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3,105,351

HIGH ENERGY FUEL CONSISTING OF A MIXTURE OF BRIDGED POLYCYCLICHYDROCARBONS AND METHODS

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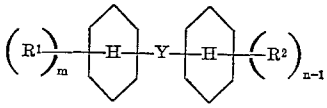
No Drawing. Filed Aug. 17, 1959, Ser. No. 833,996
24 Claims. (Cl. 60—35.4)

This invention relates to mixtures of position isomers of bridged saturated polycyclic hydrocarbons having various uses, but particularly as a high energy fuel for jet, turbojet, rocket, missile and other reaction engines; to processes for forming such hydrocarbon mixtures: to intermediate mixtures useful in said processes; and to operation of jet engines by combustion of said hydrocarbon mixtures therein.

Other secondary uses for my mixture of compounds in the lower viscosity ranges include heat transfer fluids, hydraulic fluids, and transformer oils. In the higher viscosity ranges and particularly including polymeric forms of my compounds, they are also useful as new high stability lubricants. They are also useful as plasticizers, extenders and softeners of elastic and plastic materials.

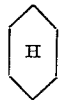
Hydrocarbon mixtures of my compounds having from 14 to 30 carbon atoms are usefully liquid over wide temperature ranges, they have relatively high boiling points and relatively low depressed freezing points. More particularly, hydrocarbon mixtures hereof have a high energy content, that is, a high B.t.u. value per gallon and relatively high density or specific gravity. This combination of characteristics makes the present hydrocarbon mixture of position isomers outstanding for use as jet fuels.

My compositions for jet fuel use comprise a mixture my position isomers of hydrocarbon compounds comprising di-(lower alkylcyclohexyl)alkanes and lower alkylcyclohexyl-cyclohexylalkanes having the following formula:



I

in which R^1 and R^2 are each linear or branched lower alkyl radicals having 1 to 13, preferably 1 to 5 carbon atoms; Y is an alkylene bridge radical having 1 to 13 carbon atoms of either linear or branched chain configuration; m is an integer from 1 to 3 and n is an integer from 1 to 4,



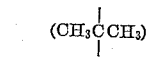
represents a saturated benzene (cyclohexyl) nucleus, and the total carbon atom content of my compounds, when they are liquid, ranges from 14 to about 30 carbon atoms. At higher carbon atom contents, the compounds can be viscous liquid to solid mixtures.

The specific gravity of such liquid mixtures will generally exceed about 0.8, and by the term "high gravity" as used herein, I mean a liquid having this minimum or higher gravity. The B.t.u. value will usually exceed about 125,000 B.t.u. per gallon and by the term "high energy" as used herein, I mean a combustible mixture having this minimum or higher B.t.u. value. For instance, the gravity of the jet fuels hereof usually lie in the range of about 0.85 up to about 0.91, and the B.t.u. value preferably ranges from about 132,000 up to about 140,000 B.t.u. per gallon.

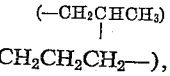
In the hydrocarbon formulae hereof, the lower alkyl radicals R^1 and R^2 include C_1 to C_{14} alkyl radicals such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-amyl, the iso-amyls, tert-amyl, n-hexyl, the iso-hexyls, tert-hexyl, diisopropyl, n-heptyl, isoheptyl, diisobutyl, 2-ethylhexyl, triisopropyl, n-nonyl, n-dodecyl, tetraisopropyl, triisobutyl, tridecyl and other isomeric forms of these and R^1 and R^2 may be selected to be either the same or different alkyl radicals.

In the hydrocarbons Formulae I through IX herein, the term alkylene or bridge radical Y includes all divalent acyclic C_1 to C_{13} hydrocarbon radicals which bridge the two ring hydrocarbon radicals through the same carbon atom or through different carbon atoms of the bridge Y and thus the term alkylidene bridge Y defines a specific type of alkylene bridge Y.

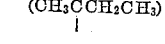
In the hydrocarbon formulae hereof, the alkylene radical Y may be illustrated by the following formulations: methylene ($—CH_2—$), ethylidene ($=CHCH_3$), ethylene ($—CH_2CH_2—$), n-propylidene-1,1 ($=CHCH_2CH_3$), propylidene-2,2



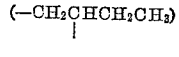
propylene-1,2



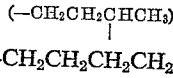
propylene-1,3 ($—CH_2CH_2CH_2—$), n-butylidene-1,1 ($=CHCH_2CH_2CH_3$), isobutylidene-1,1 ($=CHCH(CH_3)_2$), n-butylidene-2,2



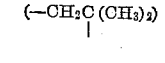
n-butylene-1,2



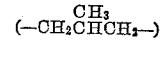
n-butylene-1,3



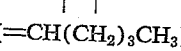
n-butylene-1,4 ($—CH_2CH_2CH_2CH_2—$), isobutylene-1,2



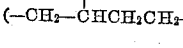
isobutylene-1,3



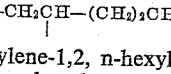
n-butylene-2,3



n-pentylidene-1,1 ($=CH(CH_2)_3CH_3$), isopentylene-1,4



n-pentylene-1,2



n-hexylidene, n-hexylene-1,2, n-hexylene-1,3, n-hexylene-1,4, n-hexylene-1,5, n-hexylene-1,6, isohexylidenes, isohexylene-1,2, n-heptylidene, iso-octylene-1,7, n-nonylidene, n-undecylidene, n-dodecylidene, and n-tridecylidene, including the various isomeric configurations of these compounds and homologues thereof having not more than 13 carbon atoms.

As formed by the methods as further described below such compounds will constitute mixtures of numerous position isomers. For instance, in its simplest form, where R=methyl, Y=methylene, $m=1$ and $n=1$, there will be at least 3 isomers of the several position types, but where $m=1$ and $n=2$, there will be 6 position isomers, and where $m=2$ and $n=3$, there will be at least 36 position isomers. Of course where position isomerism can result by variation of attachment of the ring nuclei

to the alkylene bridge —Y— then the number is considerably greater. The number further increases with the variations in number and isomeric form among the alkyls. Moreover, as described below some of the cyclic radicals themselves are often derived from hydrocarbon fractions comprising multicomponent mixtures of alkyl substituted aromatic hydrocarbons from which the final products hereof may be made, and, as thus formed, may comprise mixtures of even greater complexity.

Thus my compositions comprise mixtures of a great number of position isomers as well as homologues, as formed by the methods described below. This is desirable because as a mixture it allows the production for example, of a jet fuel usually in liquid form when the carbon atom content is in the range of 14 to 30, a product of relatively high boiling point, relatively constant high gravity, and at moderate temperatures, fluid viscosity. My mixture of numerous position isomers has also a relatively low depressed freezing point, often as much as 50° C. below that of a corresponding pure isomer.

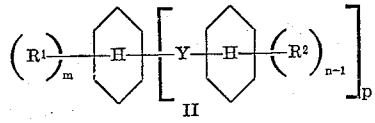
A further advantage of my mixture of position isomer compounds is that they may be produced to desirably close specifications, most desirable for a jet fuel, not withstanding that they are a mixture of so many distinct compounds, by methods which in themselves are highly economic.

As pointed out, the total number of carbon atoms is in the range of 14 to about 30 where my compounds are used as normally liquid fuels at ambient temperatures. Within these limits, the alkyl and alkylene substitutions of the benzene radicals will be selected in number and size whereby liquid compounds are produced. For example, the alkylene bridging group can be reduced in carbon chain size, preferably in the range from 1 to 5 carbon atoms, while simultaneously the alkyl groups attached to the ring can be increased in number and size, and vice versa, for purposes of maintaining the size of the compounds within the 14 to about 30 carbon atom limits to define a liquid fuel.

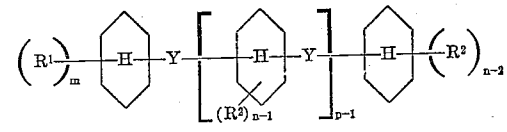
Outside of these limits my mixture of isomeric compounds can be viscous oil or a solid mixture of position isomers. These too can be used as fuel, but for liquid fuel use may have to be heated to reduce their viscosity or even melted. These, including the normally liquid types, have other uses as stated above.

An advantage of the variation of my liquid fuel in the range 14 to about 30 carbon atoms, and the variation to produce a large number of position isomers in each product is that my mixture is usually or can be made relatively uniform with respect to the number of carbon atoms of each product in any of its uses. For instance as set forth in many of the examples below each product may be composed of a mixture of compounds of the same number of carbon atoms. When the ring substituents are derived from a commercial mixture of C_7 to C_9 aromatics, the total carbon atom of compounds count in the several compounds of the resulting mixture would generally vary only in this corresponding narrow range. Of course, side reactions such as further condensation, produce compounds having a higher number of carbon atoms such as the tricyclic or polycyclic alkanes, for example, the di-(alkylcyclohexyl-methyl)-alkylcyclohexane, di-(alkylcyclohexyl-ethyl)-alkylcyclohexane, and the like. The polymeric multi-bridge and multi-ring compounds being higher boiling are readily separated by distillation. Where a wide boiling range fuel is not objectionable and where the final products are highly viscous liquids or even solids, such heavy ends need not be removed from the fuel.

These heavy ends may be illustrated by the formulae:



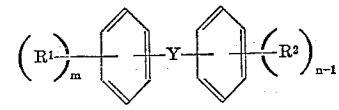
II



III

where p is an integer having the value 2 or 3 and R^1, R^2, Y, m and n have the same definition as in Formula I.

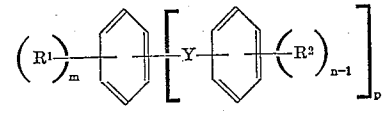
My compounds represented by Formula I are preferably produced by hydrogenation of an intermediate di-(alkylphenyl)-alkane or (phenyl) (alkylphenyl)-alkane compound having the formula:



IV

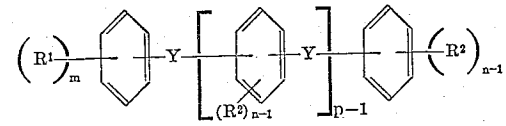
wherein R^1, R^2, m and n have the same significance as given in Formula I, and Y may be any 1 to 13 carbon atoms acyclic bridging compound preferably having 1–5 carbon atoms.

My compounds represented by Formula II and Formula III are produced by hydrogenation of an intermediate compound having the formulae:



V

and

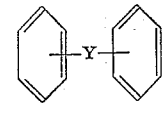


VI

wherein R^1, R^2, Y, p, m and n have the same significance as given in formula III.

The intermediate mixture of isomeric compounds of Formulae IV, V and VI is preferably formed by reacting a bridging compound with an alkyl benzene compound for a mixture of different alkyl benzene compounds in which benzene can be substituted for one of the alkyl benzene compounds.

Alternatively, but less economically, it is possible to first form a di-(phenyl)-alkylene bridge compound of the formula:



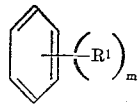
VII

in which Y has the same significance as in Formulae I and IV formed by the same bridging reactions as for Formula IV compounds, the Formula VII compound then being alkylated by usual alkylation methods to add 1 or more alkyl groups of the formula R^1 or R^2 or a mixture of both to the rings; thereby, forming a mixture of intermediate isomers of the formula IV.

In a further alternate procedure, a mixture of compounds of Formula VII may be formed by bridging two phenyl groups with the alkylene bridging group and alkylating one or both rings with one or more lower alkyl groups in the presence of a suitable catalyst to promote both reactions in the same reaction mixture.

The preferred bridging methods involve alkylation of two phenyl groups with a single alkane such as acetylene; or a hydrocarbon diene; or an oxygen or dihalogen bear-

ing aliphatic compound, at least one of said phenyl groups being an alkylphenyl group of the formula



as defined above, employing an alkylating catalyst which may be an acid catalyst, usually a string mineral acid like sulfuric, phosphoric and/or hydrofluoric acid; or a compound, e.g., like a boron halide or boron fluoride or their complexes, such as boron fluoride-phenylate, boron fluoride-etherate, boron fluoride dissolved in sulfuric acid, and other acid alkylation and condensing agents with or without the Friedel-Crafts type catalysts. Where the bridging group carries two halogen atoms, a Friedel-Crafts type catalyst such as aluminum chloride may be used alone.

When using sulfuric acid as a catalyst, the usual alkylating strength is above about 80%, but generally below about 98%, above which sulfonation of the aromatic rings, or excessive condensation to polycyclic compounds may occur.

Particularly, such catalysts will be used to incorporate a bridging group derived from an aliphatic material comprising an aldehyde, a glycol, an alkylene oxide, an acetylene or alkyne, a diene, especially a conjugated diene, and a dihalo-alkane or the like. Acetylene itself and higher alkyne compounds may be used as the bridging compound. For purposes of joining the alkyl benzene rings in the case of acetylene or other alkynes, the usual catalyst is mercuric sulfate, activated with strong acid such as 85–98% sulfuric acid or a boron fluoride-phosphoric acid complex. Alkylation reactions, as known in the art, generally are employed at ambient temperatures and sometimes lower temperatures, such as 0° to ±30° C. Certain catalysts such as hydrogen fluoride, known in the art, can operate at temperatures considerably below ambient temperatures such as —20° C. or lower.

Typically useful alkylphenyl producing groups are toluene, the ortho, meta or para xylenes and their mixtures, the trimethylbenzenes including mesitylene, ethylbenzene, the di- and tri-ethyl benzenes, the methylethyl benzenes, the dimethylethyl benzenes, the diethylmethyl benzenes, the mono-, di, and tri-propyl benzenes, the n-butyl, sec-butyl, tert-butyl benzenes, the isopropyl benzenes including cumene and pseudocumene, diisopropyl benzene, mono and di-amyl benzene, di-decyl benzene, with mixed alkyl groups including those with both normal and branched C_1 through C_{13}, preferably C_1 to C_5 alkyl substituents, and the various combinations of alkyls within the limits of Formula IV.

When the bridging component is aldehyde, it can be formaldehyde, acetaldehyde, propionaldehyde, iso-butyraldehyde, decylaldehyde, do-decyl aldheyde and the like; when it is alkyne, it can be acetylene, methyl-acetylene, ethyl acetylene, and the like; when it is a hydrocarbon diene, it can be butadiene-1,3, allene, isoprene, piperylene, dimethyl butadiene and the higher dienes; when it is a glycol it can be ethylene glycol, propylene glycol-1,3, butylene glycol-1,4, hexylene glycol-1,6, hexylene glycol-1,2, decylene glycol-1,10 and the like; when it is dihaloalkane, it is preferably a dichloro, dibromo or chlorobromo compound within the limits of the Formula I or IV as given above; when it is alkylene oxide, it can be ethylene oxide, propylene oxide, epichlorohydrin; or ketenes such as ketene and the like.

In commercial practice an aromatic extract of a reformation or aromatization reaction (termed petroleum reformate) may be used in its entirety, usually comprising the C_6 to C_9 aromatics which may also contain up to 50% benzene, or select C_7, C_8 or C_9 fractions of such extract may be used singly. The C_8 fraction comprising the three isomeric xylenes and ethyl benzene sometimes

contaminated with toluene and/or with some other C_9 aromatics may most economically be used in its entirety. This valuable C_8 aromatic fraction may often first be distilled to separate the ortho xylene isomer leaving the mixed meta and para xylene isomers. The latter fraction can have its para xylene extracted for even more valuable uses, and the ortho and meta xylenes fractions recombined for use herein. Any of these select xylene fractions or the entire C_8 fraction, are useful in the practice of this invention. Thus any petroleum refinery reformate having an economically recoverable quantity of aromatics may comprise a useful source material from which an aromatic extract may be obtained and used as a source of the alkyl benzenes, either as a whole extract, or as select fractions thereof. A typical preferred C_8 fraction may comprise about 2% toluene, 10% p-xylene, 48% m-xylene, 19% o-xylene and about 21% ethylbenzene.

In carrying out the bridging reaction, where predominantly the bicyclic compound is desired, the alkyl benzene is usually used in substantial excess, e.g., a 2 to 3 times molar excess in respect to the molar quantity of bridging group material employed, and where higher polycyclic compounds are desirable such as the tricyclic and higher polycyclic side reaction compounds (such as shown in Formulae II, III, V and VI), a lower ratio down to about ½ to 3 moles of alkyl benzene per mole of bridging compound is used. The catalyst may be usually added thereto at room temperature, and if the bridging compound is difficult to react, the temperature may be raised; if the bridging compound is highly reactive, the temperature may be lowered, applying cooling or refrigeration as needed, and the bridging group material is usually added slowly, such as dropwise over a several hour period, usually about 4 to 12 hours, with continued agitation in order to avoid excessive side reactions thereof, the conditions being modified depending on the activity of the reagents.

When the bridging reaction does not terminate by joining of only two ring groups, it is preferred to allow the reaction to convert only a portion, such as about ⅓ of the available alkyl benzene to the Formula IV compound, before terminating the reaction. The reaction product Formula IV compounds are then recovered from the reaction mixture and the excess unreacted compounds such as alkyl benzene are recycled to the reactor.

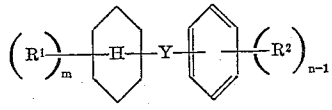
Olefinic compounds generally are to be avoided with bridging reagents except where both alkylation and alkylene bridging of two rings in the same reaction in the presence of a selected catalyst for both reactions is desired.

In the instance of reacting dihaloalkanes as the bridging group catalyzed with aluminum chloride, or an equivalent Friedel-Crafts catalyst, the alkyl benzene compound and the dihaloalkane are first mixed, and usually is cooled to about 0° C. or less, and then the aluminum chloride can be added in any suitable manner, even rapidly. Such reactions are run with typical bridging compounds as ethylidene dichloride, butylidene dichloride-1,4, hexylidene dichloride-1,6, isobutylidene dichloride-1,2, butylene bromochloride-1,4, propylene dibromide-1,3, ethylene dichloride-1,2, propylene dichloride-2,2, isobutylene dibrombide-1,3 and the like.

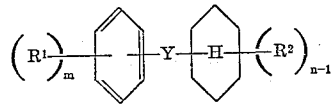
After the position isomeric compounds of Formula IV are prepared, such are freed of catalyst residues by decantation, filtration and/or water washing with or without the aid of acid for Friedel-Crafts catalysts removal, followed by an alkaline aqueous wash; or in the case of the acid catalyst by only water and/or alkaline aqueous wash. If the unreacted materials are not hydrogenated under the conditions employed for such hydrogenation, then such unreacted materials need not be removed; and the whole product may be hydrogenated; however, in most instances the unreacted materials are removed usu-

ally by distillation and the position isomeric compounds of Formula IV may be hydrogenated. Before hydrogenation, the Formula IV product may be further distilled for greater purity to remove any side reaction product, such as the tricyclic and polycyclic compounds. The hydrogenation is usually carried out in a diluent, e.g., a paraffin solvent in the presence of a hydrogenation catalyst such as nickel or cobalt or other catalyst capable of hydrogenating aromatic compounds, etc. In the example an active Raney nickel or Raney cobalt catalyst was preferred.

In order that hydrogenation of the aromatic rings of Formula IV compounds proceed at a reasonable rate, hydrogen is employed at non critical elevated pressures, usually about 500 p.s.i. to 5,000 p.s.i. To hydrogenate these aryl compounds, the temperature is raised non critically above a minimum temperature, usually 100–200° C., or sometimes higher, until hydrogenation commences. Each aryl ring usually has a minimum threshold hydrogenation temperature which must be exceeded and this depends on the activity of the catalyst employed and on the position of the alkyl substituents in the individual aryl rings. Thus by selective hydrogenation (control of catalyst activity, temperature and hydrogen pressure and which is sometimes influenced by the solvent selected) one can hydrogenate only a single aromatic ring of these biaromatic ring compounds thus producing intermediate compounds of formulae:



VIII



IX

wherein R^1 and R^2, Y, *m* and *n* have the same significance as in Formula I.

Accordingly, these partial hydrogenation position isomeric products of Formulae VIII and IX are intermediates having more hydrogen than compounds of Formula IV and less hydrogen than compounds of Formula I and in a like manner compounds of Formulae V and VI can be partially hydrogenated.

Each of the partial hydrogenation products of these formulae are intermediates per se, such as for further hydrogenation to form the jet fuels of Formula I, e.g., hydrogenation of phenyl methyl-cyclohexyl methane position isomeric mixture to the cyclohexyl methylcyclohexyl methane position isomeric mixture.

The hydrogenated bicyclic compounds of Formula IV can contain a minor quantity, less than about 50%, of diphenyl bridged compound in the reaction mixture, for example, when a benzene and alkyl benzene mixture is bridged, which does not need to be separated from the alkylphenyl bridged compound of Formula IV but may economically be fully hydrogenated therewith to a final hydrocarbon mixture, also useful for a jet fuel mixture.

As noted my products are a very complex mixture of position isomers even in the simplest form, such as when produced with a methylene bridge, for example, by condensation of alkyl-benzenes with methylene chloride or formaldehyde followed by hydrogenation. There are six position isomeric di-(methylcyclohexyl)-methanes which are present in a synthetic fuel prepared by hydrogenation of di-(tolyl)-methane (prepared for example from toluene and formaldehyde, e.g., with sulfuric acid catalyst). They are di-(2-methylcyclohexyl)-methane, di-(3-methylcyclohexyl)-methane, di-(4-methylcyclohexyl)-methane, (2-methylcyclohexyl) (3-methylcyclohexyl)-methane, (2-methylcyclohexyl) (4-methylcyclohexyl)-methane, and (3-methylcyclohexyl) (4-methylcyclohexyl)-methane.

Four other isomers formed by other methods of synthesis are: di-(1-methylcyclohexyl)-methane, (1-methylcyclohexyl) (2-methylcyclohexyl)-methane, (1-methylcyclohexyl) (3-methylcyclohexyl)-methane and (1-methylcyclohexyl) (4-methylcyclohexyl)-methane.

Even though there are some perfectly symmetrical "bis" compounds possibly present, any one of these can be present only as a minor portion of even the simplest complex position isomer mixture.

For example, the di-(methylcyclohexyl)-methanes have six isomers, but the di-(dimethylcycohexyl) methanes have 144 possible position isomers, and 36 of these position isomers can be obtained by condensation of formaldehyde or methylene chloride with mixed xylenes, followed by hydrogenation.

A typical specific exemplification of the preparation of a mixture of isomers of the present inventions is as follows: a mixture of ortho-, meta- and para-ethyltoluenes obtained from petroleum or coal tar refining is reacted with formaldehyde (e.g., using sulfuric acid catalyst at 30° C.) to produce di-(methylethylcycohexyl)-methane containing all possible position isomers (100) in varying amounts dependent on relative activities of the formaldehyde with the four different hydrogens of each of the ethyltoluene isomers present in the starting materials of the synthesis.

It has been further found that the heat of combustion of isomeric mixtures of such di-(dialkylcyclohexyl)-methanes is partially dependent on variations in ratios of the amounts of respective isomers present in a given product. Thus, the hydrogenated products derived from (*a*) reaction of a commercial xylene with formalin (37% formaldehyde) at 30° C. followed by hydrogenation and from (*b*) reaction of the same commercial xylene with formalin (37% formaldehyde) at 60° C. contained different amounts of the various isomers and showed respectively 19,500 gross B.t.u./lb. and 19,815 gross B.t.u./lb. for the heat of combustion. Similarly, the reaction of methylene chloride with xylene using anhydrous aluminum chloride as catalyst, followed by hydrogenation gave a fuel of 19,605 B.t.u./lb. Thus the broad fractions of a given position isomer mixture of di-(mono- or di-alkylcyclohexyl)-methane from two or more sources will differ in properties including the energy of combustion. The constancy of energy output of fuels from a given synthesis is an important advantage of the fuels of the present invention, particularly for rocket fuels since target calculations are based in part on the basis of known energy available from the fuel charge. The operating variables of the methods of synthesis of the fuels of the present invention are readily controlled to give a reproducible product, hence reproducible heat of combustion.

By the reaction of formaldehyde with a mixture of the three xylenes and three methylethylbenzenes, followed by hydrogenation of the condensation product, there was obtained a fuel containing a large number of isomeric (methylethylcyclohexyl) - (dimethylcyohexyl)-methanes and di-(methylethylcyclohexyl)-methanes, in addition to the many di-(dimethylcyclohexyl)-methane position isomers; the various xylyl and ethylphenyl combinations as substituents for methane (in the formaldehyde condensation product) thus increased the number of isomers obtained in the final hydrogenated products of this invention in comparison to the hydrogenated xylene-formaldehyde reaction product also of this invention.

Thus di-(alkylphenyl)-methane can be made by reacting the alkyl benzene hydrocarbons or their mixtures with (*a*) formaldehyde (employing a Friedel-Crafts catalyst for example at 5–25° C.) and converted to fuels of the present invention by hydrogenation. Other catalysts and temperatures may be used to obtain a final hydrogenated

fuel of a different isomeric composition; i.e., different amounts of the various isomeric di-(alkylcyclohexyl)-methanes in comparison to these preparations.

The precursors (Formulae IV, V and VI compounds) were then hydrogenated over Raney nickel catalyst (e.g., Girdler's G–49 catalyst) using about 8 pts. by weight of methylcyclohexane as solvent for 1 to 4 pts. by weight of precursor. The hydrogenation was conducted at 100 to 200° C. under 65 to 100 atmospheres of hydrogen pressure in a batch reactor with agitation for 2 to 8 hours. The methylcyclohexane solvent was removed by distillation, the remainder being water white to light yellow fuels of this invention.

In the examples, the terms used are defined:

(*a*) By the term "gross heating value" of a fuel is meant the total heat developed on burning a fuel after the products are cooled back to the initial temperature (usual practice 60° F.), assuming that all the water produced by combustion is condensed.

(*b*) By the term "net heating value" of a fuel is meant the total heat developed on burning a fuel after the products are cooled back to the initial temperature (usual practice 60° F.), assuming the water of combustion is uncondensed.

INDEX OF EXAMPLES

Materials Employed in Forming Hydrocarbon Precursor Compounds

	Alkylbenzene	Bridge	Bridging compound (or alkylation)[2]
Example I	Toluene	Methyl	Paraformaldehyde.
Table I	C_8 thru C_{12} [1]	do	Do.
Example:			
II	Toluene	do	Do.
III	C_8 aromatic	do	Do.
IV	Toluene	do	Formaldehyde (37%).
V	Toluene	do	1,1-dichloromethane.
VI	Crude xylenes	do	Do.
VII	p-Xylene	do	Paraformaldehyde.
VII–A	Crude xylenes	do	Do.
VIII	Ethylbenzene	do	Do.
VIII–A	Diphenylmethane	do	Alkylated with ethylene.[2]
IX	Cumene	do	Paraformaldehyde.
IX–A	Diphenylmethane	do	Alkylated with ethylene.[2]
X	Sec-butylbenzene	do	Paraformaldehyde.
XI	Toluene	Ethyl	Acetaldehyde.
Table II	C_8 thur C_{11} [1]	do	Do.
Example:			
XII	Toluene	do	Acetylene.
XIII	do	do	Do.
XIV	do	do	Acetylene, ethylene.
XIV–A	do	do	Do.[2]
XV	do	do	Acetylene.
XVI	Xylenes	do	Do.
XVII	Toluene	do	Ethylene glycol.
XVIII	Cumene	do	1,2 dichloroethane.
XIX	Toluene	Propyl	Propionaldehyde.
Table III	C_8 thru C_{11}	do	Do.
Example:			
XX	Xylenes	do	Do.
XXI	do	do	1,2-dichloropropane.
XXII	Toluene	do	2,2-dichloropropane.
Table III [2]	C_8 thru C_{11} [1]	do	Do.
Example:			
XXIII	C_8 aromatic	do	1,2-propyleneoxide.
XXIV	Toluene	Butyl	Butyraldehyde.
XXV	Xylenes	do	Do.
XXVI	Toluene	do	Butadiene.
XXVII	do	Pentyl	Piperylene.
XXVIII	do	Undecyl	Undecylenic aldehyde.
XXIX	do	Decyl	Decamethylene-dibromide-1,10.

[1] Aromatic.
[2] By reference.

EXAMPLE I

(*a*) *Isomeric Mixture of Di-(Tolyl)-Methanes*

In this example, 1660 grams (18.04 moles) of toluene, 96 grams (3 moles) methanol, 200 grams of a mixture of 96.7% sulfuric acid (1.973 moles) containing 2.8 grams (0.01 mole) ferrous sulfate heptahydrate were placed in a glass flask equipped with a stirrer, a reflux condenser, a thermometer, an opening for addition of reagents, and cooled in a water bath held at a temperature 18 to 21° C. To this mixture while stirring were added 90 grams paraformaldehyde (equivalent to 3 moles of anhydrous formaldehyde) over a period of 25 minutes. Stirring was continued for 60 minutes at about 25° C. The water bath temperature was then raised to 95° C. over a period of 2.5 hours, with continuous stirring, and the mixture was then refluxed for an additional hour. About 24 grams of formaldehyde vapors were lost through the condenser and the remainder of the formaldehyde (2.2 moles) from depolymerization of the paraformaldehyde under conditions of the reaction, condensed with the toluene. The mixture was cooled, the hydrocarbon layer was separated from the acid, and washed with 2 liters of water followed by 2 liters of 1% sodium carbonate solution. The hydrocarbon was then heated to distill excess toluene at 760 mm. of mercury pressure. The mixture of di-(tolyl)-methane position isomers distilled over at 137 to 152° C. at 11 mm. mercury pressure; 354 grams of this isomeric mixture were obtained: $N_D^{20}=1.5700$; $D_4^{20}=0.996$, M.P.=65° C.; viscosity=0.65 poises at −25° C.

(*b*) *Isomeric Mixture of Di-(Methylcyclohexyl)-Methanes*

To 294.4 grams of the di-(tolyl)-methane position isomers obtained in (*a*) was added 800 g. of methylcyclohexane, together with 58.9 g. of Raney type nickel catalyst (Girdler G–49 catalyst, Girdler Corp.) and the mixture was placed in a gallon autoclave unit equipped with a magnetic stirrer and pressured with 1000 p.s.i. of hydrogen at 22° C., and the autoclave was heated to 120° C., the temperature being maintained over a period of 4 hours while stirring. During this period three additional pressurings of hydrogen were added to raise the hydrogen pressure each respective time from 400, 500 and 625 p.s.i. to 1000 p.s.i., indicating partial hydrogenation in stages. After the third addition, the temperature was held at 120 to 125° C. for 80 minutes. The pressure dropped to 975 p.s.i. and remained constant for the last 30 minutes. The autoclave was cooled, the contents removed, filtered and the methylcyclohexane was separated therefrom by distillation. A quantitative yield of over 300 grams of a position isomeric mixture of di-(methylcyclohexyl)-methanes was obtained. H=13.15%, C=87.08%, $N_D^{20}=1.4750$; $D_4^{20}=0.876$; B.P.=111–120° C. @ 7 mm. Hg; melting point=below −70° C.; viscosity=1.4 poises at −25° C.; heat of combustion=19,787 B.t.u./lb. (gross), 18,555 B.t.u./lb. (net), 136,070 B.t.u./gallon (net).

Substituting for the 1660 grams of toluene used in this example, 1910 grams of o-xylene yields a mixture of the di-(o-xylyl)-methane which are hydrogenated to the di-(-1,2-dimethylcyclohexyl)-methanes; or 1910 grams of m-xylene yields the di-(m-xylyl)-methanes which are hydrogenated to the di-(1,3-dimethylcyclohexyl)-methanes; or 1910 grams of p-xylene yields the di-(p-xylyl)-methanes which are hydrogenated to the di-(1,4-dimethylcyclohexyl)-methanes; or 1910 grams of mixtures of 2 or more of o-xylene, m-xylene and p-xylene are likewise converted to the mixture of di-(mixed xylyl)-methanes and hydrogenated to the di-(mixed dimethylcyclohexyl)-methanes; or 1910 grams of ethylbenzene is converted to the di-(ethylphenyl)-methanes and hydrogenated to the di-(ethylcyclohexyl)-methanes; 1910 grams of a C_8 aromatic fraction are also converted to the di-(mixed C_8, alkylphenyl)-methanes and hydrogenated to the di-(mixed C_8, di (di-alkylcyclohexyl)-methanes.

In this example, the quantity of alkylbenzene can be varied from 0.5 mole of alkylbenzene per mole of formaldehyde, up to the 18 moles of alkyl benzene or even higher per mole of formaldehyde. The excess of the alkylbenzene usually at least twice the molar requirement tends to keep the system sufficiently dilute to minimize formation of tricyclic compounds and higher polycyclic; conversely use of lower proportions down to 0.5 mole, produces substantial quantities of the higher cyclic com-

pounds. The process can be carried out continuously by separating hydrocarbon and acid layers and recycling the acid to the system. In this formaldehyde reaction water is split off, therefore the acid concentration may be restored by adding fuming sulfuric or sulfur trioxide intermittently or continuously. To bind the water released in the reaction, one may add phosphorous pentoxide or like compound. In this example for convenience paraformaldehyde was used; however, gaseous formaldehyde or formaldehyde solutions can also be employed.

While ferrous sulfate has been employed as a co-catalyst in this example, other Friedel-Crafts transition metal salts, e.g., other sulfates may be employed with the sulfuric acid hereof. The reaction may be catalyzed with the Lewis acid catalysts alone, e.g., with hydrofluoric acid, and in such case usually lower temperatures are employed. Especially useful are the catalysts set forth under Example II below. Depending on the degree of dilution and acid concentration, the temperature is correspondingly lowered or raised. The conditions of reaction chosen should be such as to minimize resin formation, as such by-products result in lower yields of the desired products.

Following the procedure of Example I but for the 18.04 moles of toluene substituting 18.04 moles (a substantial excess) of other alkyl benzenes, corresponding di-(alkylphenyl)-methane position isomer mixtures are produced which, when hydrogenated, give the corresponding di-(alkylcyclohexyl)-methane position isomers as set forth in the following Table I.

In the tables herein the designating numerals referring to the alkyl substitution positions on the phenyl or cyclohexyl rings have been maintained the same for the reactants and for the products and have not been altered in the conventional manner to assign number I to the position of attachment of the Y bridging group to said rings.

TABLE I.—MIXTURE OF POSITION ISOMERS

No.	Alkylbenzene	Di-(alkylphenyl)-methanes	Di-(alkylcyclohexyl)-methanes
1	o-ethyltoluene	di-(o-ethyltolyl)-methanes	di-(o-ethyl-methylcyclohexyl)-methanes.
2	m-ethyltoluene	di-(m-ethyltolyl)-methanes	di-(m-ethyl-methylcyclohexyl)-methanes.
3	p-ethyltoluene	di-(p-ethyltolyl)-methanes	di-(p-ethyl-methylcyclohexyl)-methanes.
4	1,2,3-trimethylbenzene	di-(1,2,3-trimethylphenyl)-methanes	di-(1,2,3-trimethylcyclohexyl)-methanes.
5	1,2,4-trimethylbenzene	di-(1,2,4-trimethylphenyl)-methanes	di-(1,2,4-trimethylcyclohexyl)-methanes.
6	1,3,5-trimethylbenzene	di-(1,3,5-trimethylphenyl)-methanes	di-(1,3,5-trimethylcyclohexyl)-methanes.
7	n-propylbenzene	di-(n-propylphenyl)-methanes	di-(n-propylcyclohexyl)-methanes.
8	isopropylbenzene	di-(isopropylphenyl)-methanes	di-(isopropylcyclohexyl)-methanes.
9	C_9 aromatic fraction	di-(C_3[a] alkylphenyl)-methanes	di-(C_3[a] alkylcyclohexyl)-methanes.
10	o-n-propyltoluene	di-(o-propyltolyl)-methanes	di-(o-propylmethylcyclohexyl)-methanes.
11	m-n-propyltoluene	di-(m-n-propyltolyl)-methanes	di-(m-propylmethylcyclohexyl)-methanes.
12	p-n-propyltoluene	di-(p-propyltolyl)-methanes	di-(p-propylmethylcyclohexyl)-methanes.
	mixed isomers of propyltoluene	di-(o-, m-, and p-propyltolyl)-methanes	di-(o-, m-, and p-propylmethylcyclohexyl)-methanes.
13	o-isopropyltoluene	di-(o-isopropyltolyl)-methanes	di-(o-isopropylmethylcyclohexyl)-methanes.
14	m-isopropyltoluene	di-(m-isopropyltolyl)-methanes	di-(m-isopropylmethylcyclohexyl)-methanes.
15	p-isopropyltoluene	di-(p-isopropyltolyl)-methanes	di-(p-isopropylmethylcyclohexyl)-methanes.
16	1,2-diethylbenzene	di-(1,2-diethylphenyl)-methanes	di-(1,2-diethylcyclohexyl)-methanes.
17	1,3-diethylbenzene	di-(1,3-diethylphenyl)-methanes	di-(1,3-diethylcyclohexyl)-methanes.
18	1,4-diethylbenzene	di-(1,4-diethylphenyl)-methanes	di-(1,4-diethylcyclohexyl)-methanes.
19	1,2-dimethyl-3-ethylbenzene	di-(1,2-dimethyl-3-ethylphenyl)-methanes	di-(1,2-dimethyl-3-ethylcyclohexyl)-methanes.
20	1,2-dimethyl-4-ethylbenzene	di-(1,2-dimethyl-4-ethylphenyl)-methanes	di-(1,2-dimethyl-4-ethylcyclohexyl)-methanes.
21	1,3-dimethyl-2-ethylbenzene	di-(1,3-dimethyl-2-ethylphenyl)-methanes	di-(1,3-dimethyl-2-ethylcyclohexyl)-methanes.
22	1,3-dimethyl-4-ethylbenzene	di-(1,3-dimethyl-4-ethylphenyl)-methanes	di-(1,3-dimethyl-4-ethylcyclohexyl)-methanes.
23	1,3-dimethyl-5-ethylbenzene	di-(1,3-dimethyl-5-ethylphenyl)-methanes	di-(1,3-dimethyl-5-ethylcyclohexyl)-methanes.
24	1,4-dimethyl-2-ethylbenzene	di-(1,4-dimethyl-2-ethylphenyl)-methanes	di-(1,4-dimethyl-2-ethylcyclohexyl)-methanes.
25	n-butylbenzene	di-(n-butylphenyl)-methanes	di-(n-butylcyclohexyl)-methanes.
26	sec-butylbenzene	di-(sec-butylphenyl)-methanes	di-(sec-butylcyclohexyl)-methanes.
27	tert-butylbenzene	di-(tert-butylphenyl)-methanes	di-(tert-butylcyclohexyl)-methanes.
28	C_{10} aromatic fraction	di-(C_4[b] alkylphenyl)-methanes	di-(C_4[b] alkylcyclohexyl)-methanes.
29	1,2-diethyl-3-methylbenzene	di-(1,2-diethyl-3-methylphenyl)-methanes	di-(1,2-diethyl-3-methylcyclohexyl)-methanes.
30	1,2-diethyl-4-methylbenzene	di-(1,2-diethyl-4-methylphenyl)-methanes	di-(1,2-diethyl-4-methylcyclohexyl)-methanes.
31	1,3-diethyl-2-methylbenzene	di-(1,3-diethyl-2-methylphenyl)-methanes	di-(1,3-diethyl-2-methylcyclohexyl)-methanes.
32	1,3-diethyl-4-methylbenzene	di-(1,3-diethyl-4-methylphenyl)-methanes	di-(1,3-diethyl-4-methylcyclohexyl)-methanes.
33	1,3-diethyl-5-methylbenzene	di-(1,3-diethyl-5-methylphenyl)-methanes	di-(1,3-diethyl-5-methylcyclohexyl)-methanes.
34	1,4-diethyl-2-methylbenzene	di-(1,4-diethyl-2-methylphenyl)-methanes	di-(1,4-diethyl-2-methylcyclohexyl)-methanes.
35	o-methyl-n-butylbenzene	di-(o-methyl-n-butylphenyl)-methanes	di-(o-methyl-n-butylcyclohexyl)-methanes.
36	m-methyl-n-butylbenzene	di-(m-methyl-n-butylphenyl)-methanes	di-(m-methyl-n-butylcyclohexyl)-methanes.
37	p-methyl-n-butylbenzene	di-(p-methyl-n-butylphenyl)-methanes	di-(p-methyl-n-butylcyclohexyl)-methanes.
38	o-methyl-isobutylbenzene	di-(o-methyl-isobutylphenyl)-methanes	di-(o-methyl-isobutylcyclohexyl)-methanes.
39	m-methyl-isobutylbenzene	di-(m-methyl-isobutylphenyl)-methanes	di-(m-methyl-isobutylcyclohexyl)-methanes.
40	p-methyl-isobutylbenzene	di-(p-methyl-isobutylphenyl)-methanes	di-(p-methyl-isobutylcyclohexyl)-methanes.
41	o-methyl-tert-butylbenzene	di-(o-methyl-tert-butylphenyl)-methanes	di-(o-methyl-tert-butylcyclohexyl)-methanes.
42	m-methyl-tert-butylbenzene	di-(m-methyl-tert-butylphenyl)-methanes	di-(m-methyl-tert-butylcyclohexyl)-methanes.
43	p-methyl-tert-butylbenzene	di-(p-methyl-tert-butylphenyl)-methanes	di-(p-methyl-tert-butylcyclohexyl)-methanes.
44	o-ethyl-n-propylbenzene	di-(o-ethyl-n-propylphenyl)-methanes	di-(o-ethyl-n-propylcyclohexyl)-methanes.
45	m-ethyl-n-propylbenzene	di-(m-ethyl-n-propylphenyl)-methanes	di-(m-ethyl-n-propylcyclohexyl)-methanes.
46	p-ethyl-n-propylbenzene	di-(p-ethyl-n-propylphenyl)-methanes	di-(p-ethyl-n-propylcyclohexyl)-methanes.
47	o-ethyl-isopropylbenzene	di-(o-ethyl-isopropylphenyl)-methanes	di-(o-ethyl-isopropylcyclohexyl)-methanes.
48	m-ethyl-isopropylbenzene	di-(m-ethyl-isopropylphenyl)-methanes	di-(m-ethyl-isopropylcyclohexyl)-methanes.
49	p-ethyl-isopropylbenzene	di-(p-ethyl-isopropylphenyl)-methanes	di-(p-ethyl-isopropylcyclohexyl)-methanes.
50	1,2-dimethyl-3-propylbenzene	di-(1,2-dimethyl-3-propylphenyl)-methanes	di-(1,2-dimethyl-3-propylcyclohexyl)-methanes.
51	1,2-dimethyl-4-propylbenzene	di-(1,2-dimethyl-4-propylphenyl)-methanes	di-(1,2-dimethyl-4-propylcyclohexyl)-methanes.
52	1,3-dimethyl-2-propylbenzene	di-(1,3-dimethyl-2-propylphenyl)-methanes	di-(1,3-dimethyl-2-propylcyclohexyl)-methanes.
53	1,3-dimethyl-4-propylbenzene	di-(1,3-dimethyl-4-propylphenyl)-methanes	di-(1,3-dimethyl-4-propylcyclohexyl)-methanes.
54	1,3-dimethyl-5-propylbenzene	di-(1,3-dimethyl-5-propylphenyl)-methanes	di-(1,3-dimethyl-5-propylcyclohexyl)-methanes.
55	1,4-dimethyl-2-propylbenzene	di-(1,4-dimethyl-2-propylphenyl)-methanes	di-(1,4-dimethyl-2-propylcyclohexyl)-methanes.
56	1,2-dimethyl-3-propylbenzene	di-(1,2-dimethyl-3-propylphenyl)-methanes	di-(1,2-dimethyl-3-propylcyclohexyl)-methanes.
57	1,2-dimethyl-4-isopropylbenzene	di-(1,2-dimethyl-4-isopropylphenyl)-methanes	di-(1,2-dimethyl-4-isopropylcyclohexyl)-methanes.
58	1,3-dimethyl-2-isopropylbenzene	di-(1,3-dimethyl-2-isopropylphenyl)-methanes	di-(1,3-dimethyl-2-isopropylcyclohexyl)-methanes.
59	1,3-dimethyl-4-isopropylbenzene	di-(1,3-dimethyl-4-isopropylphenyl)-methanes	di-(1,3-dimethyl-4-isopropylcyclohexyl)-methanes.
60	1,3-dimethyl-5-isopropylbenzene	di-(1,3-dimethyl-5-isopropylphenyl)-methanes	di-(1,3-dimethyl-5-isopropylcyclohexyl)-methanes.
61	1,4-dimethyl-2-isopropylbenzene	di-(1,4-dimethyl-2-isopropylphenyl)-methanes	di-(1,4-dimethyl-2-isopropylcyclohexyl)-methanes.
62	n-amylbenzene	di-(n-amylphenyl)-methanes	di-(n-amylcyclohexyl)-methanes.
63	pri-isoamylbenzene	di-(2-isoamylphenyl)-methanes	di-(2-isoamylcyclohexyl)-methanes.
64	sec-isoamylbenzene	di-(3-isoamylphenyl)-methanes	di-(3-isoamylcyclohexyl)-methanes.
65	tert-amylbenzene	di-(tert-amylphenyl)-methanes	di-(tert-amylcyclohexyl)-methanes.
66	C_{11} aromatic fraction	di-(C_5[c] alkylphenyl)-methanes	di-(C_5[c] alkylcyclohexyl)-methanes.
67	n-amyl-o-toluene	di-(n-amyl-o-tolyl)-methanes	di-(n-amyl-o-methylcyclohexyl)-methanes.
68	n-amyl-m-toluene	di-(n-amyl-m-tolyl)-methanes	di-(n-amyl-m-methylcyclohexyl)-methanes.
69	n-amyl-p-toluene	di-(n-amyl-p-tolyl)-methanes	di-(n-amyl-p-methylcyclohexyl)-methanes.
70	2-isoamyl-o-toluene	di-(2-isoamyl-o-tolyl)-methanes	di-(2-isoamyl-o-methylcyclohexyl)-methanes.
71	2-isoamyl-m-toluene	di-(2-isoamyl-m-tolyl)-methanes	di-(2-isoamyl-m-methylcyclohexyl)-methanes.
72	2-isoamyl-p-toluene	di-(2-isoamyl-p-tolyl)-methanes	di-(2-isoamyl-p-methylcyclohexyl)-methanes.
73	3-isoamyl-o-toluene	di-(3-isoamyl-o-tolyl)-methanes	di-(3-isoamyl-o-methylcyclohexyl)-methanes.
74	3-isoamyl-m-toluene	di-(3-isoamyl-m-tolyl)-methanes	di-(3-isoamyl-m-methylcyclohexyl)-methanes.
75	3-isoamyl-p-toluene	di-(3-isoamyl-p-tolyl)-methanes	di-(3-isoamyl-p-methylcyclohexyl)-methanes.
76	ter-amyl-o-toluene	di-(ter-amyl-o-tolyl)-methanes	di-(ter-amyl-o-methylcyclohexyl)-methanes.

See footnotes at end of table.

TABLE I.—MIXTURE OF POSITION ISOMERS—Continued

No.	Alkylbenzene	Di-(alkylphenyl)-methanes	Di-(alkylcyclohexyl)-methanes
77	ter-amyl-m-toluene	di-(ter-amyl-m-tolyl)-methanes	di-(ter-amyl-m-methylcyclohexyl)-methanes.
78	ter-amyl-p-toluene	di-(ter-amyl-p-tolyl)-methanes	di-(ter-amyl-p-methylcyclohexyl)-methanes.
79	o-ethyl-n-butylbenzene	di-(o-ethyl-n-butylphenyl)-methanes	di-(o-ethyl-n-butylcyclohexyl)-methanes.
80	m-ethyl-n-butylbenzene	di-(m-ethyl-n-butylphenyl)-methanes	di-(m-ethyl-n-butylcyclohexyl)-methanes.
81	p-ethyl-n-butylbenzene	di-(p-ethyl-n-butylphenyl)-methanes	di-(p-ethyl-n-butylcyclohexyl)-methanes.
82	o-ethyl-isobutylbenzene	di-(o-ethyl-isobutylphenyl)-methanes	di-(o-ethyl-isobutylcyclohexyl)-methanes.
83	m-ethyl-isobutylbenzene	di-(m-ethyl-isobutylphenyl)-methanes	di-(m-ethyl-isobutylcyclohexyl)-methanes.
84	p-ethyl-isobutylbenzene	di-(p-ethyl-isobutylphenyl)-methanes	di-(p-ethyl-isobutylcyclohexyl)-methanes.
85	o-ethyl-tert-butylbenzene	di-(o-ethyl-tert-butylphenyl)-methanes	di-(o-ethyl-tert-butylcyclohexyl)-methanes.
86	m-ethyl-tert-butylbenzene	di-(m-ethyl-tert-butylphenyl)-methanes	di-(m-ethyl-tert-butylcyclohexyl)-methanes.
87	p-ethyl-tert-butylbenzene	di-(p-ethyl-tert-butylphenyl)-methanes	di-(p-ethyl-tert-butylcyclohexyl)-methanes.
88	2,3-dimethyl-n-butylbenzene	di-(2,3-dimethyl-n-butylphenyl)-methanes	di-(2,3-dimethyl-n-butylcyclohexyl)-methanes.
89	2,4-dimethyl-n-butylbenzene	di-(2,4-dimethyl-n-butylphenyl)-methanes	di-(2,4-dimethyl-n-butylcyclohexyl)-methanes.
90	3,4-dimethyl-n-butylbenzene	di-(3,4-dimethyl-n-butylphenyl)-methanes	di-(3,4-dimethyl-n-butylcyclohexyl)-methanes.
91	3,5-dimethyl-n-butylbenzene	di-(3,5-dimethyl-n-butylphenyl)-methanes	di-(3,5-dimethyl-n-butylcyclohexyl)-methanes.
92	2,3-dimethyl-sec-butylbenzene	di-(2,3-dimethyl-sec-butylphenyl)-methanes	di-(2,3-dimethyl-sec-butylcyclohexyl)-methanes.
93	2,4-dimethyl-sec-butylbenzene	di-(2,4-dimethyl-sec-butylphenyl)-methanes	di-(2,4-dimethyl-sec-butylcyclohexyl)-methanes.
94	3,4-dimethyl-sec-butylbenzene	di-(3,4-dimethyl-sec-butylphenyl)-methanes	di-(3,4-dimethyl-sec-butylcyclohexyl)-methanes.
95	3,5-dimethyl-sec-butylbenzene	di-(3,5-dimethyl-sec-butylphenyl)-methanes	di-(3,5-dimethyl-sec-butylcyclohexyl)-methanes.
96	2,3-dimethyl-tert-butylbenzene	di-(2,3-dimethyl-tert-butylphenyl)-methanes	di-(2,3-dimethyl-tert-butylcyclohexyl)-methanes.
97	2,4-dimethyl-tert-butylbenzene	di-(2,4-dimethyl-tert-butylphenyl)-methanes	di-(2,4-dimethyl-tert-butylcyclohexyl)-methanes.
98	3,4-dimethyl-tert-butylbenzene	di-(3,4-dimethyl-tert-butylphenyl)-methanes	di-(3,4-dimethyl-tert-butylcyclohexyl)-methanes.
99	3,5-dimethyl-tert-butylbenzene	di-(3,4-dimethyl-tert-butylphenyl)-methanes	di-(3,4-dimethyl-tert-butylcyclohexyl)-methanes.
100	1,2-dipropylbenzene	di-(1,2-dipropylphenyl)-methanes	di-(1,2-dipropylcyclohexyl)-methanes.
101	1,3-dipropylbenzene	di-(1,3-dipropylphenyl)-methanes	di-(1,3-dipropylcyclohexyl)-methanes.
102	1,4-dipropylbenzene	di-(1,4-dipropylphenyl)-methanes	di-(1,4-dipropylcyclohexyl)-methanes.
103	1,2-diisopropylbenzene	di-(1,2-diisopropylphenyl)-methanes	di-(1,2-diisopropylcyclohexyl)-methanes.
104	1,3-diisopropylbenzene	di-(1,3-diisopropylphenyl)-methanes	di-(1,3-diisopropylcyclohexyl)-methanes.
105	1,4-diisopropylbenzene	di-(1,4-diisopropylphenyl)-methanes	di-(1,4-diisopropylcyclohexyl)-methanes.
106	1,2,3-triethylbenzene	di-(1,2,3-triethylphenyl)-methanes	di-(1,2,3-triethylcyclohexyl)-methanes.
107	1,2,4-triethylbenzene	di-(1,2,4-triethylphenyl)-methanes	di-(1,2,4-triethylcyclohexyl)-methanes.
108	1,3,4-triethylbenzene	di-(1,3,4-triethylphenyl)-methanes	di-(1,3,4-triethylcyclohexyl)-methanes.
109	n-hexylbenzene	di-(n-hexylphenyl)-methanes	di-(n-hexylcyclohexyl)-methanes.
110	2-isohexylbenzene	di-(2-isohexylphenyl)-methanes	di-(2-isohexylcyclohexyl)-methanes.
111	3-isohexylbenzene	di-(3-isohexylphenyl)-methanes	di-(3-isohexylcyclohexyl)-methanes.
112	tert-hexylbenzene	di-(tert-hexylphenyl)-methanes	di-(tert-hexylcyclohexyl)-methanes.
113	C_{12} aromatic fraction	di-(C_6[d] alkylphenyl)-methanes	di-(C_6[d] alkylcyclohexyl)-methanes.

[a] C_3 alkyl groups include three methyl-, methyl- and ethyl-, propyl- and isopropyl-groups.
[b] C_4 alkyls groups include two methyl-, and one ethyl-, two ethyl-, a methyl- and propyl-, a methyl- and isopropyl-, n-butyl-, isobutyl-, tert-butyl-groups.
[c] C_5 alkyl groups include two ethyl- and one methyl-, one ethyl- and one propyl-, one ethyl- and one isopropyl-, one methyl- and one n-butyl-, one methyl-, and one isobutyl-, one methyl- and one sec-butyl-, one methyl- and one tert-butyl-, one n-pentyl-, the several branched and unbranched primary pentyl-, the several isopentyls-, two sec-pentyls, tert-pentyl-groups.
[d] C_6 alkyl groups include three ethyl-, methyl- and ethyl- and propyl-, methyl- and ethyl- and isopropyl-, two propyl-, two isopropyl-, two methyl- and one n-butyl-, two methyl- and one sec-butyl-, two methyl- and one tert-butyl-, one ethyl- and one n-butyl-, one ethyl- and one sec-butyl-, one ethyl- and one tert-butyl-, methyl- and amyl-, the methyl- and sec-amyl, the methyl- and tert-amyl-, the seven branched and unbranched pri-hexyl-, the six sec-hexyls-, the two isohexyls-, and three tert-hexyl-groups.

In Example I and in the examples of Table I, the alkylbenzenes employed for illustrative purposes include alkyl substituted benzenes for which: (*a*) the total carbon count of the alkyl group or groups on the benzene is 1 to 6, it being understood that the 7 to 13 carbon count alkylbenzenes likewise can be employed; (*b*) alkylbenzenes with two different alkyl groups are substituted on the benzene, it being understood that alkylbenzenes with three different alkyl groups substituted on the benzene likewise can be employed; (*c*) position isomer mixtures are prepared from a single alkylbenzene, it being understood that the mixtures of different alkylbenzenes or one or more alkylbenzenes and benzene can likewise be employed to produce a larger number of position isomer precursor compounds and their hydrogenated products in which R_1 and R_2 of Formulae I and IV are different alkyl substituents.

While Table I and the tables hereinafter show examples of the position isomers according to Formula IV and the hydrogenated products according to Formula I, the tables are understood to also exemplify the partial hydrogenated products according to Formulae VIII and IX; and it is further understood that there are exemplified herein the higher position isomers (prepared by increasing the ratio of bridging compound to the alkyl benzene compound in the reaction) according to Formulae V and VI, and the hydrogenated products thereof according to Formulae II and III, and also the partial hydrogenated products of Formulae V and VI and combinations of these.

EXAMPLE II

(*a*) *Mixture of Di-(Tolyl)-Methanes*

The procedure of Example I was repeated using 3 moles of paraformaldehyde in the same apparatus. The catalyst was 1.5 moles of 78% sulfuric acid and the paraformaldehyde was added in small increments over 3 hours with the temperature being raised from 20° C. to 59° C. during the course of the addition and held at an average temperature of 48° C. for 1 hour. The product di-(tolyl)-methane distilled at 175–180/10 mm. Hg pressure to give less than 5 grams of di-(tolyl)-methanes. This example illustrates the approximate lower useful limit of acid concentration of the reaction.

EXAMPLE III

(*a*) *Mixture of Di-(Xylyl)-Methanes*

Example I was repeated using instead of toluene, a commercial synthetic xylene mixture with the following analysis:

0.5% toluene, 20.0% ethylbenzene, 20.0% p-xylene, 42% m-xylene, 16% o-xylene, 1.5% higher boiling (e.g., ethyltoluene). Eighteen moles (1910 grams) of this xylene mixture was reacted with 4 moles paraformaldehyde, 3 moles methanol and 4 moles 96.7% sulfuric acid containing 0.01 mole of ferrous sulfate heptahydrate. The time of addition of the paraformaldehyde was 25 minutes and the temperature during addition was gradually raised from 29 to 59° C. The temperature was then raised slowly to about 70° C. and maintained while stirring for an hour. It was estimated that the loss of formaldehyde was 29 g. or 0.97 mole. The product after water washing and caustic washing as in Example I was distilled to yield 416.3 g. of product distilling at 152 to 167° C./2 mm. Hg and 200 grams residue, a higher condensation product of di-(xylyl)-methane with xylene and formaldehyde, apparently di-(xylyl)-methylxylene having the structure of Formula VI R_1 and R_2=CH_3, Y=CH_2 P=2, m=2 and n=3. The above 416.3 grams was a mixture containing the position isomers of di-(ethylphenyl)-methane, di-(xylyl)-methane, and (xylyl)-(ethylphenyl)-methane represents 1.86 moles of product. This mixture had an N_D^{20}=1.5663; D_4^{20}=0.978; M.P.=−40° C.; viscosity=27 poises at

—25° C. The yield was 61.5% of theory based on formaldehyde reacted, or 67.5 wt. percent of the total condensation products.

(b) Mixed Di-(Dimethylcyclohexyl)-Methanes and Higher Homologues

One mole of the di-(xylyl)-methane product of Example III (*a*) (224 g.) was hydrogenated according to the procedure of Example I using 38.8 g. Raney nickel catalyst and 800 g. methylcyclohexane as solvent. The conditions of hydrogenation were: 130–134° C. for 70 minutes at 350 to 750 p.s.i. hydrogen pressure. The water white product was a mixture of three components, namely di-(dimethylcyclohexyl)-methane, di-(ethylcyclohexyl)-methane, and (dimethylcyclohexyl)-(ethylcyclohexyl)-methane and each component comprised numerous position isomers, obtained in about 90% yield and its properties were: B.P.=120–130° C./1 mm. Hg; M.P.=below —70° C.; N_D^{20}=1.4760; D_4^{20}=0.876; viscosity=5 poises at —25° C. The elemental analysis was 88.65% carbon and 13.39% hydrogen. The energy of combustion was 19,760 B.t.u./lb. (gross), 18,513 B.t.u./lb. (net), 137,420 B.t.u./gallon (net). Substitution of sulfuric acid-phosphorous pentoxide combination (0.33 mole P_2O_5 per mole of formaldehyde), the concentration of the sulfuric acid does not change during the reaction since the water of condensation converts the P_2O_5 to phosphoric acid:

(*a*) $3HCHO+6CH_3C_6H_5 \rightarrow 3(CH_3C_6H_5)_2CH_2+3H_2O$

(*b*) $3H_2O+P_2O_5 \rightarrow 2H_3PO_4$

When operating in this manner, the productivity of the sulfuric acid catalyst is much higher. Also substitution of hydrofluoric acid for the sulfuric acid in the above procedure produces high yields of di-(alkylaryl)-methanes which is hydrogenated to a fuel having an energy of combustion greater than 135,000 B.t.u./gallon.

EXAMPLE IV

(a) Mixtures of Di-(Tolyl)-Methanes

In this example toluene was reacted with formalin (37% formaldehyde) instead of paraformaldehyde used in Example I. 820 grams (7.5 moles) of 89.5 sulfuric acid containing 2.8 g. (0.01 mole) ferrous sulfate heptahydrate was added dropwise to a mixture of 1842 grams (20 moles) toluene, 203 grams (2.5 moles) 37% formalin and 40 grams (1.25 moles) methanol while stirring. The temperature of reaction was maintained in the range of 18 to 29° C. by a cold water bath. The time of the acid addition was 77 minutes. The mixture turned dark purple during the acid addition. Stirring was continued for 1 hour at 19–21° C. after the addition of the acid was completed. The mixture was then diluted with 1 liter water and well shaken, the upper hydrocarbon layer was separated, washed and distilled from a Claisen flask to separate the unreacted toluene and 179 g. (0.91+ mole) of di-(tolyl)-methane was obtained distilling at 149 to 184° C./10 mm. Hg pressure with a residue of 95 g. having a refractive index of N_D^{20} of 1.601. The residue is isomers of di-(tolylmethyl)-toluene (0.32 mole). Thus it is estimated that 1.55 moles HCHO reacted, 0.95 mole HCHO escaped through the condenser or was washed out of the final reaction mixture. The yield of di-(tolyl)-methane was 59% based on formaldehyde reacted, and the di-(tolyl)-methane comprised 66% of the aryl-hydrocarbon reaction products. The characteristics measured on this di-(tolyl)-methane product were: N_D^{20}=1.5618; D_4^{20}=0.979; F.P.=below —65° C.; viscosity=5 poises at —50° C.

(b) Mixtures of Di-(Methylcyclohexyl)-Methanes

This material when hydrogenated over Raney nickel according to the procedure of Example I gave a fuel having over 136,000 B.t.u./gallon. When xylene (20 moles) is substituted for toluene in the above example, the final hydrogenated fuel comprises mixed isomers of di-(dimethylcyclohexyl)-methane. When trimethylbenzene (20 moles) is substituted for toluene in the above example, the final fuel comprises isomers of di-(trimethylcyclohexyl)-methane.

EXAMPLE V

(a) Mixtures of Di-(Tolyl)-Methanes

One mole of 1,1-dichloromethane (85 grams) was weighed into a 4-liter glass vessel equipped with condenser, agitator, thermometer, an opening for addition of components, the vessel being immersed in an ice/water bath. To it was added six moles (552 grams) of dry toluene while stirring; when the temperature of the very mildly stirring mixture had fallen to 5° C. about one-half mole (65 g.) of powdered aluminum chloride (anhydrous) was added over a period of 15 minutes. HCl fumes were evolved slowly and after addition of the $AlCl_3$ was completed the stirrer was stopped and the flask was allowed to stand 24 hours, the ice in the cooling bath being allowed to melt, the temperature rising gradually to room temperature. The reaction mixture was poured into 700 grams of ice and 30 ml. conc. hydrochloric acid, the whole heated to near reflux, then cooled to 50° C. The hydrocarbon layer was separated, washed with an equal volume of 1% hydrochloric acid solution, and heated to distill off the unreacted toluene along with small amounts of water; 118 g. of a fraction, di-(tolyl)-methanes, distilling at 135–150° C./2–3 mm. Hg (n_D^{20}: 1.5680) (and leaving a tarry residue of about 30 grams) was obtained following a xylene fraction distilling at 135–145° C. (30 g.).

(b) Mixtures of Di-(Methylcyclohexyl)-Methanes

Of this di(-tolyl)-methane, 100 grams was hydrogenated as in Example I to yield di-(methylcyclohexyl)-methane; B.P.=110–120/7 mm. Hg, in substantially quantitative yield.

Alternatively, following the procedure of Example V other Friedel-Crafts catalysts may be substituted for the aluminum chloride. Thus BF_3, VCl_4, $BeCl_2$, and the like produce di-(tolyl)-methane from toluene and methylene chloride. The position isomeric composition of the final hydrogenated fuel is different for each catalyst, but in every case the energy value is greater than 135,000 B.t.u./gallon.

EXAMPLE VI

(a) Mixed Di-(Xylyl)-Methanes

In Example VI the procedure of Example V was repeated using currently produced commercial xylenes having the following analysis: 2% toluene, 10% p-xylene, 48% m-xylene, 19% o-xylene, 21% ethylbenzene.

(b) Mixed Di-(Dimethylcyclohexyl)-Methanes

The final hydrogenated product was similar but not identical to that obtained in Example V, having slightly lower density and slightly higher combustion energy.

EXAMPLE VII

(a) Mixtures of Di-(Xylyl)-Methanes

In this example, the procedure of Example III was repeated using a xylene of about 90% p-xylene content, and 10% o- and m-xylene combined. The tendency to form resins with formaldehyde resulted in lower yields of the desired di-(xylyl)-methane position isomers product when the same reaction conditions were employed.

(b) Mixtures of Di-(Dimethylcyclohexyl)-Methanes

This product of (*a*) was hydrogenated to produce a fuel of net heat of combustion greater than 135,000 B.t.u./gallon.

EXAMPLE VII–A

(a) Mixture of Di-(Xylyl)-Methanes

The procedure of Example III was employed to react commercial xylenes (of same composition as set forth in Example VI) with formaldehyde. Forty moles (4247 grams) of the xylenes were placed in the reaction vessel (used in Example I) together with 10 moles methanol (320 g.), 0.02 mole ferrous sulfate heptahydrate (5.6 g.), and 10 moles 96.1% sulfuric acid (1021 g.). Ten moles paraformaldehyde (300 g.) were added over a period of 3 hours and fifty minutes to the reaction vessel while stirring and maintaining at 40–45° C. After 45 minutes' additional stirring, 2 more moles of 96.1% sulfuric acid (204 g.) were added over a period of 1.5 hours and heat was applied during this addition so that the temperature of the reaction mixture gradually increased to 52° C. when the acid was all added. The acid layer was removed, the upper layer was washed once with 1 liter of water, once with 1 liter of 3% Na_2CO_3 solution, and three times with three successive liters of water. Distillation of the hydrocarbon products at 745/mm. Hg gave the following fractions boiling above 200° C.:

Fractions	° C./745 mm. Hg	$n_D^{23.5}$	Yield (g.)
1	200–300	1.5300	7.8
2	300–319	1.5560	26.8
3	319–326	1.5638	1,500.0
4	326–340	1.5653	106.3
5	340–380	1.5710	31.7
6	380–400	1.5862	158.1
7	>400	1.5700	48.8
8	Residue	Solid	115.5
Total			1,995.0

Fractions 2–6 weighing 1822.9 grams distilling from 300 to 400° C. is the mixture of isomeric di-(xylyl)-methane precursors of this invention.

(b) Mixture of Di-(Dimethylcyclohexyl)-Methanes

Hydrogenation of 673 grams of fraction 3 above was carried out using the procedure and autoclave of Example I. Pentane solvent (1800 ml.) was used instead of methylcyclohexane solvent, and 101 grams of Girdler's nickel catalyst G–49–A was used. After maintaining the autoclave at 155 to 195° C. under 500 to 800 p.s.i. hydrogen pressure for 16 hours, no further hydrogen was absorbed. The contents of the autoclave were filtered, the pentane removed by distillation, and 662 grams of di-(dimethylcyclohexyl)-methanes was obtained having the following properties:

The product was redistilled to yield a principal fraction having the following properties: B.P.=295–302° C./745 mm. Hg; n_D^{25}=1.4759; D_4^{30}=0.865; M.P.=below −50° C.; viscosity=<0.5 poise at 30° C.; and the gross heat of combustion was 19,615 B.t.u./lb.

(c) Mixtures of Di-(C_2-Alkylphenyl)-Methanes and Hydrogenated Products Thereof

This example was repeated as in (*a*) above employing 2120 grams of mixed xylenes and 2120 grams of ethylbenzene to yield a mixture of mixed isomers of di-(xylyl)-methanes, di - (ethylphenyl) - methanes, and (ethylphenyl)-(xylyl)-methanes.

The C_{17} distillation cut containing these mixed position isomers was hydrogenated as in (*b*) above to yield a fuel of net heat of combustion greater than 135,000 B.t.u./gallon.

EXAMPLE VIII

(a) Mixtures of Di-(Ethylphenyl)-Methanes

A glass flask equipped with a stirrer, a reflux condenser, a thermometer and an opening for addition of reagents was warmed in a water bath at an average temperature of 50° C. To the reaction vessel was added

1910 grams (18 moles) of ethylbenzene, 406 grams (4 moles) of 96.9% sulfuric acid, 5.3 grams (0.02 mole) of ferrous sulfate heptahydrate, 64 grams (2 moles) of methanol and 120 grams (4 moles) of paraformaldehyde was added in small increments over a 2 hour period; the temperature of the reactants averaged 51° C. Stirring was continued at 50° C. for another half hour. During the reaction, the color changed to dark purple. The hydrocarbon layer was decanted, washed with a liter of water followed by a liter of 3% aqueous solution of sodium carbonates and then finally washed with 1 liter of water. The unreacted material was distilled off and the product distilled as follows:

Fractions	B.P., ° C. 1 mm. Hg	N_D^{20}	Yield (g.)
1	148–150	1.5540	12.2
2	150–152	1.5541	475
3	[1] 152		141

[1] Residue.

Fraction 1 was an amber fluid, fraction 2 was a clear fluid and fraction 3 was a dark red viscous fluid.

(b) Mixtures of Di-(Ethylcyclohexyl)-Methanes

The combined products of fractions (1) and (2) were hydrogenated according to the procedure of Example I. A mixture of position isomers of di-(ethylcyclohexyl)-methanes was obtained having a net fuel value greater than 135,000 B.t.u./gallon.

EXAMPLE VIII–A

(a) Mixtures of Di-(Ethylphenyl)-Methanes

To a pressure vessel with agitator and cooling jacket is added 168 grams (1 mole) of diphenylmethane, 102 grams (1 mole) of 97% sulfuric acid, 13.5 grams of gaseous boron fluoride and the pressure vessel is attached to a 100 p.s.i. ethylene line and pressured therewith. The reactants are rapidly agitated and the reaction temperature is maintained at 300° C. After the reaction mixture has taken up 56 grams (2 moles) of ethylene, the ethylene is shut off and the vessel vented and the reactants removed. The hydrocarbon layer is separated from the acid layer and poured onto a kilogram of ice, followed by washing with 1 liter of 3% aqueous sodium carbonate solution and 1 liter of water. Any unreacted diphenyl-methane is distilled off and the product is a mixture of position isomers of di-(ethylphenyl)-methane (or other di-(ethylphenyl)-alkanes) containing small amounts of mono-tri- (and higher) ethyl-di-(phenyl)-methanes.

(b) Mixtures of Di-(Ethylcyclohexyl)-Methanes

To an autoclave is added 40 grams of di-(ethylphenyl)-methane (or other di(ethylphenyl)-alkanes) of (*a*) above, 160 grams of cyclohexane and 9 grams of Raney type nickel catalyst (Girdler #49–A catalyst) and hydrogenated at 160° C., with 1000 p.s.i. of hydrogen. The catalyst is removed by filtration and the cyclohexane removed by distillation. The resulting fuel product comprises a mixture of position isomers of di-(ethylcyclohexyl)-methanes (or di-(ethylcyclohexyl)-alkanes) having a net energy of combustion greater than 135,000 B.t.u./gallon.

(c) Mixtures of Di-(Alkylcyclohexyl)-Alkanes Prepared From Benzene or Alkylbenzene, a Compound Providing the Y Bridge and an Olefin

In place of the 1 mole of diphenyl-methane employed in Example (*a*) above, 2 moles of benzene and 1 mole of a bridging compound such as a hydrocarbon diene, e.g., butadiene, isoprene, piperylene and the like homologues up to and including C_{13} homologues, or mixtures of these (see Examples XIV–C, XXVI and XXVII) may be added concurrently or alternately with 1 to 3

moles of olefin, e.g., ethylene, propylene, butylene, isobutylene and the like homologues up to and including C_{13} homologues, or mixtures of these olefins and with the aid of a suitable alkylating catalyst, e.g., sulfuric acid and boron fluoride as set forth in (*a*) hereof, and converted to the mixture of position isomers of the corresponding di-(alkylphenyl)-alkane (Formula IV) which is subsequently hydrogenated as set forth in (*b*) above to the mixture of position isomers of the corresponding di-(alkylcyclohexyl)-alkanes (Formula I) or the partially hydrogenated compounds corresponding to Formulae VIII or IX herein.

When it is desired to produce di-(alkylcycohexyl)-alkanes or di-(trialkylcyclohexyl)-alkanes with the same or different alkyl substituents on the cyclohexyl radicals then one can employ benzene together with two or more olefins and a compound supplying the Y bridging radical; or one may employ one or more C_1 to C_{13}-alkylbenzenes together with one or more olefins and a compound supplying the Y bridge; and these materials are converted in a like manner as set forth in this example or in the other examples herein with the aid of an alkylation catalyst to the position isomers corresponding to Formula IV herein and with subsequent hydrogenation these same are converted to position isomers corresponding to Formula I or VIII or IX herein (refer to Example XIV–A).

EXAMPLE IX

(*a*) *Mixtures of Di-(Isopropylphenyl)-Methanes*

A glass flask equipped with a stirrer, a reflux condenser, a thermometer and an opening for addition of reagents was heated in a water bath at a temperature 45 to 50° C. To this reaction flask was added 480 g. (4 moles) of cumene, 100 g. (1 mole) 96.9% sulfuric acid, 32 g. (1 mole) of methanol, 1.1 g. (0.005 mole) of ferrous sulfate heptahydrate and over a 2 hour period was added in small increments 30 g. (1 mole) of paraformaldehyde. The hydrocarbon layer was separated, washed with 1 liter of 3% sodium carbonate aqueous solution followed by 1 liter water. The unreacted cumene was removed by distillation. The product was distilled as follows:

Fractions	B.P. at° C./ 745 mm. Hg	N_D^{23}	Yield (g.)[1]
1	225–325	1.5225	10.2
2	325–335	1.5406	76.7
3	335–340	1.5407	26.2
4	340–350	1.5429	21.7
Residue	above 350	1.5670	31.8

[1] Distillates had slight greenish tinge.

(*b*) *Mixtures of Di-(Isopropylcyclohexyl)-Methanes*

Fractions 1 through 4 were combined for hydrogenation (and if desired the residue could also be included). The hydrogenation was carried out as in Example I and the di-(isopropylcyclohexyl)-methane position isomer mixture had a net fuel value greater than 135,000 B.t.u./gallon.

EXAMPLE IX–A

(*a*) *Mixtures of Di-(Isopropylphenyl)-Methanes*

To a glass vessel equipped with a stirrer in a water bath at 20° C. is added 168 grams (1 mole) of diphenyl methane, 102 grams (1 mole) of 97% sulfuric acid and over a period of 4 hours propylene is bubbled into the rapidly agitated reactants so that 105 grams (2.5 moles) of propylene are reacted. The hydrocarbon layer is separated from the acid layer and washed with 1 liter of water, 1 liter of 3% aqueous sodium carbonate and again with 1 liter of water and any unreacted diphenylmethane is removed by distillation. The resulting product is primarily di-(isopropylphenyl)-methane with a small amount of (isopropylphenyl) - (phenyl)-methane and (diisopropylphenyl)-(isopropylphenyl)-methane position isomers.

(*b*) *Mixtures of Di-(Diisopropyl-Phenyl)-Methanes*

The preparation of these position isomers is conducted similarly as described in (*a*) of this example, only the reaction temperature is maintained at 2° C. with the aid of an ice bath and propylene is bubbled in over a 6-hour period or until the reactants take up 172 grams (4.1 moles) of propylene, and the acid layer is decanted and the hydrocarbon layer washed yielding mainly di-(isopropylphenyl)-methane. In Examples IX–A (*a*) or (*b*) a half mole of boron fluoride can be added to speed up the reaction and shift the ratio of position isomers.

(*c*) *Mixtures of (Isopropylphenyl)-(Phenyl)-Methane*

Alternately in Example IX–A 46 grams (1.1 moles) of propylene can be combined, chiefly forming the (isopropylphenyl)-(phenyl)-methane.

(*d*) *Mixtures of Di-(Isopropylcycloxhexyl)-Methane*

To an autoclave is added 20 grams of principally di-(isopropylphenyl)-methane from (*a*) above, 80 grams of cyclohexane solvent and 5 grams of Raney type nickel catalyst (Girdler #G–49A catalyst) and hydrogenated at 160° C. with 1000 p.s.i. of hydrogen. The catalyst is removed by filtration and cyclohexane removed by distillation. The resulting fuel product is a mixture of position isomers of di-(isopropylcyclohexyl)-methanes having a net energy of combustion greater than 135,000 B.t.u./gallon.

(*e*) *Mixtures of Di-(Diisopropyl-Cyclohexyl)-Methane*

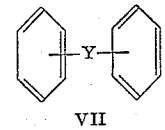
This example is conducted similarly to Example IX–A (*d*) above except that 20 grams of principally di-(diisopropyl-phenyl)-methane is employed and the product from hydrogenation is di-(diisopropyl-cyclohexyl)-methane which is useful as a fuel having a net energy of combustion greater than 135,000 B.t.u./gallon.

(*f*) *Mixtures of (Isopropylcyclohexyl)-(Cyclohexyl)-Methane*

This example is conducted similarly to Example IX–A (*d*) except that 20 grams of (isopropylphenyl)-(phenyl)-methane is employed and the product from hydrogenation is (isopropylcyclohexyl)-(cyclohexyl)-methane which is a useful fuel having a net energy of combustion greater than 135,000 B.t.u./gallon.

In place of the 1, 2 and 4 moles of propylene in Examples IX–A (*c*), (*a*) and (*b*) alpha-isoolefins can be employed such as isobutylene, isopentylene, isohexylene, diisopropylene, tri-propylene, diisobutylene, triisobutylene and the like or other alphaolefins such as ethylene, butene-1, pentene-1, hexene-1 and the like and when employing these alpha-olefins, it is sometimes necessary to increase the sulfuric acid catalyst efficiency by adding boron fluoride (e.g. 0.5 mole boron fluoride per 1 mole of concentrated sulfuric acid see Example VIII–A).

In place of the 1 mole of diphenyl-methane may be added 1 mole of one or more of the diphenyl derivative of ethane, propane, butanes, isobutane, the pentanes, the hexanes or any compound of Formula VII, i.e.



VII

in which Y is an alkane bridge radical having 1 to 13 carbon atoms. These various position isomers produced by alkylating compounds of the type of Formula VII produce compounds of the type of Formula IV which when hydrogenated (as per Example IX–A (*d*)) produces position isomer fuels of Formula I according to this invention.

EXAMPLE X

(*a*) *Mixture of Di-(Sec-Butylphenyl)-Methanes*

A glass flask equipped with a stirrer, a reflux condenser,

a thermometer and an opening for addition of reagents was heated in a water bath at a temperature of 50° C. To the reaction vessel was added 805 grams (6 moles) of sec-butylbenzene, 152 grams (1.5 moles) of 96.9% sulfuric acid, 24 grams (0.75 mole) of methanol, 1.1 grams (0.005 mole) of ferrous sulfate heptahydrate and over a period of 1.5 hours was added in small increments 45 grams (1.5 moles) of paraformaldehyde. During the reaction the average temperature of the reactants was 55° C. After 0.5 hour continued stirring, the hydrocarbon product was decanted from the acid layer and washed with 1 liter of water followed by 1 liter of 3% aqueous sodium carbonates and finally with 1 liter of water, and the unreacted materials removed by distillation.

The product was distilled as follows:

Fractions	B.P., ° C./745 mm. Hg	N_D^{23}	Yield (g.)
1	300–350	1.5211	7.9
2	350–360	1.5421	131.6
3	360–370	1.5451	34.8
4	370–390	1.5511	16.5
5	390–395	1.5619	12.4
6	395–405	1.5688	15.0
7	[1] >405	Solid	43.0

[1] Residue.

Fractions 1 to 4 were liquids some solid material separated from fraction 5 and fraction 6 solidified with a melting point about 50° C.

(b) Mixed Di-(Sec-Butylcyclohexyl)-Methanes and Higher Fractions

Fractions 2 to 5 were combined and hydrogenated according to the procedure of Example I to yield a position isomer mixture which had a net fuel value greater than 135,000 B.t.u./gallon.

EXAMPLE XI

(a) Mixtures of 1,1-Di-(Tolyl)-Ethanes

In a 4-liter glass reaction vessel identical with that of Example I were placed 1658 g. (18 moles) of toluene and 406 g. (4 moles) of 96.7% sulfuric acid. The flask was cooled in an ice bath to 5° C. and while vigorously agitating the toluene-acid mixture, acetaldehyde (4 moles) was added dropwise over a period of 35 minutes. The temperature rose to a maximum of 15° C. during the addition of the aldehyde, the initially colorless mixture gradually turned orange, red and dark brown successively. Some

aldehyde (B.P. 21° C.) vapors were lost through the condenser. Stirring was continued for 85 minutes during which time the temperature decreased to 3° C. indicating most of the reaction was over. The dark brown mixture was allowed to warm to 25° C. The acid layer did not readily separate and soda ash (400 g.) was added gradually with stirring to neutralize the acid. The solution warmed up and some unreacted acetaldehyde distilled out of the mixture during this process. It was calculated from product weights that a total of 2.24 moles of the added aldehyde was lost by vaporization. The aqueous layer was removed, the hydrocarbon layer was water-washed with 1500 ml. water and the toluene distilled off. The toluene-free product was distilled at atmospheric pressure and the fractions collected were as follows:

Fractions	B.P., ° C./745 mm. Hg	N_D^{20}	Yield (g.)
1	255–298	1.5421	14.0
2	298–300	1.5551	27.1
3	300–304	1.5587	10.6
4	304–306	1.5601	30.3
5	306–308	1.5611	97.8
6	308–310	1.5620	55.7
7	310–315	1.5618	28.7
8	315–325	1.5628	21.0
9	325–365	1.5618	18.5
10	365–380	1.5539	12.8
11	[1]	[2]	40.0

[1] Resinous residue.
[2] Dark solid.

Fractions 1 to 10 combined weighed 316.5 grams which distilled at 255–380° C., with the main portion distilling from 298–325° C. This total distillate had the following properties: D_4^{20}=0.976; N_D^{20}=1.5600; M.P.=below −65° C.; viscosity=5 poises at −25° C.

(b) Mixtures of 1,1-Di-(Methylcyclohexyl)-Ethane

Fractions 1 through 10 were combined and hydrogenated by the procedure of Example I to yield the position isomers of 1,1-di-(methylcyclohexyl)-ethane having a density of D_4^{20}=0.891 and N_D^{20}=1.4800 and a heat of combustion of over 136,000 B.t.u./gallon.

Following the procedure of Example XI, but for the 18 moles of toluene substituting 18 moles (a substantial excess over that required for stoichiometric reaction with the acetaldehyde) of other alkylbenzenes, corresponding 1,1-di-(alkylphenyl)-ethane position insomer mixtures are produced which, when hydrogenated, give the corresponding 1,1-di-(alkylcyclohexyl)-ethane position isomers as set forth in Table II.

TABLE II.—MIXTURE OF POSITION ISOMERS

No.	Alkylbenzene	1,1-di-(alkylphenyl)-ethanes	1,1-di-(alkylcyclohexyl)-ethanes
1	ethylbenzene	di-(ethylphenyl)-ethanes	di-(ethylcyclohexyl)-ethanes.
2	o-xylene	di-(o-xylyl)-ethanes	di-(1,2-dimethylcyclohexyl)-ethanes.
3	m-xylene	di-(m-xylyl)-ethanes	di-(1,3-dimethylcyclohexyl)-ethanes.
4	p-xylene	di-(p-xylyl)-ethanes	di-(1,4-dimethylcyclohexyl)-ethanes.
5	C_8 aromatic fraction	di-(C_8[a] alkylphenyl)-ethanes	di-(C_8[a] alkylcyclohexyl)-ethanes.
6	o-ethyltoluene	di-(o-ethyltolyl)-ethanes	di-(o-ethyl-methylcyclohexyl)-ethanes.
7	m-ethyltoluene	di-(m-ethyltolyl)-ethanes	di-(m-ethyl-methylcyclohexyl)-ethanes.
8	p-ethyltoluene	di-(p-ethyltolyl)-ethanes	di-(p-ethyl-methylcyclohexyl)-ethanes.
9	1,2,3-trimethylbenzene	di-(1,2,3-trimethylphenyl)-ethanes	di-(1,2,3-trimethylcyclohexyl)-ethanes.
10	1,2,4-trimethylbenzene	di-(1,2,4-trimethylphenyl)-ethanes	di-(1,2,4-trimethylcyclohexyl)-ethanes.
11	1,3,5-trimethylbenzene	di-(1,3,5-trimethylphenyl)-ethanes	di-(1,3,5-trimethylcyclohexyl)-ethanes.
12	n-propylbenzene	di-(n-propylphenyl)-ethanes	di-(n-propylcyclohexyl)-ethanes.
13	isopropylbenzene	di-(isopropylphenyl)-ethanes	di-(isopropylcyclohexyl)-ethanes.
14	C_9 aromatic fraction	di-(C_9[b] alkylphenyl)-ethanes	di-(C_9[b] alkylcyclohexyl)-ethanes.
15	o-n-propyltoluene	di-(o-n-propyltolyl)-ethanes	di-(o-n-propylmethylcyclohexyl)-ethanes.
16	m-n-propyltoluene	di-(m-n-propyltolyl)-ethanes	di-(m-n-propylmethylcyclohexyl)-ethanes.
17	p-n-propyltoluene	di-(p-n-propyltolyl)-ethanes	di-(p-n-propylmethylcyclohexyl)-ethanes.
	mixed isomers of propyltoluene	di-(o-, m-, and p-propyltolyl)-ethanes	di-(o-, m-, and p-propylmethylcyclohexyl)-ethanes.
18	o-isopropyltoluene	di-(o-isopropyltolyl)-ethanes	di-(o-isopropylmethylcyclohexyl)-ethanes.
19	m-isopropyltoluene	di-(m-isopropyltolyl)-ethanes	di-(m-isopropylmethylcyclohexyl)-ethanes.
20	p-isopropyltoluene	di-(p-isopropyltolyl)-ethanes	di-(p-isopropylmethylcyclohexyl)-ethanes.
21	1,2-diethylbenzene	di-(1,2-diethylphenyl)-ethanes	di-(1,2-diethylcyclohexyl)-ethanes.
22	1,3-diethylbenzene	di-(1,3-diethylphenyl)-ethanes	di-(1,3-diethylcyclohexyl)-ethanes.
23	1,4-diethylbenzene	di-(1,4-diethylphenyl)-ethanes	di-(1,4-diethylcyclohexyl)-ethanes.
24	1,2-dimethyl-3-ethylbenzene	di-(1,2-dimethyl-3-ethylphenyl)-ethanes	di-(1,2-dimethyl-3-ethylcyclohexyl)-ethanes.
25	1,2-dimethyl-4-ethylbenzene	di-(1,2-dimethyl-4-ethylphenyl)-ethanes	di-(1,2-dimethyl-4-ethylcyclohexyl)-ethanes.
26	1,3-dimethyl-2-ethylbenzene	di-(1,3-dimethyl-2-ethylphenyl)-ethanes	di-(1,3-dimethyl-2-ethylcyclohexyl)-ethanes.
27	1,3-dimethyl-4-ethylbenzene	di-(1,3-dimethyl-4-ethylphenyl)-ethanes	di-(1,3-dimethyl-4-ethylcyclohexyl)-ethanes.
28	1,3-dimethyl-5-ethylbenzene	di-(1,3-dimethyl-5-ethylphenyl)-ethanes	di-(1,3-dimethyl-5-ethylcyclohexyl)-ethanes.
29	1,4-dimethyl-2-ethylbenzene	di-(1,4-dimethyl-2-ethylphenyl)-ethanes	di-(1,4-dimethyl-2-ethylcyclohexyl)-ethanes.
30	n-butylbenzene	di-(n-butylphenyl)-ethanes	di-(n-butylcyclohexyl)-ethanes.

See footnotes at end of table.

TABLE II.—MIXTURE OF POSITION ISOMERS—Continued

No.	Alkylbenzene	1,1-di-(alkylphenyl)-ethanes	1,1-(di-alkylcyclohexyl)-ethanes
31	sec-butylbenzene	di-(sec-butylphenyl)-ethanes	di-(sec-butylcyclohexyl)-ethanes.
32	tert-butylbenzene	di-(tert-butylphenyl)-ethanes	di-(tert-butylcyclohexyl)-ethanes.
33	C_{10} aromatic fraction	di-(C_4[c] alkylphenyl)-ethanes	di-(C_4[c] alkylcyclohexyl)-ethanes.
34	1,2-diethyl-3-methylbenzene	di-(1,2-diethyl-3-methylphenyl)-ethanes	di-(1,2-diethyl-3-methylcyclohexyl)-ethanes.
35	1,2-diethyl-4-methylbenzene	di-(1,2-diethyl-4-methylphenyl)-ethanes	di-(1,2-diethyl-4-methylcyclohexyl)-ethanes.
36	1,3-diethyl-2-methylbenzene	di-(1,3-diethyl-2-methylphenyl)-ethanes	di-(1,3-diethyl-2-methylcyclohexyl)-ethanes.
37	1,3-diethyl-4-methylbenzene	di-(1,3-diethyl-4-methylphenyl)-ethanes	di-(1,3-diethyl-4-methylcyclohexyl)-ethanes.
38	1,3-diethyl-5-methylbenzene	di-(1,3-diethyl-5-methylphenyl)-ethanes	di-(1,3-diethyl-5-methylcyclohexyl)-ethanes.
39	1,4-diethyl-2-methylbenzene	di-(1,4-diethyl-2-methylphenyl)-ethanes	di-(1,4-diethyl-2-methylcyclohexyl)-ethanes.
40	o-methyl-n-butylbenzene	di-(o-methyl-n-butylphenyl)-ethanes	di-(o-methyl-n-butylcyclohexyl)-ethanes.
41	m-methyl-n-butylbenzene	di-(m-methyl-n-butylphenyl)-ethanes	di-(m-methyl-n-butylcyclohexyl)-ethanes.
42	p-methyl-isobutylbenzene	di-(p-methyl-n-butylphenyl)-ethanes	di-(p-methyl-n-butylcyclohexyl)-ethanes.
43	o-methyl-isobutylbenzene	di-(o-methyl-isobutylphenyl)-ethanes	di-(o-methyl-iso-butylcyclohexyl)-ethanes.
44	m-methyl-isobutylbenzene	di-(m-methyl-isobutylphenyl)-ethanes	di-(m-methyl-iso-butylcyclohexyl)-ethanes.
45	p-methyl-isobutylbenzene	di-(p-methyl-isobutylphenyl)-ethanes	di-(p-methyl-iso-butylcyclohexyl)-ethanes.
46	o-methyl-tert-butylbenzene	di-(o-methyl-tert-butylphenyl)-ethanes	di-(o-methyl-tert-butylcyclohexyl)-ethanes.
47	m-methyl-tert-butylbenzene	di-(m-methyl-tert-butylphenyl)-ethanes	di-(m-methyl-tert-butylcyclohexyl)-ethanes.
48	p-methyl-tert-butylbenzene	di-(p-methyl-tert-butylphenyl)-ethanes	di-(p-methyl-tert-butylcyclohexyl)-ethanes.
49	o-ethyl-n-propylbenzene	di-(o-ethyl-n-propylphenyl)-ethanes	di-(o-ethyl-n-propylcyclohexyl)-ethanes.
50	m-ethyl-n-propylbenzene	di-(m-ethyl-n-propylphenyl)-ethanes	di-(m-ethyl-n-propylcyclohexyl)-ethanes.
51	p-ethyl-n-propylbenzene	di-(p-ethyl-n-propylphenyl)-ethanes	di-(p-ethyl-n-propylcyclohexyl)-ethanes.
52	o-ethyl-isopropylbenzene	di-(o-ethyl-isopropylphenyl)-ethanes	di-(o-ethyl-isopropylcyclohexyl)-ethanes.
53	m-ethyl-isopropylbenzene	di-(m-ethyl-isopropylphenyl)-ethanes	di-(m-ethyl-isopropylcyclohexyl)-ethanes.
54	p-ethyl-isopropylbenzene	di-(p-ethyl-isopropylphenyl)-ethanes	di-(p-ethyl-isopropylcyclohexyl)-ethanes.
55	1,2-dimethyl-3-propylbenzene	di-(1,2-dimethyl-3-propylphenyl)-ethanes	di-(1,2-dimethyl-3-propylcyclohexyl)-ethanes.
56	1,2-dimethyl-4-propylbenzene	di-(1,2-dimethyl-4-propylphenyl)-ethanes	di-(1,2-dimethyl-4-propylcyclohexyl)-ethanes.
57	1,3-dimethyl-2-propylbenzene	di-(1,3-dimethyl-2-propylphenyl)-ethanes	di-(1,3-dimethyl-2-propylcyclohexyl)-ethanes.
58	1,3-dimethyl-4-propylbenzene	di-(1,3-dimethyl-4-propylphenyl)-ethanes	di-(1,3-dimethyl-4-propylcyclohexyl)-ethanes.
59	1,3-dimethyl-5-propylbenzene	di-(1,3-dimethyl-5-propylphenyl)-ethanes	di-(1,3-dimethyl-5-propylcyclohexyl)-ethanes.
60	1,4-dimethyl-2-propylbenzene	di-(1,4-dimethyl-2-propylphenyl)-ethanes	di-(1,4-dimethyl-5-propylcyclohexyl)-ethanes.
61	1,2-dimethyl-3-isopropylbenzene	di-(1,2-dimethyl-3-isopropylphenyl)-ethanes	di-(1,2-dimethyl-3-isopropylcyclohexyl)-ethanes.
62	1,2-dimethyl-4-isopropylbenzene	di-(1,2-dimethyl-4-isopropylphenyl)-ethanes	di-(1,2-dimethyl-4-isopropylcyclohexyl)-ethanes.
63	1,3-dimethyl-2-isopropylbenzene	di-(1,3-dimethyl-2-isopropylphenyl)-ethanes	di-(1,3-dimethyl-2-isopropylcyclohexyl)-ethanes.
64	1,3-dimethyl-4-isopropylbenzene	di-(1,3-dimethyl-4-isopropylphenyl)-ethanes	di-(1,3-dimethyl-4-isopropylcyclohexyl)-ethanes.
65	1,3-dimethyl-5-isopropylbenzene	di-(1,3-dimethyl-5-isopropylphenyl)-ethanes	di-(1,3-dimethyl-5-isopropylcyclohexyl)-ethanes.
66	1,4-dimethyl-2-isopropylbenzene	di-(1,4-dimethyl-2-isopropylphenyl)-ethanes	di-(1,4-dimethyl-2-isopropylcyclohexyl)-ethanes.
67	n-amylbenzene	di-(n-amylphenyl)-ethanes	di-(n-amylcyclohexyl)-ethanes.
68	pri-isoamylbenzene	di-(pri-isoamylphenyl)-ethanes	di-(pri-isoamylcyclohexyl)-ethanes.
69	sec-isoamylbenzene	di-(sec-isoamylphenyl)-ethanes	di-(sec-isoamylcyclohexyl)-ethanes.
70	tert-amylbenzene	di-(tert-amylphenyl)-ethanes	di-(tert-amylcyclohexyl)-ethanes.
71	C_{11} aromatic fraction	di-(C_5[d] alkylphenyl)-ethanes	di-(C_5[d] alkylcyclohexyl)-ethanes.

[a] C_2 alkyl groups include ethyl-, and two methyl groups.
[b] C_3 alkyl groups include three methyl-, methyl- and ethyl-, propyl- and isopropyl groups.
[c] C_4 alkyl groups include two methyl- and one ethyl-, two ethyl-, a methyl- and propyl-, a methyl- and isopropyl-, n-butyl-, isobutyl-, tert-butyl groups.
[d] C_5 alkyl groups include two ethyl- and one methyl-, ethyl-, and one propyl-, one ethyl-, and one isopropyl-, one methyl- and one n-butyl-, one methyl- and one isobutyl-, one methyl- and one sec-butyl-, one methyl- and one tert-butyl-, one n-pentyl-, the several branched and unbranched primary pentyl-, the several isopentyls-, two sec-pentyls-, tert-pentyl, and neopentyl groups.

In Example XI and in the examples of Table II, the alkyl benzenes employed for illustrative purposes include alkyl substituted benzenes for which: (*a*) the total number of carbon atoms of the alkyl group or groups on the benzene is 1 to 5, but other alkyl groups containing 6 to 13 carbon atoms likewise can be employed; (*b*) alkyl benzenes with two different alkyl groups are substituted on the benzene, but alkyl benzene with three different alkyl groups substituted on the benzene likewise can be employed; (*c*) position isomer mixtures are prepared from a single alkyl benzene, but the mixture of different alkyl benzenes or one or more alkylbenzenes and benzene can likewise be employed to produce a larger number of position isomer precursors compounds and their hydrogenated products in which R_1 and R_2 of Formulae I and IV are different alkyl substituents.

While Table II and the tables hereinafter show examples of the position isomers according to Formulae II and the hydrogenated products according to Formula I, the tables are understood to also exemplify the partial hydrogenated products according to Formulae VIII and IX; and it is further understood that there are exemplified herein the higher position isomers (prepared by increasing the ratio of bridging compound to the alkyl benzene compound in the reaction) according to Formulae V and VI, and the hydrogenated products thereof according to Formulae II and III, and also the partial hydrogenated products of Formulae V and VI and combinations of these.

The condensation of acetaldehyde with toluene of Example XI and the condensation of the examples of Table II can alternately be carried out with boron fluoride catalysts or with BF_3-phenol complex, BF_3-ether complex, BF_3-methanol complex, and the like BF_3 catalysts. A preferred catalyst is P_2O_5 or polyphosphoric acids in H_2SO_4, since these serve to remove the water of reaction according to the following reactions and thus maintain constant concentration of the sulfuric acid:

(1)
$$CH_3CHO + 2CH_3C_6H_5(\text{toluene}) \xrightarrow{H_2SO_4} CH_3CH(CH_3C_6H_5)_2 + H_2O$$

(2)
$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

with such a catalyst higher production per unit weight of H_2SO_4 is obtained.

EXAMPLE XII

(*a*) *Mixture of 1,1-Di-(Tolyl)-Ethanes*

A 4-liter glass reaction vessel, cooled with an ice/water bath, was charged with 1,196 grams toluene (13 moles), 14 grams mercuric sulfate, and 257 grams of 97.4% sulfuric acid. Commercial acetylene from its pressure tank (containing acetone solvent to stabilize it) was bubbled through a water scrubber and sulfuric acid drying chamber, and thence into the toluene-acid catalyst mixture, wherein the acetylene was rapidly absorbed and reacted. The rate of acetylene addition was adjusted to maintain a reaction temperature not over about 15° C. Over a period of 10 hours about 4.50 moles (117 grams) acetylene were absorbed. During the absorption of the acetylene, the color of the mixture turned gradually to yellow, orange, red, brown, and dark brown successively. Upon termination of the reaction, one liter of water was added and after thorough mixing the acid layer was separated, the upper layer was again washed with 1 liter of water followed by 1 liter of aqueous 3% sodium carbonate solution. The hydrocarbon layer was then dis-

tilled from a Claisen flask. Following the toluene removal by distillation, the product was distilled as follows:

Fractions	B.P., ° C./2 mm. Hg	n_D^{13}	Yield (g.)
1	154–164	1.5668	555
2	164–245	1.5868	125
3	[1] 245		164

[1] Residue.

Fraction 1 was 1,1-di-(tolyl)-ethanes and fraction 2 was di-(1-tolylethyl)-toluenes, Formula VI, $R^1=CH_3$, $m=1$, $n=2$, $p=1$ and fraction 3 was higher condensation products according to Formulae V and VI.

(b) Mixture of 1,1-Di-(Methylcyclohexyl)-Ethanes

Fraction 1, the 1,1-di-(tolyl)-ethanes in quantity of 210 grams (1 mole) was hydrogenated as in Example I, employing 41 grams of Raney nickel catalyst (Girdler G–49 catalyst) and 800 grams of methylcyclohexane as solvent. The time of hydrogenation and maximum temperature were 3.5 hours and 261° C. respectively. After removal of catalyst by filtration and methylcyclohexane by distillation and almost a quantitative yield of 1,1-di-(methylcyclohexyl)-ethane position isomers were obtained having the following properties: B.P. °C.=174–6/36 mm. Hg; M.P.=below —65° C.; $D_4^{20}=0.891$; $N_D^{20}=1.4816$; Gardner viscosity=50 centipoises @ —5° C. The elemental analysis of this position isomer mixture of 1,1-di-(methylcyclohexyl)-ethane was carbon 86.65% and hydrogen 13.48% and the combustion energy was 19,670 B.t.u./lb. (gross), 18,400 B.t.u./lb. (net) and 136,710 B.t.u./gal. (net).

Alternatively, the acetylene can be preliminarily passed through sulfuric acid-$HgSO_4$ combination to convert it to acetaldehyde which is then passed into sulfuric acid-toluene mixture. From a practical standpoint this method has the advantage of maintaining the life of the acid catalyst since the following scheme may be employed.

Step A:

$$\text{1 mole acetylene} + \text{1 mole water} \xrightarrow[H_2SO_4]{\text{Hg salt}} \text{1 mole acetaldehyde}$$

Step B:

$$\text{1 mole acetaldehyde} + \text{2 moles toluene} \xrightarrow{H_2SO_4} \text{1 mole 1,1-di-(tolyl)-ethane} + \text{1 mole water}$$

As the sulfuric acid in step A becomes depleted in water, the acid in step B is becoming diluted. Thus when equal volumes of 97% sulfuric acid are used to start operations in both steps A and B then the acid in step A becomes 100% while the acid in step B falls to 94% the acids are exchanged and the process repeats itself. When the 94% sulfuric acid in step A builds up to 100% (by supplying water to the acetylene to form acetaldehyde) and in step B when the 100% sulfuric acid is diluted to 94% (by removing water from the acetaldehyde) then the acids in the two steps can again be exchanged. The toluene, of course, may be replaced by other alkyl benzenes as set forth in Table II following Example XI.

EXAMPLE XIII

(a) Mixtures of 1,1-Di-(Tolyl)-Ethanes

This example otherwise similar to Example XII illustrates the effect when higher temperatures are employed during the acetylene absorption and reaction; 2.27 moles of acetylene were absorbed over a period of 3.75 hours at a temperature ranging from 10 to 28° C. The yield of (*a*) 1,1-di-(tolyl)-ethane position isomers was 58% of theory based on acetylene reacted and (*b*) higher condensation products accounted for the remainder of the yield (42%). The (*a*) fraction product was 214–244° C./90 mm. Hg; $N_D^{20}=1.5600$ and $D_4^{20}=0.976$.

(b) Mixtures of 1,1-Di-(Methylcyclohexyl)-Ethanes

Hydrogenation of (*a*) according to the procedure of Example I yielded quantitatively 1,1-di-(methylcyclohexyl)-methane position isomers with the following properties B.P.=167–185° C./36 mm. Hg; M.P.=below —65° C.; $D_4^{20}=0.890$; $N_D^{20}=1.4895$; viscosity=320 centipoises at —20° C. and the energy of combustion=19,550 B.t.u./lb. (gross); 18,280 B.t.u./lb. (net); 135,640 B.t.u./gallon (60° F.) (net).

In an alternative procedure under the same conditions, I can employ BF_3 complexes with water or, alcohols or, phenols or, ethers or acids, etc. in the presence of a mercuric compound such as mercuric oxide, mercuric acetate or sulfate, to replace the sulfuric acid of the above preparation. In this case, addition of a trace amount of water to the reaction mixture is helpful to initiate the reaction.

EXAMPLE XIV

(a) Mixture of 1,1-Di-(Tolyl)-Ethanes

The procedure of Example XII was repeated using a mixture of ethylene and acetylene (ratio 40/60). In this example 828 grams of toluene, (9 moles), 119 grams of 97.3% sulfuric acid (1.28 moles), 7 grams $HgSO_4$ (0.023 mole), and 0.465 mole acetylene (12.1 g.) together with ethylene were reacted at a temperature of 4 to 6° C. in a reaction time of 2 hours. The reaction mixture was poured into 700 ml. water after the reaction was completed. The hydrocarbon layer was separated and washed free of acid and distilled. The mixture of 1,1-di-(tolyl)-ethane position isomers were obtained in 88% yield based on the acetylene absorbed. The properties thereof were: B.P.=115–123° C./1 mm. Hg, and $N_D^{20}=1.5665$.

(b) Mixtures of 1,1-Di-(Methylcyclohexyl)-Ethanes

Hydrogenation of the position isomers of this 1,1-di-(tolyl)-ethane as in Example XII yielded a similar high energy fuel comprising a mixture of the position isomers of 1,1-di-(methylcyclohexyl)-ethanes.

EXAMPLE XIV–A

(a) Mixture of 1,1-Di-(Ethylmethylphenyl)-Ethanes

The procedure of Example XIV was repeated employing 368 grams (4 moles) of toluene, 408 grams (4 moles) of 97% sulfuric acid, 68 grams (1 mole) of boron fluoride and in a pressure vessel was added 112 grams (4 moles) of ethylene (as in Example VIII–A) and after the ethylene reacted then 26 grams (1 mole) of acetylene was gradually added and reacted. The product was recovered (as in Example XIV) yielding principally a mixture of position isomers of 1,1-di-(ethylmethylphenyl)-ethanes.

(b) Mixture of 1,1-Di-(Ethylmethylcyclohexyl)-Ethanes

The 1,1-di-(ethylmethylphenyl)-ethanes of (*a*) above was hydrogenated according to Example XII (*b*) and the recovered product was principally a mixture of position isomers of 1,1-di-(ethylmethylcyclohexyl)-ethanes which had a net fuel value greater than 135,000 B.t.u./gallon.

EXAMPLE XV

(a) Mixture of 1,1-Di-(Tolyl)-Ethanes

Example XIV was repeated, but omitting the ethylene from the feed. The results were similar. From 11.1 g. of acetylene a 90% yield of 1,1-di-(tolyl)-ethanes resulted having $N_D^{20}=1.5650$; $D_4^{20}=0.981$; M.P.=below —65° C.; and a viscosity=50 poises @ —25° C.

(b) Mixture of 1,1-Di-(Methylcyclohexyl)-Ethanes

Hydrogenation of 84 g. of this product was conducted at 100–180° C. with 700 to 1100 p.s.i. hydrogen over Raney nickel (16.8 g.) as the catalyst for a 6 hour period. About 90% yield of a mixture of position isomers of 1,1-di-(methylcyclohexyl)-ethane resulted after filtering the

product and distilling to remove methylcyclohexane solvent and without further fractionation, the product had the following properties: D_4^{20}=0.891; N_D^{20}=1.4815; M.P.=below −65° C.; viscosity=5 poises @ −25° C. and energy of combustion=19,825 B.t.u./lb. (gross); 18,555 B.t.u./lb. (net); 137,865 B.t.u./gallon (net).

EXAMPLE XVI

(a) *Mixture of 1,1-Di-(Xylyl)-Ethanes*

In this example 1378 grams (13 moles) of mixed xylenes (xylene fraction of same composition as set forth in Example VI) was reacted with 104 grams of acetylene (freed of acetone) in the presence of 257 grams 97.4% sulfuric acid and 14 grams $HgSO_4$ over a period of 7 hours at 5 to 20° C. A 57% yield was obtained of a mixture of 1,1-di-(xylyl)-ethanes, 1,1-di(ethylphenyl)-ethanes and 1-(xylyl)-1-(ethylphenyl)-ethanes containing small amounts of analogous components containing the tolyl substituents. The properties of the 1,1-di-(xylyl)-ethanes were: B.P.= 136–160° C./4 mm. Hg, N_D^{20}=1.5665.

(b) *Mixture of 1,1-Di-(Dimethylcyclohexyl)-Ethanes*

In this Example XVI a material, 238 grams (one mole) in 800 grams methylcyclohexane was hydrogenated over Raney nickel (48 grams) according to the procedures of Example I, at 1000 to 1300 p.s.i. hydrogen pressure and in the temperature range 140 to 214° C. for 6 hours. The recovered high energy fuel (95% yield) had the following properties: B.P.=136–141° C. at 2 mm. Hg, M.P.= below −70° C., D_4^{20}=0.893, N_D^{20}=1.4845, viscosity= 50 centipoises @ 20° C. or 98.5 poises @ −30° C.

The elemental analysis was 86.90% carbon and 13.52% hydrogen and the energy of combustion was 19,715 B.t.u./lb. (gross), 18,440 B.t.u./lb. (net), 137,285 B.t.u./gallon (net).

EXAMPLE XVII

(a) *Mixtures of 1,2-Di-(Tolyl)-Ethanes*

The procedure of Example XI was repeated substituting ethylene glycol for the acetaldehyde. In this example, 1244 grams (13.5 moles) of toluene was combined with 609 grams (6 moles) of 97.3% sulfuric acid as catalyst, and 186 grams (3 moles) of ethylene glycol were added over a period of 3 hours, the mixture being maintained at 2–4° C. After addition was complete, the temperature of the mixture was raised to and maintained at 40° C. for 1.5 hours. The acid layer was separated, the upper layer was washed with 1 liter of water and then with 1 liter 1% soda ash solution. Distillation of the washed product removed the unreacted toluene and yielded di-(tolyl)-ethane position isomers having N_D^{20}=1.5371.

(b) *Mixtures of 1,2-Di-(Methylcyclohexyl)-Ethanes*

The 1,2-di-(tolyl)-ethanes were hydrogenated as in Example I to give a high energy fuel of this invention, a mixture of the position isomers of 1,2-di-(methylcyclohexyl)-ethanes.

EXAMPLE XVIII

(a) *Mixtures of 1,2-Di-(Isopropylphenyl)-Ethanes*

A 4-liter glass vessel equipped with a condenser, agitator, thermometer and opening for addition of reactants was immersed in an ice bath and the following reactants were added: 720 grams (6 moles) of cumene, 85 grams (1 mole) 1,2-dichloroethane. The temperature of the reactants were allowed to fall to 5° C. and 65 grams (0.5 mole) of freshly sublimed aluminum chloride added in increments over 15 minutes and hydrogen chloride fumes were given off. The mixture was allowed to stand overnight with the temperature rising to room temperature as the ice in the cooling bath melted. The reaction mixture was added to 700 grams of ice and 30 ml. of concentrated hydrochloric acid and the mass heated to reflux then cooled to 50° C. and the hydrocarbon layer separated and washed first with 1 liter of 1% hydrochloric acid and then with 1 liter of water and the unreacted cumene distilled off. The resulting hydrocarbon was principally a mixture of the position isomers of 1,2-di-(isopropylphenyl)-ethanes.

(b) *Mixtures of 1,2-Di-(Isopropylcyclohexyl)-Ethanes*

The product comprising 1,2-di-(isopropylphenyl)-ethanes was hydrogenated employing Raney nickel catalyst and methylcyclohexane as solvent according to the procedure of Example I and the resulting fuel after removal of the catalyst and the methycyclohexane was a mixture of position isomers of 1,2-di-(isopropylcyclohexyl)-methanes having a net fuel value greater than 135,000 B.t.u./gallon.

In this Example XVIII, the 720 grams of cumene (which is a substantial excess over that required for stoichiometric reaction with the 1,2-dihalopropane) may be substituted by any of the alkyl benzenes employed in Examples 1 to 12 and 14 to 70 of Table II and the di-(alkylphenyl)-ethanes formed are the same as those set forth in Table II except that the ethane bridge is substituted in the 1,2-positions instead of the 1,1-position and these products are hydrogenated to yield the di-(alkylcyclohexyl)-ethanes except that the ethane bridge is substituted in the 1,2-positions instead of the 1,1-position. In the just set forth alternate examples, the alkyl benzene employed for illustrative purposes include alkyl substituted benzenes for which: (*a*) the total carbon count of the alkyl group or groups on the benzene is 1 to 5, but 6 to 13 carbon atoms containing alkyls on the alkyl benzenes likewise can be employed; (*b*) alkyl benzenes with two different alkyl groups can be substituted on the benzene, but alkyl benzenes with three different alkyl groups substituted on the benzene likewise can be employed; (*c*) position isomer mixtures are prepared from a single alkyl benzene, but the mixture of different alkyl benzenes or one or more alkylbenzenes and benzene can likewise be employed to produce a larger number of position isomer precursor compounds and their hydrogenated products in which R_1 and R_2 of Formulae I and IV are different alkyl substituents.

EXAMPLE XIX

(a) *Mixtures of 1,1-Di-(Tolyl)-Propanes*

In this example, 1658 grams (18 moles) of toluene were condensed with 162.4 grams (2.8 moles) of propionaldehyde, and 406 grams (4 moles) of 97.6% sulfuric acid was used as catalyst as in Example XI. The reaction was conducted in an agitated glass vessel cooled in an ice bath. The propionaldehyde was added dropwise over a period of 125 minutes and the temperature of the reactants held at 6–10° C. On completion of addition of the aldehyde, the reaction was allowed to run another 25 minutes then the hydrocarbon layer separated and washed free of acid and distilled. The yield of 1,1-di-(tolyl)-propane position isomers was 144.5 grams (23% yield) and about 68 grams of 1-tolyl)-propane (18% yield). The properties of the 1,1-di-(tolyl)-propane position isomers were: B.P. 275–375° C. @ 760 mm. Hg, N_D^{20}=1.5310; D_4^{20}=0.958, F.P.=below −65° C.

(b) *Mixture of 1,1-Di-(Methylcyclohexyl)-Propanes*

One hundred grams of the product the 1,1-di-(tolyl)-propane position isomers was hydrogenated with 20 grams of Raney nickel catalyst according to the procedure at 1000 p.s.i. hydrogen pressure and a temperature of 200 to 236° C. for 24 hours. The recovered mixed position isomers of 1,1-di-(methylcyclohexyl)-propane had the following properties: B.P=285–330° C.; 760 mm. Hg (90% cut), N_D^{20}=1.4790; D_4^{20}=0.891; F.P.=below −65° C.; viscosity=35 poises at −25° C. The energy of combustion was 19,407 B.t.u./lb. (gross), 18,130 B.t.u./lb. (net), 134,670 B.t.u./gallon (net). Following

the procedure of Example XIX, but for the 18 moles of toluene, substituting 18 moles (a substantial excess over that required for stoichiometric reaction with the propionaldehyde) of other alkylbenzenes, corresponding 1,1-di-(alkylphenyl)-propane position isomer mixtures are produced which, when hydrogenated, give the corresponding 1,1-di-(alkylcyclohexyl)-propane position isomers as set forth in the following table:

zene likewise can be employed; (*c*) position isomer mixtures are prepared from a single alkylbenzene, but the mixture of different alkylbenzenes or one or more alkylbenzenes and benzene can likewise be employed to produce a larger number of position isomer precursor compounds and their hydrogenated products in which R_1 and R_2 of Formulae I and IV are different alkyl substituents.

Alternately, the method of Example XIX and Exam-

TABLE III.—MIXTURE OF POSITION ISOMERS

No.	Alkylbenzene	1,1-di-(alkylphenyl)-propanes	1,1-di-(alkylcyclohexyl)-propanes
1	ethylbenzene	di-(ethylphenyl)-propanes	di-(ethylcyclohexyl)-propanes.
2	o-xylene	di-(o-xylyl)-propanes	di-(1,2-dimethylcyclohexyl)-propanes.
3	m-xylene	di-(m-xylyl)-propanes	di-(1,3-dimethylcyclohexyl)-propanes.
4	p-xylene	di-(p-xylyl)-propanes	di-(1,4-dimethylcyclohexyl)-propanes.
5	C_8 aromatic fraction	di-(C_8[a] alkylphenyl)-propanes	di-(C_8[a] alkylcyclohexyl)-propanes.
6	o-ethyltoluene	di-(o-ethyltolyl)-propanes	di-(o-ethyl-methylcyclohexyl)-propanes.
7	m-ethyltoluene	di-(m-ethyltolyl)-propanes	di-(m-ethyl-methylcyclohexyl)-propanes.
8	p-ethyltoluene	di-(p-ethyltolyl)-propanes	di-(p-ethyl-methylcyclohexyl)-propanes.
9	1,2,3-trimethylbenzene	di-(1,2,3-trimethylphenyl)-propanes	di-(1,2,3-trimethylcyclohexyl)-propanes.
10	1,2,4-trimethylbenzene	di-(1,2,4-trimethylphenyl)-propanes	di-(1,2,4-trimethylcyclohexyl)-propanes.
11	1,3,5-trimethylbenzene	di-(1,3,5-trimethylphenyl)-propanes	di-(1,3,5-trimethylcyclohexyl)-propanes.
12	n-propylbenzene	di-(n-propylphenyl)-propanes	di-(n-propylcyclohexyl)-propanes.
13	isopropylbenzene	di(isopropylphenyl)-propanes	di-(isopropylcyclohexyl)-propanes.
14	C_9 aromatic fraction	di-(C_9[b] alkylphenyl)-propanes	di-(C_9[b] alkylcyclohexyl)-propanes.
15	o-n-propyltoluene	di-(o-n-propyltolyl)-propanes	di-(o-n-propylmethylcyclohexyl)-propanes.
16	m-n-propyltoluene	di-(m-n-propyltolyl)-propanes	di-(m-n-propylmethylcyclohexyl)-propanes.
17	p-n-propyltoluene	di-(p-n-propyltolyl)-propanes	di-(p-n-propylmethylcyclohexyl-)propanes.
	mixed isomers of propyltoluene	di-(o-, m-, and p-propyltolyl)-propanes	di-(o-, m-, and p-propylmethylcyclohexyl)-propanes.
18	o-isopropyltoluene	di-(o-isopropyltolyl)-propanes	di-(o-isopropylmethylcyclohexyl)-propanes.
19	m-isopropyltoluene	di(m-isopropyltolyl-)propanes	di-(m-isopropylmethylcyclohexyl)-propanes.
20	p-isopropyltoluene	di-(p-isopropyltolyl)-propanes	di-(p-isopropylmethylcyclohexyl)-propanes.
21	1,2-diethylbenzene	di-(1,2-diethylphenyl)-propanes	di-(1,2-diethylcyclohexyl)-propanes.
22	1,3-diethylbenzene	di-(1,3-diethylphenyl)-propanes	di-(1,3-diethylcyclohexyl)-propanes.
23	1,4-diethylbenzene	di-(1,4-diethylphenyl)-propanes	di-(1,4-diethylcyclohexyl)-propanes.
24	1,2-dimethyl-3-ethylbenzene	di-(1,2-dimethyl-3-ethylphenyl)-propanes	di-(1,2-dimethyl-3-ethylcyclohexyl)-propanes.
25	1,2-dimethyl-4-ethylbenzene	di-(1,2-dimethyl-4-ethylphenyl)-propanes	di-(1,2-dimethyl-4-ethylcyclohexyl)-propanes.
26	1,3-dimethyl-2-ethylbenzene	di-(1,3-dimethyl-2-ethylphenyl)-propanes	di-(1,3-dimethyl-2-ethylcyclohexyl)-propanes.
27	1,3-dimethyl-4-ethylbenzene	di-(1,3-dimethyl-4-ethylphenyl)-propanes	di-(1,3-dimethyl-4-ethylcyclohexyl)-propanes.
28	1,3-dimethyl-5-ethylbenzene	di-(1,3-dimethyl-5-ethylphenyl)-propanes	di-(1,3-dimethyl-5-ethylcyclohexyl)-propanes.
29	1,4-dimethyl-2-ethylbenzene	di-(1,4-dimethyl-2-ethylphenyl)-propanes	di-(1,4-dimethyl-2-ethylcyclohexyl)-propanes.
30	n-butylbenzene	di-(n-butylphenyl)-propanes	di-(n-bthylcyclohexyl)-propanes.
31	Sec-butylbenzene	di-(sec-butylphenyl)-propanes	di-(sec-butylcyclohexyl)-propanes.
32	tert-butylbenzene	di-(tert-butylphenyl)-propanes	di-(tert-butylcyclohexyl)-propanes.
33	C_{10} aromatic fraction	di-(C_4[c] alkylphenyl)-propanes	di-(C_4[c] alkylcyclohexyl)-propanes.
34	1,2-diethyl-3-methylbenzene	di-(1,2-diethyl-3-methylphenyl)-propanes	di-(1,3-diethyl-3-methylcyclohexyl)-propanes.
35	1,2-diethyl-4-methylbenzene	di-(1,2-diethyl-4-methylphenyl)-propanes	di-(1,2-diethyl-4-methylcyclohexyl)-propanes.
36	1,3-diethyl-2-methylbenzene	di-(1,3-diethyl-2-methylphenyl)-propanes	di-(1,3-diethyl-2-methylcyclohexyl)-propanes.
37	1,3-diethyl-4-methylbenzene	di-(1,3-diethyl-4-methylphenyl)-propanes	di-(1,3-diethyl-4-methylcyclohexyl)-propanes.
38	1,3-diethyl-5-methylbenzene	di-(1,3-diethyl-5-methylphenyl)-propanes	di-(1,3-diethyl-5-methylcyclohexyl)-propanes.
39	1,4-diethyl-2-methylbenzene	di-(1,4-diethyl-2-methylphenyl)-propanes	di-(1,4-diethyl-2-methylcyclohexyl)-propanes.
40	o-methyl-n-butylbenzene	di-(o-methyl-n-butylphenyl)-propanes	di-(o-methyl-n-butylcyclohexyl)-propanes.
41	m-methyl-n-butylbenzene	di-(m-methyl-n-butylphenyl)-propanes	di-(m-methyl-n-butylcyclohexyl)-propanes.
42	p-methyl-isobutylbenzene	di-(p-methyl-n-butylphenyl)-propanes	di-(p-methyl-n-butylcyclohexyl)-propanes.
43	o-methyl-isobutylbenzene	di-(o-methyl-isobutylphenyl)-propanes	di-(o-methyl-isobutylcyclohexyl)-propanes.
44	m-methyl-isobutylbenzene	di-(m-methyl-isobutylphenyl)-propanes	di-(m-methyl-isobutylcyclohexyl)-propanes.
45	p-methyl-isobutylbenzene	di-(p-methyl-isobutylphenyl)-propanes	di-(p-methyl-isobutylcyclohexyl)-propanes.
46	o-methyl-tertbutylbenzene	di-(o-methyl-tert-butylphenyl)-propanes	di-(o-methyl-tertbutylcyclohexyl)-propanes.
47	m-methyl-tertbutylbenzene	di-(m-methyl-tertbutylphenyl)-propanes	di-(m-methyl-tertbutylcyclohexyl)-propanes.
48	p-methyl-tertbutylbenzene	di-(p-methyl-tertbutylphenyl)-propanes	di-(p-methyl-tertbutylcyclohexyl)-propanes.
49	o-ethyl-n-propylbenzene	di-(o-ethyl-n-propylphenyl-propanes	di-(o-ethyl-n-propylcyclohexyl)-propanes.
50	m-ethyl-n-propylbenzene	di-(m-ethyl-n-propylphenyl)-propanes	di-(methyl-n-propylcyclohexyl)-propanes.
51	p-ethyl-n-propylbenzene	di-(p-ethyl-n-propylphenyl)-propanes	di-(p-ethyl-n-propylcyclohexyl)-propanes.
52	o-ethyl-iso-propylbenzene	di-(o-ethyl-isopropylphenyl)-propanes	di-(o-ethyl-isopropylcyclohexyl)-propanes.
53	m-ethyl-iso-propylbenzene	di-(m-ethyl-isopropylphenyl)-propanes	di-(m-ethyl-isopropylcyclohexyl)-propanes.
54	p-ethyl-iso-propylbenzene	di-(p-ethyl-isopropylphenyl)-propanes	di-(p-ethyl-isopropylcyclohexyl)-propanes.
55	1, 2-dimethyl-3-propylbenzene	di-(1,2-dimethyl-3-propylphenyl)-propanes	di-(1, 2-dimethyl-3-propylcyclohexyl)-propanes.
56	1, 2-dimethyl-4-propylbenzene	di-(1,2-dimethyl-4-propylphenyl)-propanes	di-(1, 2-dimethyl-4-propylcyclohexyl)-propanes.
57	1, 3-dimethyl-2-propylbenzene	di-(1,3-dimethyl-2-propylphenyl)-propanes	di-(1-3-dimethyl-2-propylcyclohexyl)-propanes.
58	1, 3-dimethyl-4-propylbenzene	di-(1,3-dimethyl-4-propylphenyl)-propanes	di-(1, 3-dimethyl-4-propylcyclohexyl)-propanes.
59	1,3-dimethyl-5-propylbenzene	di-(1,3-dimethyl-5-propylphenyl)-propanes	di-(1,3-dimethyl-5-propylcyclohexyl)-propanes.
60	1,4-dimethyl-2-propylbenzene	di-(1,4-dimethyl-2-propylphenyl)-propanes	di-(1,4-dimethyl-2-propylcyclohexyl)-propanes.
61	1,2-dimethyl-3-iscpropylbenzene	di-(1,2-dimethyl-3-isopropylphenyl)-propanes	di-(1,2-dimethyl-3-isopropylcyclohexyl)-propanes.
62	1,2-dimethyl-4-isopropylbenzene	di-(1,2-dimethyl-4-isopropylphenyl)-propanes	di-(1,2-dimethyl-4-isopropylcyclohexyl)-propanes.
63	1,3-dimethyl-2-iscpropylbenzene	di-(1,3-dimethyl-2-isopropylphenyl)-propanes	di-(1,3-dimethyl-2-isopropylcyclohexyl)-propanes.
64	1,3-dimethyl-4-isopropylbenzene	di-(1,3-dimethyl-4-isopropylphenyl)-propanes	di-(1,3-dimethyl-4-isopropylcyclohexyl)-propanes.
65	1,3-dimethyl-5-isopropylbenzene	di-(1,3-dimethyl-5-isopropylphenyl)-propanes	di-(1,3-dimethyl-5-isopropylcyclohexyl)-propanes.
66	1,4-dimethyl-2-isopropylbenzene	di-(1,4-dimethyl-2-isopropylphenyl)-propanes	di-(1,4-dimethyl-2-isopropylcyclohexyl)-propanes.
67	n-amylbenzene	di-(n-amylphenyl)-propanes	di-(n-amylcyclohexyl)-propanes.
68	2-isoamylbenzene	di-(2-isoamylphenyl)-propanes	di-(2-isoamylcyclohexyl)-propanes.
69	3-isoamylbenzene	di-(3-isoamylphenyl)-propanes	di-(3-isoamylcyclohexyl)-propanes.
70	tert-amylbenzene	di-(tert-amylphenyl)-propanes	di-(tert-amylcyclohexyl)-propanes.
71	C_{11} aromatic fraction	di-(C_5[d] alkylphenyl)-propanes	di-(C_5[d] alkylcyclohexyl)-propanes.

[a] C_8 alkyl groups include ethyl-, and two methyl- groups.
[b] C_9 alkyl groups include three methyl-, methyl- and ethyl-, propyl-, and isopropyl-groups.
[c] C_4 alkyl groups include two methyl- and one ethyl-, two ethyl-, a methyl- and propyl-, a methyl- and isopropyl-, n-butyl-, isobutyl-, tert-butyl groups.
[d] C_5 alkyl groups include two ethyl- and one methyl,- ethyl-, and one propyl-, one ethyl-, and one isopropyl-, one methyl- and one n-butyl-, one methyl- and one isobutyl-, one methyl- and one sec-butyl-, one methyl- and one tert-butyl-, one n-pentyl-, the several branched and unbranched primary pentyl-, the several isopentyls-, two sec-pentyls-, tert-pentyl and neopentyl groups.

In Example XIX and in the examples of Table III, the alkyl benzenes include alkyl substituted benzenes for which: (*a*) the total carbon atom content of the alkyl group or groups on the benzene is 1 to 5, but 6 to 13 carbon atom alkyls can likewise be employed on the alkyl benzenes; (*b*) alkylbenzenes with two different alkyl groups are substituted on the benzene, but alkylbenzenes with three different alkyl groups substituted on the benzene likewise can be employed; (*c*) position isomer mixtures are prepared from a single alkylbenzene, but the mixture of different alkylbenzenes or one or more alkylbenzenes and benzene can likewise be employed to produce a larger number of position isomer precursor compounds and their hydrogenated products in which R_1 and R_2 of Formulae I and IV are different alkyl substituents.

Alternately, the method of Example XIX and Examples 1 to 70 of Table III can be modified by employing in place of the sulfuric acid such acids as hydrofluoric, or combinations such as sulfuric acid with phosphorous pentoxide or sulfuric acid with the polyphosphoric or metaphosphoric acids. Slightly different position isomer compositions were obtained in the final hydrogenated fuels in comparison with the compositions obtained when using sulfuric acid catalyst, indicating that variations of

catalyst can vary the particular position isomer relationship of the mixture.

While Table III and the tables herein after show examples of the position isomers according to Formulae II and the hydrogenated products according to Formula I, the tables are understood to also exemplify the partial hydrogenated products according to Formulae VIII and IX; and it is further understood that there are exemplified herein the higher position isomers (prepared by increasing the ratio of bridging compound to the alkyl benzene compound in the reaction) according to Formulae V and VI, and the hydrogenated products thereof according to Formulae II and III, and also the partial hydrogenated products of Formulae V and VI and combinations of these.

EXAMPLE XX

(*a*) *Mixture of 1,1-Di-(Xylyl)-Propanes*

Propionaldehyde was reacted with xylenes (the commerical xylenes employed are described in Example VI). In this reaction 1698 grams (16 moles) of mixed xylenes (Sinclair Petrochemicals Inc.) were reacted with 169 grams (2.9 moles) of propionaldehyde employing 507.5 grams (5 moles) of 97.4% sulfuric acid as catalyst. The glass reactor was cooled with ice and the temperature of the reactants was 3–4° C. during the period of 5.6 hours required for the propionaldehyde addition and was 2° C. for the 0.9 hour of stirring thereafter. After removal of excess xylenes by distillation about 50 grams of product was obtained distilling between 165–300° C. at 745 mm. Hg with refractive index $N_D^{20}=1.5500$, $D_4^{20}=0.970$, F.P.=−54° C. and a viscosity of 85 centipoises at 35° C. A residue of 15 grams dark solid remained. The main fraction represented a yield of 1.6 moles of 1,1-di-(xylyl)-propanes admixed with 1,1-di-(ethylphenyl)-propanes and 1-(xylyl)-1-(ethylphenyl)-propanes.

(*b*) *Mixtures of 1,1-Di-(Dimethylcyclohexyl)-Propanes*

Hydrogenation of 258 grams of the product of (*a*) above with the aid of 52 grams of Raney nickel catalyst (Girdler catalyst #G–49) at 200 to 236° C. with 800 grams methylcyclohexane as solvent according to the procedure of Example I gave about 90% yield of hydrogenated fuel comprising: 1,1-di-(dimethylcyclohexyl)-propanes mixed with 1,1-di-(ethylcyclohexyl)-propanes and 1-(dimethylcyclohexyl)-1-(ethylcyclohexyl)-propanes, containing the numerous position isomers of each of the total mixture having the following characteristics: B.P.=300–400° C./745 mm. Hg, F.P.=below −65° C., $D_4^{20}=0.907$, $N_D^{20}=1.4988$, viscosity=0.5 poise @ 31° C., 148 poises at −25° C., and with an energy of combustion of 19,510 B.t.u./lb. (gross), 18,230 B.t.u./lb. (net), 137,825 B.t.u./gallon (net).

EXAMPLE XXI

(*a*) *Mixture of 1,2-Di-(Xylyl)-Propanes*

A 4 liter glass vessel equipped with a condenser, agitator, thermometer and opening for addition of reactants was immersed in a 20° C. water bath and the following reactants were added: 848 grams (8 moles) of mixed xylenes, 120 grams (0.9 mole) of freshly sublimed aluminum chloride and over 2.5 hours 226 grams (2 moles) of 1,2-dichloropropane was added dropwise. The temperature of the reactants remained at 25° C. during addition of the 1,2-dichloropropane. The reaction vessel was removed from the water bath and heated with an electric heating jacket at 37° C. and the temperature of the stirred reactants was 35° C. for 2.5 hours. The hydrocarbon reaction mixture was diluted with 1 liter of mixed xylenes and 50 ml. of concentrated hydrochloric acid and the mixture poured onto 2 kilos of ice and warmed to the reflux temperature and the hydrocarbon layer separated. The hydrocarbon layer was washed with 1 liter of water containing 25 ml. of concentrated hydrochloric acid and then washed twice again with 1 liter of water and the excess xylenes removed by distillation at atmospheric pressure.

The hydrocarbon fuel product was distilled as follows.

Fractions	B.P., ° C./745 mm. Hg	n_D^{23}	Yield (g.)
1	165–200	1.5001	56.7
2	200–300	1.5069	36.5
3	300–375	1.5501	136.4
4	375–405	1.5532	6.8
5	[1] 405	Dark oil	6.0

[1] Residue.

Fractions 1 and 2 chiefly comprise isomers of monoxylylpropane while fractions 3 and 4 contain the mixed position isomers of 1,2-di-(xylyl)-propanes.

(*b*) *Mixture of 1,2-Di-(Dimethylcyclohexane)-Propanes*

The 1,2-di-(xylyl)-propanes were hydrogenated according to the method of Example I to yield a position isomer mixture which had a net fuel value greater than 135,000 B.t.u./gallon.

Other mixtures of position isomers similar to those set forth in Examples 1 to 70 of Table III except that the propylene bridge is substituted in the 1,2-position instead of the 1,1-position are prepared in the manner set forth in (*a*) and (*b*) above.

EXAMPLE XXII

(*a*) *Mixture of 2,2-Di-(Tolyl)-Propanes*

A 4 liter glass vessel equipped with condenser, agitator, thermometer and opening for addition of reactants was immersed in a 20° C. water bath and the following reactants added: 368 grams (4 moles) of toluene, 134 grams (1 mole) of freshly sublimed aluminum chloride and over a 2 hour period was added dropwise 113 grams (1 mole) of 2,2-dichloropropane while agitating vigorously and then the temperature was raised to 35° C. and the reactants agitated for another 2 hours. The reaction mixture was worked up as in example XXI only using half the quantity of materials. The resulting product was distilled to yield a fuel comprising the position isomers of 2,2-di-(tolyl)-propane.

(*b*) *Mixture of 2,2-Di-(Methylcyclohexyl)-Propanes*

The 2.2-di-(tolyl)-propane fractions were hydrogenated according to Example I to yield a fuel of mixed position isomers of 2,2-di-(methylcyclohexyl)-propane which had a net fuel value greater than 135,000 B.t.u./gallon and excellent thermal stability.

In this Example XXII, the 368 grams (4 moles) of toluene (which is a substantial excess over that required for stoichiometric reaction with the 2,2-dichloropropane) may be substituted by any of the alkyl benzenes employed in Examples 1 to 70 of Table III except that the propylene bridge is substituted in the 2,2-position instead of the 1,1-position and these products are hydrogenated to yield the di-(alkylcyclohexyl)-propanes, except that the propane bridge is substituted in the 2,2-position instead of the 1,1-position. In the just set forth alternate examples, the alkyl benzene employed for illustrative purposes include alkyl substituted benzenes for which: (*a*) the total carbon count of the alkyl group or groups on the benzene is 1 to 5, but 6 to 13 carbon atom content alkyl groups may be present in the alkyl benzenes likewise can be employed: (*b*) alkyl benzenes with two different alkyl groups are substituted on the benzene, but alkyl benzenes with three different alkyl groups substituted on the benzene likewise can be employed: (*c*) position isomer mixtures are prepared from a single alkyl benzene, but the mixture of different alkyl benzenes or one or more alkyl benzenes and benzene can likewise be employed to produce a larger number of position isomer precursor compounds and their

hydrogenated products in which R_1 and R_2 of Formulae I and IV are different alkyl substituents.

EXAMPLE XXIII

(a) *Mixtures of Di-(Xylyl)-Propanes*

In this example, 1700 grams (16 moles) of mixed xylenes (toluene 2%, o-xylene 19%, m-xylene 48%, p-xylene 10%, ethylbenzene 21%) were reacted in a manner similar to the procedure of Example XI, with 232 grams (4 moles) of 1,2-propylene oxide instead of paraformaldehyde, using 406 grams (5 moles) of 96.98% sulfuric acid. The propylene oxide was added dropwise over a 3 hour period to the stirring mixture of xylenes and sulfuric acid maintained at a temperature between 10 and 11° C. in a glass reaction vessel cooled with an ice bath. The reaction vessel was then heated and stirred for 2 hours, the temperature remaining in the range 40–52° C. During addition of the propylene oxide, the color changed to slight orange and then to purple, during the heating stage the color changed to deep orange.

The hydrocarbon layer was separated and washed first with 1 liter of water, and then 1 liter of 3% sodium carbonate aqueous solution, then again with 1 liter of water and the residual xylenes removed by distillation.

The following fractions were obtained:

Fractions	B.P., ° C./745 mm. Hg	N_D^{20}	Yield (grams)
1	154–177	1.4970	36.2
2	177–205	1.4989	14.2
3	205–232	1.4998	18.0
4	232–260	1.5100	14.6
5	260–288	1.5260	9.4

(b) *Mixtures of Di-(Dimethylcyclohexyl)-Propanes*

Fractions 2 to 5 were combined and this mixed fraction containing the di-(xylyl)-propane position isomers. This mixed fraction when hydrogenated according to the procedure of Example I yields a high energy fuel with a net energy of combustion greater than 135,000 B.t.u./gallon.

(c) *Mixture of 1,3-Di-(Xylyl)-Propanes*

The 4 moles of 1,2 propylene oxide are substituted by 304 grams (4 moles) of propanediol-1,3 and the reaction carried out as in (a) above to pield the position isomers of 1,3-di-(xylyl)-propane.

(d) *Mixture of 1,3-Di-(Dimethylcyclohexyl)-Propanes*

The mixtures of 1,3-di-(xylyl)-propanes prepared according to (c) above was hydrogenated as in (b) above to yield the position isomers of 1,3-di-(dimethylcyclohexyl)-propanes which was a high energy fuel of net energy of combustion greater than 135,000 B.t.u./gallon.

Other mixtures of position isomers similar to those set forth in Examples 1 to 70 of Table III except that the propylene bridge is substituted in the 1,3-position instead of the 1,1-position, are prepared in the manner set forth in (c) and (d) above.

EXAMPLE XXIV

(a) *Mixtures of 1,1-Di-(Tolyl)-Butanes*

Following the procedure of Example XI, 1566 grams (17 moles) of toluene was reacted with 288 grams (4 moles) of n-butyraldehyde employing 500 grams (5 moles) of 96.7% sulfuric acid as catalyst. The aldehyde addition time was 3.5 hours and the temperature of the reactants was maintained at 3–6° C. by cooling the reaction vessel with an ice bath. After about 2 hours of additional stirring at 2–3° C. the product was diluted with 1500 ml. water and worked up as in Example XI. The unreacted toluene containing some butyraldehyde were removed by distillation and the following fractions were obtained:

Fractions	B.P., ° C./745 mm. Hg	N_D^{20}	Yield (grams)
1	163–300	1.4644–1.4703	97.8
2	320–365	1.5228–1.5469	312.6
3	Residue	Dark solid	23.3

Fraction 3 had D_4^{20} of 0.956 and by analysis corresponds to the expected mixture of position isomers of 1,1-di-(tolyl)-butane. Fraction 1 appears to contain some 1-tolyl-butane and 1-tolyl-octane (from reaction of butyraldehyde condensation product with toluene). The amount of butyraldehyde reacted was 3 moles with one mole (72 grams) being recoverable for re-use by distillation directly from the reaction mixture. Based on 3 moles butyraldehyde the yields were approximately: 43% 1,1-di-(tolyl)-butane, 22% 1-tolyl-butane, 4% higher condensation products.

(b) *Mixtures of 1,1-Di-(Methylcyclohexyl)-Butanes*

Of this di-(tolyl)-butane, 119 grams was hydrogenated, according to the procedure of Example I, in 800 grams of methylcyclohexane with 24 grams Raney type nickel catalyst (Girdler 49–A catalyst) at 100–210° C. under 1000 p.s.i. hydrogen pressure. The recovered product from the hydrogenation amounted to 144 grams which represents the position isomers of 1,1-di-(methylcyclohexyl)-butane in substantially quantitative yield after consideration of handling losses.

The properties of this 1,1-di-(methylcyclohexyl)-butane fraction was as follows: B.P.=300°–330° C. at 745 mm. Hg, N_D^{20}=1.4798, D_4^{20}=0.884, F.P.=below −65° C., viscosity=98.5 poises @ −25° C., and the energy of combustion 19,630 B.t.u./lb. (gross), 18,350 B.t.u./lb. (net), 135,240 B.t.u./gallon (net).

Alternatively, anhydrous hydrofluoric acid was substituted for the sulfuric acid catalyst in the above procedure and a similar but different position isomeric composition resulted for the final hydrogenated fuel in comparison to the above fuel.

EXAMPLE XXV

(a) *Mixtures of 1,1-Di-(Xylyl)-Butanes*

The procedure of Example X was employed to react butyraldehyde with 1910 grams (18 moles) of commercial xylene mixture composition given in Example VI, 137 grams (1.9 moles) of butyraldehyde were reacted in the presence of 96 grams (3 moles) of methanol and 408 grams (4 moles) of 96.7% sulfuric acid containing 2.2 grams (0.01 mole) of ferrous sulfate. The aldehyde was added over a period of 45 minutes to the xylene-acid methanol mixture maintained at 73 to 87° C. and stirring was continued 3 hours followed by 15 minutes at 75 to 85° C. From the reaction mixture after freeing of xylene by distillation, the following fractions were obtained:

Fractions	B.P., ° C./ 2 mm. Hg	N_D^{20}	Yield, grams
1	38–92	1.4951–1.4964	258.9
2	92–130	1.5110–1.5280	105.6
3	Residue	Dark solid	84.0

Fraction 1 had zero bromine number and has the properties of 1-xylyl-butane. Fraction 2 is the desired 1,1-di-(xylyl)-butane and its density (D_4^{20}) was 0.922 and N_D^{20}=1.5248.

(b) *Mixtures of Di-(Dimethylcyclohexyl)-Butanes*

Hydrogenation according to the procedure of Example I was conducted on about 80 grams of fraction 2 above, employing 16.0 grams Raney type nickel catalyst (Gir-

dler G–49 catalyst) at a pressure of 1150 p.s.i. of hydrogen at 100–130° C. After removal of the 800 grams of methycyclohexane solvent 62.1 grams of the hydrogenated product consisting of the position isomers of 1,1-di-(dimethylcyclohexyl)-butane isomers in mixtures with 1,1-di-(ethyl-cyclohexyl)-1 - (ethylcyclohexyl) - butanes were obtained with the following physical properties: B.P.=300 to 355° C. at 760 mm. of Hg, N_D^{20}=1.4805, D_4^{20}=0.875, viscosity=148 poises at −25° C., and the energy of combustion was 19,505 B.t.u./lb. (gross), 18,220 B.t.u./lb. (net), 132,915 B.t.u./gallon (net).

EXAMPLE XXVI

(*a*) *Mixtures of Di-(Tolyl)-Butanes*

In this example, the position isomers of di-(tolyl)-butanes were prepared by reacting butadiene-1,3 with toluene. In a glass vessel fitted with a stirrer and cooled in a salt-ice bath having a temperature of −6 to −9° C. was charged 2211 grams (24 moles) of toluene and 406 grams (4 moles) of 96.9% sulfuric acid. Over a period of 35 minutes a slow stream of cooled butadiene gas was introduced under the surface of the agitating toluene-sulfuric acid mixture. The butadiene gas flow (about 60 grams charged) over a 2.5 hour period was adjusted so that the temperature of the reaction mixture was held at −2° C. and during the reaction the color changed from green to orange. The hydrocarbon layer was decanted from the reaction mixture and washed with 1 liter of water followed by 1 liter of 3% sodium carbonate aqueous solution and washed again with 1 liter water and the toluene was distilled off. The reaction products were distilled yielding the following fractions:

Fractions	B.P., ° C./745 mm. Hg	N_D^{20}	Yield (g.)
1	200–250	1.5058	11.2
2	250–300	1.5226	16.3
3	300–320	1.5381	12.3
4	320–325	1.5458	18.1
5	325–330	1.5480	28.0
6	330–335	1.5498	28.3
7	335–340	1.5512	8.4
8	340–350	1.5524	15.2
9	350–360	1.5525	11.8
10	360–380	1.5540	18.0
11	380–400	1.5561	16.3
12	400–405	1.5561	10.2
13	Residue		13.7

In this reaction are obtained position isomers of (*a*) tolyl-butane, (*b*) tolyl-dibutane, (*c*) di-(tolyl)-butane, (*d*) (methyl-butenyl-phenyl-(tolyl)-butane and (*e*) di(tolyl)-butyl-(tolyl)-butane. It is believed that the fractions boiling between 200 and 300° C. contain position isomers of type set forth under (*a*) and (*b*) above; the fraction boiling between 360 and 405° C. contains isomers of the type set forth under (*d*) and (*e*) above.

(*b*) *Mixtures of 1,1-Di-(Methylcyclohexyl)-Butanes*

Hydrogenation of fractions 1 to 12 of Example XXVI (*a*) combined, in Example I, gave a mixture containing position isomers of di-(methylcyclohexyl)-butane, which as a fuel has a net energy of combustion greater than 135,000 B.t.u./gallon (net).

In place of the 60 grams of butadiene of this example or the 288 grams of n-butyraldehyde of Example XXV, the following bridging compounds can be substituted: butadiene-1,2 (allene); the mono-unsaturated C_4 alcohols such as 1-butenol-3 (methylvinyl-carbinol); or 1-butenol-4 (allylcarbinol); or the C_4 acetylenes such as 1-butine (ethylacetylene) 2-butine (dimethylacetylene); or the C_4 diols such as 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 2,3-butylene glycol, or 2,4-butylene glycol or the C_4 alkylene oxides such as 1,2-butylene oxide or 2,3-butylene oxide and mixtures of these. If a Friedel-Crafts catalyst is employed in place of the Lewis acid, e.g. aluminum chloride, then the C_4 dichlorides may be employed such as 1,1-dichlorobutane, 2,2-dichlorobutane, 1,2-dichlorobutane, 1,-3-dichlorobutane, 1,4-dichlorobutane or 2,3-dichlorobutane or even similar bromine or mixed chloro-bromine C_4 compounds or mixtures of these.

EXAMPLE XXVII

(*a*) *Mixtures of Di-(Tolyl)-Pentane*

In this example, the procedure of Example XXVI is followed except in place of the 60 grams of butadiene-1,3 there was added slowly 204 grams (3 moles) of piperylene to the same quantity of toluene and acid and the reaction vessel was cooled with ice instead of salt and ice. The piperylene was added over a 3 hour and 45 minute period with reaction temperature maintained at 2° C. and during the course of the reaction the color changed to dark orange. The hydrocarbon product layer was separated and freed of acid by water washing including an alkaline water wash and the residual toluene removed by distillation. The product was fractionated as follows:

Fractions	B.P., ° C./mm. Hg	N_D^{20}	Yield (grams)
1	101–105/15	1.5040	23.7
2	101–112/15	1.5080	6.7
3	178–180/13	1.5351	49.0
4	187–190/13	1.5400	27.2
5	[1] 190/13	[2]	212

[1] The kettle temperature was 400° C.
[2] Fluid residue.

Fractions 1 and 2 were amber colored fluids and fraction 3 and 4 were navy blue colored fluids and the undistillable residue was a viscous amber liquid.

Fractions 1 and 2 contained tolyl pentane and fractions 3 and 4 contained di-(tolyl)-pentane and (pentenyl-tolyl)-(tolyl)-pentane position isomers.

(*b*) *Mixtures of Di-(Methylcyclohexyl)-Pentanes*

Hydrogenation of the above precursor fractions 3 and 4, as in Example I, gave a mixture of position isomers of di(methylcyclohexyl) pentane and methyl-amylcyclohexyl-methylcyclohexyl-pentanes which as a fuel has a net energy of combustion greater than 135,000 B.t.u./gallon.

In place of piperylene as the C_5 diene bridging compound of this example, one can employ other aliphatic C_5 dienes such as pentadiene-1,2, pentadiene-1,4-pentadiene-2,3, isoprene; or the C_6-dienes and higher such as hexadiene-1,2, hexadiene-1,3, hexadiene-1,4, hexadiene-1,5, hexadiene-1,6, hexadiene-2,3, hexadiene-2,4, hexadiene-2,5, hexadiene-3,4, 2,3-dimethyl butadiene and other higher homologues of these dienes containing 7 to 13 carbon atoms. Further as bridging compounds in place of the piperylene can be employed aldehydes, diols, mono-unsaturated carbinols, alkylene oxides and in some instances reactive saturated and unsaturated ketones having both branched and straight chain C_5 to C_{13} carbon skeleton and mixtures of these. If Friedel-Crafts catalysts are used, then the middle dihalides containing chloro- and/or bromo-groups having C_5 to C_{13} branched or unbranched carbon skeleton may be employed singly or as mixtures for bridging.

EXAMPLE XXVIII

(*a*) *Mixtures of (Tolyl)-Undecenes*

To a 4 liter glass vessel equipped with a condenser, agitator and thermometer, placed in water bath was added 685 grams (7 moles) of toluene, 102 grams (1 mole) of 96.19% sulfuric acid and during 1 hour and 15 minutes was added dropwise 168 grams (1 mole) of undecylenic aldehyde and during this addition of aldehyde the temperature of the reactants rose from 32° C. to 41° C. Then was added dropwise an additional 50.7% grams (0.5 moles) of 96.19% sulfuric acid over 1 hour and 15 minutes with the temperature of the reactants dropping to 33° C. The hydrocarbon layer was separated and

washed with 1 liter of water, 1 liter of 3% aqueous solution of sodium carbonate and 1 liter of water and the unreacted toluene removed by distillation. The product was distilled as follows:

Fractions	B.P., ° C./ 745 mm. Hg	N_D^{23}	Yield (g.)
1	383-393	1.4819	18.1
2	390-400	1.4900	15.3
3	400-409	1.5185	27.1
4	Residue		Ca. 30

Water of dehydration during distillation showed the presence of 1-tolyl-1-hydroxy-undecane in the reaction products, which yielded tolylundecadiene by dehydration. The properties of fractions 1 and 2 correspond to those of a mixture of tolyl-undecene and tolyl-undecadiene isomers. The properties of fraction 3 corresponds to those of di-tolyl-undecene position isomers. The residue contains some tritolylundecene.

(b) Mixtures of Position Isomers of Di-(Methylcyclohexyl)-Undecane

Hydrogenation of fractions 1 to 3 combined above according to the procedure of Example I yields a high energy fuel comprising mono- and di-(methylcyclohexyl)-undecane position isomers having a combustion energy greater than 135,000 B.t.u./gallon (net).

EXAMPLE XXIX

(a) Mixtures of 1,10-Di-(Tolyl)-Decane

To a liter glass vessel equipped with reflux condenser, stirrer and thermometer, and placed in a water bath at 90° C. was added 552 grams (6 moles) of toluene and 40 grams (0.3 mole) of freshly sublimed aluminum chloride and was further added dropwise, 150 grams (0.5 mole) of decamethylene dibromide-1,10 (refractive index was N_D^{23}:1.4940) of over a period of 3 hours with the temperature of the reactants remaining at 85° C. for the first 2 hours and rising to 93° C. during the third hour and then stirred at a temperature of about 90° C. for 2.5 hours. The reaction mixture was poured into 650 grams of ice to which 65 ml. of 37% hydrochloric acid had been added. The hydrocarbon layer was separated and washed with 300 ml. of 6.2% aqueous solution of hydrochloric acid and dried by passing through a bed of sodium chloride.

Fractions	B.P., ° C./ mm. Hg	N_D^{23}	Yield (g.)
1	83-114/747	1.4944	[1] 400
2	114-120/747	1.4924	50
3	40-93/2-3	1.5020	28
4	93-136/1-2	1.5096	26.5
5	136-172/1-2	1.5225	53
6	172-240/2-4	1.5550	18
7	[2]		9

[1] Ml.
[2] Residue dark oil.

Fraction 5 had a density of D_4^{30}=0.903 and fraction 6 a density of D_4^{30}=0.950 and these fractions contained the 1,10-di-(tolyl)-decane in a mixture with lesser amounts of tolyl decane and di-(10-tolyldecyl)-toluene isomers.

(b) Mixtures of 1,10-Di(Methylcyclohexyl)-Decanes

To a high pressure autoclave was added 20 grams of fractions 5 and 6 combined comprising the position isomers of 1,10-di-(tolyl)-undecane as shown above, 80 grams of cyclohexane and 4.6 grams of Raney type nickel catalyst (Girdler #49-A catalyst) and the autoclave was pressured to 1000 p.s.i. with hydrogen. The temperature was raised to 150° C. and the product agitated until hydrogenation was complete. The catalyst was filtered off and the cyclohexane removed by distillation. The resulting product in approximate quantitative yield was a mixture of position isomers of 1,10-di-(methylcyclohexyl)-decane mixed with smaller amounts of methylcyclohexyldecane and di-(10-methylcyclohexyldecyl)-methylcyclohexane isomers, which mixture had a net fuel value greater than 135,000 B.t.u./gallon.

The di-(alkylcyclohexyl)-alkane position isomer mixtures represented by Formula I are used as high energy fuels per se, but such fuels sometimes may be mixed with other high energy hydrocarbon and non-hydrocarbon fuels in minor proportion. Thus the high energy liquid fuels of this invention can be employed in quantity at least in the order of 25% or more to enhance the fuel value of presently used hydrocarbon fuels such as kerosene, dialkyl cyclohexane, cumene, hydrogenated cumene, di-(cumene), hydrogenated di-(cumene), paramenthane and the like; and they can also be employed with such high energy fuels as boron hydride, decaborane, the alkyl boron hydrides, the trialkyl borons, and the like to minimize fire and toxicity hazards inherent with these boron derivatives per se.

It has been found that by increasing the number of carbon atoms in the alkyl groups, even increasing the total number of carbon atoms in the compound above the preferred range of 14 to 30 for a jet fuel liquid mixture, higher more viscous liquid and solids are produced still of high energy content useful for fuels which need to be heated to reduce their viscosity or to melt them for combustions as free flowing liquids.

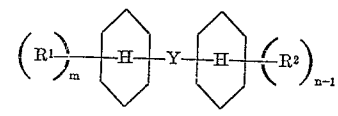
These saturated compounds, including the partially hydrogenated precursor compounds have fuel uses also other than in jet fuels, and may also be used in other uses as stated above.

Thus compounds of the several Formulae I to III wherein R^1 and R^2 are alkyl radicals having 1 to 13 carbon atoms, and Y is an alkylene bridge having 1 to 13 carbon atoms, and *m* is an integer of 1 to 3 and *n* is an integer from 1 to 4 and the total carbon atoms content of compounds above the range of 14 to 30 for example in the range of 30 to 54 are useful fuels, and the higher hydrogenated compounds also are useful for less convenient fuel uses, as well as other uses. The intermediate partially hydrogenated and non-hydrogenated compounds of Formulae IV through VI, and VIII through IX, are useful precursors for fuels by hydrogenation, and may be used as solid fuel hydrocarbons, which can be melted for use as liquid fuel. They also can be burned as solid fuels. They may also be used as lubricants, heat transfer media, hydraulic fluids, plasticizers for elastomers and plastomers, adhesives, and like materials in coatings, films or plastically formed articles.

The higher homologues and their isomers are produced by the same methods employing more or less molar proportions of the various reactants, as the fuel and fuel precursor products of this invention, the bridging compounds employed are the same. It will be obvious to those skilled in the art that minor modifications and changes may be made without departing from the essence of the invention. For example, while in liquid form, my products are outstandingly useful for high energy fuels, and can be burned as fuel for jet and other heat engines where the high energy content is of advantage. It is therefore to be understood that the exemplary embodiments are illustrative and not restrictive to the invention, the scope of which is defined in the appended claims, and that all modifications that come within the meaning and range of equivalency of the claims are intended to be included therein.

I claim:

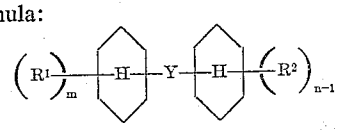
1. A high energy fuel consisting essentially of a mixture of position isomers of at least three compounds having the formula:



wherein R^1 and R^2 are alkyl radicals each having from 1

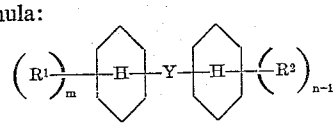
to 13 carbon atoms and Y is an alkylene bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3 and *n* is an integer from 1 to 4.

2. A high energy fuel consisting essentially of a mixture of position isomers of at least three compounds having the formula:



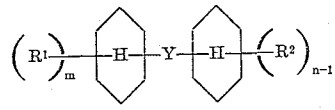
wherein R^1 and R^2 are alkyl radicals each having from 1 to 4 carbon atoms and Y is an alkylene bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3 and *n* is an integer from 1 to 4 and the total number of carbon atoms in the molecule is in the range of 14 to 30.

3. A high energy fuel consisting essentially of a mixture of position isomers of at least three compounds having the formula:



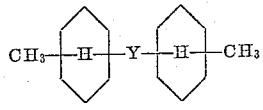
wherein R^1 and R^2 are alkyl radicals each having from 1 to 13 carbon atoms and Y is an alkylene bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3 and *n* is an integer from 1 to 4 and in which the alkylcyclohexyl radicals of said compound are derived from C_7 to C_9 petroleum fractions, linked as shown by the bridging group Y, and hydrogenated.

4. A composition of matter consisting essentially of a mixture of at least three position isomers having the formula:



wherein R^1 and R^2 are lower alkyl radicals each having from 1 to 13 carbon atoms, Y is an alkylene bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3, and *n* is an integer from 1 to 4.

5. A composition of matter consisting essentially of a mixture of at least three hydrocarbon position isomers having the formula:

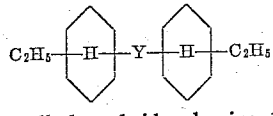


wherein Y is an alkylene bridge having 1 to 13 carbon atoms.

6. A composition of matter according to claim 5 in which Y is a methylene radical.

7. A composition of matter according to claim 5 in which Y is an ethylene radical.

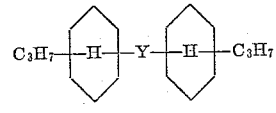
8. A composition of matter consisting essentially of a mixture of at least three hydrocarbon position isomers having the formula:



wherein Y is an alkylene bridge having 1 to 13 carbon atoms.

9. A composition of matter according to claim 8 in which Y is a methylene radical.

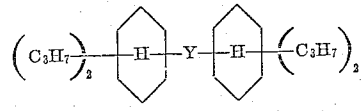
10. A composition of matter consisting essentially of a mixture of at least three hydrocarbon position isomers having the formula:



wherein Y is an alkylene bridge having 1 to 13 carbon atoms.

11. A composition of matter according to claim 10 in which Y is a methylene radical.

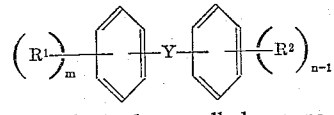
12. A composition of matter consisting essentially of a mixture of at least three hydrocarbon position isomers having the formula:



wherein Y is an alkylene radical having 1 to 13 carbon atoms.

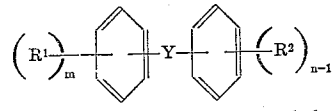
13. A composition of matter according to claim 12 in which Y is a methylene radical.

14. A composition of matter consisting essentially of a mixture of at least three position isomers having the formula:

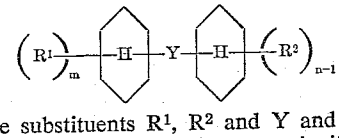


wherein R^1 and R^2 are lower alkyl groups each having from 1 to 13 carbon atoms and Y is a divalent acyclic hydrocarbon bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3, *n* is an integer from 1 to 4.

15. A composition of matter consisting essentially of a mixture of at least three position isomers of a substantially hydrogenated product of a compound having the Formula *a*:

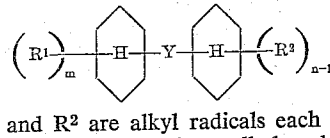


wherein R^1 and R^2 are alkyl radicals each having from 1 to 13 carbon atoms and Y is a divalent acyclic hydrocarbon bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3 and *n* is an integer from 1 to 4, said hydrogenated compound containing from an intermediate quantity up to as much; hydrogen as a compound having the Formula *b*:



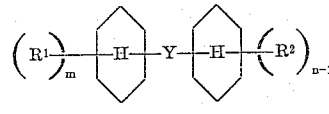
wherein the substituents R^1, R^2 and Y and the integers *m* and *n* of Formula *b* have the same significance as in Formula *a*.

16. The process of operating a jet engine comprising burning a mixture of at least three position isomers having the formula:



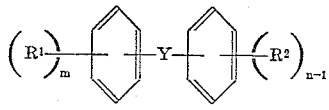
wherein R^1 and R^2 are alkyl radicals each having from 1 to 13 carbon atoms and Y is an alkylene bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3 and *n* is an integer from 1 to 4 and the total number of carbon atoms in the molecule is in the range of 14 to 30.

17. The process of forming a mixture of at least three position isomers having the Formula *a*:



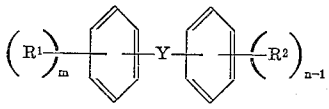
wherein R^1 and R^2 are alkyl radicals each having from 1 to 13 carbon atoms and Y is a divalent acyclic hydrocarbon bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3, and *n* is an integer from 1 to 4, comprising

hydrogenating a mixture of at least three position isomers having the Formula *b*:



wherein R^1, R^2, Y, *m* and *n* of Formula *b* have the same significance as in Formula *a*.

18. The process according to claim 17 wherein the compound having the formula:

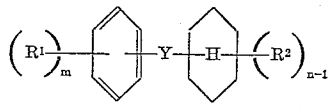


is formed by bridging two benzene-ring hydrocarbons of which at least one is an alkylbenzene, with an alkylene group Y having 1 to 13 carbon atoms.

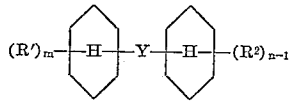
19. The process according to claim 18 in which at least one of said alkylbenezenes is xylene.

20. The process according to claim 18 in which at least one of said alkylbenzenes is cumene.

21. The process of forming a mixture of at least three position isomers having formulae of the group consisting of (*a*)

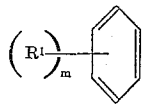


and (*b*)



wherein R^1 and R^2 are alkyl radicals each having from 1 to 13 carbon atoms and Y is an alkylene bridge having 1 to 13 carbon atoms, *m* is an integer from 1 to 3 and *n*

is an integer from 1 to 4, which comprises (step I) bridging two benzene ring hydrocarbons, at least one of which is alkyl benzene having the formula:



wherein R^1 and *m* have the same significance, the alkylene bridging compound Y being selected from the group consisting of alkynes, aliphatic aldehydes, alkylene glycols, alkylene oxides, dichloroalkanes, dibromo alkanes, chlorobromo alkanes and C_3 to C_{13} dienes, and (step II) at least partially hydrogenating said compound.

22. A process according to claim 21 in which the bridging radical Y having 1 to 13 carbon atoms is derived from an aliphatic saturated aldehyde and the bridging reaction is carried out in the presence of a strongly acidic catalyst.

23. A process according to claim 22 in which the bridging radical Y is derived from formaldehyde.

24. A high energy fuel composition as defined in claim 3 wherein R and R′ are methyl radicals, Y is a methylene bridge radical, *m* is an integer of from 1 to 2 and *n* is an integer of from 2 to 3.

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