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## Synthetic Fuel Mixtures as Standard Fuel for Overload Motor Tests

A. Suggestion for the Composition of Synthetic Fuel Mixtures as Standard Fuel for Overload Motor Tests.

By: Fromherz, Ludwigshafen, 18 Feb. 1942

1. Introduction and Synopsis

At the meeting of the DVL (Deutsche Versuchsanstalt für Luftfahrtforschung) on "The Antiknock Behavior and Storage of Motor Fuels," on June 16, & 17, 1941 in Berlin-Adlershof, the disadvantages connected with the control of overload test motors by standard fuels from production were discussed. Dr. Pier suggested to replace these by synthetic standard mixtures as actual standard fuels. This suggestion found general approval.

Based on suitable data, a suggestion is made herein for the composition of synthetic standard mixtures, which are intended to replace the present standard mixtures for $CV_2b$, $C_3$ and $C_2$, derived from current production, in the overload curve. The compositions proposed in Section 6 represent a first approximation and must be corrected and definitely determined by comparative tests in the overload motor.

2. General Data on the Character of Standard Fuels.

The following standard fuels are recognized at present:

| | |
|---|---|
| for $CV_2b$: | $CV_2b$ - RLM (Reichsluftfahrtministerium) with 50% aromatics by volume and the rest of O.N. (M.M.) = 64 + 0.12% Pb/vol. |
| for $C_3$: | 80%/vol. $CV_2b$ - RLM + 20%/vol. ET 110 (iso-oct.) with an O.N. = 96 + 0.12% Pb/vol. |
| for $C_2$: | 80%/vol. VT 706 (50%/vol. aromatics + 50%/vol. with an O.N. = 74) + 20%/vol. ET 110 + 0.12% Pb/vol. |
| Std.-$C_3$, | therefor, contains 40%/vol. aromatics, 40%/vol. residual gasoline with an O.N. = 64, and 20%/vol. ET 110 with an O.N. = 96. For the 60%/vol. of residual gasoline and ET 110 an O.N. = 74.6 is figured by the mixture rule. |
| Std.-$C_2$, | therefor, contains 40%/vol. aromatics, 40%/vol. residual gasoline with an O.N. = 74, and 20%/vol. ET 110 with an O.N. = 96. For the 60%/vol. of residual gasoline and ET 110 an O.N. = 81.4 is figured. |

We must now attempt to replace each of the above standard fuels by an equal volume proportion of a definite aromatic mixture (50, 40 or 40%/vol) and by an equal volume proportion of a definite residual gasoline with an O.N. of 64, 74.6 or 81.4.

3. Replacing the Residual Gasoline.

The problem to find a definite uniformly boiling (siedegerecht) substitute for a residual gasoline can not be solved directly. I.G. standard gasoline is not available in sufficient quantities. A consultation with Dr. Ester of Leuna showed that VT 702-Leuna is produced in current production with constant characteristics for long periods of time and can, therefore, be safely used as standard component.

The following may be considered excellent components for the definite adjustment of the given residual gasoline quality:

1. - VT 702 (Leuna aviation gasoline), O.N. 70-71, aromatics content 7%/vol, resid. gasol. O.N. 69.

2. - I.G. standard gasoline, O.N. 42.

3. - ET 110, O.N. 96.

4. Synthetic Aromatic Mixture.

It is obvious that a uniform aromatic mixture for all standard mixtures in question should be found.

For this purpose the aromatics analyses of $CV_2b$ and DHD gasolines made by Dr. Hirschberger and D. Ch. Lajus in the laboratory in the course of the latter half of 1941 were compared in Table 1. The intermediate fractions were distributed in equal portions to the benzol, toluol and xylol fractions and a corresponding portion, abt. 2%/wt, of the higher aromatics added to the xylol fraction.

It may be recognized, above all, that the difference in the composition of the aromatics of the DHD bit. coal gasoline and $CV_2b$ is not appreciable. For an average uniform mixture, preferential consideration being given $CV_2b$-RLM and DHD bit. coal gasoline, the following composition is obtained:

15%/wt. benzol
40%/wt. toluol
30%/wt. xylol + ethylbenzol
15%/wt. higher aromatics.

For the higher aromatics it is preferable to use di-ethylbenzol. A division into 10% isopropylbenzol + 5% di-ethylbenzol would probably be an unnecessary refinement, because, in the first place, isopropylbenzol and diethylbenzol are very much alike in their overload behavior, and, in the second place, the difference in the influence on the boiling curve is probably imperceptible. A division of the diethylbenzol into o-m-p-components has not been made up to this time. It is probably unimportant and impossible in practice. On the contrary, it seems advisable to divide the xylol fraction into o-m-p-xylol and ethylbenzol, because of the quantitatively large proportion and the different overload behavior. In its overload behavior, o-xylol is some distance below the other components.

TABLE 1.

Aromatics Composition of $CV_2b$ and DHD High Test Fuels (-165°C)

The figures are %/wt, the intermediate fractions were distributed in equal halves to the main fractions, and abt. 2% of the fraction for higher aromatics was added to the xylol-ethylbenzol fraction.

| Fractions | DHD 4075 H from bit. coal gasoline | DHD fr. brown coal gasol. 50% c.e.p.prod. | | DHD fr. Russian aviat. gasol. heavy fraction, Eurotank, P-1471 | DHD from Ruman. gasol, C-quality | DHD from Nienhagen petrol. gasol. |
|---|---|---|---|---|---|---|
| Benzol | 13 | 12 | | 8 | 14 | 11 |
| Toluol | 40 | 43 | | 34 | 41 | 32 |
| Xylol-Ethylbenzol | 32 | 33 | | 46 | 33 | 38 |
| Higher Aromatics | 15 | 12 | | 12 | 12 | 19 |
| | $CV_2b$-RLM Std. fuel | $CV_2b$-Scholven | | $CV_2b$-Poelitz P-1012 Tank 217/12 28.9.41 | $CV_2b$-Gelsenberg (-150°C) Tank Sample 16.8.41 | $CV_2b$-France Wifo-Hitzacker (-162°C) |
| | | 24.8.41 | 28.9.41 | | | |
| Benzol | 21 | 15 | 27 | 12 | 21 | 23 |
| Toluol | 38 | 33 | 22 | 29 | 36 | 35 |
| Xylol-Ethylbenzol | 30 | 33 | 34 | 41 | 36 | 34 |
| Higher Aromatics | 11 | 19 | 17 | 18 | 7 | 8 |

## 5. Determination of the Composition of the Xylol Fraction by Raman Spectra and Infra-Red Absorption.

The composition of the xylol fraction was unknown until now. An analysis by fractional distillation is out of the question because of the partially identical position of the boiling points. A separation by freezing results in insufficient enrichment.

On the other hand, the simultaneous investigation of the Raman spectra and the infra-red absorption proved successful.

The independent investigations of the fraction 135-137°C of the aromatics extract obtained in the laboratory by Dr. Hirschberger and D. Ch. Lajus from $CV_2b$-RLM showed that:

| | According to infra-red absorption | According to the Raman spectra | Mean Value |
|---|---|---|---|
| ethylbenzol = | 66-67%/wt. | 67-68%/wt. | 67% |
| m-xylol | 23 | 27 | 25 |
| p-xylol | 8 | 5 | 7 |
| o-xylol | <3 | <1 | 1 |

The agreement is satisfactory, since the limits of errors overlap.

Accordingly, the Raman spectra of the other fractions under consideration were evaluated and the constituent of the 4 components calculated altogether, as may be seen from Table 2.

Table 2 shows that o-xylol is present in very small quantities. The p-xylol constituent is also relatively small. Because of the overlead behavior of p- and o-xylol, relatively opposite to m-xylol (p somewhat better than m, o much worse than m), one may, for simplification, assume in the first approximation that the differences caused by the presence of these small o- and p-xylol constituents compensate each other and together act like m-xylol. Accordingly, the xylol fraction in the uniform mixture, 30%/wt, can be divided into 20%/wt. ethylbenzol and 10%/wt. m-xylol, for simplification.

### TABLE 2.

Composition of the Xylol Fraction of $CV_2b$-RLM

| Fraction °C | Total Quantity g | %/wt. in total fraction: Ethyl-Benzol | m- | p- | o-xylol | Quantity, g: Ethyl-Benzol | m- | p- | o-xylol |
|---|---|---|---|---|---|---|---|---|---|
| 130-135 | 11.6 | 75 | 20 | 5 | 0 | 8.7 | 2.3 | 0.6 | 0 |
| 135-137 | 403.7 | 67 | 25 | 7 | 1 | 270.5 | 101.0 | 28.2 | 4.0 |
| 137-138 | 29.5 | 47 | 40 | 5 | 8 | 13.9 | 11.8 | 1.5 | 2.3 |
| 138-140 | 22.3 | 46 | 36 | 3 | 15 | 10.3 | 8.0 | 0.7 | 3.3 |
| 140-145 | 20.1 | 37 | 38 | 3 | 22 | 7.5 | 7.6 | 0.6 | 4.4 |
| Total, g | 487.2 | | | | | 310.9 | 130.7 | 31.6 | 14.0 |
| Total, % | 100 | | | | | 63.8 | 26.8 | 6.5 | 2.9 |
| | | | | | | | 36.2% o-xylol | | |

6. Composition of High Test Standard Fuels.

1. The uniform aromatic mixture (Einheitsmischung) is derived from Sections 4 and 5:

15%/wt. benzol
40 " toluol
20 " ethylbenzol
10 " m-xylol
15 " diethylbenzol (or 10% isopropylbenzol + 5% diethylbenzol)

2. From Sections 2 and 3 we can compute the following composition, based on the mixture rules for standard gasolines with 50,40 or 40%/vol. total aromatics and an octane number of the rest = 64, 74.6 or 81.4:

a) Substitute Std. C7$_2$b:
47%/vol. synthetic aromatics mixture
44 " VT 702
9 " I.G. std. gasoline
+ 0.12% Pb.

b) Substitute Std. C$_2$ (new):
either 80%/vol. subst. std. C7$_2$b
+ 20%/vol. ET 110
or 36%/vol. synth. aromatics mixture
51 " VT 702
13 " ET 110
+ 0.12% Pb.

c) Substitute Std. C$_3$:
37%/vol. synth. aromatics mixture
35 " VT 702
28 " ET 110
+ 0.12% Pb.

These mixtures probably agree with the old standard fuels in their overload curves within an error of ± 1 atm, considering the approximations made (using the mixture rules for octane number and overload curve, standardizing the aromatics composition). It is proposed to make 2 independent determinations of the overload curves and a comparative measurement of the corresponding present standard fuel of each of the synthetic mixtures of the given compositions.

A comparison of the series of measurements shows the correction, which must be applied to the calculated compositions to obtain the best adaptation of the synthetic curves to the present standard curves.

B. Synthetic Standard Fuels for Overload Tests and Dependence of the Overload Curves on the Naphthene Content.

By: Fromherz, Ludwigshafen, 10 April, 1943

(With 5 figures, not available)

I. Introduction and Preliminary Work.

In the report of 13.February 1942, proposals were worked out for the composition of synthetic standard mixtures as standard fuels for overload tests, in substitution for $CV_2b$, $C_3$ and $C_2$ samples taken from current production, based on Roman investigations and with the rules for calculating overload curves. The new synthetic standard fuels must have such characteristics that their overload curves practically agree with the old standard curves for $CV_2b$, $C_3$ and $C_2$.

The following standard aromatics mixture component was found to come closest to the aromatics composition of our high test fuels:

| | |
|---|---|
| 15%/wt. | benzol |
| 40 " | toluol |
| 20 " | ethylbenzol |
| 15 " | m-xylol |
| 10 " | diethylbenzol. |

For the residual gasoline component we must select a mixture which has an octane number (ON) of 64 in the case of $CV_2b$ substitution, one of 73.7 in the case of $C_3$(new) substitution, and one of 82.4 in the case of $C_2$ substitution.

The following may be considered excellent components by definite adjustment of this residual gasoline quality:

1. - VT 702 (Leuna aviation gasoline) O.N. 70-72, aromatics content 7%/vol, residual gasoline O.N. 69, naphthene content 41%/vol.

2. - I.G. std. gasoline, O.N. 42, practically free of naphthene.

3. - ET 110, O.N. 96, free of naphthene.

The following compositions of the standard gasolines were calculated therefrom in the first mixture, (percentages by volume):

1. - Substitute $CV_2b$,
   47%/vol. synthetic aromatics mixture,
   44 " VT 702
   9 " I.G. std. gasoline + 0.12% Pb,
   corresponds to $CV_2b$-ELM with 50% aromatics and 50% residual gasoline with an O.N. of 64 + 0.12% Pb.

2. - Substitute $C_2$,
   37%/vol. synthetic aromatics mixture,
   35 " VT 702
   28 " ET 110
   + 0.12% Pb,
   corresponds to 80% VT 706 (50% aromatics + 50% residual gasoline with O.N. 74) + 20% ET 110 + 0.12% Pb.

3. - Substitute $C_3$ (new)

   a). 80% subst. $CV_2b$ + 17.6% ET 110 + 2.4% VT 702 + 0.12% Pb.
   i.e., 37.6% synth. arom. mixture
   37.6% VT 702
   7.2% I.G. std. gasol. + 0.12% Pb.
   17.6% ET 110.

b). 36% synth. arom. mixture
54% VT 702
10% ET 110,
corresponds to 80% $CV_2b$-RLM
+ 20% captured iso-octane with O.N. 93
+ 0.12% Pb.

4. - Substitute $C_3$ (upper limit),

a). 80% subst. $CV_2b$ + 20% ET 110 + 0.12% Pb.

b). 36% synth. arom. mixture
51% VT 702
13% ET 110
+ 0.12% Pb,
corresponds to 80% $CV_2b$ + 20% ET 110
with an O.N. 96 + 0.12% Pb, a mixture,
whose overload curve is abt. 0.2 atm
above $C_3$ (new).

2. Experimental Determination of the Overload Curve of Standard Mixtures.

Mixtures 1, 2, 4a and 4b were made twice, independent of each other, for experimental testing and their overload curves determined in 2 series with a time interval of several days. Series I, Fig. 1a, b & c, Series II, Fig. 2a, b & c. Besides, the corresponding original standard gasoline overload curve was always measured, in order to eliminate irregularities of the test motor. This seemed necessary for reliable evaluation of results because of the great variations in the measurements of the overload curves, at least ±0.5 atm.

Figures 1a, b, c and 2a, b, c show that the synthetic mixtures have better overload curves throughout, actually an average of 1 atm higher, although the aromatics composition, see above, practically corresponds to that of the original standard gasolines and the residual gasoline component is adjusted to the same octane number.

In detail, the positive differences Δ of the new overload curves of the synthetic mixtures (Δ in atm) compared to those of the original standard gasolines are shown in Table Ia.

TABLE Ia

| | $CV_2b$ (compare 1) Series I | $C_3$ (upp. limit, compare 4a) Series I | $C_3$ (upp. limit, compare 4b) Series I | $C_2$ (compare 2) Series I |
|---|---|---|---|---|
| Δ (bottom) | 0.8 | 0.9 | | 0.7 |
| Δ (top) | 1.6 | 1.4 | | 1.3 |
| Δ (mean) | 1.2 | 1.1 | 0 | 1.0 |
| | | Series II | | |
| Δ (top) | | | | |
| Δ (bottom) | | | | |
| Δ (mean) | 1.2 | 1.0 | 0.5 | 0.5 |
| Naphthene Content | 18% | 14% | 22% | 14% |
| Naphth. Content of original std. gasoline | 33% | 26% | | 28% |

### 3. Dependence of the Overload Curves on the Naphthene Content.

Table Ia, section 2, shows the reason for the more favorable position, by abt. 1 atm, of the overload curves of the synthetic mixtures. Since, as shown in section 1, the aromatics composition and octane number of the residual gasoline is the same in the synthetic mixtures as in the original standard gasolines, the only difference is the considerably lower naphthene content of the synthetic gasolines. A complete absence of naphthene with equal octane number of the residual gasoline would, accordingly extrapolated, indicate a more favorable position, by abt. 2 atm, of the overload curve.

The highest possible grades of gasolines are, therefore, obtained, if the naphthenes are removed, at the same time keeping the octane number of the residual gasoline constant, or by dehydrogenating aromatics made from naphthenes to a relatively naphthene-poor gasoline, like VT 702 or iso-octane, or polymer gasoline, or adding them to mixtures of these.

### 4. Final Composition of Synthetic Standard Mixtures.

To lower the overload curve of synthetic mixtures without changing the slope, the octane number of the residual gasoline must be lowered, at the same time keeping the aromatics content constant.

The following mixtures, representing closest approximations, were made and their overload curves determined:

Series III, Fig. 3a, b & c.

1. - Substitute $CV_2b$, Fig. 3a,

| | |
|---|---|
| 48% synth. arom. mixt, | arom. content 50% |
| 50% aromatic content, | resid. gasol. O.N. 58, |
| 34% VT 702 | naphth. content 14% |
| 18% I.G. std. gasoline, | △ (mean) 0.6 atm. |
| + 0.12% Pb. | |

2. - Substitute $C_2$, Fig. 3b,

| | |
|---|---|
| 37% synth. arom. mixt., | arom. content 40% |
| 44% VT 702 | resid. gasol. O.N. 78 |
| 19% ET 110 | naphth. content 15% |
| + 0.12% Pb | △ (mean) 0.5 atm. |

3. - Substitute $C_3$ (new), Fig. 3c,

a). 

| | |
|---|---|
| 80% mixt. 1 ($CV_2b$ sinth), | arom. content 40% |
| 17.6% ET 110 | resid. gasol. O.N. 70.5 |
| 2.4% VT 702 | naphth. content 12% |
| + 0.12% Pb | △ (mean) 0.5 atm. |

b).

| | |
|---|---|
| 36% synth. arom. mixt, | arom. content 40% |
| 58% VT 702 | resid. gasol. O.N. 71.8 |
| 6% ET 110 | naphth. content 24% |
| + 0.12% Pb | △ (mean) 0.8 atm. |

It is apparent that the overload curves are still too high, in spite of appreciable lowering of the residual gasoline octane number.

Another correction showed that the overload curves of the synthetic mixture agrees with the original standard gasolines, within the limits of errors. The overload curves of 2 independently produced series (Series IV and V) were again measured at intervals of some weeks (Series IV in Fig. 4a,b,c, Series V in Fig. 5a,b,c).

The Compositions of the Final Standard Mixtures are as follows:

1. - Substitute $CV_2b$, Fig. 4a and 5a,

| | |
|---|---|
| 48% arom. mixt. | arom. content 50% |
| 24% VT 702 | resid. gasol. O.N. 54 |
| 28% I.G. std. gasol. | naphth. content 10% |
| + 0.12% Pb | △ Series IV +0.3 atm. |
| | △ " V +0.4 atm. |

2. - Substitute $C_2$, Fig. 4b and 5b,

| | |
|---|---|
| 36.5% arom. mixture, | arom. content 40% |
| 52% VT 702 | resid. gasol. O.N. 74.2 |
| 11.5% ET 110 | naphth. content 21% |
| + 0.12% Pb | △ Series IV +0.4 atm. |
| | △ " V -0.5 atm. |

3. - Substitute $C_3$, 4c and 5c,

a). 

| | |
|---|---|
| 80% mixture 1, | arom. content 40% |
| 17.6% ET 110 | resid. gasol. O.N. 67 |
| 2.4% VT 702 | naphth. content 9% |
| + 0.12% Pb | △ Series IV +0.2 atm. |
| | △ " V +0.4 atm. |

b). 

| | |
|---|---|
| 36% arom. mixt. | arom. content 40% |
| 60% VT 702 | resid. gasol. O.N. 67 |
| 4% I.G. std. gasol. | naphth. content 24% |
| + 0.12% Pb | △ Series IV -0.2 atm. |
| | △ " V +0.2 atm. |

It may be seen that, in agreement with the statements made in Section 3, due to the low naphthene content, $CV_2b$ quality may already be obtained with a residual gasoline with an octane number of 54, instead of 63, $C_3$ quality with a residual gasoline with an octane number of 67, instead of 73.7, and $C_2$ quality with a residual gasoline with an octane number of 74.2 instead of 81.4. In particular, it is evident that by raising the aromatics content of VT 702 to 40%, residual gasoline octane number 69, a highly qualified gasoline can be obtained, the quality of which is above that of $C_3$, without having to add ET 110 iso-octane.

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