ROCKET PROPELLANTS

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Propellant is the chemical mixture burned to produce thrust in rockets and consists of a fuel and an oxidizer. A *fuel* is a substance that burns when combined with oxygen producing gas for propulsion. An *oxidizer* is an agent that releases oxygen for combination with a fuel. The ratio of oxidizer to fuel is called the *mixture ratio*. Propellants are classified according to their state - liquid, solid, or hybrid.

The gauge for rating the efficiency of rocket propellants is *specific impulse*, stated in seconds. Specific impulse indicates how many pounds (or kilograms) of thrust are obtained by the consumption of one pound (or kilogram) of propellant in one second. Specific impulse is characteristic of the type of propellant, however, its exact value will vary to some extent with the operating conditions and design of the rocket engine.

Liquid Propellants

In a liquid propellant rocket, the fuel and oxidizer are stored in separate tanks, and are fed through a system of pipes, valves, and turbopumps to a combustion chamber where they are combined and burned to produce thrust. Liquid propellant engines are more complex than their solid propellant counterparts, however, they offer several advantages. By controlling the flow of propellant to the combustion chamber, the engine can be throttled, stopped, or restarted.

A good liquid propellant is one with a high specific impulse or, stated another way, one with a high speed of exhaust gas ejection. This implies a high combustion temperature and exhaust gases with small molecular weights. However, there is another important factor that must be taken into consideration: the density of the propellant. Using low-density propellants means that larger storage tanks will be required, thus increasing the mass of the launch vehicle. Storage temperature is also important. A propellant with a low storage temperature, i.e. a cryogenic, will require thermal insulation, thus further increasing the mass of the launcher. The toxicity of the propellant is likewise important. Safety hazards exist when handling, transporting, and storing highly toxic compounds. Also, some propellants are very corrosive; however, materials that are resistant to certain propellants have been identified for use in rocket construction.

Liquid propellants used in rocketry can be classified into three types: petroleum, cryogens, and hypergols.

Petroleum fuels are those refined from crude oil and are a mixture of complex hydrocarbons, i.e. organic compounds containing only carbon and hydrogen. The petroleum used as rocket fuel is a type of highly refined kerosene, called RP-1 in the United States. Petroleum fuels are usually used in combination with liquid oxygen as the oxidizer. Kerosene delivers a specific impulse considerably less than cryogenic fuels, but it is generally better than hypergolic propellants.

Specifications for RP-1 where first issued in the United States in 1957 when the need for a clean burning petroleum rocket fuel was recognized. Prior experimentation with jet fuels produced tarry residue in the engine cooling passages and excessive soot, coke and other deposits in the gas generator. Even with the new specifications, kerosene-burning engines still produce enough residues that their operational lifetimes are limited.

Liquid oxygen and RP-1 are used as the propellant in the first-stage boosters of the Atlas and Delta II launch vehicles. It also powered the first-stages of the Saturn 1B and Saturn V rockets.

Cryogenic propellants are liquefied gases stored at very low temperatures, most frequently liquid hydrogen (LH_2) as the fuel and liquid oxygen (LO_2 or LOX) as the oxidizer. Hydrogen remains liquid at temperatures of -253 ^oC (-423 ^oF) and oxygen remains in a liquid state at temperatures of -183 ^oC (-297 ^oF).

Because of the low temperatures of cryogenic propellants, they are difficult to store over long periods of time. For this reason, they are less desirable for use in military rockets that must be kept launch ready for months at a time. Furthermore, liquid hydrogen has a very low density (0.071 g/ml) and, therefore, requires a storage volume many times greater than other fuels. Despite these drawbacks, the high efficiency of liquid oxygen/liquid hydrogen makes these problems worth coping with when reaction time and storability are not too critical. Liquid hydrogen delivers a specific impulse about 30%-40% higher than most other rocket fuels.

Liquid oxygen and liquid hydrogen are used as the propellant in the high efficiency main engines of the Space Shuttle. LOX/LH_2 also powered the upper stages of the Saturn V and Saturn 1B rockets, as well as the Centaur upper stage, the United States' first LOX/LH_2 rocket (1962).

Another cryogenic fuel with desirable properties for space propulsion systems is liquid methane (-162 ^oC). When burned with liquid oxygen, methane is higher performing than state-of-the-art storable propellants but without the volume increase common with LOX/LH_2 systems, which results in an overall lower vehicle mass as compared to common hypergolic propellants. LOX/methane is also clean burning and non-toxic. Future missions to Mars will likely use methane fuel because it can be manufactured partly from Martian in-situ resources. LOX/methane has no flight history and very limited ground-test history.

Liquid fluorine (-188 ^oC) burning engines have also been developed and fired successfully. Fluorine is not only extremely toxic; it is a super-oxidizer that reacts, usually violently, with almost everything except nitrogen, the lighter noble gases, and substances that have already been fluorinated. Despite these drawbacks, fluorine produces very impressive engine performance. It can also be mixed with liquid oxygen to improve the performance of LOX-burning engines; the resulting mixture is called FLOX. Because of fluorine's high toxicity, it has been largely abandoned by most space-faring nations.

Some fluorine containing compounds, such as chlorine pentafluoride, have also been considered for use as an 'oxidizer' in deep-space applications.

Hypergolic propellants are fuels and oxidizers that ignite spontaneously on contact with each other and require no ignition source. The easy start and restart capability of hypergols make them ideal for spacecraft maneuvering systems. Also, since hypergols remain liquid at normal temperatures, they do not pose the storage problems of cryogenic propellants. Hypergols are highly toxic and must be handled with extreme care.

Hypergolic fuels commonly include hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH). Hydrazine gives the best performance as a rocket fuel, but it has a high freezing point and is too unstable for use as a coolant. MMH is more stable and gives the best performance when freezing point is an issue, such as spacecraft propulsion applications. UDMH has the lowest freezing point and has enough thermal stability to be used in large regeneratively cooled engines. Consequently, UDMH is often used in launch vehicle applications even though it is the least efficient of the hydrazine derivatives. Also commonly used are blended fuels, such as Aerozine 50 (or "50-50"), which is a mixture of 50% UDMH and 50% hydrazine. Aerozine 50 is almost as stable as UDMH and provides better performance.

The oxidizer is usually nitrogen tetroxide (NTO) or nitric acid. In the United States, the nitric acid formulation most commonly used is type III-A, called inhibited red-fuming nitric acid (IRFNA), which consists of HNO_3 + 14% N_2O_4 + 1.5-2.5% H_2O + 0.6% HF (added as a corrosion inhibitor). Nitrogen tetroxide is less corrosive than nitric acid and provides better performance, but it has a higher freezing point. Consequently, nitrogen tetroxide is usually the oxidizer of choice when freezing point is not an issue, however, the freezing point can be lowered with the introduction nitric oxide. The resulting oxidizer is called mixed oxides of nitrogen (MON). The number included in the description, e.g. MON-3 or MON-25, indicates the percentage of nitric oxide by weight. While pure nitrogen tetroxide has a freezing point of about -9 ^oC, the freezing point of MON-3 is -15 ^oC and that of MON-25 is -55 ^oC.

USA military specifications for IRFNA were first published in 1954, followed in 1955 with UDMH specifications.

The Titan family of launch vehicles and the second stage of the Delta II rocket use NTO/Aerozine 50 propellant. NTO/MMH is used in the orbital maneuvering system (OMS) and reaction control system (RCS) of the Space Shuttle orbiter. IRFNA/UDMH is often used in tactical missiles such as the US Army's Lance (1972-91).

Hydrazine is also frequently used as a monopropellant in *catalytic decomposition engines*. In these engines, a liquid fuel decomposes into hot gas in the presence of a catalyst. The decomposition of hydrazine produces temperatures up to about 1,100 ^oC (2,000 ^oF) and a specific impulse of about 230 or 240 seconds. Hydrazine decomposes to either hydrogen and nitrogen, or ammonia and nitrogen.

Other propellants have also been used, a few of which deserve mentioning:

Alcohols were commonly used as fuels during the early years of rocketry. The German V-2 missile, as well as the USA Redstone, burned LOX and ethyl alcohol (ethanol), diluted with water to reduce combustion chamber temperature. However, as more efficient fuels where developed, alcohols fell into general disuse.

Hydrogen peroxide once attracted considerable attention as an oxidizer and was used in Britain's Black Arrow rocket. In high concentrations, hydrogen peroxide is called high-test peroxide (HTP). The performance and density of HTP is close to that of nitric acid, and it is far less toxic and corrosive; however it has a poor freezing point and is unstable. Although HTP never made it as an oxidizer in large bi-propellant applications, it has found widespread use as a monopropellant. In the presence of a catalyst, HTP decomposes into oxygen and superheated steam and produces a specific impulse of about 150 s.

Nitrous oxide has been used as both an oxidizer and as a monopropellant. It is the oxidizer of choice for many hybrid rocket designs and has been used frequently in amateur high-powered rocketry. In the presence of a catalyst, nitrous oxide will decompose exothermically into nitrogen and oxygen and produce a specific impulse of about 170 s.

Solid Propellants

Solid propellant motors are the simplest of all rocket designs. They consist of a casing, usually steel, filled with a mixture of solid compounds (fuel and oxidizer) that burn at a rapid rate, expelling hot gases from a nozzle to produce thrust. When ignited, a solid propellant burns from the center out towards the sides of the casing. The shape of the center channel determines the rate and pattern of the burn, thus providing a means to control thrust. Unlike liquid propellant engines, solid propellant motors cannot be shut down. Once ignited, they will burn until all the propellant is exhausted.

There are two families of solids propellants: homogeneous and composite. Both types are dense, stable at ordinary temperatures, and easily storable.

Homogeneous propellants are either simple base or double base. A simple base propellant consists of a single compound, usually nitrocellulose, which has both an oxidation capacity and a reduction capacity. Double base propellants usually consist of nitrocellulose and nitroglycerine, to which a plasticiser is added. Homogeneous propellants do not usually have specific impulses greater than about 210 seconds under normal conditions. Their main asset is that they do not produce traceable fumes and are, therefore, commonly used in tactical weapons. They are also often used to perform subsidiary functions such as jettisoning spent parts or separating one stage from another.

Modern composite propellants are heterogeneous powders (mixtures) that use a crystallized or finely ground mineral salt as an oxidizer, often ammonium perchlorate, which constitutes between 60% and 90% of the mass of the propellant. The fuel itself is generally aluminum. The propellant is held together by a polymeric binder, usually polyurethane or polybutadienes, which is also consumed as fuel. Additional compounds are sometimes included, such as a catalyst to help increase the burning rate, or other agents to make the powder easier to manufacture. The final product is rubber like substance with the consistency of a hard rubber eraser.

Composite propellants are often identified by the type of polymeric binder used. The two most common binders are polybutadiene acrylic acid acrylonitrile (PBAN) and hydroxy-terminator polybutadiene (HTPB). PBAN formulations give a slightly higher specific impulse, density, and burn rate than equivalent formulations using HTPB. However, PBAN propellant is the more difficult to mix and process and requires an elevated curing temperature. HTPB binder is stronger and more flexible than PBAN binder. Both PBAN and HTPB formulations result in propellants that deliver excellent performance, have good mechanical properties, and offer potentially long burn times.

Solid propellant motors have a variety of uses. Small solids often power the final stage of a launch vehicle, or attach to payloads to boost them to higher orbits. Medium solids such as the Payload Assist Module (PAM) and the Inertial Upper Stage (IUS) provide the added boost to place satellites into geosynchronous orbit or on planetary trajectories.

The Titan, Delta, and Space Shuttle launch vehicles use strap-on solid propellant rockets to provide added thrust at liftoff. The Space Shuttle uses the largest solid rocket motors ever built and flown. Each booster contains 500,000 kg (1,100,000 pounds) of propellant and can produce up to 14,680,000 Newtons (3,300,000 pounds) of thrust.

Hybrid Propellants

Hybrid propellant engines represent an intermediate group between solid and liquid propellant engines. One of the substances is solid, usually the fuel, while the other, usually the oxidizer, is liquid. The liquid is injected into the solid, whose fuel reservoir also serves as the combustion chamber. The main advantage of such engines is that they have high performance, similar to that of solid propellants, but the combustion can be moderated, stopped, or even restarted. It is difficult to make use of this concept for vary large thrusts, and thus, hybrid propellant engines are rarely built.

A hybrid engine burning nitrous oxide as the liquid oxidizer and HTPB rubber as the solid fuel powered the vehicle *SpaceShipOne*, which won the Ansari X-Prize.

PROPERTIES OF ROCKET PROPELLANTS

Compound	Chemical Formula	Molecular Weight	Density	Melting Point	Boiling Point
Liquid Oxygen	O_2	32.00	1.14 g/ml	-218.8 ^oC	-183.0 ^oC
Liquid Fluorine	F_2	38.00	1.50 g/ml	-219.6 ^oC	-188.1 ^oC
Nitrogen Tetroxide	N_2O_4	92.01	1.45 g/ml	-9.3 ^oC	21.15 ^oC
Nitric Acid	HNO_3	63.01	1.55 g/ml	-41.6 ^oC	83 ^oC
Hydrogen Peroxide	H_2O_2	34.02	1.44 g/ml	-0.4 ^oC	150.2 ^oC
Nitrous Oxide	N_2O	44.01	1.22 g/ml	-90.8 ^oC	-88.5 ^oC
Chlorine Pentafluoride	ClF_5	130.45	1.9 g/ml	-103 ^oC	-13.1 ^oC
Ammonium Perchlorate	NH_4ClO_4	117.49	1.95 g/ml	240 ^oC	N/A
Liquid Hydrogen	H_2	2.016	0.071 g/ml	-259.3 ^oC	-252.9 ^oC
Liquid Methane	CH_4	16.04	0.423 g/ml	-182.5 ^oC	-161.6 ^oC
Ethyl Alcohol	C_2H_5OH	46.07	0.789 g/ml	-114.1 ^oC	78.2 ^oC
n-Dodecane (Kerosene)	$C_{12}H_{26}$	170.34	0.749 g/ml	-9.6 ^oC	216.3 ^oC
RP-1	$C_nH_{1.953n}$	≈175	0.820 g/ml	N/A	177-274 ^oC
Hydrazine	N_2H_4	32.05	1.004 g/ml	1.4 ^oC	113.5 ^oC
Methyl Hydrazine	CH_3NHNH_2	46.07	0.866 g/ml	-52.4 ^oC	87.5 ^oC
Dimethyl Hydrazine	$(CH_3)_2NNH_2$	60.10	0.791 g/ml	-58 ^oC	63.9 ^oC
Aluminum	Al	26.98	2.70 g/ml	660.4 ^oC	2467 ^oC
Polybutadiene	$(C_4H_6)_n$	≈3000	≈0.93 g/ml	N/A	N/A

NOTES:
- Chemically, kerosene is a mixture of hydrocarbons; the chemical composition depends on its source, but it usually consists of about ten different hydrocarbons, each containing from 10 to 16 carbon atoms per molecule; the constituents include n-dodecane, alkyl benzenes, and naphthalene and its derivatives. Kerosene is usually represented by the single compound n-dodecane.
- RP-1 is a special type of kerosene covered by Military Specification MIL-R-25576. In Russia, similar specifications were developed under specifications T-1 and RG-1.
- Nitrogen tetroxide and nitric acid are hypergolic with hydrazine, MMH and UDMH. Oxygen is not hypergolic with any commonly used fuel.
- Ammonium perchlorate decomposes, rather than melts, at a temperature of about 240 ^oC.

ROCKET PROPELLANT PERFORMANCE

Combustion chamber pressure, P_c = 68 atm (1000 PSI) ... Nozzle exit pressure, P_e = 1 atm

Oxidizer	Fuel	Hypergolic	Mixture Ratio	Specific Impulse (s, sea level)	Density Impulse (kg-s/l, S.L.)
Liquid Oxygen	Liquid Hydrogen	No	5.00	381	124
	Liquid Methane	No	2.77	299	235
	Ethanol + 25% water	No	1.29	269	264
	Kerosene	No	2.29	289	294
	Hydrazine	No	0.74	303	321
	MMH	No	1.15	300	298
	UDMH	No	1.38	297	286
	50-50	No	1.06	300	300
Liquid Fluorine	Liquid Hydrogen	Yes	6.00	400	155
	Hydrazine	Yes	1.82	338	432
FLOX-70	Kerosene	Yes	3.80	320	385
Nitrogen Tetroxide	Kerosene	No	3.53	267	330
	Hydrazine	Yes	1.08	286	342
	MMH	Yes	1.73	280	325
	UDMH	Yes	2.10	277	316
	50-50	Yes	1.59	280	326
Red-Fuming Nitric Acid (14% N_2O_4)	Kerosene	No	4.42	256	335
	Hydrazine	Yes	1.28	276	341
	MMH	Yes	2.13	269	328
	UDMH	Yes	2.60	266	321
	50-50	Yes	1.94	270	329
Hydrogen Peroxide (85% concentration)	Kerosene	No	7.84	258	324
	Hydrazine	Yes	2.15	269	328
Nitrous Oxide	HTPB (solid)	No	6.48	248	290
Chlorine Pentafluoride	Hydrazine	Yes	2.12	297	439
Ammonium Perchlorate (solid)	Aluminum + HTPB (a)	No	2.12	277	474
	Aluminum + PBAN (b)	No	2.33	277	476

NOTES:
- Specific impulses are theoretical maximum assuming 100% efficiency; actual performance will be less.
- All mixture ratios are optimum for the operating pressures indicated, unless otherwise noted.
- LO_2/LH_2 and LF_2/LH_2 mixture ratios are higher than optimum to improve density impulse.
- FLOX-70 is a mixture of 70% liquid fluorine and 30% liquid oxygen.
- Where kerosene is indicated, the calculations are based on n-dodecane.
- Solid propellant formulation (a): 68% AP + 18% Al + 14% HTPB.
- Solid propellant formulation (b): 70% AP + 16% Al + 12% PBAN + 2% epoxy curing agent.

SELECTED ROCKETS AND THEIR PROPELLANTS

Rocket	Stage	Engines	Propellant	Specific Impulse
Atlas/Centaur (1962)	0 1 2	Rocketdyne YLR89-NA7 (x2) Rocketdyne YLR105-NA7 P&W RL-10A-3-3 (x2)	LOX/RP-1 LOX/RP-1 LOX/LH_2	259s sl / 292s vac 220s sl / 309s vac 444s vacuum
Titan II (1964)	1 2	Aerojet LR-87-AJ-5 (x2) Aerojet LR-91-AJ-5	NTO/Aerozine 50 NTO/Aerozine 50	259s sl / 285s vac 312s vacuum
Saturn V (1967)	1 2 3	Rocketdyne F-1 (x5) Rocketdyne J-2 (x5) Rocketdyne J-2	LOX/RP-1 LOX/LH_2 LOX/LH_2	265s sl / 304s vac 424s vacuum 424s vacuum
Space Shuttle (1981)	0 1 OMS RCS	Thiokol SRB (x2) Rocketdyne SSME (x3) Aerojet OMS (x2) Kaiser Marquardt R-40 & R-1E	PBAN Solid LOX/LH_2 NTO/MMH NTO/MMH	242s sl / 268s vac 363s sl / 453s vac 313s vacuum 280s vacuum
Delta II (1989)	0 1 2	Castor 4A (x9) Rocketdyne RS-27 Aerojet AJ10-118K	HTPB Solid LOX/RP-1 NTO/Aerozine 50	238s sl / 266s vac 264s sl / 295s vac 320s vacuum

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