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METHOD FOR MAKING A ROCKET AND MISSILE FUEL

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This application is a continuation-in-part application
derived from copending application Serial No. 793,152,
filed February 13, 1959, now abandoned.

The present invention is directed to a rocket and mis-
sile fuel, specifically an improved fuel for rockets and
missiles consisting of certain alkyl cyclohexanes. The present invention also relates to a method of obtaining the
fuel.

The present invention may briefly be described as a
rocket and missile fuel consisting essentially of an admix-
ture of C_{10} alkyl cyclohexanes, the admixture contain-
ing less than 1% paraffins and substantially no bicyclic
compounds, wherein each alkyl carbon atom alpha to the
cyclohexane ring has at least two hydrogen atoms attached thereto, and wherein the admixture has a boiling range from 319° F. to 358° F., and a hydrogen-to-carbon ratio of 2.1. Further, thermally unstable alkyl cyclo-
hexanes which have tertiary or quaternary carbon atoms alpha to the ring are avoided. For example, tertiary butyl cy-
clohexane and isopropyl cyclohexane are deleterious ma-
terials since they are not thermally stable. The methylated and/or ethylated derivatives of these compounds also
are undesirable and also are excluded from the present
invention.

Further, bicyclic compounds and paraffins which nor-
mally boil in the same range as the alkyl cyclohexanes of
the novel fuel are present in the reformation streams which
would be a source for the alkyl cyclohexanes. Therefore, these deleterious materials must be separated from the de-
sired alkyl cyclohexanes.

It is important that the fuel be reproducible in that
each successive batch which is produced must have ex-
actly the same quality and characteristics as the preceding
batches. Of particular importance is the control of the paraffinic content of the fuel. Since paraffins may not be
separated from the alkyl cyclohexanes by the generally
accepted methods such as distillation, extraction, etc., the
control of the amount of paraffins is particularly difficult.
The hydrogen-to-carbon ratio of paraffins is higher than
than that of alkyl cyclohexanes. Since the amount of paraffins in the feedstock will vary, depending on the crude oil
source, the paraffin content of the missile fuel product
would be expected to vary. This would result in a varia-
tion in the average hydrogen-to-carbon ratio. The ratio of
hydrogen to carbon in the product has an important effect
upon the specific impulse of the fuel so that small changes in the hydrogen-to-carbon ratio will result in
significant changes in the thrust of a missile using such
fuel. By removing substantially all of the paraffins, the
variation in paraffin content is virtually eliminated, and
the problem avoided.

It is quite important, of course, that the thrust of the
missile be accurately known so that the exact flight path
of the missile may be accurately precalculated.

Likewise, the hydrogen-to-carbon ratio of the methyl
hydrocarbons is substantially lower than that of the desired
fuel. Thus, the presence of these materials would be
deleterious to the performance of the missile using this
fuel, as the specific impulse would be lowered by the presence of these undesirable compounds.

The presence in the fuel of compounds having tertiary
or quaternary carbon atoms adjacent to the cyclo-
hexane ring is thermally unstable and are cracked at the
thrust chamber wall which operates at a temperature of
about 5000° F. This cracking results in the deposition of
coke on the thrust chamber wall, thereby substantially
reducing the heat transfer from the thrust chamber wall
to the hydrocarbon liquid, which eventually causes a
mechanical rupture of the thrust chamber wall. The present invention avoids this problem by removing the
unstable compounds from the fuel.

The liquid hydrocarbon fuel of the present invention is
oxidized in the missile by liquid oxygen. This requires
that the hydrocarbon be subjected to low temperatures
during its installation in the missile. Therefore, the
presence of high freezing point compounds in the fuel is
deleterious. Accordingly, 1,2,4,5-tetramethylecyclohexane
must be eliminated from the mixture to avoid freezing of
that compound at the low temperatures involved.

Briefly, the process of the present invention may be
described as a method which comprises fractionating a
virgin naphthenic crude oil to obtain a first fraction boil-
ing within the range of about 250° F. to about 400° F.
which contains paraffins, C_{10} alkyl cyclohexanes, and
methyl hydridanes as well as methyl isopropyl cyclo-
hexane, methyl-t-butyl cyclohexanes, and t-butyl cyclo-
hexanes. This admixture cannot be separated by simple
distillation to yield the desired alkyl cyclohexanes since
the undesirable materials fall in the same boiling range
as the desired alkyl cyclohexanes. Nor can extraction
be relied upon as a direct means of separation, since there is
no selective affinity upon which to base an extractive
separation.

Therefore, the first fractionation product is contacted
in a hydroforming zone with a hydroforming catalyst
under conditions operative to aromatize the alkyl cy-
clohexanes into alkyl benzenes, and to aromatize the methyl
hydridanes into methylnapthenes. Tertiary butyl groups
are destroyed during the hydroforming process, presum-
ably being cleft from the cyclohexane ring. Thus, the
term "hydroforming" is seen to encompass reactions
wherein aromatics are produced by dehydrogenation of
naphthenes and cyclization.

The hydroforming step is accomplished at a tempera-
ture within the range of 800° F. to 1000° F., a pressure
from 100 to 400 p.s.i.g., a space velocity of 0.75 to 2.25
v/v/hr., and a hydrogen rate of 1000 to 3000 s.c.f./b. A
hydroforming catalyst such as platinum on alumina
or molybdena may be used, however, the preferred
catalyst is platinum on alumina.

The aromatized stream is then fractionated to obtain
an aromatized fraction boiling within the range of 350°
F. to 381° F. In order to obtain the desired alkyl ben-
zenes while excluding methyl isopropyl benzenes (such
as 1-methyl-2-isopropyl benzene) and lighter materials,
and durene and heavier materials. Some of the paraffinic
materials present in the feedstock will form azeotropes
with the aromatic materials and will be removed from
the stream during the fractionation step.

The aromatized fraction is then hydrogenated in order
to regain the alkyl cyclohexane structure. Thishydro-
genation step is accomplished by contacting the aromatized fraction with a hydrogenation catalyst such as nickel-
tungsten sulfide, cobalt molybdate, nickel on kieselguhr,
platinum on alumina, or copper-promoted nickel. The
preferred catalyst is 40% nickel on kieselguhr.

Standard hydrogenation conditions are used, being
within the range of 300° F. to 600° F., from 100 to 1000
p.s.i.g., from 3000 to 15,000 s.c.f. of hydrogen per barrel
of feedstock, and the liquid space velocity of 0.25 to 2 v./v./hr.

The paraffins remaining in the stream form azoetropes with alkyl cyclohexanes which boil at different temperatures from the azoetropes previously formed with the aromatic materials. Thus, when the hydrogenated stream is fractionated to obtain a heart cut boiling within the range of 319° F. to 358° F., a substantially paraffin-free C10 alkyl cyclohexane product is obtained. A missile fuel prepared by the process of the present invention was found to contain substantially no paraffins or olefins, and was made up of the following C10 alkyl cyclohexanes:

1,4-dimethyl-2-ethylcyclohexane
1,2-dimethyl-3-ethylcyclohexane
1,2-dimethyl-4-ethylcyclohexane
1,3-dimethyl-2-ethylcyclohexane
1,3-dimethyl-4-ethylcyclohexane
1-methyl-3-n-propylcyclohexane
1,3-dimethyl-5-ethylcyclohexane
1,3-diethylcyclohexane
1-methyl-4-n-propylcyclohexane
1,2-diethylcyclohexane
1,4-diethylcyclohexane
1-methyl-2-n-propylcyclohexane
n-Butylcyclohexane

In sum, the present combination of steps provides a useful and novel process for the production of the desired C10 alkyl cyclohexane admixture which finds high utility as a rocket and missile fuel.

The present invention may be more fully appreciated by reference to the drawing wherein is schematically shown the process of obtaining the novel rocket and missile fuel by the present invention.

Referring now to the drawing, a virgin naphthenic crude such as Conroe, Coastal, etc., is introduced by way of line 100 into a fractionator 101 in order to make the first separation. Fractionator or distillation zone 101 is provided with all the necessary equipment and is operated under conditions to make the desired separation. A 250° F. through 400° F. rough heart cut is removed by way of line 102, whereas the fraction including 250° F. and lighter material is withdrawn overhead by way of line 104, the 400° F. and heavier materials being discharged by line 106. The cut rough stream boiling from 250° F. to 400° F. contains paraffins, naphthenes, hydridanes, and the naphthenes including 1-methyl-2-isopropylcyclohexane, t-butylcyclohexane, and methyl-t-butylcyclohexane. This rough cut is charged into hydroforming zones 108, which contains all of the equipment normally associated with hydroforming. In the hydroformer 108 the stream is aromatized and the t-butyl groups cleft from the cyclohexene rings.

The aromatized product is withdrawn by way of line 110 and introduced into a second fractionator or distillation zone 112 wherein the 1-methyl-2-isopropylbenzene and lighter materials are removed overhead and the durene and heavier materials are dropped out in the bottom of the line 116. The fractions of t-butyl cyclohexanes are discharged as benzene and as C6 and lighter paraffins through line 114.

A heart cut boiling within the range from 355° F. to 381° F. is removed from the fractionator 112 by way of line 120. This heart cut contains about 10% paraffins, 80% aromatics, and 10% indanes, and is charged into the hydrogenation zone 122 where it is contacted in the presence of a hydrogenation catalyst with from 3000 to 15,000 s.c.f./b. of hydrogen at a temperature within the range from 300° F. to 600° F. and a pressure from 100 to 1000 p.s.i.g. Suitable space velocities are from 0.25 to 2.0 v./v./hr. In the hydrogenator 122, the aromatics are converted to alkyl cyclohexanes and the indanes are converted to hydridanes.

The hydrogenated stream is withdrawn by way of line 124 and charged into the fractionator 126 from which an overhead stream boiling from 319° F. and lower is withdrawn by line 128 and a high boiling stream containing paraffins and hydridanes is withdrawn by way of line 130. The stream withdrawn by way of line 130 boils at 358° F. and higher.

A hydrogenated fraction boiling within the range of 319° F. to 358° F. and containing less than 1% paraffins is withdrawn by way of side stream 132. This side stream 132 is the alkyl cyclohexane product boiling within the desired range.

The desired alkyl cyclohexanes are obtained in a desired concentration free of undesirable paraffins, bicyclic compounds, and alkyl cyclohexanes having a t-butyl or isopropyl group attached thereto. Thus, an improved rocket and missile fuel may be obtained from a virgin naphthenic crude oil.

As used in the present application, the term "naphthenic crude" embraces those crude oils which contain a substantial amount of naphthenes. Actually, any crude oil which contains even a small amount of naphthenic material including C10 alkyl cyclohexanes would be suitable for use as a feedstock in the present process. However, to be commercially attractive, the crude should contain a minimum of about 10% naphthenic material. As an example, Coastal crude yields a naphtha boiling within the range from 200° F. to 430° F. which contains 8% aromatics, 49% paraffins, and 43% naphthenes. This naphtha cut can be treated by the process of the present invention to yield the desired alkyl cyclohexane product stream with no aromatics or paraffins admixed therewith. Thus, the present invention is useful with respect to a wide range of feedstocks.

**EXAMPLE**

As exemplary of the practice of the present invention, a Coastal crude oil was fractionated in order to produce a feedstock boiling within the range from 300° F. to 350° F. The fractionated feedstock was charged to a hydroformer and contacted with a platinum on alumina catalyst at 900° F. and 300 p.s.i.g. at a space velocity of 1.5 v./v./hr. and a hydrogen treat rate of 4000 s.c.f./b. of feed. During passage through the hydroforming zone, the stream was aromatized and yielded a product containing 80% C6+, material and 20% C6 and lower, as shown in Table I below:

<table>
<thead>
<tr>
<th>Table I—Aromatized product</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4 and heavier</td>
<td>81</td>
</tr>
<tr>
<td>Paraffins</td>
<td>26</td>
</tr>
<tr>
<td>Naphthene</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aromatics</th>
<th>Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>3</td>
</tr>
<tr>
<td>C7</td>
<td>8</td>
</tr>
<tr>
<td>C8</td>
<td>17</td>
</tr>
<tr>
<td>C9</td>
<td>16</td>
</tr>
<tr>
<td>C10</td>
<td>10</td>
</tr>
<tr>
<td>C5 and lighter</td>
<td>19</td>
</tr>
</tbody>
</table>

| C0                       | 5      |
| C1                       | 5      |
| C2                       | 2      |
| C1                       | 2      |

The breakdown of the C6 stream indicates the splitting off of alkyl groups (including t-butyl radicals) during aromatization.

This hydroformed product was then fractionated to yield a heart cut boiling within the range of 355° F. to 381° F., and the aromatized fraction was then hydrogenated at 400° F. and 800 p.s.i.g. with 11,600 s.c.f./b. hydrogen in contact with a 40% nickel on kieselguhr catalyst, at a space velocity of 0.75 v./v./hr. The hydrogenated product was removed and fractionated to obtain...
a hydrogenated fraction boiling within the range of 319° F. to 358° F., which contained no paraffin and was substantially entirely C₁₈ alkyl cyclohexanes.

The hydrogenated product had a gravity of 0.8046, a hydrogen-to-carbon ratio of 2:1 and a heat of combustion of 18,647 B.t.u./lb. The net paraffins and other materials were less than 1% and the purity of C₁₈ alkyl cyclohexanes was greater than 99%. An Engler distillation of the product indicated an IBP of 330° F. and a 95% point of 338° F. This compares to an actual boiling range of about 319° F. to 358° F.

An inspection of a typical missile fuel produced by the present invention is as follows:

<table>
<thead>
<tr>
<th>Hydrogenated product</th>
<th>0.8031</th>
</tr>
</thead>
</table>

**Distillation:**

<table>
<thead>
<tr>
<th>IBP, °F.</th>
<th>331</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBP, °F.</td>
<td>356</td>
</tr>
<tr>
<td>Boiling Range, °F.</td>
<td>25</td>
</tr>
<tr>
<td>Viscosity at 68° F., cs.</td>
<td>1.385</td>
</tr>
<tr>
<td>Freezing Point, °F.</td>
<td>-100</td>
</tr>
<tr>
<td>Aromatics, percent</td>
<td>0.8</td>
</tr>
<tr>
<td>Olefins, percent</td>
<td>0.01</td>
</tr>
<tr>
<td>Br. No.</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulphur, percent</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

**Hydrogen/Carbon:**

- By analysis: 1.995/1
- By calculation: 2.00/1

**Net Heat of Combustion, B.t.u./lb.**

18,720

This hydrogenated product is an excellent rocket and missile fuel in that it burns evenly and does not place a load on the guidance system of a missile. By providing a fuel such as described herein, it is possible to obtain speeds in excess of about 25,000 miles per hour and thus allow the missiles to escape earth's gravity and to proceed into space. Furthermore, by providing a missile fuel which burns evenly, the guidance systems may then be used to place the missile in orbit as may be desired. The present invention is, therefore, quite important, advantageous, and useful.

Having disclosed the present invention in detail, and having included a preferred best mode and embodiment of the present invention, what is desired to be covered by Letters Patent should not be limited to the specific examples herein given but rather by the appended claims.

I claim:

1. A method which comprises fractionating a virgin naphthenic crude oil to obtain an first fraction boiling within the range of about 250° F. to about 400° F. and containing paraffins, C₈ and C₁₀ alkyl cyclohexanes, and methyl hydridanes, said alkyl cyclohexanes including 1-methyl-2-isopropyl cyclohexane, methyl-1-butyl cyclohexanes, and t-butyl cyclohexanes, contacting said first fraction in a hydroforming zone at a temperature within the range from 800° F. to 1000° F. and a pressure with the range from 100 to 400 psi, with from 1000 to 5000 s.c.f./b. of hydrogen in the presence of a hydroforming catalyst and at a liquid space velocity within the range from 0.75 to 2.25 v/v/hr, to obtain an aromatized stream containing alkyl benzenes, methyl indanes, and paraffins, said alkyl benzenes including 1-methyl-2-isopropyl benzene and being substantially free of t-butyl and methyl-1-butyl benzenes, fractionating said aromatized stream to obtain an aromatized fraction boiling within the range of 335° F. to 381° F., whereby 1-methyl-2-isopropyl benzene and lighter materials and durenes and heavier materials are removed, contacting said aromatized fraction in a hydrogenation zone at a temperature within the range of 300° F. to 600° F. and a pressure within the range from 100 to 1000 psi, with from 3000 to 15,000 s.c.f./b. of hydrogen in the presence of a hydrogenation catalyst and at a liquid space velocity of from 0.25 to 2.0 v/v/hr, to obtain a hydrogenated stream containing alkyl cyclohexanes in which each alkyl carbon alpha to the ring has at least two attached hydrogen atoms, paraffins, and methyl hydridanes, and fractionating said hydrogenated stream to obtain a substantially paraffin-free alkyl cyclohexane product boiling within the range of 319° F. to 358° F.

2. A method according to claim 1 wherein the hydroforming catalyst is chosen from the group consisting of platinum on alumina and molybdena, and the hydrogenation catalyst is chosen from a group consisting of nickel-tungsten sulfide, cobalt molybdate, platinum on alumina, nickel on kieselguhr, and copper-promoted nickel.

3. A method according to claim 1 wherein the aromatization is accomplished over a platinum catalyst at about 900° F. and about 200 psi, with a hydrogen rate of about 3000 s.c.f./b. and a liquid space velocity of about 1.5 v/v/hr, and the hydrogenation is accomplished over a 40% nickel on kieselguhr catalyst at about 400° F. and 800 psi, with a hydrogen rate of about 11,000 s.c.f./b. and a liquid space velocity of about 0.75 v/v/hr.

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