NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

REPORT No. 476

RELATION OF HYDROGEN AND METHANE
TO CARBON MONOXIDE IN EXHAUST GASES
FROM INTERNAL-COMBUSTION ENGINES

By HAROLD C. GERRISH and ARTHUR M. TESSMANN

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AERONAUTICAL SYMBOLS

1. FUNDAMENTAL AND DERIVED UNITS

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2. GENERAL SYMBOLS, ETC.

- W, Weight = mg
- g, Standard acceleration of gravity = 9.80665 m/s² = 32.1740 ft./sec.²
- m, Mass = W/g
- ρ, Density (mass per unit volume).
- Standard density of dry air, 0.12497 (kg·m⁻¹·s⁻²) at 15°C and 750 mm = 0.002378 lb./ft.⁻³.
- Specific weight of “standard” air, 1.2255 kg/m³ = 0.07651 lb./ft.³.

3. AERODYNAMICAL SYMBOLS

- V, True air speed.
- q, Dynamic (or impact) pressure = 1/2 ρ V².
- L, Lift, absolute coefficient C_L = L/qS
- D, Drag, absolute coefficient C_D = D/qS
- D₁, Profile drag, absolute coefficient C_D₁ = D₁/qS
- D₂, Induced drag, absolute coefficient C_D₂ = D₂/qS
- D₃, Parasite drag, absolute coefficient C_D₃ = D₃/qS
- C, Cross-wind force, absolute coefficient C_C = C/qS
- R, Resultant force.
- i_w, Angle of setting of wings (relative to thrust line).
- i_t, Angle of stabilizer setting (relative to thrust line).
- mk², Moment of inertia (indicate axis of the radius of gyration k, by proper subscript).
- S, Area.
- Sₚ, Wing area, etc.
- G, Gap.
- b, Span.
- c, Chord.
- b², Aspect ratio.
- ρ, Coefficient of viscosity.
- μ, Coefficient of viscosity.
- Q, Resultant moment.
- Ω, Resultant angular velocity.
- ρ V₁², Reynolds Number, where l is a linear dimension.
- e.g., for a model airfoil 3 in. chord, 100 mi./hr. normal pressure, at 15°C, the corresponding number is 234,000;
- or for a model of 10 cm chord 40 m/s, the corresponding number is 274,000.
- Cₚ, Center of pressure coefficient (ratio of distance of c. p. from leading edge to chord length).
- α, Angle of attack.
- ε, Angle of downwash.
- α∞, Angle of attack, infinite aspect ratio.
- αᵣ, Angle of attack, induced.
- αᵣ, Angle of attack, absolute.
- (Measured from zero lift position.)
- γ, Flight path angle.
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By HAROLD C. GERRISH and ARTHUR M. TESSMANN
Langley Memorial Aeronautical Laboratory
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS
NAVY BUILDING, WASHINGTON, D.C.

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By Harold C. Gerrish and Arthur M. Teissmann

SUMMARY

The relation of hydrogen and methane to carbon monoxide in the exhaust gases from internal-combustion engines operating on standard-grade aviation gasoline, fighting-grade aviation gasoline, hydrogenated safety fuel, "Laboratory Diesel" fuel, and "Auto Diesel" fuel was determined by analysis of the exhaust gases. Two liquid-cooled single-cylinder spark-ignition, one 9-cylinder radial air-cooled spark-ignition, and two liquid-cooled single-cylinder compression-ignition engines were used.

The results of more than 100 exhaust-gas analyses showed that a linear relation existed between the carbon monoxide and the hydrogen found in the exhaust gas from engines using hydrogenated fuels. A small amount of CH₄ was found to be always present in the exhaust gas, but the amount was independent of the air-fuel ratio and of the H-C ratio of the fuel. These relationships and the use of the Ostwald combustion diagram make available all the information of a complete exhaust-gas analysis when any two factors (CO₂, CO, O₂, or air-fuel ratio) are known. The preparation and use of an Ostwald combustion diagram are described. It is also shown that the air-fuel ratio supplied to the engine may be determined with a precision of ±2 percent without measuring the air taken in by the engine, thus making the method of particular value for work outside the laboratory.

INTRODUCTION

The importance of the complete analysis of the exhaust gases from internal-combustion engines is not generally realized but, inasmuch as information relating to composition of the fuel used, air-fuel ratio, fuel wasted due to incomplete combustion, and in particular the carbon-monoxide content of the exhaust may be readily obtained from such analyses, it is evident that the analyses are of considerable importance, although little reliable data on exhaust-gas relationships are available. The value of a partial analysis of the exhaust gas in adjusting carburetors is clearly recognized today and several automatic instruments for analyzing exhaust gas have been made available to engine operators.

The simple type of Orsat apparatus has been largely used to determine the amounts of carbon dioxide (CO₂), carbon monoxide (CO), and oxygen (O₂) in the exhaust gas. The determination of the amount of CO is not as satisfactory as that of the other constituents because of the poor absorption characteristics of the solutions used. If relationships could be established between the O₂ and CO₂ of the exhaust gas and the other constituents (carbon monoxide (CO), hydrogen (H₂), and methane (CH₄)) the usefulness of the simple Orsat apparatus would be materially increased.

Little experimental evidence has been published on the correlation of CO, H₂, and hydrocarbons in exhaust gases from internal-combustion engines. Fenning (reference 1), using gasoline in a single-cylinder sleeve-valve engine operating at 800 r.p.m., found that in the exhaust gases $H_2 = 1.30$ CO and that $OH_4$ was almost entirely absent. He refers to an earlier experimenter, Ballentyne, who had found that in the exhaust gas of a gasoline engine $H_2 = 0.36$ CO and $CH_4 = 0.12$ CO. Judge (reference 2, p. 103) states that the just-mentioned empirical relations are sufficiently accurate for estimating the percentages of $H_2$ and $CH_4$ present in the exhaust.

The purpose of this investigation was (1) to determine the relation between $H_2$, $CH_4$, and CO in the exhaust of 4-stroke-cycle engines using standard grade and fighting grade aviation gasoline, hydrogenated safety fuel, "Laboratory Diesel" fuel, and "Auto Diesel" fuel; and (2) to prepare combustion diagrams, the use of which would permit the estimation of CO, $H_2$, and $CH_4$ in the exhaust gas from the determination of CO₂ and O₂. This investigation was conducted by the National Advisory Committee for Aeronautics between 1931 and 1933.

APPARATUS AND METHOD

A modification of the Bureau of Mines gas-analysis apparatus was used during this investigation and is shown in figure 1. Special forms of pipettes developed by the Bureau of Standards (reference 3, p. 133) were used to obtain more efficient absorption.
The percentages of CO₂ and O₂ were determined in the usual manner by absorption in potassium hydroxide and alkaline pyrogallol, respectively. These solutions were prepared as recommended by Shepherd (reference 3, p. 145). Percentages of H₂, CH₄, and CO were computed from data obtained by the combustion of the residual gas and air in the slow-combustion pipette (reference 3, p. 162). Tests with fuming sulphuric acid showed no unsaturated hydrocarbons present.

Gas samples were obtained by inserting a steel tube into the exhaust pipe immediately behind the exhaust valve of the single-cylinder test engines and approximately 5 feet from the open end of the exhaust pipe of the 9-cylinder radial engine. Several minutes after the engine had attained a stable condition, the samples were collected in glass sampling tubes. Samples were first taken by displacement of mercury, but later evacuated sampling tubes were used, employing only those that would hold an absolute pressure of 0.1 mm of mercury for several hours. Samples by either method gave consistent results. Portions of several check samples were analyzed immediately and at intervals of 1 and 2 weeks and no difference was found in the analyses.

In this investigation four single-cylinder 4-stroke liquid-cooled test engines and one 9-cylinder radial air-cooled engine were used. Table I shows the engine test conditions and the fuels used. The distillation curves (A.S.T.M.) for the fuels are shown in figure 2.

FIGURE 2.—Distillation curves (A.S.T.M.).

The H-C ratio of hydrogenated safety fuel was given by the manufacturer as 0.130. As the gasolines conformed to the Air Service specifications, they have been considered to have an H-C ratio of approximately 0.175 (reference 4, p. 461).

Fuel consumption was measured directly by weight, and air consumption by means of an 80-cubic-foot-capacity gasometer. The start and stop of the gasometer were synchronized electrically with the engine revolution counter and a stop watch.

RESULTS AND DISCUSSION

Relation of H₂ and CH₄ to CO.—The percentages of H₂, CH₄, and CO found in the exhaust gases of the engines using standard grade and fighting grade aviation gasolines, Auto Diesel fuel, and Laboratory Diesel fuel are plotted in figure 3. A mean curve drawn
through all the data gives a reasonably accurate approximation for the H-CO ratio. The test points for the various engines and fuels lie surprisingly near a mean curve for all the data. However, there is a small deviation of the mean curve for each set of data from the mean curve for all the data, indicating a slight shift in the H-CO ratio with changes in fuels and engines.

The maximum deviation of the experimental points from this mean curve is about 20 percent for the large quantities of CO. The relation of H₂ to CO, considering all the test points, is

\[ H_2 = 0.51CO \]

whereas \( CH_4 = 0.22 \) percent.

In figure 3 a comparison is also made between the results obtained when using a carburetor and when using a fuel-injection system with spark ignition. It is evident that the relation of H₂ to CO is unaffected by the manner in which the fuel is introduced into the engine cylinder.

The experimental data establishing the relationship between H₂ and CO in the exhaust gas from an engine using hydrogenated safety fuel are given in figure 4. The relationship was found to be

\[ H_2 = 0.33CO \]

amount of CH₄ was found to be constant and equal to 0.27 percent.

No satisfactory explanation for the constancy of the percentage of CH₄ in the exhaust gas of spark-ignition and compression-ignition engines, irrespective of the load or type of fuel employed, is available at this time.

Figure 5 shows the relation of O₂ and CO₂ in the exhausts of three single-cylinder test engines and one 9-cylinder radial engine. The fuels used were standard-grade aviation gasoline, fighting grade aviation gasoline, Auto Diesel fuel, and Laboratory Diesel fuel. It will be noted that for lean mixtures the experimental and theoretical results agree. For rich mixtures Dicksee (reference 5) found no free oxygen present. Fenning found oxygen present when using rich mixtures in a single-cylinder sleeve-valve test engine, but found none in his bomb experiments. He states (reference 1, p. 204) that the free oxygen found for rich mixtures was probably due to leakage past the sleeve valves during compression. Best (reference 6) analyzed the exhaust gases from separate exhaust stacks of a 6-cylinder engine operating at 1,300 r.p.m., full throttle, and with an air-fuel ratio of 11.9 (by measurement of air and fuel). He found oxygen present in each stack. It is believed that the presence of free oxygen with rich mixtures may be attributed either to the lack of a perfectly homogeneous charge in the engine cylinder or to the dissociation of the oxides of nitrogen that are formed during the combustion process.

It is evident that if the quantity of O₂ present in the exhaust for lean mixtures is known the corresponding quantity of CO₂ can be readily determined from the curve shown in figure 5. However, for rich or near-rich mixtures it would be necessary to measure both gases, for in this range the O₂ content is practically constant.
The Ostwald combustion diagram shows in graphical form the theoretical relationships among the products of combustion of hydrocarbons. The interdependence of CO, O₂, CO, and air-fuel ratio is given and it is possible to determine CO and air-fuel ratio when the values for CO₂ and O₂ are known. Such diagrams are shown in figures 6 and 7 and their development is given in the appendix. The simplest type of Orsat apparatus enabling determinations of CO₂ and O₂ to be made is all that is needed in conjunction with an Ostwald diagram and knowledge of the relation of H₂ and CH₄ to CO to give a complete analysis of exhaust gas with an accuracy comparable to that of direct measurement. This fact should cause the diagrams to be of considerable value to engineers interested in the composition of exhaust gas from internal-combustion engines.

Figure 6 is an Ostwald combustion diagram for standard and fighting grade aviation gasolines having H-C ratios of 0.175. It is also applicable to Auto Diesel and Laboratory Diesel fuels since the H-C ratio of these fuels was found to be approximately the same as for the gasolines. An Ostwald combustion diagram for hydrogenated safety fuel (H-C ratio of 0.128) is shown in figure 7. The differences in the relationships of the two charts are due to the H-C ratio of safety fuel being different from that of the other fuels.

The dotted lines in figure 6 illustrate the use of the diagram. It is readily apparent that for an exhaust gas containing 10.5 percent CO₂ and 2.0 percent O₂ the CO content will be 4.5 percent and \( \eta \) will be 1.09, \( \eta \) being the reciprocal of the excess-air coefficient. The percentages of H₂ can be determined from the relation \( H₂ = 0.51 CO \). The amount of CH₄ is constant and equal to 0.22 percent.

The agreement of the values for air-fuel ratio obtained from the Ostwald diagram and those derived by calculation from the results of complete exhaust-gas analyses is shown in figure 8. The agreement of the values for CO obtained by the two methods is good and is shown in figure 9.

In figure 10 air-fuel ratios determined from analyses of the exhaust gases are compared to air-fuel ratios supplied to the engine and determined by weighing the fuel and measuring the air. For rich mixtures the air-fuel ratios found from exhaust-gas analyses were, for all engines tested, somewhat greater than those supplied to the engine, which is probably due to incomplete combustion of the fuel in the cylinder with consequent carbon formation not accounted for in the exhaust-gas analysis. The determination of the percentages of CO₂ and O₂ in the exhaust gas and the use of the Ostwald combustion diagram to obtain the exhaust air-fuel ratio make possible, by means of figure 10, the determination of the air-fuel ratio supplied to the engine with a precision of \( \pm 2 \) percent without measuring the air taken in by the engine.

In table II is shown the composition of the fuels used, as supplied by the manufacturers or reported in the literature and as determined from exhaust-gas analyses. The averages of laboratory analyses are chiefly those of rich mixtures. It seems that values computed from mixtures a little leaner than the theoretically correct air-fuel ratios would have been more accurate than any others since deposition of carbon is more likely to occur in very lean and in rich mixtures.

The agreement between reported values and values computed from laboratory gas analyses is quite good for the gasolines and the safety fuel. The results from gas analyses of Laboratory Diesel fuel indicate it to have approximately the same composition as Auto Diesel fuel.

Table II and the relations found between H and CO for the different fuels indicate that there is a definite connection between the H-C ratio of the fuel and the H-CO ratio of the exhaust gases of internal-combustion engines because an increase in the H-C ratio of the fuel results in an increase in the H-CO ratio of the exhaust gas.

**CONCLUSIONS**

The experimental data presented in this report indicate that:
Figure 6.—Ostwald combustion diagram for standard and fighting grades of aviation gasolines, Auto Diesel fuel, and Laboratory Diesel fuel. The amount of CH₄ is constant, 0.22 percent. The amount of H₂ varies linearly with CO, H₂ = 0.51CO.

Note.—Excess-air coefficient = 1/φ; percent excess air = 100 (1/φ - 1); air-fuel ratio = 14.8φ/φ.
Figure 7.—Ostwald combustion diagram for hydrogenated safety fuel. The amount of CH₄ is constant, 0.27 percent. The amount of H₂ varies linearly with CO, H₂ = 0.33 CO.

Note.—Excess-air coefficient = L/V; percent excess air = 100 (L/V-1); air-fuel ratio = 14.06/L.
1. The exhaust gases from internal-combustion engines burning hydrocarbon fuels contain $H_2$ and CO.

2. A small amount of $CH_4$ was found to be always present in the exhaust gas, but the amount was independent of the air-fuel ratio and of the H-C ratio of the fuel.

3. Oxygen was also found in the exhaust gas from internal-combustion engines using hydrocarbon fuels even when the fuel was in excess of that required for complete combustion.

4. The determination of any two components ($CO_2$, $CO$, $O_2$, air-fuel ratio), employment of the H-CO relationship, and the use of the Ostwald combustion diagram provide a rapid means of obtaining the quantities of the products of combustion in the exhaust gas of internal-combustion engines.

5. The air-fuel ratio supplied to the engine may be determined from the exhaust-gas analysis with a precision of ±2 percent without measuring the air taken in by the engine, thus rendering the method particularly valuable for work outside the laboratory.
APPENDIX

DEVELOPMENT OF AN OSTWALD COMBUSTION DIAGRAM

The following development of the Ostwald diagram for the combustion of a hydrocarbon, when the products of combustion contain the gases \( \text{H}_2, \text{H}_2\text{O}, \text{O}_2, \text{N}_2, \text{CH}_4, \text{CO}_2, \) and \( \text{CO} \), is similar to that of Theodorsen (reference 7).

The relative weights of carbon and hydrogen appearing in the exhaust as products of combustion are

\[
\begin{align*}
C &= 12(\text{CO}_2 + \text{CO} + \text{CH}_4) \\
H &= 2.015(\text{H}_2 + \text{H}_2\text{O} + 2\text{CH}_4)
\end{align*}
\]

Then

\[
\begin{align*}
\frac{H}{C} &= \frac{2.015(\text{H}_2 + \text{H}_2\text{O} + 2\text{CH}_4)}{12(\text{CO}_2 + \text{CO} + \text{CH}_4)} = K
\end{align*}
\]

where \( K \) is the weight ratio of the hydrogen to carbon and the chemical symbols refer to percentage by volume.

From equation (1):

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

Considering dry air to contain 20.9 percent \( \text{O}_2 \) and 79.1 percent \( \text{N}_2 \) by volume, then

\[
\text{N}_2 = \frac{79.1}{20.9}(\text{O}_2 + \text{O}_2')
\]

where \( \text{O}_2' \) is the oxygen consumed and \( \text{O}_2 \) is the excess oxygen. The oxygen consumed is obtained as follows:

\[
\text{O}_2' = \text{CO}_2 + \frac{1}{2}\text{CO} + \frac{1}{2}\text{H}_2\text{O}
\]

Substituting the value of \( \text{H}_2\text{O} \) of equation (2) in equation (4) and then the resulting value of \( \text{O}_2' \) in equation (3), we have

\[
\begin{align*}
\text{N}_2 &= 3.785\text{O}_2 + 3.785\text{CO}_2 + 1.892\text{CO} - 1.892\text{H}_2 \\
&- 3.785\text{CH}_4 + 11.268K(\text{CO}_2 + \text{CO} + \text{CH}_4)
\end{align*}
\]

Nitrogen may also be determined by difference.

\[
\text{N}_2 = 100 - \text{O}_2 - \text{CO}_2 - \text{CO} - \text{H}_2 - \text{CH}_4
\]

From equations (5) and (6), we obtain

\[
\begin{align*}
\text{O}_2 + \text{CO}_2(1 + 2.355K) + \text{CO}(0.604 + 2.355K) \\
- 0.186\text{H}_2 - \text{CH}_4(0.582 - 2.355K) &= 20.9
\end{align*}
\]

Equation (7) is the general equation of the theoretical relationships among the products of combustion of hydrocarbons.

The reciprocal (\( \eta \)) of the excess-air coefficient is obtained as follows:

\[
\eta = \frac{\text{O}_2 \text{ required for complete combustion}}{\text{O}_2 \text{ present}}
\]

then

\[
\eta = \frac{\text{CO}_2 + \text{CO} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{H}_2\text{O} + 2\text{CH}_4}{\text{O}_2 + \text{CO}_2 + \frac{1}{2}\text{CO} + \frac{1}{2}\text{H}_2\text{O}}
\]

Substituting the value of \( \text{H}_2\text{O} \) of equation (2), we have

\[
\eta = (1 + 2.977K)(\text{CO}_2 + \text{CO} + \text{CH}_4) + \text{O}_2 + \text{CO}_2(1 + 2.977K) + \text{CO}(0.5 + 2.977K) \\
- \text{CH}_4(1 - 2.977K) - \frac{1}{2}\text{H}_2
\]

Equation (9) is the general equation of the theoretical relationships of the excess-air coefficient and the products of combustion of hydrocarbons.

Substituting the value of \( \text{H}_2\text{O} \) of equation (2), we have

\[
\begin{align*}
\text{O}_2 + 1.412\text{CO}_2 + 0.921\text{CO} &= 20.937
\end{align*}
\]

and equation (9) becomes

\[
\eta = \frac{1.521\text{CO}_2 + 1.521\text{CO} + 0.333}{\text{O}_2 + 1.521\text{CO}_2 + 0.765\text{CO} - 0.105}
\]

The combustion triangle is formed from the solution of equation (10) for \( \text{CO}_2, \text{CO}, \) and \( \text{O}_2 \) and is plotted in figure 6.

By means of equations (10) and (11), equations for \( \text{CO}_2, \text{CO}, \) and \( \text{O}_2 \) in terms of \( \eta \) may be obtained. The solution of these equations for a common value of \( \eta \) makes it possible to construct the \( \eta \) lines in the Ostwald diagram (fig. 6).

From the H-C ratio and the stoichiometric equations for complete combustion, the quantity of air required was calculated to be 14.89 pounds per pound of fuel and the air-fuel ratio was 14.89/\( \eta \).

REFERENCES


**BIBLIOGRAPHY**


**TABLE I**

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<td>Engine speed, r.p.m.</td>
<td>1,600</td>
<td>1,600</td>
<td>1,600</td>
<td>1,600</td>
<td>1,600</td>
</tr>
</tbody>
</table>

**TABLE II**

<table>
<thead>
<tr>
<th>AUTO DIESEL FUEL</th>
<th>LABORATORY DIESEL FUEL</th>
<th>AVIATION GASOLINE</th>
<th>FIGHTING GASOLINE</th>
<th>STANDARD GASOLINE</th>
<th>HYDROGENATED SAFETY FUEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer's report</td>
<td>Average, 17 laboratory gas analyses</td>
<td>Manufacturer's report</td>
<td>Average, 16 laboratory gas analyses</td>
<td>Reference 4, p. 461</td>
<td>Average, 13 laboratory gas analyses</td>
</tr>
<tr>
<td>C.</td>
<td>85.3</td>
<td>85.5</td>
<td>85.1</td>
<td>85.1</td>
<td>84.5</td>
</tr>
<tr>
<td>H</td>
<td>14.7</td>
<td>14.5</td>
<td>14.9</td>
<td>14.9</td>
<td>15.5</td>
</tr>
<tr>
<td>H/C</td>
<td>1.72</td>
<td>1.69</td>
<td>1.75</td>
<td>1.75</td>
<td>1.18</td>
</tr>
</tbody>
</table>

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Positive directions of axes and angles (forces and moments) are shown by arrows.

<table>
<thead>
<tr>
<th>Axis</th>
<th>Moment about axis</th>
<th>Angle</th>
<th>Velocities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designation</td>
<td>Symbol</td>
<td>Designation</td>
<td>Symbol</td>
</tr>
<tr>
<td>Longitudinal</td>
<td>$X$</td>
<td>$L$</td>
<td>roll</td>
</tr>
<tr>
<td>Lateral</td>
<td>$Y$</td>
<td>$M$</td>
<td>pitch</td>
</tr>
<tr>
<td>Normal</td>
<td>$Z$</td>
<td>$N$</td>
<td>yaw</td>
</tr>
</tbody>
</table>

Absolute coefficients of moment

\[ C_t = \frac{L}{q_0 S} \]
\[ C_n = \frac{M}{q_0 S} \]
\[ C_a = \frac{N}{q_0 S} \]

Angle of set of control surface (relative to neutral position), $\delta$. (Indicate surface by proper subscript.)

4. PROPELLER SYMBOLS

- $D$: Diameter.
- $p$: Geometric pitch.
- $p/D$: Pitch ratio.
- $V'$: Inflow velocity.
- $V_n$: Slipstream velocity.
- $T$: Thrust, absolute coefficient $C_T = \frac{T}{q_0 D^3}$
- $Q$: Torque, absolute coefficient $C_Q = \frac{Q}{q_0 D^3}$

5. NUMERICAL RELATIONS

1 hp. = 76.04 kg/m/s = 550 lb./ft./sec.
1 kg/m/s = 0.01315 hp.
1 mi./hr. = 0.44704 m/s
1 m/s = 2.23693 mi./hr.
1 lb. = 0.4535924277 kg.
1 kg = 2.2046224 lb.
1 mi. = 1609.35 m = 5280 ft.
1 m = 3.2808333 ft.