REPORT No. 616

INTERRELATION OF EXHAUST-GAS CONSTITUENTS

By HAROLD C. GERRISH and FRED VOS

SUMMARY

An investigation was made to determine the interrelation of the constituents of the exhaust gases of internal-combustion engines and the effect of engine performance on these relations. Six single-cylinder, liquid-cooled test engines and one 9-cylinder radial air-cooled engine were tested. Various types of combustion chambers were used and the engines were operated at compression ratios from 5.1 to 7.0 using spark ignition and from 13.6 to 16.6 using compression ignition. The investigation covered a range of engine speeds from 1,600 to 2,100 r. p. m. The fuels used were two grades of aviation gasoline, Auto Diesel fuel, and Laboratory Diesel fuel. Power, friction, and fuel-consumption data were obtained from the single-cylinder engines at the same time that the exhaust-gas samples were collected.

Definite relations, which were independent of engine design and operating conditions, were found among the constituents of exhaust gases, air-fuel ratio, water of combustion, and combustion efficiency. Combustion efficiency and amount of water of combustion increased approximately linearly with air-fuel ratio for rich mixtures and were independent of mixture strength for lean mixtures. These relations make it possible to obtain a complete exhaust-gas analysis simply by determining the air-fuel ratio or the CO₂ and O₂ content. The results also showed that compression-ignition engines may be operated at the same air-fuel ratio as spark-ignition engines without loss in combustion efficiency.

INTRODUCTION

The mixture strength, or ratio of air to fuel, of internal-combustion engines is of paramount importance, not only because it is a fundamental factor for the correlation of all engine-performance data but because of its effect on the specific fuel consumption and the temperature of the engine cylinder.

The direct method of determining the mixture strength of conventional engines is to measure the air and fuel entering the engine cylinder. The inconvenience of such a procedure necessitates the substitution of some indirect method, such as noting the decrease of engine speed with a constant-pitch propeller when the mixture is leaned, noting the temperature of the cylinder head, or analyzing the exhaust gases.

Various instruments are commercially available for indicating the mixture strength. As the operation of the more promising types of instruments for aircraft depends upon one or more constituents or on some property of the constituents of the exhaust gases, it is essential to know the correlation of these constituents with mixture strength. If the relation of all the products of combustion to one particular component could be established, especially to one that could readily be determined, the measurement and control of the mixture strength of aircraft engines, especially for cruising conditions, would come into more general use.

This investigation was made to establish the relationship among the constituents of the exhaust gases of internal-combustion aircraft engines and to determine the influence of engine design and operating conditions upon these relationships.

APPARATUS AND METHOD

A modified Bureau of Mines gas-analysis apparatus with Bureau of Standards type pipettes was used for the analysis of the exhaust-gas samples. (See reference 1.) Caustic potash was used for absorbing CO₂ and alkaline pyrogallol for absorbing O₂. By means of simple stoichiometric equations and “oxygen and nitrogen balances,” the air-fuel ratio, H–C ratio of the fuel, and water of combustion were computed.

Combustion efficiency was computed from the heat liberated, which is the heat evolved by the formation of CO₂, H₂O, and CO, and from the potential heat, which is the sum of the amount of heat liberated and the amount that could be evolved by the combustion of the unburned combustibles, CO, H₂, and CH₄. Values of the molecular heats of combustion given in reference 2 were used in the calculations.

Six single-cylinder, liquid-cooled test engines and one commercial 9-cylinder radial air-cooled engine were used in this investigation. Table I shows the engine test conditions and the fuels used. The fighting grade
aviation gasoline complied with Army Specification No. Y-3557-G and the standard grade aviation gasoline with Aeronautical Specification No. 7G3. The distillation curves of these fuels are given in figure 1. In spite

![Figure 1: Distillation curves (A. S. T. M.)](image)

of the differences in distillation characteristics, all the fuels had practically the same H-C ratio, 0.175, as determined from exhaust-gas analyses. (See reference 1.)

Power, friction, and fuel-consumption data were obtained from the test engines at the same time that the exhaust-gas samples were collected. The i. m. e. p. was obtained by the addition of the f. m. e. p. and the b. m. e. p.

**COMBUSTION CHARACTERISTICS OF AVIATION GASOLINES AND DIESEL FUELS**

**Exhaust-gas composition.**—The combustion of a hydrocarbon with excess air in an internal-combustion engine results in the formation of $\text{H}_2\text{O}$ and $\text{CO}_2$ with $\text{N}_2$ and $\text{O}_2$ left from the air. The combustion of a hydrocarbon with a deficiency of air produces $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{N}_2$, only a trace of $\text{O}_2$, and also $\text{CO}$, $\text{H}_2$, and $\text{CH}_4$. Some investigators have shown the presence of unsaturated hydrocarbons but tests at this laboratory with fuming sulphuric acid gave no indication of their presence.

Figure 2 shows the composition (by volume) of the exhaust gases from spark- and compression-ignition engines using fuels with an H-C ratio of 0.175. As the composition is given on the usual dry basis, the

![Figure 2: Composition of exhaust gases from spark- and compression-ignition engines using fuels with H-C ratio of 0.175.](image)
clusion of H$_2$O gives a total percentage greater than 100. The largest constituent is N$_2$, varying from 77 to 85 percent of the exhaust gases; CO$_2$ varies from 9 to approximately 14 percent; and H$_2$O varies from 9 to about 16 percent. The maximum values of N$_2$, CO$_2$, and H$_2$O occur at approximately the chemically correct mixture. The amount of CO and O$_2$ varied from 0 to 9 percent, O$_2$ being small in the rich region and CO small in the lean region. The amount of H$_2$ is approximately half the quantity of CO. The amount of CH$_4$ is small and approximately constant for all mixtures.

The presence of O$_2$ in rich mixtures and of CO in lean mixtures has been questioned by different investigators. Dicksee (reference 3) found neither constituent, but Best (reference 4) gives analyses that contain both CO and O$_2$. Minter (reference 5) states that O$_2$ is always present in the exhaust even when rich mixtures are used and concludes that the presence of O$_2$ is due to unequal distribution of the fuel. D’Alleva and Lovell (reference 6) also found O$_2$ present in the exhaust gas of rich mixtures, the O$_2$ content averaging 0.2 percent.

For rich mixtures the solid line (fig. 2) drawn through the test points for CO$_2$ was assumed to be straight and was located by the method of least squares. For lean mixtures a curve similar to the theoretical one was drawn. The point of intersection of the two solid curves corresponds to an air-fuel ratio of 14.4. The O$_2$ curve was calculated from the relation of air-fuel ratio to CO$_2$ and O$_2$ (equation (12)) and the CH$_4$ curve, from equation (2). All of the other curves were calculated by substituting the determined values of CO$_2$ and O$_2$ in equations (8), (7), (8), and (10). The equations are presented in the appendix and were developed from the empirical relations established in reference 1. Note that these equations are applicable only to fuels having H–C ratios of 0.175.

The dashed lines of figure 2 for lean mixtures (air-fuel ratios greater than 15) show the amounts of O$_2$, CO$_2$, H$_2$O, and N$_2$ that would result from complete combustion of the fuel. The theoretical values of CO$_2$ and H$_2$O are larger than the empirical values, which indicates incomplete combustion of the C and H$_2$. The empirical value of O$_2$ is larger than the theoretical on account of the O$_2$ that was not used to burn the C to CO$_2$ and the H$_2$ to H$_2$O.

The results obtained at this laboratory are compared in figure 3 with those obtained by Fenning (reference 7) and D’Alleva and Lovell (reference 6). Fenning’s exhaust-gas samples were obtained from a single-cylinder sleeve-valve engine of 4½-inch bore and 5½-inch stroke, operating at 800 r. p. m. He used a high-grade commercial gasoline designated as “Bowley’s Special petrol.” D’Alleva and Lovell used commercial gasoline in one 8-cylinder and two 6-cylinder automobile engines. Exhaust-gas samples were taken from an exhaust pipe common to all the cylinders. The three investigations show approximately the same relationship. This agreement is especially interesting in view of the fact that over 20 years elapsed between Fenning’s and the other two investigations.

Water of combustion.—The weight ratio of the water formed by combustion of the fuel to the amount of fuel used is of importance when water recovery is considered as a means of maintaining the equilibrium of an airship. Under normal operating conditions the amount of water recovered is from 90 to 100 percent of the fuel used (reference 8). This percentage depends upon the water of combustion, the efficiency of the condenser, and the humidity of the air.

Figure 4 shows the effect of air-fuel ratio on the ratio of the water of combustion to the amount of fuel used. The water of combustion increases approximately linearly with the air-fuel ratio for rich mixtures and is independent of mixture strength for lean mixtures. The curve drawn through the points was obtained from a solution of equation (14), proper values of CO$_2$ and O$_2$ being used. The dashed line is the ratio that would result from complete combustion of the hydrogen in the fuel.
Figure 5 is a chart constructed from equation (14) correlating the ratio of water of combustion to fuel burned with \( \text{CO}_2 \) and \( \text{O}_2 \). The water of combustion in the exhaust may be rapidly determined for any period of time from the weight of the fuel used during this interval and the percentages of \( \text{CO}_2 \) and \( \text{O}_2 \) present. Figure 6 has been prepared to show the agreement between the values of the ratio of water of combustion to fuel burned obtained from figure 5 and from the experimental values. The agreement is not particularly good, there being a deviation of approximately \( \pm 10 \) percent. The discrepancy may be due to inaccurate determinations of the experimental values of water of combustion (see fig. 4) inasmuch as any error in the determination of \( \text{N}_2 \), \( \text{CO}_2 \), \( \text{O}_2 \), and \( \text{CO} \) enters into the experimental determination of these values.

Combustion efficiency.—Figure 4 also shows the influence of air-fuel ratio on combustion efficiency. Note that combustion efficiency increases approximately linearly with air-fuel ratio for rich mixtures and is approximately constant at a value of about 97 percent for lean mixtures. The increase in combustion efficiency with air-fuel ratio indicates the large improvement possible in thermal efficiency and, therefore, the economy of present-day aircraft engines.
The data also show that combustion in the compression-ignition engine and in the spark-ignition engine is equally good for all mixtures. The curve (fig. 4) was determined by the method used for figure 2 except that equation (16) was used. This equation, correlating combustion efficiency with CO₂ and O₂, is shown graphically in figure 7. By means of this figure and a simple Orsat apparatus the combustion efficiency may readily be determined. Figure 8 shows the agreement between values of combustion efficiency determined from figure 7 and those determined by experiment.

Combustion of hydrogen and carbon.—The effect of mixture strength on the ratio of the products of complete combustion (H₂O/CO₂) is plotted in figure 9. The solid curve through the points was obtained from the empirical values of CO₂ and H₂O. The data show
that, for lean mixtures, there is sufficient O$_2$ to burn both H$_2$ and C and the ratio of the products of complete combustion is constant. Theoretically this ratio for complete combustion is 1.04 but, owing to the incompleteness of combustion in this region, the ratio is slightly less. For rich mixtures the H$_2$ burns more readily than the C in the fuel. The fuel does not burn as free H$_2$ and free C but, probably, as various hydrocarbons in such a manner that relatively more H$_2$ is consumed than C. Gerrish and Foster (reference 9) have shown that, when sufficient Diesel fuel is present in the engine cylinder to utilize all the O$_2$, the addition of H$_2$ increases the quantity of H$_2$O formed and decreases the amount of CO$_2$.

**Engine performance.**—In figure 10 the engine performance has been shown as a factor of the air-fuel ratio for the compression-ignition engines 2, 3, and 4 and the spark-ignition engines 5 and 6 operating with a carburetor under the conditions shown in table I. The positions of maximum power for the different engines and conditions on this basis are identical and occur at a definite air-fuel ratio, approximately 13. All engines investigated are on an equivalent basis as regards air-fuel ratio and combustion efficiency; the differences in their performance are due to the amount of charge present and the efficiency of the cycle.

It was thought that some of the differences in the performance of the engines might be the cause of the scatter of the experimental data presented in figures 2, 4, and 9. It was impossible, however, to obtain closer agreement by grouping the data according to engines or engine conditions and it is therefore concluded that the exhaust-gas constituents, air-fuel ratio, water of combustion, combustion efficiency, and their relationships are independent of engine design and manner of operation.

**CONCLUSIONS**

The following conclusions have been drawn from the results presented.

1. The constituents of the exhaust gases from internal-combustion engines bore a definite interrelation.
2. Factors computed from exhaust-gas analyses, such as air-fuel ratio, water of combustion, and combustion efficiency, bore a definite relation to one another and to the constituents of the exhaust gas.
3. Engine performance and operating conditions, such as compression ratio, engine speed, injection advance angle, and method of ignition, did not affect the relations between the exhaust-gas constituents and the factors computed from them.
4. The relations of the constituents and factors make it possible to obtain a complete exhaust-gas analysis simply by determining the air-fuel ratio or the amount of CO$_2$ and O$_2$.
5. For rich mixtures the H$_2$ of hydrocarbon fuels burned more readily than the C.
6. Compression-ignition engines were operated at the same air-fuel ratio as spark-ignition engines without loss in combustion efficiency.
7. Combustion efficiency and water of combustion increased approximately linearly with air-fuel ratio for rich mixtures and were independent of mixture strength for lean mixtures.

Langley Memorial Aeronautical Laboratory,
National Advisory Committee for Aeronautics,
Langley Field, Va., September 7, 1937.
APPENDIX

DEVELOPMENT OF EMPIRICAL RELATIONSHIPS AMONG THE CONSTITUENTS OF THE EXHAUST GASES FROM INTERNAL-COMBUSTION ENGINES

According to reference 1 for standard grades of aviation gasolines, Auto Diesel fuel, and Laboratory Diesel fuel

\[ H_2 = 0.51 \text{ CO} \]  
\[ \text{CH}_4 = 0.22 \text{ CO} \]  
\[ K = \frac{H}{C} = 0.175 \]

\[ H_2O = 5.955 K (\text{CO} + \text{CO}_2 + \text{CH}_4) - H_2 - 2\text{CH}_4 \]  

and

\[ O_2 + \text{CO}_2 (1 + 2.355 K) + \text{CO}(0.604 + 2.355 K) - 0.186 H_2 - \text{CH}_4 (0.583 - 2.355 K) = 20.9 \]  

Inserting the values of \( H_2, \text{CH}_4, \) and \( K \) in equation (5) and then solving for \( \text{CO} \),

\[ \text{CO} = 22.733 - 1.086 O_2 - 1.533 \text{CO}_2 \]  

Inserting this value of \( \text{CO} \) in equation (1),

\[ H_2 = 11.594 - 0.554 O_2 - 0.782 \text{CO}_2 \]  

Inserting the values of \( H_2, \text{CH}_4, K, \) and \( \text{CO} \) in equation (4),

\[ H_2O = 11.885 - 0.578 O_2 + 0.226 \text{CO}_2 \]  

By differences there is obtained

\[ N_2 = 100 - \text{CO}_2 - O_2 - \text{CO} - H_2 - \text{CH}_4 \]  

Substituting the values of \( H_2, \text{CH}_4, \) and \( \text{CO} \) in equation (9),

\[ N_2 = 65.453 + 0.6395 O_2 + 1.3148 \text{CO}_2 \]  

The air-fuel ratio \( (A/F) \) is

\[ \frac{A}{F} = 28.84 \left( \frac{N_2}{0.791} \right) \]  

where the values outside the parentheses are the molecular weights of air, carbon, and hydrogen and 0.791 is the volumetric ratio of \( N_2 \) to air.

Substituting in equation (11) the values previously found for \( N_2, \text{CH}_4, H_2, \text{CO}, \) and \( H_2O \),

\[ \frac{A}{F} = 1.523 \left( \frac{102.350 + O_2 + 2.056 \text{CO}_2}{21.139 - O_2 - 0.491 \text{CO}_2} \right) \]  

The ratio of the water of combustion to the fuel present \( (W/F) \) is

\[ \frac{W}{F} = \frac{18.015 H_2O}{12(\text{CO}_2 + \text{CO} + \text{CH}_4) + 2.015(H_2 + H_2O + 2\text{CH}_4)} \]  

Substituting the values previously found for \( H_2O, \text{CO}, \text{CH}_4, \) and \( H_2 \),

\[ \frac{W}{F} = 0.650 \left( \frac{20.582 - O_2 + 0.391 \text{CO}_2}{21.139 - O_2 - 0.491 \text{CO}_2} \right) \]  

In the determination of the combustion efficiency, the heat of vaporization of \( H_2O \) is not included because the cylinder gases are exhausted at a temperature considerably above the boiling point of water. The heats of combustion of the fuels have been computed from the heats of combustion of the elementary constituents. This method is in error by the heat of formation of the fuel. The error is small, however, amounting to about 1 percent in combustion efficiency for air-fuel ratios giving maximum power. The heats of combustion utilized in the calculations are given in kilojoules (absolute) at 18° C. and 1 atmosphere (reference 2).

The heat liberated by the formation of \( \text{CO}_2, H_2O, \) and \( \text{CO} \) is

\[ 395 \text{CO}_2 + 110.6 \text{CO} + 242 H_2O \]

The heat that could be evolved by the combustion of the unburned combustibles is

\[ 242 H_2 + 284.4 \text{CO} + 799 \text{CH}_4 \]

The combustion efficiency may be expressed as the ratio of the heat liberated to the sum of the heat liberated and the heat that still could be evolved.

Combustion efficiency

\[ \text{Combustion efficiency} = \frac{\text{CO}_2 + 0.280 \text{CO} + 0.613 \text{H}_2O}{\text{CO}_2 + \text{CO} + 0.613 \text{H}_2O + 0.613 \text{H}_2 + 2.023 \text{CH}_4} \]  

Substituting the values previously found for \( H_2O, \text{CO}, \text{CH}_4, \) and \( H_2 \),

Combustion efficiency

\[ = 0.370 \left( \frac{20.74 - O_2 + 1.079 \text{CO}_2}{21.11 - O_2 - 0.491 \text{CO}_2} \right) \]  

A summary of the solution of the equations is given in table II.

REFERENCES


145

<table>
<thead>
<tr>
<th>Air Fuel</th>
<th>CO (per cent)</th>
<th>O (per cent)</th>
<th>CO (per cent)</th>
<th>H (per cent)</th>
<th>N (per cent)</th>
<th>H2O (per cent)</th>
<th>H2O (per cent)</th>
<th>Combustion efficiency (per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>0.78</td>
<td>0.15</td>
<td>0.14</td>
<td>4.68</td>
<td>77.08</td>
<td>12.78</td>
<td>1.57</td>
<td>0.972</td>
</tr>
<tr>
<td>12</td>
<td>10.18</td>
<td>0.44</td>
<td>0.83</td>
<td>3.29</td>
<td>74.13</td>
<td>18.23</td>
<td>1.27</td>
<td>1.043</td>
</tr>
<tr>
<td>13</td>
<td>11.60</td>
<td>0.80</td>
<td>0.83</td>
<td>2.59</td>
<td>81.09</td>
<td>14.18</td>
<td>1.19</td>
<td>1.129</td>
</tr>
<tr>
<td>14</td>
<td>13.02</td>
<td>1.22</td>
<td>1.59</td>
<td>1.07</td>
<td>85.59</td>
<td>14.48</td>
<td>1.11</td>
<td>1.366</td>
</tr>
<tr>
<td>15</td>
<td>15.23</td>
<td>1.52</td>
<td>1.99</td>
<td>0.59</td>
<td>85.72</td>
<td>14.02</td>
<td>1.06</td>
<td>1.247</td>
</tr>
<tr>
<td>16</td>
<td>17.52</td>
<td>2.12</td>
<td>2.41</td>
<td>0.16</td>
<td>83.45</td>
<td>13.53</td>
<td>1.04</td>
<td>1.254</td>
</tr>
<tr>
<td>17</td>
<td>19.00</td>
<td>2.55</td>
<td>2.85</td>
<td>0.15</td>
<td>82.51</td>
<td>13.54</td>
<td>1.05</td>
<td>1.261</td>
</tr>
<tr>
<td>18</td>
<td>20.45</td>
<td>3.05</td>
<td>3.26</td>
<td>0.15</td>
<td>82.59</td>
<td>13.54</td>
<td>1.05</td>
<td>1.272</td>
</tr>
<tr>
<td>19</td>
<td>21.90</td>
<td>3.50</td>
<td>3.69</td>
<td>0.15</td>
<td>82.26</td>
<td>13.22</td>
<td>1.05</td>
<td>1.272</td>
</tr>
<tr>
<td>20</td>
<td>23.40</td>
<td>4.01</td>
<td>4.13</td>
<td>0.15</td>
<td>82.07</td>
<td>12.78</td>
<td>1.05</td>
<td>1.272</td>
</tr>
<tr>
<td>21</td>
<td>24.90</td>
<td>4.50</td>
<td>4.54</td>
<td>0.15</td>
<td>82.70</td>
<td>12.18</td>
<td>1.05</td>
<td>1.271</td>
</tr>
<tr>
<td>22</td>
<td>26.40</td>
<td>5.01</td>
<td>5.02</td>
<td>0.15</td>
<td>82.71</td>
<td>11.55</td>
<td>1.05</td>
<td>1.271</td>
</tr>
<tr>
<td>23</td>
<td>27.90</td>
<td>5.50</td>
<td>5.52</td>
<td>0.15</td>
<td>82.23</td>
<td>11.12</td>
<td>1.05</td>
<td>1.270</td>
</tr>
<tr>
<td>24</td>
<td>29.40</td>
<td>6.00</td>
<td>6.03</td>
<td>0.15</td>
<td>82.37</td>
<td>10.77</td>
<td>1.05</td>
<td>1.265</td>
</tr>
</tbody>
</table>