REPORT No. 760

A METHOD OF ESTIMATING THE KNOCK RATING OF HYDROCARBON FUEL BLENDS

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SUMMARY

The usefulness of the knock ratings of pure hydrocarbon compounds would be increased if some reliable method of calculating the knock ratings of fuel blends was known. The purpose of this study was to investigate the possibility of developing a method of predicting the knock ratings of fuel blends.

Two blending equations have been derived from an analysis based on certain assumptions relative to the cause of fuel knock. One of these equations may be used for calculating the knock limit of fuel blends when tested in a supercharged test engine. This equation indicates that the reciprocal of the knock-limited inlet-air density of a fuel equals the weighted average of the reciprocals of the knock-limited inlet-air densities of the pure components. The same law applies when indicated mean effective pressure is used in place of inlet-air density.

The second blending equation may be used for calculating the knock limit of fuel blends when tested by critical-compression-ratio methods. The equation relates the blending characteristics of fuels to the knock limits of the pure fuels and to blending constants that appear in the equation.

The limited amount of experimental data available seems to be in agreement with the theory except in the case of benzene. Although the blending equations do not apply to all fuels and the experimental data are not extensive enough to delineate the limits of applicability, it is believed that the analysis presented will be of assistance in understanding the relations that exist between the knock-testing of pure and of blended fuels.

INTRODUCTION

The knock ratings of a large number of pure hydrocarbon compounds have been determined and checked by several investigators. The value of these determinations has been limited by the fact that all practicable fuels used in spark-ignition engines consist of blends of many hydrocarbons, and the knock limit of fuel blends could not, in general, be calculated from knowledge of the knock limits of the pure components. This fact was illustrated by Lovell and Campbell (reference 1) when they showed that the various hydrocarbons do not exhibit the same blending relationships. The recent work reported in reference 2 likewise clearly illustrates that the blending characteristics of fuel blends depend upon the nature of the components.

Eastman (reference 3) has proposed an empirical formula for determining the knock ratings of fuel blends from the ratings of the pure components. The principal objection to this method is that it is highly empirical and does not give a clear picture of blending problems.

The purpose of the present study is to investigate the possibility of developing a method of predicting the knock limits of fuel blends tested either by the supercharged-engine method or by the critical-compression-ratio method. In this paper, fuel-blend tests by the critical-compression-ratio method rather than by the supercharged-engine method are emphasized because more complete data are available for them and a more involved analysis is required.

REVIEW OF KNOCK-TESTING

It is necessary to have the principles of knock-testing clearly in mind in order to understand the present paper. A very brief review of these fundamentals is given here.

Engine knock tests fall within two classes: critical-compression-ratio tests and supercharged-engine tests. In the critical-compression-ratio tests the fuel-air ratio, the inlet-air pressure, and the inlet-air temperature are held constant and the compression ratio is raised until standard knock intensity is observed. The compression ratio at standard knock intensity is the measure of the knock limit of the fuel.

In the supercharged-engine knock tests, the inlet-air temperature and the compression ratio are held constant and the inlet-air pressure is increased until standard knock intensity is observed. The indicated mean effective pressure or the density of air in the cylinder charge may be used as a measure of the knock limit of the fuel being tested.

Changes of inlet-air pressure do not affect any of the cyclic temperatures; an increase of the compression ratio, however, increases the temperature at the end of compression, the combustion temperature, and the end-gas temperature. The fundamental difference, therefore, between test methods employing the critical compression ratio and those in which the supercharged engine is involved is that the critical-compression-ratio tests measure the knock limits of fuels at varying end-gas temperatures whereas the supercharged-engine tests measure the knock limits of all fuels at the same end-gas temperature. (See reference 4.)

BLENDING EQUATIONS

Some assumptions regarding the mechanism of knock have been made to provide a basis for deriving blending equations. In the following assumptions and derivations it was assumed that the blends and the components of the blends were tested at the stoichiometric fuel-air ratio. It is understood, of course, that all fuels and blends are tested under the same engine conditions.

ASSUMPTIONS

1. Knock is the result of the reaction of some intermediate products or agents during combustion. The nature of these products and the reaction between them are the same regardless of the fuel used.

2. At any end-gas temperature, knock occurs when the mass of the knock-producing agents per unit volume reaches a given value.

3. At any one end-gas temperature and for any one fuel component, the mass per unit volume of the knock-producing agent evolved by that component is directly proportional to the mass of the component per unit volume.

4. At any one end-gas temperature, the mass per unit volume of the knock-producing agents is a function of the molecular structure of the fuel.

5. The increase in temperature during combustion of all fuels or fuel blends under consideration is the same.

DISCUSSION OF ASSUMPTIONS

Assumption 1 is introduced in order that the knocking properties of fuels may be treated as additive properties.

Assumption 2 states the conditions under which knock is assumed to occur.

Assumption 3 is introduced in order that the effect of blending on the generation of the knock-producing agent may be evaluated. The assumption states in effect that a unit mass of a particular component will generate a certain mass of knock-producing agent regardless of the other components in the blend.

Assumption 4 permits consideration of the differences of knock limits of the fuel components.

Assumption 5 is introduced in order that the knock limit of fuels may be related to engine-compression density and temperature instead of end-gas density and temperature, thereby simplifying the analysis. Many hydrocarbon fuels of current interest fulfill this condition, but some classes of fuels, notably alcohols and ethers, do not.

DERIVATIONS

If M is the mass per unit volume of the knock-producing agent at the condition of incipient knock, then, because of assumptions 1 and 2, the following equation may be written:

$$M = \rho_1 + \rho_2 + \rho_3 + \ldots \qquad (1)$$

where

$\rho_1, \rho_2, \rho_3, \ldots$ mass per unit volume of the knock agent produced by each component under conditions at which the blend will knock

It was explained in the section Review of Knock Testing that the end-gas temperatures are constant for supercharged-engine tests but vary with the critical compression ratio of the fuel for critical-compression-ratio tests.

From assumptions 3 and 4, the following relations hold for supercharged-engine knock tests:

$$\rho_1 = k_1 D N_1$$

$$\rho_2 = k_2 D N_2$$

$$\rho_3 = k_3 D N_3$$

where

ρ_1, ρ_2, ρ_3 mass of knock agent produced per unit volume by components 1, 2, 3, respectively

N_1, N_2, N_3 mass fractions of components 1, 2, 3, respectively, in the fuel blend

D total mass of fuel per unit volume

k_1, k_2, k_3 quantity of knock-producing agent generated per unit mass by components 1, 2, 3, respectively

When the pure compound 1 is tested, the knock-limited density of fuel in the charge is D_1 and

$$M = \rho_1 = k_1 D_1 \qquad (2)$$

Therefore

$$k_1 = \frac{M}{D_1}$$

and

$$\rho_1 = \frac{M}{D_1} D N_1$$

Similarly

$$\rho_2 = \frac{M}{D_2} D N_2$$

and

$$\rho_3 = \frac{M}{D_3} D N_3$$

Substitute these values of ρ_1, ρ_2, ρ_3, $\ldots$ in equation (1).

$$M = \frac{M}{D_1} D N_1 + \frac{M}{D_2} D N_2 + \frac{M}{D_3} D N_3 + \ldots$$

and

$$\frac{1}{D} = \frac{N_1}{D_1} + \frac{N_2}{D_2} + \frac{N_3}{D_3} + \ldots \qquad (3)$$

Equation (3) is the blending equation applicable to knock tests with supercharged engines as limited by the original assumptions. The knock-limited inlet-air densities may be used instead of the fuel densities for values of D, D_1, D_2, D_3, $\ldots$ because the compression ratio and the fuel-air ratio are the same in all cases. The relation given in equation (3) may be expressed in words as follows: The reciprocal of the knock-limited inlet-air density of a fuel blend tested by a supercharged-engine method is the weighted average of the reciprocals of the knock-limited inlet-air densities of the pure components.

The same law applies when the indicated mean effective pressure is used in place of the inlet-air density because they are proportional under the conditions of supercharged-engine knock tests. The following equation is applicable to these tests:

$$\frac{1}{\text{imep}} = \frac{N_1}{(\text{imep})_1} + \frac{N_2}{(\text{imep})_2} + \frac{N_3}{(\text{imep})_3} + \ldots \qquad (3b)$$

where

imep   knock-limited indicated mean effective pressure of the fuel blend

(imep)$_1$, (imep)$_2$, knock-limited indicated mean effective
(imep)$_3$ pressures of components 1, 2, 3, respectively, when tested individually

N_1, N_2, N_3 mass fractions of components 1, 2, 3, respectively, in the fuel blend

In the case of critical-compression-ratio knock tests, the inlet-air density is held constant and the compression ratio is changed. The charge density at the end of compression is therefore proportional to the compression ratio. An equation similar to equation (2) may be used for relating ρ_1 to the compression ratio instead of to the mass of fuel per unit volume. The value of k_1, however, varies with the compression ratio because the compression temperature varies with the compression ratio. In order to account for the variation of k_1 with the compression ratio, the following relation between ρ_1 and compression ratio R is assumed:

$$\rho_1=(A_1+B_1R)N_1 \qquad (4)$$

where

A_1, B_1 constants characteristic of fuel 1 and the engine operating conditions

Similarly

$$\rho_2=(A_2+B_2R)N_2$$

and

$$\rho_3=(A_3+B_3R)N_3$$

where

A_2, B_2, A_3, B_3 constants characteristic of fuels 2 and 3, respectively, and the engine operating conditions

Substitute these values in equation (1).

$$M=N_1(A_1+B_1R)+N_2(A_2+B_2R)+N_3(A_3+B_3R)+. \quad . \quad . (5)$$

The value of A_1 may be determined by letting $N_1=1$, $N_2=0$, $N_3=0$, and $R=R_1$ when R_1 is the critical compression ratio of fuel 1 when tested individually.

$$M=A_1+B_1R_1$$
$$A_1=M-B_1R_1$$

Likewise

$$A_2=M-B_2R_2$$

and

$$A_3=M-B_3R_3$$

Substitute these values in equation (5). The following equation is obtained:

$$R=\frac{N_1B_1R_1+N_2B_2R_2+N_3B_3R_3+\ \cdots}{N_1B_1+N_2B_2+N_3B_3+\ \cdots} \qquad (6)$$

Equation (6) is the blending equation applicable to critical-compression-ratio knock tests.

The quantities B_1, B_2, B_3, . . . are named blending constants. Each fuel has a blending constant, the value of which is independent of the other fuels in the blend and is determined by the critical compression ratio of the fuel and the rate of change of knock limit with inlet-air temperature.

In the case of two-component blends, $N_2=1-N_1$ and equation (6) becomes:

$$R=\frac{N_1(B_1R_1-B_2R_2)+B_2R_2}{N_1(B_1-B_2)+B_2} \qquad (7)$$

which is the equation of an equilateral hyperbola asymptotic to

$$N=\frac{B_2}{B_2-B_1}=N_a$$

and

$$R=\frac{B_1R_1-B_2R_2}{B_1-B_2}=R_a$$

where

N_a the value of N_1 at the asymptote

R_a the value of R at the asymptote

The asymptotic form of equation (7) is

$$(R-R_a)(N_a-N_1)=N_a(R_2-R_a) \qquad (8)$$

In equations (6) and (7) the absolute values of the constants are not required, but the relative values must be known. If one compound is assigned an arbitrary value of the constant, the values of the constants for all other compounds are fixed. The value of B for other compounds may be found by determining the critical compression ratio of the pure compound and of one blend of the compound with another compound whose blending constant is known. These values may be used in the blending equation and the equation solved for the value of the unknown blending constant. When the relative values of B for all compounds have been determined, the knock limits of all blends may be computed from the blending equation.

GRAPHICAL SOLUTION

A chart may be constructed suitable for graphical determination of the blending characteristics of fuels when tested by a critical-compression-ratio method. Equation (7) may be put into the following form:

$$F=RG \qquad (9)$$

where

$$F=N_1(B_1R_1-B_2R_2)+B_2R_2$$

$$G=N_1(B_1-B_2)+B_2=N_1B_1+(1-N_1)B_2$$

If R is held constant, F is proportional to G. In figure 1, the value of F has been plotted against the value of G for values of R between 2 and 15. The abscissa G is actually the weighted average value of B_1 and B_2 (see equation (9)) for the mixture, and the abscissa has therefore been marked G or B. The positions of all compounds whose critical compression ratios and blending constants are known may be plotted on the chart.

All points representing blends of two components will lie on a straight line joining the two components because F and G are linear functions of N_1 and, consequently, F is a linear function of G. Furthermore, a point representing any blend of the two components will divide the line in the same ratio as that in which the components exist in the blend. A mix-

ture composed of 60-percent isooctane and 40-percent n-heptane, for example, will be on the straight line joining the two components and the point will be 60 percent of the distance from n-heptane to isooctane. The basis for the proportional division comes from the fact that G (or B) is a linear function of N_1 and that the blending equation is linear.
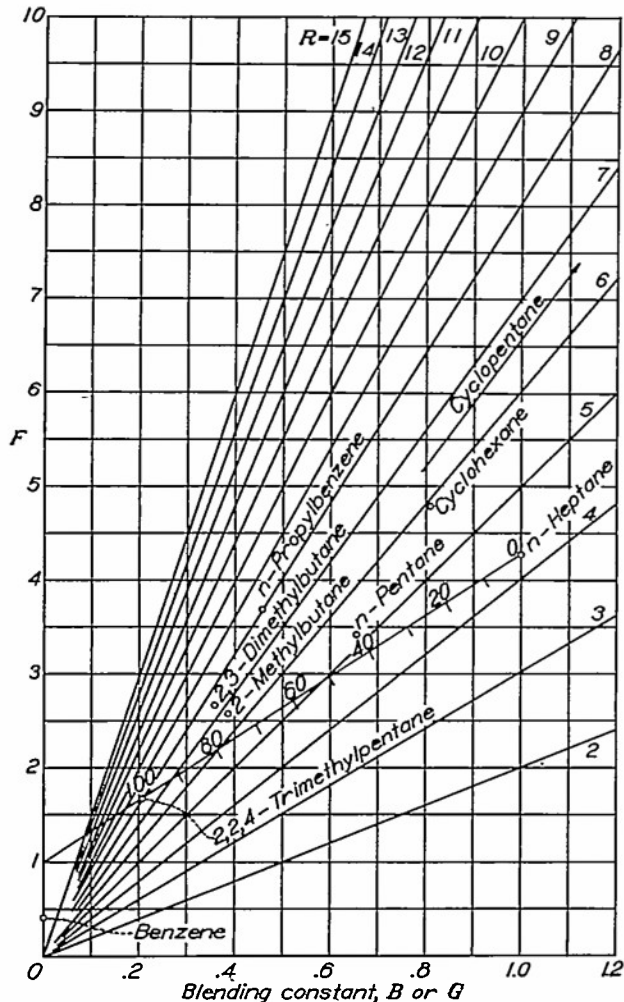

FIGURE 1.—Knock-limit chart for fuel blends. (A. S. T. M. (Motor) Method data.) $F=RB$; R=critical compression ratio; B=blending constant; F=constant.

EXPERIMENTAL DATA

Experimental verification of the supercharged-engine blending equation (equation (3)) is taken from the work of Heron and Beatty reported in reference 5. Reference 5 shows that, if the reciprocal of the knock-limited indicated mean effective pressures of blends of reference fuels are plotted against the octane numbers of the blends, the data will fall on a straight line. Figure 2 illustrates this relationship. The fact that the data fall on a straight line confirms equation (3).

Tests on a supercharged CFR test engine were run at the Aircraft Engine Research Laboratory of the National Advisory Committee for Aeronautics for the purpose of testing the blending equation. Figure 3, which is similar to figure 2, is a cross plot from full mixture-response curves on various blends of S-2 and M-3 reference fuels. The figure shows that the data at rich and lean mixtures follow the reciprocal law.
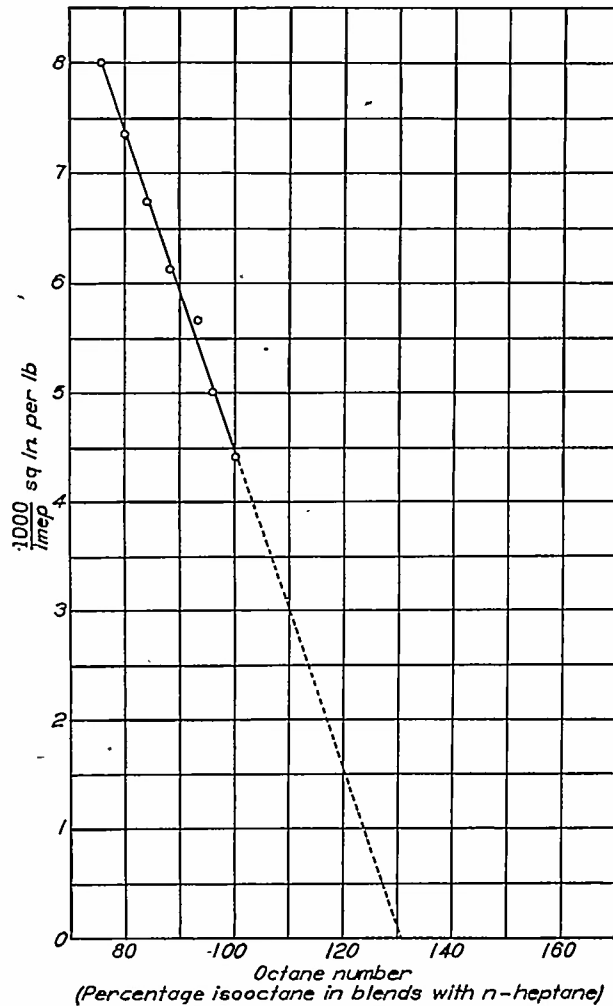

FIGURE 2.—Supercharged knock ratings of blends of isooctane and n-heptane, 17.6 engine. (Data from fig. 5 of reference 5.)
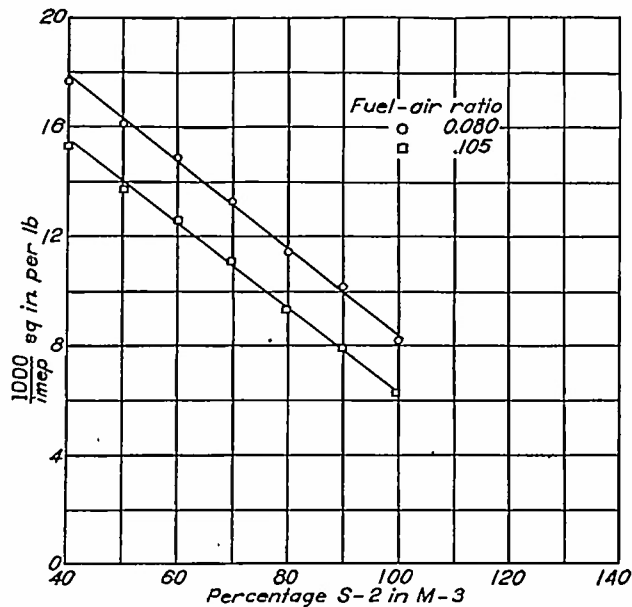

FIGURE 3.—Supercharged knock ratings of blends of S-2 and M-3 reference fuels. CFR engine; bore, 3¼ inches; engine speed, 2000 rpm; spark advance, 35° B. T. C.; compression ratio, 7.0; coolant inlet temperature, 250° F; inlet-air temperature, 250° F.

Data for verifying the hyperbolic blending relationship of n-heptane and isooctane when tested by critical-compression-ratio methods are taken from references 2 and 6. Reference 2 shows that the critical compression ratios of blends of isooctane and n-heptane, when tested by the A. S. T. M. (Motor) Method, fit the following equation:

$$N=\left(\frac{1.369-H}{1.954-H}\right)178$$

where

N percentage of isooctane in blend

H height of compression chamber, inches

The value of N was given on a volumetric basis but, because the densities of the components are practically equal, N may be used as the mass fraction.

The length of the engine stroke was 4.5 inches, and therefore the relation between compression ratio R and H is

$$R=\frac{4.5+H}{H}$$

If H is eliminated from this equation and from the preceding equation, the following equation is obtained:

$$(R-3.3)(125-N)=123$$

This equation is that of an equilateral hyberbola asymptotic to $R=3.3$ and $N=125$. The relation between octane number and critical compression ratio is shown in figure 4. The curve was drawn from the preceding equation and the data points were taken from reference 2. The data from figure 4 are replotted in figure 5 with octane number as the abscissa and the reciprocal of $R-3.3$ as the ordinate. The fact that the data fall on a straight line is confirmation of the hyperbolic blending relationship. Knock-test data on isooctane and n-heptane as reported in reference 6 are given in figure 6. The data were obtained by the CFR (Research) Method. The reciprocal of $R-4.2$ is plotted against th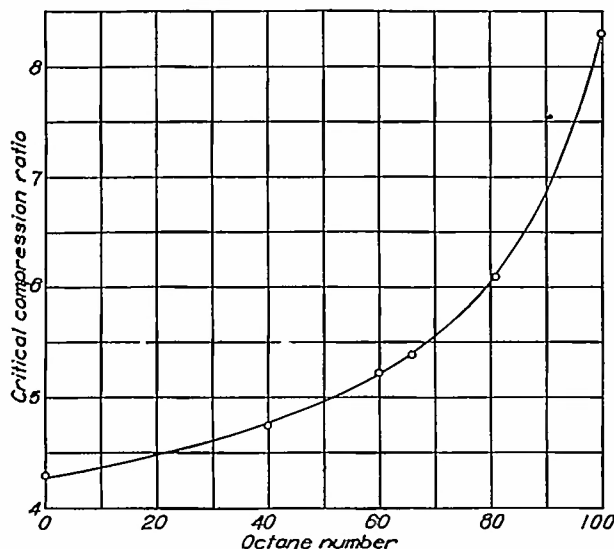e octane number. The data fell on a straight line, the intercepts of which are 120 and 1.53. The data, therefore, fit the following equation:

$$(R-4.2)(120-N)=78.3$$

The asymptotes to the hyperbola representing the preceding equation are 4.2 and 120 as compared with 3.3 and 125 obtained from the A. S. T. M. (Motor) Method tests. It is concluded that the asymptotes of the blending hyperbola change with changing engine conditions.
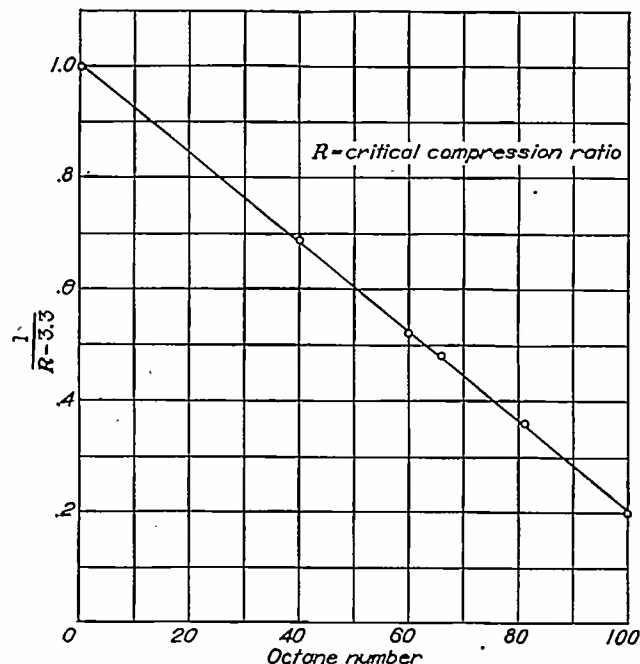

FIGURE 5.—Blending characteristics of 2,2,4-trimethylpentane and n-heptane. (Replot of data in figure 4.)

FIGURE 4.—Blending characteristics of 2,2,4-trimethylpentane and n-heptane, A. S. T. M. (Motor) Method. (Data calculated from reference 2.)
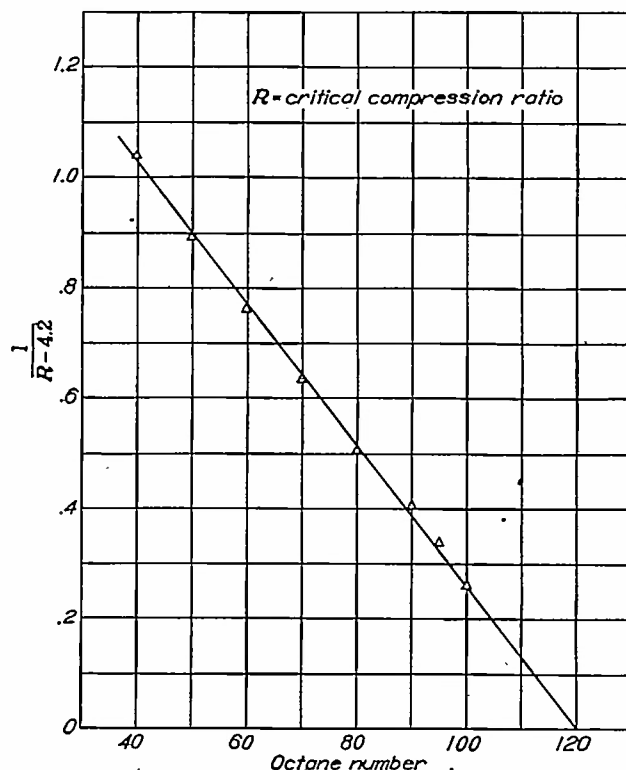

FIGURE 6.—Critical-compression-ratio data for isooctane and n-heptane mixtures by the CFR (Research) Method. (Data calculated from reference 6.)

Figure 7, plotted from data in reference 2, shows that the following blends also have hyperbolic blending characteristics:

n-heptane and 2,3-dimethylbutane
n-pentane and n-octane
n-heptane and 2,4-hexadiene
2,2,4-trimethylpentane and cyclohexane
n-heptane and cyclohexane

The following blends do not follow the hyperbolic relationship:

n-heptane and diisobutylene
n-heptane and benzene
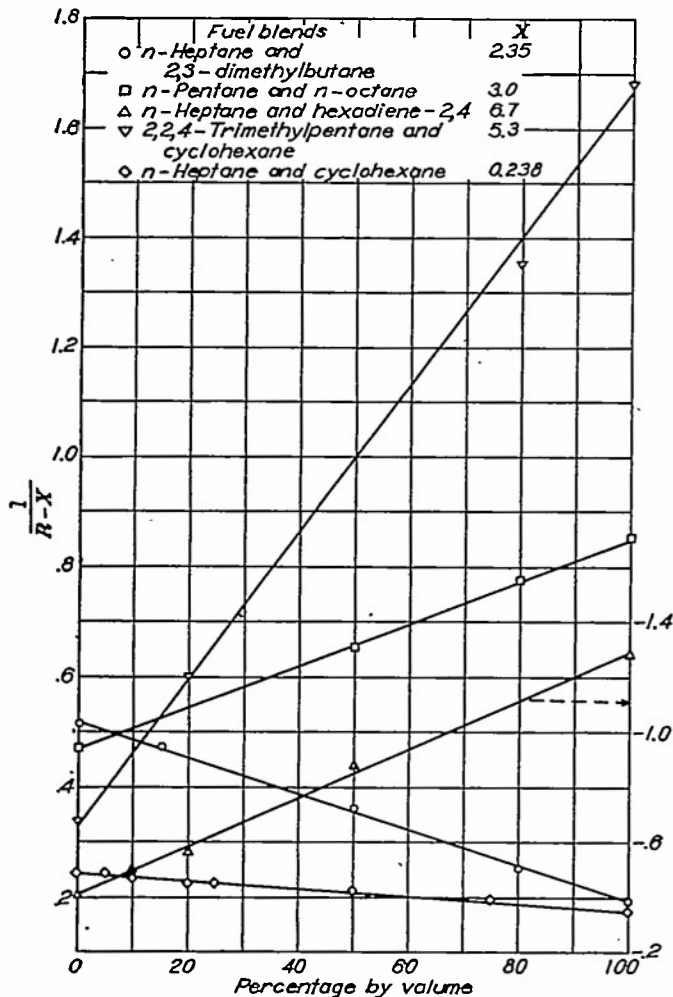n-heptane and toluene

FIGURE 7.—Test of hyperbolic blending relation for knock ratings of fuel blends by A. S. T. M. (Motor) Method. (Data calculated from reference 2.) Equation of hyperbola: $(R-X)(Y-N)=W$; where R, compression ratio; N, percentage of first component in blend; X, Y, and W, constants.

The blending characteristics of these three families of blends are shown in figure 8. The data were calculated from reference 2. The data for n-heptane and diisobutylene are irregular, and it is possible that there is a break in the blending characteristics of the compounds.

The blending characteristic of benzene and n-heptane between 0 and 90 percent of benzene in the blends is hyperbolic. The rating of pure benzene does not fit the hyperbolic relation.
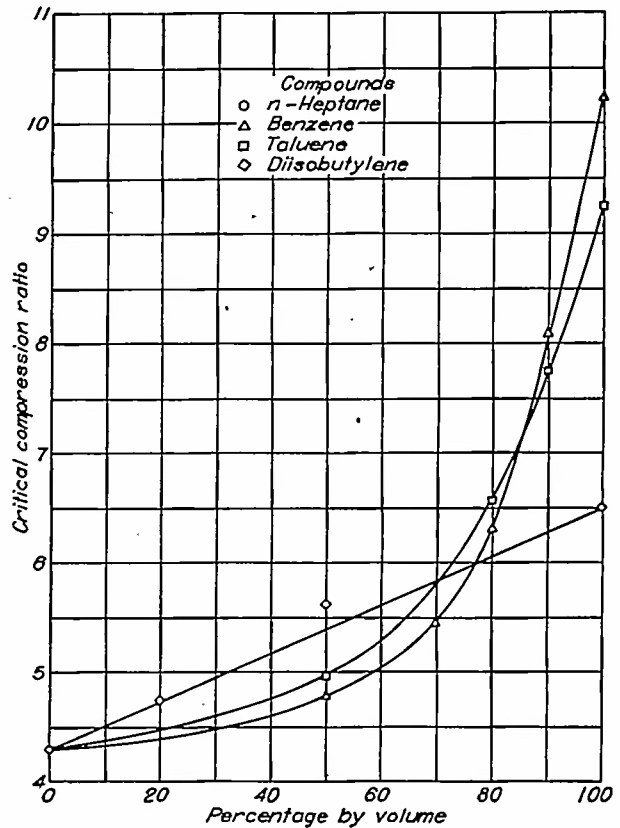

FIGURE 8.—Blending characteristics of diisobutylene, benzene, and toluene in n-heptane. (Data calculated from reference 2.)

The invariance of the blending constant B may be tested if the blending relationships among three compounds are known. The method is explained by an example: The knock rating of pure cyclohexane is 77 and the knock rating of a blend of 50-percent cyclohexane and 50-percent n-heptane is 51. From these data, the value of B for cyclohexane was calculated. The knock rating of a blend of 50-percent cyclohexane and 50-percent isooctane was calculated and found to be 84.6, which is a good agreement with the experimental value of 84. This fact shows that the value of B was the same for cyclohexane in blends with n-heptane or isooctane.

The ratings of 50-percent blends of isooctane with the compounds listed in the following table have been calculated from the ratings of the pure compounds and of the 50-percent blends with n-heptane. The calculated ratings and experimental ratings are listed.

Hydrocarbon	Octane number of pure fuel	Octane number of 50-50 blend in isooctane	
		Calculated	Experimental [1]
2-methylbutane	89	94	93
n-pentane	61	79	79
2,3-dimethylbutane	95	97	97
cyclohexane	77	85	84

[1] Data from reference 5.

The average deviation of the calculated values from the observed values is 0.5. This close agreement between calculated and experimental values shows that B is invariant for the four cases. This conclusion may not hold for tests at other engine conditions.

The compounds listed in the preceding table are shown in figure 1. In addition to these compounds, benzene (reference 2), cyclopentane (reference 6), and n-propylbenzene (reference 6) are shown. Reference 7 gives the blending octane number based upon 20 percent of the compound in a 60–40 mixture of isooctane and n-heptane. The values of the blending constant for cyclopentane and n-propylbenzene were calculated from this blending octane number.

DISCUSSION

Limitations.—The following limitations must be observed in the use of the blending equations:

1. The blending formula does not apply to fuels with heating values that differ greatly from the heating value of the commonly used hydrocarbon fuels. (See assumption 2.)

2. All fuels and blends must be tested at the stoichiometric fuel-air ratio. Test data indicate that the blending equation may be valid when all fuels and blends are tested with the same percentage of excess fuel.

3. The blending formula does not apply to leaded or otherwise doped fuels unless the concentration of antiknock dope is the same in all components. This restriction is necessary because of assumption 3.

4. Certain fuels may not show continuous variation of knock limit with temperature. For some of the blends with such fuels, the blending equation is invalid.

Blends of gasolines.—Use of the blending equations is not restricted to pure compounds. Mixtures such as gasoline may be used in the blending equations in the identical manner in which pure compounds are used. The rating of the mixture may be found as well as the value of the blending constant for the mixture.

Justification of assumptions.—The close agreement between calculated knock ratings of fuel blends and experimental knock ratings does not necessarily prove the correctness of the assumptions. The assumptions are, however, compatible with the data presented in this report.

In the derivation of the blending equation for critical-compression-ratio tests, the production of knocking agent by fuels was assumed to be in accordance with equation (4). This particular form of equation was assumed because a simple blending equation could be derived from it. The

justification for equation (4) lies in the accuracy of the results obtained from the blending equation derivable therefrom.

Application to leaded fuels.—The blending equation cannot be applied directly to leaded fuels except in special cases. Data reported in reference 5 show that the blending equation is valid for blends of isooctane plus 4 ml of tetraethyl lead per gallon and for n-heptane plus 4 ml of tetraethyl lead per gallon. Although isooctane and n-heptane show the same percentage increase in knock-limited power with this addition, some fuels do not. Blends with such compounds may not be in accord with the blending equation.

Expressions of blend composition.—The blending equations have been derived assuming that the fuel composition is expressed on a weight basis. The blending equations (3) and (6) are equally valid when the blend compositions are expressed on a volume basis provided that the volume of the blend equals the sum of the volumes of the pure components and that the densities of the components are approximately equal.

AIRCRAFT ENGINE RESEARCH LABORATORY,
  NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS,
  CLEVELAND, OHIO, *August 1, 1943.*

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ABSTRACT

A method is presented of estimating the knock rating of hydrocarbon fuel blends. Two blending equations have been derived from an analysis based upon certain assumptions relative to the cause of fuel knock. One of these equations may be used for calculating the knock limit of fuel blends when tested in a supercharged engine. The second blending equation may be used for calculating the knock limit of fuel blends when tested by critical-compression ratio methods. It is believed that the analysis presented will be of assistance in understanding the relations that exist between the knock-testing of pure and blended fuels.

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ABSTRACT:

Blending equations were derived from assumptions relative to fuel knocking. They are to be used for determination of fuel knock limit tested by supercharged or critical-compression-ratio methods. Blending constant of a compound was found to have a fixed value independent of the compounds with which it is blended. Variables affecting blending equation are discussed. The equation may be applicable to leaded-fuel blends.

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