

# Bi-Phase Chemical Propellant

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**Abstract** - Any composition of propellant showing similar performance characteristics in its solid and liquid phase can be called a Bi-Phase Chemical Propellant. These propellants can operate in the liquid state as well as the solid state with minor loss in performance. They are actualized by altering the phase (either by freezing or with additives that increase the melting point or both) of conventional liquid propellants and making them usable in their solid form. Considering materials that require cooling to remain in the solid state, Bi-Phase propellants offer virtually unlimited choice of propellant constituents that can be selected depending on the characteristics ( $I_{sp}$ ,  $C^*$ ) required[1]. The main idea behind Bi-Phase propellant is to find a propellant composition that can be used in all the different stages of a rocket. In current scenario conventional liquid cryogenic propellants cannot be eliminated due to lack of other practical compositions offering such high performance. Bi-Phase propellants are aimed to replace the comparatively low performing composite solid propellants that are used in the initial stages of a rocket, thus increasing the overall performance of a system and reducing complexity by using single composition in all the different stages. Facilities that manufacture and handle cryogenic liquids can also handle Bi-Phase propellants. Use of frozen liquid fuels and oxidizers enables a substantial increase of performance as compared to conventional solid propellants, but can make use of their simple process conditions.

**Key Words:** Bi Phase Propellant, Cryogenic propellant, Rocket Propulsion.

## 1. INTRODUCTION

Rockets are the only devices capable of taking man and objects to space and they get their power from the chemical propellants that burn and produce thrust. Mainly there are three varieties of chemical propellants - Solid propellants, Liquid propellants and Hybrid propellants. Solid propellants are used in large and small motors in a wide variety of applications. Their simplicity warrants a high degree of reliability and the cost of development of large solid motors is much lower than with their liquid counterparts. However, neglecting minor variations, they all have in common that specific impulses are low compared with cryogenic liquid propellants and production requires tedious operations such as casting, mixing and curing. Liquid propellants are high performing but they are associated with complex operating conditions. Solid propellants are currently used in booster and lower stages where huge thrust is required but they are not ideal for upper stages, similarly liquid propellants are great for upper stages as they provide more control but they aren't ideal for lower stages owing to their comparatively lower density. Bi-Phase propellants are conceptualized to tackle this very problem of finding a propellant that is versatile enough to be used in all rocket stages without significantly compromising on performance.

Bi-Phase chemical propellant is a new concept in which, conventional high performing liquid propellants are converted to their solid state (by freezing) and used like a solid propellant grain with Phase loss less than 5%. Phase loss of a Bi-Phase propellant is the loss of  $I_{sp}$  of propellant in solid state compared to propellant in liquid state due to the extra energy required to go from solid to liquid state.

$$\% \text{ Phase loss} = (I_{sp}(\text{liquid}) - I_{sp}(\text{solid})) * 100 / I_{sp}(\text{liquid})$$

As the name indicates Bi-Phase propellant can be used in two physical phases i.e. liquid and solid. The liquid phase of the propellant is simply a conventional liquid propellant composition. While the solid part is the frozen phase of that specific propellant composition. The Solid Bi-Phase propellant can be used in two ways :

**1.1 Mono BPP** - In this type the fuel and oxidizer are premixed in their liquid or gaseous state and the frozen to get a single propellant grain. Mono BPPs resemble the burning behaviour of classical solid propellants. Mono-BPPs show stable burning behavior with a constant regression rate which obeys the exponential Law of Vieille under varying pressure conditions. Above the surface they form a thin liquid layer that has constant thickness under isobaric conditions and decreases with pressure. The use of premixed mono-BPPs is limited to compatible compounds. The ignition requires more energy due to the low initial temperature and the two phase transitions compared to conventional solid propellants. The modeling of the burning behavior corresponds to classical modeling of transient burning monopropellants and homogeneous propellants like double base or nitramine propellants. It includes the heating and phase transitions energies within the condensed phase without a surface reaction.

**1.2** In the second method the oxidizer and fuel are arranged as separate grains. This results in highly safe propellant configurations and allows to influence the burning behavior by grain geometry within a broad range. In this method two types are distinguished as: externally sustained systems (e.g. by heat from an external gas generator) and self-sustained systems.

One of the initial difficulties that comes to mind against such a concept or similar ones is the danger of combustion instability and detonation. Many quasi-homogeneous mixtures of cryogenic solid fuels and oxidizers might be very well behaved, but this is a concern for the majority of propellant combinations. This can be solved by transforming deflagration into boundary layer combustion by dissecting the grain into a number of homogeneous subunits.

Using BPP in the solid phase in place of conventional solid propellants gives substantially increased performance and at the same time retains the easy operating process of solid grains. Most of the current rockets use Composite solid propellants in the booster stage and cryogenic or semi-cryogenic liquid propellants in their main and upper stages. One of the most lucrative advantage of BPPs (apart from the increased performance) is that a whole rocket with its different stages can use a single propellant composition in solid and liquid phase. This reduces the complexity of rocket manufacturing and operating because the issues associated with acquiring/manufacturing, storage and handling and operating of more than one propellant composition is eliminated.

The phase conversion from liquid to solid state comes with slightly decreased performance due to the enthalpy of fusion and sensible heat required to comeback to the liquid state during combustion. However, thermodynamic calculations confirm that the reduction of the chamber temperature corresponding to this has only a minor influence on the  $C^*$  and Isp of the solid phase compared to the liquid phase (less than 5%). Therefore the Bi-Phase propellants in solid state retain the high performance characteristics of liquids.

Use of frozen liquid fuels and oxidizers enables a substantial increase of performance as compared to conventional solid propellants, but can make use of their simple process conditions. Two stage rockets that currently use solid propellant in the first stage and cryogenic liquids in upper stages can use a single Bi-Phase composition in its solid and liquid phase for the first and second stage respectively. This eliminates issues associated with acquiring/manufacturing, storage and handling of more than one propellant composition. The use of higher performing solid state Bi-Phase propellant in the initial stages of the rocket (in place of the currently used Composite solid propellants) comes with increased performance and can prove to be more financially sustainable than the current system. Using solid BPP composition of SH<sub>2</sub>-SO<sub>2</sub> with Isp close to 400 in the S-200 booster stage of the GSLV-Mk3 will require nearly 50% less propellant to achieve the required thrust.

## 2. LITERATURE SURVEY

There are no previous papers explicitly devoted to the study of Bi-Phase Chemical Propellant. The topic that most relates with this study is Cryogenic Solid Propellants and the idea of using frozen liquids as propellants was addressed by R.E.Lo in a paper[1] dating back to 1998. In a subsequent paper[2] R.E.Lo suggested transforming deflagration of CSP grain into boundary layer combustion by dissecting the grain into a number of homogenous subunits. In the case of dissected solid propellant grains the source is a melting and/or evaporating solid oxidizer located inside the same combustion chamber.

Experiments and modelling to study the burning behaviour of frozen liquid propellants (CSP) was done by V. Weiser and coworkers[3] by using model substances methanol/H<sub>2</sub>O<sub>2</sub> and nitromethane/H<sub>2</sub>O<sub>2</sub>. The test configurations were modular combustion as Rod-In-Matrix under pressure and atmospheric and pressurized a disc stack burner. Their results showed that combustion of cryogenic solid propellants behaves similar to that of solid rocket propellants and various combinations of mono-CSPs and modular CSPs show burning rates described by Vieille's law.

Further experiments were performed by V.Weiser et al and the burning behaviour of some other CSP combinations were investigated[4]. For the first time a propellant strand of polymer rods embedded in solid oxygen was prepared and burnt. The experiments with CSPs end in the combustion of a small rocket motor showing no serious technical obstacles.

## 3. MOTIVATION AND OBJECTIVE

The primary motivation of this study is to find a versatile propellant that can be used in different stages of rocket operation without significant loss in performance. (in boosters, upper stages, etc).

Objective of this study is to calculate theoretical performance characteristics of SH<sub>2</sub>-SOX propellant (a prospective Bi-Phase propellant) and compare it with presently used propellant combinations.

## 4. METHODOLOGY

Ideally the chemical reaction of H<sub>2</sub>-O<sub>2</sub> gives completely oxidized H<sub>2</sub>O as the product but at high temperatures, the completely oxidized products of combustion like H<sub>2</sub>O dissociate into OH, H and O. The dissociation is favored at lower pressures as there is less resistance to the breaking up from the neighboring molecules. Therefore the global reaction is written as

$$H_2 + a_1 O_2 = b_1 H_2O + b_2 H_2 + b_3 OH + b_4 H + b_5 O$$

The atom balance equations for this reaction are

$$2 = 2b_1 + 2b_2 + b_3 + b_4 \quad \& \quad 2a_1 = b_1 + b_3 + b_5$$

In terms of partial pressures these equations are written as

$$2P/n = 2PH_2O + 2PH_2 + POH + PH \quad \& \quad 2a_1P/n = PH_2O + POH + PH$$

$$b_i = P_i \cdot n / P$$

Where P is the total chamber pressure.

Equilibrium equations

Completely oxidized H<sub>2</sub>O in the product gets dissociated to H and OH at high temperatures,  $H_2O = H + OH$

$$[PH_2O] = [PH] \cdot [POH] / K_1$$

OH further dissociates into O and H,  $OH = O + H$

$$[POH] = [PO] \cdot [PH] / K_2$$

H<sub>2</sub> in the product dissociates to 2 H,  $H_2 = 2H$

$$[PH_2] = [PH]^2 / K_3$$

Where K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub> are the equilibrium constant for the specific reactions whose values varies with temperature.

Solving equilibrium equations with the atom balance equations gives the partial pressures of the product gases, which are used to calculate the number of moles of products.

Energy balance equation

$$[b_1 \Delta H_{foH_2O} + b_2 \Delta H_{foH_2} + b_3 \Delta H_{foOH} + b_4 \Delta H_{foH} + b_5 \Delta H_{foO}] - [\Delta H_{foH_2} + a_1 \Delta H_{foO_2}] +$$

$$[HH_2 + a_1 HO_2](T_i - 298) + [b_1 HH_2O + b_2 HH_2 + b_3 HOH + b_4 HH + b_5 HO](T_f - 298) = 0$$

Here T<sub>f</sub> is the assumed temperature of the combustion products and T<sub>i</sub> is the temperature of the reactants. H denotes the enthalpy which includes the sensible heat (C<sub>p</sub>T) and the latent heat where applicable. ΔH<sub>fo</sub> is the standard heat of formation. If the assumed value of temperature T<sub>f</sub> is not correct, the above equation will not be satisfied. A new value of temperature is assumed, equilibrium constants at the new temperature calculated, the moles b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub> and b<sub>4</sub> determined and the enthalpy balance checked. The procedure is repeated till two successive iterations give values of temperature within a prescribed accuracy.

An iterative procedure is used to calculate the chamber temperature and the composition (b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub>, b<sub>4</sub>, b<sub>5</sub>) of product gases. Algorithm of the procedure is given below

Step 1 - Assume Temperature of combustion products T<sub>b</sub>

Step 2 - Assume total moles in products n based on completely oxidized products

Step 3 - Solve the atom balance equations and equilibrium equations for b<sub>i</sub>

Step 4 - If  $\sum b_i = n$  proceed to the next step, otherwise repeat steps 2 & 3 until  $\sum b_i = n$

Step 5 - Calculate T<sub>b</sub>' from energy balance equation

Step 6 - If T<sub>b</sub>' = T<sub>b</sub> Stop, otherwise repeat steps 1 to 5 until T<sub>b</sub>' = T<sub>b</sub>.

Next, the C\* and Isp is calculated using the formula

$$C^* = ((R_0/m) \cdot T_c)^{1/2} / \Gamma$$

m is the molar mass of the products it is given by,  $m = \sum b_i \cdot m_i / n$

Γ is a function of specific heat ratio γ

$$I_{sp} = (C^*) \cdot (CF)$$

CF is the Thrust Coefficient of the nozzle

Frozen equilibrium condition is assumed to prevail in this whole process and therefore the results obtained will be lower than the results expected from practical tests.

All the calculations are done by a computer program written specifically for this purpose using Python programming language.

## 5. RESULTS

As expected the Bi-Phase propellant composition H2-O2 gives lower performance in its solid state as compared to its performance in liquid state. The difference of performance between liquid phase propellant and solid phase propellant is called Phase Loss.

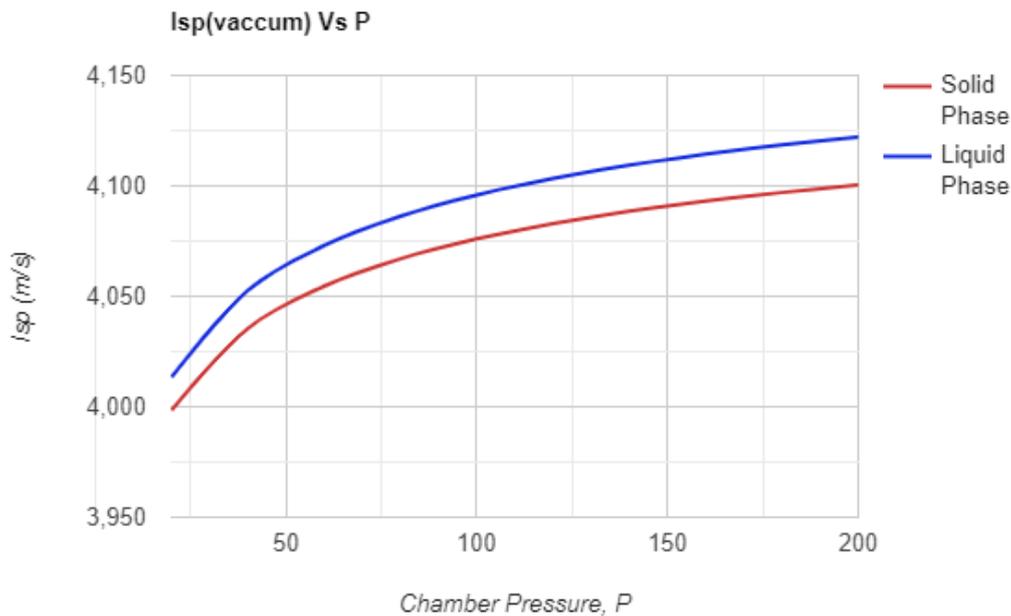
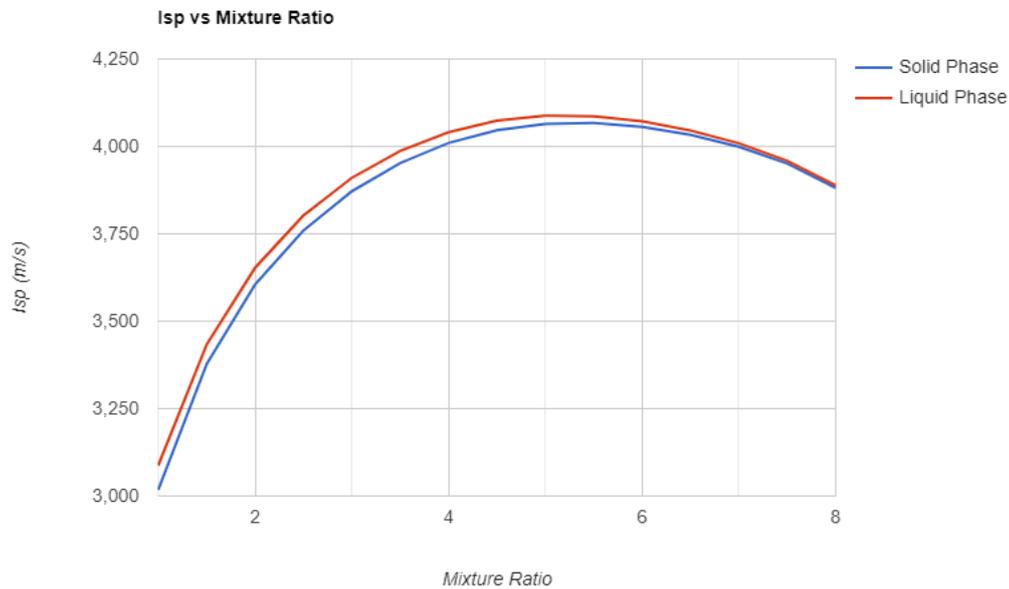
At Chamber Pressure  $P = 80$  bar and Supersonic Area Ratio  $AR = 40$ . The  $C^*$  value for LH2-LOX composition ranges from 1949.48 m/s at mixture ratio = 1 to 2238.88 m/s at  $MR = 3.5$ ,  $I_{sp}(\text{vacuum})$  ranges from 314.77 s at  $MR = 1$  to 416.69 s at  $MR = 5.5$ . For SH2-SOX composition,  $C^*$  ranges from 1909.56 m/s at  $MR=1$  to 2221.89 m/s at  $MR=3.5$ ,  $I_{sp}(\text{vacuum})$  ranges from 307.64 s at  $MR=1$  to 414.57 s at  $MR=5.5$ .

The results obtained for different values of mixture ratio for  $P = 80$  bar and  $AR=40$  are listed in the table below

MR	Liquid H2-O2				Solid H2-O2			
	TC (K)	$C^*(\text{m/s})$	$I_{sp}(\text{vacuum})(\text{s})$	$I_{sp}(\text{sl})(\text{s})$	TC(K)	$C^*(\text{m/s})$	$I_{sp}(\text{vacuum})(\text{s})$	$I_{sp}(\text{sl})(\text{s})$
1	848.05	1949.48	3087.9	2530.37	815	1909.56	3018	2455.79
1.5	1213	2106.07	3434.29	3027.47	1179.8	2075.74	3378	2965.99
2	1540.55	2183.36	3652.97	3359.8	1507	2158.38	3604.73	3307.26
2.5	1837.35	2221.19	3802.63	3590.34	1803.45	2199.73	3759.89	3544.53
3	2107.85	2236.99	3910.06	3754.84	2073.65	2218	3871.42	3714.08
3.5	2354.05	2238.88	3987.50	3872.46	2319.9	2221.89	3952	3836.23
4	2576.35	2231.17	4040.98	3954.15	2542.795	2212.93	4009.85	3922.318
4.5	2774.27	2216.36	4073.55	4006.44	2741.95	2202.7	4046.36	3979.06
5	2947.45	2196.20	4087.74	4034.44	2916.98	2183.99	4064.6	4011.497
5.5	3095.9	2172.08	4086.25	4042.74	3067.67	2161.13	4066.99	4023.97
6	3219.6	2144.97	4071.64	4035.19	3193.84	2135.12	4055.99	4020.19
6.5	3318.25	2115.50	4045.77	4014.48	3294.98	2106.57	4033.27	4002.77
7	3390.6	2083.86	4008.96	3981.40	3369.65	2075.65	3999.13	3972.45
7.5	3433.45	2049.59	3958.94	3933.83	3414.29	2041.89	3951.12	3926.95
8	3439.13	2011.13	3888.62	3864.46	3420.46	2003.62	3881.58	3858.39

For a fixed mixture ratio and area ratio,  $MR = 5.5$ ,  $AR = 40$ , with increasing chamber pressure  $I_{sp}$  increases for the propellant in both of its phases. It is seen that the %Phase Loss in Solid Phase increases with increasing pressure.

After correcting for the lower performance given by Frozen equilibrium analysis, the the results obtained for LH2-LOX composition through this program are in sync with the results given by the NASA CEA software at any given set of boundary conditions.



## 6. CONCLUSIONS

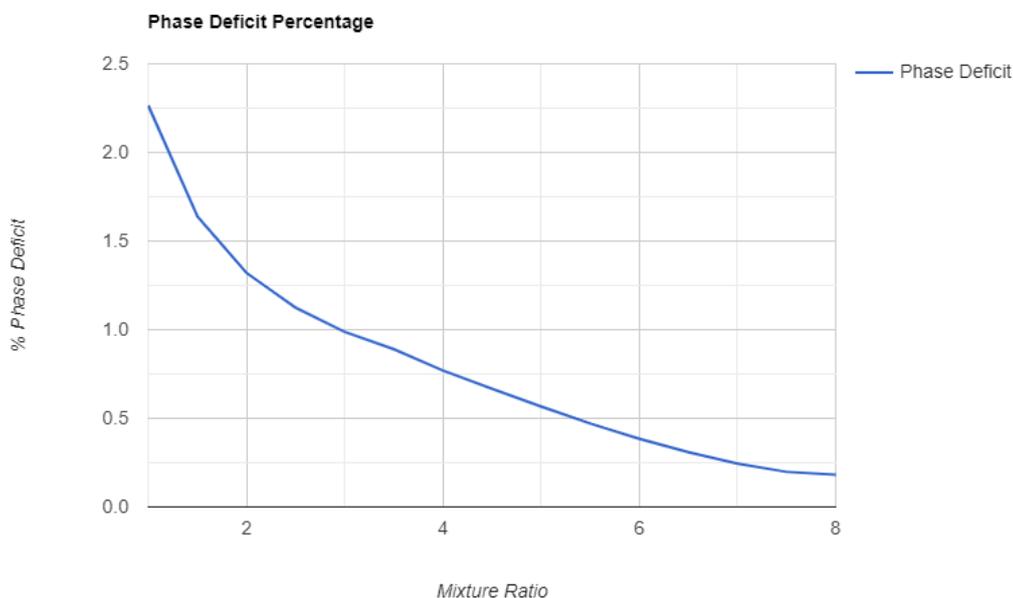
The results show that H<sub>2</sub>-O<sub>2</sub> propellant composition can be used in solid rocket boosters (with some extra effort to make and keep it in solid form), LH<sub>2</sub>-LOX is already widely used in upper stages. This study also suggests that other high performing liquid propellants can also be used in their solid phase with minor Phase Loss, that is they too can be Bi-Phase Propellants. It also suggests that some high performing compositions which cannot be used in their liquid phase due to instabilities might be usable when converted to their solid phase.

The major drawback in using Solid H<sub>2</sub>-O<sub>2</sub> propellant instead of current composite solid propellants is the low density of solid H<sub>2</sub> & solid O<sub>2</sub>, but there might be some high energy liquid propellants which have higher densities and these compositions can be very useful.

An interesting result is the very low Phase Loss, this low Phase Loss enables the use of SH2-SOX with very minor loss in performance compared to LH2-LOX.

It should also be noted that % Phase Loss is highest when MR = 1 and as MR increases % Phase Loss decreases. The energy released during reaction increases rapidly with increasing MR while the energy required by the reactants (to reach their standard state from initial state) increase at a lower rate with increasing MR, these two phenomenon when compounded explain the trend of decreasing % Phase Loss with increasing MR.

MR	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8
% Phase Loss	2.26	1.64	1.32	1.12	0.99	0.89	0.77	0.67	0.57	0.47	0.38	0.31	0.24	0.20	0.18



Solid rocket booster of the GSLV Mk3 uses 206690 kg of HTPB based solid propellant to give 3578.2 kN average thrust at sea level, initial calculations show that solid H2-O2 can give similar performance with less than half the propellant, mass. In other words it can be said that replacing the solid rocket boosters with SH2-SOX boosters will increase the payload mass capability of GSLV Mk3 by several folds.

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