REPORT No. 616

INTERRELATION OF EXHAUST-GAS CONSTITUENTS

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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 13.5 to 15.6 using compression ignition. The investigation covered a range of engine speeds from 1,500 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 CO_2 and O_2 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 CO_2 and alkaline pyrogallol for absorbing O_2. 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 CO_2, H_2O, 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, H_2, and CH_4. 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

TABLE I.—ENGINE TEST CONDITIONS

Engine	Number of cylinders	Displacement (cubic inches)	Type of combustion chamber	Type of ignition	Type of cooling	Fuel system	Fuel	Compression ratio	Engine speed (r.p.m.)	Valve timing
1	1	137	Pent roof	Spark	Liquid	Carburetor and injection.	Standard grade aviation gasoline.	5.5	1,500	Standard.
2	1	137	Bulb prechamber	Compression	do	Injection	Auto Diesel and Laboratory Diesel.	13.5	1,500	Do.
3	1	137	Vertical disk	do	do	do	Auto Diesel	15.6	1,500	19° overlap.
4	1	137	Vertical disk with displacer piston.	do	do	do	do	15.3	1,500	60° overlap.
5	1	143	Pent roof	Spark	do	Carburetor and injection.	Standard grade aviation gasoline.	5.8	1,500	Standard.
6	1	143	do	do	do	do	do	7.0	1,500 to 2,100	130° overlap.
7	9	1,750	Spherical	do	Air	Carburetor	Fighting grade aviation gasoline.	5.1	1,475 to 1,550	Standard.

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

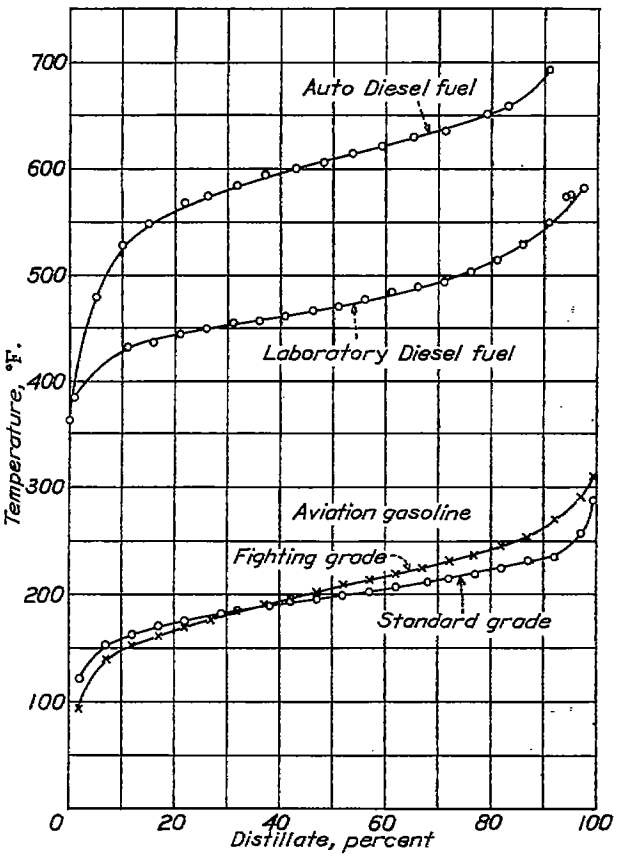

FIGURE 1.—Distillation curves (A. S. T. M.).

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 H_2O and CO_2 with N_2 and O_2 left from the air. The combustion of a hydrocarbon with a deficiency of air produces H_2O, CO_2, N_2, only a trace of O_2, and also CO, H_2, and 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 in-

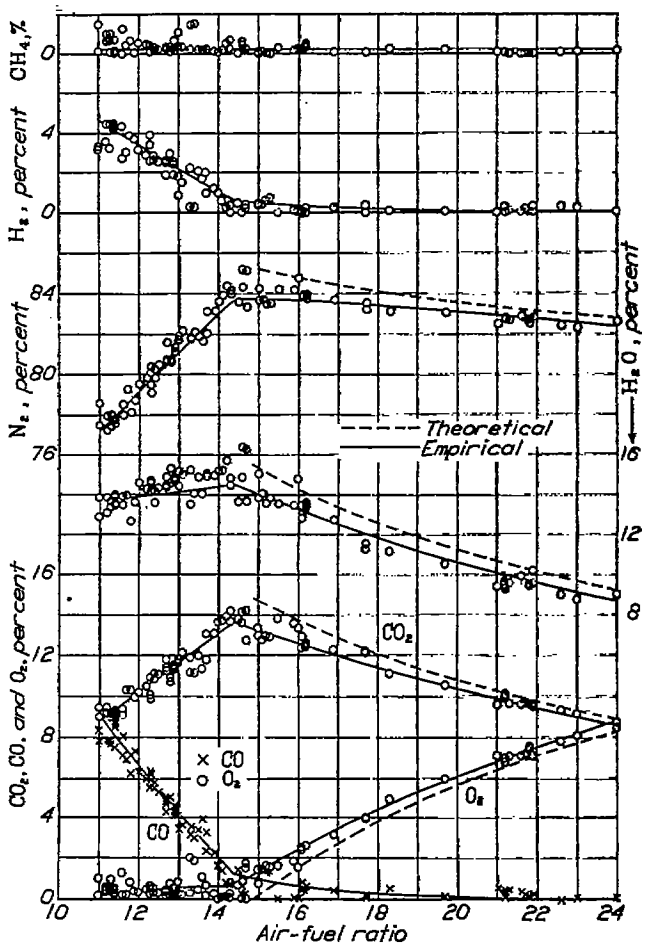

FIGURE 2.—Composition of exhaust gases from spark- and compression-ignition engines using fuels with H-C ratio of 0.175.

clusion of H_2O 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_2O varies from 9 to about 16 percent. The maximum values of N_2, CO_2, and H_2O 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 investi-

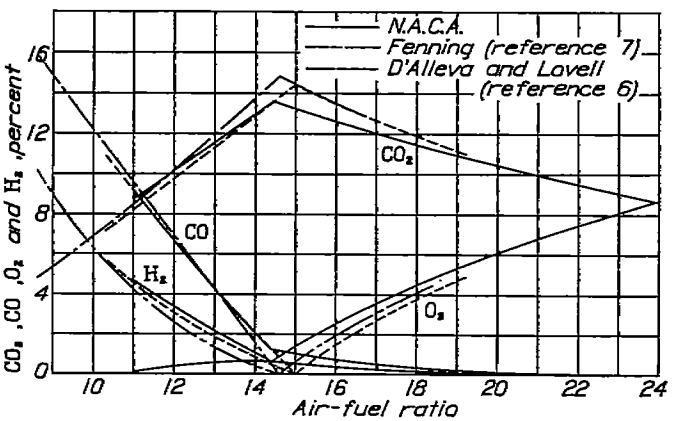

FIGURE 3.—Comparison of exhaust-gas analyses.

gators. 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 (6), (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_2O, and N_2 that would result from complete combustion of the fuel. The theoretical values of CO_2 and H_2O 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_2O.

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 4 1/16-inch bore and 5 5/16-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.

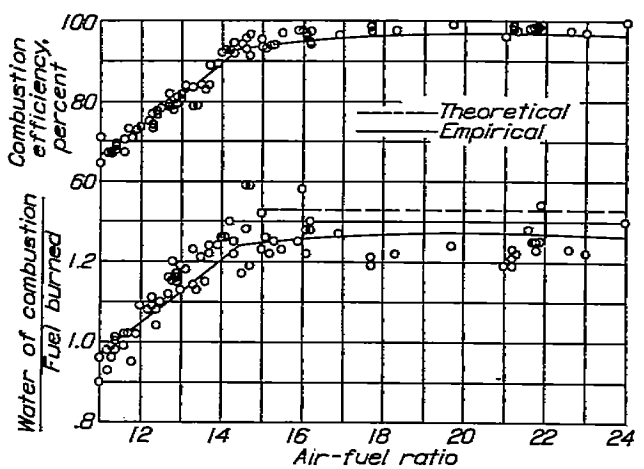

FIGURE 4.—Combustion efficiency and water of combustion.

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.

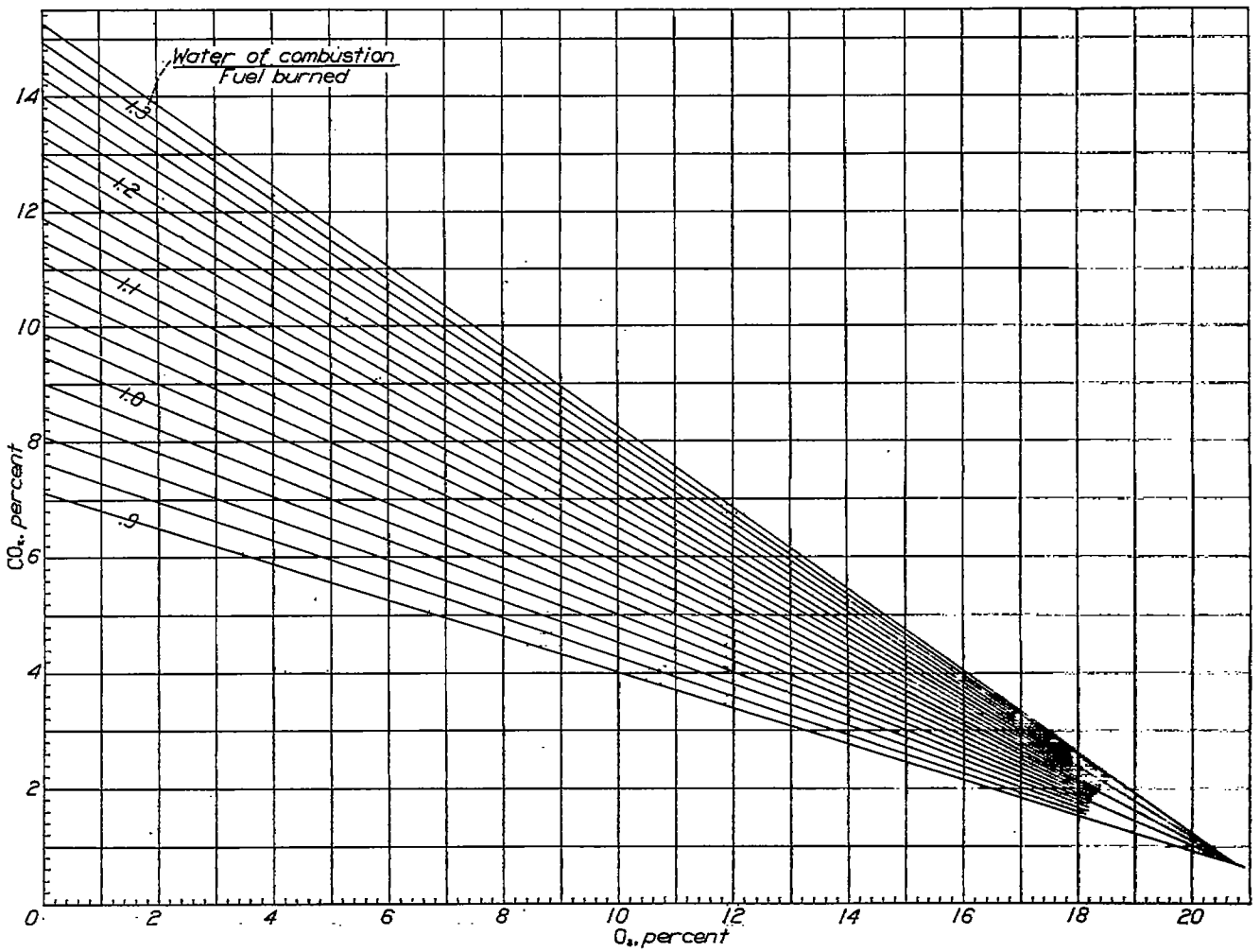

FIGURE 5.—Water-of-combustion chart (empirical).

Figure 5 is a chart constructed from equation (14) correlating the ratio of water of combustion to fuel burned with CO_2 and 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 CO_2 and 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 ± 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 N_2, CO_2, O_2, and 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.

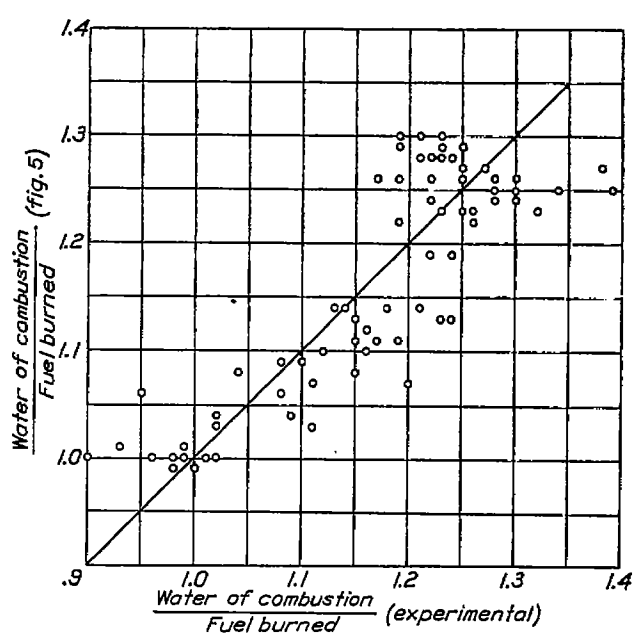

FIGURE 6.—Agreement of empirical and experimental values of water of combustion.

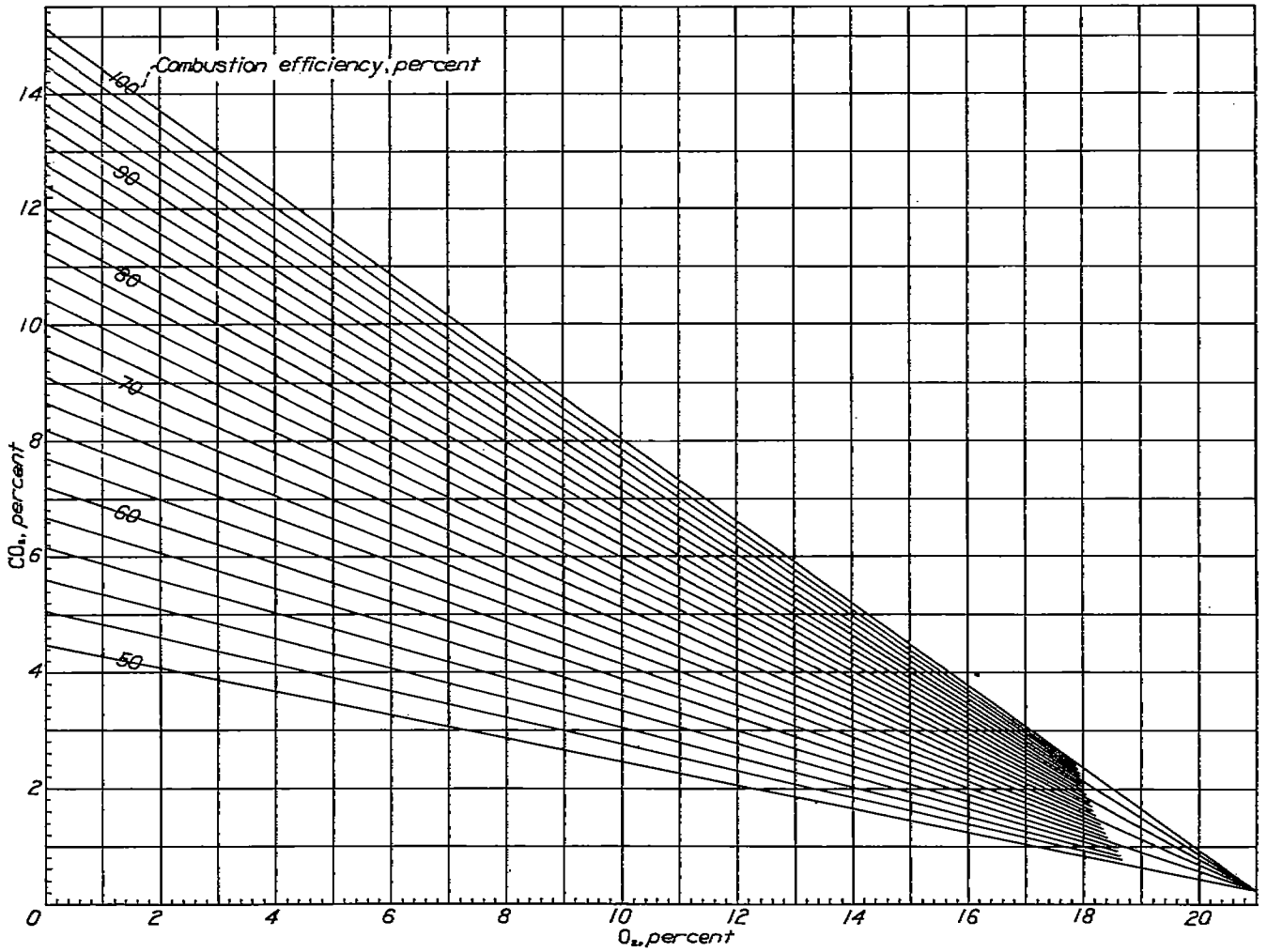

FIGURE 7.—Combustion-efficiency chart (empirical).

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 CO_2 and O_2, 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.

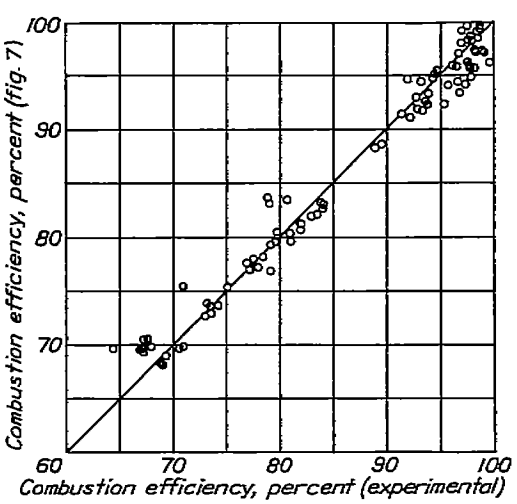

FIGURE 8.—Agreement of empirical and experimental values of combustion efficiency.

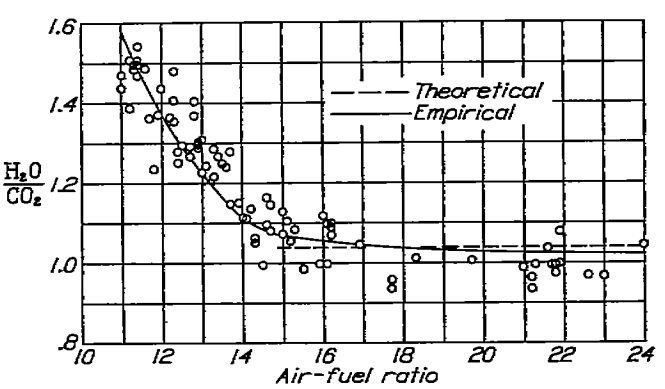

FIGURE 9.—Relative combustion of hydrogen and carbon.

Combustion of hydrogen and carbon.—The effect of mixture strength on the ratio of the products of complete combustion (H_2O/CO_2) is plotted in figure 9. The solid curve through the points was obtained from the empirical values of CO_2 and H_2O. 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

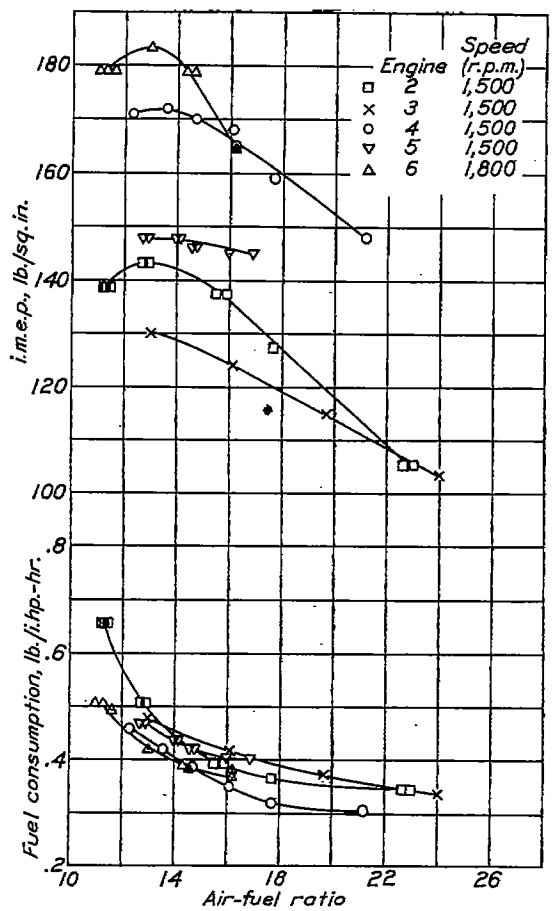

FIGURE 10.—Effect of air-fuel ratio on engine performance.

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_2O 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.

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APPENDIX

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

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

$$H_2=0.51\ CO \tag{1}$$

$$CH_4=0.22 \tag{2}$$

$$K=\frac{H}{C}=0.175 \tag{3}$$

$$H_2O=5.955\ K\ (CO_2+CO+CH_4)-H_2-2CH_4 \tag{4}$$

and

$$O_2+CO_2(1+2.355\ K)+CO(0.604+2.355\ K)-0.186\ H_2-CH_4(0.582-2.355\ K)=20.9 \tag{5}$$

Inserting the values of H_2, CH_4, and K in equation (5) and then solving for CO,

$$CO=22.733-1.086\ O_2-1.533\ CO_2 \tag{6}$$

Inserting this value of CO in equation (1),

$$H_2=11.594-0.554\ O_2-0.782\ CO_2 \tag{7}$$

Inserting the values of H_2, CH_4, K, and CO in equation (4),

$$H_2O=11.885-0.578\ O_2+0.226\ CO_2 \tag{8}$$

By differences there is obtained

$$N_2=100-CO_2-O_2-CO-H_2-CH_4 \tag{9}$$

Substituting the values of H_2, CH_4, and CO in equation (9),

$$N_2=65.453+0.6395\ O_2+1.3148\ CO_2 \tag{10}$$

The air-fuel ratio (A/F) is

$$\frac{A}{F}=\frac{28.84\left(\frac{N_2}{0.791}\right)}{12(CO_2+CO+CH_4)+2.015(H_2+H_2O+2CH_4)} \tag{11}$$

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, CH_4, H_2, CO, and H_2O,

$$\frac{A}{F}=1.523\left(\frac{102.350+O_2+2.056\ CO_2}{21.139-O_2-0.491\ CO_2}\right) \tag{12}$$

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

$$\frac{W}{F}=\frac{18.015\ H_2O}{12(CO_2+CO+CH_4)+2.015(H_2+H_2O+2CH_4)} \tag{13}$$

Substituting the values previously found for H_2O, CO, CH_4, and H_2,

$$\frac{W}{F}=0.680\left(\frac{20.562-O_2+0.391\ CO_2}{21.139-O_2-0.491\ CO_2}\right) \tag{14}$$

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 CO_2, H_2O, and CO is

$$395\ CO_2+110.6\ CO+242\ H_2O$$

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

$$242\ H_2+284.4\ CO+799\ CH_4$$

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

$$=\frac{CO_2+0.280\ CO+0.613\ H_2O}{CO_2+CO+0.613\ H_2O+0.613\ H_2+2.023\ CH_4} \tag{15}$$

Substituting the values previously found for H_2O, CO, CH_4, and H_2,

Combustion efficiency

$$=0.370\left(\frac{20.74-O_2+1.079\ CO_2}{21.11-O_2-0.491\ CO_2}\right) \tag{16}$$

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

REFERENCES

1. Gerrish, Harold C., and Tessmann, Arthur M.: Relation of Hydrogen and Methane to Carbon Monoxide in Exhaust Gases from Internal-Combustion Engines. T. R. No. 476, N. A. C. A., 1933.
2. National Research Council: International Critical Tables, vol. V, McGraw-Hill Book Company, Inc., 1929, pp. 176 and 181.

3. Dicksee, C. B.: Exhaust Gas Analysis. Auto. Eng., vol. XXI, no. 285, Oct. 1931, pp. 401–406.
4. Best, H. W.: Report on Air-Fuel-Ratio Tests. S. A. E. Jour., vol. XXV, no. 5, Nov. 1929, pp. 532–534.
5. Minter, Clarke C.: Interpretation of Exhaust Gas. S. A. E Jour., vol. XXI, no. 5, Nov. 1927, pp. 573–575.
6. D'Alleva, B. A., and Lovell, W. G.: Relation of Exhaust Gas Composition to Air-Fuel Ratio. S. A. E. Jour., vol. 38, no. 3, March 1936, pp. 90–98, p. 116.
7. Fenning, Robert W.: The Composition of the Exhaust from Liquid-Fuel Engines. Jour. Inst. Mech. Eng., March 1916, pp. 185–236.
8. Fulton, Garland: Improving Airship Performance. A. S. M. E. Trans., AER-56-8, vol. 56, no. 5, May 1934, pp. 301–303.
9. Gerrish, Harold C., and Foster, Hampton H.: Hydrogen as an Auxiliary Fuel in Compression-Ignition Engines. T. R. No. 535, N. A. C. A., 1935.

TABLE II.—SUMMARY OF VALUES COMPUTED FROM EMPIRICAL EQUATIONS

Air/Fuel	CO_2 (percent)	O_2 (percent)	CO (percent)	H_2 (percent)	N_2 (percent)	H_2O (percent)	H_2O/CO_2	Water/Fuel	Combustion efficiency (percent)
11	8.76	0.15	9.14	4.66	77.08	13.78	1.57	0.972	56.7
12	10.18	.44	6.65	3.39	79.13	13.93	1.37	1.043	73.8
13	11.60	.59	4.31	2.20	81.09	14.16	1.22	1.122	81.5
14	13.02	.63	2.09	1.07	82.99	14.46	1.11	1.205	89.6
15	13.23	1.35	.99	.50	83.72	14.09	1.06	1.247	93.8
16	12.62	2.49	.68	.35	83.65	13.30	1.05	1.256	94.8
17	12.00	3.55	.48	.25	83.51	12.54	1.05	1.261	95.5
18	11.45	4.49	.30	.16	83.39	11.88	1.04	1.267	96.2
19	10.90	5.36	.20	.10	83.23	11.25	1.03	1.269	96.5
20	10.40	6.15	.11	.06	83.07	10.68	1.03	1.272	96.9
21	9.92	6.86	.08	.04	82.90	10.16	1.03	1.271	96.9
22	9.44	7.55	.06	.03	82.71	9.65	1.02	1.268	96.8
23	9.00	8.18	.05	.03	82.53	9.19	1.02	1.266	96.7
24	8.60	8.74	.06	.03	82.37	8.78	1.02	1.264	96.6