GREEN PROPELLANTS OPTIONS FOR LAUNCHERS, MANNED CAPSULES AND INTERPLANETARY MISSIONS.

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ABSTRACT

The quest for green propellants justifies a thorough review of all foreseeable applications involving MMH / NTO and hydrazine (satellite applications being excluded).
The relative merits of various fuels and monopropellants are compared and several trade-offs enable to select a preferred solution for a given mission.

1. INTRODUCTION:

The green propellant candidates are numerous and include already known combinations like LOX - LH2 and LOX - pure hydrocarbons.
The propellant combinations to be replaced are MMH or UDMH or UH25 / NTO (bipropellants) and hydrazine for monopropellants.
Solid propellant boosters could be also replaced by green liquid propellants but green solid candidates exist also.
A first review of candidate chemical products (e. g. hydrocarbons, HTP, nitrates) revealed that no perfect green exist. The maximum allowable concentration in air for workers (TWA) is sometimes very low for some green candidates. Other can form very easily explosive mixtures with air. Some risks should be accepted when greens are selected and they could be mitigated by appropriate measures (e. g. cooling to reduce vapour pressure).

2. GREEN PROPELLANTS APPLICATIONS

In fact, the foreseen application is the main driver for the selection of a given green propellant as illustrated by three examples:

♦ **<u>Boosters</u>**

Boosters applications are driven mainly by the required Delta V (around 2 km/s) and the stage cross section (aerodynamic drag). Since the propellant quantity is huge (from 50 to 300 tons) the propellant cost has some impact on the selection. The explosion risk is also an important factor: oxidisers or fuels having potential monopropellant behaviour are not very good candidates from the safety point of view.
All these constraints are satisfied by LOX - hydrocarbons combinations.
<u>Kerosene:</u>
Many US and Russian launchers are using "kerosene". It was selected in the fifties to replace ethyl alcohol as a fuel, but the chamber pressure was limited by coking in the cooling channels and combustion instabilities.
The most recent engines are sophisticated and expensive: they use staged combustion cycle and LOX rich gas generator. By this design, two main drawbacks of kerosene are avoided: soot formation in gas generator and combustion instabilities in main chamber.
Special kerosene blends reduce coking.
This risk could be also eliminated by LOX cooling. This technique has been used by MBB to cool the first high pressure chamber (P 101). Of course, when a LOX rich gas generator is used, only a part of LOX flow could be used for cooling.
Last, simplified LOX – kerosene engines could use an ablative chamber, thus eliminating the coking problem (e. g. FASTRACK engine).
<u>Methane:</u>
The big advantage of methane over kerosene is the possibility to use a fuel rich gas generator without soot formation and the very high cooling efficiency of methane. Methane is injected in gaseous state thus lowering the risk of combustion instabilities. Thus the overall engine design is very close to a classical LOX – LH2 engine.
<u>Other light hydrocarbons:</u>
Besides the classical LOX - kerosene and LOX - methane combination, some light hydrocarbons and ethers offer attractive properties:

- Ø Isp greater than either kerosene or methane,
- Ø density higher than methane,
- Ø Gaseous injection following heating in regenerative cooling, thus offering same protection against combustion instabilities than methane and hydrogen.

The Isp of some light hydrocarbons, i.e. cyclopropane and propene are even higher than methane despite their higher molecular mass.
This is linked to their chemical structure: in some cases their decomposition is exothermic; the enthalpy of reacted gases is therefore higher than with paraffins.
The table 2.1 shows the specific impulse of the oxygen – fuels combinations and the mixture ratio. H_2 – O_2 and N_2O_4 / MMH are given as references. It is easy to verify the specific impulse increase from propanol to propane, propene and propyne.
It can be seen also that for some oxidisers (HTP and N_2O) the mixture ratio is very high, but the variation of Isp with MR is quite low (especially for N_2O hybrids).
N_2O hybrids are not treated in this study but could be interesting (simplicity).

♦ **<u>Manned capsules RCS and landing retrorockets</u>**

Manned capsules RCS and landing retrorockets obey to different selection criteria. Today the reference propellants are MMH / N_2O_4. The replacement by non toxic propellants would offer a considerable improvement for the crew safety (the tanks are generally located inside the re-entry body aeroshell) and for post recovery operations. Two attractive solutions appear:

- Ø new monopropellants (organic nitrates salts and combinations).
- Ø safe combinations like N_2O and organic liquids.

Of course, they provide a lower Isp than MMH - N2O4 but they are much safer. A critical point would be the ignition reliability which is absolutely necessary for the crew safety. For monopropellants, the critical point would be catalytic or non catalytic ignition and for N2O / hydrocarbons, the catalytic (N2O decomposition) or electric ignition.

- **Automatic Interplanetary missions**

They are dominated today by MMH - N2O4 or hydrazine.

Depending on required Delta V, cryogenic or semi cryogenic combinations would be beneficial (pending on the use of active refrigeration). This would extend to low propellant masses the present domain of LOX based combinations.

The preferred ignition method is a torch fed with evaporated propellants. Torch and main chamber have separate valves (Fig. 2.2).
For manned missions, LOX - LH2 is probably the best choice but may require substantial improvements (throttling) for the landing phase. It could be inferred from the DC-X tests that the LOX - LH2 engines could be throttled safely from 30 % to 100 % of the nominal thrust.
For less severe Delta V requirements, N2O / hydrocarbons or new monopropellants (ADN or HAN) are attractive solutions.

This remark is also valid for small upper stages.
Fig. 2.1 shows a possible small upper stage design with four N2O tanks and one fuel tank to handle the much larger N2O volume.

The reviewed mission cases are listed in table 2.2.

3. TOXICITY and HANDLING

Many green candidate are indeed quite toxic (TLV - TWA in the 1 to 100 ppm range) i. e. not very different from N2O4. (TLV - TWA = Threshold limit value - time weighed average, weekly exposure, 8 hours per day).
Some green candidates present surprisingly low limits:
For HTP, TLV - TWA is 1 ppm (like NTO) and it is 25 ppm for ammonia.
However, the effective exposure risk is lower for HTP (whose vapour pressure is fairly low) than for NTO, boiling at 21°C. This is even worse in the case of ammonia.
On the other hand, light hydrocarbons and nitrous oxide are not toxic, they have only a narcotic effect at very high concentrations.

This toxicity risk can be mitigated in some cases by sub cooling; this is developed in the chapter “handling”.

The main rejection criterion is the carcinogenic risk.

The explosion hazard should be also analysed carefully especially if large propellant quantities are used. This is a special concern for monopropellants, but N2O and HAN / ADN seem quite safe from this point of view.

Handling:
Many propellants exhibit a large density variation versus temperature. This is especially true for N2O (relative density 1.2 near boiling point and 0.7 near 30°C). From the system point of view, it is very efficient to increase the propellant density.
This means that most light hydrocarbons and N2O should be cooled before tank filling for large quantities (boosters). The added advantage of cooling is the reduced vapour pressure (preferably below atmospheric pressure, except for N2O) resulting in low pressure operation for all ground equipment.
In addition, the cooling requirements are much more lax than for cryogenic liquids. A classical industrial refrigerator, like those used in deep freeze industry, is sufficient to cool the propellant, vapours can be easily recondensed.
The added advantage of cooling is the lowering of vapour pressure for toxic or very flammable products. This will reduce the risk of toxic fumes (e. g. N2O4) or explosion (air / light HC vapour mixture) in case of spillage.
All these points are taken into account for the trade-off.

4. SELECTION TRADE-OFF

Trade off rationale

The trade off were performed for each mission case, using weighing factors adapted the mission, e. g. for upper stages the Specific impulse is very important and the weighing factor is very high. It is lower for boosters while propellant density weighing factor is higher.

The table 4.1 provides the list of trade criteria and the weighing factors in case of APOLLO mission (CSM). The first two coefficients are related to pure performance (mean density and Isp) and total thirty points. A second set is related to mission and operational aspects (62 points). It shall be noted that some coefficients are set to zero for this particular mission (throttling, short term storage), while other get a very high level for this mission (long term storage and chill down). The last set deals with development aspects (risk and cost), 18 points are allotted.

The quotation marks are allotted on a 10 points span. The table 2.1 shows how specific impulse values are translated into marks.

The table 4.2 shows an example of trade off table for lunar manned mission (APOLLO like). On the pure performance point of view, LOX / LH2 is obviously the best combination, when operational aspects are taken into account, storable propellants present the best mark and especially N2O / propane (or other light HC). HTP has a negative rating due to the storage unknowns. The development aspects do not affect the results in this case.

Fig. 4.1 shows the trade off result in the case of boosters. The purely technical parameters (density and Isp) appear as yellow bars, while the overall performance appears in blue and the total rating including development and recurring cost bars are in red.
The LOX / CH4 and LOX / light HC provide a very good global technical solution, slightly better than LOX / LH2 (the high density plays an important role for boosters). However, the global note favours the storable solutions as they offer a very low development and recurring cost (provided existing engines could be used with small modifications).

Development cost is also a selection criterion!
It can be seen on this example that the cost issue can favour technical solutions with limited Isp, thanks to a very low development cost (reuse of existing engines and facilities).
Some combinations could be attractive from the technical view point but would be very costly to implement, especially for large liquid propulsion. Some "less green" combinations (retaining one toxic but non carcinogenic propellant) could be more financially accessible as they use slightly modified thrusters and tanks (The development of a brand new thruster is very costly in the case of large liquid propulsion).
Among non cryogenic oxidizers, N2O is a very interesting one (non toxic) but with a very high mixture ratio (the MR is also very high for HTP).
This cost argument is clearly not valid for lower thrust levels: since the absolute development cost is much lower; the spectrum of new green propellants is more widely opened.

<u>Other study cases:</u>
The launcher large upper stage with high ΔV capability favour LOX / LH2.
For some cases, automatic landing (VIKING like) or RCS, the new nitrate blends are the best choice but require more work on ignition techniques (catalyst is not the unique solution).
When all cases are merged, LOX / light HC appear as a good compromise for many missions.

This selection is based on theoretical values. Uncertainties on the real behaviour of new propellants shall be eliminated by testing. The phase one of the on-going ESTEC contract will end up by the establishment of technology experimentation plans. The tests could be performed in an optional second phase.

5. PROPOSED FUTURE WORKS

The encouraging data on specific impulse values of oxygen / light hydrocarbons need to be verified by tests (for two mixture ratios: optimum specific impulse and gas generator). In addition, these tests will enable to verify the ignition characteristics and combustion stability of the candidate propellants.
Some test facilities in Europe are compatible with the test objectives (simplicity of use and reduced thrust level, yielding moderate test costs). Separate facilities are required to test oxygen based and nitrogen oxides based combinations. ONERA (MASCOTTE and FAUGA) as well as DLR (M3) test benches are good candidates.
To test HAN or ADN thrusters in the 1 kN range, new facilities may be needed since existing ones are devoted to satellite thrusters tests (1 to 20 N).

6. SYNTHESIS and CONCLUSION

LARGE BOOSTERS
For VIKING class boosters, the trade off indicate that N2O4 / HC is the best combination.
If N2O4 is not accepted, LOX / LH2 and LOX / methane are the most obvious <u>industrial</u> choices.
In addition, light hydrocarbons like cyclopropane and propene could be even more interesting than methane.
Light hydrocarbons enable to conciliate high performance, regenerative cooling by fuel and high density.
Unsaturated light hydrocarbons surpass kerosene and even methane in Isp. In addition, they present a higher density than the saturated hydrocarbons with same carbon atoms number. Best performance is obtained with propyne and ethylene, but the stability in a large engine has to be verified.
Ethers (DME) present also a good density with a specific impulse higher than alcohol and equal to kerosene.

MEDIUM STAGES:
Present UH25 / MON stages can be converted to kerosene / N2O4 with a slight deficit in specific impulse and the added complication of separate hypergolic fuel for “automatic” ignition. N2O4 is still very toxic but the potentially carcinogenic fuel is deleted with minor modifications on engine, stage and ground facilities.
Otherwise, LOX/ light HC is an attractive solution but requires more work (and more expenses) on engine development.

LARGE UPPER STAGES
When volume is not a problem, LOX / LH2 is by far the best solution. If volume is constrained and if the required Delta V is not too high (lower than 2.5 km/s), the present practice is to use MMH / MON (high density and simplicity of use). LOX / light hydrocarbons could be a very efficient replacement.

SMALL UPPER STAGES
They use hydrazine (PEGASUS) or NTO / MMH / UDMH (VEGA).
New monopropellants (HAN, ADN) could be a very efficient substitute as well as N2O / hydrocarbons. N2O could be used also as a monopropellant for attitude control engines.

MANNED or UNMANNED PLANETARY MISSIONS
When LOX - LH2 is not used, LOX / light HC is the second best choice. LOX can be stored indefinitely with superinsulated tanks and existing cryorefrigerators. For small LOX quantities (lower than 1.5 ton) double wall insulation can be used with a moderate mass penalty.

The synthesis of the findings shows that three main propellants sets deserve further testing:

- LOX - light HC usable from small planetary missions to large boosters.
- Light HC or alcohols combined to NTO (half green) or N2O (fully green) as a low cost replacement of MMH / NTO.
- HAN or ADN based monopropellants. "High thrust" non catalytic thrusters could be a new way to explore.

The ongoing work will determine if it is possible to test only one set or test the three propellants sets in parallel.

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Table 2.1: Specific impulses and mixture ratios of studies propellant combinations

Chamber pressure = 1.03 MPa, ε = 40 (LOX and H_2O_2), ε = 100 (N_2O_4 and N_2O)

propellants	MR	Vac, Isp	quotation mark	
LOX/LH2	6	**460,0**	**0**	¬ **reference**
LOX/CH4	3,28	365,0	-5,4	
LOX / Kerosene	*2,62*	*354,0*	*-6,2*	
LOX / DME	1,72	350,0	-6,5	
LOX / Ethanol	1,81	342,0	-7,2	
LOX / ethylene	2,44	366,0	-5,3	
LOX / propane	2,86	360,0	-5,8	
LOX / propyne	2,05	**370,0**	**- 5**	¬ **n**
…/…				
H2O2/Kero	7,96	315,0	-9,2	
N2O4 / MMH	2,4	336,0	-7,6	
N2O4 / Kerosene	4,6	324,0	-8,5	
N2O4 / propane	5	328,0	-8,2	
N2O / propane	8,7	**305,0**	**- 10**	¬ **n-5 = -10**

Table 2.2: mission cases

Application	***Reference mission***	***Overall DV or total impulse***	***Number of ignition***	***Mission duration***
Boosters	Replacement of A5ECB solid boosters	3200 m/s	1	2 min
Upper stage	1) Trans-lunar / Trans-earth propulsion 2) Generic green upper stage	2200 m/s 3000 m/s	6 to 8 2	2 weeks 6 hours
Planet ascent / descent	Lunar descent/ascent module	4200 m/s	2 + throttling	2 weeks
Orbit transfer	LEO-GEO orbit transfer	4000 m/s	2	Not specified
RCS / OMS	RCS for a reusable TSTO launch vehicle	350 kN.s	> 100	2 weeks

Fig. 2.1 Small N2O / light HC upper stage design

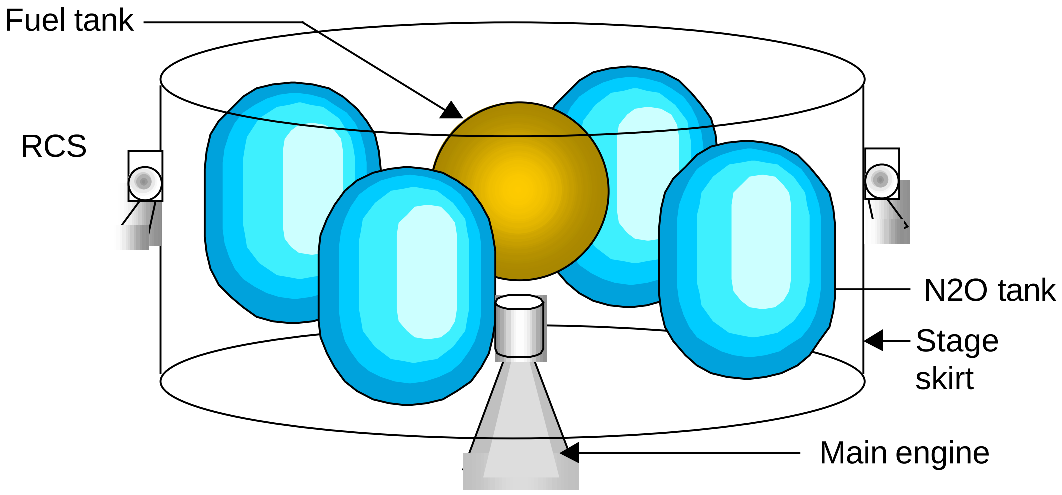

Fig. 2.2 LOX – HC engine with torch ignitor

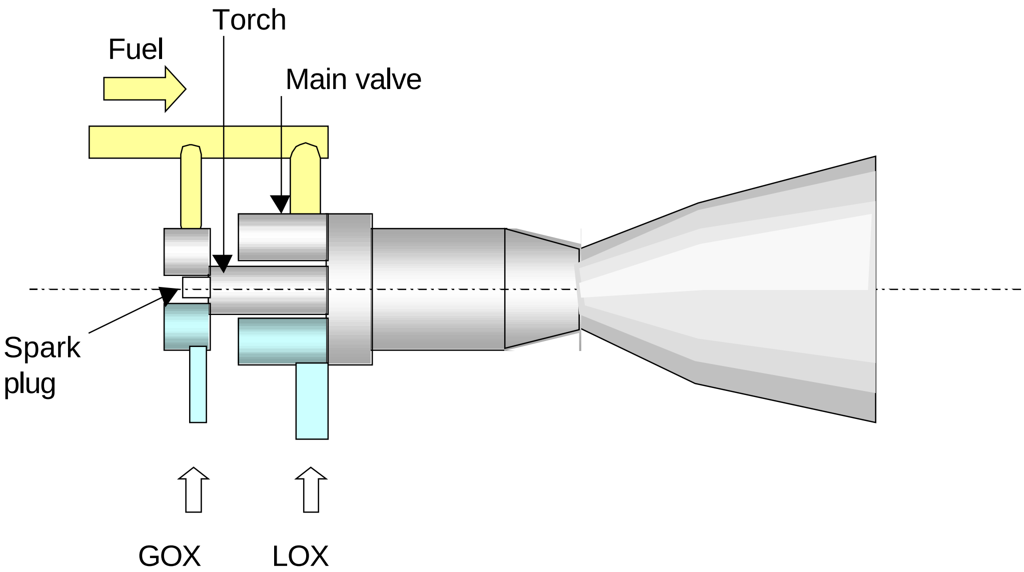

Table 4.1 Example of trade off coefficients for trans-lunar upper stage

mean density (oxidiser + fuel)	vacuum Isp	Launcher dimensioning assessment	Ignition and re-ignition	Combustion stability	Engine pollution (soot,...)	Throttling / pulsing capability	Cooling capability (Cp , T cr.,)	Short term storage	Long term storage	chilling down operations	Flammability and explosion risk	toxicity of propellants	toxicity of combustion / decomposition products	compatibility with materials	Procurement (easy, reliable)	Delivery (transport) storage (ground facilities)	Global technical assessment	Development risks (existing background)	Cost of test facilities (existing, adaptation or new)	Development cost	Recurring cost	Global assessment
5	**25**	**30**	**10**	**3**	**1**	**0**	**4**	**0**	**20**	**10**	**3**	**3**	**1**	**4**	**2**	**1**	**92**	**7**	**3**	**7**	**1**	**110**

Table 4.2 Example of trade off for trans-lunar upper stage (CSM)

Propellants	Performance	Global technical	Global
LOX / LH2	0	0	0
LOX / CH4	-60	46	47
LOX / Kerosene	-69,5	10,5	28.5
LOX / DME	-80	40	37
LOX / ethanol	-96	20	45
LOX / ethylene	-53,5	63,5	60.5
LOX / propane	-64,5	49	46
LOX / propene	-61,5	52	49
LOX / propyne	-43,5	47	44
LOX / cyclopropane	-52,5	59	56
LOX / isopropyl alcohol	-88,5	20.5	24.5
H2O2 (90%) / Kero	-135	-359	-351
H2O2 (90%) / ethanol	-152	-333	-318
N2O4 / UDMH	-104	-141	-93.5
N2O4 / MMH	-99	-136	-89
N2O4 / Kerosene	-119	80	120
N2O4 / propane	-115	118	138
N2O / propane	-162	83.5	103.5
N2O4 / ethanol	-139	96.5	14.5

Fig. 4.1 Example of trade of result for boosters