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Calculated Data for the Combustion with Liquid Oxygen of Water-diluted Alcohols and Paraffin in Rocket Motors

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COMMUNICATED BY THE PRINCIPAL DIRECTOR OF SCIENTIFIC RESEARCH (AIR),
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Summary.—Flame compositions, combustion temperatures, and specific impulses have been calculated for the combustion with liquid oxygen of

(1) methyl alcohol with varying additions of water,
(2) ethyl alcohol with varying additions of water,
(3) aviation turbine paraffin.

Calculations have been confined to propellant combinations with an excess of alcohol or paraffin and which produce combustion temperatures below about 2,700 deg K. An expansion ratio of 20:1 has been assumed in obtaining the specific impulses, and the methods of calculation are fully explained. The various propellant combinations are assessed from several points of view as to their usefulness for rocket propulsion.

1. *Introduction.*—The purpose of this note is to present information on the combustion with liquid oxygen of aviation turbine paraffin and of ethyl or methyl alcohol diluted with varying percentages of water. Calculations of the composition of the gaseous products, the combustion temperature and the specific impulse were made in order to assess these fuels and fuel mixtures for use in a regeneratively cooled combustion chamber. It was hoped to be able to replace paraffin by an alcohol-water fuel mixture and thereby obtain more efficient jacket cooling without any undue rise in combustion temperature at the required specific impulse. Results of tests so far made are encouraging.

2. It was also hoped that, by the use of these new fuel mixtures, the radar attenuation across the rocket jet would be greatly reduced. Of possibly considerable importance in this case are mixtures in which dilution beyond stoichiometric proportions is by water and not alcohol. The jet produced by the combustion of these mixtures should contain no free carbon and no after burning, both of which are believed to be a possible cause of attenuation.

3. The method used in making the calculations, together with a worked example, are given in the appendices. This should enable those not conversant with this type of problem to make similar calculations themselves.

4. Results of the calculations are given in Tables 1 to 3 and Figs. 1 to 8. They are discussed in paras. 13 to 22 and the conclusions presented in paras. 23 to 27.

5. The data on aviation turbine paraffin is complementary to that given by F/Lt. Beeton, but covers a lower range of specific impulses. Agreement between the two sets of results appears to be good.

6. An appreciation of the relative value as coolants of the three types of fuel or fuel mixture is to be made in a further technical note, but for the purpose of this note it will be sufficient to realise that the alcohols when used alone are a considerable improvement on paraffin, and that the water mixtures of dilutions likely to be used (up to 50 per cent water) are probably very much the same as undiluted alcohols.

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7. *Presentation of Results.*—Calculations have been made of the composition of the gaseous products, the combustion temperature and the specific impulse, assuming no recombination in the nozzle, and an adiabatic expansion from 20 atmospheres to 1 atmosphere for the following fuels and fuel mixtures at various fuel/oxygen ratios:—

(i) Methyl alcohol with varying additions of water.
(ii) Ethyl alcohol with varying additions of water.
(iii) Aviation turbine paraffin.

8. The results of these calculations are presented in Tables 1 to 3 and shown graphically in Figs. 1 to 8.

9. For each alcohol-water mixture a grid (Figs. 1 and 2) shows the variation of combustion temperature with varying water dilution for various oxygen to alcohol ratios (= R) and various specific impulses. This was first carried out for methyl alcohol for the ratios R = 0·667, 0·8, 1·0 and 1·25 where R = 1·5 is the stoichiometric ratio. Similar values of R for ethyl alcohol were obtained by multiplying the above by 2·08/1·5 in each case, since the stoichiometric ratio for ethyl alcohol-oxygen is 2·08. Corresponding values of R for the two alcohols then give lines of equal fuel richness.

10. In the case of paraffin fuel there can be no water dilution, and curves are given of the variation of combustion temperature and specific impulse with the mixture ratio of fuel and oxygen (Fig. 3).

11. In Figs. 4 and 5 for the two alcohols the mass flow of the fuel mixture is shown as a fraction of the total propellant flow with varying water dilution and for various specific impulses. This enables one to calculate the mass flow of fuel mixture which will be required in a rocket motor working with given thrust, specific impulse and fuel mixture.

12. The compositions of the gaseous products of reaction are shown in the remaining figures.

13. *Discussion of Results.*—In order to assess the results it must be borne in mind that for the same mass flow ethyl alcohol is a considerably better coolant than paraffin (film conductance = 1·8 times that of paraffin), methyl alcohol is slightly better still (2·4) and water is better than both (5·8 to 6·7). It is expected to be shown that alcohol-water mixtures with up to 50 per cent water have a film conductance not greatly better than the undiluted alcohol in question.

14. *Undiluted Alcohols and Paraffin.*—At low oxygen to alcohol ratios (*i.e.* low temperatures), methyl alcohol gives similar specific impulses at slightly lower temperatures than ethyl alcohol. At higher ratios the position is reversed. In neither case, however, is the difference more than 100 deg C and it is usually a good deal less. Paraffin shows a small advantage over both, but again it is of the order of 100 deg C, the maximum advantage being about 150 deg C at a specific impulse of 220 seconds.

15. Over the range of specific impulses taken, the mass flows of methyl alcohol are some 7 to 10 per cent higher than those of ethyl alcohol in each case, and these in turn are 22 to 25 per cent higher than those of paraffin. Combined with the above mentioned cooling properties this gives methyl alcohol a moderate advantage over ethyl alcohol and both alcohols a very considerable advantage over paraffin.

16. *Alcohols Diluted with Equal Percentage of Water.*—As the alcohol dilution is replaced by water dilution, the temperature for any given specific impulse rises considerably (200 or 300 deg C) especially at high specific impulses. Ethyl alcohol-water mixtures give temperatures up 100 deg C lower than corresponding mixtures with methyl alcohol; and paraffin which cannot be diluted gives temperatures 300 or 400 deg C lower than both.

17. Over the range of specific impulses and dilutions taken, the mass flows of methyl alcohol-water mixtures are from 0 to 7 per cent higher than those of corresponding mixtures with ethyl alcohol. These in turn are 20 to 35 per cent higher than those of paraffin.

18. Since the film conductances of the alcohol-water mixtures (up to 50 per cent water) appear nearly equal to those of the undiluted alcohols, and the combustion temperatures are somewhat higher, it seems disadvantageous to use water dilution from the point of view of jacket cooling. However, we may still expect methyl alcohol-water mixtures to have a slight advantage over mixtures of ethyl alcohol with the same percentage of water, and both to have a considerable advantage over paraffin.

19. *Near Stoichiometric Mixtures.*—It should be noted that the mixtures dealt with in the immediately preceding paragraphs contained numerically equal percentages of water. Consequently, at the same specific impulses the methyl alcohol propellant mixtures are more nearly stoichiometric than those containing ethyl alcohol.

20. It may be necessary, in order to minimise radar attenuation, to use alcohol-oxygen ratios near the stoichiometric ratio and dilute each alcohol with water so as to give the (same) desired specific impulse. Under these conditions ethyl alcohol requires a greater percentage of water than methyl alcohol and ignition difficulties may arise. Leaving these aside however, and comparing lines of similar R value (or 'fuel richness') near the stoichiometric value, we find that the two alcohols give very nearly the same temperature for any given specific impulse. It is of course, as before, some 300 or 400 deg C above that given by paraffin for the same specific impulse.

21. Under these conditions and over the range of specific impulses and dilutions taken, the mass flow of methyl alcohol-water mixtures are from 0 to 5 per cent higher than those of corresponding mixtures with ethyl alcohol. These in turn are as before some 20 to 35 per cent higher than those of paraffin.

22. As before, the alcohol-water mixtures should both be a considerable improvement over paraffin due to their better cooling properties and higher rates of flow. In this case, however, owing to the greater dilution of the ethyl alcohol, the two mixtures will probably have almost equal film conductivities and there will be very little to choose between them. Owing to the greater combustion temperature the overall advantage from the cooling point of view is not so great as when undiluted alcohols are used.

23. *Conclusions.*—Used undiluted, there is very little difference between the combustion temperatures given by the three fuels. For reasons of regenerative cooling methyl alcohol will be slightly better than ethyl alcohol, and both will be considerably better than paraffin.

24. As water is added to replace either alcohol as a diluent, the temperature for any given specific impulse rises. At higher specific impulses (200 to 300 sec) the rise is quite considerable.

25. Preliminary calculations indicate that this rise in combustion temperature will not be accompanied by any very significant improvement in jacket cooling as the percentage of water dilution rises from 0 to 50 per cent.

26. In general, therefore, it will probably be best to use undiluted alcohols where possible, though mixtures with water, if required for other reasons, will show an advantage over paraffin.

27. In the case of near stoichiometric alcohol-water-oxygen mixtures, required to reduce radar attenuation, the water dilution will be greater with ethyl alcohol mixtures than with methyl alcohol mixtures. For reasons of ignition methyl alcohol may therefore be preferable. Otherwise there will probably be little to choose between the two alcohols, both, however, being preferable to paraffin.

APPENDIX I

Method of Calculation of Combustion Temperatures and Specific Impulses.

1. For the combustion temperatures dealt with, we can assume that there is no dissociation of the products of combustion into O, OH or H, and that the only molecules present are CO, H_2O, H_2, CO_2. Results based on these assumptions hold good up to 2,500 or 2,700 deg K. For higher performance mixtures the calcultated temperatures will be too high. We also assume that there is no recombination during expansion through the venturi. The first and major stage is the calculation of the combustion temperature. The specific impulse follows relatively simply from this.

2. *Outline of the Method.*—We first make an intelligent estimate of the expected combustion temperature and calculate the composition of the gases in equilibrium at this temperature. We then assume that the propellant decomposes into gases of this composition at room temperature (300 deg K) and at the combustion pressure. The heat evolved is calculated from the difference between the heats of formation of the gases and the propellant at 300 deg K and the combustion pressure. This is compared with the amount of heat required to heat the gases at constant pressure from 300 deg K to the estimated combustion temperature. If these figures disagree, a second and more accurate guess is made of the expected combustion temperature.

3. *Initial Composition.*—The first step is to write down the number of gram atoms (*i.e.*, the fraction of the atomic weight expressed in grams) of each element present in one gram of the propellant. These numbers are proportional to the actual number of atoms of each element present.

4. *Equilibrium of Gaseous Products.*—By equating the number of atoms of each type present before and after the reaction we obtain three equations giving the amounts of CO, H_2O and H_2, in the products in terms of the amounts of C, H, O (known) and CO_2 (not known). Expressed in gram moles,

$$\text{(i)}\quad (CO) = (O) - (CO_2),$$

$$\text{(ii)}\quad (H_2O) = (O) - (C) - (CO_2),$$

$$\text{(iii)}\quad (H_2) = \tfrac{1}{2}(H) - (O) + (C) + (CO_2).$$

The fourth equation is given by the water-gas equilibrium which is known at any temperature,

$$\text{(iv)}\quad \frac{(CO) \times (H_2O)}{(CO_2) \times (H_2)} = K_0.$$

The constant K_0 is found from tables using the estimated combustion temperature. The last equation is then solved for CO_2 using the previous three equations to eliminate (CO), (H_2O) and (H_2).

5. *Heat Available.*—The heats of formation of the gaseous products from their constituent elements at 300 deg K are added, and from the total is subtracted the heat of formation of the propellant from these same constituent elements at the same temperature. The difference gives the heat liberated in the decomposition of the propellant at 300 deg K and constant pressure. This pressure is the combustion pressure, but the heat of formation is nearly independent of pressure and is tabulated for a pressure of one atmosphere, so this value may be used.

6. *Correction of Estimated Temperature.*—Using tables of total heat or of the mean specific heat at constant pressure of the gaseous products we find the amount of heat required to raise them from 300 deg K to the estimated combustion temperature. If this is less than the heat available we must estimate a higher temperature and vice versa. A rough estimate of the error is obtained by dividing the difference between the heat available and the heat required by the specific heat in calories per gram around the estimated temperature.

7. If the originally estimated temperature is very far in error, *i.e.* by 100 or 200 deg C, it will be necessary to re-estimate K_0, and, using the new equilibrium, to recalculate the heat available. This latter, is not, however, very sensitive to small changes in the composition.

8. *Specific Impulse.*—This is found by a relatively simple calculation involving no approximations. Mean values of γ (the ratio of the specific heats) and M (the molecular weight) are found by averaging on a basis of the number of molecules present. Values of γ at the combustion temperature are near enough for reasonable accuracy, the expression for the specific impulse being relatively insensitive to changes in γ, though values at a mean temperature over the expansion period should strictly be used. We get, therefore,

$$\text{(i) Mean } \gamma = \frac{\Sigma\gamma \times \text{Number of gm moles}}{\Sigma\text{ Number of gm moles}}$$

$$\text{(ii) Mean } M = \frac{\Sigma M \times \text{Number of gm moles}}{\Sigma\text{ Number of gm moles}} = \frac{1}{\Sigma\text{ Number of gm moles}}$$

Mean values of γ and M are best found by constructing another table and using the above relations. The specific impulse is then obtained from the following equation where P_e and P_c are the exit and combustion pressures respectively and T is the combustion temperature.

$$S.I. = 9{\cdot}25\left[\frac{T}{M}\cdot\frac{2\gamma}{(\gamma-1)}\left\{1-(P_e/P_c)^{(\gamma-1)/\gamma}\right\}\right]^{1/2} \text{ seconds.}$$

APPENDIX II.

Worked Example.

1. *Data.*

CH_3OH 0·45 gm — Heat of formation = 0·45 × 1,793 = 807 cal
O_2 0·45 gm — Heat of formation = 0·45 × 106 = 48 cal
H_2O 0·10 gm — Heat of formation = 0·10 × 3,790 = 379 cal
Heat of formation of 1 gm propellant = 1,234 cal

2. *Initial Composition.*

(C) = 0·45 × 1/32 = 0·0141 gm atom,
(H) = 0·45 × 4/32 + 0·10 × 2/18 = 0·0563 + 0·0111 = 0·0674 gm atom
(O) = 0·45 × 1/32 + 0·45 × 2/32 + 0·1 × 1/18 = 0·0422 + 0·0056
= 0·0478 gm atom
[Check = (0·0141 × 12) + (0·0674 × 1) + (0·0478 × 16) = 1·001]

3. *Equilibrium of gaseous products.*

(CO) = 0·0141 — (CO_2)
(H_2O) = 0·0478 — 0·0141 — (CO_2) = 0·0337 — (CO_2)
(H_2) = 0·0337 — 0·0478 + 0·0141 + (CO_2) = (CO_2) — (a chance simplification)
Estimate temperature at 2,600 deg K so that K_0 = 6·33 (from tables).

$$\text{Hence } \frac{[0{\cdot}0141 - (CO_2)]\ [0{\cdot}0337 - (CO_2)]}{(CO_2) \times (CO_2)} = 6{\cdot}33.$$

Hence, solving, (CO_2) = 0·0059 gm mole
giving (CO) = 0·0082 gm mole
(H_2O) = 0·0278 gm mole
(H_2) = 0·0059 gm mole.

4. *Heat Available and Correction of Estimated Temperature*

Gaseous Product	Quantity Present gram mole per gram propellant	Heat of Formation (from tables) cals per gram mole	Hence Heat of formation of Amount Present cals	Mean C_v between 300°K and 2600°K (from tables) cals per gram mole per °K	Mean C_p between 300°K and 2600°K ($= C_v + 1{\cdot}987$) cals per gram mole per °K	Hence Heat required to Raise Temperature through 2300°K cals
CO	0·0082	26,400	216	6·191	8·178	154
H_2O	0·0278	57,810	1607	8·768	10·755	688
CO_2	0·0059	94,030	555	11·373	13·360	181
H_2	0·0059	—	—	5·697	7·684	104
Sum	0·0478		2378			1127

Heat available = 2378 — 1234 = 1144 cals.
Heat required to raise temperature from 300 to 2600 deg K = 1127 cals.
So estimate was low by about (1144 — 1127)/0·5 = 30 deg C.
So combustion temperature = 2630 deg K.

5. *Specific Impulse.* (*combustion temperature* = 2630 deg K)

Gaseous Product	Quantity Present	Actual C_v at 2600°K	Actual C_p at 2600°K ($= C_v + 1{\cdot}987$)	γ	$\gamma \times$ gram moles Present	$M \times$ gram mole Present
CO	0·0082	6·841	8·828	1·291	0·01058	0·230
H_2O	0·0278	10·788	12·775	1·184	0·03292	0·500
CO_2	0·0059	12·854	14·841	1·154	0·00681	0·260
H_2	0·0059	6·604	8·591	1·301	0·00768	0·012
Sum	0·0478				0·05799	1·002

Mean $\gamma = 0{\cdot}05799/0{\cdot}0478 \doteq 1{\cdot}213$

Mean $M = 1/0{\cdot}0478 \doteq 20{\cdot}9$

$$\text{Therefore } S.I. = 9{\cdot}25\left[\frac{2630}{20{\cdot}9} \times \frac{2{\cdot}426}{0{\cdot}213} \times \left\{1 - \left(\frac{1}{20}\right)^{0{\cdot}1756}\right\}\right]^{1/2} = 224 \text{ seconds.}$$

TABLE 1

Calculated Data for Methyl Alcohol-Water-Liquid Oxygen Propellant Combinations

(*Expansion ratio* 20:1)

$R\left(=\frac{\text{oxygen gm}}{\text{alcohol gm}}\right)$	0·667	0·667	0·667	0·80	0·80	0·80	1·0	1·0	1·0	1·0	1·25	1·25
Methyl alcohol, gm	0·60	0·48	0·36	0·555	0·435	0·357	0·45	0·40	0·333	0·25	0·3636	0·3077
Water, gm	0	0·20	0·40	0	0·217	0·357	0·10	0·20	0·333	0·50	0·1818	0·3077
Liquid oxygen, gm	0·40	0·32	0·24	0·445	0·348	0·286	0·45	0·40	0·333	0·25	0·4545	0·3846
Water as percentage of alcohol ..	0	41·7	111·1	0	50	100	22·2	50	100	200	50	100
Water as percentage of fuel mixture	0	29·4	52·6	0	33·3	50	18·2	33·3	50	66·7	33·3	50
Combustion temperature, deg K ..	2000	1500	1010	2445	1760	1355	2630	2250	1780	1170	2800	2230
Specific impulse, sec	208	179	146	223	190	166	224	208	186	152	225	204
(CO), gm moles	0·0147	0·0097	0·0031	0·0128	0·0081	0·0047	0·0080	0·0064	0·0041	0·0014	0·0036	0·0025
(H_2O), gm moles	0·0209	0·0258	0·0291	0·0233	0·0282	0·0313	0·0277	0·0300	0·0330	0·0370	0·0307	0·0340
(CO_2), gm moles	0·0041	0·0053	0·0081	0·0045	0·0055	0·0064	0·0060	0·0061	0·0063	0·0064	0·0078	0·0071
(H_2), gm moles	0·0166	0·0153	0·0156	0·0113	0·0110	0·0108	0·0060	0·0061	0·0063	0·0064	0·0021	0·0023

Note: All quantities are for one gram of propellant.

TABLE 2

Calculated Data for Ethyl Alcohol-Water-Liquid Oxygen Propellant Combinations

(*Expansion ratio* 20:1)

$R\left(=\frac{\text{oxygen gm}}{\text{alcohol gm}}\right)$	0·928	0·928	0·928	1·113	1·113	1·113	1·391	1·391	1·391	1·391	1·391	1·391	1·739	1·739	1·739
Ethyl alcohol, gm	0·5188	0·4119	0·3416	0·4733	0·3686	0·302	0·4182	0·3716	0·347	0·3134	0·2949	0·2570	0·2908	0·2605	0·2359
Water, gm	0	0·2060	0·3416	0	0·2212	0·363	0	0·1115	0·173	0·2507	0·2949	0·3855	0·2035	0·2865	0·3539
Liquid oxygen, gm	0·4812	0·3820	0·3168	0·5267	0·4103	0·336	0·5818	0·5169	0·480	0·4359	0·4102	0·3575	0·5057	0·4530	0·4102
Water as percentage of alcohol	0	50	100	0	60	120	0	30	50	80	100	150	70	110	150
Water as percentage of fuel mixture	0	33·3	50	0	37·5	54·5	0	23	33·3	44·4	50	60	41·2	52·4	60
Combustion temperature, deg K	2150	1590	1240	2680	1920	1480	3380	2875	2580	2300	2120	1750	3000	2580	2270
Specific impulse, sec	215	184	162	231	198	173	247	231	221	209	201	185	229	215	204
(CO), gm mole	0·0191	0·0127	0·0075	0·0166	0·0109	0·0066	0·0123	0·0101	0·0089	0·0074	0·0064	0·0048	0·0043	0·0035	0·0028
(H_2O), gm mole	0·0153	0·0212	0·0240	0·0186	0·0248	0·0282	0·0213	0·0244	0·0258	0·0281	0·0292	0·0318	0·0283	0·0307	0·0327
(CO_2), gm mole	0·0035	0·0052	0·0074	0·0040	0·0051	0·0065	0·0059	0·0060	0·0062	0·0063	0·0064	0·0063	0·0083	0·0078	0·0075
(H_2), gm mole	0·0185	0·0171	0·0173	0·0122	0·0115	0·0116	0·0059	0·0060	0·0062	0·0063	0·0064	0·0063	0·0020	0·0022	0·0023

Note : All quantities are for one gram of propellant.

TABLE 3

Calculated Data for Aviation Turbine Paraffin—Liquid Oxygen Propellant Combinations
(*Expansion ratio* 20:1)

$R\left(=\frac{\text{oxygen gm}}{\text{paraffin gm}}\right)$	1·13*	1·25	1·375	1·50	1·75
Paraffin, gm	0·468	0·444	0·421	0·400	0·365
Liquid oxygen, gm	0·532	0·555	0·579	0·600	0·635
Combustion temperature, deg K	1300	1620	1950	2250	2800
Specific impulse, sec	178	196	211	222	248
(CO), gm mole	0·0332	0·0306	0·0286	0·0268	0·0233
(H_2O), gm mole	0	0·0024	0·0051	0·0076	0·0114
(CO_2), gm mole	0	0·0009	0·0012	0·0016	0·0025
(H_2), gm mole	0·0351	0·0309	0·0264	0·0224	0·0160

Notes: (i) All quantities are for one gram of propellant

* This is a somewhat approximate calculation

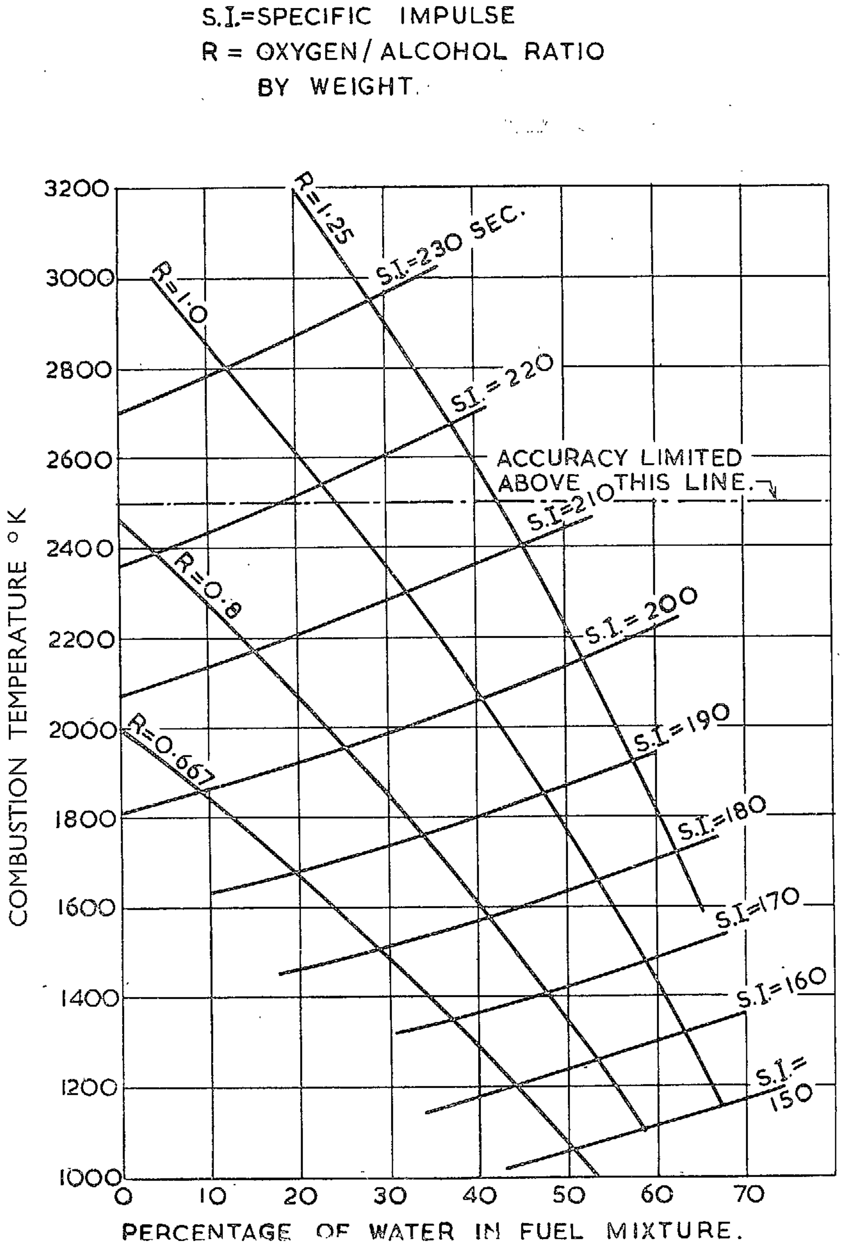

Fig. 1. Combustion temperatures and specific impulses for methyl alcohol–water–liquid oxygen propellant combinations at an expansion ratio of 20:1.

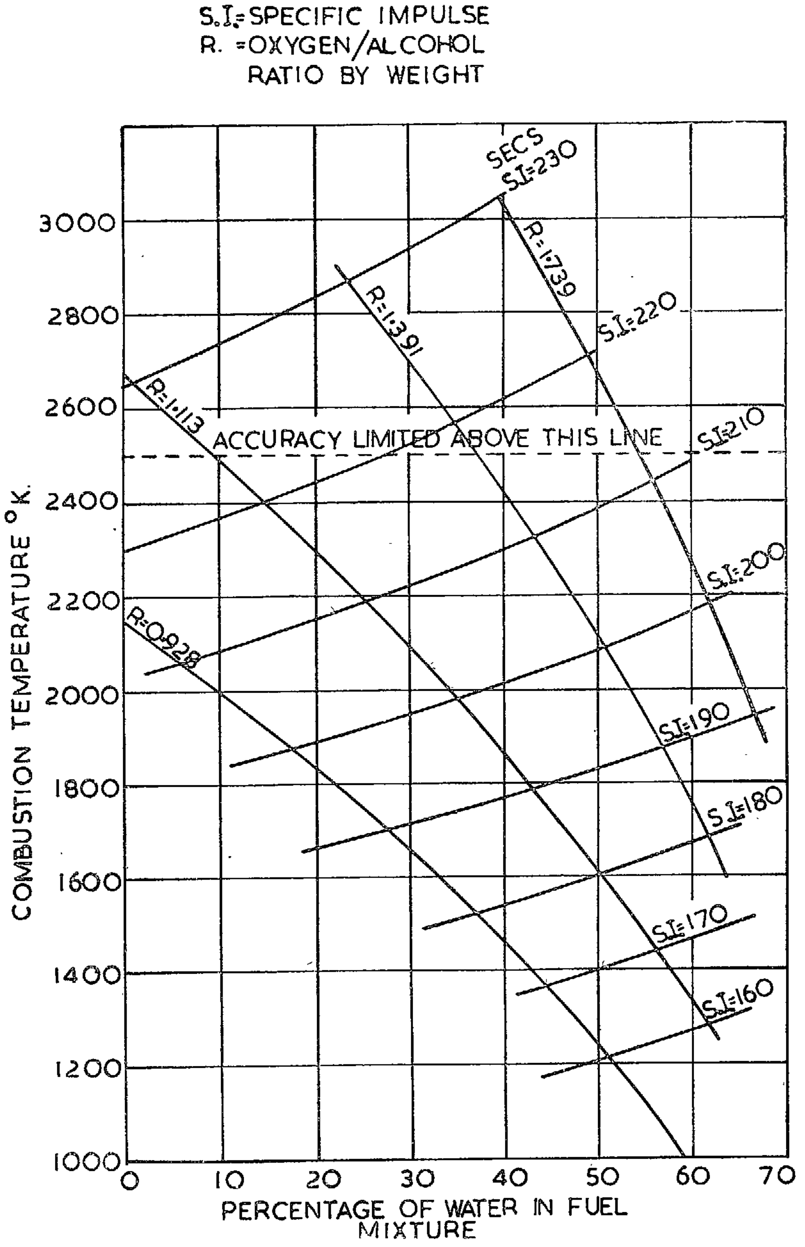

Fig. 2. Combustion temperatures and specific impulses for ethyl alcohol–water–liquid oxygen propellant combinations at an expansion ratio of 20:1.

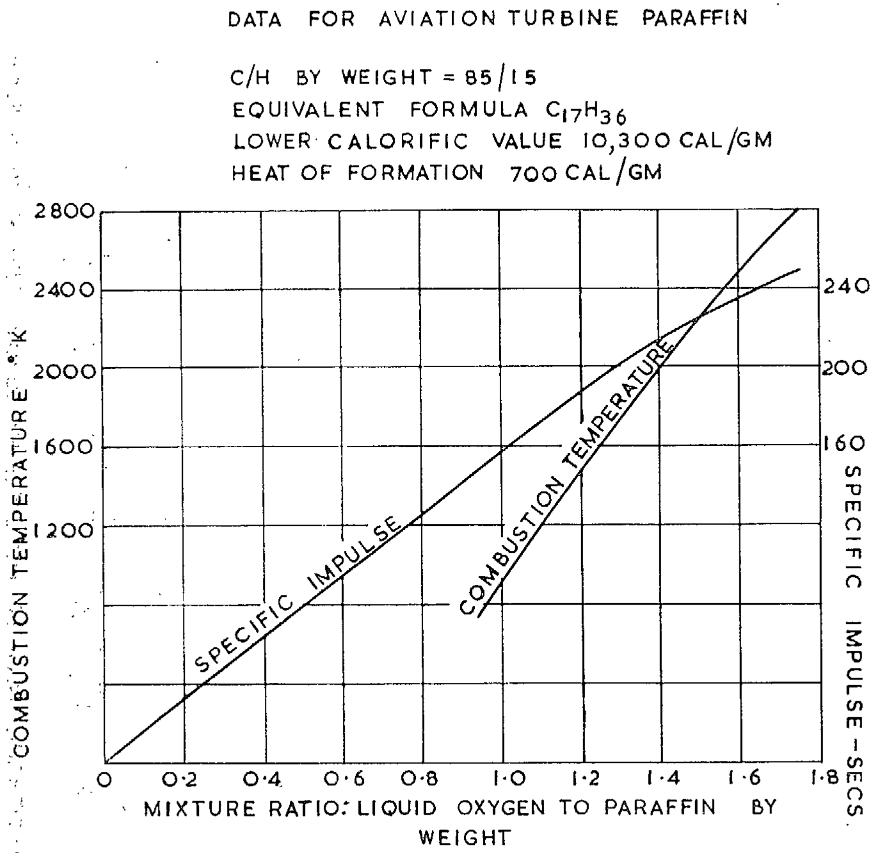

FIG. 3. Combustion temperatures and specific impulses for paraffin–liquid oxygen propellant combinations at an expansion ratio of 20:1.

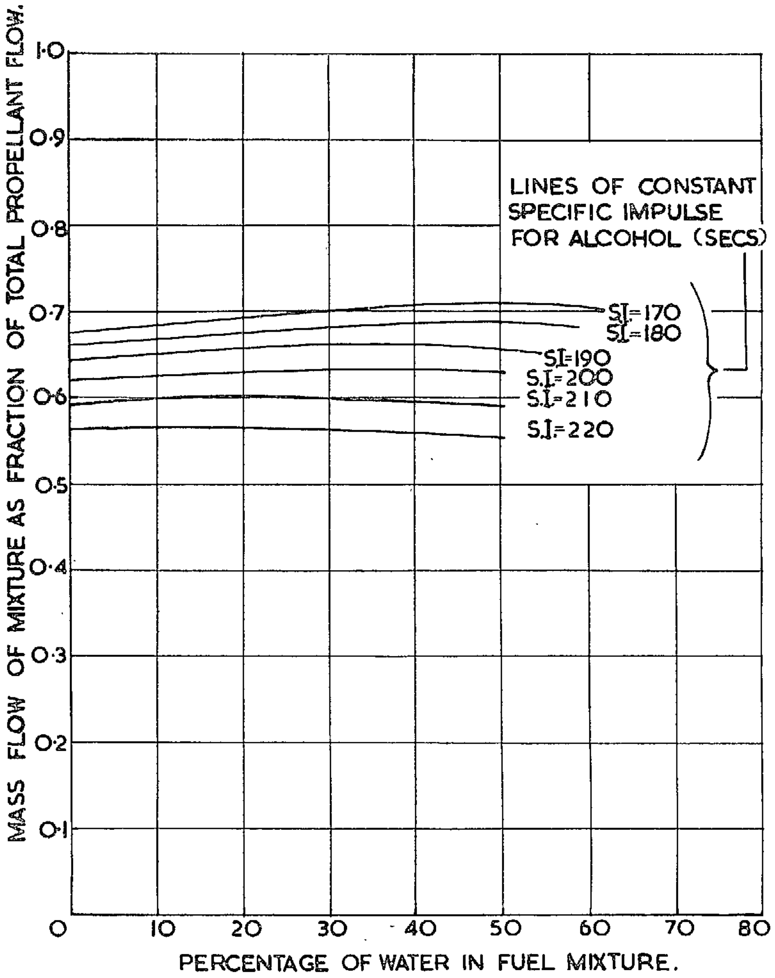

FIG. 4. Mass flow of fuel mixture for methyl alcohol–water mixtures (specific impulses for an expansion ratio of 20:1).

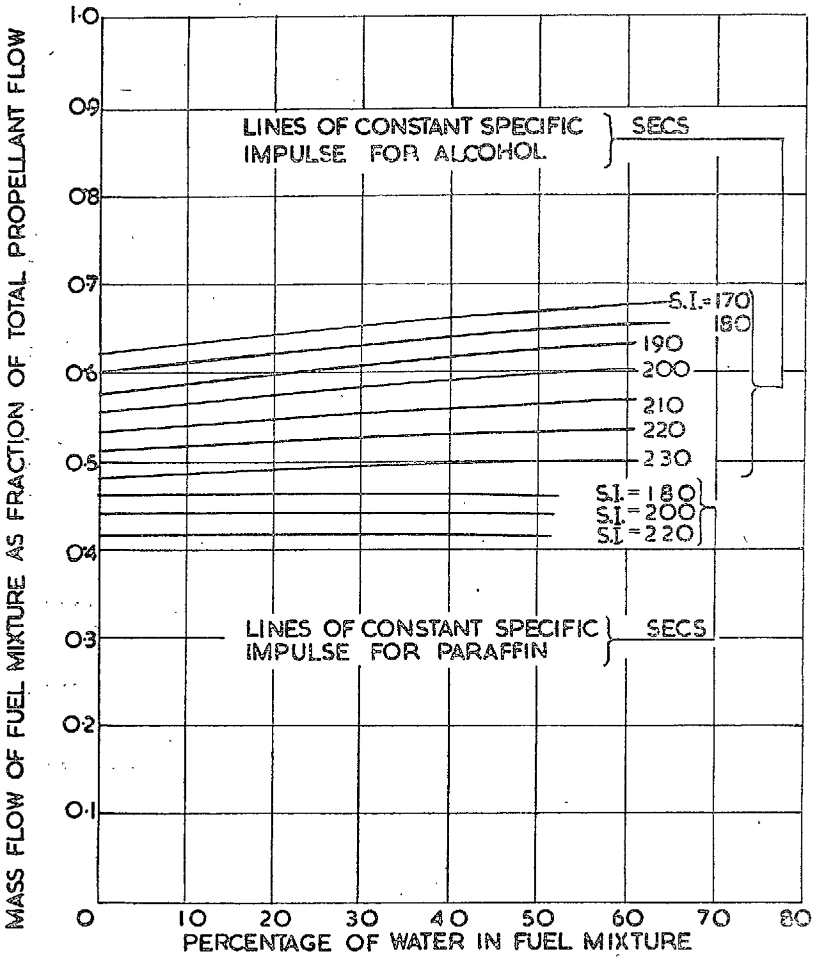

FIG. 5. Mass flow of fuel mixture for ethyl alcohol–water mixtures and paraffin (specific impulses at an expansion ratio of 20:1).

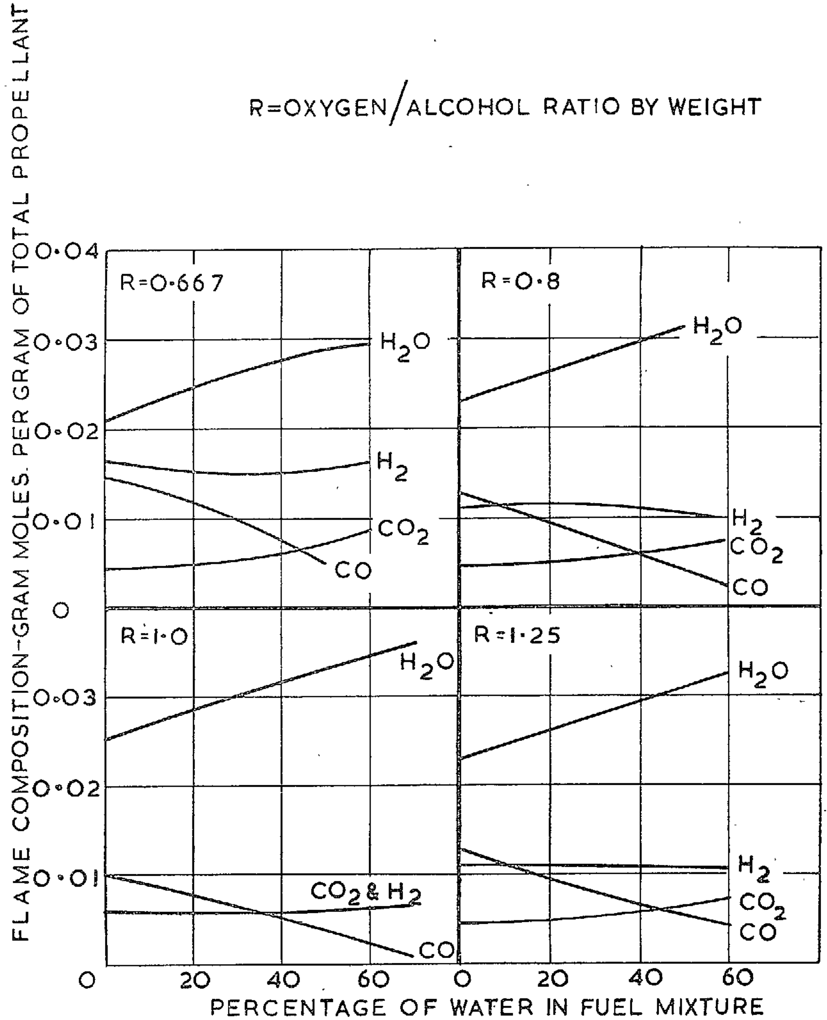

FIG. 6. Flame compositions for methyl alcohol–water–liquid oxygen propellant combinations.

J4258 Wt.14/806 K8 4/51 D&Co. 34-263

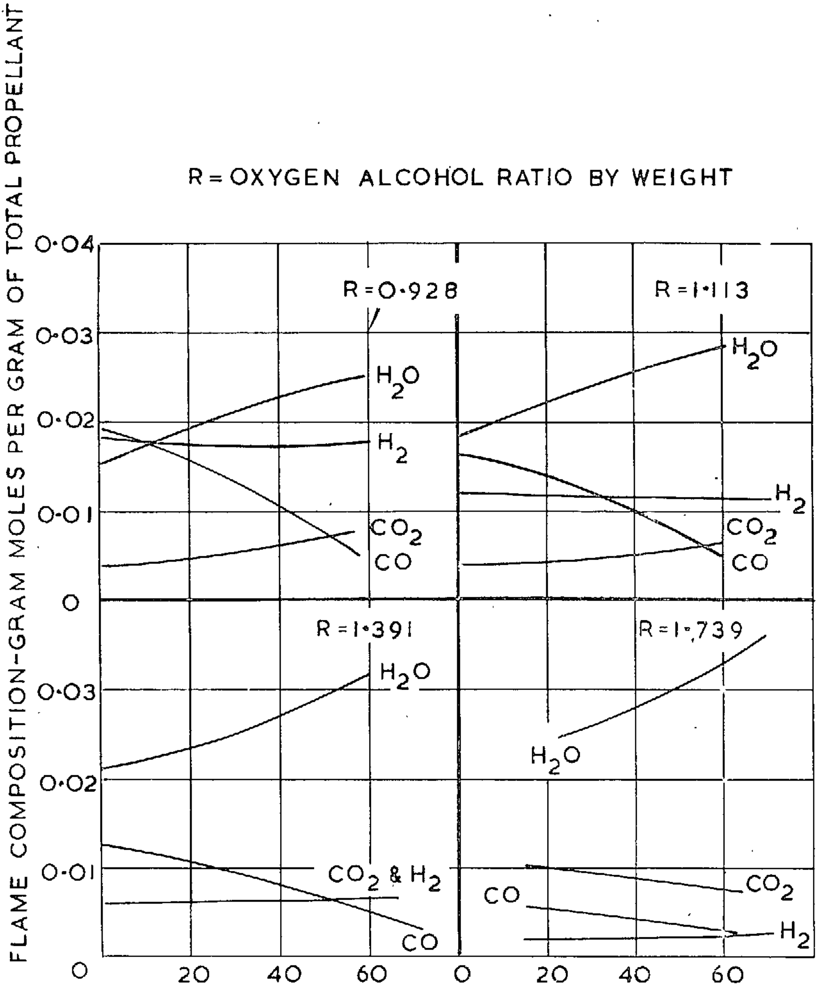

Fig. 7. Flame compositions for ethyl alcohol–water–liquid oxygen propellant combinations.

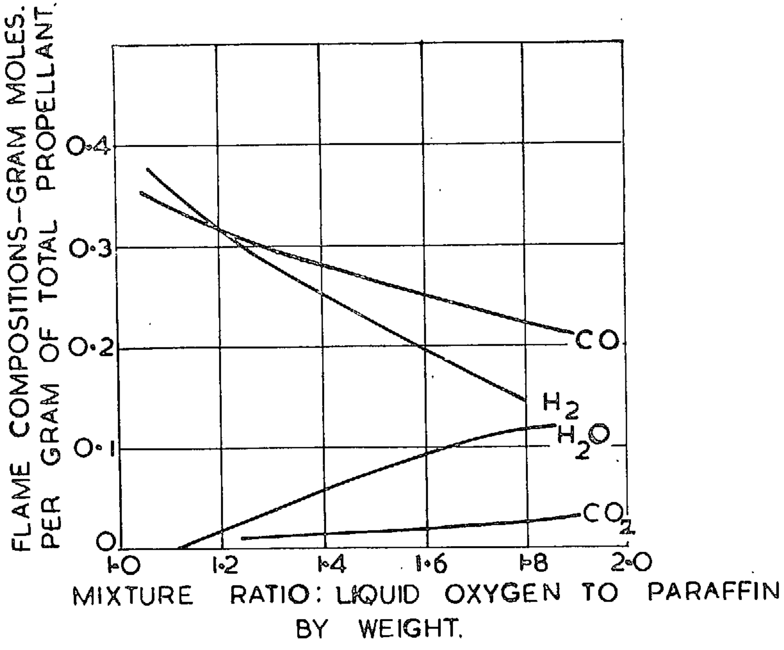

Fig. 8. Flame compositions for paraffin–liquid oxygen propellant combinations.

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