

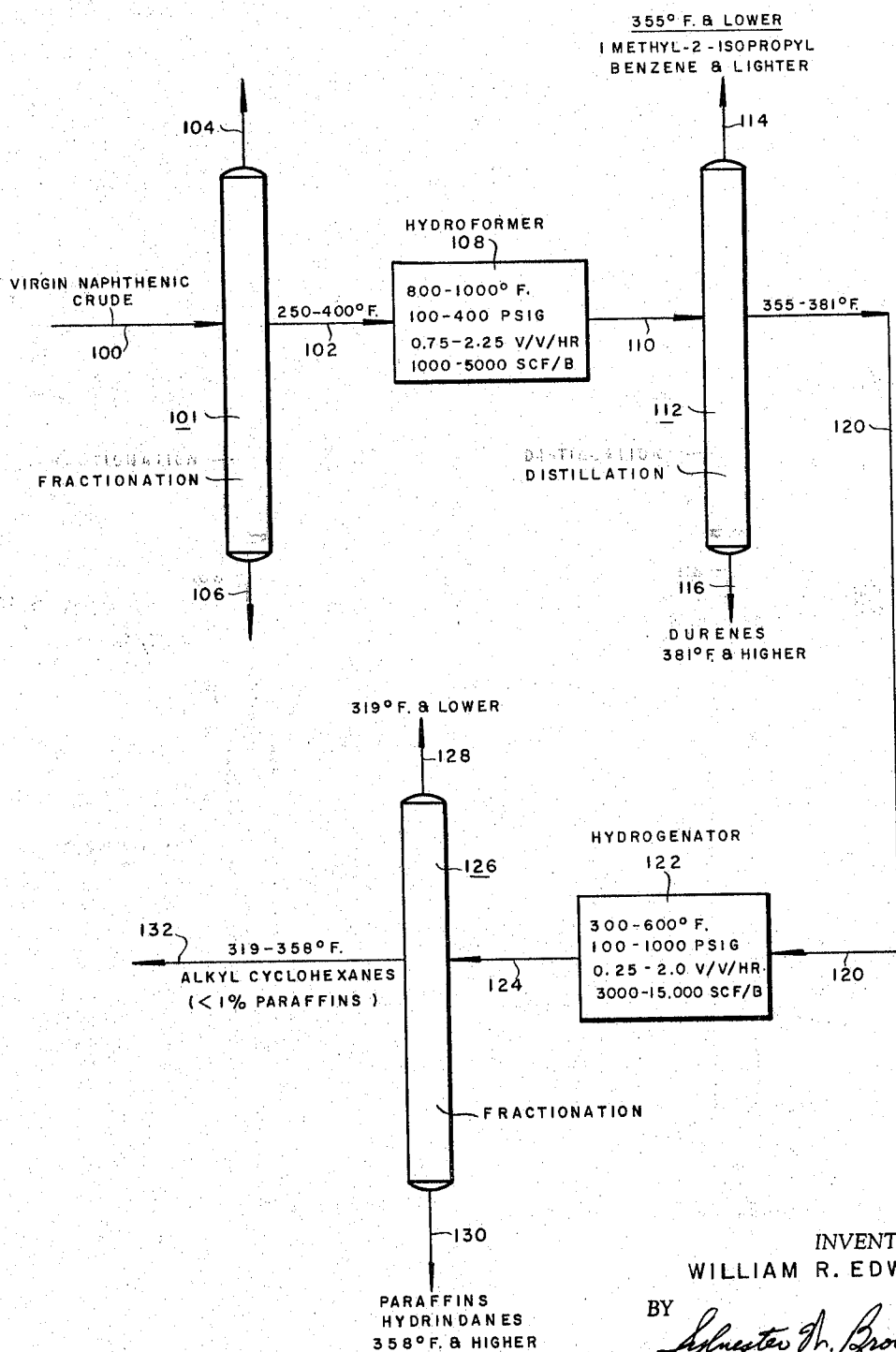
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METHOD FOR MAKING A ROCKET AND MISSILE FUEL

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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 missile 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 admixture of C_{10} alkyl cyclohexanes, the admixture containing 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 cyclohexanes which have tertiary or quaternary carbon atoms alpha to the ring are avoided. For example, tertiary butyl cyclohexane and isopropyl cyclohexane are deleterious materials 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 normally boil in the same range as the alkyl cyclohexanes of the novel fuel are present in the refinery streams which would be a source for the alkyl cyclohexanes. Therefore, these deleterious materials must be separated from the desired alkyl cyclohexanes.

It is important that the fuel be reproducible in that each successive batch which is produced must have exactly 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 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 variation 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 hydrindanes 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 carbons adjacent to the ring is highly undesirable. In addition to being burned to provide thrust

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for the missile, the liquid hydrocarbon fuels are also led around the thrust chamber to abstract heat therefrom and serve as a coolant therefor to prevent failure of the metal wall of the thrust chamber. Compounds having tertiary and quaternary carbons adjacent to the cyclohexane ring are 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-tetramethylcyclohexane 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 boiling within the range of about 250° F. to about 400° F. which contains paraffins, C_{10} alkyl cyclohexanes, and methyl hydrindanes as well as methyl isopropyl cyclohexane, methyl-t-butyl cyclohexanes, and t-butyl cyclohexanes. 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 cyclohexanes into alkyl benzenes, and to aromatize the methyl hydrindanes into methylindanes. Tertiary butyl groups are destroyed during the hydroforming process, presumably 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 temperature 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 5000 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 benzenes 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. This hydrogenation 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 2.0 v./v./hr.

The paraffins remaining in the stream form azeotropes with alkyl cyclohexanes which boil at different temperatures from the azeotropes 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 advertence 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 rough cut stream boiling from 250° F. to 400° F. contains paraffins, naphthenes, hydrindanes, and the naphthenes including 1-methyl-2-isopropyl-cyclohexane, 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 cyclohexane 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 fragments of t-butyl cyclohexanes are discharged as benzene and as C₅ 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 hydrindanes.

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 hydrindanes 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% C₅ and lower, as shown in Table I below:

Table I.—Aromatized product

	Percent
C ₆ and heavier	81
Paraffins	26
Naphthene	1
Aromatics:	
C ₆	Trace
C ₇	3
C ₈	8
C ₉	17
C ₁₀	16
C ₁₁ +	10
C ₅ and lighter	19
C ₅	5
C ₄	5
C ₃	5
C ₂	2
C ₁	2

The breakdown of the C₅ 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

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a hydrogenated fraction boiling within the range of 319° F. to 358° F., which contained no paraffin and was substantially entirely C₁₀ 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 C₁₀ 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:

	Hydrogenated product
Sp. Gr. 60/60	0.8031
Distillation:	
IBP, ° F.	331
FBP, ° F.	356
Boiling Range, ° F.	25
Viscosity at 68° F., cs.	1.382
Freezing Point, ° F.	-100
Aromatics, percent	0.8
Olefins, percent	0.01
Br. No.	0.01
Sulphur, percent	0.0035
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 a first fraction boiling within the range of about 250° F. to about 400° F. and containing paraffins, C₁₀ and C₁₁ alkyl cyclohexanes, and methyl hydrindanes, said alkyl cyclohexanes including 1-methyl-2-isopropyl cyclohexane, methyl-t-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 within the range from 100 to 400 p.s.i.g. with from 1000 to 5000 s.c.f./b. of hydrogen in the presence of a hydroforming

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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-t-butyl benzenes, fractionating said aromatized stream to obtain an aromatized fraction boiling within the range of 355° 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 p.s.i.g. 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 hydrindanes, 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 p.s.i.g. 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 p.s.i.g. with a hydrogen rate of about 11,600 s.c.f./b. and a liquid space velocity of about 0.75 v./v./hr.

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