WAR limite Performance of Blends of AN-F-28 Fuel Containing 2 Percent Aromatic Amines - I

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MEMORANDUM REPORT

for the

Army Air Forces, Materiel Command

KNOCK-LIMITED PERFORMANCE OF BLENDS OF AN-F-28 FUEL
CONTAINING 2 PERCENT AROMATIC AMINES - I

By J. Robert Branstetter

SUMMARY

Tests were conducted to investigate the effect of 2-percent additions of 11 aromatic amines on the knock-limited performance of AN-F-28 fuel. A total of 48 aromatic amines are being prepared at the Aircraft Engine Research Laboratory for knock tests. This report presents results for the first 11: aniline, N,N-dimethylaniline, N,N-diethylaniline, N-isopropylaniline, N-butylaniline, N-methyl-p-toluidine, N-isopropyl-p-toluidine, p-isopropylaniline, 2,6-xylidine, 4-isopropyl-2-methylaniline, and o-methoxyaniline. The knock-limited performance of an AN-F-28 fuel with and without 2-percent additions of each of the aromatic amines was determined in a CFR engine under three sets of operating conditions (including F-4 conditions). The report contains only information on the antiknock effectiveness of the aromatic amines and does not consider other phases of the fuel problem, such as their effect on lubrication and synthetic rubbers.

The results are summarized as follows:

1. These tests indicate that the following aromatic amines (in addition to xylidines) might be considered of interest as antiknock agents: N-methyl-p-toluidine, p-isopropylaniline, and aniline.

2. Of the aromatic amines tested, N-methyl-p-toluidine gave the best rich-mixture performance. Its antiknock effectiveness at rich fuel-air mixtures was nearly twice that of xylidines.

3. At rich fuel-air mixtures the antiknock effectiveness of the aromatic amines in AN-F-28 fuel was both greater and more independent of engine conditions than at lean fuel-air mixtures.

4. All of the aromatic amines tested with the exception of N-isopropylaniline showed pronounced sensitivity to engine operating conditions at low fuel-air ratios. Because of low or negative response, N-isopropylaniline is not of interest.
5. With the exception of the xylidines and p-isopropylaniline, all the aromatic amines tested depreciated the knock-limited performance of AN-F-28 fuel at fuel-air ratios of both 0.062 and 0.070 under F-4 conditions. At the least extreme engine conditions, however, the antiknock effectiveness of the aromatic amines, on a percentage basis, was almost independent of fuel-air ratio.

**INTRODUCTION**

The data presented in this report are part of a general program, being conducted at the request of the Army Air Forces, to determine the effects of aromatic amines on the knock-limited performance of a currently used aviation gasoline.

Because of the suggested use of xylidines as an antiknock additive for aviation gasolines, it was thought advisable to knock test a series of aromatic amines. A total of 48 aromatic amines are being prepared. This report, part I of a series of five reports, presents knock data for 11 aromatic amines. In this report no attempt is made to evaluate the amines from any consideration other than that of their effect on fuel knock as indicated by the results recorded on a small-scale engine.

Some of the aromatic amines have been tested in other laboratories prior to the tests for which the results are presented herein. The NACA data, in conjunction with the results of other laboratories, provide a reasonably satisfactory evaluation of the antiknock characteristics of these compounds within the limits of the significance of the engine conditions employed.

This work is being conducted at the Aircraft Engine Research Laboratory of the NACA at Cleveland, Ohio. The data presented were obtained in the period from October to December 1943.

**APPARATUS AND TEST PROCEDURE**

Each aromatic amine tested (table I) was distilled through a fractionating column, and a narrow (approximately 10°C) fraction in the middle of the boiling range was selected. The purity of the additives was estimated at 95 percent or more. The preparation and purification of the amines were performed under the direction of Dr. W. T. Olson of the laboratory staff.
The tests were performed on a CFR engine described in reference 1. In the present tests the injection elbow was altered to allow for the installation of an independent "warm-up" fuel system in order that the test fuel could be conserved.

Because a small-scale engine operating at one set of conditions does not predict the full-scale, knock-limited-performance characteristics of a fuel over a wide range of engine variables, three sets of conditions, varying in severity, were used for the present tests.

The three sets of operating conditions are as follows:

<table>
<thead>
<tr>
<th>Inlet-air temperature (°F)</th>
<th>Spark advance (deg B.T.C.)</th>
<th>Coolant temperature (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-4 method</td>
<td>225</td>
<td>45</td>
</tr>
<tr>
<td>Modification A</td>
<td>250</td>
<td>30</td>
</tr>
<tr>
<td>Modification B</td>
<td>150</td>
<td>30</td>
</tr>
</tbody>
</table>

At each of these sets of conditions, 0- and 2-percent blends of the aromatic amines were tested in one lot of AN-F-28, Amendment-1, fuel on the same day. The value of 2 percent was selected for blending purposes because it represents approximately the amount that would be of greatest interest. Tests of 1- and 3-percent blends would have been useful in extending the data, but limitations in the quantities of the amines available prevented these choices.

DISCUSSION OF RESULTS

A bracketed AN-F-28 fuel reference curve (data compiled from several tests made during the course of the project) is presented in figure 1.

The knock-limited performance data obtained on the aromatic amines are presented in figures 2 to 12. Each figure compares the effects of the transition from severe to mild test conditions on blends of 0 and 2 percent aromatic amines and AN-F-28 aviation gasoline.

Table I summarizes the relative power obtained by the addition of aromatic amines. They showed decidedly greater sensitivity for a change in fuel-air ratio under F-4 than under either of the two less severe conditions. When the engine was operated under F-4 specifications, none of the amines increased the knock-limited power more than the base fuel at fuel-air ratios of 0.062 and 0.070 (with
the exception of commercial xyldines at 0.062), however, N-methyl-p-
toluidine, p-isopropylaniline, xyldines, and 4-isopropyl-2-methyl-
aniline exhibited desirable rich-mixture characteristics.

The antiknock effectiveness of the aromatic amines approached
independence of the fuel-air mixture when the severity of conditions
was decreased. When the columns in table I at the inlet-air tem-
perature of 150° F were averaged, an improvement of 1 percent in
relative knock-limited power was noted with an increase in fuel-air
ratio from 0.062 to 0.110.

Again, when the relative knock-limited powers (table I) were
averaged, the amines showed progressive improvement with a transi-
tion from severe to mild test conditions except that, at very rich
fuel-air mixtures, the severity of conditions had little effect on
the relative knock-limited performance. The effect of conditions
was most outstanding at lean fuel-air ratios.

In general, p-isopropylaniline and N-methyl-p-toluidine resulted
in higher knock-limited performance than both 2,6-xyldine and com-
mmercial xyldines and, of the additives tested, N-methyl-p-toluidine
gave the highest permissible power at an inlet-air temperature of
150° F at all fuel-air ratios. Also, under F-4 conditions this
additive showed marked superiority at very high fuel-air ratios but
acted as a proknock agent at lean mixtures. With the exception of
4-isopropyl-2-methylaniline and o-methoxyaniline, N-methyl-p-toluidine
showed greater sensitivity to engine conditions than any of the other
amines tested.

The indicated specific fuel consumption of the aromatic-amine
curves coincided with that of the base fuel on more than half the
tests; several additives, however, showed more economy improvements
in the rich region than in the lean region. Because sufficient
material was not available for check runs, the significance of these
differences in indicated specific fuel consumption is questionable.

SUMMARY OF RESULTS

From tests of the antiknock effectiveness of 2-percent additions
of 11 aromatic amines to AN-F-28 fuel under three sets of conditions
in a CFR engine, the following results were obtained:

1. The aromatic amines (in addition to xyldines) that might be
considered of interest as antiknock agents are N-methyl-p-toluidine,
p-isopropylaniline, and aniline.
2. Of the aromatic amines tested, N-methyl-p-toluidine gave the best rich-mixture performance. Its antiknock effectiveness at rich fuel-air mixtures was nearly twice that of xyldines.

3. At rich fuel-air mixtures the antiknock effectiveness of the aromatic amines in AN-F-28 fuel was both greater and more independent of engine conditions than at lean fuel-air mixtures.

4. All of the aromatic amines tested with the exception of N-isopropylaniline showed pronounced sensitivity to engine operating conditions at low fuel-air ratios. Because of low or negative response, N-isopropylaniline is not of interest.

5. With the exception of the xyldines and p-isopropylaniline, all the aromatic amines tested depreciated the knock-limited performance of AN-F-28 fuel at fuel-air ratios of both 0.062 and 0.070 under F-4 conditions. At the least extreme engine conditions, however, the antiknock effectiveness of the aromatic amines, on a percentage basis, was almost independent of fuel-air ratio.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, April 17, 1944.

REFERENCE

TABLE I - SUMMARY OF ANTITKNOCK EFFECTIVENESS OF AROMATIC-AMINE ADDITIONS TO AN-F-28 FUEL

[F-4 method: inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.
Modification A: inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.
Modification B: inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.]

<table>
<thead>
<tr>
<th>Aromatic amines (2-percent addition to AN-F-28 fuel)</th>
<th>Relative power = ( \frac{\text{imep (aromatic amine plus AN-F-28)}}{\text{imep (AN-F-28)}} )</th>
<th>Fuel-air ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F-4 method</td>
<td>Modification A</td>
</tr>
<tr>
<td>AN-F-28</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Aniline</td>
<td>1.14</td>
<td>1.11</td>
</tr>
<tr>
<td>N,N-dimethylaniline</td>
<td>0.99</td>
<td>1.01</td>
</tr>
<tr>
<td>N,N-diethylaniline</td>
<td>1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>N-isopropylaniline</td>
<td>0.96</td>
<td>0.91</td>
</tr>
<tr>
<td>N-butylaniline</td>
<td>1.00</td>
<td>1.03</td>
</tr>
<tr>
<td>N-methyl-p-toluidine</td>
<td>0.98</td>
<td>1.13</td>
</tr>
<tr>
<td>N-isopropyl-p-toluidine</td>
<td>0.89</td>
<td>0.90</td>
</tr>
<tr>
<td>p-isopropylaniline</td>
<td>1.00</td>
<td>1.09</td>
</tr>
<tr>
<td>2,6-xylidine</td>
<td>0.95</td>
<td>0.97</td>
</tr>
<tr>
<td>4-isopropyl-2-methylaniline</td>
<td>.86</td>
<td>1.10</td>
</tr>
<tr>
<td>o-methoxyaniline</td>
<td>.76</td>
<td>1.00</td>
</tr>
<tr>
<td>Xylidines (^c) (commercial)</td>
<td>1.03</td>
<td>1.01</td>
</tr>
</tbody>
</table>

\(^a\) Insufficient fuel to complete performance test.

\(^b\) Values obtained by extrapolation.

\(^c\) Unpublished data.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS
Figure 1. - Knock-limited F-4 performance of AN-F-28 fuel and corresponding S reference curves. Inlet-air temperature, 225°F; spark advance, 45° B.T.C.; coolant temperature, 375°F; engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165°F.
Fuel-air ratio

(a) Inlet-air temperature, 250° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 2. - Effect of addition of 2-percent aniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 2. - Concluded. Effect of addition of 2-percent aniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

(b) Inlet-air temperature, 150° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.
(a) Inlet-air temperature, 250° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 3. - Effect of addition of 2-percent N, N-dimethylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 3. Concluded. Effect of addition of 2-percent N,N-dimethyl-
aniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 185°F.
(a) Inlet-air temperature, 225° F; spark advance, 45° B.T.C.; coolant temperature, 375° F.

Figure 4. Effect of addition of 2-percent N, N-diethylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Effect of addition of 2-percent N,N-diethyl-aniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 1650°F.
(c) Inlet-air temperature, 150° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 4. - Concluded. Effect of addition of 2-percent N, N-diethyl- aniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Inlet–air temperature, 225° F; spark advance, 45° B.T.C.; coolant temperature, 375° F.

Figure 5. - Effect of addition of 2-percent N-isopropylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 5. - Continued. Effect of addition of 2–percent N-isopropyl-aniline to AN-F-28 fuel on knock–limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

(b) Inlet–air temperature, 250° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.
Figure 5. – Concluded. Effect of addition of 2-percent N-isopropyl-aniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

(c) Inlet-air temperature, 150° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.
Figure 6. - Effect of addition of 2-percent N-butylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

(a) Inlet-air temperature, 225° F; spark advance, 45° B.T.C.; coolant temperature, 375° F.
Figure 6. - Continued. Effect of addition of 2-percent N-butylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Fuel-air ratio

Inlet-air temperature, 150° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 6. Concluded. Effect of addition of 2-percent N-butylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 7. - Effect of addition of 2-percent N-methyl-p-toluidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

(a) Inlet-air temperature, 225° F; spark advance, 45° B.T.C.; coolant temperature, 375° F.
Figure 7. - Continued. Effect of addition of 2-percent N-methyl-p-toluidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165°F.
Figure 7. - Concluded. Effect of addition of 2-percent N-methyl-p-toluidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 8. - Effect of addition of 2-percent N-isopropyl-p-toluidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 185°F.
Fuel-air ratio

Inlet-air temperature, 250° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 8. – Continued. Effect of addition of 2-percent N-isopropyl-p-toluidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Fuel-air ratio

(c) Inlet-air temperature, 150° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 8. - Concluded. Effect of addition of 2-percent N-isopropyl-p-toluidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 9. - Effect of addition of 2-percent \( p \)-isopropylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165 \(^\circ\) F.
Figure 10. - Effect of addition of 2-percent 2, 6-xylidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1900 rpm; compression ratio, 7.0; oil temperature, 165° F.
(b) Inlet-air temperature, 250° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 10. - Continued. Effect of addition of 2-percent 2, 6-xylidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Inlet-air temperature, 130°F; spark advance, 30° B.T.C.; coolant temperature, 250°F.

Figure 10. - Concluded. Effect of addition of 2-percent 2,6-xylidine to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165°F.
(a) Inlet-air temperature, 225° F; spark advance, 45° B.T.C.; coolant temperature, 375° F.

Figure 11. - Effect of addition of 2-percent 4-isopropyl-2-methylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 11. – Continued. Effect of addition of 2-percent 4-isopropyl-2-methylaniline to AN-F-23 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Figure 11 - Concluded. Effect of addition of 2-percent 4-isopropyl-2-methylaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Fuel-air ratio

Inlet-air temperature, 225° F; spark advance, .45° B.T.C.; coolant temperature, 375° F.

Figure 12. - Effect of addition of 2-percent o-methoxyaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Inlet-air temperature, 250° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 12. - Continued. Effect of addition of 2-percent o-methoxyaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
I

Fuel-air ratio

(c) Inlet-air temperature, 150° F; spark advance, 30° B.T.C.; coolant temperature, 250° F.

Figure 12. - Concluded. Effect of addition of 2-percent o-methoxyaniline to AN-F-28 fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.
Anti-knock effectiveness of 2% additions of 11 aromatic amines in AN-F-28 fuel were tested in CFR engine under three operating conditions. Results show that N-methyl-p-toluidine gave best rich-mixture performance. Anti-knock effectiveness of all aromatic amines was greater at rich fuel/air mixtures. All fuels except N-isopropyl-aniline showed sensitivity to engine operating conditions.