

Performance Evaluation and Experimental Studies on Metallised Gel Propellants

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ABSTRACT

Metallised gel propellants offer higher specific impulse and volumetric loading, reduced vaporisation loss, spillage and slosh problems and easy storage in comparison to the conventional liquid propellants. Theoretical performance analysis of gel propellant containing *Al* in unsymmetrical dimethyl hydrazine-dinitrogen tetroxide (UDMH- N_2O_4) system shows peak Isp (vacuum condition) of 316.7 s and 318.3 s at oxidiser/fuel (O/F) ratios of 1.5 and 1.0, respectively for 30 per cent and 40 per cent UDMH-*Al* gel propellants, under standard conditions. The effect of other parameters like area ratio and chamber pressure on performance has been brought out in view of mission oriented applications. Aluminium has been found to be a better choice over magnesium in metallised gel propellants. Experimental studies on UDMH gellation using propellant grade (15 μm) and pyrotechnic grade (1.5 μm) *Al* in 500 g batch level show that gellant (methyl cellulose) concentration could be reduced by 50 per cent using pyrotechnic grade *Al*. The pseudoplastic-thixotropic behaviour, flow rate through die holes, burst pressure tests and bulk density are studied. UDMH - 25 to 30 per cent *Al* gels with both grades of *Al* are found to be stable, pseudoplastic (shear thinning) and thixotropic (time-dependent shear thinning), but their flow pattern through die holes differ in nature.

1. INTRODUCTION

The important axiomatic fact of the propulsion system is always a demand for high performance. As one moves from solids to storable liquids and then to cryogenic propellants, the performance increases but the storage and handling requirements and safety imposes high restrictions. Metallised gel propellants belong to a new class of storable liquid propellants^{1,2} and offer higher specific impulse (Isp) and volumetric loading, reduced vaporisation loss, spillage and slosh problems and easy storage, in comparison to the conventional liquid propellants³. They are emerging as a choice candidate for future liquid engines. The metallic

fuel *Al* has been found to be a better choice over *Mg*, based on its higher performance, easy availability and low cost.

The first part of this paper presents the results of detailed thermochemical analysis using Gordon and McBride computer program^{4,5} for the calculation of complex chemical equilibrium compositions with free-energy minimisation considerations. NASA-SP-273 program using equilibrium flow conditions is used for computations. These results are used to find the impact of payload on operational launch vehicles. The experimental part details the

development and characterisation of metallised unsymmetrical dimethyl hydrazine (UDMH) gel propellant using propellant grade (15 μm) *Al* and pyrotechnic grade (1.5 μm) *Al*.

2. MATERIALS & METHODS

UDMH	Unsymmetrical dimethyl hydrazine. Purity: minimum, 98.5 per cent; moisture content: maximum, 0.3 per cent. (Source- Andhra Sugars (P) Ltd., Tanuku, A.P).
N_2O_4	Dinitrogen tetroxide. Purity: minimum, 99.9 per cent; <i>Fe</i> content: maximum 2 ppm; moisture content: maximum, 0.17 per cent. (Source: Hindustan Organic Chemicals, Bombay).
Agar-Agar	Sea weed carbohydrate (powder form) having the structure of alternating copolymer 3-linked beta-D-galacto pyranose and 4-linked 3,6, anhydro-alpha-L-galacto pyranose units. (Source: CDH (P) Ltd., Bombay).
Cab-o-sil (M5)	Trade name of fused silica containing 99 per cent SiO_2 , 1 per cent volatile matter and with particle size of 8 μm . (Source: Cabot Corp., USA).
MC	Methyl cellulose. Viscosity of 2 per cent aqueous solution at 20 °C is 4000 cps. (Source: SISCO Chemical Industries, Bombay).
EC	Ethyl cellulose with degree of substitution 2.42 to 2.50. (Source: CDH (P) Ltd., Delhi).
HMC	Hydroxy methyl cellulose. (Source: CDH (P) Ltd., Delhi).
CMC	Carboxy methyl cellulose (sodium salt), assay 99 per cent with degree of substitution 0.7 to 0.8. (Source: CDH (P) Ltd., Delhi).
OPC Complex	Organophilic clay complex (smectone clay) passing through 200 specific BSS 95 per cent, specific gravity 1.7. (Source: David & Co (P) Ltd., Gujarat).

Silicone oil Metroark DM Silicone fluid of viscosity 1000 centistocks (Source: Metroark (P) Ltd., Calcutta).

The heat of formation used for the equilibrium flow condition is +12.7 kcal/mole for UDMH ($C_2H_8N_2$), - 4.676 kcal/mole for N_2O_4 and zero for *Al*. NASA-SP-273 program using equilibrium flow conditions is used for theoretical computations.

3. PERFORMANCE EVALUATION

The actual performance of gel propellant can only be evaluated by static test firing in a liquid engine using small thrusters. However, thermochemical analysis would give a clear picture on the energetics of the gel propellant. A typical UDMH-*Al* gel propellant with N_2O_4 is analysed under equilibrium conditions.

The effect of *Al* loading (0-40 %) and oxidiser/fuel (O/F) ratio (0.5 - 4.0) on (Isp) of UDMH-*Al* gel with N_2O_4 under standard conditions [$P_c/P_e = 70$, area ratio (AR) = 10] is shown in Fig. 1. When *Al* is introduced in UDMH fuel, the maximum performance in Isp is 318.3 s with 40 per cent *Al* and 316.6 s with 30 per cent *Al* at O/F ratio of 1.0 and 1.5, respectively as against 263.0 and 287.4 s for virgin UDMH- N_2O_4 system. Figure 2 shows that increase in AR from 10 to 500 increases Isp with a marginal shift in O/F ratio. The AR for stage motors differ with altitude for a particular mission. For example, the AR of liquid engine for PSLV second stage and GSLV cryo stage are 30 and 200, respectively. The effect of chamber pressure on Isp shown in Fig. 3 is found to be only marginal over 10 to 60 ksc beyond which the Isp gain is negligible.

The combined effect of enhanced Isp and improved density of the gel propellant can boost the payload capability of launch vehicles. Data analysis has shown that for an operational launch vehicle like PSLV which has earth storable liquid propellant in the second stage of 37.5 tonnes,

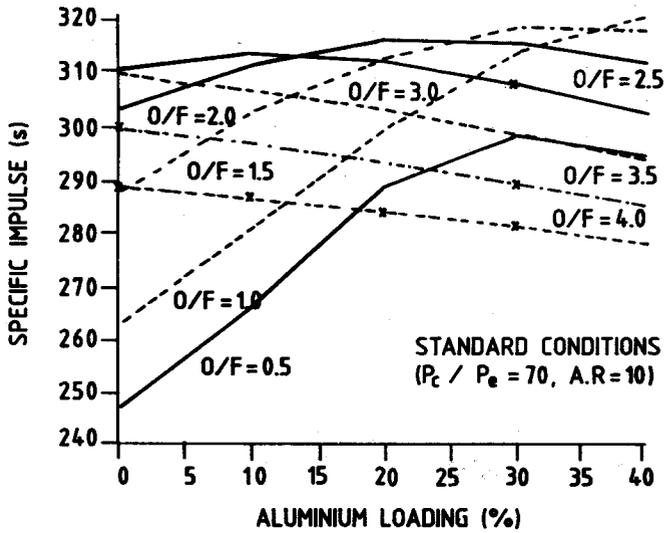


Figure 1. Effect of O/F ratio and Al loading on the performance of UDMH-N₂O₄ propellant.

substituted with UDMH-Al gel propellant, the payload gain is 20 per cent (260 kg).

4. GELATION EXPERIMENTS

Gelation experiments⁶ were conducted at 15-20 °C in a sealed reaction kettle fitted with high speed emulsifier. UDMH was charged to the kettle and then cooled to 15-20 °C in a water bath using immersion cooler. Methyl cellulose (MC) gellant was added pinch by pinch under mechanical agitation. This was followed by the addition of surfactant (silicone oil) and stepwise addition of Al powder. The system was kept undisturbed and gelation was found to occur within 30-60 min for propellant grade (15 µm) Al and 15-30 min for pyrotechnic grade (1.5 µm) Al. Nitrogen gas was purged in the initial and final phase of gelation to avoid air oxidation. The gelation experiments were conducted in 500 g batch level.

Table 1. Characteristics of aluminium powder

Properties	Propellant grade	Pyrotechnic grade
Purity (%)	99.30	95.00
Volatile matter (%)	0.05	0.25
Coating agent (%)	0.00	1.00
Particle size (µm)	15.00	1.50
Specific surface area (m ² /g)	0.10-0.20	2-3

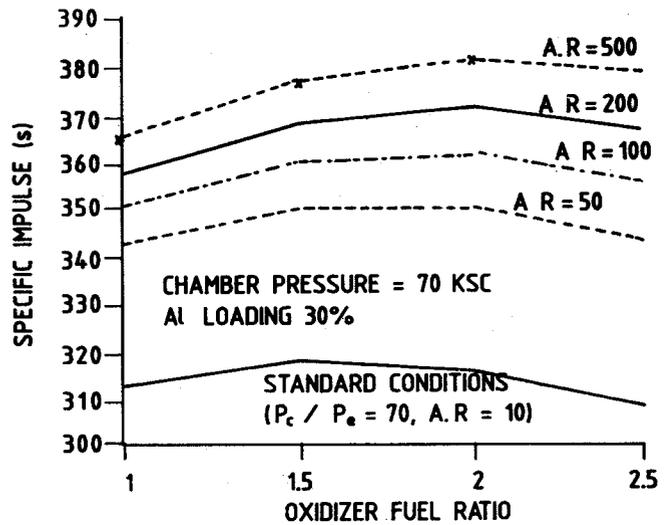


Figure 2. Effect of area ratio and O/F ratio on Isp of UDMH-30% Al-N₂O₄ propellant.

Propellant grade (15 µm) Al and pyrotechnic grade (1.5 µm) Al were used and the properties of both grades are given in Table 1.

The pseudoplastic and thixotropic behaviour of the gels was studied using Brookfield viscometer at different rpm and time intervals. The flow rate of the gel was measured using 500 ml pressure vessel and die holes of 0.45 to 2 mm under nitrogen pressure of 1 to 3 kg f/cm². Burst pressure tests were also carried out using different diaphragm materials like mylar film, kapton film, copper foil,

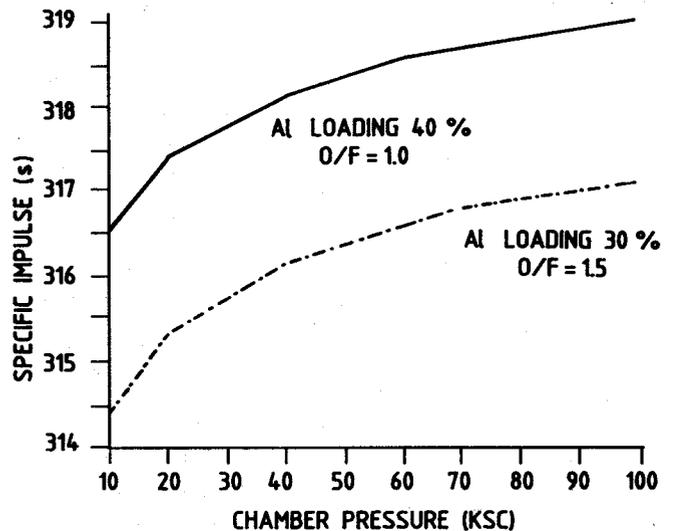


Figure 3. Effect of chamber pressure on Isp of metallised UDMH-N₂O₄ propellant.

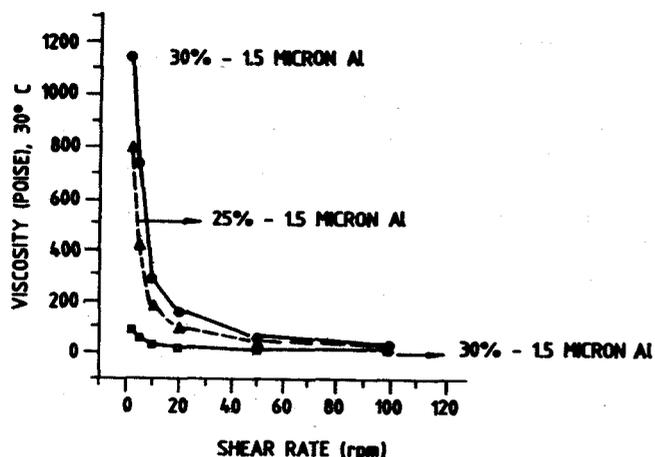


Figure 4. Effect of rpm on viscosity of UDMH-Al gel

etc., as a step for controlling the flow during testing of liquid engine.

5. RESULTS & DISCUSSION

Among the hydrocolloid (Agar-agar, ethyl cellulose, carboxymethyl cellulose (CMC), hydroxymethyl cellulose (HMC)) and particulate (cab-o-sil, organophilic clay complex) gellants, MC was found to be the most suitable gellant for UDMH gelation. The influence of the above gellants on UDMH gelation was detailed earlier⁶. Small concentration of silicone oil was found to improve the flow characteristics of UDMH-Al gel. The composition details are given in Table 2. The gellant concentration could be reduced by the use of pyrotechnic grade Al (1.5 μm) which has larger surface area compared to propellant grade Al (15 μm).

5.1 Pseudoplastic Behaviour

The pseudoplastic behaviour of UDMH-Al gel is shown in Fig. 4. The drastic reduction in viscosity with increase in rpm (\propto shear rate) is indicative of pseudoplasticity. This is more pronounced in the gel with pyrotechnic grade Al than the one with propellant grade Al. However, the viscosity values are higher with pyrotechnic grade Al and hence, proper consistency and stability of the gel was achieved with 25 per cent metal loading.

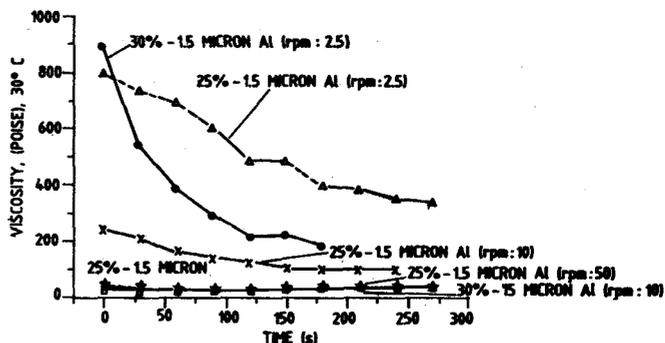


Figure 5. Time dependency and rpm on viscosity of UDMH-Al gel.

5.2 Thixotropic Behaviour

The time dependency on viscosity of UDMH-Al gel is shown in Fig. 5. Here also the reduction in viscosity is more distinct with the gel containing pyrotechnic grade Al. The changes in viscosity with time is more at lower rpm than at higher rpm.

These results show that UDMH-Al gel with pyrotechnic grade Al is more pseudoplastic and thixotropic than the one with propellant grade Al.

5.3 Gel Flow Rate

The flow rate data of UDMH-Al gel is shown in Table 3. Die hole diameters of 0.45 to 2 mm were used at applied pressure range 0.5-2.0 kg f/cm². Though the gel with pyrotechnic grade Al was expected to give higher flow rate due to smaller particle size, flow rate was found to be very poor. While the gel with propellant grade Al flows through 0.75 mm die hole at 2 kg f/cm², the gel with pyrotechnic grade Al shows a slower rate even through 2 mm die hole at the same pressure. This could be attributed to the flat nature of the particles of pyrotechnic grade Al even though that have low

Table 2. Compositions of UDMH-Al gel

Composition	UDMH-Al gel		
	With propellant grade Al	With pyrotechnic grade Al	
		1	2
UDMH (%)	67.2	68.2	73.0
MC (%)	2.1	0.7	1.0
Silicone oil (%)	0.7	1.0	1.0
Al powder (%)	30.0	30.0	25.0

Table 3. Flow rate of UDMH-*Al* gel

Applied pressure (kg f/cm ²)	Die hole (mm)	Number of holes	Flow rate (g/min)	
			30 % (propellant grade) 15 μ m <i>Al</i>	25 % (pyrotechnic grade) 1.5 μ m <i>Al</i>
0.5-3.0	0.45	1	0	0
0.5-1.0	0.75	1	0	0
2.0	0.75	1	27	0
0.5	1.0	3	72	0
1.0	1.0	3	224	0
1.0	2.0	3	720	0
2.0	2.0	3	-	140

average particle size (expressed as that of the equivalent sphere), compared to propellant grade *Al*. Hence UDMH gel with propellant grade *Al* is superior to the one with pyrotechnic grade *Al* wrt flow characteristics.

5.4 Burst Pressure Tests

Diaphragm burst pressure tests were carried out to find a suitable diaphragm material for use in the flow path. The results are shown in Table 4. Even though the burst pressure for copper foil is 3 kg f/cm², copper was getting tarnished with UDMH gel. Kapton and mylar films do not burst even at 6 kg f/cm². Kapton film with a larger opening diameter of 24 mm bursts at 5.5 kg f/cm², and hence, may be a suitable diaphragm material.

5.5 Bulk Density

The experimental value of density of UDMH-30 per cent *Al* gel system is 1.074 g/cc

Table 4. Burst pressure test with UDMH-*Al*-gel

Diaphragm material	Thickness (mm)	Hole opening (mm)	Results
Mylar film	0.04	12	No bursting up to 6 kg f/cm ²
<i>Al</i> sheet sandwiched with polythene	0.09	12	Bursting at 6 kg f/cm ²
Copper foil	0.04	12	Bursting at 3 kg f/cm ²
Kapton film	0.06	12	No bursting up to 6 kg f/cm ²
Kapton film	0.06	24	Bursting at 5.5 kg f/cm ²

which is higher by 37 per cent over UDMH fuel. For the same tankage volume of UDMH-*N*₂*O*₄, this higher bulk density of metallised system enhances the propellant loading by 20 per cent and density impulse by 17 per cent.

6. CONCLUSIONS

Performance evaluation of metallised UDMH-*Al* gel propellant with *N*₂*O*₄ showed peak Isp values of 318.3 and 316.7 for 40 per cent and 30 per cent *Al* at O/F ratio of 1 and 1.5, respectively. Specific impulse increased with increase in AR. For peak performance, O/F ratio shifted from 1.5 to 2 and 1 to 1.5 for 30 per cent and 40 per cent *Al*, respectively, when the AR was increased from 10 to 500. Marginal Isp gain was seen when the chamber pressure was increased from 10 to 60 kg f/cm² beyond which the Isp gain was negligible.

Metallised UDMH gel propellants containing 25-30 per cent propellant grade and pyrotechnic grade *Al* were prepared in 500 g level. Gellant concentration could be reduced when pyrotechnic grade *Al* was used. Both systems were found to be pseudoplastic and thixotropic. However, the gel flow characteristics were superior with propellant grade *Al*. Actual firing of UDMH-*Al* gel propellant with *N*₂*O*₄ is planned with suitable modification of solenoid valve, injector design and nozzle.

REFERENCES

- Palaszewki, B.A. Upper stages using liquid propulsion and metallised propellants. National Aeronautics & Space Administration, USA, 1992. NASA-TP-3191.

2. Munjal, N.L. *Prop. Explos. Pyrotech.*, 1985, **10**, 111-17.
3. Green, J.M. Flow visualisation of rocket injector spray using gelled propellant simulants. American Institute of Aeronautics & Astronautics. AIAA-91-2198.
4. Gordon, S. & McBride, B.J. Computer program for complex chemical equilibrium composition rocket performance and applications., National Aeronautics & Space Administration, USA, 1976. NASA-SP-273.
5. Glassman, I. & Sawyer, R.F. The performance of chemical propellants. Technivision Services Slough, England, January 1969.
6. Varghese, T.L.; Gaidhar, S.C.; John, David.; Josekutty, Jose.; Muthiah, Rm.; Rao, S.S.; Ninan, K.N. & Krishnamurthy, V.N. Developmental studies on metallised UDMH and kerosene gels. *Def. Sci. J.*, 1995, **45** (1), 25-30.

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