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LANGLEY GRANT

IN-77-CR

150137

P-18

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Final Report
For the period ended April 30, 1988,

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Under
NASA Contract NAS1-17993
Task Authorization No.'s 60 and 77
Dr. Jag J. Singh, Technical Monitor
Instrument Research Division

Submitted by the
Old Dominion University Research Foundation
P.O. Box 6369
Norfolk, Virginia 23508

July 1988
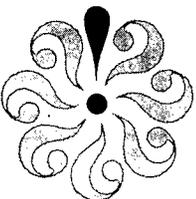
ON-LINE MEASUREMENT OF HEAT OF COMBUSTION

By

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ABSTRACT

An experimental method for an on-line measurement of heat of combustion of a gaseous hydrocarbon fuel mixture of unknown composition is developed. It involves combustion of a test gas with a known quantity of air to achieve a predetermined oxygen concentration level in the combustion products. This is accomplished by a feedback controller which maintains the gas volumetric flow rate at a level consistent with the desired oxygen concentration in the products. The heat of combustion is determined from a known correlation with the gas volumetric flow rate. An on-line micro-computer accesses the gas volumetric flow data, and displays the heat of combustion values at desired time intervals.

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1. INTRODUCTION

Several well known techniques are currently available for the measurement of heats of combustion of hydrocarbon fuels. For example, constant volume bomb calorimeters are commonly used for determination of heats of combustion of liquid and solid fuels. Similarly, constant pressure flame calorimeters are employed for measuring the heat of combustion of gaseous fuels (Ref. 1). Although these methods are reasonably accurate for most applications, they are not suitable for applications which require an on-line measurement of heat of combustion of fuels of unknown composition. This is particularly the case in natural gas transmission industry where the heat of combustion of natural gas of unknown composition may be required at certain time intervals.

In the present study, we have developed a new experimental technique for an on-line measurement of heat of combustion of a gaseous fuel of an unknown composition. Preliminary results indicate that the technique has the potential of measuring the heat of combustion values with a precision approaching 0.30 percent. The proposed method is an extension of a method developed by Singh and associates (Ref. 2). Their method involves combustion of fuel with air of known oxygen concentration. The combustion bound air is sufficiently enriched with oxygen so that the oxygen concentration in the products equals that of the incoming air. It is further shown in Ref. 2 that the heat of combustion is correlated with the ratio of volumetric flow rates of injected oxygen and the fuel. Although this study clearly demonstrates the feasibility of the method, it has the drawback of oxygen enrichment requirement which makes it unsuitable for an on-line field

measurement. A simplified theoretical method, eliminating the requirement of oxygen enrichment, has also been proposed (Ref. 3). This procedure involves combustion of a fuel with a fixed amount of air of a known oxygen concentration. The fuel flow rate is adjusted until a desired oxygen concentration is achieved in the combustion products. The heat of combustion, for a given air flow rate, is shown to be correlated with only one variable, namely the volumetric flow rate of the gaseous fuel. Two correlations are presented for calculating the heat of combustion in the high and low fuel volumetric flow rate regimes.

In the present study, following the ideas presented in Ref. 3, an on-line gas calorimeter is developed for measuring the heat of combustion of hydrocarbon gas fuel mixtures of unknown composition. The technique employs a digital feedback controller to maintain the oxygen concentration in the combustion products at a predetermined level dictated by the combustion stability of the burner, and the oxygen sensor sensitivity. The volumetric fuel flow rate is monitored and controlled at a level consistent with the desired oxygen concentration in the products. The data from the experiment is channeled to an on-line micro-computer which uses a software to display the heat of combustion at desired time intervals. The details of the method are described in the next section.

2. EXPERIMENTAL SET-UP

The prototype gas calorimeter is shown in Fig. 1. A photograph of the set-up is included in Appendix A. The fuel gas and air of known oxygen concentration was premixed and led into a specially designed burner. The volume flow rate of the fuel was measured by a volumetric flowmeter with an optical encoder mounted on its shaft. The volume flowrate (cc/min) was
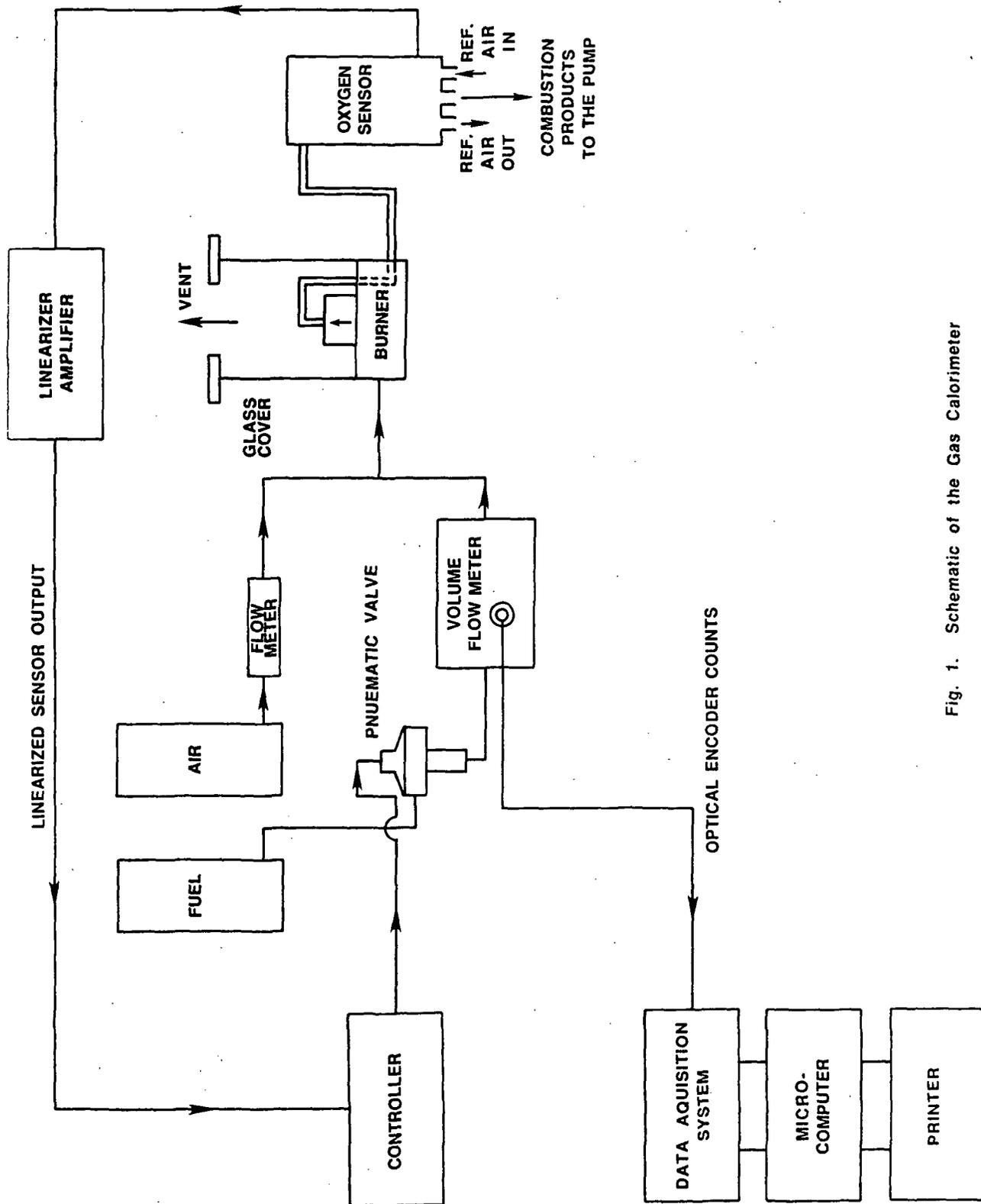
Fig. 1. Schematic of the Gas Calorimeter

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determined by measuring the counts (number/min) of the lines etched on the disk of the encoder. The counts were recorded on a Hewlett Packard (HP) data acquisition system and were also transmitted to a HP micro-computer and a printer.

Initially, the burner presented severe combustion instability problems, and the combustion could not be sustained with a porous plug type burner over a wide range of operating conditions. Depending on the air and fuel flow rates, either a blow-off or a flash-back of the flame resulted. These problems of inflammability are common at low burning velocities (Ref. 4), and special care was required in the burner design to sustain stable combustion. Finally, a burner with internal honeycomb structure was employed to damp out any large disturbances that might have resulted in combustion instability. The use of this burner resulted in a stabilized flat flame front over wide ranges of air and fuel flow rates. The burner was enclosed in a glass container with a vented top. This eliminated any fluctuations of oxygen concentration caused by diffusion of atmospheric oxygen toward the combustion products.

The oxygen concentration in the products was measured by pumping the products through a Y_2O_3 - stabilized ZrO_2 oxygen sensor. Since the sensor's operational characteristics are similar to those described in Ref. 5, we omit the details here. The mili-volt output of the oxygen sensor which correlated uniquely with oxygen concentrations was linearized and amplified during the experiment. The resultant output was directed to a MYCRO-352 single loop digital controller. A similar signal corresponding to 3.0 percent oxygen concentration, a value used in all experiments in the present study, was also dialed into the controller. The controller using the

difference of the two signals, namely the one corresponding to the actual oxygen concentration in products, and the one corresponding to the desired 3.0 percent value, manipulated a pneumatic control valve to vary the fuel flow rate. A higher than desired value of oxygen concentration prompted the controller to open the valve wider and caused higher fuel flow rate through the system. This led to faster depletion of oxygen due to enhanced combustion, resulting in the return of oxygen concentration toward the desired level.

Due to unsteadiness introduced by the volumetric flow meter and the combustion process, the oxygen concentration in the products exhibited small fluctuations around the mean value of three percent oxygen concentration. To average the fluctuations in oxygen concentration, the mean and standard deviation of a set of data points of heat of combustion at equal time intervals was obtained. The experimental procedure and results are described in the next two sections.

EXPERIMENTAL PROCEDURE

Prior to taking the data for heat of combustion, several preparatory steps had to be taken to ready the set-up for experimentation. First, the oxygen sensor was calibrated with air samples of known oxygen concentrations, so that a mV-oxygen concentration calibration curve could be obtained. After this step, the system was flushed for several minutes with air to scavenge any fuel left inside the system from the previous experiment. The bottled air was used for combustion, and its oxygen concentration was measured with the oxygen sensor before the start-up of the experiment. The gas flowmeter was also calibrated so that the number of counts per minute from the optical encoder can be readily converted into

flow rate in cubic centimeter per minute (ccm).

A fixed amount of air flow rate from a pressurized tank was initiated, and the fuel flow rate was gradually increased to a level until a stable flat flame front was established over the burner. The three percent oxygen concentration was dialed as a set-point in the controller, and the controller was activated to monitor the fuel flow rate. The fuel flow was varied by controlling the valve opening until the set-point value was achieved. As pointed out earlier, the oxygen concentration value in combustion products could not be set exactly at three percent level due to inherent unsteadiness of the combustion process and due to unsteadiness introduced by the internal mechanism in the gas flowmeter.

The fuel flow rate data, in terms of counts per minute, was recorded at three minute intervals. This value was then used in a correlation given in Appendix B to obtain a value of heat of combustion at three minutes interval. Several data points over a period of 15 to 30 minutes, depending on the experiment, were recorded, and a mean value and the standard deviation was computed for the period.

4. RESULTS

The present technique was applied to three gas samples, namely methane, a mixture of methane and nitrogen, and ethane. The case of methane was used to calibrate the procedure by using its known value of heat of combustion. The remaining two cases served as examples for validating the procedure. Table 1 shows the experimental data involving optical encoder counts, the flow rate in ccm and the heat of combustion, calculated from the correlation discussed in Appendix B. The oxygen concentration of the supply air was 20.93 percent and the air flow rate was 7000 ccm for this case. We note

TABLE 1

DATA FOR PURE METHANE

COUNTS/180 SEC.	FUEL FLOWRATE (ccm)	HEAT OF COMBUSTION (Kcal/Kmol)
2125	590.3	211.7
2118	588.3	212.5
2108	585.6	213.5
2115	587.5	212.8
2116	587.8	212.7
2108	585.6	213.6
2110	586.1	213.4
2118	588.3	212.5
2112	589.4	212.1

Mean = 212.8 Kcal/Kmol

Standard Deviation = .62 Kcal/Kmol

that the standard deviation of the heat of combustion data points was 0.28 percent for this case.

Table 2 shows the data for the methane (92.5%) and nitrogen (7.5%) mixture. The air flow rate and its oxygen concentration values remained at the same levels. Based on a 7.5 percent non-combustible fraction in the fuel, the heat of combustion of the sample was calculated to be 196.8 Kcal/Kmol. The mean value of nine data points, recorded at three minute intervals, was 197.5, and the standard deviation of the data was 0.77 percent.

Table 3 shows the data for ethane. The air flow rate for this case was 7000 ccm, and the oxygen concentration measured prior to the experiment was 20.95 percent. The standard deviation of 16 data points showed a standard deviation of 0.3%, while the mean value of the data was 376.7 Kcal/Kmol. The corresponding heat of combustion reported in the literature is 372.8 Kcal/Kmol.

5. CONCLUSIONS

An experimental technique for measuring heat of combustion of gas mixtures of unknown composition was developed and tested. The technique is specially attractive for applications where an on-line measurement of heat of combustion is required. The system worked reasonably well during the course of this investigation, and the results validated the technique. Although the data-base generated during the course of this study is somewhat limited, the results indicate that the technique is potentially capable of measuring the heat of combustion of widely ranging hydrocarbon gas mixtures of unknown composition with a precision approaching 0.30 percent.

TABLE 2

DATA FOR METHANE (92.5%) AND N_2 (7.5%) MIXTURE

COUNTS/180 SEC.	FUEL FLOW RATE (ccm)	HEAT OF COMBUSTION (Kcal/Kmol)
2297	671.7	195.6
2265	662.3	198.4
2284	667.9	196.8
2288	669.0	196.4
2260	660.8	198.9
2246	656.7	200.1
2262	661.4	198.7
2301	672.8	195.3
2280	666.7	197.1

Mean Value = 197.5 Kcal/Kmol

Standard Deviation = 1.5 Kcal/Kmol

TABLE 3

DATA FOR PURE ETHANE

COUNTS/300 SEC.	FUEL FLOW RATE (ccm)	HEAT OF COMBUSTION (Kcal/Kmol)
2122	353.7	374.8
2119	353.2	375.4
2121	353.5	375.0
2122	353.7	374.8
2117	352.8	375.7
2112	352.0	376.6
2113	352.2	376.4
2113	352.2	376.4
2112	352.0	376.6
2107	351.2	377.5
2102	350.3	378.4
2108	351.3	377.3
2103	350.5	378.2
2103	350.5	378.2
2101	350.2	378.6
2104	350.7	378.1

Mean Value = 376.7 Kcal/Kmol

Standard Deviation = 1.3 Kcal/Kmol

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APPENDIX A

Photograph of the Set-Up of the Prototype Gas Calorimeter
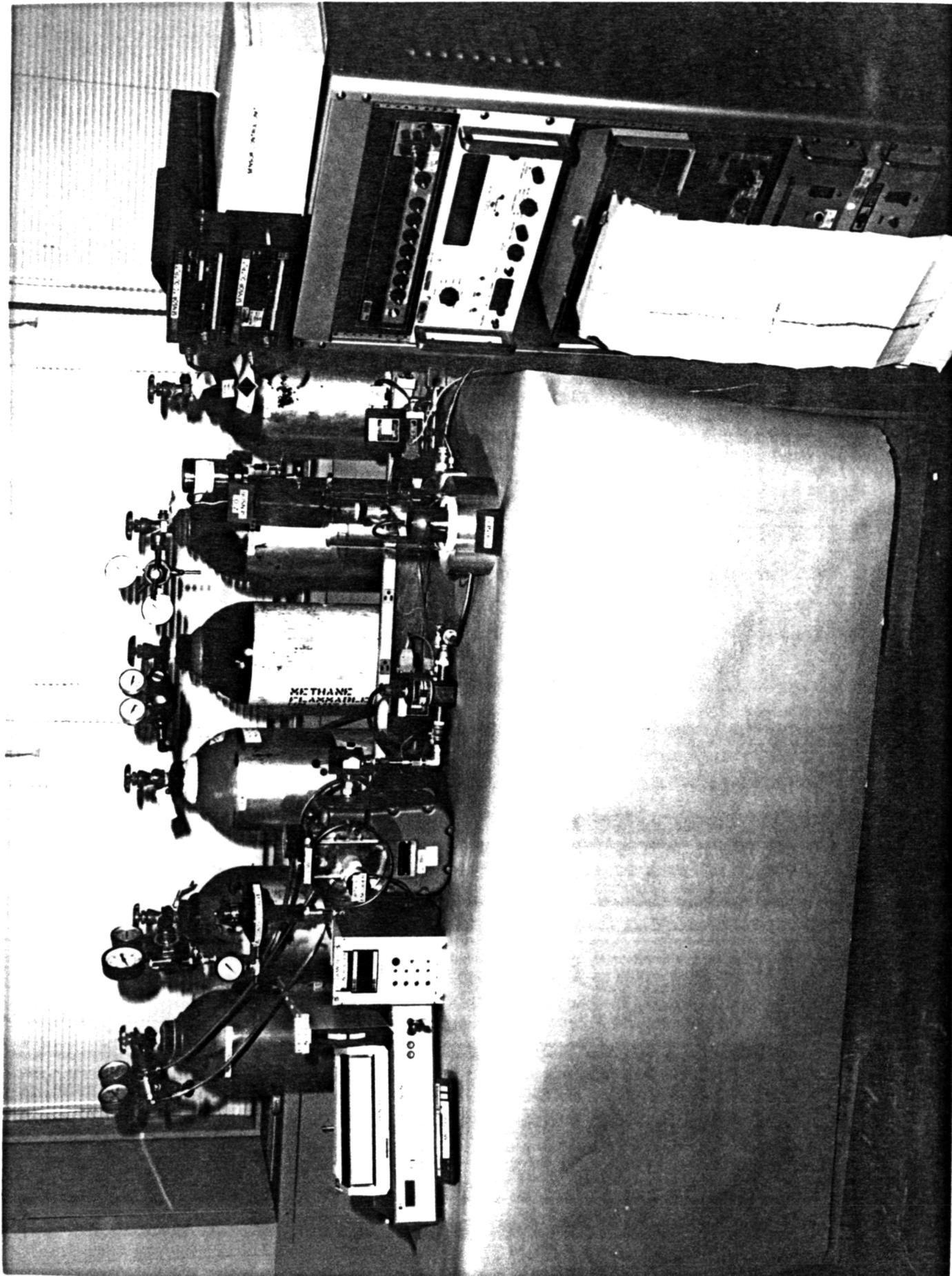
APPENDIX B

Expression for Heat of Combustion of Gas Mixtures

EXPRESSION FOR HEAT OF COMBUSTION OF GAS MIXTURES

The heat of combustion, ΔH_{mix}, of a gas mixture of a pure hydrocarbon $(C_x H_y)$ and non-combustible inert chemical species is given by the expression:

$$\Delta H_{mix} = f \Delta H_{C_x H_y} \tag{1}$$

where f is the combustible fraction by volume of the mixture. If this gas is mixed with air and burned, the amount of oxygen in the products of combustion can be expressed as:

$$P = \frac{4Q1 - nf(4x + y)}{41 + 4n + nf(y-4)} \tag{2}$$

where,

P = oxygen fraction of combustion products;

f = combutible fraction of test gas;

n = volumetric flow rate of test gas;

Q = oxygen fraction of air;

1 = volumetric flow rate of air;

x = carbon atoms in the fuel;

y = hydrogen atoms in the fuel;

Solving Eq. 2 for f, one gets:

$$f = \frac{41(Q-P) - 4\,Pn}{n(4x + (1 + P)y - 4P)} \tag{3}$$

Substituting for f in Eq. 1, one gets:

$$\Delta H_{mixture} = \Delta H_{C_x H_y} \left(\frac{41(Q-P) - 4\,Pn}{n(4x + (1 + P)y - 4P)} \right) \tag{4}$$