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Stoichiometric Air/Fuel Ratios of Automotive Fuels

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Submitted for Recognition as an American National Standard

SAE The Engineering Society For Advancing Mobility Land Sea Air and Space

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FUELS AND LUBRICANTS PRACTICE

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STOICHIOMETRIC AIR/FUEL RATIOS OF AUTOMOTIVE FUELS

1. INTRODUCTION: The mass of air required to burn a unit mass of fuel with no excess of oxygen or fuel left over is known as the stoichiometric air-fuel ratio. This ratio varies appreciably over the wide range of fuels - gasolines, diesel fuels, and alternative fuels - that might be considered for use in automotive engines.

   Although performance of engines operating on different fuels may be compared at the same air-fuel ratio or same fuel-air ratio, it is more appropriate to compare operation at the same equivalence ratio, for which a knowledge of stoichiometric air-fuel ratio is a prerequisite.

   This report summarizes the computation of stoichiometric air-fuel ratios from a knowledge of a composition of air and the elemental composition of the fuel without a need for any information on the molecular weight of the fuel.

2. EQUIVALENCE RATIOS: When the actual air-fuel ratio supplied to the engine is higher than the stoichiometric air-fuel ratio, there is excess air and the engine is operating "lean". Conversely, when the air-fuel ratio is lower than stoichiometric, fuel combustion will be incomplete and engine operation is "rich".

   The ratio of the actual fuel-air ratio to the stoichiometric fuel-air ratio is the fuel-air equivalence ratio.

$$\frac{\left(\frac{\text{Fuel}}{\text{Air}}\right)_{\text{actual}}}{\left(\frac{\text{Fuel}}{\text{Air}}\right)_{\text{stoichiometric}}} = \text{fuel-air equivalence ratio} = \text{phi} = \emptyset \qquad (1)$$

   The inverse of the fuel-air ratio is the air-fuel ratio. The ratio of the actual air-fuel ratio to the stoichiometric air-fuel ratio is the air-fuel equivalence ratio.

$$\frac{\left(\frac{\text{Air}}{\text{Fuel}}\right)_{\text{actual}}}{\left(\frac{\text{Air}}{\text{Fuel}}\right)_{\text{stoichiometric}}} = \text{air-fuel equivalence ratio} = \text{lambda} = \lambda \qquad (2)$$

When the term "equivalence ratio" is used, it is necessary to indicate whether the fuel-air equivalence ratio (eq. 1) or the air-fuel equivalence ratio (eq. 2) is intended. The air-fuel equivalence ratio has frequently been labeled as "excess air ratio."

3. ATOMIC WEIGHTS AND COMPOSITION OF FUELS AND AIR: The following atomic weights of elements present in many fuels are:

Carbon	- 12.011	
Hydrogen	- 1.00794	$\pm$ 0.00007
Oxygen	- 15.9994	$\pm$ 0.0003
Nitrogen	- 14.0067	
Sulfur	- 32.066	$\pm$ 0.006

These atomic weights have been adopted by the Commission on Atomic Weights and Isotopic Abundances of the International Union of Pure and Applied Chemistry[1].

The composition of air is shown in Table 1.

In the computations below, the atomic weights and mass of air containing one mass unit of oxygen are rounded to five significant digits. Measured values of actual air-fuel ratios and elemental analyses are seldom more precise than four significant digits.

[1]N. E. Holden and R. L. Martin, Pure and Applied Chemistry, 56, 663 (1984)

Table 1

Molecular Weights and Assumed Fractional Volume

Composition of Sea Level Dry Air

Gas Species	Fractional Volume[1]	Molecular Weight[2] kg/kmole	Relative Mass[3]
N_2	0.78084	28.0134	21.873983
O_2	0.209476	31.9988	6.702981
Ar	0.00934	39.948	0.373114
CO_2	0.000314	44.0098	0.013819
Ne	0.00001818	20.179	0.000365
He	0.00000524	4.002602	0.000021
Kr	0.00000114	83.80	0.000092
Xe	0.000000087	131.29	0.000011
CH_4	0.000002	16.04276	0.000032
H_2	0.0000005	2.01588	0.000001
			28.964419

Thus, $\frac{\text{Mass of Air}}{\text{Mass of Oxygen}} = \frac{28.964419}{6.702981} = 4.3211$

1. Data from Table 3 of "U.S. Standard Atmosphere, 1976", National Oceanic and Atmospheric Administration; National Aeronautics and Space Administration; United States Air Force, Washington, DC, October 1976.

2. Calculated from 1983 IUPAC Atomic Weights, N. E. Holden and R. L. Martin, Pure and Applied Chemistry, 56, 663 (1984).

3. Relative mass = fractional volume x molecular weight.

4. CALCULATION OF STOICHIOMETRIC AIR-FUEL RATIOS OF HYDROCARBONS: The stoichiometric oxidation of pure compounds such as methane and ethane can be expressed by balanced chemical equations, e.g.:

Methane: $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ (3)

Ethane: $C_2H_6 + 3.5\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$ (4)

Thus, the stoichiometric oxygen-methane mass ratio is:

$$\left(\frac{\text{oxygen}}{\text{methane}}\right)_{\text{stoich}} = \frac{15.999 \times 2 \times 2}{(12.011 \times 1) + (1.0079 \times 4)} = \frac{63.996}{16.043} = 3.9891 \quad (5)$$

Similarly, the stoichiometric oxygen/ethane mass ratio is:

$$\left(\frac{\text{oxygen}}{\text{ethane}}\right)_{\text{stoich}} = \frac{15.999 \times 3.5 \times 2}{(12.011 \times 2) + (1.0079 \times 6)} = \frac{111.99}{30.069} = 3.7245 \quad (6)$$

A general equation applicable to all hydrocarbons and mixtures thereof can be expressed in terms of the amount of hydrogen per carbon atom, that is, the atomic ratio of hydrogen-to-carbon (H/C).

Thus, $$\left(\frac{\text{oxygen}}{\text{hydrocarbon}}\right)_{\text{stoich}} = \frac{15.999\ [2 + 0.5\ H/C]}{[(12.011 \times 1) + (1.0079\ H/C)]} \quad (7)$$

The bracketed term in the numerator, namely, [2 + 0.5 H/C], indicates that 2 atoms of oxygen are needed to oxidize each atom of carbon to carbon dioxide plus another 0.5 atom of oxygen is needed to oxidize each atom of hydrogen to water.

For illustration, Equation 5 can then be rewritten as:

$$\left(\frac{\text{oxygen}}{\text{methane}}\right)_{\text{stoich}} = \frac{15.999\ [2 + (0.5 \times 4)]}{[(12.011 \times 1) + (1.0079 \times 4)]} = 3.9891 \quad (5')$$

and Equation 6 can be rewritten as:

$$\left(\frac{\text{oxygen}}{\text{ethane}}\right)_{\text{stoich}} = \frac{15.999\ [2 + (0.5 \times 3)]}{[(12.011 \times 1) + (1.0079 \times 3)]} = 3.7245 \quad (6')$$

The stoichiometric oxygen-hydrocarbon ratio can readily be converted to stoichiometric air-fuel ratio by multiplying by the mass of air containing unit mass of oxygen, i.e.,

$$\left(\frac{\text{oxygen}}{\text{hydrocarbon}}\right)_{\text{stoich}} \times \frac{\text{mass air}}{\text{mass oxygen}} = \left(\frac{\text{air}}{\text{hydrocarbon}}\right)_{\text{stoich}} = \left(\frac{\text{Air}}{\text{Fuel}}\right)_{\text{stoich}} \tag{8}$$

For automotive engine applications, the analysis of dry air can be regarded as essentially constant throughout the lower atmosphere. As shown in Table 1, the mass of air per unit mass of oxygen is:

$$\frac{\text{mass air}}{\text{mass oxygen}} = \frac{28.964}{6.7030} = 4.3211 \tag{9}$$

Combining Equations 7, 8 and 9 leads to the general relationship

$$\left(\frac{\text{Air}}{\text{Fuel}}\right)_{\text{stoich}} = \left(\frac{A}{F}\right)_s = 4.3211 \times \frac{15.999\ [2 + (0.5)\ (H/C)]}{(12.011 \times 1) + (1.0079\ H/C)} \tag{10}$$

which applies to <u>all hydrocarbons and mixtures thereof</u>.

5. <u>CALCULATION OF STOICHIOMETRIC AIR-FUEL RATIOS OF OXYGENATES</u>: Equation 10 can be modified to include not only all hydrocarbons but also all oxygenated compounds and blends with hydrocarbons. This modification includes the addition of quantities expressed in terms of the oxygen-to-carbon atomic ratio, O/C, to both the numerator and denominator of Equation 10. Thus, the general equation now becomes:

$$\left(\frac{A}{F}\right)_s = 4.3211 \times \frac{15.999\ [2 + (0.5)\ (H/C) - (O/C)]}{[(12.011 \times 1) + (1.0079)\ (H/C) + (15.999)\ (O/C)]} \tag{11}$$

The quantity added to the numerator reflects that the total oxygen required is decreased by the oxygen-to-carbon atomic ratio since oxygen is present in the fuel and need not be supplied by the air.

The stoichiometric air-fuel ratio of a mixture can be determined either by calculation from the known composition or by the chemical analysis of the mixture.

If the H/C, O/C and mass of each component in a mixture are known, the (A/F)s of each component can be calculated and summed for the amount of each component present. Thus,

$$\sum\left(\frac{A}{F}\right)_s = \frac{\left[\text{mass } F_1 \times \left(\frac{A}{F_1}\right)_s\right] + \left[\text{mass } F_2 \times \left(\frac{A}{F_2}\right)_s\right] + \ldots \text{mass } F_n \times \left(\frac{A}{F_n}\right)_s]}{[\text{mass } F_1 + \text{mass } F_2 + \ldots F_n]} \tag{12}$$

In many cases, however, the composition of the fuel may be unknown. The H/C and O/C ratios of the mixture can then be determined by a precision combustion analysis. In such an analysis, the mass % hydrogen and mass % carbon are usually calculated from the weights of water and carbon dioxide produced from combustion and the mass % of oxygen may be determined by difference, i.e.;

mass % oxygen = 100% - (mass % carbon + mass % hydrogen) (13)

The atomic ratios of hydrogen-to-carbon (H/C) and of oxygen-to-carbon (O/C) can be calculated from mass percentages as follows:

$$\frac{H}{C} = \left(\frac{\text{mass \% hydrogen}}{1.0079}\right) \Big/ \left(\frac{\text{mass \% carbon}}{12.011}\right) = \frac{\%H}{\%C} \times \frac{12.011}{1.0079} = \frac{\%H}{\%C} \times 11.917 \quad (14)$$

$$\frac{O}{C} = \left(\frac{\text{mass \% oxygen}}{15.999}\right) \Big/ \left(\frac{\text{mass \% carbon}}{12.011}\right) = \frac{\%O}{\%C} \times \frac{12.011}{15.999} = \frac{\%O}{\%C} \times 0.75073 \quad (15)$$

These values for the mixture can then be inserted into general equation 11 to obtain the stoichiometric air-fuel ratio of the blend containing carbon and hydrogen or carbon, hydrogen, and oxygen.

6. CALCULATION OF STOICHIOMETRIC AIR-FUEL RATIOS OF FUELS CONTAINING SULFUR: Sulfur (at.wt. = 32.066) forms numerous oxides, e.g., SO or S_2O_3, SO_2, SO_3, SO_4, and S_2O_7. Of these, SO_2 predominates in the exhaust gas of internal combustion engines[2].

General equation 11 can be modified further to include sulfur containing fuels. For this purpose, a quantity is added to the denominator, representing the mass added by the sulfur per carbon atom and a quantity is added to the numerator indicating that 2 oxygen atoms are required to burn the sulfur to SO_2.

Thus, Equation 11 becomes:

$$\left(\frac{A}{F}\right)_S = \frac{4.3211 \times 15.999\,[2 + (0.5)(H/C) - (O/C) + 2(S/C)]}{[(12.011 \times 1) + (1.0079)(H/C) + (15.999)(O/C) + (32.066)(S/C)]} \quad (16)$$

If engine exhaust gases containing excess oxygen either from "lean" operation or from injection of air into the exhaust manifold is passed over a catalyst used for emission control, additional oxidation of SO_2 to SO_3 can result. In this case, 3 atoms of oxygen are needed to oxidize the sulfur and the numerator quantity should be changed from 2(S/C) to 3(S/C).

7. CALCULATION OF STOICHIOMETRIC AIR-FUEL RATIOS OF FUELS CONTAINING NITROGEN: Nitrogen (at.wt. = 14.007) like sulfur forms numerous oxides, e.g., NO, NO_2, NO_3, N_2O and N_2O_5. The major product in automotive engine exhaust is nitric oxide, NO. Thus, a quantity is added to the denominator representing the mass added by the nitrogen per carbon atom and a quantity is added to the numerator indicating that 1 oxygen atom is required to burn the nitrogen atom to NO. Equation 16 then becomes:

$$\left(\frac{A}{F}\right)_S = \frac{4.3211 \times 15.999\,[2 + (0.5)(H/C) - (O/C) + 2(S/C) + 1(N/C)]}{[(12.011 \times 1)+(1.0079)(H/C)+(15.999)(O/C)+(32.066)(S/C)+(14.007)(N/C)]} \quad (17)$$

Equation 17 is then the general equation for calculating the stoichiometric air-fuel ratio of fuels containing carbon and hydrogen along with oxygen, sulfur and nitrogen. In summary in this equation:

[2]W. R. Pierson, Chemtech, May, 1976, p. 332

H/C = atomic hydrogen-to-carbon ratio
O/C = atomic oxygen-to-carbon ratio
S/C = atomic sulfur-to-carbon ratio
N/C = atomic nitrogen-to-carbon ratio

and

12.011 = atomic weight of carbon
1.0079 = atomic weight of hydrogen
15.999 = atomic weight of oxygen
32.066 = atomic weight of sulfur
14.007 = atomic weight of nitrogen
4.3211 = weight of air per unit weight of oxygen

It should be noted that Equation 17 assumes that sulfur oxidizes to SO_2 and nitrogen to NO which is generally applicable to internal combustion engines. However, these approximations should be verified for engines optimized for different operating conditions for alternative fuels that may become available. In general, however, the effect on stoichiometric air-fuel ratio is expected to be small since the atomic ratios of S/C and N/C for most fuels are usually small. The user should recognize that during combustion, oxygen will also combine with nitrogen from the air to form oxides of nitrogen.

In vehicles equipped with reducing catalysts, generally part of the "three-way catalysts", the oxides of nitrogen from the engine are reduced to nitrogen and therefore the nitrogen term in the numerator, 1N/C, should be eliminated if the overall stoichiometry of engine plus catalyst is considered.

8. CALCULATION OF STOICHIOMETRIC AIR-FUEL RATIOS OF FUELS CONTAINING WATER: Some alternative automotive fuels may contain appreciable quantities of water. For example, the ethanol-water azeotrope which contains 4 mass percent water[3] has been used as a spark-ignition engine fuel and a microemulsion of 10 volume percent of water in diesel fuel has been considered as a fire-resistant fuel for military use.

The water adds to the weight of fuel without adding to the amount of oxygen required for combustion. Therefore, the stoichiometric air-fuel ratio of the wet fuel will differ from that of the dry fuel. However, Equation 11 will apply to the wet fuel if the H/C and O/C atomic ratios were determined for that wet fuel.

9. FUELS WITHOUT CARBON ATOMS: Several substances which do not contain carbon atoms, such as ammonia and hydrazine, have been investigated as potential alternative fuels for automotive engines. For such fuels, the equations listed above do not apply. However, the same principles can be used; namely, the calculations can be based on a "per nitrogen atom" basis.

[3] L. M. Horsley, "Azeotropic Data III", Advances in Chemistry Series 116, American Chemical Society, Washington.

10. EFFECT OF HUMIDITY IN AIR: Stoichiometric air-fuel ratios should always be calculated on the basis of the mass of dry air required to burn a unit mass of fuel as is done in the preceding equations. However, it may also be desirable to determine the required mass of ambient air which usually contains water vapor. The mass of water vapor present can be determined from measured temperatures and relative humidities of the ambient air using psychrometric charts[4, 5].

At room temperature and humidity, the relative mass of water vapor to dry air is small. For example, at 21°C (70°F) and 50% relative humidity, the damp air will contain 0.008 mass units of water vapor for each 1.000 mass units of dry air. The actual mass of ambient air at 21°C (70°F) and 50% relative humidity required for stoichiometric burning will therefore be 1.008 times higher than the mass of dry air computed in the equations above.

[4] O. T. Zimmerman and I. Lavine, "Industrial Research Services Psychrometric Tables and Charts", 1945.

[5] A. Wexler, "Humidity and Moisture - Measurement and Control in Science and Industry", Vol. 1, p. 97, Reinhold Publishing Corp., New York, NY 1965.

APPENDIX

The method described above is applicable to wet fuels as well as dry fuels as shown by the following two methods of calculating the stoichiometric air-fuel ratio of the ethanol-water azeotrope. The first method calculates the (A/F)s from the elemental composition of the wet fuel and the second calculates it from the elemental composition of the dry fuel and then corrects the (A/F)s by adding the weight of water to the dry fuel.

In the illustration below, the following values are used:

- The ethanol-water azeotrope consists of 96.0 mass percent of ethanol and 4.0 mass percent of water[3].
- The atomic weights to five significant figures are:

Carbon = 12.011
Hydrogen = 1.0079
Oxygen = 15.999

Method 1

In the absence of direct measurement of the elemental analysis of the azeotrope, the carbon, hydrogen, and oxygen contents are calculated in this example from the known composition of the azeotrope and its constituents.

1. Weight of elements in 96.0 grams of ethanol (C_2H_5OH)

		Relative Weight	Weight Fraction	g in 96.0 g
Carbon	- 2 x 12.011 =	24.022	0.52144	50.058
Hydrogen	- 6 x 1.0079 =	6.0474	0.13127	12.602
Oxygen	- 1 x 15.999 =	15.999	0.34729	33.340
	mol. wt. =	46.068	$\sum$=1.00000	$\sum$=96.000

2. Weight of elements in 4.0 grams of water (H_2O)

		Relative Weight	Weight Fraction	g in 4.0 g
Carbon	- 0			
Hydrogen	- 2 x 1.0079 =	2.0158	0.11190	0.4476
Oxygen	- 1 x 15.999 =	15.999	0.88810	3.5524
	mol. wt. =	18.0148	$\sum$=1.00000	$\sum$=4.0000

3. Weight of elements in 100 g of azeotrope

	From Ethanol	From Water	Total
Carbon	50.058	-	50.058
Hydrogen	12.602	0.4476	13.050
Oxygen	33.340	3.5524	36.892
	96.000	4.0000	100.000

4. Thus, a direct measurement of the elemental composition of the azeotrope should be:

% carbon = 50.058
% hydrogen = 13.050
% oxygen = 36.892

5. Calculation of H/C and O/C atomic ratios

(Eq. 14) $$\frac{\%H}{\%C} \times 11.917 = \frac{13.050}{50.058} \times 11.917 = 3.1067$$

(Eq. 15) $$\frac{\%O}{\%C} \times 0.75073 = \frac{36.892}{50.058} \times 0.75073 = 0.55328$$

6. Using H/C and O/C from (5) in Equation 11:

$$\left(\frac{A}{F}\right)_s = 4.3211 \times \frac{15.999\,[2 + (0.5)(H/C) - (O/C)]}{[(12.011 \times 1) + (1.0079)(H/C) + (15.999)(O/C)]}$$

$$= 4.3211 \times \frac{15.999\,[2 + (0.5)(3.1067) - (0.55328)]}{[12.011 + (1.0079)(3.1067) + (15.999)(0.55328)]}$$

$$= 69.133 \times \frac{[3.0001]}{[23.994]}$$

$$\left(\frac{A}{F}\right)_s = 8.6438 \text{ of azeotrope}$$

Method 2

The direct measurement of the elemental composition of pure dry ethanol as shown in (1) above should be 52.144% carbon, 13.127% hydrogen and 34.729% oxygen. A fuel with this analysis would have H/C and O/C ratios as follows:

(Eq. 14) $$\frac{\%H}{\%C} \times 11.917 = \frac{13.127}{52.144} \times 11.917 = 3.0$$

(Eq. 15) $$\frac{\%O}{\%C} \times 0.75073 = \frac{34.729}{52.144} \times 0.75073 = 0.5$$