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FINAL REPORT

(NASA-CF-146729) SOOT FORMATION IN THE METHANE/OXYGEN AND METHANE/OXYGEN/HYDROGEN FLAME Final Report (Newark Coll. of Engineering) 46 p HC $4.00 CSCL 211 Unclas 63/28 01043

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NEWARK COLLEGE OF ENGINEERING
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INTRODUCTION

The purpose of this study was to ascertain the feasibility of using methane, recovered from carbon dioxide by the Sabatier- Senderens reaction, as a fuel in a reaction control engine.

A problem which had to be avoided was the emission of soot particles. It was thought that such particles would remain in the environment of the spacecraft and, thereby, adversely affect optical sightings and, also, such particles might have an effect upon communications.

The initial studies were of a practical nature. The first was the influence of the spatial arrangement of the fuel and oxygen injectors on soot formation. In the second study, inhibition of soot formation was considered. Considering the given situation, it was impractical to use an additive. However, since methanol combustion does not produce soot, and methanol can be produced from methane in situ, the possibility that methanol could act as an inhibitor was studied. In the third study, since these are restartable engines, the effect of shutdown on the rapidity of soot formation was studied.

On a fundamental level, we attempted to analyze spectroscopically a situation similar to the "unmixing" phenomena which results from the back-diffusion of light gases. As a result of the back-diffusion, the composition of the unburnt fuel mixture changes so that a mixture which might have been expected to burn soot-free, does form soot. And, once formed, the soot is kinetically-stabilized and, therefore, will probably appear in the gas which is emitted.
1. THE FACTOR OF FUEL PYROLYSIS IN INJECTOR DESIGN
Leonard Dauerman* and G. E. Salser+
Department of Chemistry and Chemical Engineering
Newark College of Engineering
Newark, New Jersey
[published in AIAA JOURNAL, 11, No. 1, 99 (January, 1973)]

The purpose of this Note is to suggest an experiment related to the performance of rocket motors which we cannot carry out because we lack the necessary facilities. Levine suggested that the recovery of water from CO₂, produced as a result of respiration, via the Sabbatier - Senderens reaction would be of value provided that the second reaction product, methane, could be oxidized without the formation of soot as an exhaust product. Soot is deleterious because the particles would be expected to act like a shroud around the spacecraft interfering with visual sightings and instrumentation performance.

The question raised is what special factors peculiar to the performance of a rocket engine affect soot formation. It has been established that to suppress soot formation the amount of oxygen needed is above that calculated thermodynamically. Soot-formation is a kinetically-controlled process. Of course, then sufficient oxygen will suppress soot formation. This is trivial recommendation.

Index Category: Liquid Rocket Engines
* Associate Professor, nonmember
+ Research Associate, member AIAA
Recent work on pre-mixed flames\textsuperscript{2} and turbulent diffusion flames\textsuperscript{3} indicate that the "kinetic-control" ascribed to soot formation processes involves not only slow chemical reactions, but perhaps, even more significantly, an unmixing effect. Reactants are diluted by hot product gases before the reaction occurs. It is also possible that reactive species in the recirculating gas promotes pyrolysis. Hydrocarbon pyrolysis occurs in a non-oxidizing atmosphere and the soot particles formed oxidize slowly in an oxidizing atmosphere.\textsuperscript{4,5}

An experiment carried out in this laboratory is suggestive of the results to be expected in a space engine. Using a six-on-one single element septad as the burner, and gaseous methane and oxygen as reactants, the effect of reversing the positions of the respective gases was studied in an atmospheric shielded flame. The glass shield, 1.5 inches in diameter, was loosely plugged with glass wool at the top to promote the recirculation of the hot product gases.

The criteria used to establish the sooting tendency associated with the respective flow patterns was the acetylene concentration. It has recently been shown that in aliphatic flames, acetylene is a measure of the expected degree of sooting.\textsuperscript{6,7}

Flames were sampled with a critical orifice quartz probe into a mass spectrometer. Representative total analyses are presented in Table 1. It is found that the acetylene concentration is twice as high when the oxygen feed is surrounded by the fuel feed. This observation is consistent with the proposed suggestion.
The above described mechanism of soot formation is enhanced to the maximum extent if one applies the prevailing criteria for injector selection, also if one uses methane as a film coolant. Since hydrocarbon oxidation occurs in a non-hypergolic manner, the prevailing philosophy would be to design the injector so that mixing occurs in the gas phase with the heat necessary to bring about vaporization and mixing coming from the hot product gases in the turbulent diffusion flame. Furthermore, the outer injector would be the one containing the fuel stream.

It is proposed that if the suppression of soot is desirable an injector be used in which the fuel injector is surrounded by oxygen injectors and, therefore, it is not possible for hydrocarbon pyrolysis to occur in a non-oxidizing atmosphere. The nature of the oxidizer is not critical in this analysis. \( \text{F}_2 \) or \( \text{OF}_2 \) or mixed oxidizers should lead to similar results. Furthermore, it is recommended that whenever a fuel is used in which a solid can form on pyrolysis as for example, diborane, the usual injector relationship should be reversed. Not only because of the "shroud" effect but for the reason that performance will be less than predicted because the assumed thermodynamic equilibrium is not achieved. Although in many respects the suggestion made is trivial, at least from the viewpoint of a chemist, it is the authors' experience that the design engineer tends to consider chemical phenomena in rocket design solely from an energy viewpoint and, in general, tends to disregard chemical phenomena.
Table 1 Mass Spectrometric Analysis of Sampled Flames

<table>
<thead>
<tr>
<th></th>
<th>Oxygen (Inside feed)</th>
<th>Oxygen (Outside feed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole %</td>
<td>Mole %</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>21.26</td>
<td>13.23</td>
</tr>
<tr>
<td>Methane</td>
<td>30.53</td>
<td>38.79</td>
</tr>
<tr>
<td>Water</td>
<td>24.88</td>
<td>26.74</td>
</tr>
<tr>
<td>Acetylene</td>
<td>2.03</td>
<td>1.00</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.09</td>
<td>0.68</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>15.59</td>
<td>13.30</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.38</td>
<td>0.26</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>4.23</td>
<td>5.99</td>
</tr>
</tbody>
</table>

Feed Conditions: Methane 7.1265 cc/sec
Oxygen 3.091 cc/sec

Analytical Precision:

<table>
<thead>
<tr>
<th></th>
<th>Hydrogen/Carbon Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzed</td>
<td>Input</td>
</tr>
<tr>
<td>Inside Feed</td>
<td>3.93 4</td>
</tr>
<tr>
<td>Outside Feed</td>
<td>3.90 4</td>
</tr>
</tbody>
</table>
REFERENCES


2. Effect of Methanol on Methane/Oxygen Flames

AUTHORS: G. E. Salser and L. Dauerman
Department of Chemistry and Chemical Engineering
Newark College of Engineering
Newark, New Jersey

A talk presented at the
Central States Combustion Institute Meeting
at the Bureau of Mines, Bartlesville, Oklahoma
on March 23, 1972
INTRODUCTION

The objective of this study is to determine whether or not intermediates in the oxidation of hydrocarbons can act as inhibitors of soot formation in methane oxidation. Practically, if such inhibitors were found, then it might be possible to form the inhibitor continuously in a pre-combustion region.

The oxidation of methane was studied in pre-mixed flames. Intermediates projected for study are methanol, formaldehyde, and formic acid.

The study on methanol has been completed. From prior studies it was difficult to predict how CH₃OH would act. CH₃OH flames are not sooty (1). OH radicals, considered the major species in the destruction of soot particles (2), have been reported in the methanol flames but no concentrations have been assigned (3). On the other hand, in slow combustion studies, the proposed mechanism involves the stripping off of hydrogen atoms without the scission of the C--O bond (4). Thus, an inhibitory effect is to be expected if OH radical formation is an important mechanism but not if the predominant mechanism is the stripping off of hydrogen atoms.

Experimental

Overall, flames were analyzed by continuous sampling into a rapid-scanning mass spectrometer. Temperature measurements were made with thermocouples. We have chosen to use the acetylene concentration as an indicator of the tendency to form soot. It has been shown that the amount of unsaturated
hydrocarbons is proportional to the amount of soot in aliphatic flames; furthermore, the major unsaturated compound in methane flames is acetylene \((5a,b)\).

**Burner** — A premixed flat flame burner with a water cooled porous metal plate for flame control was used in this investigation. The burner was operated at atmospheric pressure. A schematic diagram of the burner is shown in Figure 1. The space below the porous plate was filled with glass beads to insure mixing and flow distribution.

Combustibles, to the burner, were metered as gases through rotameters using Moore Flow controllers for regulation. The rotameters were calibrated using calibrated wet test meters and other volumetric techniques for the actual gas mixtures used.

The fuel stream was methane with 10\% Argon and the oxidizer stream, 100\% Oxygen. Methanol was added to the fuel stream by passing it after metering through a temperature controlled saturator. The actual concentration of methanol was checked by Mass Spectrometric analysis. Where methanol was added to the fuel stream the flow ratios were adjusted to maintain the O/C ratio.

**Sampling and Analysis**

Combustion gases were sampled by a quartz probe placed above the flame. The sampling system is illustrated schematically in Figure 2. In order to avoid fractionation of the sample the pressure reduction to the mass spectrometer was carried out in stages.
In the first stage through the quartz probe, the pressure drop was from atmospheric to about 22 torr. Since all flow is laminar, no fractionation occurs. The second stage drops the pressure to 100 u. Since gas enters this stage through a 0.005" hole at 22 torr but exits at 100 u through a 1 inch hole, flow both into and out of this stage is in the transition region and no net fractionation occurs. Flow into the source is through 5 holes approximately 0.001" in diameter and is molecular. Flow from the source at 5 X 10^{-6} torr is also molecular. In molecular flow the molecules of gas move independently of one another and although the composition in the source may not be that of the inlet system, the partial pressure of each component in the source is a direct function of the partial pressure of that component in the inlet system. Pure gases may be admitted to the inlet system for calibration under these conditions. The criteria used in the design of such a system is as follows: The mode of flow into a region must be the same as the mode of flow out of the region.

Analysis of combustion water is possible with this inlet system because of the continuous flow which brings fresh sample quickly to the source leak. The surfaces of the vacuum system are rapidly brought to equilibrium with the sample. There is, of course, a small amount of water which is recycled by the vacuum pumps but the stripping produced by surface adsorption in the normal static system is largely avoided. The analytical accuracy for water of this flow system is probably better by
at least an order of magnitude than that of any static system. This holds true for other polar compounds although water in undoubtedly the worst case.

An example of the accuracy of this system under flow conditions is indicated in Table 1.

Run Ratio

The burner was run at the molar O/F ratios shown in Table 2.

Temperature of Flame

The temperature record of the flame was taken in runs separate from the analytical runs to avoid too much disturbance of the flame. Although many workers have used Platinum thermocouples and other devises to obtain temperatures, we found that the temperature of our flame was such that all of these devices melted in the flame. In fact the sampling probe itself had to be treated by heating with potassium salts to promote crystallization. This reduced the viscous flow properties and raised the emissivity of the quartz probe. Even a probe so treated was not stable enough to use as a pneumatic thermometer.

We had available, wire for a Tungsten-Tungsten Rhenium thermocouple and found that in our flame the rate of oxidation was slow enough to allow the use of one thermocouple for a complete run.

The Tungsten couple was not catalytic to the flame gases. This was checked by coating a thermocouple with Silica and checking the temperature of the coated vs the uncoated after
using equation B. \( h_c \) was estimated using the data of Mc Adams.

The temperature was taken at three distances from the burner face, corresponding to the mass spectrometer probe positions. In addition from the gas stream composition data, the adiabatic flame temperature was calculated. Representative temperature data is shown in Table 3 for one probe distance.

It will be noted that the adiabatic temp is higher than the gas temperature calculated from the experimental data. A considerable portion of the combustion heat is lost to the cooled burner plate. In a run under vacuum conditions such that the burner flame lifted from the plate, much higher temperatures were measured. It is doubtful that the gas temperature is accurate to closer than 100°F, because of the heat balance which must be made. Relatively small changes in \( c \) and \( h_c \) will cause large changes in the calculated gas temperature. Under conditions of luminosity the heat balance breaks down more or less completely since the thermocouple is radiating to a semitransparent luminous gas rather than to room temperature surroundings. Under such conditions the rate of heat loss from radiation increases greatly and the temperature is much closer to that directly measured with the thermocouple.

**DATA**

Representative data are shown in Table 4. Although molar O/F ratios from 0.8 - 1.10 were run in seven equal steps, only 4 ratios are shown for simplicity. The 0.80 and 0.85 ratios
always had a yellow carbon tint to the flame. It will be noted that the values of the runs with methanol added agree well with those without methanol. In particular the concentration of C_2H_2 seems relatively stable with addition of methanol; visual observation indicates that addition of methanol does not change the free carbon content of the flame.

The sampling at 20 mm and 10 mm probe distance to the burner face is relatively stable. Closer spacing of the probe to the burner face leads to more variable results since the flame front position is a function of the O/F ratio. It is unlikely that data taken with these probe distances is of much value for comparative purposes. It is interesting to note that methanol is found only with the closest probe distance and that the ratio of methanol to methane indicates that methanol was being consumed faster than methane.

A material balance based on the analyzed products is shown in Table 5. This indicates that reasonable analytical accuracies were achieved and that in the region where carbon was formed (i.e., O/F of 0.80 and 0.85) there is a detectable loss in carbon.

CONCLUSIONS

It would appear that the addition of methanol had little if any effect on the formation of carbon. It must be remembered that these were rich premixed systems in which the carbon was formed and to reduce carbon one must disturb the competition for oxygen which exists between carbon and hydrogen.
A slight increase in CO₂ is noted with the addition of methanol. Such an increase would reduce the available oxygen and thus have a tendency to increase the formation of carbon.

It has been our experience that premixed gaseous flames with O/F ratios reasonably stoichiometric do not give carbon. Carbon arises in gaseous diffusion flames where mixing is inadequate or in liquid fueled flames where rich zones must exist in the neighborhood of the vaporizing droplet. Oil droplets, where pyrolysis must occur to achieve gasification may give carbon by a pyrolysis mechanism.

Therefore our rich flames, from the viewpoint of gas fed flames is perhaps unrealistic. However such rich zones do occur with other fuels and consequently justify this investigation as a simplified attempt to treat these conditions.

It would appear that with methanol, the C-H bonds are broken in preference to the C-O bond. Thus methanol gives no carbon because H⁻C⁻H, the methyl radical does not exist to form acetylenics. However its products of combustion do not help form the C-O bond in the methane combustion anymore than do those of methane itself.

The mechanistic insight provided by this study has to be qualified because the contention that the OH radicals are responsible for the consumption of soot particles is denied by others who claim that the O₂ molecule is the most important species(6).
REFERENCES


### TABLE 1.

<table>
<thead>
<tr>
<th>Make up (Gravimetric)</th>
<th>Component</th>
<th>Analyzed (Flow)</th>
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<tbody>
<tr>
<td>23.9</td>
<td>H₂</td>
<td>22.22</td>
</tr>
<tr>
<td>26.1</td>
<td>CH₄</td>
<td>25.52</td>
</tr>
<tr>
<td>26.2</td>
<td>CO</td>
<td>27.26</td>
</tr>
<tr>
<td>23.8</td>
<td>CO₂</td>
<td>24.98</td>
</tr>
<tr>
<td>Ratio (Molar)</td>
<td>Ratio (wt)</td>
<td>Ratio (Analyzed) Molar</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>1.10</td>
<td>2.20</td>
<td>1.095</td>
</tr>
<tr>
<td>1.05</td>
<td>2.10</td>
<td>1.03</td>
</tr>
<tr>
<td>1.00</td>
<td>2.00</td>
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</tr>
<tr>
<td>0.95</td>
<td>1.90</td>
<td>0.931</td>
</tr>
<tr>
<td>0.90</td>
<td>1.80</td>
<td>0.885</td>
</tr>
<tr>
<td>0.85</td>
<td>1.70</td>
<td>0.838</td>
</tr>
<tr>
<td>0.80</td>
<td>1.60</td>
<td>0.792</td>
</tr>
<tr>
<td>O/F Ratio</td>
<td>Thermocouple Temp °C</td>
<td>20 mm Adiabatic Temp</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>1.10</td>
<td>1305</td>
<td>2828</td>
</tr>
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<td>1.00</td>
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</tr>
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<td>0.90</td>
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<td>2441</td>
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<tr>
<td>0.80</td>
<td>1255</td>
<td>2159</td>
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</table>

2-12


TABLE 4.

Representative Analytical Results

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>A-Methane-9.6% Ar, O₂</th>
<th>B-Methane-9.6%A + 8% Methanol, O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/F</td>
<td>H₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>1.00 20 mm</td>
<td>A 0.36</td>
<td>B 35.93</td>
</tr>
<tr>
<td>0.90 20 mm</td>
<td>37.55</td>
<td>38.77</td>
</tr>
<tr>
<td>0.85 20 mm</td>
<td>39.75</td>
<td>39.64</td>
</tr>
<tr>
<td>0.80 20 mm</td>
<td>40.20</td>
<td>39.41</td>
</tr>
<tr>
<td>1.00 10 mm</td>
<td>36.55</td>
<td>36.17</td>
</tr>
<tr>
<td>0.90 10 mm</td>
<td>40.54</td>
<td>38.65</td>
</tr>
<tr>
<td>0.85 10 mm</td>
<td>41.30</td>
<td>39.55</td>
</tr>
<tr>
<td>0.80 10 mm</td>
<td>41.59</td>
<td>39.57</td>
</tr>
<tr>
<td>1.00 2 mm</td>
<td>33.04</td>
<td>34.07</td>
</tr>
<tr>
<td>0.90 2 mm</td>
<td>37.47</td>
<td>36.65</td>
</tr>
<tr>
<td>0.85 2 mm</td>
<td>34.50</td>
<td>37.54</td>
</tr>
<tr>
<td>0.80</td>
<td>Probe softened during B run</td>
<td></td>
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</tbody>
</table>

FOLDOUT FRAME
<table>
<thead>
<tr>
<th>CO</th>
<th>O₂</th>
<th>Ar</th>
<th>CO₂</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>27.49</td>
<td>28.09</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>28.86</td>
<td>28.68</td>
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<td>nil</td>
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<tr>
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<td>28.42</td>
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<td>nil</td>
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<td>26.97</td>
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<td>nil</td>
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<tr>
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<td>28.81</td>
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<td>nil</td>
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<tr>
<td>27.77</td>
<td>29.03</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>27.69</td>
<td>28.94</td>
<td>0.10</td>
<td>nil</td>
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<td>27.09</td>
<td>27.72</td>
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<td>nil</td>
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<tr>
<td>25.10</td>
<td>28.14</td>
<td>0.22</td>
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<tr>
<td>22.93</td>
<td>27.50</td>
<td>0.21</td>
<td>nil</td>
</tr>
<tr>
<td>22.06</td>
<td>26.76</td>
<td>0.79</td>
<td>nil</td>
</tr>
</tbody>
</table>
TABLE 5.

* Range switch malfunction

<table>
<thead>
<tr>
<th>O/F Ratio</th>
<th>$\Sigma , \text{H}_2$</th>
<th>$2 \times \Sigma , \text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.10</td>
<td>64.5</td>
<td>64.5</td>
</tr>
<tr>
<td>* 1.05</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1.00</td>
<td>64.9</td>
<td>64.8</td>
</tr>
<tr>
<td>0.95</td>
<td>66.0</td>
<td>65.5</td>
</tr>
<tr>
<td>0.90</td>
<td>65.7</td>
<td>65.8</td>
</tr>
<tr>
<td>0.85</td>
<td>67.2</td>
<td>66.4</td>
</tr>
<tr>
<td>0.80</td>
<td>69.6</td>
<td>67.5</td>
</tr>
</tbody>
</table>

* Range switch malfunction
Figure 1. Premix Burner
Premix Burner

Total Combustibles
45 cc/sec

Velocity
25.48 cm/sec

Quartz Probe

Porous Plate
Glass Beads
Cooling Coil
Figure 2. Mass Spectrometer Sampling System
Mass Spectrometer
Sampling System
3. The Effect on Soot Formation of Restarting Engines

A. Introduction

It is probable that in the small reaction control engines soot formation is most likely to occur during start-up and shut-down because during these stages the fuel to oxygen ratios fluctuate over a wide range and, also, the combustion temperature drops. This temperature drop favors the formation of soot thermodynamically because the equilibrium

$$2 \text{CO} \rightarrow \text{CO}_2 + \text{C}_{\text{solid}}$$

is well over to the right below 1000°K and, also, the rate of combustion decreases.

The purpose of this study was to determine whether or not the sudden quenching of combustion caused by a drop in the oxygen flow rate, even at very low chamber pressures, will lead to soot formation.

B. Experimental

The experimental set-up is shown in Figure 3-1. Precisely metered streams of fuel and oxygen flow mix and then are ignited in a pyrex pipe cross. At a controlled pressure, the absorption and the emission spectra are monitored with the Warner-Swazey spectrometer; the temperature is also observed. Quenching of the flame is initiated by interrupting the flow of oxygen. This is effected by a foot actuated solenoid valve.
which, also, actuates a small light located on the top of the oscilloscope screen on which the time-resolved spectra are recorded.

The spectra displayed on the oscilloscope were either recorded on Polaroid film or on motion picture film using a Bolex 16mm camera. The Warner-Swazey Model 501 Rapid Scanning Spectrometer is a single beam instrument that can be operated in the infrared and the UV-visible spectral regions. While it is possible to scan limited regions of the spectra up to 0.001 second, for practical reasons, the fastest scan rate in this study was 0.01 second.

Figures 3-2 to 3-3 are indicative of the data obtained. In Figure 3-2, the IR spectra of the butane/oxygen system in the 2-5\(\mu\) range are shown. Two spectra are displayed simultaneously in each frame. The upper is the absorption spectrum and the lower spectrum in each frame is the emission spectrum. The source was chopped at a rate of 10 cps and the film speed is 32 frames per second. The left hand series represent the steady-state spectra. On the right, oxygen flow has been quenched and spectra, reading downward, represent the process of quenching. In the spectra on the right, note the smudge in the left hand corner. This is the light bulb signal actuated by the foot switch which causes the oxygen flow to stop. In Figure 3-3, U.V.
spectra in the region from 2800Å to 4000Å are shown during the quenching process. The output from the thermocouple, which is an index of the temperature, is recorded on each frame as a straight line. The height of this line is proportional to the temperature.

With the available spectrometer components, we were limited to scanning in the IR from 2.5 to 5 microns and, in the UV-Visible, from 2300 to 8000Å. Within these perimeters, species that could be detected were the following: in the IR, CO, CO₂, H₂O, hydrocarbons; in the UV-Visible, OH, CH, C₂ (Swan bands).

C. Results and Discussion

As in the previous study, the formation of acetylene was used to indicate the presence of soot in the flame. The C-H stretch emission band in the IR at 3.05 is distinctive because the other hydrocarbon C-H stretch emissions occur at significantly lower frequencies: olefins, 3.2; and aliphatics, 3.35. The band associated with acetylene is observed under steady-state conditions as the flame becomes sooty. See Figure 3-4. Note that in going from the lean flame, Figure 3-4b, to the richer flames, Figures 3-4a,c, an emission band appears at 3.05. Also, visual observations support the inference from the spectra that the emergence of the acetylene
emission band indicates the formation of soot because the leanest flame is not luminous whereas the others are.

Coincident with the emergency of the acetylene emission band, the O-H stretch band at 2.7 associated with water disappears. It is not clear at this point whether the concentration of H₂O emitters falls below the limits of detection in sooty flames or the soot absorbs the water. That similar species can be absorbed on soot in sooty flames has been inferred previously in a study of propellant flames in the IR region. [H. A. Bent and B. Crawford, Jr., "Infrared Studies of Propellant Flames," J. Phys. Chem., 63, 941 (1959)].

In the methane/oxygen system, the minimum pressure at which it was possible to sustain non-sooting combustion with a 1:1 molar composition in the system used was 70 mm. The flow rate of each gas was 22 cc/sec. Under these conditions, during quenching brought about by the abrupt stopping of the oxygen flow, no emission band appears at 3.05μ, therefore, it is inferred that soot formation does not occur.

The observed changes in the relative intensities of the emission bands characteristic of CO₂ CO₁ and H₂O as a function of the time after quenching are plotted in Figure 3-5. It can be seen that the CO₂
intensity decreases at the greatest rate. It is not surprising that as less oxygen is available for combustion, CO should become the favored product. Note that these are emission spectra. The relative intensities may not reflect precisely the gas composition because as the flame temperature drops, the relative emissions may not drop proportionately.

To observe sooting on quenching, we next used a longer chain hydrocarbon, butane. In this system, non-sooting combustion was sustained in the pressure region between 110 and 125 mm and for a molar ratio of butane to oxygen of 1:2.5.

The emission peak which is assigned to soot, 3.05μ, is observed as the flame temperature drops 200°F, from 3100°F to 2900°F. This occurs in about \( \frac{1}{16} \) second. When this occurs, the OH, CH, and C\(_2\) emission bands in the UV disappear.

The data obtained on CO, CO\(_2\), and H\(_2\)O in the infrared region are plotted in Figure 3-6. The UV-visible data are plotted in Figure 3-7 for C\(_2\), CH and OH.

These results indicate that in the methane/oxygen system non-sooting combustion can be maintained at extremely low pressures, and that the quenching of such a system will not cause soot formation. The probability is that proper conditions for shutdown can be achieved without soot formation being a problem.
Figure 3-1  System Used to Study Spectra of Quenched Flames
SCHEMATIC DIAGRAM OF APPARATUS
Figure 3-2  IR Spectra Before Quenching (on the left) and After Quenching; Absorption and Emission Spectra are Displayed.
Figure 3-3 UV-Visible Spectra of Quenched Flame
Figure 3-4 a-c. Steady-State IR Spectra of Sooty v. Non-Sooty Flames. (Lean Flame Spectra in No. 2. No. 1 and 3 are the richer flame. No. 3 is the richest flame.)
Figure 3-5  Composition of Flame From IR Spectra During
Quenching of 1:1 CH₄ to O₂ v. Time
Fig. Fuel Mixture: 1:1 (molar) methane to oxygen
Pressure: 70 mm
Data taken from six different runs; Infrared spectra

- : CO
△: CO
○: H₂O

Intensity (Relative Peak Height)

Time (second)
Figure 3-6  Composition of Flame From IR Spectra During Quenching of 1:2.5 Butane to O₂ v. Time
Fig. Fuel Mixture: 1:2.5 (molar) butane to oxygen
Pressure: 115 mm
Data taken from 4 different runs; Infrared spectra

Intensity (Relative Peak Height)

\[ \text{Intensity} = \text{Relative Peak Height} \]

\[ \times: \text{CO}_2 \]
\[ \triangle: \text{CO} \]
\[ \bigcirc: \text{H}_2\text{O} \]

Temperature (°F)

Time (second)

0 1/32 2/32 3/32 4/32

2000 2500 3000 3500
Figure 3-7  Composition of Flame from UV-Visible Spectra During Quenching of 1:2.5 Butane to O₂ v. Time
Fig. Fuel mixture: 1:2.5 (molar) butane to oxygen
Pressure: 115 psia
UV-Visible spectra

Intensity
(Relative Peak Height)

OH (4298.71)

C₂ (4692.96)

OH (3130.57)

Time (second)
4. Simultaneous Analysis of Transient Phenomena Using Optical and Mass Spectrometry

Jost, Wagner, and Homan have shown that in order to understand the nature of soot formation in flames, it is necessary to probe the flame using both mass spectrometry and optical spectrometry. A major source of their papers in this area are the biannual Combustion (International) Symposia beginning with the 10th [U. Bonne, K. H. Homann, and H. Gg. Wagner, "Carbon Formation in Premixed Flames," Tenth Symposium (International) on Combustion, pp. 503-512, The Combustion Institute, 1965.] One of their major conclusions was that the back-diffusion of hydrogen causes "unmixing" of premixed flames. This mechanism explains why soot is formed from a stoichiometric mixture which theoretically should not produce a sooty flame.

Many combustion systems are unstable. The purpose of this study was to investigate soot formation in such systems using rapid-scanning spectroscopic systems. It was our ultimate aim to study an unstable flame using simultaneously rapid-scanning optical and mass spectrometry. It was hoped that an investigation of soot formation in an unstable system might lead to criteria for deciding whether or not a process in a stable flame is kinetically or thermodynamically stabilized.
The mass spectrometer to be used in these studies was the Finnigan 1015 quadrupole, a rapid scanning instrument, which is relatively small and portable and, thus, appeared to be appropriately designed for the intended experiments. However, during the original period of the grant and the period of the extension, the mass spectroscopist on this project, G. Salser, concluded that the instrument was not suitable because the spectra were unstable and the instrument was not analytically accurate.

We have delayed submitting the final report in the hope that data could be obtained using this mass spectrometer. At this time, we have been able to eliminate the instability and to obtain analytical accuracy.

A calibration gas mixture was made with the following composition on a mole % basis: hydrogen ($H_2$), 23.9%; methane ($CH_4$), 26.1%; carbon monoxide ($CO$), 26.2%; carbon dioxide ($CO_2$), 23.8%. Based upon sensitivities taken at 40 microns pressure for the individual gases, the mole % shown in Table 4-1 were calculated from the spectra of the standard gas mixture obtained over pressures ranging from 57.4 to 116 microns. The hydrogen value is low but hydrogen is usually difficult to quantitate in gas mixtures using mass spectrometry. Fortunately, the hydrogen values
are low consistently and do not fluctuate unreasonably, therefore, the inaccuracy can be largely "corrected" out.

After these hurdles had been overcome, there is another which has thus far proven to be impassable. Scan-rates of interest, on the basis of the optical studies, lie within the 0.1 to 0.01 second range. However, with the sampling systems available or that could easily be fabricated, the smallest transit time is 0.6 second, given the flow and pressure regimes of interest. To get below this value, it appears that a high pressure molecular beam system is needed. Such a system is beyond our capabilities at the present time.
Table 4-1

<table>
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<th>Pressure (Microns)</th>
<th>( \text{H}_2 )</th>
<th>( \text{CH}_4 )</th>
<th>CO</th>
<th>( \text{CO}_2 )</th>
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<tr>
<td>116</td>
<td>19.25</td>
<td>26.60</td>
<td>28.68</td>
<td>25.47</td>
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<tr>
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<td>26.1</td>
<td>26.2</td>
<td>23.8</td>
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