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PROBLEMS IN CHEMICAL PROPULSION SYSTEMS AND LIMITING FACTORS

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ABSTRACT

The energy limitations of chemical propulsion systems are discussed in terms of molecular weight, bond energy and molecular dissociations. Based on the above consideration, a specific impulse in the order of 425 seconds appears to be the maximum value attainable. Other factors affecting the performance of chemical propulsion systems are mass ratio and combustion efficiency.

Problems associated with advancing the state of technology in chemical propulsion in solids, liquids and hybrid engines are discussed. These include the sensitivity of energetic ingredients used in solid propellants, the design and engineering of liquid engines employing cryogenic oxidizers and fuels, the use of more energetic and dense propellants in storable liquid engines, and problems in combustion and development of hybrid engines.

INTRODUCTION

For many years, rocket propulsion has been synonymous with chemical reaction systems. Today, as a result of the latest advances in nuclear, thermoelectric and other related technologies, rocket motors based on physical rather than chemical properties are now being developed. It is not anticipated that these new developments will materially affect the position of chemical propulsion systems; instead, these new systems will find their own unique place fulfilling special functions based on new requirements now being established for outer space and other missions.

It is important that we define the area in which chemical systems operate and to indicate the limitation on performances set by the maximum available energy in chemical propellants. These performance limitations are real but this in no way implies that no further advancements are possible. Although ultimate performance limitations can be indicated with a fair degree of accuracy, these limits have not yet been attained and further advances in the state of the art will permit significant improvements over our present capabilities. This paper will discuss the energy limitations of chemical propulsion systems and outline the problem areas which need resolution if we are to develop higher energy and more efficient chemical propulsion systems.

The most serious limitations to chemical propulsion systems are those that are imposed by the laws of nature. The maximum available energy that can be obtained from known chemical structures can be determined from a consideration of bond energies, heats of formation and reaction. It is possible then to establish a maximum value for specific impulse which is a fundamental parameter depicting the performance of a propellant. In its simplest form, specific impulse can be described by the following equation:

$$I_s = \frac{F}{W} \ ;$$

F = Thrust in pounds force
W = Rate of propellant consumption in pounds/second or the thrust generated by a flow of one pound of propellant per second.

From Table I, the relative position of various rocket propulsion systems is shown. In terms of specific impulse chemical systems are the least energetic. Non-chemical systems are capable of performance of at least one order of magnitude over any performance possible by chemical propulsion systems, although chemical air-breathers employing oxygen from the atmosphere as an oxidizer offer the possibility of extending the impulse performance by a factor of 2-3.

TABLE I

COMPARISON OF PROPULSION SYSTEMS

System	Specific Impulse (lb(F)sec/lbm)
Chemical	130 - 450
Chemical Air Breathers	300 - 1,200
Solar Heating	300 - 600
Nuclear	500 - 7,000
Arc Jet	1,000 - 5,000
Ion Jet	5,000 - 15,000
Plasma	3,000 - 6,000

The use of specific impulse as a basis of comparison can lead to misleading conclusions. Although some of the non-chemical systems are capable of generating high specific impulse, the mass flow rate of the thrust is extremely low limiting these systems to only certain applications where high thrust requirements do not have to be met. Thrust can be shown to be equivalent to the product of the velocity of the exhaust particle and the mass flow rate. The advantage of the chemical propulsion system is that by varying the burning rate of the propellant and the internal design of the grain tremendous mass expulsion rates can be attained to give thrusts equivalent to hundreds of thousands of pounds. By reducing the burning rate, the same propellants may be useable in sustainer operations where lower thrusts but increased burning times are required.

A specific impulse of about 425 appears to be the maximum value attainable in chemical propulsion systems. The reasons for this are essentially related to the reactions of chemical constituents in rocket combustion chambers. The barriers preventing the attainment of performance higher than this are: bond energy, molecular weight and molecular dissociation. To appreciate these factors, we need to redefine specific impulse in terms of thermochemical and dynamic relationships such as:

$$I_s = \sqrt{\frac{2J}{g} (H_c - H_e)}$$

where

J = Mechanical Equivalent of Heat
g = Gravitational Constant
H_c = Combustion Enthalpy
H_e = Exit Enthalpy.

Another representation of the specific impulse equation is:

$$I_s = 9.797 \sqrt{\frac{k}{k-1} \times \frac{Tc}{M} \left[1 - \left(\frac{Pe}{Pc}\right)^{\frac{k-1}{k}}\right]}$$

where

k = Average Specific Heats C_p/C_v
Pe = Exit Pressure
Pc = Chamber Pressure
M = Average Molecular Weight
Tc = Combustion Chamber Temperature.

The significant points in this equation are that specific impulse is defined by the temperature of the combustion process Tc and the molecular weight of the reactant gases, M. The specific heat, k, and pressure effects are contributing factors but not of major consideration in this discussion. The above equation can be reduced to the following:

$$I_s \sim \sqrt{\frac{Tc}{M}}$$

Table II lists theoretical values for specific impulse for some typical liquid propellants. From these values, it is possible to establish relationships between specific impulse and composition, temperature and molecular weight. From consideration of molecular weight according to the foregoing equation, the approach to higher specific impulse is the selection of propellants which result in low molecular weight combustion products. The absolute minimum which can be achieved of course is hydrogen--with a molecular weight of 1.5 to 2 involving both molecular and atomic species. However, since reactions between different atomic and molecular species other than hydrogen will be involved in chemical propulsion molecular weights greater than 2 will generally result, the latter being possible only in a nuclear rocket employing hydrogen as a fuel. Some typical rocket exhaust compositions are shown in Table III. Typical rocket exhaust molecular weights generally range from 18 to 32. From Table III, it can also be seen that second period light metals such as lithium, beryllium and boron with molecular weights of 7, 9 and 11 permit them to be considered as possible constituents in rocket engine combustion. A value for the hydrogen-fluorine system is 8.9 which is the minimum molecular weight attainable. The limiting value, of course, is one but this value is unattainable for chemical propulsion systems. The species hydrogen, carbon, nitrogen, oxygen and fluorine have long been and will probably be for some years to come the basic atomic species participating in the rocket combustion and expansion cycle. It is here then, with the molecular weight that the first barrier to extremely high specific impulse values is to be found.

The temperature is a measure of the thermal energy imparted to the combustion products as a result of the fuel-oxidizer reaction in the combustion chamber resulting from the breaking of valence bonds and forces in the oxidizer and fuel and forming of new and usually stronger valence bonds in the reaction products. Table IV shows comparative values of chemical bond energies of reactants and products.

TABLE II

SPECIFIC IMPULSE VALUES

Oxidizer	Fuel	Tc (°F)	$\dot{M}$	k	Isp (500 psi)	
Hydrogen Peroxide	Gasoline	4830	21	1.20	248	(286)
Hydrogen Peroxide	Hydrazine	4690	19	1.22	262	
Nitric Acid	Gasoline	5150	--	1.23	240	
Nitric Acid	Aniline	5100	21	--	235	
Nitric Acid	Ammonia	4220	22	1.24	237	
Oxygen	Alcohol	5560	22	1.22	259	
Oxygen	Gasoline	5770	22	1.24	264	
Oxygen	Hydrazine	5370	18	1.25	280	(313)
Oxygen	Hydrogen	4500	9	1.26	360	(391)
Fluroine	Ammonia	7224	19	1.33	306	(357)
Fluorine	Hydrazine	7940	19	1.33	316	(363)
Fluorine	Hydrogen	5100	8.9	1.33	373	(410)

Bracketed figures -- 1000 → 14.7 psia

TABLE III

MOLECULAR WEIGHTS

Reactants			Combustion Products		
Hydrogen	-	1.00	H	-	1.00
Helium	-	4.00	H_2	-	2.02
Lithium	-	6.94	C	-	12.01
Beryllium	-	9.01	N	-	14.01
Boron	-	10.82	O	-	16.00
Carbon	-	12.01	OH	-	17.01
Nitrogen	-	14.01	H_2O	-	18.02
Oxygen	-	16.00	F	-	19.00
Fluorine	-	20.18	HF	-	20.01
Sodium	-	23.00	CO	-	28.01
Magnesium	-	24.32	NO	-	30.01
Aluminum	-	26.97	CF	-	31.01
Silicon	-	28.06	O_2	-	32.00
Phosphorus	-	30.98	F_2	-	38.00
Sulfur	-	32.07	CO_2	-	44.01
Chlorine	-	35.45	CF_2	-	50.01
			C_2F_2	-	62.02
			COF_2	-	66.01
			CF_3	-	69.01
			CF_4	-	88.01

TABLE IV

VALENCE BOND ENERGIES
(Kcal/mol)

Reactants		Combustion Products	
C-O	81	C=O	256
C-C	78	N≡N	225
C-N	70.5	N=O	150
O-O	117	N-F	134
H-H	33	C-F	106
N-H	85	H-O	103
C-H	80		
F-F	36		

In selecting propellant combinations that will yield high combustion temperatures, the choice of fuel and oxidizer will be centered on compounds which in themselves have positive heats of formation and will in reaction lead to products which have high bond energies and very negative heats of formation. One of the objectives of the ingredient synthesis program for higher energy propellant is to prepare chemical structures which have low negative or even positive heats of formation so as to produce the maximum heat balance. The bond energies or heats of formation of basic chemical structures then represent another limitation in the attainment of higher specific impulse since the combustion temperature on which specific impulse depends is directly related to the energy balance resulting from the combustion reaction.

Another limitation is that there is a temperature level beyond which it is extremely difficult to go. At higher temperatures, the exhaust products begin to absorb substantial quantities of energy by first dissociating to free radicals. Unless these radicals recombine in the nozzle this energy absorbed in dissociation is not available to do useful work. In Table V, the lower order flame temperatures

TABLE V

DISSOCIATION OF EXHAUST SPECIES

Species	% Dissociation			
	(4,000°F)	(6,000°F)	(8,000°F)	(10,000°F)
CO_2	5	40	--	--
H_2O	2	12	22	--
H_2	1	6	18	--
O_2	1	5	14	--
HF	--	1	2	--
CO	--	--	--	2
N_2	--	--	--	2

are low primarily because of lower order bond energy, although in some cases the low temperatures are a result of advanced dissociation of some of the reactant ingredients, particularly water and carbon dioxide. Water begins to dissociate low in the temperature scale, 5% being dissociated at 5000°F. Rocket engine flame temperature, Tc, is therefore limited by the dissociation of the reaction products which begin about 5000°F and reach advanced levels at 8000°F to 10,000°F. However, the practical limit in combustion temperature is approximately 7000°F. Table V shows the percent dissociation of various exhaust species against temperature at 500 psi. From this, one can gather that higher temperature systems are more probable in those reactions which have a minimum of CO_2 and H_2O and an optimum amount of N_2 and CO. Theoretical considerations and experimental firings prove that this is the case.

To the propulsion engineers, performance is generally expressed in terms of vehicle range, size, payload or velocity at burnout. The latter parameter which can be shown to be related to the other performance criteria is described by the following equation:

$$V_b = I_s \, g \log \frac{W_i}{W_b}$$

$$\frac{W_i}{W_b} = \text{mass ratio} = \frac{\text{vehicle initial weight}}{\text{vehicle burn-out weight}}$$

The mass ratio can also be written as:

$$\frac{W_i}{W_b} = \frac{W_b + W_p}{W_b} = 1 + \frac{W_p}{W_b} = 1 + \frac{vd}{W_b}$$

where

v = volume of propellant
d = density of propellant
W_p = propellant weight.

There is little doubt that these performance parameters are all enhanced to a greater or lesser degree by the increase in specific impulse. However, there are certain aspects of the foregoing equation apart from specific impulse which are limiting factors in achieving maximum performance in a chemical propulsion system. These aspects are discussed below:

Combustion Efficiency

The specific impulse is generally calculated to give a theoretical value assuming 100% efficiency and assuming complete equilibrium flow along the nozzle. In actual practice, the performance is limited by the combustion efficiency of the propellant and of the motor, and the efficiency or available energy is generally around 90 to 97% of the theoretical value. The difference between theoretical and actual delivered specific impulse may be attributable to several factors. Heat losses from the motor, failure to maintain equilibrium flow throughout the nozzle, and thermal-velocity lags of condensed phases in the exhaust all lead to reduced efficiency. This factor is of considerable importance in that the selection of a propellant for a given motor is not necessarily based on its theoretical value but on the delivered impulse. It is possible that some propellant may actually deliver higher impulse even though their theoretical values may be somewhat less than other propellants.

The addition to metals to propellants either as a fuel or as a means of increasing density may seriously affect the combustion efficiency. The use of Al as a fuel, for example, will give significant increases in specific impulse but large amounts of Al are increasingly more difficult to burn efficiently so that the improvement in performance is less than proportional. The presence of Al_2O_3 in the exhaust creates two phase flow in which there exists thermal and velocity lags which dissipate the energy in the system. There is also the problem of obtaining complete combustion of the aluminum to aluminum oxide. If the aluminum particles are only oxidized on the surface during the combustion process then the full potential of the aluminum as a fuel is not realized. This type of combustion inefficiency may occur where metal fuels are present in the propellant formulation. As other metals are employed, one of the major problems anticipated is that of obtaining acceptable combustion efficiencies in the development of higher energy propellants. In general, values below 90% are undesirable and may result in deliverable impulses not significantly above available systems. Considerable effort is being placed on the combustion efficiency problem with the idea of understanding the basic mechanisms affecting the dissipation of energy and in developing propellants and propulsion systems in which combustion efficiencies of 95% or over for solid fuels are possible.

Mass Ratio

The mass ratio factor in the equation for burnout velocity shows that improved performance can be obtained through an increase in the proportion of propellant by weight to the inert constituents of the motor. Motor designs are generally optimized to give the highest mass ratio consistent within the state of the art. Table VI shows the variation in range and velocity of a one stage rocket for different

TABLE VI

MASS RATIO EFFECTS

Mass Ratio $\frac{W_f}{W_i}$	Isp (lb. sec)	Range (mile)	Burnout Velocity (ft sec)
1. 43	200	50	2, 305
	300	75	3, 460
	400	140	4, 610
	500	200	5, 760
	600	275	6, 900
2. 00	200	130	4, 460
	300	250	6, 700
	400	440	8, 920
	500	700	11, 160
	600	1, 050	13, 400
3. 33	200	330	7, 750
	300	750	11, 600
	400	1, 450	15, 550
	500	2, 700	19, 400
	600	4, 850	23, 200
10. 1	200	1, 300	14, 800
	300	4, 150	22, 200
	400	Satellite	29, 000
	500	Escape	37, 000
	600	Escape	44, 400

specific impulses. It is apparent that the rewards for achieving high mass ratio propulsion systems are significant in terms of increased performance. Even for relatively low impulse such as 200 seconds, a mass ratio increase from 200 (50% propellant and 50% inerts) to 10 (90% propellant to 10% inerts) can increase the range from 130 to 1300 miles.

The limiting factors on which the mass ratio depends are as follows:

Pressure: A higher specific impulse can be obtained by designing the motor for higher combustion pressures. Increased combustion pressure results in decreased dissociation of some species, thereby increasing the flame temperatures and making possible a more complete combustion. There is a practical limit to the increase in pressure as determined by the trade-off between the improvement in specific impulse and the increase in the thickness and therefore weight of combustion chamber to accommodate the increase in pressure. In some instances, it may be desirable to operate the motor at lower pressures; for example, in the upper stage of some of the space motors at some sacrifice in impulse so that higher mass ratios can be attained. The development and use of higher strength light weight materials may make it possible to operate motors at higher pressure realizing higher impulse values and reducing at thickness and weight of the chamber so that simultaneously an increase in mass ratio is obtained. On the other hand, the increase in impulse and temperature may offset this improvement since the use of additional insulation in the chamber and nozzle to resist thermal erosive effects may be required thereby effectively reducing the mass ratio.

Propellant Density: For volume limited applications, it is sometimes desirable to incorporate the maximum amount of propellant by weight. This is essentially accomplished by using a propellant with a relatively high density. This maneuver not only is effective in increasing the mass ratio but also can result in a higher total impulse for the motor. The addition of metals to the propellant is