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The Calculated Performance of Ethyl Alcohol-Water Mixtures as Rocket Fuels with Liquid Oxygen

By

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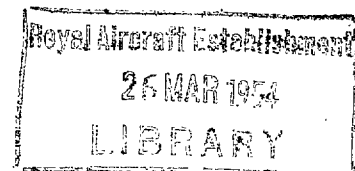
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Summary.—Specific impulses and combustion temperatures have been calculated for rocket propellants consisting of liquid oxygen and ethyl alcohol-water mixtures. This system appears to have a number of advantages compared with the corresponding liquid oxygen and petrol system.

1. *Introduction.*—1.1. Several recent investigations have been made into the performance of various rocket fuels with liquid oxygen. The general conclusion is that there are no fuels (except perhaps liquid hydrogen) which show any startling increase in specific impulse over the values obtainable with petrol or with alcohol. Moreover the vast quantity of rocket fuel which is required for aircraft or missile propulsion would make it necessary to create a small new industry if an unorthodox fuel were used.

1.2. The choice, then, seems likely to lie between petrol and ethyl alcohol, both of which can be obtained in quantity at a very low price.

1.3. Some time ago the theoretical specific impulses and combustion temperatures were calculated for the case of petrol and liquid oxygen. The present investigation has considered the corresponding case when the fuel is ethyl alcohol diluted with different proportions of water.

1.4. Hutcheon and Green have recently made an independent analysis, which covers the range of lower temperatures and greater water contents with both ethyl and methyl alcohol. By taking dissociation and recombination effects fully into account, the present investigation extends these calculations to cover the high temperature range with accuracy.

2. *Note on Combustion Temperatures.*—2.1. Rocket gases produced by combustion with liquid oxygen may reach temperatures of up to 3,500 deg K, and the construction of combustion chambers to withstand such temperatures is a problem of considerable difficulty. It seems probable, at least for motors designed for continuous operation and 100 per cent reliability, that steps must be taken to reduce these peak temperatures.

2.2. Temperatures may in general be lowered either by using one or other propellant component in excess ratio, or by introducing a 'ballast' of inert substances. The former method is perhaps the easiest from many points of view, but it does rely for its effect on complete mixing during combustion. If the fuel control mechanism is momentarily upset, a high temperature mixture may be inadvertently supplied which could cause failure of the combustion chamber. Even if the overall mixture ratio is not in error, it is difficult to guarantee that local variations in mixture will not occur within the combustion chamber.

* R.A.E. Tech. Note Aero. 1943, received 4th June, 1948.

2.3. An inert diluent, on the other hand, already mixed with one of the component liquids, makes it virtually impossible for the designed maximum temperature ever to be exceeded. In choosing a diluent, it is preferable to use one having as high as possible a proportion of hydrogen atoms in its composition, since this always tends to increase specific impulse for a given combustion temperature.

2.4. When using fuels in the neighbourhood of their chemically-correct ratio, the specific impulse, as well as the combustion temperature, is fairly insensitive to changes in mixture ratio. The very rich mixture, on the other hand, just as it may lead to overheating if the proportion of fuel falls short of the designed value, may lose considerably on performance if too much fuel is supplied.

2.5. A further disadvantage of using over-rich mixtures may result from the after-burning of the hot gases with the oxygen of the atmosphere. Long flames are undesirable for several reasons; perhaps the most important one for some applications is the very bad effect they seem to have on radio signals in the vicinity.

2.6. Owing to the considerable degree of dissociation present at the highest temperatures, it must be expected that a relatively large amount of inert diluent will be required to cause a given drop in maximum temperature. For given pressure conditions, the specific impulse will chiefly be a function of these maximum temperatures. For fuels containing hydrogen, or diluted with hydrogen compounds, better specific impulses for a given maximum temperature are always to be obtained on the fuel-rich side of the mixture for maximum temperature, which is never far from the chemically correct mixture.

2.7. The alternative method of using nitrogen to dilute the liquid oxygen is not practicable because the liquid is continually evaporating, and the nitrogen content would become progressively less on storing for any length of time.

2.8. To sum up, the best way of reducing combustion temperatures seems to be to dilute the fuel component with quite a high proportion of some inert liquid rich in hydrogen, while keeping the mixture ratio of oxidant to fuel as close as possible to that for maximum specific impulse with the diluted fuel. Water is clearly the obvious choice of diluent, and since this does not mix with hydrocarbon liquids to any extent, we are led to consider mixtures of water and alcohol.

3. *Comparison between Petrol and Alcohol.*—3.1. The manufacture and storage of alcohol present no great difficulty, particularly if the water content is not critical. The cost of alcohol is probably rather higher than that of petrol, but both are so cheap that cost is unlikely to be a determining factor.

3.2. From an operational point of view, petrol may be preferred because it is already required in vast quantities for aircraft and mechanical transport vehicles, and large-scale supply and distribution organisations are in existence.

3.3. Maximum temperatures may be controlled in the case of alcohol fuel by diluting with water, with which it mixes in all proportions. With petrol, on the other hand, it is necessary to use over-rich mixtures: a method which has been shown to be open to several objections.

3.4. Alcohol and alcohol-water mixtures have the advantage of being chemically stable in contact with the hot walls of the combustion chamber coolant jacket. Under such conditions, petrol would be liable to crack, and leave a carbon deposit which would interfere with cooling. Apart from their stability, alcohol-water mixtures are found to be greatly superior to petrol in the important respect of heat transfer. The relative cooling properties have been considered by Hutcheon in Ref. 2.

3.5. The density of alcohol is higher than that of petrol: an important point in view of the volumetric tankage limitations. The density is further increased as the water content is raised, as is shown in Fig. 1. This effect is, however, largely counteracted by the fact that the relative proportion of fuel to oxidant is greater with alcohol mixtures, and since liquid oxygen is considerably more dense than either fuel, the differences in mean propellant density are only small.

3.6. On the other hand since the cooling of the combustion chamber is usually performed by the fuel component, the smaller proportion of fuel used with the petrol system makes cooling more difficult.

3.7. The freezing point for 100 per cent alcohol is -114 deg C, and for 70 per cent alcohol it is -50 deg C. The range of mixtures considered should therefore be free from freezing troubles at altitude, and would be under no disadvantage compared with petrol on this account. The boiling point is also satisfactory (78 deg C for 100 per cent, 80 deg C for 70 per cent alcohol).

3.8. Hutcheon and Green give the performance of both methyl and ethyl alcohol at lower temperatures, but the difference seems to be very small. Methyl alcohol should have some slight advantage due to its greater hydrogen content. The difference between petrol and paraffin is negligible as far as performance goes: paraffin has the advantage of a higher density, but its higher viscosity leads to difficulties in other directions.

4. *Scope of Present Investigations.*—4.1. The methods and thermal data used for calculating the combustion temperatures and specific impulses are the same as those set out in Ref. 1.

4.2. In the present case the propellants are taken as pure liquid oxygen at -183 deg C, with various mixtures of ethyl alcohol and water at 25 deg C. The combustion chamber pressure is fixed at 20 atm. and the exit pressure at 1 atm. in all cases. The lower calorific value of pure alcohol is taken as 6410 C.H.U./lb.

4.3. The fuels investigated consisted of 100 per cent, 85 per cent and 70 per cent alcohol by weight, the remainder being water. In each case, three different mixture ratios were taken in the range between chemically correct and about 75 per cent excess fuel. The results were as follows:—

100 per cent C_2H_5OH

Mixture ratio oxygen to fuel	2.0	1.5	1.2
Combustion temperature (deg K)	3285	3185	2810
Specific Impulse (sec)	246	249.5	239

85 per cent C_2H_5OH

Mixture ratio oxygen to fuel	1.8	1.4	1.1
Combustion temperature (deg K)	3200	3140	2775
Specific Impulse (sec)	241	245.5	233

70 per cent C_2H_5OH

Mixture ratio oxygen to fuel	1.46	1.15	0.90
Combustion temperature (deg K)	3075	2945	2450
Specific Impulse (sec)	237	236	220.5

4.4. In order more easily to present the results for each fuel as one of a family of curves, they are plotted against the function $r/(r+r')$, where r is the mixture ratio, and r' the ratio for chemically correct combustion to carbon dioxide and water. On this basis, the combustion temperatures are plotted in Fig. 2, and the specific impulses in Fig. 3. For comparison, the curves for petrol are also included, reproduced from previous calculations (Ref. 1).

4.5. The important values to be seen from these curves for each alcohol percentage are:—

- (a) The maximum combustion temperature reached at any mixture ratio, since this is the temperature which may have to be withstood if fuel metering and injection is not perfect.
- (b) The maximum specific impulse at any mixture ratio.
- (c) The mixture ratio for maximum specific impulse.

4.6. These quantities are plotted against the alcohol percentage in Figs. 4 and 5. It will be appreciated that since each fuel is only calculated for three mixtures, the exact forms of the curves have to some extent to be guessed. The possible variations are only very small, but the curves are so flat at the top that it is not possible to pick out with certainty the mixture ratio for maximum performance.

It may therefore be that the values indicated in Fig. 5 do not represent the absolute maxima: all that should be inferred is that mixtures in the neighbourhood of these values will give a negligible fall-off from the optimum performance.

4.7. In the Appendix it is shown that curves plotted against the function $r/(r + r')$, as in Figs. 2 and 3, give a correct representation of the sensitivity to changes in mixture strength. In Fig. 3 the width is indicated of the band of mixtures covered by possible ± 5 per cent metering errors in either component in the neighbourhood of the mixture for optimum performance.

5. *Conclusions.*—5.1. Petrol has a theoretical specific impulse under optimum conditions about 3 per cent higher than pure ethyl alcohol, but the combustion temperature at the same time is nearly 200 deg C higher.

5.2. Considerable quantities of water may be added to the alcohol without having any very great effect either on specific impulse or on combustion temperature. With 30 per cent water by weight, the performance is reduced about 5 per cent, and the combustion temperature by 200 deg C.

5.3. When operating near the mixture ratio for optimum specific impulse, errors in metering of ± 5 per cent in either component cannot cause more than about 2 seconds fall-off in performance.

5.4. The balance of advantages appears to lie more with alcohol fuel than with petrol, though it is admitted that this conclusion is open to modification in the light of practical experience with both systems.

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No.	<i>Author</i>	<i>Title, etc.</i>
1	A. B. P. Beeton	High Temperature Rocket Performance Calculations. A.R.C. 11,460. October, 1947. (Unpublished.)
2	I. C. Hutcheon	Comparison of some Rocket Fuels as Regenerative Coolants. A.R.C. 11,509. January, 1948. (Unpublished.)

APPENDIX

Graphical Representation for showing the Effect of Metering Inaccuracies

Consider a rocket system being supplied by its metering unit with two fluids, at rates x and y lb/sec. These may be regarded as independent variables, of which the mixture ratio r is a function given by

$$r = \frac{x}{y}.$$

Differentiating:

$$\frac{dr}{r} = \frac{dx}{x} - \frac{dy}{y}.$$

If an error of $\pm 100\varepsilon$ per cent is possible in either of the components metered, then the maximum error in mixture ratio will clearly occur when $\frac{dx}{x} = -\frac{dy}{y} = \pm \varepsilon$, and so

$$\frac{dr}{r} = \pm 2\varepsilon.$$

Suppose now it is desired to plot together on one graph the characteristics of a number of different propellants as a function of mixture ratio. We wish to know what function of r we must use as abscissa in order that the relative flatness or otherwise of the individual curves shall be a true indication of the sensitivity of the propellant system to metering variations. If φ is the characteristic to be plotted (combustion temperature, specific impulse, etc.), then we want to associate the slope $d\varphi/df$ with the sensitivity $d\varphi/\varepsilon$. Hence we must clearly have everywhere $df \propto \varepsilon$, whatever the value of r . With the relation already obtained between ε and r , we can write

$$df = k \left(\frac{dr}{r} \right),$$

which gives

$$f = k \log r.$$

Plotting against the logarithm of the mixture ratio therefore always gives a true picture of the relative sensitivity to metering errors.

It has previously been the practice to plot against the function $r/(r + r')$, where r' is the chemically correct ratio. This was done in order to keep the curves within a finite area and to make them all more or less similar in shape.

So in this case $f = \frac{r}{r + r'}$, therefore $r = \frac{r'f}{1-f}$

therefore, $\frac{dr}{df} = \frac{r'}{(1-f)^2}$ therefore, $\frac{dr}{r} = \frac{df}{f(1-f)}$.

But the required condition was shown to be $dr/r \propto df$, which is therefore satisfied either when all the points considered have exactly the same value of f , or when they have approximately the same value of f in the neighbourhood of the stationary value of $1/f(1-f)$. In other words the points must either be in the same vertical line on the diagram, or else not far from the condition corresponding to $r = r'$, or $f = 0.50$. But the effect of taking r' as the chemically correct ratio for each fuel has the effect of bringing all the points of maximum specific impulse relatively close together in the neighbourhood of $f = r/(r + r') = 0.45$, as is seen in Fig. 3, and this is sufficiently close to the value 0.50 for the present purpose.

The sensitivity to metering errors is therefore correctly represented when the characteristics are plotted against $r/(r + r')$, where r' is the chemically correct mixture.

The stationary value of $1/f(1-f)$ in the neighbourhood of $f = 0.5$ is 4.

Therefore, $\frac{dr}{r} = \frac{df}{f(1-f)} = 4df$.

Since also $\frac{dr}{r} = \pm 2\varepsilon$, we have $df = \pm \frac{1}{2}\varepsilon$.

The variation in mixture represented by df in the diagram is therefore numerically equal to one half of ε , the possible metering error in either component. For instance, if both the fuel and the oxidant flow can be controlled only to within ± 5 per cent, then points must be considered up to 0.025 on the scale of $r/(r + r')$ either side of the designed operating point.

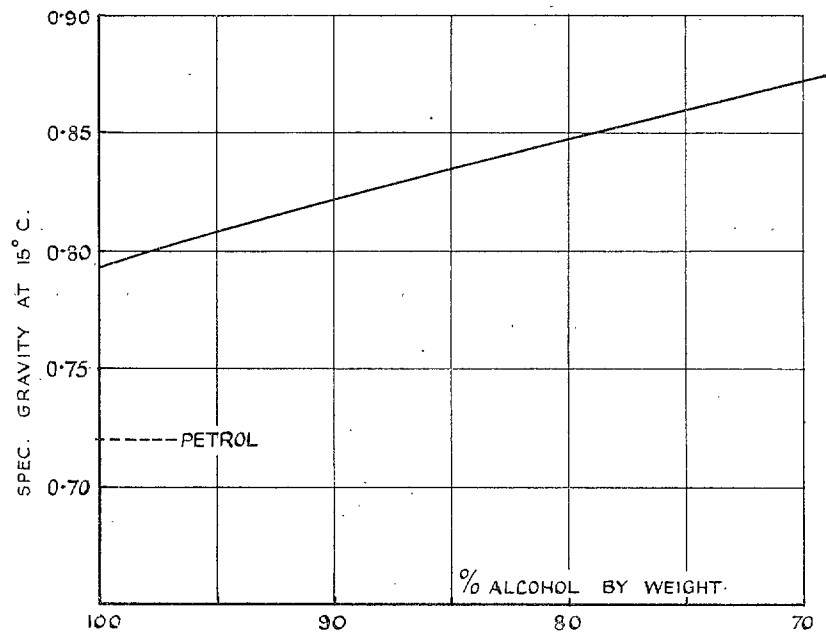


FIG. 1. Specific gravity of ethyl alcohol-water mixtures.

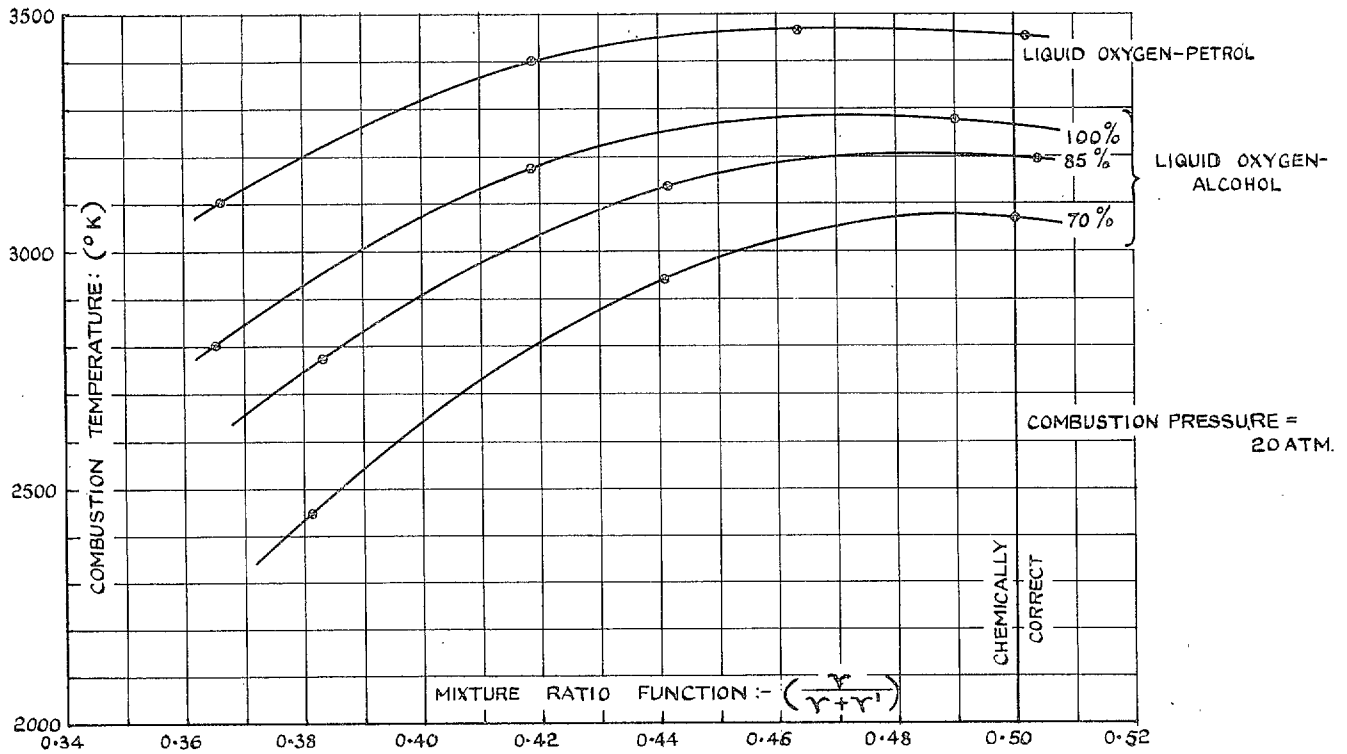


FIG. 2. Calculated variations of combustion temperature.

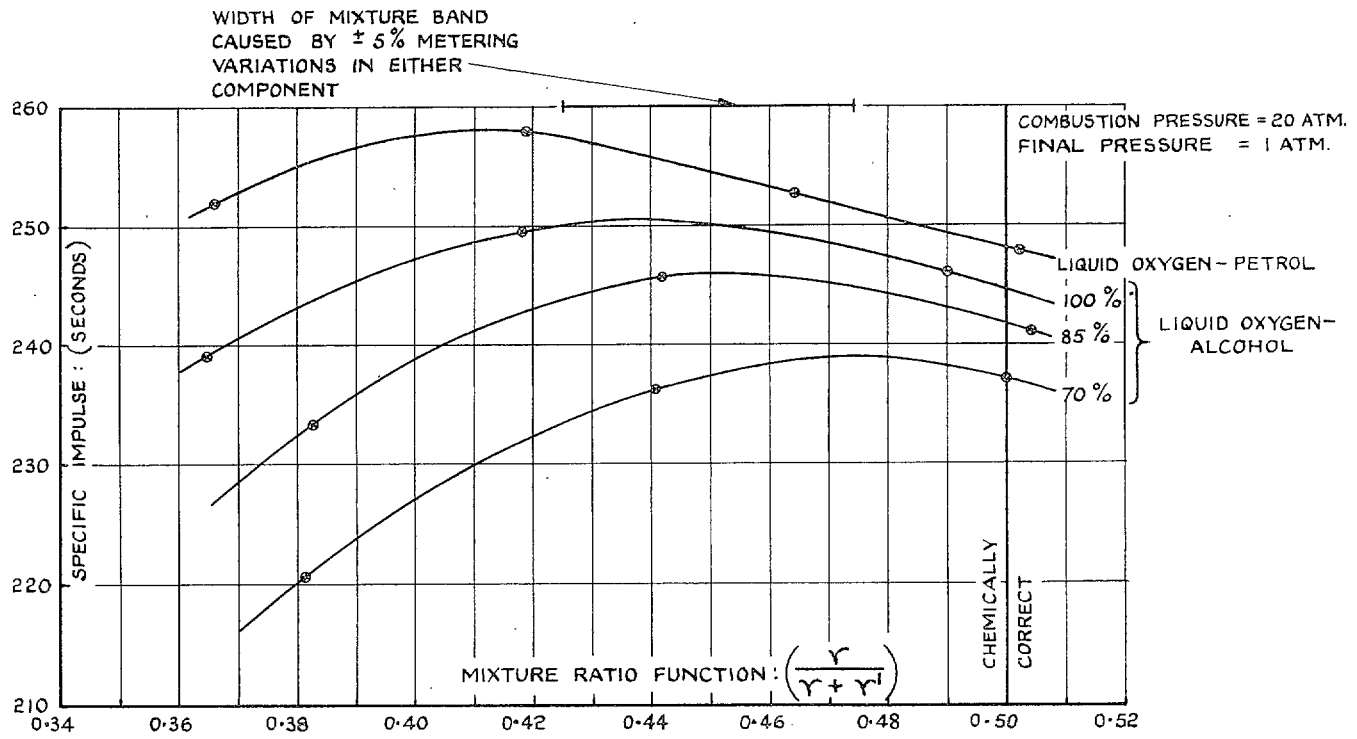


FIG. 3. Calculated variations of specific impulse.

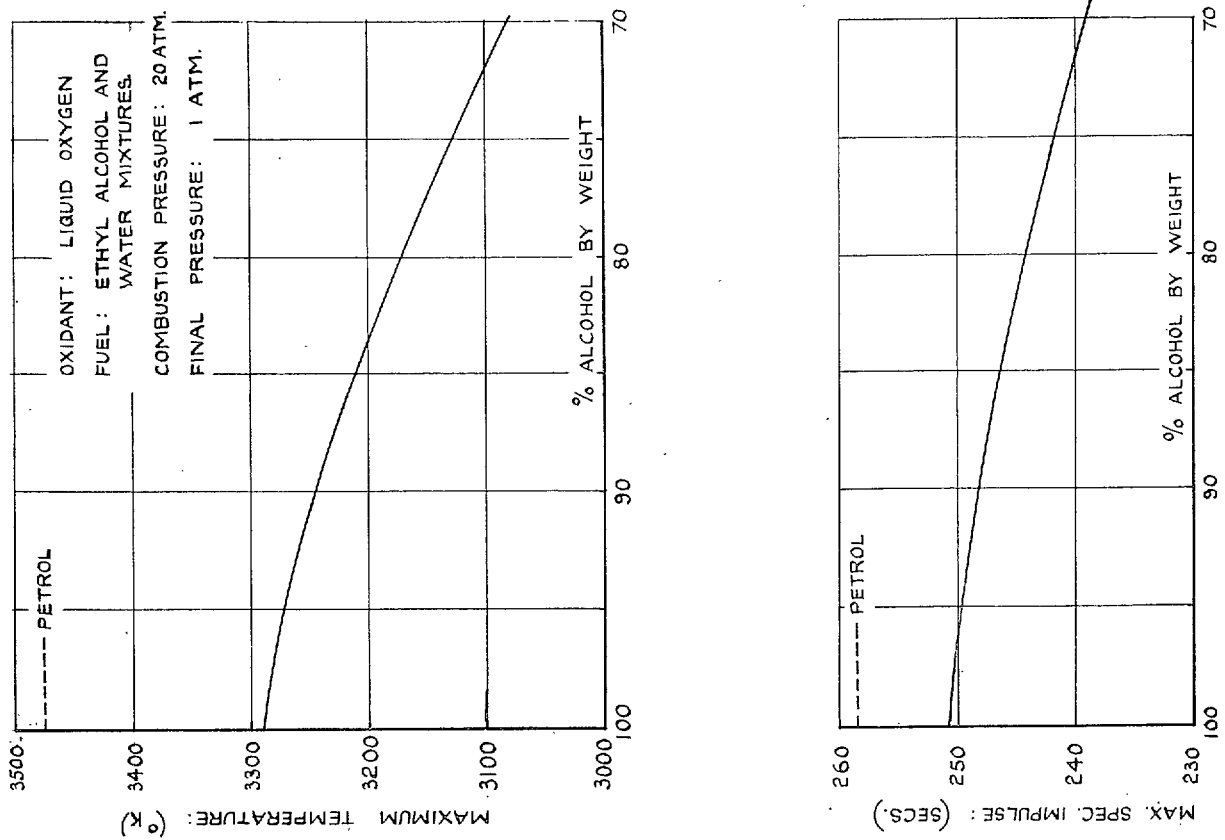


FIG. 4. Calculated maximum temperature and maximum specific impulse as functions of alcohol content.

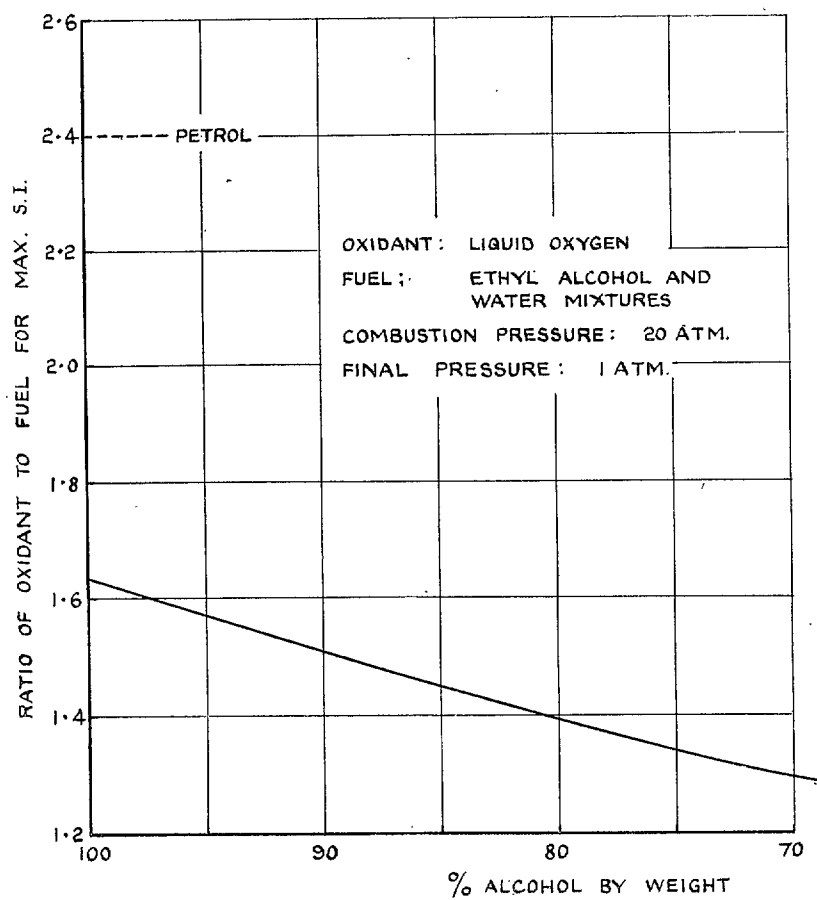


FIG. 5. Approximate variation of optimum mixture ratio with alcohol content.

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