May 6, 1947. R. C. BRANDON 2,420,030

MOTOR FUELS AND PREPARATION THEREOF

Filed April 13, 1943 2 Sheets-Sheet 1

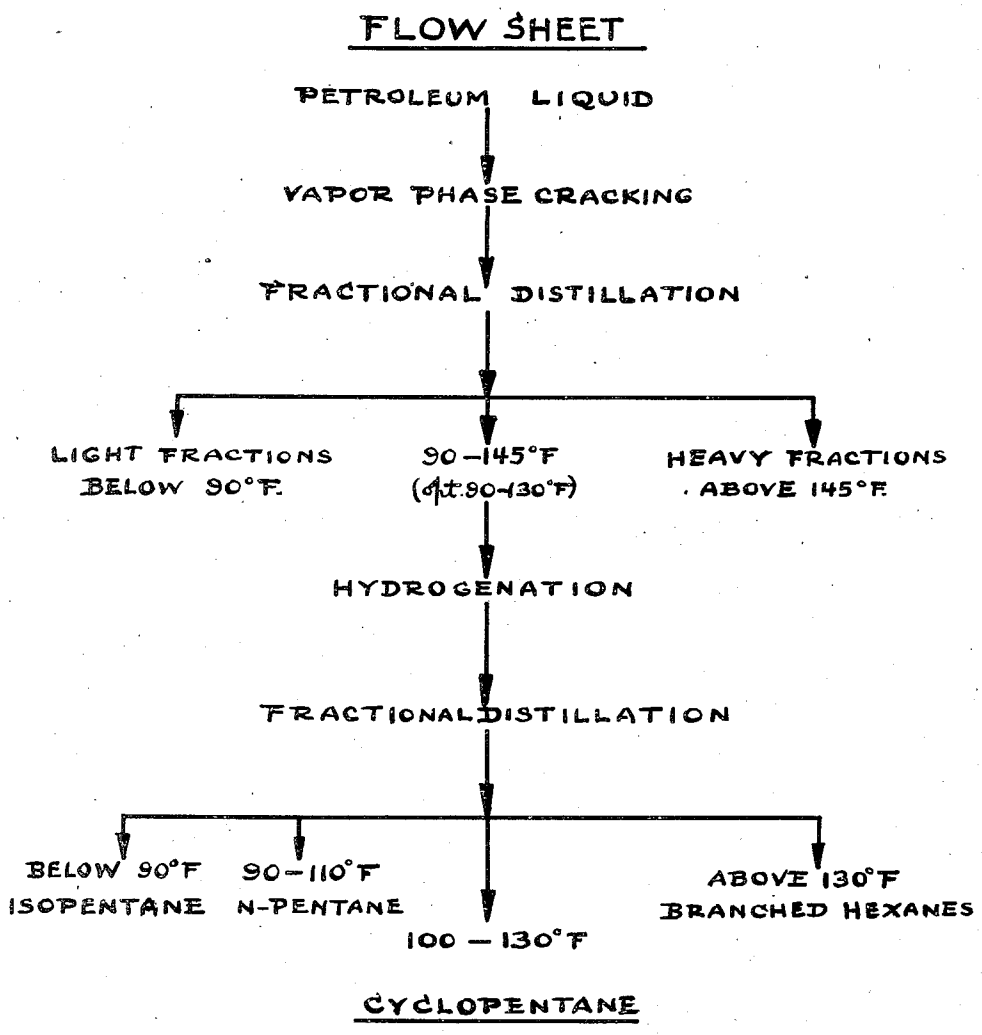

Fig. 1

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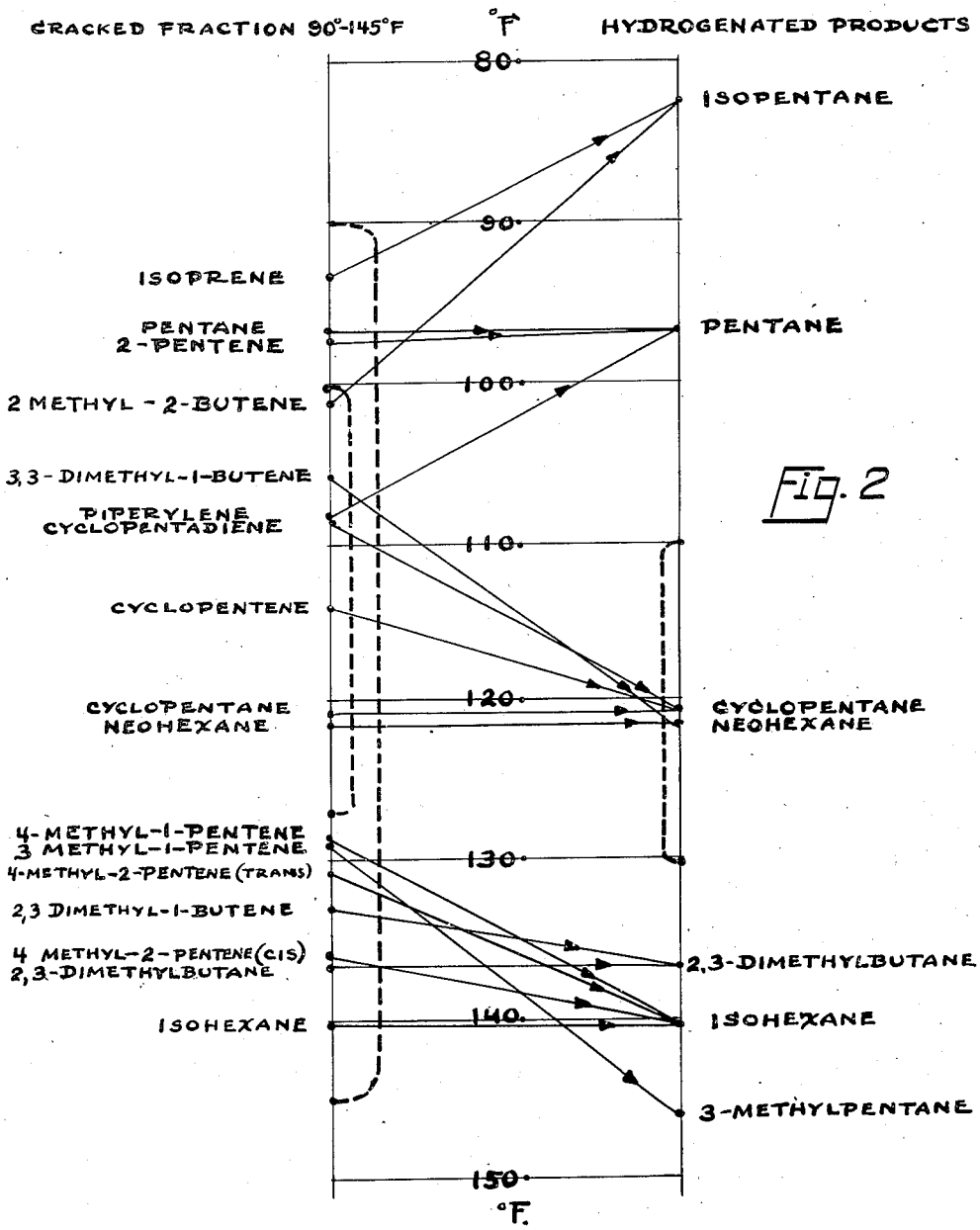

Fig. 2

BOILING POINT CHART

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UNITED STATES PATENT OFFICE

2,420,030

MOTOR FUELS AND PREPARATION THEREOF

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2 Claims. (Cl. 196—61)

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This invention relates to novel motor fuels and methods of preparing same and more particularly to a novel method of preparing an improved addition agent for motor fuels, especially for preparing cyclopentane in relatively pure form from petroleum raw materials.

It has been known for some time that cyclopentane is a suitable addition agent for motor fuels because it has a boiling point of 120.7° F., a Reid vapor pressure of about 9 lbs. per square inch, and an octane number (by the A. S. T. M. motor method) of about 85 to 90. Recently it has been found to be even much more valuable as an addition agent in leaded aviation motor fuels to be used in supercharged engines under rich mixture conditions, because under such conditions it tremendously increases the power output of the engine, provided the fuel contains 3 cc. or more of tetraethyl lead (T. E. L.) per gallon. For instance, in the so-called 3–C blending value test for motor fuels, identified as Army-Navy test AN–VV–F–748 (for determining fuel characteristics in the supercharged engine with various fuel-air weight ratios), cyclopentane with 4 cc. T. E. L. per gallon shows a power output or I. M. E. P. (indicated mean effective pressure) of more than 450 lbs. per square inch (blending value in 20% by volume concentration) in an alkylate base stock, whereas the more desirable of the other saturated hydrocarbons boiling in the same vicinity and having a sufficiently high vapor pressure to be used as the volatility-imparting agent in a motor fuel blend, have substantially lower 3–C blending values, such as 290 for 2,3-dimethyl butane, 235 for neohexane (which is 2,2-dimethyl butane) and 218 for isopentane.

Thus it is one object of the present invention to provide a practical, economical and plentiful supply of cyclopentane for use as the sole volatility-improver in aviation motor fuel blends for supercharged engines. Such fuels require the use of special base stocks which per se have an A. S. T. M. octane number of at least 85, and preferably at least 90, and a power output of at lease 180 I. M. E. P. in the 3-C test, when containing 3 cc. of tetraethyl lead per gallon.

Suitable base stocks for the purpose of this invention are the hydrocarbon liquids made by alkylation of lower olefins (alkenes) having 2

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to 6, preferably 3 to 5, carbon atoms with isoparaffins (iso-alkanes) having 4 to 5 carbon atoms, particularly isobutane having 4 carbon atoms. Such alkylates may be made by known methods such as by reaction in the presence of sulfuric acid or other catalyst, and generally have a boiling range of about 90–350° F. and preferably about 100–320° F., and usually have a Reid vapor pressure of about 2 to 3. Another suitable base stock is the material known commercially as iso-octane but which is chemically referred to as 2,2,4-trimethyl pentane and which is made commerically by hydrogenation of di-isobutylene. This product has a boiling range in the vicinity of about 200–230° F. and a Reid vapor pressure of about 2.

When preparing aviation fuels for supercharged engines, it is normally considered desirable to make a finished blend which has a Reid vapor pressure of about 5 to 7 lbs./sq. in., because if the vapor pressure is much below 5, difficulties would be encountered in starting the engine, and if it is much above 7, vapor locking and other troubles may result. On the other hand, for maximum power output which is very desirable, if not essential, especially for military purposes, when an airplane takes off, it is obviously desirable to incorporate into the motor fuel base stock in addition to tetraethyl lead as much cyclopentane as possible (due to its high blending I. M. E. P. in alkylates of more than 450 lbs. per square inch) without exceeding the Reid vapor pressure limit of 7.

Now one of the difficulties of the past has been that pure cyclopentane could be derived essentially only by the hydrogenation of a relatively pure cyclopentadiene obtained as a by-product during the destructive distillation of coal into coke, and the amount of it which can be obtained from this source is so insignificantly small that it is not only expensive but the amount available could not possibly supply the tremendous demand for motor fuel purposes. On the other hand, some cyclopentane has also been produced by straight distillation or fractionation of certain crude petroleum stocks in which it occurs by nature in relatively small amounts. Here again, however, there are two disadvantages, namely, that the amount actually available is still relatively small and furthermore it

generally contains inseparably admixed therewith a small amount of a branched paraffinic hydrocarbon called neohexane (chemically referred to as 2,2-dimethyl butane, which has a boiling point of 121.5° F., which is almost identical with that of cyclopentane itself, i. e. 120.7° F.). It is believed that by even the best methods of fractionation which are available from a practical or commercial point of view, a cyclopentane product cannot be obtained which has a purity greater than about 90–95%. As shown in the following data, the small amount, i. e. 5–10% of saturated hydrocarbon impurities (perhaps neohexane) very greatly reduces the 3-C blending value of such cyclopentane obtained by distillation from natural petroleum products and this reduction in 3-C blending value may be very much greater in proportion than might be expected from the actual percentage of impurities present, because small amounts of impurities often exert a deleterious influence far greater than would be calculated arithmetically on a percentage basis.

Pure cyclopentane was subjected to a 3-C blending value test in 20% concentration in an alkylate base stock having an octane number of 90, and with an addition of 3 cc. of tetraethyl lead per gallon. For comparison, the pure cyclopentane cut obtainable from fractionation of crude oil was similarly tested, except that 4 cc. per gallon of tetraethyl lead were used instead of 3 cc. The following table shows the test results:

Cyclopentane	Boiling Range, ° F.	Refractive Index at 20° C.	Per cent Purity	Clear ASTM-O. N.	3-C Blending Value	
					cc. TEL/Gal.	IMEP
Pure	120.6	1.4065	99+	85.0	3	425
Distilled from Crude	120.2 to 121.2	1.4030	90+	91.1	4	370

These tests show that the pure cyclopentane gave a power output (I. M. E. P.) of 425 with only 3 cc. of tetraethyl lead, whereas the narrow cut cyclopentane fraction distilled from crude petroleum only gave a power output of 370 even with 4 cc. of tetraethyl lead (the pure cyclopentane shows an I. M. E. P. greater than 450 when 4 cc. of tetraethyl lead are used). It is also interesting to note that these results are quite contrary to what would be expected from a comparison of the A. S. T. M. octane number of the plain cyclopentane, without any alkylate or tetraethyl lead, because the pure cyclopentane only had an octane number of 85.0, whereas the fraction distilled from crude oil had an octane number of 91.1.

Accordingly one of the primary objects of this invention is to provide a substantially pure cyclopentane having a purity substantially greater than 95%, and generally greater than 98%, and to provide this purer cyclopentane by a process which uses petroleum hydrocarbons as raw materials and converts them chemically into cyclopentane in large enough amounts for use on a commercial scale as a high power-output addition agent for supercharged aviation engines operating under rich mixture conditions.

Broadly the invention comprises, as outlined briefly in the flow sheet shown on the accompanying drawing marked Sheet 1, subjecting to vapor-phase cracking a petroleum hydrocarbon stock composed of hydrocarbons having at least 5 carbon atoms, under conditions to produce substantial quantities of unsaturated 5-carbon ring hydrocarbons, fractionating the resultant cracked products to separate therefrom a fraction boiling within the approximate limits of 90–145° F., hydrogenating said fraction under conditions to saturate the unsaturated hydrocarbons therein, and finally fractionating the hydrogenated product to separate therefrom a fraction boiling within the approximate limits of 100–130° F. and consisting essentially of cyclopentane.

A primary feature of the invention is carrying out the cracking under conditions which tend to produce a relatively large amount of olefinic or di-olefinic hydrocarbons, the amount of carbon-to-carbon linkages to be split depending upon the molecular size of the raw material being treated, which may consist of various petroleum fractions such as naphthas, kerosene, gas oil, light and heavy lubricating oil stocks. If a very light stock is used as raw material such as a light naphtha containing a substantial amount of C_5 hydrocarbons, the treating process may comprise essentially a dehydrogenation with little or no splitting of C—C linkages. Some ring formation, i. e., conversion of chain compounds into corresponding ring compounds, is not objectionable and in fact is desirable.

Although this vapor-phase cracking may be carried out by a batch operation and in various types of equipment known to the art, it is preferably carried out continuously by heating the hydrocarbon feed material, together with a diluent, as will be explained, in a pipe coil where it is rapidly heated to a temperature of about 1200–1600° F., and maintained thereat for a relatively short time, such as less than 5 seconds, and generally less than 1 second, equivalent contact time at peak temperature. The diluent, calculated on a diluted hydrocarbon vapor basis, should be from 40 to 90 mol percent of a suitable gaseous material such as air or steam. The use of a gaseous diluent of any type has the effect of reducing the partial pressure of the hydrocarbons present and therefore tends to increase cracking and unsaturation with relatively little tendency toward polymerization. The actual pressure at which the cracking is carried out should be in any case lower than about 200 lbs. per square inch absolute pressure, and preferably about 15 lbs. per sq. in. gauge, although, if desired, the operation may be carried out under vacuum, i. e., by the use of pressures ranging from atmospheric down to 1 lb. per square inch absolute pressure or even less.

After the desired amount of cracking has been effected, the cracked products are quickly cooled below the temperature at which harmful polymerization of the desired unsaturated materials might occur with any substantial speed, namely, to a temperature at least as low as 800° F. and perhaps down to 200° F., and this may be done by injecting water or unheated oil as a quenching medium into the transfer line as close as possible to the coil outlet, and/or fractionating the cracked products in a tower cooled by injection of water or oil.

After the cracked products have been cooled

sufficiently, they are subjected to distillation to separate a fraction having a lower boiling limit of about 90–100° F. and an upper boiling limit somewhere between about 130° F. and 145° F., this fraction being the one in which cyclopentadiene formed in the cracking will appear as well as any cyclopentene similarly formed during the cracking. This fractionation should be carried out as promptly as possible after the cracking so as to avoid unnecessary loss of cyclopentadiene by polymerization into dicyclopentadiene or higher polymers during storage, which would, of course, boil at a substantially higher temperature than the 90–145° F. fraction.

The next step according to this invention is the hydrogenation of the selected cracked distillate fraction. This hydrogenation may be carried out in a number of ways, but in any case should be carried out under relatively mild hydrogenating conditions with admixed hydrogen under a pressure of at least 0 lbs. per square inch gauge so as to completely saturate the hydrocarbons present without causing any splitting of C—C linkages. One suitable procedure is to hydrogenate the 90–145° F. cracked distillate fraction with a Raney nickel catalyst or other suitable hydrogenation catalyst at a pressure of about 500–1,000 lbs. per square inch and at a temperature of about 200–500° F., preferably about 300–350° F. Other alternative hydrogenation procedures include the use of such catalysts as nickel sulfide-tungsten sulfide, molybdenum sulfide supported on a carrier such as alumina, clay, pumice, etc., as well as catalysts comprising oxides or sulfides of the group VI metals, at temperatures of 500–800° F., and pressures of 50–500 lbs. per square inch in either batch or continuous equipment. As another alternative, the feed stock may be vaporized, mixed with hydrogen, and passed over a catalyst in a chamber heated to about 750° F.

The result of this hydrogenation step as will be seen more clearly by referring to the accompanying drawing marked Sheet 2, is to effect a spread in the boiling points of the various hydrocarbons in such a way as to facilitate the separation of the primarily desired cyclopentane from all other hydrocarbons, except the small amount of neohexane which may have been present initially, or any that would be formed upon hydrogenation of the corresponding olefin, namely, the 3,3-dimethyl butene-1. However, tests do not show that any such olefin had been formed by cracking, and theoretically this olefin has such a peculiar and unstable structure that it is improbable that any of it would be formed during the cracking. The accompanying chart (Sheet 2) shows clearly how hydrogenation separates two materials, one desired and one undesired, which both boil at exactly the same temperature, namely 108.5° F., the piperylene being converted into pentane and therefore changing in boiling point from 108.5° F. down to 96.8° F., whereas the cyclopentadiene changes into cyclopentane, with a rise in boiling point from 108.5° F. to 120.7° F. Thus hydrogenation has produced a spread in boiling range of about 24° F. between the highly desired cyclopentane and highly undesired normal pentane, permitting ready separation of these two materials. It is also seen that cyclopentene which boils at 114° F., which is less than 6° F. from the piperylene, is also converted into cyclopentane and therefore is much more easily separated after hydrogenation. Although the effects just described are the most important results of the hydrogenation, it is also noted that several lower boiling constituents such as the 2-methyl-2-butene which boils at 101.1° F. and isoprene which boils at 93.4° F., and therefore are both undesirably close to normal pentane at 96.8° F. and 2-pentene at 97.3° F., are both converted by hydrogenation into isopentane which boils at the much lower temperature of 82.4° F., whereas the 2-pentene is converted into pentane, thus resulting in a spread of 14.4° F. between isopentane at 82.4° F., which is a fairly desirable constituent for motor fuels, and the normal pentane at 96.8° F., which is very poor. Also, all of the hydrocarbons boiling above cyclopentane and neohexane in the cracked distillate fraction, are converted by hydrogenation into saturated hydrocarbons boiling at an even higher temperature, and therefore are even more easily separated from cyclopentane after hydrogenation than before. These heavier boiling hydrocarbons which boil between the limits of 128° F. and 140° F. before hydrogenation and boil between 136° F. and 146° F. after hydrogenation are all branched hexanes which have fairly good octane number and fair power output blending value and therefore are useful as a mixed motor fuel blending agent, even though they are not nearly as good as cyclopentane and therefore should desirably be separated therefrom.

As will be readily appreciated from the chart, it may be desirable in carrying out the present invention to select a slightly narrower cracked fraction than one having a boiling range of about 90–145° F., such as for instance 90–130° F., or preferably still about 100–127° F., particularly if it is desired to obtain a relatively high proportion of cyclopentane without having to hydrogenate a large volume of hydrocarbons other than those leading to the formation of the cyclopentane or those which cannot otherwise be separated therefrom. In other words, by selecting a vapor-phase cracked fraction boiling between about 100° and 127° F., relatively little normal pentane will have to be handled, and only a small proportion of isopentane resulting from the hydrogenation of the 2-methyl-2-butene, but none of that resulting from isoprene; and little if any of the branched hexenes or corresponding branched hexanes boiling above 128° F.

Likewise in making the final distillation, i. e., after hydrogenation, it is preferred to cut the cyclopentane fraction at about 100–130° F. or preferably at about 110°–125° F. so as to recover substantially all of the cyclopentane in the hydrogenated product, without contaminating it with any of the normal pentane or any of the branched hexanes boiling above 130° F. By carrying out the process of this invention a cyclopentane product has been produced which has a purity above 93% cyclopentane, and even higher, and this product has been obtained in relatively high yields, for instance, ranging from 1 to 2% or higher based on the volume of original petroleum liquids such as a heavy naphtha subjected to cracking.

In order to more fully explain the details as well as objects and advantages of the invention, the following experimental data are given:

Example 1

A heavy virgin naphtha having a boiling range of about 200–430° F., which was obtained from an East Texas crude and which is of the paraffinic type, was subjected to vapor phase cracking in a pipe coil at a temperature of about 1400°

F. and at a gauge pressure of about 15 lbs. per square inch, using 79.1 mol percent steam dilution and having an equivalent contact time at 1400° F. of about 0.86 second, the cracked products being immediately cooled by quenching with water injected into the fractionating tower in which the cracked products were subjected to distillation to recover a fraction boiling from the C_5 range to about 145° F., final vapor temperature. This fraction was hydrogenated over a Raney nickel catalyst (made by leaching the aluminum out of a nickel-aluminum alloy with caustic soda) at 700 lbs. per square inch pressure and at a temperature of 315° F. The liquid product was analyzed for cyclopentane by analytical distillation and was found to contain about 25% by volume of cyclopentane. The fraction boiling at 120° F. was essentially 100% cyclopentane and amounted to 16% of the liquid product. The 113–129° F. fraction contained 95% cyclopentane and amounted to 24% of the liquid product. The cyclopentane boiling at 120° F. was not only easy to separate from the lighter fractions which include isopentane and normal pentane, as well as the heavier fraction which contained branched hexanes boiling above 130° F., but as shown by refractive index and other tests was practically absolutely pure cyclopentane. It showed no presence of neohexane which is the only saturated paraffin hydrocarbon which could be present in a fraction having a boiling point of 120° F.

In this experiment no attempt was made to recover the cyclopentane or other hydrocarbons which were lost in the gas during the cracking and hydrogenation, and assuming that the C_5 portion of the lost gases contained the same proportion of pure cyclopentane as did the liquid C_5 portion, it is estimated that the amount of cyclopentane lost in the gas, and which of course would be recovered in commercial operations, was substantially equal to the amount of cyclopentane recovered in the liquid hydrogenation products.

If these same yields are calculated on the basis of the amount of fresh heavy naphtha feed, originally subjected to cracking, it is estimated that the cracked fraction boiling from 90–145° F. amounted to 2.04% by volume, the C_5 lost in the gas amounted to 1.43% by volume, the cyclopentane recovered from the liquid hydrogenated product amounted to 0.54%, the estimated potential cyclopentane lost in the gas is about 0.51% by volume, and the total estimated cyclopentane amounted to 1.05% by volume. This would mean that for every 100 barrels of heavy naphtha subjected to the cracking operations, 4 bbl. of material boiling at 90–145° F. could be obtained which on hydrogenation would produce 1 barrel of pure cyclopentane. This is a very great and unexpected improvement over the only other method used heretofore for obtaining cyclopentane commercially, namely, by distilling it from natural petroleum fractions, in which case very much more naphtha boiling at 90–145° F. would have to be distilled in order to obtain 1 barrel of cyclopentane fraction, and even the latter would not be as pure as the product obtained by the process of the present invention.

Example 2

The procedure of Example 1 was repeated, except that the raw material feed to the cracking unit was a light virgin naphtha and during the cracking a 71.8 mol percent of air dilution was used with an equivalent contact time of 0.23 second at 1400° F. which is slightly shorter than that used in Example 1. The gauge pressure was 15 lbs. per square inch, substantially the same as in Example 1. A fraction boiling from about 90–145° F. was separated from the cracked products and was hydrogenated and refractionated to obtain a cyclopentane cut. Based upon the amount of fresh feed to the cracking unit as 100%, the yields were as follows:

	Per cent by volume
Recovered C_5–145° F. V. T.[1] cut	11.90
C_5 lost in gas	5.86
Cyclopentane from hydrogenated C_5–145° F. V. T. cut	0.73
Estimated cyclopentane lost in gas	0.98
Total cyclopentane	1.71

[1] V. T. means vapor temperature. This fraction contains about 69 wt. per cent C_5; if only the C_5 cut had been hydrogenated, the cyclopentane from the hydrogenation would have been substantially higher.

Thus the total amount of cyclopentane recovered in Example 2 is slightly greater than that obtained in Example 1 when calculated on the basis of the total fresh feed to the cracking unit, since it was 1.71% in Example 2, compared to 1.05% in Example 1, but when based upon the amount of narrow cracked fraction subjected to hydrogenation (which was 11.90% based on the original feed) the yield of cyclopentane was only about 14–15%, compared to about 25% in Example 1.

The cracking conditions used in Example 1 had been selected as representative of conditions tending to give maximum aromatic production, whereas the cracking conditions used in Example 2 were representative of those tending to give maximum butadiene production. It will be obvious to those skilled in the art that considerable variation can be made in the cracking conditions to be used without departing from the general spirit and scope of the present invention, the primary requisite being reacting in the vapor phase at relatively elevated temperature with the use of about 40–90 mol percent dilution with air and/or steam or other suitable diluent, in order to produce a large amount of cyclopentadiene.

It is not intended that this invention be limited to the specific materials nor specific reaction conditions which have been given merely for the sake of illustration, but only by the appended claims.

I claim:

1. The method of preparing volatile liquid hydrocarbon products especially useful as a blending agent in leaded fuels for supercharged aviation engines to be used under rich mixture operation for maximum power output, which comprises subjecting to vapor phase cracking a petroleum hydrocarbon stock composed of hydrocarbons having at least 5 carbon atoms, under conditions to produce substantially large quantities of cyclopentadiene with other unsaturated C_5 to C_6 hydrocarbons boiling below 110° F. and above 127° F., fractionating the resultant cracked products to separate therefrom a fraction boiling within the approximate limits of 90–145° F., hydrogenating said fraction under conditions to saturate the unsaturated hydrocarbons therein, fractionating the resultant hydrogenated product to separate therefrom four fractions consisting essentially of the following four types of constituents, respectively: isopentane, normal pentane, cyclopentane, and branched hexanes, and combining the first, third and fourth of said fractions from the hydrogenated product in the desired proportions to obtain a motor fuel blend-

ing agent having the desired combination of antiknock and vapor pressure properties.

2. The method of preparing a volatile liquid hydrocarbon product especially useful as a blending agent in leaded fuels for supercharged aviation engines to be used under rich mixture operation for maximum power output, which comprises subjecting to vapor phase cracking a petroleum hydrocarbon stock composed of hydrocarbons having at least 5 carbon atoms under conditions to produce substantially large quantities of cyclopentadiene with other unsaturated C_5 to C_6 hydrocarbons boiling below 110° F. and above 127° F., fractionating the resulting cracked products to separate therefrom a fraction boiling within the approximate limits of 90–145° F., hydrogenatig said fraction under conditions to saturate the unsaturated hydrocarbons therein, fractionating the resultant hydrogenated product to separate therefrom a fraction consisting essentially of normal pentane, and combining the other components of the hydrogenated product essentially including isopentane, cyclopentane, and branched hexanes to obtain a motor fuel blending agent having the desired combination of antiknock and vapor pressure properties.

RICHARD C. BRANDON.

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