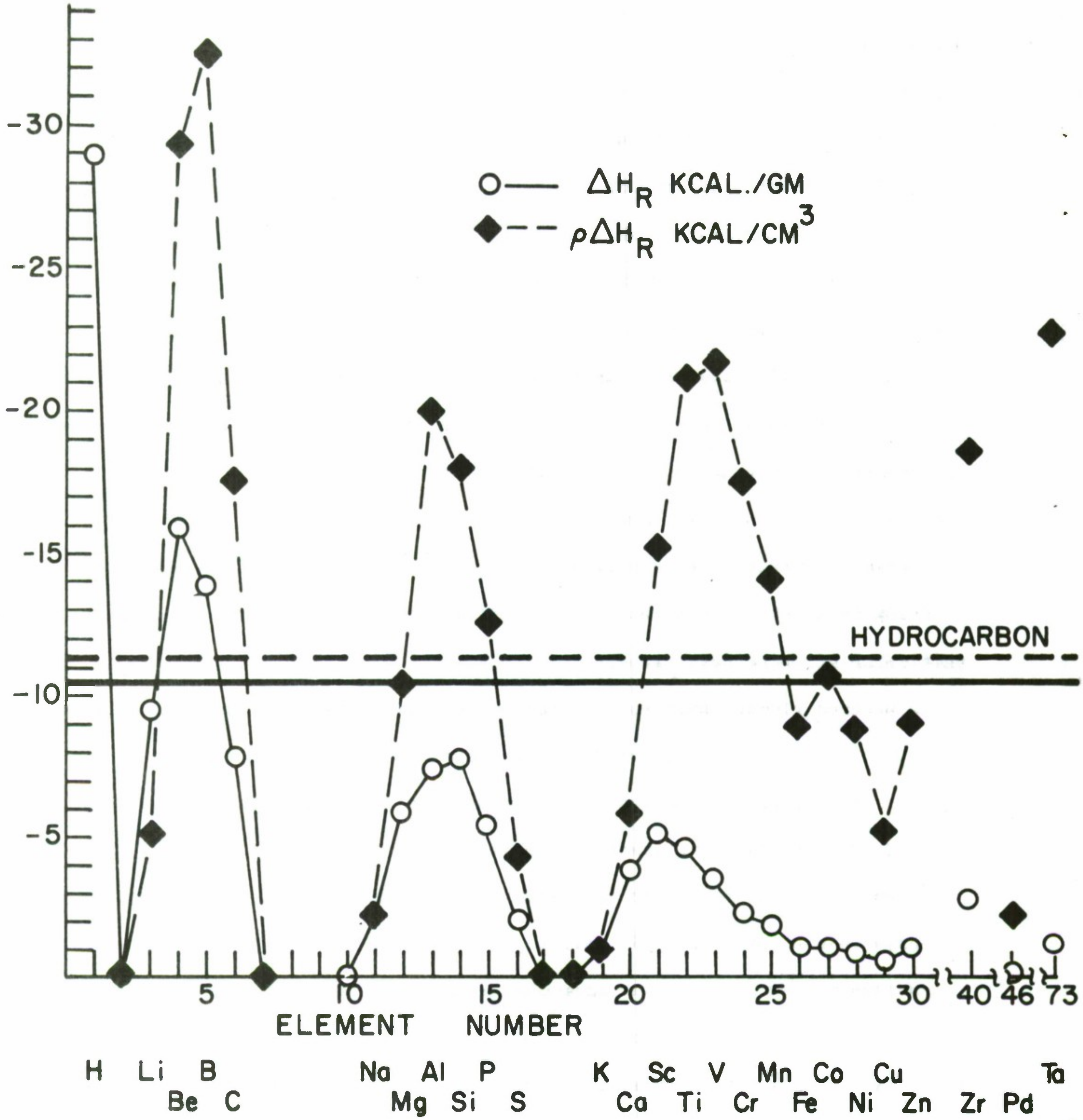

Figure 3. Heat of combustion of elements per unit mass and per unit volume, compared with the values of representative hydrocarbon.

TABLE 1

Standard Enthalpy of Combustion of Selected Elements with Oxygen

Element	ρ [g/cc]	Oxide (selected state)	ΔH°_R [kcal/g]	$\rho \Delta H^\circ_R$ [kcal/cc]	Reference
H*	*	H_2O (g)	-28.9	*	1,2,3
Li	0.534	Li_2O (s)	-10.26	- 5.48	1,2,3
		(ℓ)	- 9.52	- 5.08	1
Be	1.85	BeO (s)	-15.88	-29.38	1,3
B	2.35	B_2O_3 (s)	-14.12	-33.19	4
		(ℓ)	-13.87	-32.60	4,10
C(graphite)	2.25	CO_2 (g)	- 7.83	-17.62	1
Mg	1.74	MgO (s)	- 5.91	-10.28	1,3
Al	2.70	Al_2O_3 (s)	- 7.41	-20.01	1,3,8
Si	2.33	SiO_2 (ℓ)	- 7.72	-17.99	1
P	2.16-2.31	P_4O_{10} (g)	- 5.45	-12.59	1
S	2	SO_2 (g)	- 2.21	- 4.42	1
Ti	4.5	TiO_2 (s)	- 4.71	-21.20	6,10
V	5.96	V_2O_5 (s)	- 3.64	-21.69	8
Cr	7.20	Cr_2O_3 (s)	- 2.43	-17.50	8
Fe	7.87	FeO (s)	- 1.13	- 8.89	4
Zn	7.133	ZnO (s)	- 1.13	- 9.08	6
Zr	6.49	ZrO_2 (s)	- 2.87	-18.63	1
Pd	12.02	PdO (s)	- .193	- 2.32	6
Ta	16.6	Ta_2O_5 (s)	- 1.38	-22.9	6

*Hydrogen is the only gas on this list and its density and energy density are very low, although the enthalpy of combustion is extremely high.

$$q_{R,max}(n) = q_{R,max}(1) \cdot (.55)^n \qquad (1)$$

where n is the period number. (See Table 2).

Periodic behavior is also exhibited by the heat of combustion per unit volume ("energy density"). However, as the density of the elements generally increases with the atomic number, the differences in the peak values from period to period are not that large.

Actually, only one period (number 2) exhibits rather high peak energy density values. Boron, with the highest energy density among all the elements, (33.2 kcal/cc when forming $B_2O_3(s)$ and 32.6 kcal/cc for $B_2O_3(\ell)$), and beryllium with 29.4 kcal/cc, are the only elements with outstandingly high energy density. Other peak values are of the order of 2/3 of the boron energy density, in the range of 20 to 22 kcal/cm^3. Note that because of the low melting temperature of liquid boron oxide, $B_2O_3(\ell)$, its corresponding energy value should be used for SFRJ performance evaluation.

Solid hydrocarbon (HC) materials are the fuel ingredients most commonly considered for SFRJ propulsion systems. "CH_2" represents the highest energy HC (similar to PB or PE) with $-\Delta H^\circ_R = 10.5$ kcal/g. Only two solid elements, Be (15.88 kcal/g) and B (14.12 kcal/g) have higher heat of combustion per unit mass. However, hydrocarbons have relatively low density, of the order of 1 g/cm^3, and therefore their energy density is relatively low. Among the commonly used polymers, high-density polybutadiene is a relatively dense HC ($\rho = 1.08$ g/cc, $-\rho\Delta H = 11.3$ kcal/cc). These values will be used as a base-line for evaluating other fuel components. (See Figure 3). It should be noted that there are a number of HC materials (usually cyclic HC of special structure) with a density of about 1.6 g/cc.

Selection on the basis of energy density reveals a variety of elements with a much better potential performance than HC.

B and Be have extremely high energy densities (almost three times higher than that of HC). However, there are a number of elements in the middle range (about two times higher than HC), among them a few heavy metals with a relatively low heat of combustion per unit mass (e.g., Ta, has $-\Delta H^\circ_R=1.38$ kcal/g, $\rho=16.6$ g/cc, and $-\rho\Delta H^\circ_R=22.9$ kcal/cc). Table 3 gives the ratio of energy density of some high performance elements vs. HC's (11.3 kcal/cc).

TABLE 2

Actual and Predicted Maximum Heats of Combustion for Elements from the Periodic Chart.

Period	Peak Value Elements	Atomic Number	Heat of Combustion, $-\Delta H_R$[kcal/g] Actual	Predicted (Eq. 1)
1	H	1	28.90	(28.90)
2	Be	4	15.88	15.90
	B	5	14.12	
3	Al	13	7.41	8.74
	Si	14	7.72	
	Ca	20	3.79	
4	Sc	21	5.07	4.81
	Ti	22	4.71	
	V	23	3.64	
5	Zr	40	2.87	2.64

TABLE 3

The Ratio of Energy Density ($-\rho\Delta H^\circ_R$) of Some Elements to that of HC

Period	Elements and Performance vs. HC
1	H(gas)
2	Be(2.60), B(2.87) , C(1.56) ,
3	Mg(.91) , Al(1.77), Si(1.59), P(1.11)
4	Sc(1.35), Ti(1.88), V(1.92) , Cr(1.55), Mn(1.25)
others	Zr(1.65), Ta(2.03), W(1.87) ,

IV. ENERGETIC PERFORMANCE: METAL HYDRIDES

The energetic performance of some solid metal hydrides are summarized in Table 4. In general (from the energy standpoint), metal hydrides may be very attractive, as the existence of hydrogen in their molecule usually increases the heat of combustion per unit mass over that of the metal itself. In the calculations, the combustion products used were the metal oxides for the pure metal combustion, and water vapor. Note that liquid and gaseous hydrides are not useful for the SFRJ. Unless otherwise indicated, the values of hydride density, ρ, and standard heat of formation (ΔH°_f) were taken from Sarner [1].

Among the solid metal hydrides beryllium hydride has the highest heat of combustion per unit mass (18.13 kcal/g), higher than any metal. The solid borane $B_{10}H_{14}$ also exhibits very high heat of combustion per unit mass (over 15.5 kcal/g).

However, most metal hydrides have very low density (usually less than 1 g/cc) except for zirconium hydride (ZrH_2) with ρ=5.67 g/cc and titanium hydride (TiH_2) with ρ=3.9 g/cc.

TiH_2 has the highest energy density (heat of combustion per unit volume) of all hydrides ($-\rho\Delta H^\circ_R$=19.92 kcal/cc) while that of ZrH_2 is 16.84 kcal/cc. Note that aluminum hydride (AlH_3) and aluminum borohydride ($Al(BH_4)_3$) are liquids at room temperature.

TABLE 4

Energetic Performance of Metal Hydrides

Hydride	M	ρ [g/cc]	ΔH°_f [kcal/mole]	ΔH°_R [kcal/g]	$\rho\Delta H^\circ_R$ [kcal/cc]	Remarks
LiH	7.947	0.82(15)	-21.63(1)(8)(15)	-9.87	-8.10	$Li_2O(s)$
				-9.23	-7.57	$Li_2O(\ell)$
BeH_2	11.028	0.7	-1	-18.13	-12.69	highest value of BeH_2 density found in Ref. 1
$B_{10}H_{14}$	122.222	0.94(1)(13)(15)	-6.9	-15.75	-14.81	$B_2O_3(s)$
				-15.53	-14.60	$B_2O_3(\ell)$
MgH_2	26.328	1.42	-18.2(1)(8)(13)	-6.96	-9.89	
AlH_3	30.004	1.5	-7 ±4(2)(8)(15)	-9.33	-14.00	AlH_3 is liquid at room temp.
TiH_2	49.916	3.9(8)	-28.6(8)	-5.11	-19.92	decomposes 400°C
ZrH_2	93.236	5.67	-42.4	-2.97	-16.84	
$LiBH_4$	21.782	0.68(15)	-45.6(8)	-13.13	-8.94	
$LiAlH_4$	37.951	0.92(15)	-26.2(15)	-9.37	-8.62	
$Al(BH_4)_3$	71.54	0.54(13)(15)	-7.2(10)	-13.8(13)	-7.45	$Al(BH_4)_3$ is liquid. mp-64.5°C

V. ENERGETIC PERFORMANCE: METAL ALLOYS; INTERMETALLIC AND OTHER METAL COMPOUNDS

Metal alloys and other metal compounds may have an advantage over the corresponding mixture of the individual elements when consideration is given to combustion and ignition characteristics, density and availability. In addition, they may have very high energetic potential. Borides, metal-metal compounds, carbides and somewhat less promising compounds, metal phosphides, are the most interesting materials.

Table 5 summarizes the thermochemical properties and enthalpy of combustion of borides. Additional information on the characteristics of boron compounds can be found in Refs. 9 and 10. Table 6 gives some of the thermophysical properties of metal-metal compounds. Intermetallic compounds are discussed in details in Ref. 4. Table 7 deals with selected carbides, and Table 8 presents some metal phosphides. More information on metal phosphides can be found in Ref. 12. In all Tables, data in parentheses represent uncertain, approximate values.

TABLE 5

Thermophysical Properties and Energetic Performance of Borides

Boride	M	ρ [g/cc]	ΔH°_f [kcal/mole]	Products (state) in add. to $B_2O_3(\ell)$	ΔH°_R with O_2 [kcal/g]	$\rho\Delta H^\circ_R$ [kcal/cc]
AlB_2	46.60	3.19(8)(15)	-76(15)	$Al_2O_3(s)$	-9.10	-29.04
AlB_{12}	156.71	2.55(8)(10)(15)	-49.2(15)	$Al_2O_3(s)$	-12.45	-31.75
AlB_{12} (alloy)	156.71	2.707(15)	-94.0(15)	$Al_2O_3(s)$	-12.16	-32.93
B	10.811	2.35(15)	0		-13.87	-32.60
B_4C	55.26	2.52(8)	-12.7(1)	$CO_2(g)$	-12.33	-31.07
Be_2B	28.84	2.2-2.35(10)	(-20)	$BeO(s)$	(-14.4)	(-32.8)
Be_5B	55.87	2.1(10)	(-30)	$BeO(s)$	(-15.0)	(-31.4)
BeB_6	73.88	2.33(10)	(-30)	$BeO(s)$	(-13.7)	(-32.0)
FeB	66.66	7.15(8)				
MgB_2	45.93	2.69(15)	-22.0(15)	$MgO(s)$	-9.18	-24.70
MgB_4	67.56	(2.5)	-25.1	$MgO(s)$	-10.64	(-26.6)
MgB_6	89.18	2.46(10)	(-28)	$MgO(s)$	(-11.39)	(-28.0)
MgB_{12}	154.04	2.44(10)	(-35)	$MgO(s)$	(-12.39)	(-30.2)
B_3Si	60.52	2.52(8)	(-30)	$SiO_2(\ell)$	(-10.5)	(-26.5)
B_6Si	92.95	2.47(8)	(-40)	$SiO_2(\ell)$	(-11.6)	(-28.6)
TaB_2	202.57	11.15(8)*	-46(8)	$Ta_2O_5(s)$	-2.49	-27.71
TiB_2	69.52	4.50(8)(15)	-77.4(8)	$TiO_2(s)$	-6.45	-29.02
VB_2	72.56	5.10(8)	(-70)	$V_2O_5(\ell)$	(-5.7)	(-29)
ZrB_2	112.84	6.085(8)(15)*	-78(8)(10)	$ZrO_2(s)$	-4.28	-26.07

(Values in parentheses are approximations).

*Ref. 9 p. 132 gives somewhat higher values: 11.7 g/cc for TaB_2 and 6.17 g/cc for ZrB_2.

TABLE 6

Thermophysical Properties and Energetic Performance of Solid Intermetallic Compounds (Except Borides).

Compound	M	ρ [g/cc]	ΔH°_f [kcal/mole]	Combustion Products (& state) with O_2	ΔH°_R [kcal/g]	$\rho\Delta H^\circ_R$ [kcal/cc]
AlMg	51.29		-1.6(7)	$Al_2O_3(S)$,$MgO(s)$	-6.67	
Al_3Mg_4	178.19	2.15(11)	-5.46(14)	$Al_2O_3(S)$,$MgO(s)$	-6.57	-14.1
$FeAl_3$	136.79		-27(7)	$FeO(S)$,$Al_2O_3(s)$	-4.66	
Mg_2Si	76.71	1.94(8)	-19(4)(6)	$MgO(S)$,$SiO_2(\ell)$	-6.33	-12.27
$MgZn_2$	155.05		-12.6(7)	$MgO(S)$,$ZnO(s)$	-1.92	
NiAl	85.69		-28.3(4)(7)	$NiO(S)$,$Al_2O_3(s)$	-2.69	
TiAl	74.88		-19.2± .3(5)(14)	$TiO_2(S)$,$Al_2O_3(s)$	-5.43	
$TiAl_3$	128.84		-34.9(14)	$TiOs(S)$,$Al_2O_3(s)$	-6.14	
TiSi	75.99		-31(14)	$TiO_2(S)$,$SiO_2(\ell)$	-5.42	
Ti_5Si_3	323.76		-138.4(14)	$TiO_2(S)$,$SiO_2(\ell)$	-5.07	
VSi_2	107.11	4.42(8)	(-40)	$V_2O_5(S)$,$SiO_2(\ell)$	(-5.4)	(-23.9)
V_2Si	129.97	5.48(8)	-37(14)	$V_2O_5(S)$,$SiO_2(\ell)$	-4.2	-23.0
$ZrSi_2$	147.40		-36(14)	$ZrO_2(s)$,$SiO_2(\ell)$	-4.47	
ZrZn	156.59		-30.4(7)	$ZrO_2(S)$,$ZnO(s)$	-2.01	
$ZrZn_2$	221.96		-40.2(7)	$ZrO_2(S)$,$ZnO(s)$	-1.93	

(Values in parentheses are approximations).

TABLE 7

Thermophysical Properties and Heat of Combustion of Solid Carbides.

Carbide	M	ρ [g/cc]	ΔH°_f [kcal/mole]	Combustion Products (& state) in add. to $CO_2(g)$	ΔH°_R [kcal/g]	$\rho\Delta H^\circ_R$ [kcal/cc]
Al_4C_3	143.95	2.36	-49.0(1)	$Al_2O_3(s)$	-7.18	-16.94
B_4C	55.26	2.52	-12.7(1)	$B_2O_3(\ell)$	-12.33	-31.07
Be_2C	33.63		-28.0	$BeO(s)$	-10.47	
CaC_2	64.10		-14.3	$CaO(s)$	-5.08	
Fe_3C	179.55	7.694	+6	$FeO(s)$	-1.61	-12.39
Li_2C_2	37.90		-14.2(1)	$Li_2O(\ell)$	-8.07	
MgC_2	48.33		+20	$MgO(s)$	-7.28	
Mg_2C_3	84.66		+17	$MgO(s)$	-6.93	
Ni_3C	188.14	7.957	+16	$NiO(s)$	-1.52	-12.06
SiC	40.10	3.217	-15	$SiO_2(\ell)$	-7.38	-23.74
TaC	192.96	13.9	-38.5(5)	$Ta_2O_5(s)$	-1.58	-21.96
TiC	59.91	4.93	-44±0.15(5)(6)(8)	$TiO_2(s)$	-4.60	-22.68
VC	62.95	5.77	(-40)	$V_2O_5(s)$	(-3.80)	(-21.94)
ZrC	103.23	6.73	-48.5	$ZrO_2(s)$	-2.97	-19.99

(Data from Reference 8, unless otherwise indicated).

TABLE 8

Thermochemical Data and Heat of Combustion of Metal Phosphides.

Phosphide	M	ρ [g/cc]	ΔH°_f [kcal/mole]	Combustion Products (& state) in add. to $CO_2(g)$	ΔH°_R [kcal/g]	$\rho\Delta H^\circ_R$ [kcal/cc]
AlP	57.96	2.42(12)	-39.8	$Al_2O_3(s)$	-5.68	-13.75
BP	41.78	2.97(10)	-49(10)	$B_2O_3(\ell)$	-6.46	-19.18
FeP	86.82	6.07(12)	-30	FeO(s)	-2.33	-14.11
FeP_2	117.80	(6)	-46	FeO(s)	-3.01	-(18)
Fe_2P	142.67	6.77(12)	-39	FeO(s)	-1.79	-12.1
Fe_3P	198.51	7.11(12)	-39	FeO(s)	-1.61	-11.4
MgP_2	86.26	(2)	-51.2(4)	MgO(s)	-4.99	(-10)
Mg_3P_2	134.88	2.055	(-80)	MgO(s)	(-5.1)	(-10.5)
Ni_3P	207.10	7.7(12)	-48(12)	NiO(s)	-1.43	-11
Ni_2P	148.39	7.2(12)	-40	NiO(s)	-1.66	-12
Ni_3P_2	238.08	5.99	(-65)	NiO(s)	(-1.88)	(-11.3)
TiP	78.87	3.95(8)(12)	-67.7	$TiO_2(s)$	-4.15	-16.38
Zn_3P_2	258.06	4.55	-113	ZnO(s)	-1.84	-8.36
ZrP_2	153.17	4.77	(-60)	$ZrO_2(s)$	(-3.52)	(-16.8)

(Data from Reference 8, unless otherwise indicated. Values in parentheses are approximations).

VI. HANDLING, SAFETY, AND COST CONSIDERATIONS

A. METALS

The higher performance materials will be considered with respect to their practical use, e.g., handling, toxicity and cost.

Aluminum: rather common, easy to handle and inexpensive (to date about 70c/lb).

Beryllium: Beryllium and its combustion products are very toxic, and the use of this metal in conventional propulsion systems seems impractical. Beryllium metal in cast billet form is priced roughly at \$150/lb(8).

Boron: Elemental boron is not considered to be a poison. Note, however, that assimilation of its compounds has a cummulative poisonous effect. Crystalline boron 99% costs about \$5/g. Amorphous boron costs about \$2/g(8).

Boron Carbide: Much cheaper than elemental boron and much easier to obtain.

Lithium: A dangerous fire hazard and reacts vigorously with water, liberating hydrogen. It is the lightest metal (0.534 g/cc). Its use as a SFRJ fuel ingredient does not look especially attractive. It costs about \$20/lb(8).

Magnesium: Does not present a particular hazard and is available and easy to handle.

Scandium: Very rare and expensive and cannot be considered as a potential fuel ingredient.

Silicon: Common, available and relatively inexpensive. Regular grade (97%) costs about 50¢/lb. However, exposure to silicon dust (fine powder) may cause a serious lung disease known as "Silicosis".

Tantalum: A heavy metal. It does not cause any irritation. In powdered form it costs about \$40/lb(8).

Titanium: Considered to be physiologically inert. Titanium powder (99.7%) costs about \$25/lb(8).

Vanadium and its compounds: Somewhat toxic and should be handled with care. An extended exposure to V_2O_5 dust should not exceed the ceiling value of 0.05 mg/m^3. The cost of the metal, 95% purity, is about \$10/lb.

Zirconium: When finely divided may exhibit spontaneous ignition. The price of commercial grade zirconium metal sponge is about \$7/lb.

Safety, handling and cost considerations of metals as fuel components in a conventional SFRJ should rule out the use of beryllium because of its high toxicity. Silicon and vanadium should be handled with great care if their use is desirable, because of their unhealthy influence.

Lithium and zirconium (powders) are major fire hazards. Aluminum and magnesium are minor fire hazard, and boron presents no problems.

B. METAL HYDRIDES

1. Binary Metal Hydrides

Table 9 summarizes the properties of solid binary hydrides. Most of the data were taken from Sarner(1). Data on titanium hydride are from Reference 8. Among the solid binary metal hydrides, lithium hydride (LiH) has the highest melting point (686°C) and is relatively stable. However, it reacts vigorously with water, evolving oxygen. In fine powder form it may also ignite spontaneously with moist air or water.

Beryllium hydride (BeH_2) is quite stable up to 240°C, is relatively inert to air at room temperature and reacts only slowly with water even at 50°C.

However, as mentioned above, beryllium compounds and combustion products are very toxic. Hence, BeH_2 is not a practical candidate for the SFRJ.

Magnesium hydride (MgH_2) is relatively stable. However, in fine powder form it may undergo vigorous reaction with air.

Aluminum hydride (AlH_3) is relatively unstable. It reacts spontaneously with air to form aluminum oxide and water.

Titanium hydride (TiH_2) is a solid of a relatively high density (3.9g/cc). It decomposes at 400°C.

Zirconium hydride (ZrH_2) is a very stable hydride and is unaffected by air or moisture under normal conditions. Its ignition temperature with air is 270°C. The relatively low reactivity is advantageous, because the hydride powder can be handled as a nonreactive metal powser. Its high density (5.7g/cc) is also advantageous.

2. Boron Hydrides (Boranes)

Among the boranes, only the higher ones are solids, e.g., $B_{10}H_{14}$, melting point 99°C.

Decaborone ($B_{10}H_{14}$) is stable in air at room temperature and presents slow hydrolisis with water(1). However, the main disadvantage of all boranes is their severe toxicity. This rules out the practical possibility of their use as fuel components in the SFRJ.

3. Complex Metal Hydrides

These materials (such as lithium borohydride, $LiBH_4$, and aluminum borohydride, $Al(BH_4)_3$) present safety hazards. $LiBH_4$ decomposes at 280°C(1). It is flammable, hygroscopic and ignites on contact with water.

$Al(BH_4)_3$ is liquid at room temperature (mp -64.5°C, bp 44.5°C). In addition it is relatively unstable and explodes with water. Its fumes are unhealthy.

Other complex metals hydrides such as $LiAlH_4$, $Mg(BH_4)_2$, $Mg(AlH_4)_2$ present similar behavior and hazards. In addition, their density is usually low (0.5 to 1.0 g/cc).

TABLE 9

Properties of Solid Binary Hydrides (Refs. 1,8)

	LiH	BeH_2	MgH_2	AlH_3	$B_{10}H_{14}$	ZrH_2	TiH_2
Molecular weight	7.948	11.029	26.336	30.004	122.312	93.236	49.916
Melting point, °C	686	-	-	-	98.78	-	-
Decomposition temp., °C	972	240	280	>100	-	500	400
Density, g/cm^3	.780	(.7)	1.42	(1.5)	.94	5.67	3.9
Specific heat, cal/g °C	.842	-	.321	-	.426	-	
Heat of formation, kcal/mole	-21.63	-1	-18.2	-3	-6.9	-42.4	
Heat of fusion, kcal/mole	7.0	-	-	-	5.25	-	

VII. SELECTION OF FUEL CANDIDATES

Selection of the most promising (practical) fuel candidates for the SFRJ from the energetic performance standpoint can be made from the discussions above.

The use of beryllium and its compounds have not been considered because of their toxicity.

The values of heat of combustion per unit mass and per unit volume (energy and energy-density) of high performance hydrocarbons (HC) are used for comparison: $\Delta H°_R$ = -10.5 kcal/g, $\rho\Delta H°_R$ = -11.3 kcal/cc.

Metallic and metal containing fuel ingredients are mainly advantageous because of their high energy-density. Some of them also exhibit high heat of combustion per unit mass.

Table 10 presents a list of the highest performance fuel candidates in decreasing order of energy density. Factors such as ignitability, combustion efficiency and particular mission profiles are not considered in this discussion.

Boron has the highest energy and energy density among all the elements. Its energetic performance is markedly outstanding compared with other elements. Interestingly, several borides exhibit similar performance in terms of energy density. The borides of aluminum, magnesium and silicon also have very high heats of combustion per unit mass. Elemental boron presents difficulties in respect to ignition and combustion. Thus, it is worth considering the use of these borides, if they improve the combustion characteristics or have other advantages.

Note that AlB_{12} (alloy) has the highest energy density among all fuel candidates, about 1% higher than that of elemental boron!

Another very attractive component is boron carbide, B_4C, which is the cheapest source of boron. As its performance is very close to that of boron, it is highly recommended as a fuel candidate.

For all these high performance materials listed, the final selection should take into account factors associated with the combustion process, as these may be very significant.

TABLE 10

Selection of the Most Energetic Fuel Candidates for the SFRJ in Terms of Energy Density in Comparison to High Performance HC.

Fuel	$-\Delta H^\circ_R$ [kcal/g]	$\frac{\Delta H^\circ_R}{(\Delta H^\circ_R)_{HC}}$	$-\rho\Delta H^\circ_R$ [kcal/cc]	$\frac{\rho\Delta H^\circ_R}{(\rho\Delta H^\circ_R)_{HC}}$
AlB_{12} (alloy)	12.16	1.16	32.93	2.91
B	13.87	1.32	32.60	2.88
AlB_{12}	12.45	1.19	31.75	2.81
B_4C	12.7	1.21	31.07	2.75
MgB_{12}	(12.4)*	(1.18)	(30.2)	(2.67)
TiB_2	6.45	0.61	29.02	2.57
VB_2	(5.7)	(0.54)	(29)	(2.57)
B_6Si	(11.6)	(1.10)	(28.6)	(2.53)
TaB_2	2.49	0.24	27.71	2.45
ZrB_2	4.28	0.41	26.07	2.31

* Values in parentheses are uncertain within up to ± 5%.

Note that except for boron compounds, none of the other intermetallic compounds or metal carbides are of similar energy performance.

Although more energetic than HC, none of the metal hydrides (including boranes) look very attractive from the energy density standpoint, nor are the metal phosphides.

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