Long-Duration Firings of a Mariner Mars 1969 Catalytic Reactor

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Two long-duration tests were conducted with a surplus Mariner Mars 1969 monopropellant hydrazine reactor in an attempt to induce the "washout" phenomenon. The Mariner Mars 1969 reactor was chosen because it has a long development history and thus is well characterized. No "washout" occurred during either of the two 1000-s tests, although slow transients were observed in the reactor operation during what were nominally steady-state conditions. The 2000 s of operating time represents nearly an order of magnitude increase over the rated life of the engine.

Introduction

In recent years, a phenomenon termed "washout" has been observed in hydrazine monopropellant reactors. This "washout" is characterized by a rather slow but significant decrease in reactor performance (i.e., chamber pressure and thrust decrease while the fuel mass flowrate increases) during what is otherwise steady-state operation. Most significantly, this performance decrease first occurs *after* the reactor has reached thermal equilibrium. If allowed to proceed, the rate of the performance degradation increases and can eventually result in a complete cessation of hydrazine decomposition. Only partially reacted fuel then flows through the catalyst bed. One of the more interesting aspects of this phenomenon is that, if fuel flow is completely stopped after "washout" and is restarted after a delay as short as 1 s, the reactor again operates in a normal manner. However, "washout" will re-occur and the succeeding time interval before the next occurrence is always shorter. The "washout"-normal behavior-"washout" cycle can be repeated many times. The time until "washout" occurs is apparently affected by the previous history of the catalyst (both the operation time and the number of ambient temperature starts), by the bulk temperature of the liquid hydrazine, and by the amount of water (mil-spec hydrazine can contain up to 1.5%) in the hydrazine. Subsequent to the tests described here, "washout" has been observed at JPL, but not with the Mariner Mars 1969 reactor. These tests, described in Reference 1, identified the catalyst surface area per unit chamber volume as an additional variable significant in the "washout" process.

An attempt has been made to induce "washout" in the well-characterized reactor used in the Mariner Mars 1969 propulsion system and the results of these tests are the subject of this article. The primary purpose of these tests was to gain some insight into questions such as: Is "washout" a fundamental, but heretofore unobserved, characteristic of the Shell 405 catalyst? Is "washout" a characteristic of all monopropellant hydrazine catalytic reactors? Is "washout" hardware related (e.g., injection technique)?

Apparatus and Procedures

For the "washout" tests a surplus Mariner Mars 1969 reactor (see Figure 1), serial number S/N 008, was modified slightly from the basic design. The modifications consisted of the addition of a 10-mesh screen, made of L-605 alloy, just below the 20–30-mesh catalyst, the addition of a pressure tap to measure the reactor chamber pressure upstream of the catalyst bed and thus permit a determination of the pressure drop across the bed, and the addition of four fittings to allow the insertion of thermocouples within the lower catalyst bed to obtain direct measurements of the gas temperature.

In addition to the modifications described above, the catalyst used for these tests differed slightly from the Mariner Mars 1969 design. First, the engine was packed with used catalyst (exact history unknown) since prior use of the catalyst had been observed to promote "washout." Second, the lower bed of the engine (see Figure 1) was packed with 100% Shell 405 catalyst in place of the 75% Shell 405/25% HA-3 mixture used in the basic Mariner Mars 1969 engine. Since this mixture is peculiar to JPL and has not been widely used elsewhere, it was felt that this substitution would simplify comparisons with outside tests. Also, in an attempt to promote the "washout," the hydrazine used for these tests was cooled to approximately 280 K (45°F)[1] for both of the long-duration tests conducted.

Results and Discussion

Two tests, each nominally 1000 s in duration, were completed. No "washout" occurred during either test, although a change occurred in the engine characteristics about midway through the first test that might be interpreted as incipient "washout." This condition spontaneously disappeared and the test was completed without further incident. Reactor performance, as measured by the characteristic velocity (c^*), remained relatively constant during both tests. During the anomaly noted above, the

[1] Values in customary units are included in parentheses after values in SI (International System) units if the customary units were used in the measurements or calculations.

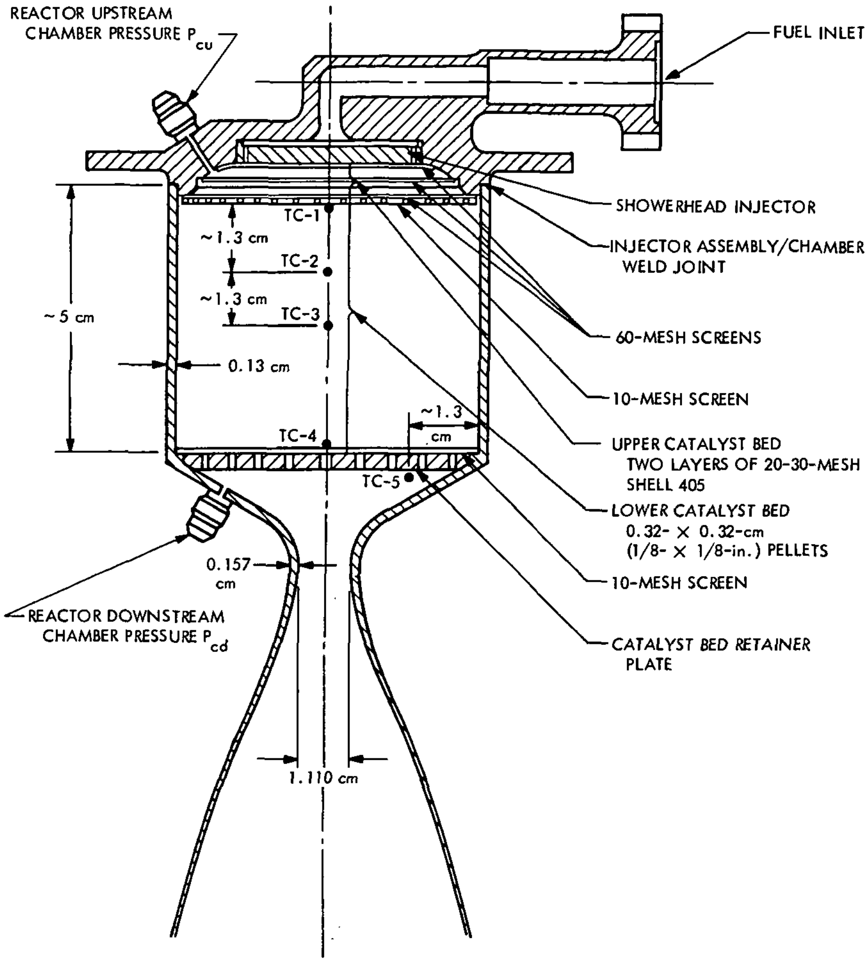

Figure 1. Internal configuration of Mariner Mars 1969 engine including modifications for "washout" tests

c^* decreased about 61 m/s (200 ft/s) but the c^* values were never below 1250 m/s (4100 ft/s). The measured value for this engine during flight acceptance testing was 1320 m/s (4320 ft/s). More significantly, there were no periods of rapid, sustained c^* decrease as is usual in "washout."

Although no "washout" was observed, the tests are of interest for several reasons. The 2000 s of operation with the same catalyst bed represents an order of magnitude increase in operation time over the nominal life of the Mariner Mars 1969 reactor. Of particular interest is the slow transient processes observed which occurred during what was nominally a steady-state operation.

A primary factor in the achievement of nearly 2000 s of test time on a single catalyst bed without excessive loss of catalyst is believed to be the 10-mesh screen (see Figure 1) added specifically for these tests. This screen provides structural rigidity for the 60-mesh screens, which in turn retain the 20–30-mesh catalyst. If the fine mesh screens do distort, a void is created in the upper catalyst bed. The catalyst particles can then move relative to one another and the upper bed can abrade itself into particles small enough to pass through a 60-mesh screen and hence out of the reactor. While the original screen design is adequate for the Mariner requirements, nominally 200 s of firing time, it is probably inadequate for the 2000 s of testing completed here. All screens were intact after the tests and only 5% of the catalyst from the upper bed was lost. The loss from the lower bed was about 1%. These are acceptable attrition rates.

The quality of a catalytic hydrazine reactor's performance is generally judged by three parameters: the characteristic velocity c^*, the "roughness" (as measured by the chamber pressure variations about the nominal steady-state pressure), and the pressure drop across the catalyst bed ($\Delta P_{\text{bed}} \equiv P_{cu} - P_{cd}$). These parameters, along with others of interest, are shown in Figures 2 and 3 as a function of time.

The plotted points of Figures 2 and 3 are taken from the data recorded by a high-speed digital recording system. Each parameter was sampled every 0.042 s. Only a few of these data are shown in Figures 2 and 3, but the long-term trends are reproduced there. Among the parameters not displayed are the fuel supply tank pressure, the fuel supply line pressure at the entrance to the reactor injector, and the fuel temperature at the injector entrance. (Note that the difference between the upstream and downstream chamber pressures (P_{cu} and P_{cd}) is plotted rather than P_{cu} itself.) The supply tank pressure was essentially constant during both tests. The injector pressure varied during the tests but the pressure drop across the injector varied directly with the fuel flowrate and agreed with the pre-test water flow calibration of the injector, and this would indicate that at no time were the injector orifices plugged. During both tests the fuel temperature increased slightly but continuously throughout the tests. The initial and final values for the first test were 282 K (48°F) and 285 K (53°F), respectively. The corresponding values for the second test were 279 K (42°F) and 280 K (45°F). The behavior of these parameters then leads to the conclusion that the variations in other measurements resulted from changes within the reactor itself and did not occur because of non-constant inlet conditions.

For a given reactor design, roughness generally increases as operating time is accumulated and is often the parameter used to define the useful life of a catalyst bed. Measured roughness for the engine during its flight acceptance testing was 3.45×10^4 N/m^2 (5 psi) as measured peak to peak. At the beginning of the first 1000-s test, the roughness level was the same as measured during acceptance testing. This relatively low level was somewhat surprising since tests early in the Mariner Mars 1969 development had

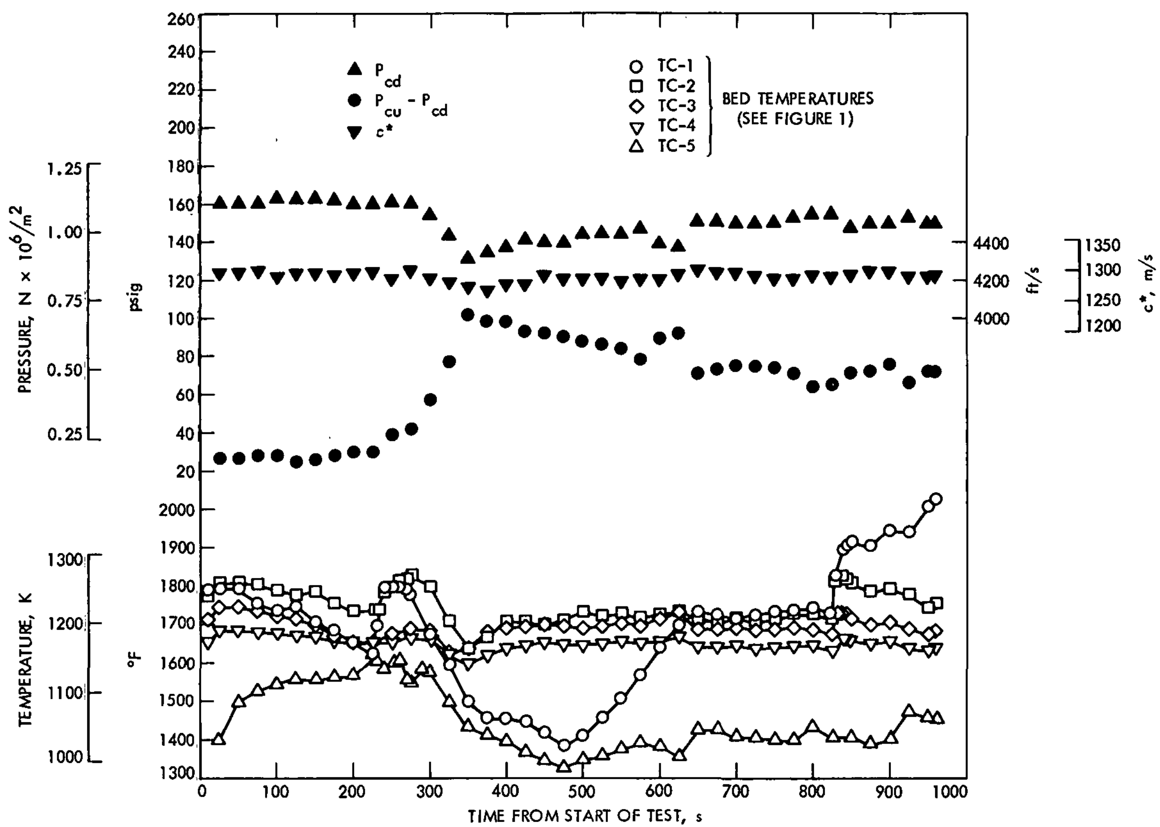

Figure 2. Results of test 1

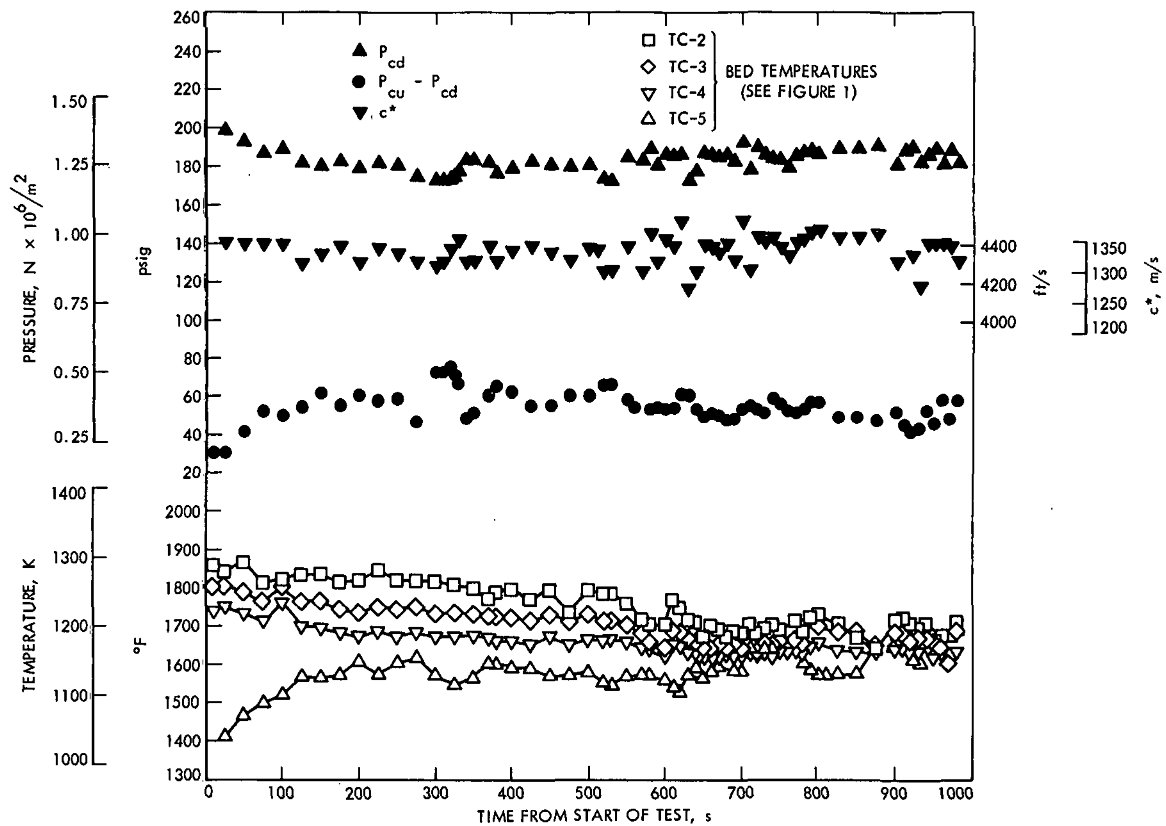

Figure 3. Results of test 2

shown that a lower bed composed of 100% Shell 405 pellets resulted in rougher operation than the mixture finally selected for the flight engines. During the first 400 s of operation, the roughness increased gradually to 4.14×10^5 N/m^2 (60 psi) peak to peak.

The usual form of the roughness associated with monopropellant reactors is a continuous, random fluctuation in chamber pressure. During both tests the reactor roughness was noticeably different and could best be described as smooth [i.e., roughness levels of 3.45×10^4 N/m^2 (5 psi) peak to peak], but interspersed with short-duration pressure pulses characterized by a rapid increase in the chamber pressure. As the roughness level increased, the time between pulses decreased. A section of an oscillogram from the first test is reproduced in Figure 4 and shows the type of chamber pressure disturbances observed. This type of pressure disturbance is generally attributed to small amounts of liquid hydrazine accumulating within the reactor which rapidly decompose after being heated enough to spontaneously react. The added catalyst retention screens could provide a place for such accumulation to occur.

Somewhat surprisingly, after the initial period of increasing roughness, the reactor operation gradually became smoother until after about 600 s when the pressure excursions were just under 1.38×10^5 N/m^2 (20 psi) peak to peak. Except for several pressure disturbances as large as 2.76×10^5 N/m^2 (40 psi) peak to peak, the roughness remained slightly under 1.38×10^5 N/m^2 (20 psi) for the remainder of the test.

During the second test the roughness began increasing from shortly after ignition and increased fairly rapidly to 1.38×10^5 N/m^2 (20 psi) peak to peak and generally remained at that level throughout the test. Again, there were several periods during which larger pressure excursions occurred but none that approached the 4.14×10^5-N/m^2 (60-psi) level observed during the first test.

As can be seen from Figures 2 and 3, the catalyst bed pressure drop ΔP_{bed}, varied noticeably during these tests. An increase in ΔP_{bed} as a function of operating time is commonly observed in hydrazine reactors. Since a pressure differential of $\sim 6.9 \times 10^5$ N/m^2 (100 psi) may result in the physical crushing of the catalyst, this valve is often used as an indication of when the bed life has been expended. This level was reached during the first test (see Figure 2), but surprisingly the ΔP_{bed} then decreased during later stages of the test and remained relatively constant during the entire second test (see Figure 3).

During both tests, but most noticeably during the first, there were apparent slow movements of the primary reaction zone or "flame front" within the catalyst bed. This was detected both by visual observation of the reactor exterior and by the temperature measurements taken within the bed itself. As is usual in experimental reactor tests, where attainment of maximum performance is not a major goal, the flight insulation was removed from the

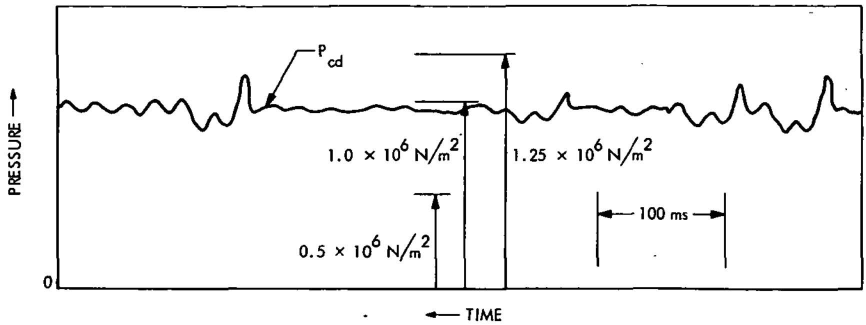

Figure 4. Typical oscillogram record

reactor walls. This allows a more convenient test stand installation, additional instrumentation, and visual observation of the reactor. Since there is no cooling other than radiation and natural convection, the reactor wall temperature is very nearly that of the reaction products, between 1100 K (~1500°F) and 1500 K (~2200°F). The chamber becomes incandescent during operation, and there is an axial temperature gradient in the catalyst bed. Thus, the color of the wall varies from a light, bright orange near the injector to a dull red at the bed exit.

During the first test, the axial location of the highest temperature (light orange) region moved slowly toward the exit of the catalyst bed and then back to its original location. The total movement was on the order of 1.27 cm (½ in.). In addition, a circular region, about 1.9 cm (¾ in.) in diameter, of low temperature developed about halfway down the chamber. This "cool" spot was observed to move slowly both axially and circumferentially. No such phenomena were observed during the second test of this series.

The description of the reactor exterior given above is of necessity general and qualitative since it is the result of visual observations by the test personnel and no photographic records were made. Definitive temperature measurements were made within the catalyst bed at the locations shown in Figure 1. The bare junction thermocouples used were similar to those described in Reference 2 except that the wire guards were not used. The data from these thermocouples are shown in Figures 2 and 3. They also indicate an apparent movement of the reaction zones during the first test and little or no movement during the second.

For a given reactor, i.e., one for which the catalyst size, the catalyst bed diameter, and catalyst bed length are fixed, the pressure drop across the bed can be correlated by means of two additional parameters. These are the propellant mass flowrate per unit cross-sectional area of the bed, G, and the catalyst bed porosity, ϵ, which is a measure of how tightly the catalyst particles are packed together. Implicit in the above statement is the assumption that the "flame front" occupies a unique axial position in the bed for each combination of ϵ and G. This is so because the pressure drop results primarily from the flow of the low-density, high-velocity gases downstream of the "flame front." Thus, any change in the position of the "flame front" would alter the length of the gas flow path and hence the pressure drop.

The possibility of the "flame front" movements resulting from changes in the degree of particle packing (i.e., porosity) was investigated.[2] This was done utilizing the computer programs described in Reference 3. The results were negative in that while reasonable changes in ϵ produced changes in ΔP_{bed} of the magnitude observed experimentally, there was virtually no change in the predicted axial temperature gradient. Thus, the conclusion must be that the experimentally observed phenomenon results from variations in some reactor property not considered in the models of Reference 3. It may be conjectured, based on the continuing work of Reference 4, that this property is the catalyst activity. The catalyst activity could vary because of adsorption of the decomposition products on the active catalytic sites. This "poisoning" might progress axially in the bed and would be expected to be reversible if the inactive catalyst were heated. Note that this could explain "washout" as well as the phenomenon described above, but it must be emphasized that this explanation is preliminary and conjectural, and is yet to be proven by experiment.

Conclusions and Recommendations

Based on the results of the two 1000-s tests described above, the following conclusions concerning "washout" and catalytic reactors in general have been reached:

(1) Our understanding of the "washout" phenomenon is only superficial. While many of the factors which play a rôle have been identified, the underlying processes remain virtually unknown.

(2) The Mariner Mars 1969 reactor is resistant to "washout," although our understanding of why this should be is incomplete. As a corollary, the Mariner Mars 1969 reactor also appears to be capable of a much longer operating time than rated, after minor internal modifications.

(3) Our knowledge of the basic processes taking place within a catalyst bed in general is only partially complete. The work of Kesten and coworkers has shed much light on this subject, but as yet the slow thermal transients observed cannot be explained except by conjecture.

[2] Variations in G were eliminated as the source since the magnitude of the ΔP_{bed} and G changes are not compatible with any existing correlations. Rather the G variations must be merely a result of changes in ϵ.

(4) Further study of the fundamental processes that occur within a catalyst bed, and even within a catalyst particle itself, is recommended. In particular the phenomenon of "washout" is the subject of an ongoing JPL program for fiscal year 1972.

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