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FOREWORD

This quarterly progress report covers the research accomplished under Contract Nonr 3016(00) through 28 February 1962. The personnel associated with this program were Dr. M. V. Peck and Dr. T. Houser. Dr. S. S. Penner was a consultant.

ABSTRACT

The combustion processes of four fuels with gaseous oxygen at two flowrates were investigated. The mass burning rates were determined for sheet stock and cast plexiglass, 30-percent aluminum in plexiglass, polystyrene and polyethylene. The burning behavior of polystyrene which was different from that of the other fuels can be explained by diffusion considerations. The mass regression rate of plexiglass was found to decrease with burning time for the two oxygen flowrates investigated, which is consistent with a diffusion mechanism.
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INTRODUCTION

The present research program in hybrid combustion has been concerned with the investigation of the processes involved in the reactions between solid fuels and gaseous oxidizers. The purpose of these studies, in the presence of a flame, has been to develop a suitable model for the hybrid combustion processes.

In previous Reports (Ref. 1, 2, 3, and 4), the experimental results for the hybrid combustion of plexiglass and gaseous oxygen were shown to be consistent with the idea that the combustion rate is largely controlled by diffusion processes. On the basis of arguments involving the hypothesis that a flame front is established not necessarily at, but correlated with, the edge of the laminar boundary layer in laminar flow and at the buffer layer in turbulent flow, a model was demonstrated for that system. By further exploiting this argument, a simplified theory of hybrid combustion of the same order of sophistication as the classical treatment of Burke and Schumann (Ref. 5) for the flame shape in cylindrical, laminar diffusion flames was presented for the plexiglass-oxygen system in the laminar regime (Ref. 1).

To test the general applicability of the postulations for the plexiglass-oxygen system, other solid fuels also were studied. The mass burning rates of polystyrene and polyethylene fuels were investigated for two gaseous oxygen flowrates. The reproducibility of data with the 30-percent aluminum in plexiglass fuel at the higher oxygen flowrates was improved with a modification of the apparatus.
EXPERIMENTAL PROCEDURE

The basic apparatus illustrated in Fig. 1 has been described in a previous report (Ref. 1). The tubular configuration is used for the present experimental program. In a standard run, a 24-inch-long fuel cylinder, composed of twelve 3 by 3 by 2-inch blocks with the 1-inch-diameter concentric holes aligned with the holes of the facing and backing plates, is burned for 60 seconds. To prevent pressure fluctuations with metalized fuels because of slag buildup at the terminal end, a backing plate with an enlarged outlet diameter of 2-1/2 inches is now employed. This is used for most runs in order to present data taken at identical conditions. A temperature probe and pressure gage at the oxidizer flowmeter were added to permit more accurate measurement of the oxidizer flowrate.
RESULTS

VARIATION OF MASS REGRESSION RATE WITH AXIAL LENGTH FOR THE PLEXIGLASS-OXYGEN SYSTEM

With the improved metering system for the oxidizer flow, the flowrates can be more accurately measured and corrected. Six runs of 60 seconds duration were made at known oxygen flowrates with sheet plexiglass fuel using the backing plate with a 1-inch-diameter outlet. In Fig. 2, the burning rate data for these runs are plotted together with the data taken previously on this system. From the new data, the correct entrance Reynolds numbers can be established for most of the previous data. The values of $Re_{2r}$ are indicated on Fig. 2. The data previously reported for entrance $Re_0$ Reynolds numbers at 58,000 and 5800 are in agreement with the present data at 56,600 and 6000, respectively.

Runs were made with 2-foot-long combustors of sheet stock plexiglass and cast plexiglass at two oxygen flowrates. A backing plate with a large-diameter outlet was utilized. Figure 3 illustrates that there is no appreciable difference in the burning characteristics of the plexiglass made by two production methods.

EFFECT OF BURNING TIME ON MASS REGRESSION RATE FOR PLEXIGLASS-OXYGEN SYSTEM

The results of the effect of burning time upon the mass burning rates of plexiglass are summarized in Fig. 4 and 5. Two-foot-long blocks were cast by the supplier of the cast metallized blocks.

R-2267-6
Figure 2. Burning Rate Based on Arithmetic Average Diameter and 60-Second Burning Time vs Axial Length

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>RUN NO.</th>
<th>Re&lt;sub&gt;2r&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>1339</td>
<td>7900</td>
</tr>
<tr>
<td>△</td>
<td>1340</td>
<td>74,900</td>
</tr>
<tr>
<td>△</td>
<td>1341</td>
<td>36,600</td>
</tr>
<tr>
<td>△</td>
<td>1342</td>
<td>99,000</td>
</tr>
<tr>
<td>□</td>
<td>1443</td>
<td>56,600</td>
</tr>
<tr>
<td>●</td>
<td>1444</td>
<td>6000</td>
</tr>
</tbody>
</table>

**NEW DATA**

**PREVIOUS DATA**

\[
m, \text{ MASS BURNING RATE} \times 10^3 (g/cm}^2 \cdot \text{SEC})
\]

\[
z, \text{ AXIAL SAMPLE LENGTH, CENTIMETERS}
\]

\[
z, \text{ AXIAL SAMPLE LENGTH, INCHES}
\]
Figure 3. Comparison of Mass Burning Rates of Sheet-Stock Plexiglass and Cast Plexiglass
Figure 4. The Effect of Burning Time on Mass Regression Rates for Plexiglass With Oxygen at ReO₂ 6000

\[ \text{mass burning rate} \times 10^3 (\text{g/cm}^2 - \text{sec}) \]
Figure 5. The Effect of Burning Time on Mass Regression Rates for Plexiglass With Oxygen at $Re_{2r_0} = 56,600$
combustors of plexiglass were burned for 30, 60, 90, and 120 seconds with oxygen at \( Re_{2r} = 6000 \). The mass burning rate vs axial length curves are shown in Fig. 4. At \( Re_{2r} = 56,600 \), runs were made for 30, 45, 60, 75, 90, and 120 seconds, and the mass burning rate vs axial length curves are presented in Fig. 5. In general, the mass burning rates decrease with increase in burning time. At \( Re_{2r} = 6000 \), the mass burning rate for all burning times first decreases, then levels off. At approximately 10 inches, the burning rates for the various burning times begin to decrease more rapidly. For the higher flowrate \( (Re_{2r} = 56,600) \), the mass burning rate decreased and then increased for all burning times.

Typical point burning rates of plexiglass at two axial positions for two oxygen flowrates are given in Table 1. In general, not only does the mass burning rate \( \dot{m} \) (g/cm\(^2\)-sec) decrease with time, but the rate of mass consumed per unit time \( \dot{m}_t \) (g/sec) also decreases.

**STUDIES OF OTHER FUELS WITH OXYGEN**

The burning characteristics of polystyrene (PS), polyethylene (PE), and 30-percent aluminum in plexiglass (30 percent Al-PMMA) with oxygen were investigated at two oxygen flowrates. The mass burning rate vs axial length curves for these fuels at \( Re_{2r} = 6000 \) and 56,600 are shown in Fig. 6 and 7, respectively; as a comparison, the curves for plexiglass were also included. Typical \( \dot{m}, r \) (surface regression rate cm/sec), and \( \dot{m}_t \) values are given in Table 2 for the fuels at \( Re_{2r} = 56,600 \).

Liquid polyethylene was observed to pour out the end of the combustor during the runs at both flowrates and, thus, the mass burning rate data which were lower than for plexiglass over most of the combustor length cannot be expected to be of much value. However, it should be noted that the mass burning rate for this fuel behaved similarly to plexiglass.
TABLE 1

THE POINT BURNING RATES* OF PLEXIGLASS

\[
\begin{align*}
\text{Re}_{2r_0} &\leq 6000 \\
\nu_{2r_0} &\leq 358 \text{ cm/sec}
\end{align*}
\]

\[
\begin{align*}
z = 5 \text{ inches} &\quad & z = 11 \text{ inches}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time, seconds</th>
<th>( \dot{m}_r ), g/cm(^2) - sec</th>
<th>( \dot{r}_r ), cm/sec</th>
<th>( \dot{m}_t ), g/sec</th>
<th>( \dot{\dot{m}}_r ), g/cm(^2) - sec</th>
<th>( \dot{r}_t ), cm/sec</th>
<th>( \dot{m}_t ), g/sec</th>
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</thead>
<tbody>
<tr>
<td>30</td>
<td>0.00561</td>
<td>0.0023</td>
<td>0.24</td>
<td>0.00494</td>
<td>0.0021</td>
<td>0.21</td>
</tr>
<tr>
<td>60</td>
<td>0.00511</td>
<td>0.0021</td>
<td>0.23</td>
<td>0.00487</td>
<td>0.0021</td>
<td>0.22</td>
</tr>
<tr>
<td>90</td>
<td>0.00486</td>
<td>0.0020</td>
<td>0.22</td>
<td>0.00473</td>
<td>0.0020</td>
<td>0.22</td>
</tr>
<tr>
<td>120</td>
<td>0.00453</td>
<td>0.0019</td>
<td>0.21</td>
<td>0.00439</td>
<td>0.0019</td>
<td>0.21</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Re}_{2r_0} &\leq 56,600 \\
\nu_{2r_0} &\leq 3360 \text{ cm/sec}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time, seconds</th>
<th>( \dot{m}_r ), g/cm(^2) - sec</th>
<th>( \dot{r}_r ), cm/sec</th>
<th>( \dot{m}_t ), g/sec</th>
<th>( \dot{\dot{m}}_r ), g/cm(^2) - sec</th>
<th>( \dot{r}_t ), cm/sec</th>
<th>( \dot{m}_t ), g/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.01515</td>
<td>0.0127</td>
<td>0.71</td>
<td>0.01394</td>
<td>0.0117</td>
<td>0.64</td>
</tr>
<tr>
<td>45</td>
<td>0.01370</td>
<td>0.0115</td>
<td>0.70</td>
<td>0.01252</td>
<td>0.0105</td>
<td>0.60</td>
</tr>
<tr>
<td>60</td>
<td>0.01268</td>
<td>0.0107</td>
<td>0.64</td>
<td>0.01176</td>
<td>0.0099</td>
<td>0.59</td>
</tr>
<tr>
<td>75</td>
<td>0.01180</td>
<td>0.0099</td>
<td>0.62</td>
<td>0.01143</td>
<td>0.0096</td>
<td>0.59</td>
</tr>
<tr>
<td>90</td>
<td>0.01190</td>
<td>0.0100</td>
<td>0.65</td>
<td>0.01090</td>
<td>0.0092</td>
<td>0.59</td>
</tr>
<tr>
<td>120</td>
<td>0.01079</td>
<td>0.0091</td>
<td>0.62</td>
<td>0.00982</td>
<td>0.0083</td>
<td>0.55</td>
</tr>
</tbody>
</table>

*Point burning rates are determined from the weight loss of each 2-inch-long block and the value is assigned to the midpoint of the block.
Figure 6. Mass Burning Rate vs Axial Length for Polymers
With Oxygen at $Re_{2r_o} \approx 6000$
Figure 7. Mass Burning Rate vs Axial Length for Polymers with Oxygen at $Re_{2r_0} = 56,600$
### Table 2

Comparison of Point Mass Burning Rates at \( \text{Re}_{2r_0} = 56,600 \) for 60-Seconds Burning Time

<table>
<thead>
<tr>
<th></th>
<th>( z = 5 ) inches</th>
<th></th>
<th>( z = 11 ) inches</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \dot{m}_2 ) ( g/cm^2 \cdot \text{sec} )</td>
<td>( \dot{r}_2 ) ( cm/\text{sec} )</td>
<td>( \dot{m}_{t2} ) ( g/\text{sec} )</td>
</tr>
<tr>
<td>PE</td>
<td>0.00985</td>
<td>0.0107</td>
<td>0.50</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.01268</td>
<td>0.0107</td>
<td>0.64</td>
</tr>
<tr>
<td>30-Percent Al-PMMA</td>
<td>0.01636</td>
<td>0.0116</td>
<td>0.85</td>
</tr>
<tr>
<td>PS</td>
<td>0.02404</td>
<td>0.0227</td>
<td>1.50</td>
</tr>
</tbody>
</table>
The aluminized fuel burned much smoother with the large-diameter end plate, and the mass burning rate vs axial length curves for aluminized fuel are reproducible and similar in shape to those of plexiglass. Both the $\dot{m}$ and $\dot{r}$ values are higher for the aluminized fuels than for plexiglass, but the differences in $\dot{r}$ appear to be less than 10 percent. Thus, it appears that the increased mass burning rate can not be explained by the density difference.

Polystyrene exhibits the only unique mass burning rate vs axial length curve. The mass burning rates and surface regression rates for this fuel are considerably higher than for any of the other fuels at the same conditions. The fuel burned with a bright luminous flame, and a great deal of black smoke and vapor was observed during the runs which were very noisy. The burned surface of the polystyrene was pitted and blackened with carbon.
DISCUSSION

Burning rate has been shown (Fig. 2) to decrease with a decrease in Reynolds number, which is in agreement with a diffusion controlled mechanism. Since the Reynolds number is inversely proportional to the diameter of the hole in the fuel blocks, at a fixed mass flowrate of gas, the Reynolds number will decrease with burning time, thus causing the burning rate to decrease; this is shown in Fig. 4 and 5 and in Table 1. It is significant that not only does the linear burning rate ($\dot{r}$) decrease, but also the total mass burned/sec ($\dot{m}_t$) becomes lower at longer burn times even though the surface area of the fuel increases. The rate of a chemically controlled process would be expected to increase with surface area if pyrolysis was rate determining. Thus, a diffusion controlled mechanism is consistent with the above observation.

An alternative explanation for the observed decrease in $\dot{m}_t$ with burning time can be given if the surface temperature as a function of burning time is considered. Assuming, for this discussion, that approximate steady-state conditions are established shortly after the combustion starts, the amount of heat available from combustion at any $z$ is constant with time. Since the surface area increases with time, the calories available/unit area and the heat transfer rates as a result of convection, because of lower Reynolds numbers, decrease. Thus, the surface recession rates may decrease for either or both of the following reasons:

1. The rate of fuel consumption may be controlled by the rate of heat addition; i.e., the chemical rate of pyrolysis is rapid enough at the surface temperature to maintain that temperature constant, although the rate of heat addition may change.
2. The chemical kinetics of polymer pyrolysis may control the rate of fuel consumption; i.e., the surface temperature will be dependent on rate of heat addition, thus resulting in a partially chemically controlled process.

Since the experimental data can be explained by a diffusion controlled mechanism, it is believed that the above is not the major contributor to combustion rates, at least with plexiglass. Further investigation must be made to determine if the contribution is significant.

The mass regression rate vs axial length curves for polyethylene and the 30-percent aluminum fuels were found to be similar in shape to that of plexiglass. While the data for polyethylene may not be expected to be reliable because of the obvious flowing of liquid fuel during burning, it is significant that all three fuels exhibit similar burning characteristics. A comparison of the linear regression rates of the fuels shown in Table 2 reveals that there are differences in the magnitude of the rate of burning that cannot be explained by the density differences. With larger proportions of metal, the metal may exert a greater and different influence upon the over-all burning characteristics, but for the percent aluminum used thus far, the previously proposed model (Ref. 1) is satisfied.

Figures 6 and 7 show a marked difference in the burning-rate behavior of polystyrene (PS) when compared to the other polymers examined. Since the density of polystyrene is about 10 percent lower than that of plexiglass, the increase in burning rate is magnified by a comparison of the linear regression rates shown in Table 2. The following thermodynamic and mass transfer considerations can be used to explain, qualitatively, the observed behavior:
Because styrene is an endothermic compound, its pyrolysis and combustion will yield significantly higher flame temperatures than the corresponding process for methyl methacrylate; approximate calculations show a difference of about 800 K, assuming the monomers to yield CO and H$_2$O. Therefore, the gas temperatures, and thus the burning rates, in the sections of the combustor which still have significant concentrations of oxygen will be higher for styrene than for MMA.

2. The increased burning rate, shortly after the entrance, results in higher mass addition rates which cause a transition to turbulent flow at a position much closer to the entrance. Figure 6 shows this transition for PS combustion occurs at the second block for the lower Re$_{2r}$, whereas at higher flowrates a laminar region does not appear to exist (Fig. 7). The increased turbulence further increases the burning rate, which is consistent with the model previously proposed for PMMA burning.

3. The oxygen is consumed much more rapidly during PS combustion because of both stoichiometry (assuming CO and H$_2$O as products) and consumption rate; thus, the downstream gas temperature should start decreasing closer to the entrance. The color of the flame at the exit of the 24-inch firings indicated that the gas temperature at that point was lower for PS (dark orange and smoky) than for PMMA (yellow to blue). Thus, the relative gas temperatures of these systems appear to have been reversed, which is consistent with a more rapid temperature drop for the PS fuel. At the higher flowrates (Fig. 7), the effect of the

Optical pyrometry will be used to substantiate this observation.

It is known that the oxygen concentration does not decrease as rapidly as stoichiometry requires because of diffusion and/or chemical reaction-rate limitations. Thus, the actual drop in gas temperature will probably occur further downstream than stoichiometry would indicate for both systems.
lowering of the PS gas temperature apparently is offset by the increased consumption rates as a result of increased turbulence, which led to the horizontal portion of the curve; but at the lower flowrates, this was not the case and a drop in the consumption rate near the exit was observed (Fig. 6). If this qualitative description is correct, the consumption rate at the higher oxygen flowrate should drop off downstream sooner for PS than for PMMA.

The relative rates of pyrolysis of the polymers may also contribute to the regression rate, but the preferred mechanism can explain the observed behavior without considering pyrolysis. Although the relative rates of polymer degradation in a vacuum (Ref. 6) indicate that PS is more stable than PMMA at 350 C, the degradation rates under combustion conditions in the presence of gases flowing at high velocities may be quite different. If the influence of oxidizing gases on combustion rates due to a change in the fuel pyrolysis rates was significant, it would be necessary to modify the diffusion-combustion model to account for oxygen reaching the surface and to accommodate chemical kinetic effects.

Other investigators (Ref. 7) have made hybrid combustion studies with an enclosed fuel system of two 5 by 5-inch flat plates of fuel. The mass flows of oxygen (0.01 lb/sec) are comparable with those used in this work. However, the operating pressures were at least 25 times larger and, therefore, the linear axial velocity is correspondingly lower and of the same order of magnitude as the normal velocity. With this large
mass addition from the wall, transition to turbulent flow is brought on at much lower Reynolds numbers, and the reported mass burning rates are above what would be expected for this entrance Reynolds number without mass addition. The regression rate of plexiglass was found to decrease with axial length, as has been reported in this program, to conform to a laminar region.

The combustion model proposed for the experiments carried out at Rocketdyne (Ref. 2 and 3) is a diffusion flame model based upon the following hypotheses:

1. A flame front is established.
2. Combustion takes place in stoichiometric proportions at this well-defined flame front.
3. In laminar flow, the location of the flame can be correlated with the edge of the laminar boundary layer.
4. In turbulent flow, the flame is located near the edge of the turbulent buffer layer.
5. The pressure gradient in the axial direction is negligible.
6. Mass addition from the wall is negligible.

This basic model has been used by others (Ref. 7). The expansion of the model (Ref. 1) yielded a simplified theory with equations for the mass regression rate, oxygen profile, fuel profile, and temperature profile in the laminar regime.
In evaluating the correlations and postulations for the experimental results presented in this program, it is important to note that the physical assumptions and analytical procedures were designed to account for the observed burning rates of plexiglass in oxygen at one atmosphere pressure, and not for the combustion processes that may be occurring in hybrid rockets at higher pressures. However, it is interesting to speculate on the important changes that are likely to occur in hybrid rockets in extrapolating the low-pressure results on plexiglass burning.

As a result of the increase in pressure, the gas density is increased. Thus, for fixed linear flow velocities, the Reynolds numbers are raised which cause transition to turbulent flow to occur nearer the entrance. In addition, burning rates should increase with increasing pressure, particularly if real hybrid propellants simulate the behavior of underoxidized solid fuels. With increasing burning rates, the mass flowrate normal to the chamber axis will also increase. This increased mass addition from the wall should cause a reduction in the transition Reynolds number to well below the values applicable for flow without mass addition, which again indicates transition will occur closer to the entrance. The net result of these considerations appears to be the conclusion that combustion in hybrid rockets is likely to involve turbulent flow; i.e., turbulence will predominate over a greater axial length and perhaps over the entire grain. Thus, the trends observed at a pressure of one atmosphere appear to give an expanded picture of what might be expected at higher pressures.

For turbulent flow, we have postulated that the flame front is located at the edge of the turbulent buffer layer. This hypothesis has not been proven, although it appears intuitively as plausible as the idea that the flame front is located within the laminar boundary layer in laminar
flow. There is no justification for assuming that the prevalence of turbulent flow over the entire hybrid grain necessarily implies that the observed gasification rate will decrease with axial distance because the oxidizer is consumed, since the reduction in oxidizer concentration will tend to be offset by heating of the main fluid stream.

No attempt has been made to calculate a priori the heat transfer to the plexiglass wall in terms of free stream conditions. One might be tempted to perform this estimate in view of the enormous complexity entailed by the development of a significant theory (Ref. 7). However, the numerical values would, in any case, be subject to considerable doubt because, without a detailed combustion model and without quantitative knowledge of the influence of mass addition on the effective transport correlation parameters (e.g., the Stanton number), on the velocity profile and on the temperature profile, it is unlikely that reliable numerical estimates can be obtained.
SUMMARY

The mass burning-rate data obtained thus far demonstrate characteristics that can be explained by the proposed diffusion flame model. The mass burning rate of plexiglass was found to decrease with burning time. Plexiglass, polyethylene, and the aluminized fuel demonstrated similar burning behavior. In the case of polystyrene, turbulent flow predominates over a greater portion of the combustor, which may be caused by turbulence being brought on at lower Reynolds numbers by greater mass addition from the wall. A similar increase in turbulence is anticipated at pressures that would be encountered in real hybrid rockets. The data obtained at one atmosphere pressure appear to give an expanded picture of the flow pattern, which includes a larger laminar regime than would be expected at higher pressures.
FUTURE WORK

The program will be directed toward obtaining data at increased pressures and demonstrating the adaptability of the proposed model to these conditions.

The effect of larger percentages of aluminum and of other metals, such as titanium in the form of the hydride, will be studied.

The effect of variations of initial diameter of the fuel grain will also be determined.

In an effort to ascertain whether the burning of polystyrene and similar materials is controlled primarily by chemical reaction and/or diffusion processes, this fuel will be preheated and precooled.

Effort will be continued toward obtaining a quantitative model for turbulent flow. In particular, the problem of large mass addition from the wall will be considered.
REFERENCES


