# Regression Rate Studies of Aniline Formaldehyde—Red Fuming Nitric Acid Hybrid System

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### Nomenclature

| | |
|---|---|
| $D$ | = diameter of port, cm |
| $G$ | = total mass flux, g/cm$^2$ sec |
| $G_o$ | = oxidizer mass flux referred to initial port area, g/cm$^2$ sec |
| $p_c$ | = combustion chamber pressure, atm |
| $\dot{r}$ | = regression rate, mm/sec |
| $x$ | = axial distance from head end, cm |
| $a, b, m, n$ | = constants |

*Subscripts*

| | |
|---|---|
| av | = average |

### Introduction

IN the design of hybrid rocket motors, it is necessary to know the manner in which the regression rate of the fuel varies with oxidizer mass flow rate and combustion chamber pressure. In a solid-gas hybrid, the combustion model consists of a diffusion flame established in a turbulent boundary layer. Theoretical analysis[1] has shown that the regression rate depends primarily on the oxidizer mass flow rate though a pressure dependence[2,3] under certain conditions has also been shown experimentally. In the case of a solid liquid hybrid, no theoretical analysis is available showing relationships between the various parameters. The combustion model[4] postulates the existence of solid-liquid heterogeneous reactions on the fuel surface giving rise to a premixed flame above which the diffusion flame is finally established. Existence of the premixed flame indicates that the regression rate may have considerable pressure dependence. Results presented here indicate that this is actually the case and that a simple relationship exists between regression rate, oxidizer mass flux, and combustion chamber pressure.

The fuel-oxidizer combination selected for this study was the aniline formaldehyde (AF)-red fuming nitric acid (RFNA) system. Condensation products of primary aromatic amines and low molecular weight aldehydes have been shown to be of interest for practical hybrid rocket motors.[5,6] In a recent study,[7] it was shown that condensation products of aniline, metatoluidine, and orthotoluidine with formaldehyde were capable of giving low ignition delays with RFNA, and regression rates with gaseous oxygen were sufficiently high to warrant consideration of these fuels for practical applications. Extensive ignition delay data for these systems was also reported.[8]

### Experimental Procedure

The fuel grain was fired in a test motor under different conditions of oxidizer mass flux and combustion chamber pressure and the regression rate was determined in each case. The test motor had a water-cooled cylindrical combustion chamber in which a fuel grain of length 27 cm, o.d. 5.05 cm, and i.d. 2.22 cm was loaded. RFNA was injected in the port with a single element swirl injector of low discharge coefficient (about 0.1). Combustion was initiated by a pyrotechnic igniter. Though the system was hypergolic, the ignition delay was long (0.9 sec) and for smooth start without flooding, a pyrotechnic igniter was necessary.

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The grain (density 1.15 g/cm$^3$) was made by pressing the fuel powder in a die at a pressure of 6 tons/in$^2$ and subsequent drilling. AF powder (melting point 150°C) was made by a process described elsewhere,[9] which consisted of direct addition of aniline to formaldehyde solution (40%) at 5°C and washing, drying, and crushing the solid product so obtained. Catalysts, 5% by weight of ammonium vanadate and 2% by weight of potassium permanganate, were added to the powder before pressing. Such large amounts of catalysts with heavy atoms of vanadium, manganese, and potassium would reduce the specific impulse. However, this was irrelevant in the present investigation which was concerned mainly with finding the dependence of regression rate on $G_o$ and $p_c$. Also for lower percentage of catalysts, the ignition delay was abnormally large and extensive flooding of grain occurred even after pyrotechnic ignition.

RFNA (density 1.5 g/cm$^3$, $N_2O_4$ content 9% by weight) was contained in an aluminum alloy tank of one liter capacity and was fed to the injector by means of a short length of pipe through an electropneumatic valve. The mass flow rate was controlled by changing the nitrogen feed pressure and its average value was estimated by carefully noting the difference in the weight of acid in the tank and feed pipe before and after a motor run.

Two sets of experiments were carried out. In the first set the combustion chamber pressure was kept at 1 atm by firing without a nozzle, with the grain held in the motor merely by a plate with a large hole. Duration of run was measured by a stop watch. In the second set, a graphite nozzle of throat diameter 0.8 cm was used to give higher chamber pressures. The pressure vs time record gave the duration of run in this case. In all cases, pressure was measured at the head end, through a hole in the injector plate, by a strain gage-type pressure transducer (accuracy 0.5 psi) and recorded by a single pen chart recorder. Regression rate was measured at the end of each run by cutting the grain at various positions and measuring average wall thickness with a micrometer.

### Results and Discussion

Twenty-five firings in all were carried out. These included those conducted initially for establishing fuel port size, maximum flow rate, and amount of catalysts on a trial-and-error basis. A significant result of these firings was the fact that for a given port area, combustion was possible only up to an upper limit of oxidizer flow rate beyond which flooding of the grain occurred. The present combination of port diameter and maximum oxidizer flow rate was arrived at in this manner. Results for nine runs are presented in Table 1. In five of these $p_c = 1$ atm, and in the other cases $p_c$ was higher.

Attempts were first made to determine if the data fitted the known pattern of solid-gas hybrid combustion by plotting[2] $\log(\dot{r}D^{0.2})$ and $\log(\dot{r}x^{0.2})$ vs $\log G$ (the total mass flux $G$ was computed by adding to $G_o$ the mass flux due to fuel regression). The plots were not straight lines but rather curves with negative slopes, showing that the analysis for solid-gas hybrid is not applicable to the solid-liquid case.

**Table 1 Regression rate data**

| Run | $G_o$ g/cm$^2$ sec | $p_c$ atm | $\dot{r}_{av}$ mm/sec |
|---|---|---|---|
| 1 | 2.41 | 1 | 0.179 |
| 2 | 3.70 | 1 | 0.207 |
| 3 | 4.17 | 1 | 0.240 |
| 4 | 4.60 | 1 | 0.250 |
| 5 | 5.22 | 1 | 0.260 |
| 6 | 2.83 | 3.65 | 0.445 |
| 7 | 3.11 | 4.40 | 0.510 |
| 8 | 4.69 | 3.93 | 0.560 |
| 9 | 5.26 | 4.20 | 0.620 |

Figure 1 shows a plot of $\log \dot{r}_{av}$ vs $\log G_o$. The data points for $p_c = 1$ atm fall on a straight line and show that, for a constant pressure of one atm, the regression rate law is of the form

$$\dot{r}_{av} = aG_o^n \quad (1)$$

$n = 0.55$ from the slope of the straight line.

It is also seen from Fig. 1 that for identical oxidizer mass flux, $\dot{r}_{av}$ is much greater for the higher pressure than for 1 atm. This indicates that pressure dependence of regression rate is considerable. Equation (1) and then be modified to a more general form

$$\dot{r}_{av} = bG_o^n p_c^m \quad (2)$$

The value of $m$ was computed by comparing $\dot{r}_{av}$ at higher pressure with that at 1 atm. For runs 6, 7, 8, and 9, the values of $m$ were found to be 0.65, 0.601, 0.62, and 0.603, respectively (average $m = 0.61$). These values are quite close and therefore Eq. (2) is a very valid description of the regression rate behavior in the present case.

The dependence of regression rate on oxidizer mass flux can be explained on the basis of convective heat transfer to the fuel surface from the diffusion flame zone, as in the case of a solid-gas hybrid. The effect is modified, however, by the presence of premixed flame near the surface and by the kinetics of the solid liquid-chemical reactions on the surface. Both these processes are modified by changes in pressure. As the pressure is increased, the premixed flame moves closer to the surface thus increasing heat transfer to it. Simultaneously, the rate of the solid-liquid surface reaction is also enhanced. The two effects combine to give the observed increase in regression rate with $p_c$. It is significant to note that increase in regression rate is considerable for comparatively small increases of $p_c$. It appears, therefore, that for the ranges of pressures and mass flows investigated, the chemical kinetic effects are very important. Since the solid-liquid reactions and the premixed flame are likely to be present in solid-liquid hybrid combustion under all conditions, it can be expected that the regression rate will show pressure dependence at higher oxidizer flow rates and combustion pressures. It cannot be said, however, that the quantitative relationship will be of the same form as that in Eq. (2). In the absence of a suitable theory combining the diffusion flame and premixed flame effects, this can be clarified only by further studies of regression rates at higher pressures and oxidizer mass flow rates.

## References


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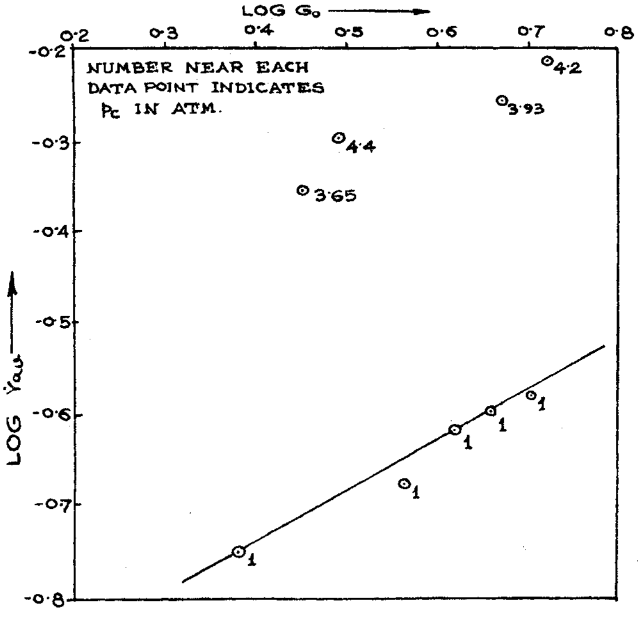


**Fig. 1 Variation of regression rate with oxidizer mass flux and combustion chamber pressure.**

# Errata

## Transition Effects on Slender Vehicle Stability and Trim Characteristics


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ON p. 8 in Fig. 11, the coordinates should be "$C_{m\alpha}$ and $C_{mq}+C_{m\dot{\alpha}}$, arbitrary scales," instead of "$C_{m\alpha}/(C_{m\alpha})d_N = 0$ and $(C_{mq}+C_{m\dot{\alpha}})/(C_{mq}+C_{m\dot{\alpha}})d_N = 0$."


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