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## A thermodynamic study on catalytic decomposition of hydrazine in a space thruster

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**Abstract** Most satellites stationed in space use catalytic propulsion systems for attitude control and orbit adjustment. Hydrazine is consumed extensively as liquid monopropellant, in the thrusters. Catalytic reactor is the most important section in the catalytic thruster. Ammonia and nitrogen gases are produced as a result of complete catalytic decomposition of hydrazine in the reactor, causing an increase in temperature and a rise in specific impulse. Ammonia is subsequently decomposed, leading to nitrogen and hydrogen gases. Decomposition of ammonia leads to a decrease in temperature, molecular weight and specific impulse. The latter phenomenon is unavoidable. The effect of ammonia decomposition on the reactor temperature, molecular weight of gaseous products and conclusively on specific impulse was studied in this article. At adiabatic state, thermodynamic analysis revealed that the maximum and minimum temperatures were 1655 K and 773 K, respectively. The highest molecular weight was obtained at ammonia conversion of zero and the lowest when ammonia conversion was 100%. The maximum specific impulse (305.4 S) was obtained at ammonia conversion of zero and completely conversion of ammonia, the minimum specific impulse (about 213.7 s) was obtained. For specific impulse, the result of thermodynamic calculation in this work was validated by the empirical results.

**Keywords:** Catalytic thruster; Hydrazine; Ammonia; Specific impulse; Thermodynamic analysis

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## Nomenclature

$A$	– empirical constant (Eq. (12))
$B$	– empirical constant (Eq. (12)), 1/K
$C$	– empirical constant (Eq.(12)), $K^2$
$C_p$	– heat capacity for outlet gas mixture at constant pressure, J/mol K
$C_{p,i}$	– heat capacity for component $i$ , J/mol K
$C_v$	– heat capacity for outlet gas mixture at constant volume, J/mol K
$D_{in}$	– diameter of orifices of showerhead injector, m
$g$	– gravitational acceleration, $m/s^2$
$H$	– enthalpy, J
$\Delta H_{p,i}$	– enthalpy change for component $i$ , J
$\Delta H_{r1,298}^o$	– standard heat for hydrazine decomposition, J/mol
$\Delta H_{r2,298}^o$	– standard heat for ammonia decomposition, J/mol
$I_{sp}$	– specific impulse for hydrazine monopropellant, s
$I_{sp,thruster}$	– specific impulse for thruster, s
$k$	– - proportional constant in Eq. (9)
$L$	– length of the catalytic bed, m
$M$	– outlet gas molecular weight, g/mol
$M_i$	– molecular weight for component $i$ , g/mol
$n_i$	– mole of component $i$ , mol
$n_{o,NH_3}$	– initial mole of ammonia, mole
$n_{NH_3}$	– present mole of ammonia, mole
$P_c$	– gas pressure in the reactor, Pa
$P_{in}$	– injection pressure, Pa
$P_e$	– outlet gas pressure from the reactor, Pa
$Q$	– amount of heat exchanged, J
$R$	– universal gas constant, 8.314 J/mol K
$T$	– temperature, K
$T_c$	– exit gas temperature from the catalytic reactor ( $= T_2$ ), K
$u$	– internal energy, J
$W_s$	– shaft work, J
$X$	– mole conversion of ammonia, %
$y_i$	– mole fraction of component $i$
$z$	– altitude, m

## Greek symbols

$\gamma$  – heat capacity ratio ( $= C_p/C_v$ )

## Subscripts

$ig$  – ideal gas

## 1 Introduction

Hydrazine ( $N_2H_4$ ) is consumed extensively in space thrusters for attitude control and orbit adjustment [1–3]. Catalytic decomposition of hydrazine produces hot gases, which contribute to the propulsion power for satellite [4]. The catalytic reactor is the most important section in a hydrazine thruster. Shell 405 (30–45 wt% Ir over  $\gamma-Al_2O_3$ ) is the most appropriate catalyst for decomposition of hydrazine [3,5]. A schematic drawing of the catalytic reactor is presented in Fig. 1.

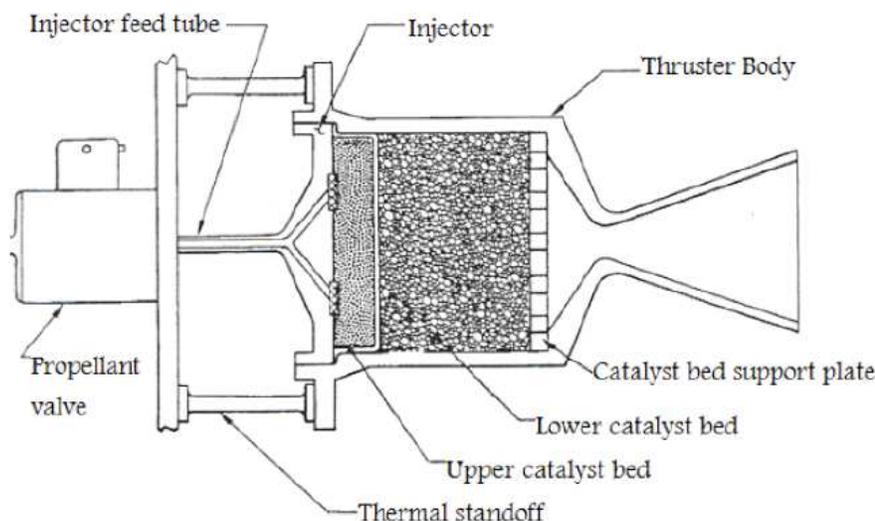
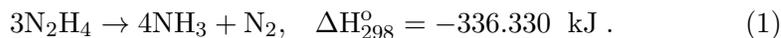
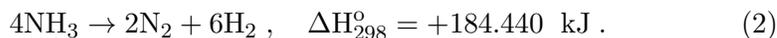


Figure 1: Schematic diagram for a catalytic reactor in hydrazine decomposition thruster [3].

Hydrazine monopropellant is decomposed into ammonia and nitrogen according to following reaction as [6]



A portion of the produced ammonia is decomposed as [6]



All substances, except hydrazine are in gaseous state. Based on general equation for specific impulse ( $I_{sp} = k(T_c/M)^{0.5}$  [2]), decomposition of ammonia is effective on outlet gaseous products, hence the effect on specific

impulse. The control of ammonia decomposition in maximizing the specific impulse is very important.

With respect to reaction thermochemistry in Eqs. (1) and (2) and the general equation for  $I_{sp}$ , there exists a paradox. Equation (1) increases the temperature of catalytic reactor, leading to an increase in  $I_{sp}$ , while Eq. (2) decreases the gas molecular weight, temperature of the reactor and  $I_{sp}$ . This is a problem in determining how much Eq. (2) should be proceeded in order to obtain an appropriate  $I_{sp}$ . In other words, it is necessary to study the changes in  $I_{sp}$  with respect to ammonia conversion. Since hydrazine is carcinogen [7], the prediction of  $\text{NH}_3$  decomposition will be helpful prior to thruster experimental tests. So, the hydrazine decomposition should be studied thermodynamically for prediction of maximum temperature, ammonia conversion, gas molecular weight and the maximum obtainable  $I_{sp,thruster}$ . The solution to the problem would assist researchers to design better catalytic reactor in hydrazine thruster.

Since 1950 the literature on this issue has been and is in progress. The studied aspects in this field are: hydrazine decomposition kinetics [8–12], hydrazine decomposition catalysts [13–17], designing and manufacturing of hydrazine thrusters [18–20] and performance of hydrazine thrusters [21–25]. In all studies, the researchers have dealt with the hydrazine thruster and catalytic decomposition of hydrazine with respect to their dynamics or kinetics but not its thermodynamic analysis. The thermodynamics of hydrazine monopropellant decomposition represents the maximum performance or specific impulse. Studying the thermodynamic aspect is the objective of this article, the results of which will be validated through the experimental work.

## 2 Extracting equations

Hydrazine is decomposed exothermically into ammonia and nitrogen, Eq. (1), and the produced ammonia is decomposed endothermically in a simultaneous manner into nitrogen and hydrogen, Eq. (2). To analyze this process, the reactions are assumed to occur in two separate sections or reactors (Fig. 2).

Hydrazine enters the reactor 1 at 289 K and is decomposed into ammonia and nitrogen adiabatically, Eq. (1). In reactor 1, the hydrazine conversion is 100% [26]. In reactor 2, ammonia is decomposed into nitrogen and hydrogen with different conversion percentages. The following assumptions

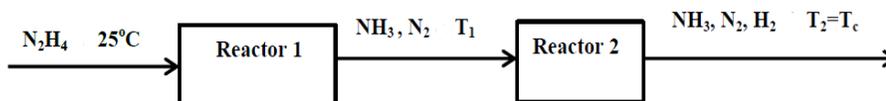


Figure 2: Virtual process for catalytic decomposition of hydrazine.

were considered for analysis of reaction Eq. (1) in virtual reactor 1:

1. Hydrazine decomposition, Eq. (1), occurs in such a rapid manner that there is no opportunity for heat exchange, hence, reactor 1 is adiabatic ( $Q = 0$ ) which is confirmed by experimental observations [27–30].
2. Due to short length of the reactor (less than 0.05 m in conventional thrusters [31–34]), the changes in kinetic energy ( $\Delta u^2/2$ ) and potential energy ( $g\Delta z$ ) are negligible. Also, there is no shaft work in the catalytic bed ( $W_s = 0$ ). According to general energy balance in reactor 1,  $\Delta H$  will be zero:

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta z = Q - W_s. \quad (3)$$

3. The temperature in hydrazine thrusters is high [27–30]. Therefore, it is assumed that the all gases are in ideal state.
4. It is assumed no changes in the catalyst morphology or no deactivation in catalyst.
5. It is assumed gravity acceleration to be constant ( $g = 9.8 \text{ m/s}^2$ ).
6. All produced gages are stable.

Since the change in enthalpy is independent on the reaction path [35], equation

$$\Delta H_{r1,298}^0 + \Delta H_P^0 = \Delta H = 0 \quad (4)$$

will be predominant in reactor 1 for hydrazine decomposition, Eq. (1).

The heat generated by hydrazine decomposition reaction enhances the temperature of the products in reactor 1. It is expressed in

$$\frac{\Delta H_{r1,298}^0}{3} = \frac{\Delta H_{p1}}{3} = n_{\text{NH}_3} \int_{298.15}^{T_1} C_{p,\text{NH}_3} dT + n_{\text{N}_2} \int_{298.15}^{T_1} C_{p,\text{N}_2} dT = \frac{4}{3} \int_{298.15}^{T_1} C_{p,\text{NH}_3} dT + \frac{1}{3} \int_{298.15}^{T_1} C_{p,\text{N}_2} dT. \quad (5)$$

The temperature of products in reactor 1,  $T_1$ , will be determined. The same assumptions hold true for reactor 2. Due to unknown level of conversion in ammonia, the mole of consumed ammonia will be a variable for second reaction in reactor 2. According to Fig. 2, the following equation will be applied:

$$\begin{aligned}\Delta H_{p1} + \Delta H_{r2,298}^o &= \Delta H_{p2} , \\ \Delta H_{p1} + \Delta H_{r2,298}^o &= \Delta H_{p2} .\end{aligned}\quad (6)$$

Here the energy balance is applied as

$$\begin{aligned}\frac{4}{3} \int_{298.15}^{T_1} C_{p,\text{NH}_3} dT + \frac{1}{3} \int_{298.15}^{T_1} C_{p,\text{N}_2} dT - \frac{X \Delta H_{r2,298}^o}{3} = \\ \left(\frac{1+2X}{3}\right) \int_{298.15}^{T_2} C_{p,\text{N}_2} dT + 2X \int_{298.15}^{T_2} C_{p,\text{H}_2} dT + \\ \left(\frac{4-4X}{3}\right) \int_{298.15}^{T_2} C_{p,\text{NH}_3} dT ,\end{aligned}\quad (7)$$

where  $T_2$  is the outlet gas temperature from reactor 2 or thrust chamber ( $T_c$ ), and  $X$  is the mole conversion of ammonia defined as reacted or consumed mole of ammonia per initial mole of ammonia (an amount between 0 and 1)

$$X = \frac{(n_{o,\text{NH}_3} - n_{\text{NH}_3})}{n_{o,\text{NH}_3}} .\quad (8)$$

Specific impulse is expressed in thermodynamic form [2,36] as follows:

$$I_{sp} \propto \sqrt{\frac{T_c}{M}} = k \sqrt{\frac{T_c}{M}} = \sqrt{\frac{2\gamma R T_c}{(\gamma - 1)g^2 M}} = \sqrt{\frac{2C_p T_c}{g^2 M}} ,\quad (9)$$

where  $\gamma = C_p/C_v$ ,  $R$  is the universal gas constant ( $C_p - C_v = R = 8.314$  J/molK) and  $g$  is the gravitational acceleration. As a thermodynamic parameter  $C_p$  is expressed as

$$C_p = \sum y_i C_{p,i} ,\quad (10)$$

and the gas molecular weight as

$$M = \sum y_i M_i .\quad (11)$$

### 3 Results and discussion

General equation for heat capacity for  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  in Eqs. (5) and (7) is presented in

$$C_p^{ig} = 8.314(A + BT + CT^{-2}) \quad (12)$$

in which  $A$ ,  $B$ , and  $C$  are material dependent constants. This relation is valid for ammonia up to 1800 K, nitrogen up to 2000 K, and hydrogen up to 3000 K [35]. The constants for the heat capacity equations are given in Tab. 1.

Table 1: Constants for specific heat capacity equation for  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  [35].

Chemical	$A$ [-]	$B \times 10^3$ [ $\text{K}^{-1}$ ]	$C \times 10^{-5}$ [ $\text{K}^2$ ]
$\text{NH}_3$	3.578	3.020	-0.186
$\text{N}_2$	3.280	0.593	0.040
$\text{H}_2$	3.249	0.422	0.083

Temperature  $T_1$  is calculated through Eq. (5) as 1654.4 K. By inserting  $T_1$  in Eq. (7), and rearranging the equation would result in  $X$  versus  $T_2$  as

$$X = \frac{46497.9 - 17.592T_2 - 6.3365 \times 10^{-3}T_2^2 - \frac{0.704 \times 10^5}{T_2}}{19498.47 + 11.742T_2 - 4.181 \times 10^{-3}T_2^2 - \frac{1.322 \times 10^5}{T_2}} \quad (13)$$

The plot of the thrust chamber temperature versus ammonia conversion according to this equation is shown in Fig. 3. As observed here, the maximum temperature is 1655 K. This temperature is obtained at no ammonia conversion ( $X = 0$ ). In the presence of the catalyst, a portion of ammonia is eventually decomposed. This fact suggests that catalysts must be found to inhibit the ammonia decomposition reaction.

Due to endothermic decomposition of ammonia, an increase in ammonia conversion leads to a decrease in gas temperature. As shown in Fig. 3, the temperature of thrust chamber decreases linearly as the ammonia conversion increases (a slope of 830 K per conversion unit). Since ammonia, nitrogen and hydrogen are stable molecules and no other molecule will be

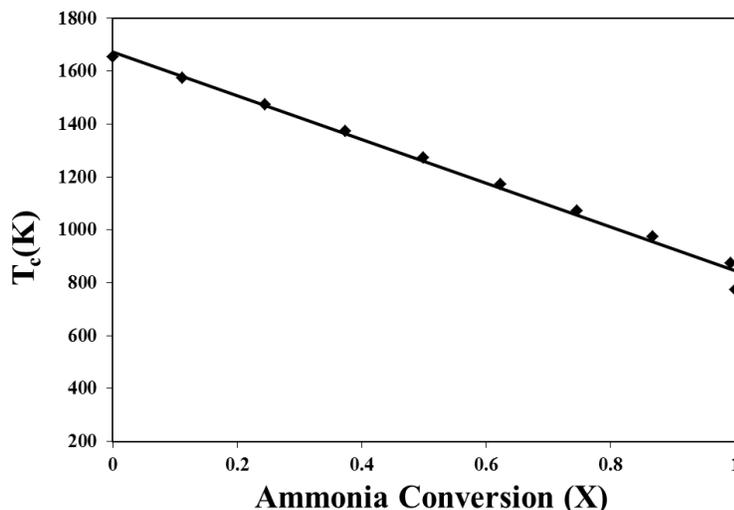


Figure 3: Changes in gas temperature in the thruster versus ammonia conversion.

formed, so the thrust chamber contains only these gases. Outlet gas molecular weight, as a thermodynamic property, is calculated through following relation, where  $M_{\text{NH}_3} = 17$  g/mol,  $M_{\text{N}_2} = 28$  g/mol, and  $M_{\text{H}_2} = 2$  g/mol:

$$\begin{aligned}
 M = \sum y_i M_i &= \frac{1-X}{1.25+X} M_{\text{NH}_3} + \frac{1+2X}{5+4X} M_{\text{N}_2} + \frac{6X}{5+4X} M_{\text{H}_2} \\
 &= \frac{148+68X}{6.25+10X+4X^2} \quad (14)
 \end{aligned}$$

The molecular weight changes of the outlet gas mixture versus ammonia conversion is shown in Fig. 4, where the highest molecular weight of outlet gas mixture is obtained when there is no ammonia conversion ( $3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2$ ). The lowest molecular weight is for complete decomposition of ammonia ( $3\text{N}_2\text{H}_4 \rightarrow 3\text{N}_2 + 6\text{H}_2$ ). In other words, hydrogen with the lowest molecular weight and the highest mole fraction reduces the total molecular weight.

Composition of the outlet gas from the reactor is one of the major parameters in evaluating the reactor performance (Fig. 5). A decrease in mole fraction of ammonia is proportional to the increase in mole fraction of nitrogen and hydrogen. As observed in figure, when hydrazine is decomposed into ammonia and nitrogen, in the absence of hydrogen the mole fractions of ammonia and nitrogen are 0.8 and 0.2, respectively. At full

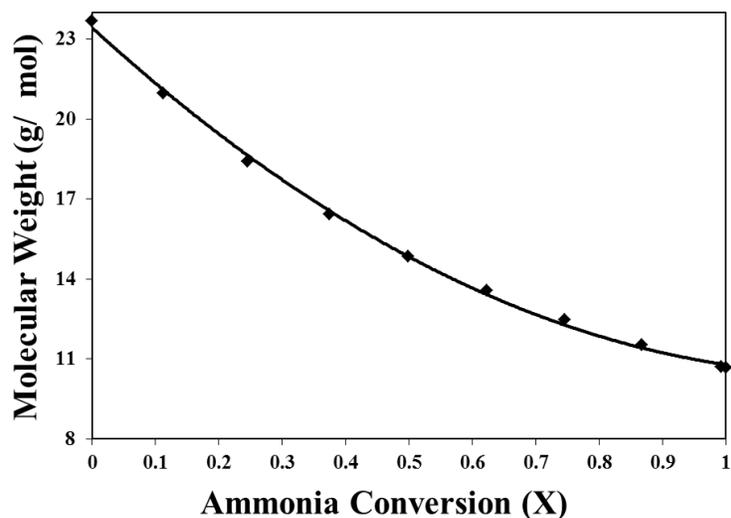


Figure 4: Variation of molecular weight for gas mixture in the reactor versus ammonia conversion.

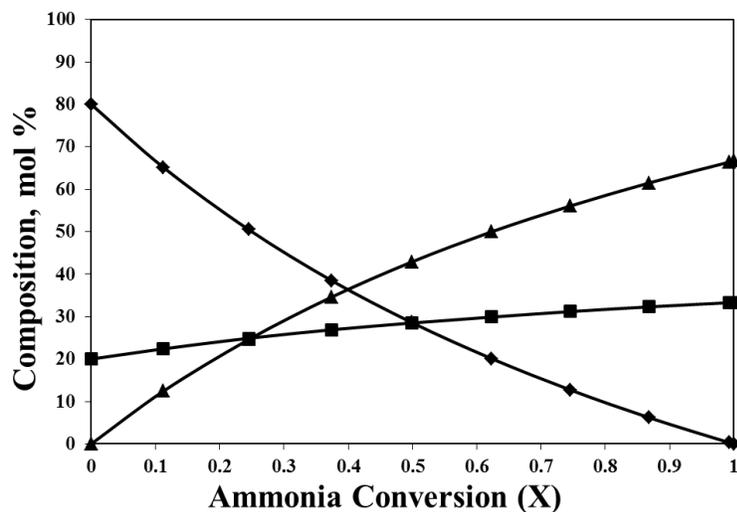


Figure 5: Variation in outlet gas composition from the reactor versus ammonia conversion (-◆-NH<sub>3</sub>, -▲-H<sub>2</sub>, -■-N<sub>2</sub>).

ammonia conversion ( $3\text{N}_2\text{H}_4 \rightarrow 3\text{N}_2 + 6\text{H}_2$ ), the nitrogen mole fraction is  $3/9$  or  $0.34$  and that of the hydrogen is  $6/9$  or  $0.66$ .

With respect to Eq. (10), the heat capacity of the gas mixture at

constant pressure is expressed through

$$C_p = \sum y_i C_{p,i} = \frac{1-X}{1.25+X} C_{p,\text{NH}_3} + \frac{1+2X}{5+4X} C_{p,\text{N}_2} + \frac{6X}{5+4X} C_{p,\text{H}_2} \quad (15)$$

The heat capacity for each component is calculated at  $T_2$  or  $T_c$  and in this relation  $C_p$  depends on temperature, while the resulting temperature depends on ammonia conversion, indicating that the  $C_p$  for the gas mixture will depend on the ammonia conversion in a complicated equation, the calculations of which will be carried out by Matlab (version 2015b) software [38]. The variation in  $C_p$  for outlet gas mixture is shown in Fig. 6, where the increase in ammonia conversion leads to a decrease in heat capacity of gas mixture. This is because  $C_p$  for ammonia is higher than nitrogen and hydrogen at any operational temperature interval [35]. Thus increase in ammonia conversion means lower composition of ammonia and therefore, a decrease in heat capacity of the gas mixture.

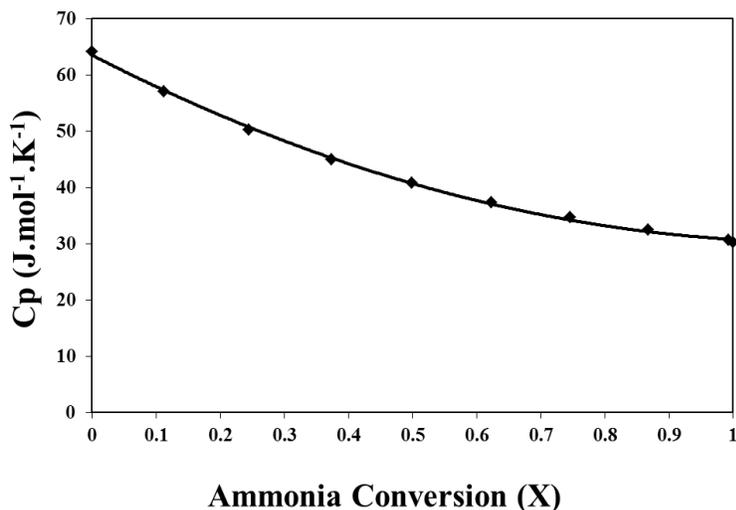


Figure 6: Variation in heat capacity for outlet gas mixture from the reactor versus ammonia conversion.

The horizontal axis (abscissa or x-axis) may represent the catalytic reactor length. In Figs. 3–6 are presented the values of temperature of thrust chamber, molecular weight, gas composition and heat capacity, respectively which vary with respect to ammonia conversion.

Specific impulse for the hydrazine monopropellant is calculated through

Eq. (9) by applying Eqs. (13)–(15) (see the results in Fig. 7). The highest specific impulse (305.4 s) is obtained when there is no ammonia conversion. If ammonia conversion is 100%, then the  $I_{sp}$  will be 213.7 s. The experimental results confirmed that ammonia is certainly decomposed in the presence of the catalyst [27–30], that is, the value of 305.4 s will not be obtained at any time.

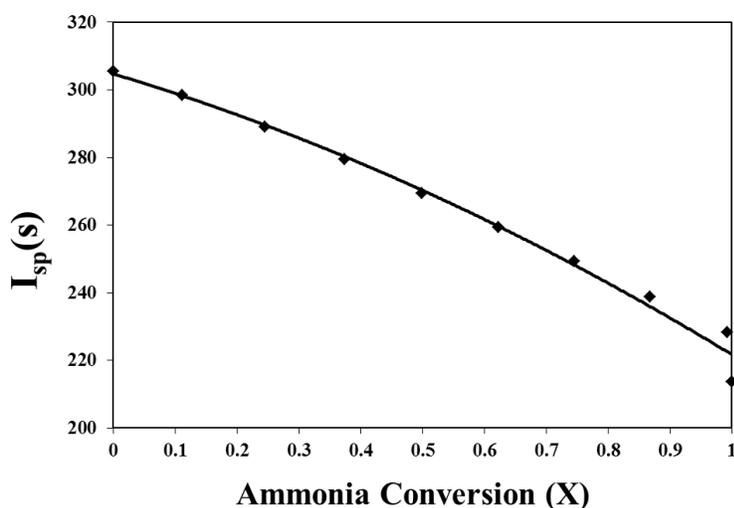


Figure 7: Variation of specific impulse for hydrazine versus ammonia decomposition.

As observed in Figs 3, 4 and 6, the change in  $T_c$  is much more than that of  $M$  or  $C_p$  (the slope of  $T_c$  versus  $X$  is 830 K/conversion unit but the slopes for  $M$  and  $C_p$  are 21.7 g/mol per conversion unit and 58.5 J/molK per conversion unit, respectively). Therefore, it is expected that  $I_{sp}$  for hydrazine monopropellant, Eq. (9), be more sensitive to  $T_c$  than  $M$  or  $C_p$ . Conclusively, ammonia conversion strongly decreases  $I_{sp}$  for hydrazine monopropellant.

The specific impulse is a character of hydrazine monopropellant, that is, Eq. (9) is provided merely for decomposition of hydrazine monopropellant. The most important advantage of Eq. (9) is that when ammonia conversion is accomplished by it, the  $I_{sp}$  value will be obtained, where  $C_p$ ,  $T_c$ , and  $M$  depend on ammonia conversion. If a nozzle is connected to the end of the reactor, the effects of pressure in the chamber and the exit of the nozzle

will be inserted in  $I_{sp}$  equation as [2]

$$I_{sp,thruster} = \sqrt{\frac{2C_p T_c}{g^2 M} \left[ 1 - \left( \frac{P_e}{P_c} \right)^{(\gamma-1)/\gamma} \right]}. \quad (16)$$

Here, the  $I_{sp,thruster}$  is a specific impulse for the thruster, not for hydrazine monopropellant. That is,  $I_{sp,thruster}$  includes  $I_{sp}$  for hydrazine monopropellant and pressure effects in the chamber and the nozzle

$$I_{sp,thruster} = I_{sp} \sqrt{\left[ 1 - \left( \frac{P_e}{P_c} \right)^{(\gamma-1)/\gamma} \right]}. \quad (17)$$

If the pressure in the thrust chamber is much more than the exit pressure, then the  $I_{sp,thruster}$  will approach  $I_{sp}$  of hydrazine monopropellant ( $I_{sp,thruster}$  is always less than  $I_{sp}$ ).

An outstanding point deduced from Eqs. (9) and (16) is that Eq. (9) represents the maximum  $I_{sp}$  for hydrazine monopropellant. By adjusting and designing modified throat and exit diameters for the nozzle, maximum specific impulse might be actuated. In other words, the maximum value of specific impulse for the thruster is the same as hydrazine monopropellant. By knowing the value of ammonia conversion, the performance condition of the reactor and the thruster will be predictable, which is a matter of concern. Moreover,  $I_{sp}$  is measured by a gas chromatograph (equipped with a thermal conductive detector) in an experimental manner while  $I_{sp,thruster}$  is measured by a load cell (to determine the thrust) with hydrazine flow meter (to determine hydrazine mass flow rate) in the experimental manner.

Based on the design type and the comments of thruster designer, the term  $\left( \frac{P_e}{P_c} \right)^{(\gamma-1)/\gamma}$  will have different values. For example, an increase in the chamber pressure through a reduction in the throat cross section area leads to increase in  $I_{sp,thruster}$ , conclusively, thermodynamic analysis will determine the maximum  $I_{sp,thruster}$ .

The obtained results here were validated through experimental work due to Adler *et al.* [37]. The specifications of design for Adler *et al.* thruster are presented below:

- injection pressure,  $P_{in}$ , between 20 and 80 kPa;
- diameter of orifices of showerhead injector,  $D_{in}$ , between 0.0008 and 0.005 m;
- length of the catalytic bed,  $L$ , from 0.0525 to 0.105 m;

- exhaust nozzle diameter,  $D_e$ , from 0.01 to 0.015 m.

Adler *et al.* obtained the optimum  $I_{sp,thruster}$  at  $P_e/P_c = 0.0175$  and ammonia conversion of 55% [37]. At this optimum conditions, they obtained  $\gamma = 1.271$ ,  $T_c = 1221$  K,  $M = 13.33$  g/mol and  $I_{sp,thruster} = 201.1$  s as well. Comparison of the results between Adler *et al.* experimental work and this work is presented in Tab. 2, indicating the confirmation of this thermodynamic analysis with only a slight difference.

Table 2: Comparison between the quantities for hydrazine thruster in this work and Adler *et al.* [37] at  $P_e/P_c = 0.0175$  and  $X_{NH_3} = 55\%$ .

Quantities	Unites	Results of Adler <i>et al.</i> [37]	Results of this work	Error (%)
$\gamma$	–	1.271	1.268	0.2
$T_c$	K	1221	1231	0.8
$M$	g/mol	13.33	14.3	0.7
$I_{sp,thruster}$	s	201.1	197.3	1.8

## 4 Conclusions

Hydrazine, as a carcinogenic monopropellant, is consumed in space thrusters. The most important section of the thruster is the catalytic reactor. In designing and manufacturing the reactor which works on hydrazine decomposition basis, it is necessary to have the reactor temperature, outlet gas molecular weight and the specific impulse. These quantities are obtainable through thermodynamic studies run on hydrazine monopropellant. At adiabatic state of the reactor, thermodynamic analysis indicated that those parameters depend on ammonia conversion. The highest and lowest temperatures in the reactor were obtained as 1655 K and 773 K, respectively. The maximum and minimum molecular weights for outlet gas from decomposition of hydrazine were obtained at zero and complete conversions of ammonia, respectively. The results from the provided analysis show that the specific impulse has its maximum (as 305.4 s) when there is no ammonia conversion. It is obtained by regulating the hydrazine flow rate into the reactor. Also, the lowest amount of the specific impulse (as 213.7 s) is obtained for the full conversion of ammonia. The results between

this thermodynamic analysis and that of the Adler experimental work at  $P_e/P_c = 0.0175$  and  $X_{\text{NH}_3} = 55\%$  indicate that there exists a 1.8% error between the thermodynamic calculations and experimental results for  $I_{sp,thruster}$ .

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