NASA TECHNICAL MEMORANDUM

NASA TM X- 73503

NASA TM X- 73503

(NASA-TM-X-73503) HIGH DENSITY PROPELLANT FOR SINGLE STAGE TO ORBIT VEHICLES (NASA) 15 p HC A02/MF A01 CSCL 22B

N77-10152

Unclas
G3/20 08957

HIGH DENSITY PROPELLANTS FOR SINGLE STAGE TO ORBIT VEHICLES

by J. J. Notardonato and Philip A. Masters
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER to be presented at the
JANNAF Propulsion Meeting
Atlanta, Georgia, December 7-9, 1976

HIGH DENSITY PROPELLANTS FOR SINGLE STAGE TO ORBIT VEHICLES

J. J. Notardonato and Philip A. Masters
Lewis Research Center
Cleveland, Ohio 44135

E-8850

ABSTRACT

Mixed mode propulsion concepts are currently being studied for advanced, single stage earth orbital transportation systems (SSTO) for use in the post-1990 time period. These propulsion concepts are based on the sequential and/or parallel use of high density impulse and high specific impulse propellants in a single stage to increase vehicle performance and reduce dry weight. Specifically, the mixed mode concept utilizes two propulsion systems with two different fuels (Mode 1 and Mode 2) with liquid oxygen as a common oxidizer. Mode 1 engines would burn a high bulk density fuel for lift-off and early ascent to minimize performance penalties associated with carrying fuel tankage to orbit. Mode 2 engines will complete orbital injection utilizing liquid hydrogen as the fuel.

Alternate and complementary paths are available for achieving higher bulk density propellant combinations for both "low" and "high" specific impulse propulsion systems. That is, "low" specific impulse systems such as RP-1 LOX can benefit by replacement of RP-1 with a more energetic, heavy hydrocarbon fuel, while "high" specific impulse systems such as LH_2 LOX can benefit by utilization of triple point and/or slush cryogens. Note that triple point LOX would be of benefit for both Mode 1 and Mode 2 propulsion systems.

This paper summarizes the current state of the art of hydrocarbon fuels and densified cryogens. An analytical study of hydrocarbon fuels is presented. Candidate fuels are compared on the basis of density, specific impulse, and cost. It is shown that high density fuels (e.g., RJ-5) currently being developed for ramjet propulsion systems are not cost effective for use in SSTO propulsion systems. An assessment is made of the technology advancements required for the practical application of slush and/or triple point cryogens to advanced propulsion systems. Performance gains that can be obtained from the use of new and/or modified propellants are summarized.

I. INTRODUCTION

Mixed mode propulsion concepts are currently being studied for advanced, single stage earth orbital transportation systems (SSTO) for use in the post-1990 time period.[1] These propulsion concepts are based on the sequential and/or parallel use of

STAR category 38

high density impulse and high specific impulse propellants in a single stage to increase vehicle performance and reduce dry weight. Specifically, the mixed mode concept utilizes two propulsion systems with two different fuels (Mode 1 and Mode 2) with liquid oxygen as a common oxidizer. Mode 1 engines would burn a high bulk density fuel for lift-off and early ascent to minimize performance penalties associated with carrying fuel tankage to orbit. Mode 2 engines would complete orbital injection utilizing liquid hydrogen as the fuel.

Higher density propellants may also be used in a number of other near term applications, including uprating of present launch vehicles, substitution of the Solid Rocket Motor (SRM) boosters on the Space Shuttle with strap-on liquid boosters, or changing propellants on the Shuttle Orbit Maneuvering Engine (OME).[2] All of these applications can potentially benefit from higher bulk density propellant combinations compared to LOX RP-1 or reduced cost compared to N_2O_4 MMH.

Alternate and complementary paths are available for achieving higher bulk density propellant combinations for both "low" and "high" specific impulse propulsion systems. That is, "low" specific impulse systems such as RP-1 LOX can benefit by replacement of RP-1 with a heavy hydrocarbon fuel, while "high" specific impulse systems such as LH_2 LOX can benefit by utilization of triple point and/or slush cryogens. Note that triple point LOX would be of benefit for both propulsion systems.

This report will summarize the current state of the art on high density hydrocarbon fuels and of triple point and slush cryogens. An assessment will be made on technology required for the practical application of the higher density propellants and of the potential benefits when this technology is applied to current and future propulsion systems.

II. DISCUSSION - HIGH DENSITY HYDROCARBON FUELS

Hydrocarbon fuels with bulk densities up to 40 percent greater than RP-1 (kerosene) have been developed in recent years for application in volume limited ramjet propulsion systems.[3,4,5] The stimulus for current research is the need to maximize range within volume limited envelopes on Air Force and Navy Cruise Missiles systems. The emphasis of the current fuel research programs is to prepare novel fuels having a net heat of combustion greater than 1.05×10^4 cal/cm^3 (160 000 Btu/gal) with a maximum viscosity of 1000 centipoise at 219 K (-65° F). Navy applications, because of more closely controlled environments, have less stringent viscosity requirements. The Navy does, however, require a flash point of at least 333 K (140° F) for safety reasons. Quantities of fuel required for both Air Force and Navy applications are limited; consequently, cost, although important, is not an overriding criteria for military systems.

Based on military systems requirements, it is unlikely that the fuel or fuels selected for Cruise Missile systems would be optimum for use in rocket propulsion systems. Fuel density is of great interest for both ramjet and rocket propulsion systems. However, ramjet fuels are being optimized on the calorific value per unit of fuel volume whereas rocket fuels must be optimized on the basis of specific impulse which is the thrust developed per unit weight rate of consumption of propellants both fuel and oxidizer. That is, rocket systems because they carry an onboard oxidizer must base fuel selection on specific impulse rather than energy content per unit volume of fuel.

However, the research being conducted for the military will provide a technological base for directing research on novel rocket fuels. The criteria used to screen potential rocket fuels will be density (ρ), specific impulse (I_{sp}), density times specific impulse to the third power ($\rho I_{sp}{}^3$), and cost. The density comparison of importance is propellant rather than fuel density at or near the point of maximum impulse. The propellant merit index, $\rho I_{sp}{}^3$, is somewhat arbitrary; however, SSTO vehicles are more sensitive to specific impulse than propellant density. (NOTE: The propellant merit index, $\rho I_{sp}{}^3$, is being used to compare hydrocarbon fuels over a relatively narrow range of density and specific impulse. It is not intended to compare hydrocarbon fuels with liquid hydrogen. The all H_2/O_2 SSTO is under study as well as the mixed mode concept. Each system has its advantages and disadvantages when compared against each other and final propulsion concept selected is dependent on many factors, including performance and cost of the hydrocarbon fuel selected for the mixed mode concept).

As a rocket fuel for combustion with liquid oxygen, the potential performance of a hydrocarbon depends on its composition, heat of formation, and density. The molecular composition of a hydrocarbon can be represented in general as C_nH_m and its empirical composition as CH_r where $r = m/n = H/C$ atom ratio. The value of r ranges from a maximum of 4.0 in methane to less than unity in condensed polyaromatics. In general with all other factors constant, specific impulse increases with increasing r (see fig. 1). Specific impulse also increases with increasing heat of formation of the hydrocarbon fuel. Qualitatively stated, specific impulse will increase with increasing heat of formation at constant r or with increasing r at constant heat of formation. Additionally, increasing fuel density is beneficial from a vehicle viewpoint in that fuel tankage volume reductions are desirable. Moreover, an increase in one or two of the critical factors (e.g., heat of formation, r-ratio, and density) is obtainable only with a concommitant decrease with the remaining factors.

For the saturated hydrocarbons that make up RP-1, the value of r is close to 2 and the heat of formation is approximately -6 K cal/gm atom. Higher (more positive) values of the heat of formation can be obtained by introducing chemical unsaturation in the form of double or triple carbon to carbon bonds into the molecule or by introducing structural strain into the molecule with polycyclic ring structures. In each case, however, an increase in heat of formation is achieved at the expense of a decrease in r, and the increase in specific impulse is less than would have been achieved if the heat of formation had been increased at constant r. Looking at candidate hydrocarbon fuels on a general basis, figure 1 can be developed to describe the dependence of I_{sp} on the heat of formation and the hydrogen/carbon ratio for known hydrocarbons. Using figure 1, one can quickly estimate the performance potential of candidate fuels by measuring the heat of formation and knowing the molecular formula.

The oxidizer/fuel ratio for maximum specific impulse is also a function of the r value for the molecule. As r increases the O/F ratio increases to obtain maximum impulse. With the exception of figure 2 which shows the specific impulse as a function of O/F for three fuels (RP-1, RJ-5, and exo-THDCP) no effort was made to calculate maximum specific impulse values for the fuels being discussed. All calculations in figure 1 and table I are based on the reaction being stoichiometric to carbon monoxide (CO) with specific impulse values calculated from the computer program listed in reference 6.

Ramjet fuels being evaluated have the goal of optimizing density and volumetric heat of combustion with no interest, per se, in specific impulse. Many of these candidate fuels do have complex polycyclic structures which may result in high heats of formation because of structural strain induced into the molecule. As such, specific impulse values for these fuels along with their high density may be in the range of interest for rocket propulsion systems. In addition, there are a series of energetic (positive heats of formation) low and intermediate density hydrocarbons that are potentially attractive for use in rocket propulsion systems. Properties of these candidate fuels are listed in table I in order of decreasing fuel density with RP-1 included as the baseline. The following comments are offered pertaining to the hydrocarbon fuels listed in table I:

1. On a unit mass basis RP-1 is likely to continue to be the lowest cost hydrocarbon fuel for rocket propulsion systems. Because of its low cost RP-1 is a strong candidate fuel for mixed mode SSTO propulsion systems which require high volume usage.

2. Depending on vehicle systems requirements, there is a series of high, intermediate, and low density hydrocarbons that are potentially attractive for use in rocket propulsion systems.

3. Of the high density fuels (greater than 1 gm/cm^3), RJ-5 (Shelldyne-H) has been studied extensively and is considered to be the baseline high density fuel. On a cost/performance basis, however, it is unlikely that RJ-5 will be a viable candidate fuel for rocket propulsion systems that require high volume fuel usage.

4. Arguments made in reference 1 and shown in figure 3 which promote the use of RJ-5 are not considered valid because of the assumption of fixed volume vehicles. Vehicles designed on the basis of fixed payload utilizing lower cost propellants (RP-1) although larger and heavier are likely to be more cost effective than vehicles using RJ-5. Cost effective is used to denote a minimum cost per unit mass of payload in orbit.

5. It is likely that most, if not `, of the high density fuels (items 2 to 8, table I) being developed for ramjet applications will not be cost effective for use in SSTO propulsion systems because of economic and performance considerations. Because of the complexity of the molecular structures and the involved synthesis routes, most of these fuels will be at least an order of magnitude more expensive than RP-1 on a unit mass basis. Additionally, it is expected that there will be little, if any, improvement in specific impulse of these fuels compared to RP-1. As shown in figure 1 and discussed previously, the specific impulse potential of hydrocarbon fuels is a function of the heat of formation of the hydrocarbon molecule and the hydrogen/carbon atom ratio. Because there is a large induced structural strain in these high density, polycyclic molecules, it is anticipated that the heats of formation will be considerably improved compared to RP-1; however, this was accomplished with a reduction in the hydrogen/carbon atom ratio of the fuel. These high density fuels with a hydrogen/carbon ratio below 1.3 are expected to have a lower specific impulse than RP-1. Overall performance as measured by pI_{sp}^{3} will be positive when compared to RP-1 but the net increase in performance is not sufficiently large to overcome the net cost differential. Of the high density fuels listed, tetrahydrotricyclopentadiene will probably offer the best combination of cost, specific impulse, and density characteristics and, as such, should be evaluated further. Dicylopropanted dimenthanohexalin will probably have acceptable performance but it is expected to have too high a cost.

6. Complex high density hydrocarbons (e.g., RJ-5) may be cost effective in limited volume applications such as a mixed mode propulsion concept proposed for the Space Tug.[7]

7. It is possible by direct hydrogeneration of refinery streams from catalytic cracking towers to obtain inexpensive, relatively high density fuel candidates for mixed mode propulsion systems. Two fuels of this type as designated by RS-A and RS-B in table I were eliminated from Air Force ramjet systems because of freezing point problems. However, for rocket propulsion systems their low cost (approx. 22¢/kg) and relatively high density makes them potentially strong candidates. These candidate fuels are mixtures of varying boiling point petroleum fractions and data is needed on an average molecular composition and heat of formation before a judgment can be made on their potential as a rocket fuel.

8. There is a series of "intermediate" density ($p = 0.95\ gm/cm^3$) and "low" density ($p = 0.80\ gm/cm^3$) hydrocarbon fuels listed in table I which have potential cost/performance advantages when compared to RP-1.

9. Exo-tetrahydrodicyclopentadiene (item 11, table I) which is being developed as a diluent for the high density ramjet fuels is a strong candidate rocket fuel. It has a higher density and approximately the same specific impulse as RP-1 with a projected cost of 55 cents/kilogram. On the basis of pI_{sp}^{3} its performance is close to that obtainable from RJ-5 at a fraction of the cost of RJ-5. Cyclopentadiene feed stock for

the synthesis of this fuel can be obtained from coal gas and in excess of 45×10^6 kilograms per year are used.

10. There is a series of low density hydrocarbons such as 1,7 octadiyne which are considerably more energetic than RP-1. These hydrocarbons offer the greatest potential for increased performance as measured by pI_{sp}^3. A verification of the properties of these fuels along with a projected cost are required before their potential can be evaluated. These lower density energetic hydrocarbons should also be evaluated for mixed mode propulsion concepts such as Item 6 above.

11. Acetylene and methane are included in table I because they represent the limits obtainable on the heat of formation and hydrogen/carbon atom ratio. Acetylene, which is highly unstable in liquid form, represents the maximum obtainable specific impulse from known hydrocarbons.

III. CONCLUSION - HIGH DENSITY HYDROCARBON FUELS

Comparison of the data presented with known properties of RP-1 results in the following conclusions:

1. Acetylene with a specific impulse 10 percent higher than RP-1 represents the maximum obtainable specific impulse from the hydrocarbon family of fuels. It is, however, not a candidate fuel because of severe instability problems of the liquid.

2. Propellant density increases of greater than 10 percent are obtainable from a series of high density hydrocarbon fuels (e.g., RJ-5, H-COT Dimer). However, these density increases are accompanied by a loss in specific impulse and greatly increased costs.

3. Increases of approximately 5 percent are obtainable in specific impulse and propellant density, for selected fuels listed in table I. These performance gains may be obtainable with minimal cost penalties.

4. Increases of up to 14 percent are obtainable in arbitrary propellant merit index (pI_{sp}^3). This increase may also be obtainable at an acceptable cost.

5. Synthesis routes, verification of chemical and physical properties, projected costs, and safety considerations need to be evaluated for most candidate fuels listed in table I before a judgment can be made on whether or not to replace RP-1 as the logical fuel selection for Mode 1 propulsion on the SSTO.

IV. DISCUSSION - TRIPLE POINT AND SLUSH CRYOGENS

Hydrogen with all its apparent advantages as a space transportation system fuel does have two major disadvantages. These are its low liquid density (0.071 gm/cm^3 at 20.3 K) and volatile nature of the liquid. Considerable technical effort was expanded during the 1960's on techniques to increase the density and extend the storage time by subcooling and/or a partial solidification of the liquid. Advanced propulsion concepts under evaluation could benefit significantly from the increased density of subcooled and/or slush cryogens depending on the economics and practicality of manufacturing and utilizing of densified cryogens. Current interest centers not only on triple point and slush hydrogen but also liquid oxygen at the triple point. Methane which has been studied extensively but is not in use as a rocket fuel should also be evaluated as a triple point liquid or slush fluid.

Past technology studies have dealt almost exclusively with triple point and slush hydrogen with few references available on subcooled liquid oxygen. Properties of interest for triple point and slush hydrogen are shown in table II.[8]

The volume advantage of 13 percent for a 50 percent mixture of hydrogen slush and of 8 percent for triple point hydrogen are the areas of prime interest in subcooled hydrogen. Additional advantages may be obtained in the storage of subcooled hydrogen because of its added heat capacity. For liquid oxygen a 14 percent increase in density can be obtained with triple point liquid (1.31 gm/cm^3 at 54.4 K) compared to the saturated liquid at the normal boiling point (1.14 gm/cm^3 at 70.2 K).

Slush oxygen utilization is of no great significance because the small additional increase in density (approx. 2 percent) is applicable to the much lower volume oxidizer tank in a space propulsion system (approx. 1/3 the volume of the hydrogen tank at an O/F ratio of 6).

Studies have shown that, in general, the most economical method for producing triple point and/or slush hydrogen is by the vacuum pumping directly over the surface of the saturated liquid.[9] This technique referred to as the "freeze-thaw" process involves very rapid pressure modulation (10 cycles/min) controlled to ± 5 mm Hg of the triple point pressure. Slush is formed during the pressure reduction cycle and the slush mass is broken during the repressurization cycle and settles to the bottom of the container. Theoretical studies show that if the freeze-thaw process was carried out under completely adiabatic conditions approximately 15 percent of the liquid hydrogen is pumped off to achieve a 50 percent mixture of slush and triple point liquid. The hydrogen pumped off can be recirculated back to the hydrogen liquefier for recovery and reuse.

At least two additional processes have been evaluated for producing subcooled hydrogen. In one process, liquid hydrogen is held in a pretreatment chamber at a pressure and temperature between saturated and triple point liquid. This partially subcooled liquid is expanded through a valve to a pressure well below the triple point pressure thereby cooling and solidifying portions of the liquid. Additionally, slush and/or triple point hydrogen can be produced by blowing helium through the liquid. Evaporated hydrogen is carried off in a stream of helium with cooling of the remainder of the liquid. This technique is of interest for upgrading triple point and/or slush hydrogen in fuel tank of a rocket where vessel walls are thin and can not withstand vacuum pumping.

The necessary conditions for producing large quantities of triple point and/or slush cryogens do not appear insurmountable. Because of the low vapor pressure of liquid hydrogen at its triple point 0.7 Newton/cm^2 (1.02 psia) precautions must be taken to prevent air from being drawn into the system. The condensation of solid oxygen from air on liquid hydrogen is hazardous and must be prevented. Either a leak tight vessel and/or a vessel surrounded with helium gas is required during production.

During fueling of space vehicles, it will be necessary to pressurize the fuel tank above atmospheric pressure with helium gas. Preliminary data indicate the solubility of helium gas in slush hydrogen is low; therefore, no significant degradation in performance will be experienced because of dilution of the fuel.

Literature data records the transport and storage of subcooled hydrogen with the most efficient equipment available.[8] For example, a 4-day trip in a railway tank Dewar would cause a reduction in the solid fraction from 50 to approximately 40 percent which can be upgraded back to 50 percent by a small vacuum pump on the launch site storage tank. Consequently, triple point and/or slush hydrogen can be produced at existing hydrogen liquefaction facilities and transferred to the point of utilization with no major precedural modifications required.

Studies have been performed on effective designs and operation of propellant management systems for liquid and slush hydrogen fueled vehicles. Included in these studies were: (1) loading of triple point liquid and/or slush hydrogen into the fuel tank on the launch pad, (2) measurement of hydrogen quantity (mass) and quality (solid content) in the fuel tank during tank fill and ground hold, (3) maintenance and/or upgrading of hydrogen quality during ground hold, (4) measurement of hydrogen quantity during flight, (5) propulsion system flow characteristics, and (6) propellant utilization systems.[10] These studies along with some minimal experimental work, while supportive in promoting the use of slush fueled vehicles would require more extensive analytical and experimental work to verify the results.

Available data indicate that the recommended technique for maintenance of hydrogen quantity and quality in a vehicle fuel tank is recirculation. This technique can be accomplished by continuous or intermittent flow of two-phase mixture of hydrogen from the storage Dewar. Adjustment of the flow rate can be used to control quality of fluid in the vehicle fuel tank. The recirculation system does have the disadvantage of requiring an additional large diameter line and umbilical for returning the liquid from the vehicle to the ground storage Dewar.

Analytical studies indicate that there are no major problems with insulation, venting, and pressurization systems for subcooled hydrogen fuel tanks. Startup pressurant requirements can be considerably higher where a subcooled hydrogen is utilized compared with standard liquid hydrogen because of the low vapor pressure of the subcooled liquid. Studies indicate that for engine startup helium is the best pressurizing medium and that warm hydrogen from the engine bleed system is best for expelling the liquid during firing.

V. CONCLUSION - TRIPLE POINT AND SLUSH CRYOGENS

Based on the data reviewed the following conclusions are offered:

1. There is no apparent technical reason why triple point and/or slush hydrogen cannot be used in advanced propulsion systems to take advantage of its increased density.

2. Production and vehicle related operation costs must be evaluated to determine on a cost/performance basis the potential benefits of subcooled cryogens.

3. Subscale testing must be performed to substantiate and expand available data on the following: (a) verification of transfer, storage, and use of subcooled hydrogen in flight type propellant tankage; (b) demonstration that helium can be used to stabilize a flight weight tank containing low vapor pressure subcooled hydrogen; (c) demonstration of the required instrumentation to determine quality and quantity of subcooled hydrogen within the accuracies required for space vehicle systems; and (d) provide data on engine and pump performance for triple point hydrogen.

VI. EFFECTS OF PROPELLANT TECHNOLOGY ON SSTO VEHICLE PERFORMANCE

Arguments made by proponents of mixed mode propulsion systems for SSTO vehicles have to a great degree been based on fixed volume vehicles. As shown in figure 3 and discussed previously increasing fuel density first by utilization of high density hydrocarbons (RJ-5) followed by slush cryogens has a striking effect on payload capability of the vehicle. While this approach is an effective argument for utilizing high density fuels, it may not result in a cost effective vehicle. A more detailed approach being evaluated internally and on contract by Langley Research Center is to design to a fixed payload and allow the vehicle size to expand or contract to accomplish the mission. Both mixed mode and all LH_2 LOX concepts are being evaluated. Fuel selections can then be made on the basis of reduced costs achieved through lower dry weight and/or gross lift-off weight as opposed to increased recurring costs associated with more complex fuels.

Effects of propellant improvements for the mixed mode (parallel burn) SSTO are summarized in figure 4 and table III. Figure 4 shows the effect on payload of increasing performance of the Mode 1 propellant as measured by $\rho I_{sp}{}^3$ for a constant volume vehicle. Significant payload improvements are obtained with the higher performance propellants; however, the projected costs for RJ-5 and the amine group of fuels are extremely high. Fuels such as exo-tetrahydrodicyclopentadiene with a performance very close to RJ-5 may be economical. Table III shows the effects of a percentage increase in I_{sp} and density on dry weight and gross lift-off weight

(GLOW). Note that the sensitivity to specific impulse is significantly higher than density sensitivity.

Table IV shows bulk density effects on both the all LH_2 LOX and the mixed mode vehicle concepts. Table IV shows performance gains that can be realized by utilizing triple point and slush hydrogen and oxygen. Reduction of close to 8 percent in dry weight and 6 percent in GLOW are obtainable by using slush cryogens for the all H-O vehicle. Vehicle size reductions obtainable by using triple point and slush cryogens must be compared to the increased cost of manufacturing the propellants and the increased complexity of using them.

VII. PROPELLANT COST PROJECTIONS

Table V gives a summary of current fuel costs and projected fuel costs for the 1990 time period. Because of the rapidly escalating cost of energy in recent years, fuel costs are difficult if not impossible to project with a high degree of confidence It is clear that petroleum based products such as RP-1 because of their high volume usage will continue to be the lowest cost fuels available. The current and projected costs for the synthetically derived speciality chemicals such as RJ-5 will limit their use to low volume applications. Recent cost increases for hydrazine based fuels resulting from governmental regulations on safety (one of the chemical intermediates is carcinogenic) will greatly reduce the utilization of these fuels. Hydrogen costs although relatively stable for the past 10 years are projected to increase rapidly in the immediate future.

VIII. CONCLUDING REMARKS

Significant gains in performance can be obtained from the utilization of new and/or modified propellants. Technological studies including cost/performance tradeoffs must be performed to evaluate the potential of applying this technology to SSTO schedules. Speciality fuels may find application in low volume applications especially as a replacement for hydrazine based fuels.

REFERENCES

1. Beichel, R.: Propulsion Systems for Single Stage Shuttles. Astronaut. & Aeronaut., vol. 12, no. 11, Nov. 1974, pp. 32-39.

2. Gregory, J. W.: Propulsion Technology Needs for Advanced Space Transportation Systems. AIAA Paper 75-1246, Sept.-Oct. 1975.

3. Schneider, A.; et al.: Air Breathing Missile Fuel Development. RDC-5000, Sun Oil Co. (AFAPL-TR-74-44-Vol-1; AD-922786L), 1974.

4. Schneider, A.; et al.: Air Breathing Missile Fuel Development. RDC-5004, Sun Oil Co. (AFAPL-TR-74-44-Vol-2; AD-B009284L), 1975.

5. Siminski, Vincent J.: Hydrocarbon Fuel Study Program Final. NWC-TP-5468 Naval Weapons Ctr. (AD-B003885L), 1975.

6. Gordon, Sanford; and McBride, Bonnie J.: Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Champan-Jouguet Detonations. NASA SP-273, 1971.

7. Salkeld, R.; and Beichel, R.: Mixed-Mode Propulsion Systems for Full Capability Space Tugs. AAS Paper 75-162, Am. Astronaut. Soc., Aug. 1975.

8. Carney, R. R.: Slush Hydrogen Production and Handling as a Fuel for Space Projects. Advances in Cryogenic Engineering. Vol. 9, K. D. Timmerhaus, ed., Plenum Press, 1964, pp. 529-535; Discussion, 535-536.

9. Slush Hydrogen Production, Storage and Distribution Study Program. (Union Carbide Corp.; Contract SNPC-41) NASA CR-81185, 1966.

10. A Study of Hydrogen Slush and/or Hydrogen Gel Utilization. Vol. 1: Saturn S-IVC Manned Mars Flyby Vehicle Application Study. (K-11-68-1K-Vol-1, Lockheed Missiles and Space Co.; NAS8-20342) NASA CR-98936, 1968. Vol. 2: Test Program 41.5-Inch Diameter Tank. (K-11-68-1K-Vol-2, Lockheed Missiles and Space Co.; NAS8-20342) NASA CR-98935, 1968.

E-8850

TABLE I. - HYDROCARBON FUELS

	Fuel	Chemical formula	$\frac{\Delta H_f(l)}{n}$, x (a)	H/C ratio	Mixture ratio, O/F, wt.% (b)	Fuel density, gm/cm^3	Cost, \$/kg (d)	Propellant density, gm/cm^3	Specific impulse, sec (c)	ρI_{sp}^3 $\frac{\text{gm-sec}^3}{\text{cm}^3}$
1	RP-1	$C_{12}H_{24}$	-6.0	2.0	2.28	0.80	0.14	1.01	327.8	3.55×10^7
2	RJ-5	$C_{14}H_{18}$	+2.5	1.28	1.96	1.08	>4.00	1.12	322.4	3.75×10^7
3	Dicyclopropanated-COT	$C_{18}H_{20}$	----	1.11	1.80	1.19	>4.00	1.15	-----	------
4	H-COT-Dimer	$C_{16}H_{20}$	+2.0	1.25	1.96	1.14	>4.00	1.14	324.0	3.87×10^7
5	Dicyclopropanated dimethanohexalin	$C_{14}H_{20}$	----	1.42	2.04	1.09	>3.00	1.11	-----	------
6	H-Binor-S	$C_{14}H_{18}$	----	1.28	1.96	1.08	>3.00	1.11	-----	------
7	Tetrahydrotricyclo-pentadiene	$C_{15}H_{22}$	-2.0	1.46	2.05	1.04	>2.00	1.09	321.7	3.63×10^7
8	Dicyclopropanated dicyclopentadiene	$C_{12}H_{16}$	----	1.33	2.00	1.03	>2 [illegible]	1.09	-----	------
9	RS-A	-------	----	----	----	1.04	.20	----	-----	------
10	RS-B	-------	----	----	----	1.01	.20	----	-----	------
11	Exo-THDCP	$C_{10}H_{16}$	-.9	1.60	2.[illegible]1	.94	.50	1.06	327.4	3.72×10^7
12	Th-Dimer	$C_{12}H_{20}$	-.9	1.66	2.14	.92	.50	1.05	329.0	3.74×10^7
13	Cyclo octatetrene (COT)	C_8H_8	+7.5	1.0	1.84	.94	-----	1.05	328.5	3.72×10^7
14	Dispiro octane	C_8H_{12}	+7.1	1.50	2.07	.846	-----	1.02	339.8	4.00×10^7
15	1,4 Cyclohexadiene	C_6H_8	+3.2	1.33	2.00	.843	-----	1.02	328.8	3.62×10^7
16	1,7 Octadiyne	C_8H_{10}	+9.8	1.25	1.96	.81	-----	1.00	339.5	3.91×10^7
17	Spiro pentane	C_5H_8	+7.6	1.60	2.11	.75	-----	.98	342.6	3.94×10^7
18	Acetylene	C_2H_2	+24.5	1.00	1.84	.62	.70	.88	361.6	4.16×10^7
19	Methane	CH_4	-21	4.00	----	.43	.14	.81	340.8	3.20×10^7

[a] Heat of formation of liquid fuel per gram atom carbon, Kcal.
[b] Stoichiometric to CO.
[c] Equilibrium expansion from 2756/10.2 Newton/cm^2 (4000/14.7 psia)
[d] Projected cost based on 4.54×10^6 kilogram/yr (10×10^6 lb/yr).

TABLE II. - PROPERTIES OF SLUSH HYDROGEN

Property	Triple point solid H_2	Slush H_2 50 percent solid	Triple point liquid H_2	Triple point H_2 vapor	Atmospheric saturated liquid H_2	Atmospheric saturated H_2 vapor
Temperature, K	13.8	13.8	13.8	13.8	20.3	20.3
Pressure, N/cm^2	0.70	0.70	0.70	0.70	10.2	10.2
Density, gm/cc	0.08666	0.08153	0.07705	1.249×10^{-4}	0.0708	0.0013455
Specific volume, cc/gm	11.54	12.265	12.98	8006.405	14.124	743.22
Enthalpy						
cal/gm (mol)	5.0961	19.106	33.129	250.0	58.92	273.73
Joules/gm (mol)	(21.322)	(79.94)	(138.61)	(1046.0)	(246.54)	(1145.28)
Specific volume below atmospheric saturated liquid, cc/gm	2.56	1.873	1.1237	----------	0	---------
Volume advantage for slush, H_2, percent	18	13	8	----------	0	---------

TABLE III. - SENSITIVITY GRADE FOR PARALLEL BURN SSTO[a, b]

Parameter	$\frac{\text{Percent GLOW}}{\text{Percent parameter}}$	$\frac{\text{Percent dry weight}}{\text{Percent parameter}}$
I_{sp}	-0.82	-0.48
ρ	-0.042	-0.074

[a]Specific impulse versus propellant bulk density.
[b]Unpublished data from NASA Langley Research Center.

TABLE IV. - BULK DENSITY EFFECTS ON SSTO VEHICLE WEIGHTS[a]

		BPO/BPH (b)	TPO/BPH	SO/BPH	TPO/TPH	SO/SH
LOX/LH	ρ, gm/cm^3 (lb/ft^3)	0.393 (24.55)	0.409 (25.55)	0.411 (25.69)	0.435 (27.20)	0.456 (28.47)
	$\Delta\rho$, percent	------------	4.07	4.64	10.79	15.97
	ΔDry weight, percent	------------	-1.97	-2.26	-5.23	-7.75
	ΔGLOW, percent	------------	-1.55	-1.77	-4.12	-6.10
		BPO/BPH+RJ	TPO/BPH+RJ	SO/BPH+RJ	TPO/TPH+RJ	SO/SH+RJ
Parallel burn	ρ, gm/cm^3 (lb/ft^3)	0.451 (28.16)	0.471 (29.45)	0.474 (29.62)	0.50 (31.19)	0.521 (32.57)
	$\Delta\rho$, percent	------------	4.58	5.18	10.76	15.66
	ΔDry weight, percent	------------	-2.22	-2.51	-5.22	-7.60
	ΔGLOW, percent	------------	-1.75	-1.98	-4.11	-5.98

[a]Unpublished data from NASA Langley Research Center.

[b]BPO - Boiling point oxygen; BPH - Boiling point hydrogen; TPO - Triple point oxygen; TPH - triple point hydrogen; SO - Slush oxygen; SH - Slush hydrogen.

TABLE V. - PROPELLANT COST PROJECTIONS

Propellant	Current cost, \$/kg (\$/lb)	Estimated 1990 cost, \$/kg (\$/lb)
LH_2	1.10 (0.50)	3.96 (1.80)
LO_2	0.059 (0.027)	0.22 (0.10)
MMH	13.24 [illegible].00)	48.48 (22.00)
N_2H_4	4.40 (2.00)	16.08 (7.30)
RP-1	0.13 (0.06)	0.48 (0.22)
RJ-5	4.40 (2.00)	16.08 (7.30)

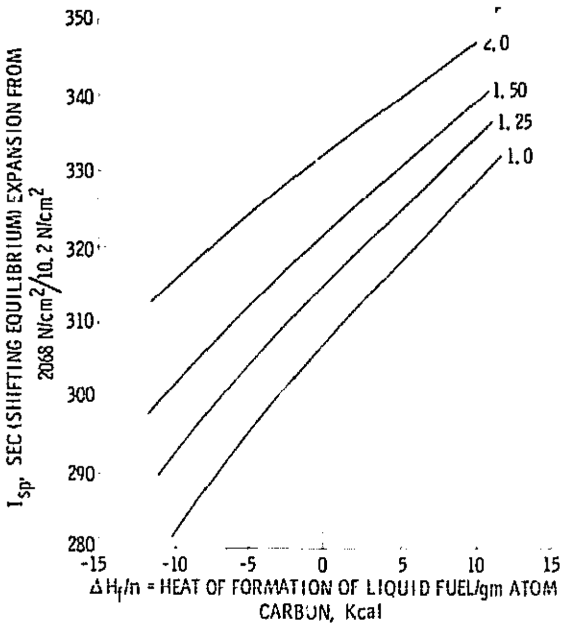

Figure 1. - Specific impulse versus $\Delta H_f/n$ at various values of atom ratio H/c = r.

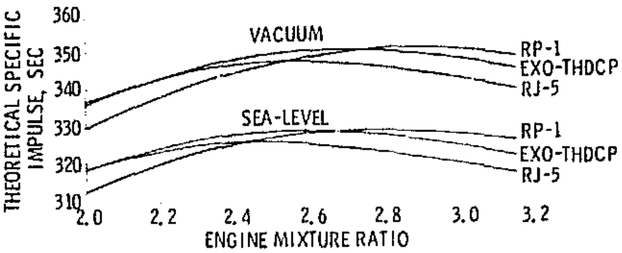

Figure 2. - Theoretical performance versus mixture ratio for LOX/hydrocarbon propellants expanded to 1 atmosphere - P_C = 2068 N/cm^2.

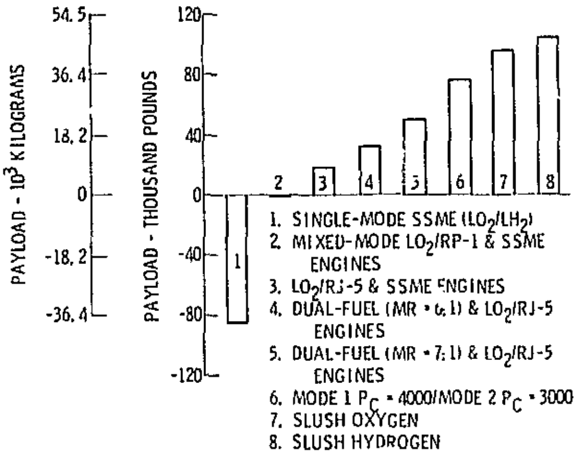

Figure 3. - Payload improvements through propulsion system optimization. (Reusable one-stage-to-orbit-and-return VTOHL; ascent propellant volume of 2377 meter^3 (84,000 ft^3).)

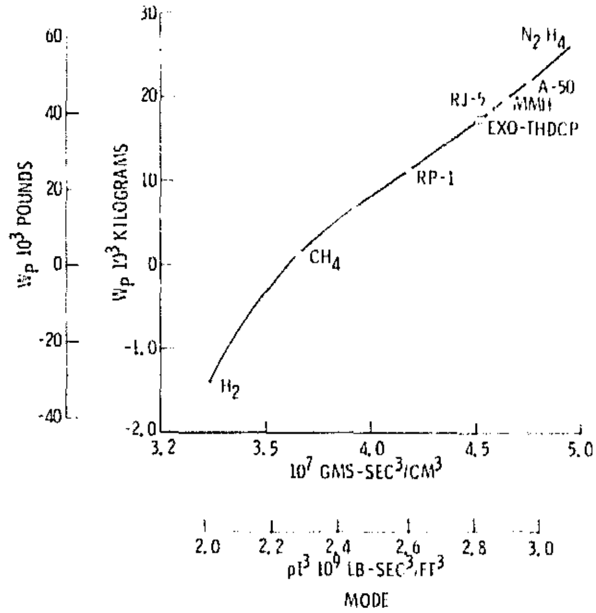

Figure 4. - Orbital payload versus model propellant index for a constant volume vehicle - 80,000 ft^3. (Obtained from Aerojet Liquid Rocket Co.)