Regression Rates of Nonmetalized Hybrid Fuel Systems

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A laboratory-scale slab burner has been used to characterize the regression rate of three different binder compounds with oxidizers varied from 100% fluorine to 100% oxygen. The oxidizer flow rate and pressure were varied from 0.014 to 0.17 lb/in.^{2}-sec and 20 to 160 psia, respectively. In the regions of low flow rate, the regression rate was independent of pressure and increased as the 0.8 power of the specific total flow rate for each of the propellant formulations studied. At the higher flow rates, the regression rate was nearly independent of flow but increased markedly with pressure. Increasing the percent oxygen resulted in a reduction in the regression rate. The classical hybrid regression rate law was extended to include the effects of condensed-phase surface products and nonunity Prandtl number. Agreement between experimental and predicted regression rates was good in the low flow-rate regions where regression rates were independent of pressure. However, the classical turbulent heat-transfer model did not account for the observed pressure dependence of regression rate in the high flow-rate regions. Rate-limiting chemical kinetic processes were postulated as the most likely cause of the observed pressure dependence.

Nomenclature

B = thermodynamic blowing-rate parameter, $h_f - h_w/\Delta h_g$
D = instantaneous duct diameter, in.
G = local total specific mass flow rate, lb/in.^{2}-sec
h_f = enthalpy of combustion gases at theoretical flame temperature, kcal/100 g
Δh_g = heat of gasification of fuel grain, kcal/100 g
h_w = enthalpy of decomposed fuel gases at equilibrium wall temperature, kcal/100 g
Pr = Prandtl number of gas mixture, $(C_p\mu/k)_{\text{mix}}$
r = local linear regression rate, in./sec
x = distance from leading edge of grain, in.
λ = weight fraction of gas in decomposed fuel grain at equilibrium wall temperature
μ = viscosity of the gas mixture, lb/in.-sec
ρ_f = solid fuel density, lb/in.^{3}

Introduction

RECENT emphasis toward the development of hybrid rocket motor systems has been accompanied by supporting fundamental studies of hybrid regression rate mechanisms. Theoretical models have been postulated previously for prediction of regression rate for both fully developed and boundary-layer flow. Predicted regression rates have been in good agreement with experimental values for simple systems for a limited number of comparisons. However, there has been a lack of reported work in comparing measured regression rates with predicted values for systems that produce condensed phases on decomposition of the fuel grain and for systems with oxidizers other than oxygen. In addition, the limited published experimental data have indicated little or no pressure dependence of regression rate.[1–3]

In the work described herein, the effects of fuel grain formulation, oxidizer formulation, oxidizer flow rate, and burner pressure were experimentally determined for nonmetalized systems using a laboratory slab burner. These regression rates were compared with values predicted using a form of the classical heat-transfer regression rate law, modified to account for condensed phases at the wall. Examinations were made of possible mechanisms of pressure dependence of regression rate and pressure flow-rate coupling.

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Regression Rate Theory

Previous experimental and theoretical research has led to the development of a mathematical model for predicting the regression rate of a hybrid grain. Models have been advanced by several investigators[1,4–7] in many cases with different approaches, but each leading to essentially the same regression rate law. In each case, the basic premise has been that the regression rate is controlled by heat transfer from a reaction zone or a freestream to the pyrolyzing wall. Probably the first proposed was that of Bartel and Rannie.[7] The work of Marxman, et al.[1] represents the most comprehensive description of characteristics of the combusting boundary layer for the heat-transfer "controlled" combustion. Influences of radiation have been treated by at least two investigators.[1,5] Influences of nonunity Prandtl, Schmidt, or Lewis number have been discussed generally for reacting boundary layers[8] and also applied to the hybrid combustion problem.[6] Green has recently summarized the theoretical developments of hybrid combustion phenomena.[6]

The Colburn analogy approach[4] to the derivation of the hybrid regression rate, including influences of radiation and Prandtl number, was extended to include the effects of con-

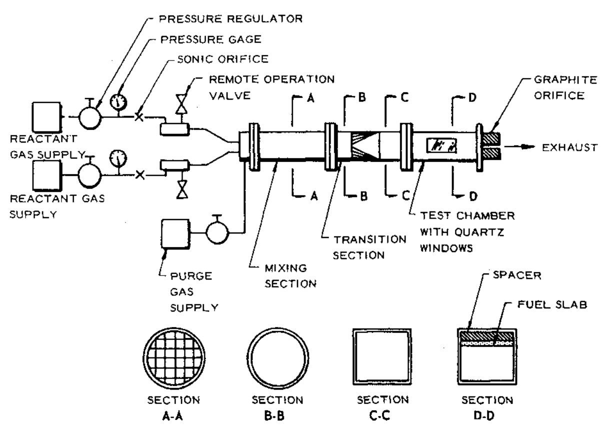

Fig. 1 High-pressure slab burner flow schematic.

densed species at the wall. Development of this regression rate law, together with assumptions, is shown in detail elsewhere in the literature.[9]

The results for the turbulent boundary layer and turbulent fully-developed flow cases are as follows:

Boundary layer

$$r = 0.03(G^{0.8}/\rho_f\lambda)\ (\mu/x)^{0.2} \ln[1 + (\lambda B/Pr^{2/3})] \quad (1)$$

Fully-developed turbulent flow cylindrical ducts

$$r = 0.023(G^{0.8}/\rho_f\lambda)\ (\mu/D)^{0.2} \ln[1 + (B\lambda/Pr^{2/3})] \quad (2)$$

The regression rate predicted by Eq. (1) is a local value at a specific distance from the leading edge of the grain. The value predicted by Eq. (2) is an instantaneous value for a specific duct diameter. The specific unit area mass flow rate is a total flow rate for both fuel and oxidizer at the point and time for which the regression rate is being evaluated.

Prediction of the regression rate required a numerical evaluation of the thermodynamic and transport quantities: μ, Pr, Δh_g, λ, h_w, and h_f. The first two quantities were predicted using conventional expressions for gas-phase mixtures.[10] For calculating Δh_g, λ, and h_w, it was assumed that the wall products were in thermodynamic equilibrium at the wall temperature. The enthalpy in the combustion region h_f was computed assuming thermal equilibrium of oxidizer and fuel at O/F ratios near the stoichiometric value, even though the O/F ratio is not precisely known. Evaluation of this enthalpy is not strongly sensitive to small changes in O/F ratio. Comparison of predicted and measured regression rates for the nonmetalized systems is shown following a presentation of experimental data.

Experimental Regression Rate Measurements

Laboratory Slab Burner

The influences of oxidizer flow and composition and total pressure on regression rate of binder/fluorine/oxygen systems were studied using a laboratory slab burner. A schematic diagram of the flow system is shown in Fig. 1. The burner operated at pressures between 20 and 160 psia.

Fuel slabs (1 in. wide, about $\frac{1}{2}$ in. thick, and up to 15 in. long, though generally 6 in. in length) were placed in the slab burner with the leading edge of the slab tapered to minimize flow disturbances. Commercial high-pressure gas containers equipped with regulator and pressure gage were used as a source of oxidizer. The metered sources of mixed reactant and diluent gases were supplied to the burner through mixing and flow straightening sections at rates from 0.014 to 0.17 lb/in.^{2}-sec. The burner itself was fitted with either a single slab or two opposing slabs. The burner walls have provision for holding optically transparent windows for photographic investigation of combustion processes. The burner pressure was controlled by a graphite orifice from which the hot gases were exhausted to the atmosphere.

The tests were generally conducted for periods of from 3 to 10 sec. Regression rate was computed from burn time together with micrometer measurement of the slab before and after the firing. Pressure and flow were recorded continuously during the firings.

Experimental Results

Summary of Experiments

Regression rate experiments were performed using binder fluorine/oxygen propellant systems. Butyl rubber, PBAA (Polybutadiene-acrylic acid copolymer), and polyurethane grains were investigated. Oxidizer composition was varied from 100% fluorine to 100% oxygen. A summary of the range of variation of fuel and oxidizer composition, oxidizer flow rate, and pressure is shown in Table 1.

Evaluation and Reproducibility of Regression Rate Measurements

No attempt was made to determine the variation of regression rate with time. All regression rates reported were averaged over the entire burn time. Regression rates were measured at five positions along the 6-in. grains and averaged with respect to length. Total flow rates also were averaged over both time and slab length. For the short burn times studied, changes in the duct cross-sectional area were small. Consequently, the average regression rate and average flow rate reported correspond very closely to the local values halfway (3 in.) down the slab. Comparison of predicted and measured regression rates are based on the latter case. Regression rates were generally reproducible within ±5%.

Effect of Flow Rate and Oxidizer Composition

Variation of flow rate and percent oxygen in the fluorine/oxygen system was extensively studied for the 100% butyl rubber grains. Data for this grain with oxygen percentages of 0, 30, 60, and 100% are shown in Fig. 2 for nominal pressures of 60 psia. Each decrease in fluorine percentage corresponded to a near exponential decrease in the regression rate. Regression rates for all oxidizers correlated with 0.8-slope lines in the low flow-rate regions (<0.07 lb/in.^{2} sec). In high flow-rate regions, rates were less dependent on flow rate for all oxidizer compositions studied. Experimental regression rates shown in Fig. 2 were for burner pressures between 50 and 80 psia.

Effect of Burner Pressure

Effects of pressure variation of regression rate coupled with variation of flow rate are shown in Figs. 3–6 for butyl rubber grains, Fig. 7 for PBAA grain, and Fig. 8 for the polyurethane. The butyl rubber data for varying oxidizer compositions shown in Figs. 3–6 indicate a strong coupling between flow and pressure. At low flow rates and for all pressures, the regression rate varied about as 0.8 power of the specific total flow rate. For higher flow rates, the regression rate becomes

Table 1 Summary of slab burner experiments

Grain formulation	Pressure range, psia	Oxidizer composition range, F_2 (wt %)	Oxidizer composition range, O_2 (wt %)	Specific oxidizer flow rate, lb/in.^{2}-sec	No. of experiments
100% Butyl rubber	21–156	0–100	100–0	0.014–0.16	72
100% PBAA	29–141	70	30	0.028–0.17	28
100% Polyurethane	18–129	0–100	100–0	0.03–0.17	11
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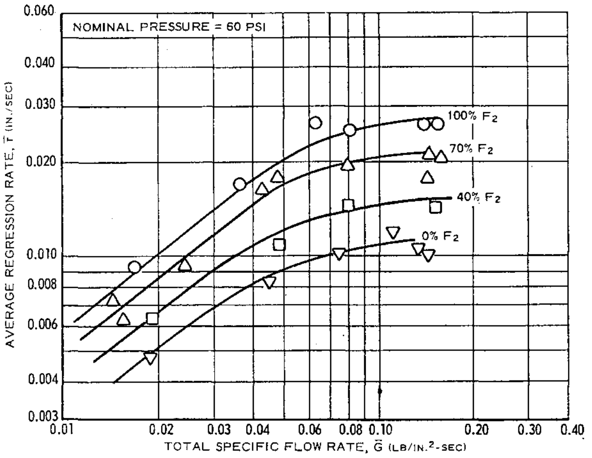


Fig. 2 Effect of total specific flow rate and oxidizer composition on the regression rate of butyl rubber grains with fluorine/oxygen oxidizer.

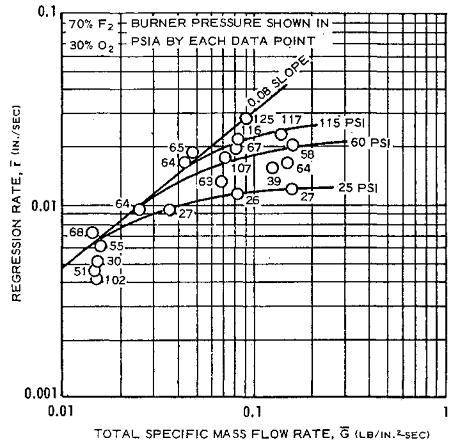


Fig. 4 Effect of total specific flow rate and pressure on the regression rate of butyl rubber grains with 70%F_2/30% O_2 oxidizer.

independent of flow rate, especially at lower pressures. For constant flow rate, increasing the pressure increases the regression rate until the 0.8-slope line is again reached, at which time further increases in pressure have little or no effect on regression rate.

The data for the PBAA grains with 70% F_2/30% O_2 oxidizer (shown in Fig. 7) are very similar in both magnitude and pressure dependence to that for the butyl rubber grains. However, for middle flow-rate ranges ($0.07 < G < 0.10$), the influence of pressure is not entirely consistent with the picture presented by the butyl rubber grains. For some cases, regression rate does not increase with increasing pressure. At higher flow rates, regression rates did continually increase with increasing pressure.

The data for the polyurethane (shown in Fig. 8) are principally with 100% fluorine, although three data points for 100% oxygen are also shown. Again a strong influence of flow rate, pressure, and oxidizer composition is shown.

Comparison of Regression Rates of Butyl Rubber, PBAA, and Polyurethane Grains

There is little evidence to indicate any difference in the regression rates of any of the three binders with the same oxidizers. The data of Figs. 3 and 8 for butyl rubber and polyurethane with 100% fluorine exhibit the same general magnitude and pressure dependence. A similar conclusion is drawn from a comparison between the data of butyl and PBAA with 70% fluorine/30% oxygen.

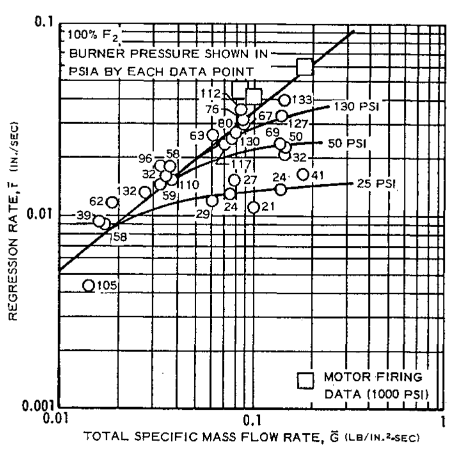


Fig. 3 Effect of total specific flow rate and pressure on the regression rate of butyl rubber grains with 100% F_2 oxidizer.

The differences in molecular structure and composition of these three binder materials, or their prepolymers, are shown in Table 2. The butyl rubber contains no oxygen, although the polyurethane binder contains over 25 wt-% of oxygen in the basic chain itself. Yet little differences were detected in the regression rates of these binders.

Comparison of Slab Burner and Motor Firing Data

Figure 3 also showed two motor regression rate values for 100% butyl rubber/100% halogen at high pressure. Agreement with the convective heat-transfer correlation is excellent, indicating only slightly higher regression rates from motor firings. The oxidizer was ClF_3 rather than pure fluorine.

Comparison of Predicted and Experimental Regression Rates

The hybrid regression rate model Eq. (1), based on turbulent boundary-layer heat transfer, predicts regression rates that are independent of pressure. The model will not account for the observed pressure dependence of regression rates shown in Figs. 3–8. However, for the lower flow-rate regions studied, regression rate was independent of pressure. Comparisons between measured and predicted regression rate have been made for this region.

Regression rates were computed as a function of wall temperature and O/F ratio using Eq. (1) for each of the binder/oxidizer systems studied. Results for butyl rubber

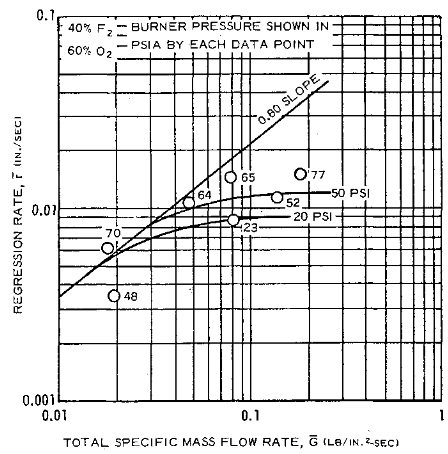


Fig. 5 Effect of total specific flow rate and pressure on the regression rate of butyl rubber grains with 40%F_2/60% O_2 oxidizer.

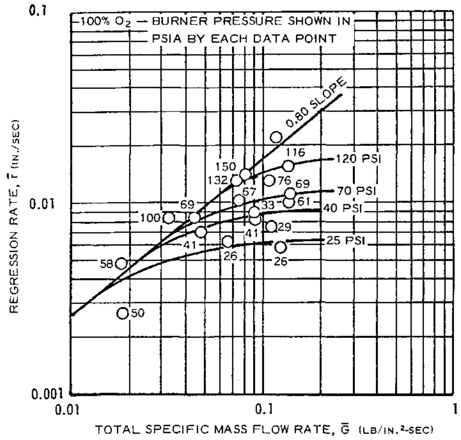


Fig. 6 Effect of total specific flow rate and pressure on the regression rate of butyl rubber grains with 100% O_2.

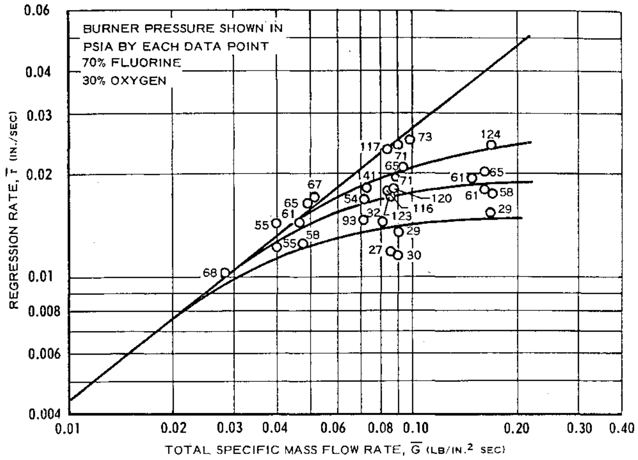


Fig. 7 Effect of total specific flow rate and burner pressure on the regression rate of polybutadiene-acrylic acid copolymer grains with fluorine/oxygen oxidizer.

grains with oxidizer compositions of 100% fluorine and 100% oxygen are illustrated in Figs. 9 and 10, together with the experimental data that were nearly pressure insensitive. A 200°K increase in assumed equilibrium wall temperature decreases predicted regression rates by 30 to 50%. Changes in O/F ratio caused only small changes in predicted regression rates.

Wall temperatures required to give exact agreement between predicted and measured regression rates are shown in Table 3 for each of the binder/oxidizer systems studied. The assumed O/F ratios for this comparison were near the stoichiometric values.

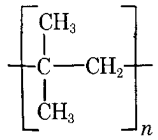
Results for butyl rubber (Table 3) indicate a slowly increasing surface temperature with increase in percent oxygen in the oxidizer. It is not certain whether the wall temperature actually does increase. It is more likely that the change in oxygen concentration causes a change in the regression rate mechanism not accounted for by Eq. (1). Predicted wall temperatures for polyurethane, PBAA, and butyl rubber grains for the same oxidizer were approximately the same.

Also of interest is the regression rate dependence on flow. The model predicts an 0.80 slope, and the data of Figs. 3–7 do

Table 2 Structure of polymer fuels

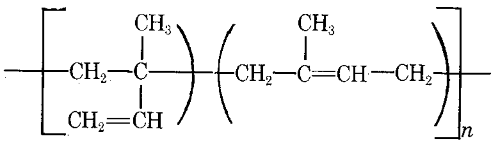
I. Butyl rubber polymer

a) Polyisobutylene, 96% (wt)

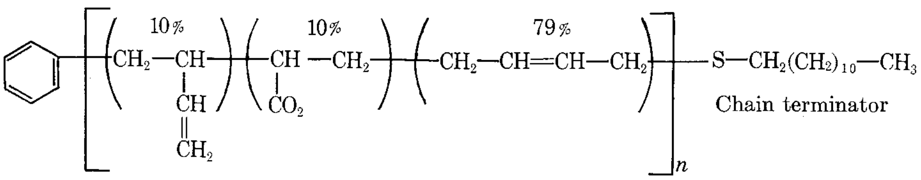


b) Polyisoprene, 2%

Minor Major

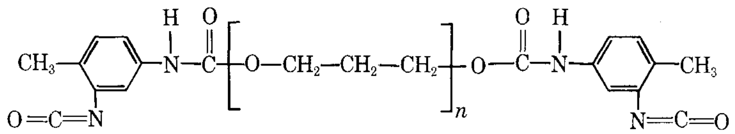


II. PBAA: Polybutadiene-acrylic acid copolymer



Chain initiator Basic chain

III. Polyurethane prepolymer



Chain initiator Basic chain Chain terminator

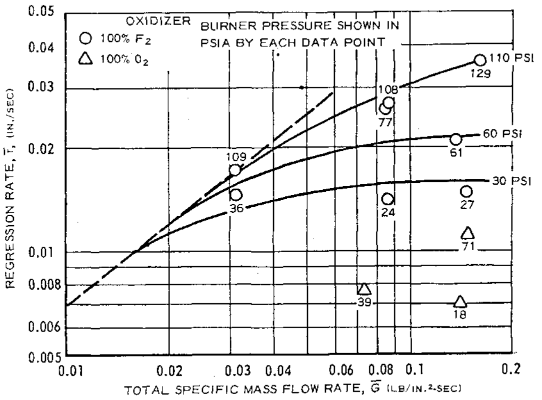


Fig. 8 Effect of total specific flow rate, burner pressure, and oxidizer composition on the regression rate of polyurethane fuel slabs.

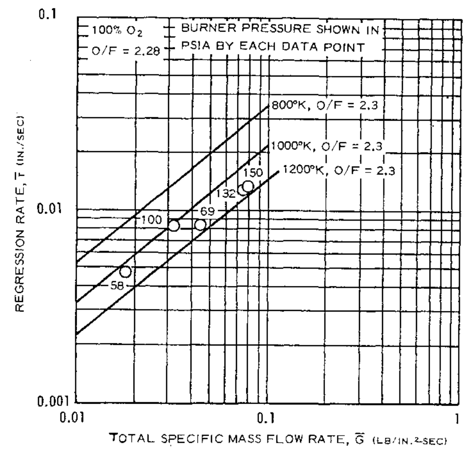


Fig. 10 Comparison of predicted and measured regression rates for butyl rubber grains with 100% O_2 oxidizer.

not support a slope different from this value.

Excellent agreement between predicted and measured regression rates for the Plexiglas system has previously been shown.[1] However, variation in pressure was not studied.

Pressure Dependent Mechanisms

A general definition of different regions of combustion for the butyl rubber system is shown in Fig. 11. For low oxidizer flow rates, the regression rate was found to vary as the 0.8 power of the flow rate and independently of pressure, as shown in region I. For the high flow rates in region III, the regression rate was found to be strongly proportional to pressure and independent of flow rate. For the intermediate region II, the regression rate varied with both flow and pressure. At a constant flow rate, increases in chamber pressure resulted in regression rate increases, until the upper limit of the line of 0.8 slope was reached. Then, further increase in pressure did not affect the regression rate. The PBAA and polyurethane binder systems behaved similarly. This same general pressure-flow-rate coupling was observed with metalized hybrid systems both in laboratory scale experiments and in motor firings.[11] However, for the metalized systems, pressure dependence was generally reduced. Possible pressure-dependent mechanisms have been considered in light of the experimental data reported.

Radiative heat-transfer rates increase with increasing pressure. For very high flow rates, when convective heat-transfer rates are high and radiative transfer small compared to convective transfer, the pressure sensitivity should be small. At very low flow rates, the convective heat-transfer contribution would eventually become negligible, in which case the regression rate would be independent of flow rate. The resultant regression rate, now dependent on radiative heat transfer, would be more pressure sensitive. The pressure dependence would then be expected to be most predominant at the lower flow rates, decreasing with increasing flow. This expected pressure flow-rate dependence from radiation-convection coupling has been predicted using the radiation-convection model[9] and is just opposite from that measured experimentally. Consequently, though radiation has in some cases been demonstrated to contribute to the magnitude of the regression rate, it is not held responsible for the observed pressure dependence of the data cited herein.

At low pressures, the heat of gasification, wall enthalpy, and weight fraction of gas at the wall are known to be pressure sensitive. However, variation of pressure from 30 to 100 psi caused only a 15% increase in the weight fraction gas, a 15% decrease in the heat of gasification, no change in the wall enthalpy, and almost no effect on the predicted regression rate. Consequently, secondary influences of pressure on the rate of heat flux to the surface cannot explain the observed pressure dependence.

Strong pressure dependence has been observed with both binder/fluorine and binder/oxygen systems. The carbon does not combust in the binder/fluorine systems. Consequently, the pressure dependence cannot be attributed to a carbon-oxidizer reaction.

It has been shown[11] that decreases in percent binder with resultant increases in metalized ingredients reduce pressure dependence while also making the ignition more difficult.

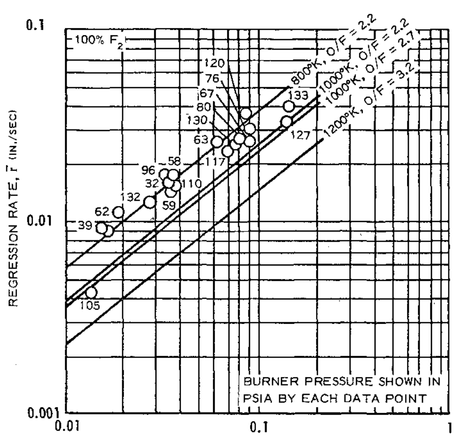


Fig. 9 Comparison of predicted and measured regression rates for butyl rubber grains with 100% F_2 oxidizer.

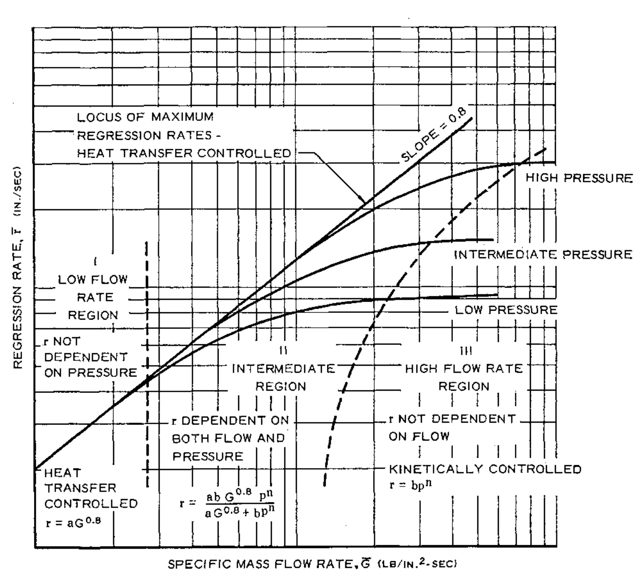


Fig. 11 Pressure and flow-rate dependence of typical nonmetalized hybrid systems.

Table 3 Equilibrium wall temperature required to produce exact agreement between predicted and experimental regression rates

Grain	Oxidizer (wt %) F_2	Oxidizer (wt %) O_2	Assumed O/F ratio	Equilibrium wall temperature, °K
Butyl rubber	100	0	2.2	800–900
Butyl rubber	70	30	3.2	800–1000
Butyl rubber	40	60	2.7	900–1000
Butyl rubber	0	100	2.3	1000–1100
PBAA	70	30	3.5	950–1000
Polyurethane	100	0	1.9	800–900

The binder systems seem to be directly associated with the observed pressure dependence. The butyl rubber, polyurethane, and PBAA binders, though different structurally and in composition, regress at nearly the same rate with nearly the same pressure dependence. Thermal pyrolysis of the binder would then not be expected to be responsible for the pressure dependence.

The reported data do not dispute the possibility of either fuel-oxidizer gas-phase reactions or gaseous oxidizer-solid fuel heterogeneous reaction. Both of the processes are pressure dependent, but the heterogeneous reaction is related only to the oxidizer partial pressure.

Recent unpublished data from this laboratory tended to support the heterogeneous mechanism as causing the observed pressure dependence. This evidence will be reported when the present work is complete.

Conclusions

For the turbulent flow range, the regression rate was predicted to be a function of the 0.8 power of total specific flow rate and independent of pressure. Unknown quantities that must presently be assumed or measured to predict regression rate are O/F ratio and equilibrium wall temperature. Predicted regression rates were insensitive to O/F ratio variation. However, 200°K increases in assumed wall temperature caused 30 to 50% decreases in predicted regression rate.

Regression rates were measured over a wide range of variation for the butyl rubber/fluorine/oxygen, PBAA/fluorine/oxygen, and polyurethane/fluorine/oxygen systems using a laboratory slab burner. Increasing percent fluorine from 0 to 100% produced substantial increases in regression rate over the entire range. The regression rate varied exponentially with percent fluorine. The nature of the pressure dependence did not seem to depend on the oxidizer composition.

Increasing burner pressure in low flow-rate regions had little or no effect on regression rate. At higher flow rates, increases in pressure caused increases in regression rate up to a maximum governed by heat-transfer limitations.

At low flow rates, regression rate varied as the 0.8 power of the flow for all propellant systems studied. At higher flow rates and lower pressures, regression rate was independent of flow rate.

Little difference in regression rate characteristics was observed between butyl rubber, PBAA, and polyurethane binder systems. For intermediate flow-rate regions, variation of PBAA regression with pressure change was irregular. Limited regression rate data for the butyl rubber system from motor firings were in good agreement with slab burner results.

The regression rate model predicted the 0.8-power flow-rate dependence of regression rate in the low but turbulent flow-rate regions. But it did not predict the observed pressure dependence of regression rate.

Several possible mechanisms were investigated to account for the observed pressure dependence. Heterogeneous attack of active oxidizer on the fuel binder offered the most feasible explanation of this pressure dependence.

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