Combustion of PMMA, PE, and PS in a Ramjet

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The combustion behavior of polymethylmethacrylate (PMMA), polyethylene (PE), and polystyrene (PS) with air was investigated in a connected pipe test facility; spectroscopy showed the presence of OH, C₂, and CH and temperatures between 1300 and 3000 K during combustion. Particular attention was focused on regression rate and combustion efficiency and the role of temperature and soot production. The present investigation gives an understanding of the most important phenomena that control (or emanate from) the combustion of a cylindrical solid fuel with a rearward facing step, and this has application for solid fuel ramjets, the safe burning of toxic waste, and hot gas generators.

The results can be summarized as follows:

1. At pressures between 0.6 and 1.1 MPa, a pressure increase causes an increase of regression rate for PMMA and PE due to enhanced radiative heat transfer from soot. At pressures below 0.5 MPa hardly any soot was observed during the combustion of PMMA and PE, whereas PS was always sooting.
2. The combustion efficiency varied from 70% to 90%, and depended on oxygen content, fuel grain length, and composition of the fuel.
3. The large vortex structure downstream of the sudden expansion at the inlet was shed at a regular rate. The shedding frequency was identified as the first longitudinal acoustic mode of pressure oscillations.

INTRODUCTION

The combustion behavior of various polymers has been investigated in a connected pipe test facility. This research attempts to give a better understanding of the flow and combustion processes in the combustion chamber of the solid fuel ramjet.

The observed trends in parameters such as the regression rate of the fuel were related to the relative importance of the various heat transfer, flow, and combustion mechanisms prevailing in a solid fuel combustion chamber. The combustion efficiency was examined as a measure of the deviation from complete combustion, i.e., equilibrium flow.

EXPERIMENTAL

Test Rig

Figure 1 is a schematic of the cylindrical ramjet combustion chamber. Directly downstream of the diaphragm, a recirculation zone is established and the rearward facing step stabilizes the flame.
The solid fuel pyrolyzes and the fuel gases mix and react with the air. Combustion products pass through an aft mixing chamber and are exhausted through a nozzle.

The gas flows were controlled by sonic control and measuring chokes, which give a constant total mass flow rate (±3%). A vitiator was used to produce air at elevated and precisely controlled temperatures and with adjustable oxygen content by burning methane with oxygen-enriched air. Ignition is achieved with the aid of a sparkplug and an H₂-O₂ gas mixture.

**Optical Instrumentation**

**Spectroscopy**

Both radially and axially emitted (via a quartz window) light was spectroscopically analyzed. Temperatures in polyethylene (PE) and polystyrene (PS) fuel grains could only be measured with the latter optical path, since these materials are not transparent. During each test run of about 30 s, 32 flame spectra were recorded successively at intervals of about 1 s.

Radiation from soot was analyzed in the wavelength region 375–385 nm, where the spectral radiance was calculated with the Planck formula to be proportional to approximately \( T^{20} \) at \( T = 1900 \) K and to \( T^{19} \) at \( T = 2000 \) K. Because of these large exponents, only the maximum temperatures along the optical path, where temperatures were fairly consistent, were determined. For this determination and for the determination of the emission coefficient of soot, the spectroscopical setup was calibrated against the spectral radiance of a calibrated tungsten ribbon lamp for the required wavelength region. Reference spectra were obtained from the ribbon lamp, and the measured soot temperature was the one that corresponds to the reference spectrum with the shape that best fitted the measured soot spectrum. It was assumed that the flame temperature was equal to the soot temperature. The inaccuracy in the temperatures found was typically 50 K. More details have been given by Wijchers [1].

**Pyrometry**

Temperatures were also obtained with the aid of a pyrometer. It determined the flame temperature in a characteristic time of 0.01 s from the radiation intensities of soot at two different wavelengths. Again, it was assumed that the difference between gas temperature and soot temperature is negligible. More details have been given elsewhere [2].

**RESULTS**

**Oscillatory behavior**

The internal surface profile of fuel charges, also called grains, was measured after each test run. For the fuels investigated [poly(methylmethacrylate) (PMMA), PE, and PS] the surface outside the recirculation zone downstream of the sudden expansion remained nearly parallel to the centerline. The region of homogeneous burning began at a distance of about nine step heights from the entrance. This point, where flow lines emerging
from the inlet reattach the solid boundary, is a kind of stagnation point, where boundary layers begin to develop and where convective heat transfer and hence the regression rate is usually higher than at places where the boundary layer is thicker.

In the recirculation zone, regression is less because of lower velocities. Downstream of the reattachment point, the flow is accelerated by the burned fuel gases, and convection is enhanced by the increasing velocity. The latter effect is seen to compensate more or less for the effect of the growing boundary layer that hampers convective heat transfer.

However, there is another phenomenon that seems to favor homogeneous burning. This is the continual refreshing of the boundary layer by the passing of the large-scale toroidal vortex that originates from the recirculation zone. High-speed cine recordings clearly revealed the regular shedding of this vortex, its sweeping through the bore, and its diffusion into the main gas stream. Mirrors on both sides of the grain revealed that the toroidal vortex remained essentially axis-symmetrical while propagating through the grain. This vortex clearly has a great influence on both the flow and the combustion.

The same oscillatory behavior was detected from pressure recordings, light emission measurements, and temperature measurements with the pyrometer. The amplitude of temperature fluctuations at 8 cm from the entrance increased from ca. 300 to ca. 600 K during a test (24 s). The fuel grain length, L, amounted to 30 cm. At 23 cm downstream of the entrance these fluctuations were less, about 200 K, probably as a result of the diffusion of the vortices in the main stream.

To investigate the nature of the oscillatory combustion, the main frequencies were computed of standing acoustical waves in the ramjet. In the one-dimensional model the inlet section has a length $L_1$, cross-sectional area $A_1$ over which is averaged, inlet reflection coefficient $\beta_1$, and cold flow throughput at speed $c_1$ and Mack number $M_1$. The high-temperature combustion chamber has similar, unindexed quantities. Acoustical damping in our test stand was found to have little effect on computed frequencies, $f$, whence they can be computed from the equation

$$(1 + c_1 A_1/c A_1)[1 - \beta_1 \beta \cos(2K_1 L_1 + 2KL)]$$

$$= (1 - c_1 A_1/c A_1)[\beta_1 \cos(2K_1 L_1)$$

$$- \beta \cos(2KL)],$$

where $K = 2\pi f / c(1 - M^2)$ denotes a modified wave number. More details have been given by Van der Geld [3], who simplified the analysis of Clark and Humphry [4].

The predicted ground frequency for the normal inlet diaphragm is 125 Hz. The one for an elongated inlet is 55 Hz. These values are to be compared with the experimentally observed frequencies, 90±15 and 40±10 Hz, respectively. In view of the simplifications of the model, the agreement with predicted ground frequencies is good.

It is concluded that the observed shedding frequencies can be identified as those corresponding to the first longitudinal acoustic mode associated with pressure oscillations in the ramjet.

Regression Rate

The following parameters were varied. Values given refer to the "standard" condition, that was set unless indicated otherwise.

- fuel grain length, $L$: 0.3 m
- initial step height, $h_0$: 12.5 mm
- initial inner bore diameter, $d_{i0}$: 40 mm
- air mass flow rate, $m_a$: 150 g/s
- chamber pressure, $P_c$: ±0.9 MPa
- aft mixing chamber length: 0.17 m
- air inlet temperature, $T_{inlet}$: 286±8 K

Dependency on Fuel Composition

At a pressure level of about 0.4 MPa, the regression rate, $r$, of PE was found to be more dependent on mass flux, $G$, than at pressures of about
1 MPa. The results were correlated with

\[ r = 6.09 \times 10^{-6} G^{0.69} \quad (0.4 < P_c \text{ (MPa)} < 0.5), \]
\[ r = 4.53 \times 10^{-5} G^{0.31} \quad (0.8 < P_c \text{ (MPa)} < 1.1), \]

with \( r \) in m/s and \( G \) in kg/m²/s. Note that the
exponent 0.31 is less than half the value of the
exponent at pressures below 0.5 MPa.

Figure 2 shows the effect of chamber pressure
on the regression rates of PE and PS.

The regression rate of PMMA was only slightly
less than that of PE, while exhibiting the same
trends. Figure 2 shows that up to 1.2 MPa the
regression rate of PS is independent of chamber
pressure, while Fig. 3 shows a distinct dependency
on mass flow rate. The regression rate of PS is
about 40% larger than that of PE and is seen to
follow a different trend (Fig. 3).

The nearby plateau burning of PS is often fa-
vorable in applications, e.g., ramjets and launch
missiles. The large soot production of PS then has
to be reduced, which can be done by increasing
the oxygen content in the oxidizer as will be seen.

Table 1 shows that the heat fluxes of all three
combustion gases are different.

**The Dependency on Chamber Pressure for
PMMA and PE**

Essentially three different pressure regions are no-
ticed (see also Fig. 2):

A. \( P_c < 0.6 \text{ MPa} \): hardly any pressure sensitivity.
B. \( 0.6 < P_c \text{ (MPa)} < 1.3 \): strong dependency on
\( P_c \)
C. \( P_c > 1.3 \text{ MPa} \): hardly any pressure sensitivity
until charring occurs.

In region A hardly any soot was observed. Con-
vective heat transfer, \( q_c \), being the main heat
transfer mechanism in this case, can be estimated
for PMMA from the product of the regression
rate, \( r = 0.15 \text{ mm/s} \), the effective heat of decom-
position of the solid phase (including depolymer-
ization heat, etc.), \( h_v = 1.3 \text{ MJ/kg} \), and the
PMMA mass density, \( \rho_F \approx 1180 \text{ kg/m}^3 \). The
result is \( q_c \approx 0.23 \text{ MW/m}^2 \).

In region B soot production becomes signifi-
cant. Measured temperatures allow for an esti-
mate of the maximum absorbed radiant heat flux:

\[ q_r = 0.29 \text{ MW/m}^2 \]. Since the net heat transfer
to the surface, \( q_w = \rho_F h_v r \), is proportional to
the regression rate, increasing values of the latter
indicate an increase of \( q_w \) by a maximum fac-
tor of 1.4. A factor of 1.5 is computed from
\[ q_w = q_r + q_c \exp(-q_r/q_c) \] with the above val-
ues of \( q_r \) and \( q_c \). The exponential accounts for
the blocking of convective by radiative heat trans-
fer [5, 6]. More details are given elsewhere [2].
This shows that the observed pressure effect can be attributed to radiative heat transfer.

### Influence of Oxygen Content and Inlet Temperature

Regression is stimulated by increasing the oxidizer concentration (Fig. 4). Spectroscopic measurements showed soot temperatures in the range 1900–2800 K, increasing with increasing oxygen content. Obviously the regression rate is enhanced by an increase in convective heat transfer resulting from the increase in the temperature of the gas mixture.

This was also observed, in a straightforward manner, by increasing the inlet air temperature.

As an example, for PMMA at 0.7 MPa the regression rate increased from 0.16 (\(T_{\text{inlet}} = 280\) K) to 0.22 mm/s (500 K) and 0.32 mm/s (800 K).

Spectroscopic measurements revealed that flame temperature and emission coefficient are unaffected by \(T_{\text{inlet}}\). This stands to reason since the temperature of the burning mixture hardly depends on oxidizer temperature, but strongly on composition and mixture ratio. Because radiation reached a maximum at about 1.2 MPa, and because the regression rate is doubled at 1.3 MPa by doubling the inlet air temperature, it is clear that the increase in regression rate with increasing \(T_{\text{inlet}}\) is entirely due to increased convective heat transfer.

### COMBUSTION EFFICIENCY

The combustion efficiency, \(\eta\), is defined [8] as the ratio \(C_{\text{exp}}/C_{\text{theo}}\). The characteristic velocity \(C^*\) depends on fuel properties, and is calculated with

\[
C_{\text{exp}}^* = \frac{P_c A_t}{(m_a + m_f)},
\]

\[
C_{\text{theo}}^* = \left(\frac{1}{\Gamma}\right)(RT_c)^{1/2},
\]

where \(m_a\) denotes the total air mass flow rate, \(m_f\) the fuel weight loss divided by the burning time, and \(A_t\) the throat area. \(T_c\) is the equilibrium temperature if burning would be adiabatic and complete, corresponding to equilibrium composition of the products, and \(\Gamma\) denotes the Vandenkerkhove function [8]:

\[
\Gamma = \sqrt{\gamma [2/(\gamma + 1)]^{(\gamma + 1)/(\gamma - 1)}}.
\]

\(R = R_a/M\), where \(M\) is the molar mass and \(R_a\) is ca. 8.3 J K\(^{-1}\) mol\(^{-1}\). The values of \(T_c\) and \(M\) are calculated with the aid of a NASA computer program [9] as a function of pressure and the mixture ratio at the throat of the combustion chamber, \(\phi = O/F = m_a/m_f\). For all three fuels, the value of \(C_{\text{theo}}^*\) under our test conditions is solely dependent on mixture ratio, and not on pressure. At constant air mass flow rate, the theoretical characteristic velocity is therefore uniquely determined by the regression rate.

#### TABLE I

<table>
<thead>
<tr>
<th>PMMA</th>
<th>PE</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression rate (mm s(^{-1}))</td>
<td>0.191</td>
<td>0.220</td>
</tr>
<tr>
<td>((m_a = 150 \text{ g s}^{-1}; P_c = 1.1 \text{ MPa}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of combustion (MJ kg(^{-1}))</td>
<td>26.2</td>
<td>46.5</td>
</tr>
<tr>
<td>Mass density (kg m(^{-3}))</td>
<td>1180</td>
<td>940</td>
</tr>
<tr>
<td>Heat fluxes (MW m(^{-2}))</td>
<td>5.9</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Fig. 4. The effect of oxygen content on the regression rate of PMMA.
Dependency on Fuel Composition and Chamber Pressure

The efficiency of PE and PS linearly decreases with increasing chamber pressure (Fig. 5). The efficiency of PMMA is only weakly dependent on pressure.

The combustion efficiency is interpreted as a measure of the deviation of the actual combustion process from thermodynamical equilibrium and complete combustion. In the case of PS, thermodynamic equilibrium is disturbed by inhomogeneous soot distributions, and in addition burning is incomplete due to the lifetime of soot particles. This is manifested by the decreasing in $C_{\text{exp}}^*$ of PS with increasing pressure. Note that for PS, $C_{\text{theo}}^*$ is independent of pressure simply because the regression rate is, making $C_{\text{exp}}^*$ proportional to the combustion efficiency. Large amounts of soot in the exhaust gases correspond to significant momentum lag and a decrease in the effective throat area, $A_t$, and hence a decreasing experimental value of the characteristic velocity (see Eq. 1).

On the other hand the combustion efficiency of PE is dominated, via $C_{\text{theo}}^*$, by the dependency of the regression rate on pressure (Fig. 6). Again, burning is more incomplete at higher pressures. Note that PE was hardly sooting as opposed to PS. The scatter in values of $C_{\text{theo}}^*$ in Fig. 6 results from the scatter in the experimental values of the regression rate at corresponding pressures.

Dependency on Oxygen Content

The increase of oxygen content clearly increases the efficiency (Fig. 7). The mixture ratio was 0.38±0.02.

That oxygen enrichment leads to lower soot production and a higher combustion temperature was clearly demonstrated by spectroscopic measurements. For low intensities the emission coefficient of soot is directly related to the soot concentration. Relative values $\varepsilon_r$ of emission coefficients $\varepsilon$ were observed from the ratio between spectral radiances detected, and the detected spectral radiances of the tungsten calibration lamp, operated at the determined temperatures. The results are shown in Fig. 8. Comparison of the spectral radiances from the flame and from the calibration lamp showed that the emission coefficient, $\varepsilon$, is unity at about 1700 K.

For the experiments with oxygen-enriched air, the emission coefficient is remarkably low, indicating little soot, and temperatures are high. The maldistribution of fuel in the chamber is compensated for by the extra amount of oxidant in the flow, making combustion more complete. This ex-
plains the increase in combustion efficiency with increasing oxygen content.

Dependency on Configuration Parameters

The following variations were investigated for PMMA: (1) increasing the stepheight from 10.5 to 14.5 mm with constant initial inner bore of the fuel grain (40 mm); increasing the fuel grain length from 0.3 to 0.9 m in steps of 0.2 m; and increasing the aft mixing chamber length to 0.17 and 0.27 m.

1. Increasing the stepheight, $h_0$, slightly reduces combustion efficiency and increases the length of the recirculation zone. Hence the flow region with minimal regression rate and at rel-
atively low temperature becomes more important. Inhomogeneity increases and the combustion efficiency diminishes.

2. The longer the grain length, the longer the average residence time of soot and combustion gases in the chamber and the more complete the combustion process. As a result the combustion efficiency was observed to increase with grain length. Soot and fuel gases from the downstream end of the fuel grain are never burned completely. If the extent of this part of the fuel grain is negligible with respect to the upstream part, an increase in grain length will hardly affect efficiency. This is reflected by the tendency of the efficiency to level off at lengths larger than 0.6 m.

3. Obviously the influence of the downstream part of the fuel grain mentioned above can also be reduced by increasing the aft mixing chamber-length. At three tests with the elongated aft mixing chamber the efficiency was found to be 0.9 (pressure 0.9 MPa). The increase of the aft mixing chamber length had effectuated an increase in efficiency of about 20%! At three tests with the elongated aft mixing chamber but at a condition with less soot (0.8 MPa), the efficiency lowered to about 0.8. Clearly the presence of soot enhances the influence of the aft mixing chamber length.

CONCLUSIONS

The combustion behavior of PMMA, PE, and PS in a solid fuel ramjet was studied. Low soot concentrations and the highest temperatures occurred at low pressures (about 0.5 MPa). Temperature fluctuations were connected to the oscillatory shedding of large coherent vortex structures. The shedding rate was identified as the one that corresponds to the first longitudinal acoustic mode associated with pressure oscillations.

The regression rate of all fuels increases with mass flux due to increasing convective heat transfer. Where the regression rate of PMMA and PE was pressure dependent, the dependence could be attributed to the formation of soot and the increasing importance of radiative heat transfer, which cannot be neglected at mass flow rates below 300 g s⁻¹. The temperature in the combustion chamber and convective heat transfer were found to be prime regression rate controlling parameters.

The combustion efficiency is a convenient measure of the deviation from adiabatic and complete burning. For different fuel compositions, different physical mechanisms were found to cause the same trend of the combustion efficiency. Combustion is made more complete by increasing grain length, aft mixing chamber length, and oxygen content, resulting in an increasing combustion efficiency.

REFERENCES


Received 6 October 1988; revised 14 March 1989