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PRODUCTION OF ROCKET FUEL

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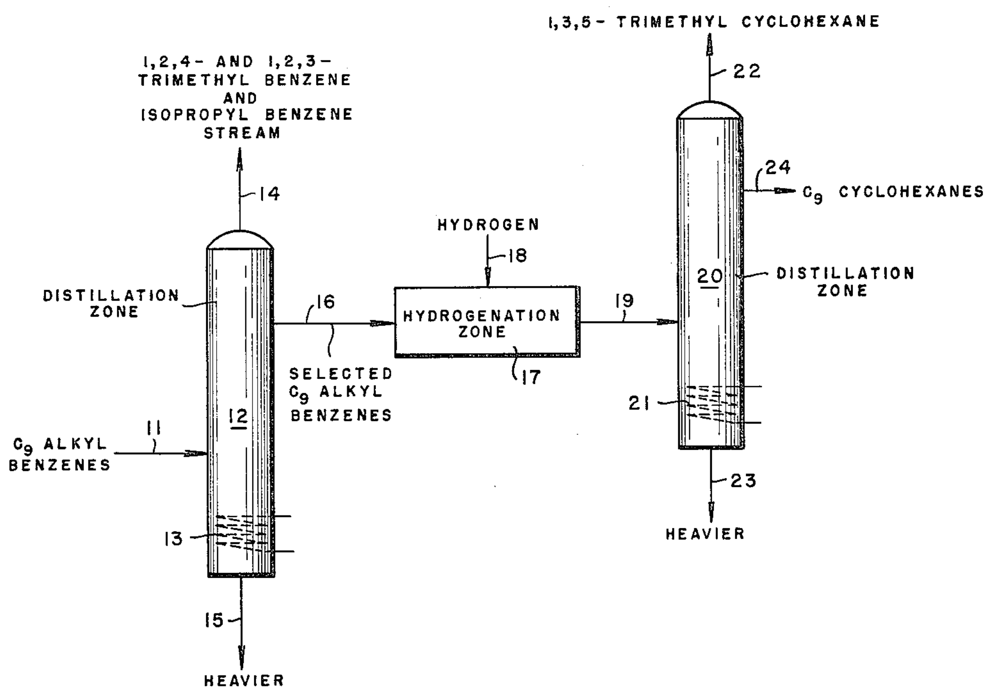

INVENTOR.
WILLIAM R. EDWARDS,

BY

ATTORNEY.

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PRODUCTION OF ROCKET FUEL

William Rogers Edwards, Baytown, Tex., assignor, by mesne assignments, to Esso Research and Engineering Company, Elizabeth, N.J., a corporation of Delaware

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The present invention is directed to a rocket and missile fuel. More specifically, the invention is directed to an improved fuel for rockets and missiles and a method of preparing same. In its more specific aspects, the invention is directed to rocket and missile fuels which fire evenly and which have high thermal stability, high hydrogen to carbon ratio, low viscosity, and high heat of combustion by weight.

The present invention may be briefly described as a rocket and missile fuel consisting essentially of n-propylcyclohexane, 1-methyl-2-ethylcyclohexane, 1-methyl-3-ethylcyclohexane, and 1-methyl-4-ethylcyclohexane. The fuel boils in the range from about 300° to about 320° F., and has an aromatic content less than 1 mol percent and is substantially free of olefins. The rocket and missile fuel of the present invention has a specific gravity of about 0.792 and has a hydrogen to carbon ratio of 2:1. Also, the rocket and missile fuel is thermally stable.

The present invention is also directed to a method of producing a rocket and missile fuel in which a C_9 alkyl benzene fraction is fractionally distilled under conditions to form a first fraction containing 1,2,4- and 1,2,3-trimethylbenzenes and isopropylbenzene and a second fraction containing other C_9 alkyl benzenes including 1,3,5-trimethylbenzene. The first fraction is discarded and the second fraction is hydrogenated under catalytic conditions to saturate the other C_9 alkyl benzenes and to form a hydrogenated product containing C_9 alkyl cyclohexanes. The product is distilled under conditions to form a third fraction containing 1,3,5-trimethylcyclohexane and a fourth fraction containing the other C_9 alkyl cyclohexanes. The third fraction is discarded and the fourth fraction which contains n-propylcyclohexane, 1-methyl-2-ethylcyclohexane, 1-methyl-3-ethylcyclohexane, and 1-methyl-4-ethylcyclohexane is recovered as a rocket and missile fuel.

The particular C_9 alkyl benzene fraction is hydrogenated at a preferred temperature of about 400° F., but temperatures in the range from about 300° to about 600° F. may be used. Pressures may range from about 100 to about 1000 pounds per square inch gauge with a suitable pressure being about 800 pounds per square inch gauge.

Liquid space velocities in hydrogenating the C_9 alkyl benzene may range from about 0.25 to about 2.00 volumes of liquid feed per volume of catalyst per hour. A suitable liquid space velocity is about 0.75 to about 1.0 v./v./hour.

The catalyst employed in the hydrogenation operation may be nickel on kieselguhr support catalyst containing about 40% by weight of nickel. While nickel on kieselguhr may be preferred, other suitable hydrogenation catalysts may be used; examples of which are as follows: nickel-tungsten sulfide, cobalt molybdate, platinum on alumina, copper, promoted nickel, and the like.

The present invention is based on several discoveries which have been made. The first discovery on which the present invention is based is that only certain C_9 alkyl cyclohexanes are suitable for use as a rocket and missile fuel because of the particularly desirable thermal stability and/or specific gravity of the fuel. The second discovery on which the present invention is based is that particular C_9 alkyl cyclohexanes have poor thermal stabilities and specific gravities and therefore are unsuitable as a rocket and missile fuel. The third discovery on which the present invention is based is that C_9 alkyl cyclohexanes of poor thermal stability and/or specific gravity may be removed only in a particular processing sequence.

The feed stock to the present invention may be obtained in several ways. One way of producing the feed stock of the present invention is by hydroforming a naphtha fraction boiling in the range from about 260° to about 300° F. boiling range to obtain a C_9 alkyl benzene fraction. If desired, the C_9 alkyl benzene may also be secured by solvent extracting an aromatic fraction from a converted hydrocarbon. Another way of obtaining the feed stock of the present invention is by solvent extraction of certain virgin distillates from selected crude petroleums such as coastal crudes and the like. A third way of obtaining the feed stock of the practice of the present invention is by catalytic cracking and possibly solvent extraction to concentrate the C_9 alkyl benzene.

The present invention will be further illustrated by reference to the drawing in which the sole FIGURE is a flow sheet of a preferred mode.

Referring now to the drawing, numeral 1 designates a feed line by way of which C_9 alkyl benzene obtained in a manner as has been described herein supra is charged into a distillation zone 12 which is illustrated as a single distillation tower provided with a heating means such as heating coil 13, line 14, and line 15, but which may be a plurality of distillation towers operating in series each of which contains suitable internal vapor-liquid contacting means, such as bell cap trays and the like, and all other auxiliary equipment, such as cooling and condensing means. Distillation zone 12 is operated in such a manner that an overhead fraction is withdrawn by line 14 and a heavier fraction is withdrawn by line 15. The overhead fraction contains essentially 1,2,4- and 1,2,3-trimethylbenzene and isopropylbenzene, whereas the heavier fraction contains any traces of heavier material which was in the C_9 alkyl benzene introduced by line 11. Selected C_9 alkyl benzenes are obtained from the zone 12 by line 16 and introduced thereby into hydrogenation zone 17 containing a catalyst of the nature described and into which hydrogen is introduced by way of line 18. Hydrogenation zone 17 is shown as a rectangle or block in the drawing, but it will be understood to include all facilities required in a modern hydrogenation zone including a catalyst and facilities for separating unused hydrogen.

The hydrogenated production from zone 17 is discharged by way of line 19 into a second distillation zone 20 which may be a single distillation tower as shown, which like zone 12 may comprise a plurality of serially interconnected distillation towers. In any event, zone 20 is provided with a heating means illustrated by steam coil 21, line 22 for withdrawal of an overhead fraction, and line 23 for discharge of heavier fractions. Conditions are adjusted in zone 20 to remove a stream consisting essentially of 1,3,5-trimethylcyclohexane by line 22. There is discharged by way of line 23 any heavier material which may have been formed in zone 17. Line 24 is provided by way of which other C_9 alkyl cyclohexanes are withdrawn from the system and recovered as a rocket and missile fuel. The stream in line 24 consists of normal propylcyclohexane, 1-methyl-2-ethylcyclohexane, 1-methyl-3-ethylcyclohexane and 1-methyl-4-ethylcyclohexane and is suitable for use as a rocket and missile fuel.

In order to illustrate further the present invention, data are set out in Table I which show the composition of one rocket and missile fuel produced in accordance with the present invention.

Table I

Component:		
n-Propylcyclohexane	mol percent	13
1-methyl-3-ethylcyclohexane	do	43
1-methyl-4-ethylcyclohexane	do	22
1-methyl-2-ethylcyclohexane	do	22
Properties:		
IBP	° F.	300
FBP	° F.	320
Hydrogen/carbon ratio		2:1
Aromatic content	mol percent	1.0
Olefin content	do	0.01
Sp. gr., 20/4° C.		0.792
Thermal stability		Very good

Referring to Table I, it will be seen that this fuel consists of four essential components, normal propylcyclohexane, 1-methyl-2-ethylcyclohexane, 1-methyl-3-ethylcyclohexane, and 1-methyl-4-ethylcyclohexane. The major component of the fuel is 1-methyl-3-ethylcyclohexane whereas equal amounts of 1-methyl-2- and 1-methyl-4-ethylcyclohexanes are present with a smaller amount of normal propylcyclohexane.

In the practice of the present invention, it is important and essential that certain of the C_9 alkyl cyclohexane be discarded in the processing sequence. For example, 1,3,5-trimethylcyclohexane must be discarded because this material has a low specific gravity. Likewise the three trimethylcyclohexanes must be discarded; however 1,2,3- and 1,2,4-trimethylcyclohexanes must be discarded before the hydrogenation operation while 1,3,5-trimethylcyclohexane must be discarded after the hydrogenation operation. The reason for this is that if an effort was made to separate the compounds by distillation without hydrogenation, the efforts would be met with failure. Isopropylbenzene may be separated by distillation but isopropylcyclohexane may not be separated practically from normal propylcyclohexane by distillation since they differ in boiling point about 1 to 3° F. depending on the literature source. Removal of the isopropylcyclohexane as isopropylbenzene is for the purpose of improving thermal stability of the fuel since isopropylcyclohexane has a poor thermal stability. Likewise, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene may be separated by distillation before hydrogenation whereas 1,3,5-trimethylbenzene may not. 1,3,5-trimethylcyclohexane may be separated by distillation after hydrogenation.

To illustrate further the separation problem which is solved in the present invention, reference is made to Table II which follows:

Table II

Component	Boiling Point, ° F.	Sp. Gr., 20/4 ° C.
n-propylcyclohexane	311	0.792
i-propylcyclohexane	310	0.802
1-methyl-2-ethylcyclohexane	308	0.804
1-methyl-3-ethylcyclohexane	298	0.788
1-methyl-4-ethylcyclohexane	303	0.790
1,3,5-trimethylcyclohexane	284	0.774
1,2,4-trimethylcyclohexane	286	0.772
1,2,3-trimethylcyclohexane	290	0.792

By reference to Table II, it will be clear that isopropylcyclohexane is not removable practically by distillation from the hydrogenated product. Likewise, it will be clear that 1,3,5-trimethylcyclohexane may be removed practically whereas the 1,2,3- and 1,2,4-trimethylcyclohexanes are more difficult to remove because of their boiling ranges. On the other hand, the 1,2,3- and 1,2,4-trimethylcyclohexane may be easily removed by distillation of the corresponding trimethylbenzene from the feed stock prior to hydrogenation. In other words, in the practice of the present invention, it is necessary to remove the isopropylcyclohexane and the 1,2,3- and 1,2,4- isopropylcyclohexane prior to hydrogenation, while it is necessary to remove the 1,3,5-trimethylcyclohexane after hydrogenation in order to secure the benefits of the present invention.

The present invention is quite important and useful in that it has a high thermal stability, a high hydrogen-carbon ratio, a low viscosity, and a high heat of combustion by weight. For example, the heat of combustion by weight of the fuel of the present invention is about 18,700 B.t.u./lb.

The thermal stability of the fuel of the present invention may be determined in accordance with the description thereof in the paper entitled: "Evaluation of the High Temperature Thermal Stability of Hydrocarbon Rocket Fuels," E. C. Jackson, 39th Annual Mtg. AIChE, March 1959, Atlantic City, New Jersey.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and secure by Letters Patent is:

1. A rocket and missile fuel consisting essentially of n-propylcyclohexane, 1-methyl-2-ethylcyclohexane, 1-methly-3-ethylycyclohexane, and 1-methyl-4-ethylcyclohexane in a mol ratio of about 1:2:4:2, said fuel boiling in the range from about 300° to about 320° F., being thermally stable, having an aromatic content less than 1 mol percent, being substantially free of olefins and having a specific gravity of about 0.792.

2. A rocket and missile fuel consisting of about 13 mol percent of n-propylcyclohexane, about 22 mol percent of 1-methyl-2-ethylcyclohexane, about 43 mol percent of 1-methyl-3-ethylcyclohexane, and about 22 mol percent of 1-methyl-4-ethylcyclohexane, said fuel boiling in the range from about 300° to about 320° F., being thermally stable and having a specific gravity of about 0.792.

3. A method for producing a rocket and missile fuel which comprises fractionally distilling a C_9 alkyl benzene fraction under conditions to form a first fraction containing 1,2,4- and 1,2,3-trimethylbenzenes and isopropylbenzene and a second fraction containing other C_9 alkyl benzenes including 1,3,5-trimethylbenzene, discarding said first fraction, contacting said second fraction with a hydrogenating catalyst at a temperature within the range from about 300° F. to about 600 F., at a pressure within the range of about 100 to about 1000 p.s.i.g., and at a space velocity within the range from about 0.25 to about 2.00 volumes of liquid feed per volume of catalyst per hour, whereby said other C_9 alkyl benzenes form a hydrogenated product containing C_9 alkyl cyclohexanes, distilling said product under conditions to form a third fraction containing 1,3,5-trimethylcyclohexane and a fourth fraction containing other C_9 alkyl cyclohexanes, discarding said third fraction and recovering said fourth fraction as a rocket and missile fuel.

4. A method for producing a rocket and missile fuel which comprises fractionally distilling a C_9 alkyl benzene fraction under conditions to form a first fraction containing 1,2,4- and 1,2,3-trimethylbenzenes and isopropylbenzene and a second fraction containing other C_9 alkyl benzenes including 1,3,5-trimethylbenzene, discarding said first fraction, hydrogenating said second fraction in the presence of a hydrogenating catalyst, at a temperature within the range from about 300° F. to about 600° F., at a pressure within the range from about 100 to about 1000 p.s.i.g. and at a space velocity within the range from about 0.25 to about 2.00 volumes of liquid feed per volume of catalyst per hour, to saturate said other C_9 alkyl benzenes and form a hydrogenated product containing C_9 alkyl cyclohexanes, distilling said product under conditions to form a third fraction containing 1,3,5-trimethylcyclohexane and a fourth fraction containing other C_9 alkyl cyclohexanes, discarding said third fraction, and recovering said fourth fraction as a rocket and missile fuel, said other C_9 alkyl cyclohexanes consisting essentially of n-propylcyclohexane, 1-methyl-2-ethylcyclo-

hexane, 1-methyl-3-ethylcyclohexane, and 1-methyl-4-ethylcyclohexane.

5. A method for producing a rocket and missile fuel which comprises hydrogenating a hydrocarbon mixture consisting of C_9 alkyl benzenes other than 1,2,3- and 1,2,4-trimethylbenzenes and isopropylbenzene over a catalyst chosen from the group consisting of nickel-tungsten sulfide, cobalt molybdate, platinum on alumina, and copper promoted nickel, at a temperature within the range of about 300° F. to about 600° F., at a pressure within the range of about 100 to about 1000 p.s.i.g., and at a space velocity within the range from about 0.25 to about 2.00 volumes of liquid feed per volume of catalyst per hour, to produce a saturated C_9 alkyl benzene mixture, fractionating the mixture to remove 1,3,5-trimethylcyclohexane, and recovering the remainder of the mixture as a substantially aromatic-free rocket and missile fuel.

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