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B. L. EVERING ET AL

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CONVERSION OF HYDROCARBON PRODUCTS

Filed Nov. 24, 1937

2 Sheets-Sheet 1

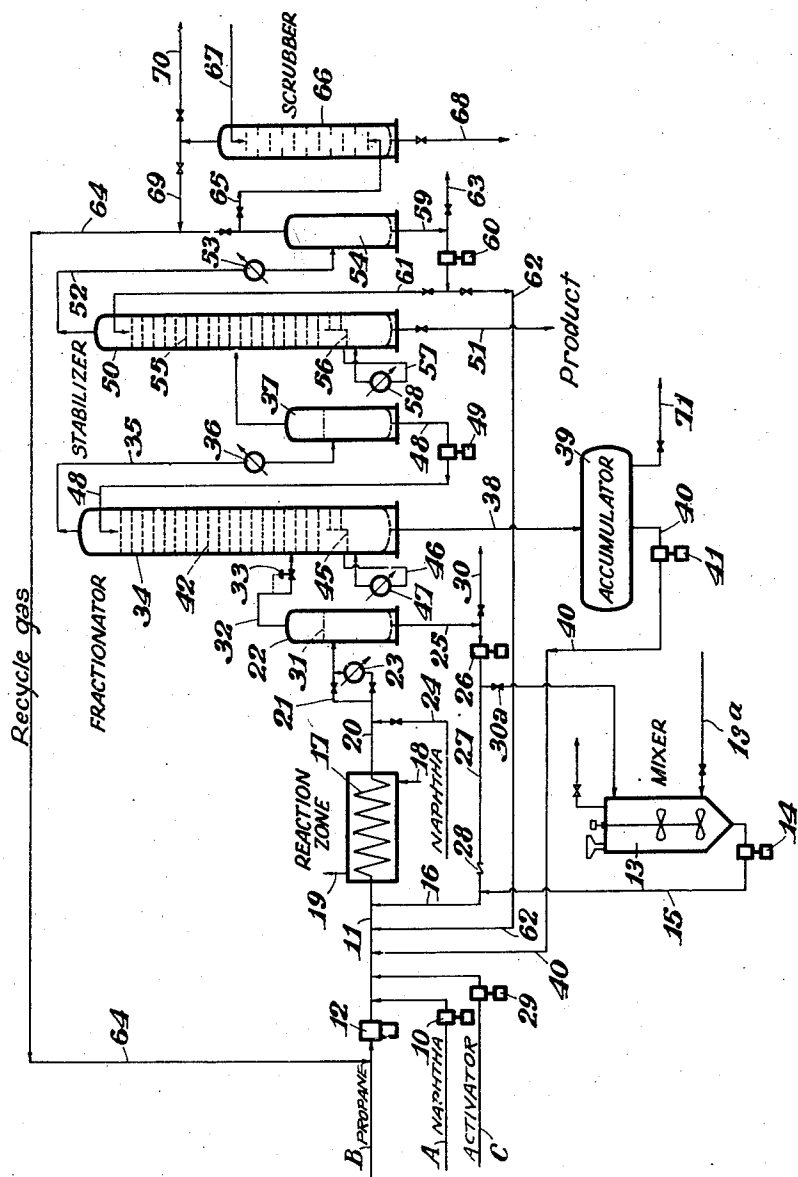


Fig. 1

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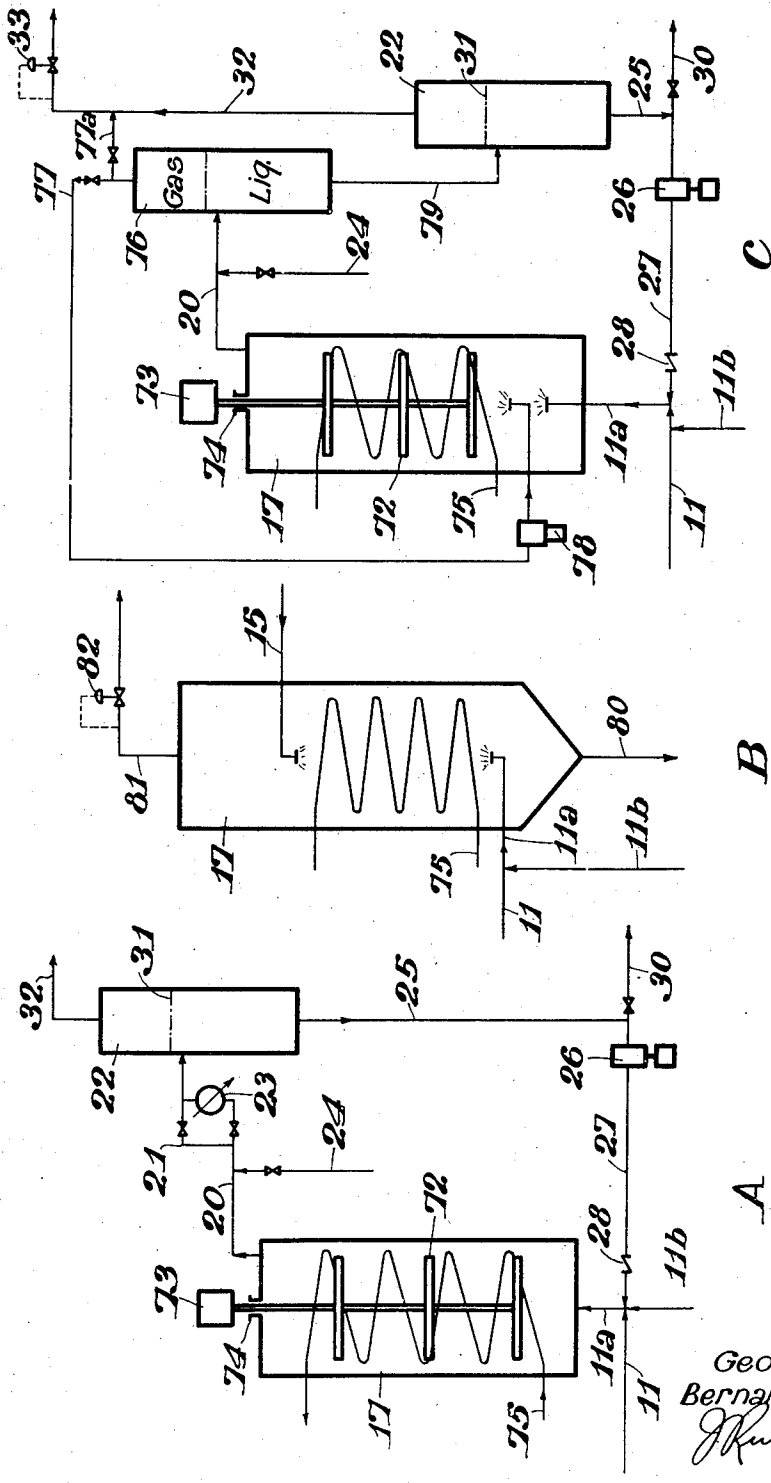


Fig. 2

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UNITED STATES PATENT OFFICE

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CONVERSION OF HYDROCARBON PRODUCTS

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Application November 24, 1937, Serial No. 176,288

7 Claims. (Cl. 196—9)

This invention relates to the preparation of a high antiknock motor fuel from an admixture of propane and straight run petroleum naphtha with the aid of catalysts. In particular, our invention relates to the preparation of a motor fuel product containing large quantities of branched-chain saturated hydrocarbons.

Saturated branched-chain hydrocarbons, and particularly mixtures of them, are very useful as motor fuels on account of their antiknock properties and high heating value. Also, the saturated branched-chain hydrocarbons have lower boiling points than the corresponding straight-chain paraffin and, consequently, motor fuels containing substantial quantities of the former have better starting characteristics than motor fuels containing large quantities of the latter. In addition, branched-chain paraffin hydrocarbons, such as the iso-hydrocarbons, are very useful as starting materials in the preparation of many chemical products.

One of the principal objects of our invention is to convert an admixture of propane and straight run naphtha of low antiknock value into a motor fuel fraction of high antiknock value. Examples of the paraffinic straight run naphtha which may be used in our process are Mt. Pleasant naphtha, Pennsylvania naphtha, Mid-Continent naphthas and the like. This conversion or branching of the admixture of hydrocarbons is effected without substantial formation of fixed gases such as hydrogen and methane. Following the conversion of the hydrocarbons into a motor fuel product of high antiknock value, the products from the reaction zone may be fractionated by any of the methods hereinafter described to give a motor fuel product of desired volatility and antiknock properties.

Other objects, advantages and methods of utilizing our process will become apparent from the description hereinafter. In the drawings, attached to and forming a part of the specification Figure 1 is a diagrammatic illustration of one arrangement of the apparatus which may be used in practicing our process. Figure 2 is a diagrammatic illustration of the types of reaction zones which may be used in our process.

Our embodiment of our process will be described with reference to the conversion of saturated straight run petroleum naphtha in the presence of a paraffinic gas consisting almost entirely of propane. The naphtha used in this example boils within the range of 150 to 400° F., however, our process may be used with petroleum naphthas having end boiling points within the

range of 230–500° F. The straight run petroleum naphtha enters the system through conduit A and is forced by pump 10 into the manifold 11. Propane enters the system through line B and is forced by compressor 12 into the manifold 11 where it is mixed with the other products therein. Also, a slurry or solution of aluminum chloride in light mineral oil is prepared in the catalyst mixer 13 and passed by pump 14 through line 15 to line 16 and then introduced into the manifold 11. A promoter or activator, namely, hydrogen chloride, hydrogen bromide, carbon tetrachloride, the alkyl halides such as methyl chloride or bromide, ethyl chloride or bromide, propyl chloride or bromide, butyl chloride or bromide, or any compound which in the presence of an aluminum halide yields a hydrogen halide is added to the reaction zone 17 through conduit C with the aid of pump or compressor 29. Also, in the place of aluminum chloride we may use other aluminum halides such as aluminum bromide. The naphtha, gas, catalyst and promoter are continuously fed to the system as above indicated and the admixture of materials is then passed through the elongated reaction zone or coil 17 which is maintained at a temperature within the range of 150–600° F., but preferably within the range of 200–500° F. or 300–475° F. At temperatures below about 475° F., substantially no fixed gases are produced during the conversion of the materials in zone 17, however, at temperatures above about 475° F. very small or negligible amounts of fixed gases may be formed. The pressure maintained in the coil or reaction zone 17 may vary over a wide range, that is, from atmospheric pressure to 6,000 pounds per square inch. In some cases the pressure may be even higher. We prefer to use a pressure within the range of about 200–4000 pounds per square inch. The time of contact employed in the reaction zone 17 may vary considerably, ranging from 1 to 150 minutes. When the naphtha in the reaction zone 17 is mostly in the liquid phase, we may use a reaction time of from 1 to 120 minutes, but preferably from 2 to 30 minutes. But when the hydrocarbon components, naphtha and feed gases, are mostly in the vapor phase, the reaction may be effected in a shorter period, namely, from 5 to 300 seconds. Any suitable heating medium, such as steam, hot oil, or thermally stable liquids, may be passed around the coil or heating zone 17 with the aid of conduits 18 and 19 to effect the desired heating or reaction between the hydrocarbon components in zone 17. Also, any suitable mixing means may be used in the reac-

tion zone to effect better contact between the hydrocarbons, catalyst and halide promoter. By keeping the materials in the reaction zone thoroughly mixed, the reaction time will be considerably reduced. Figure 2 shows three modified forms of the reaction zone 17 and these modified forms effect intimate contact between the hydrocarbons and catalysts and thereby reduce the time of contact to the lower parts of the above ranges.

The propane used in our process may be derived from any source, and the term "propane" is used herein to define a fraction of hydrocarbon gas containing no olefins and from 75 to 100% C_3H_8 . The other hydrocarbons which may be present in the propane consist almost entirely of the butanes.

As pointed out hereinafter, an aluminum halide-hydrocarbon complex, in the form of a solution, is formed in the system and it may be used as the catalyst in the reaction zone 17. Alternatively, additional amounts of fresh aluminum halide may be added to this aluminum halide-hydrocarbon complex and the admixture used as the catalyst in the reaction zone 17. When aluminum chloride is used as the catalyst this complex is called an aluminum chloride-hydrocarbon complex.

The converted products pass from the reaction zone through the transfer line 20 and valved conduit 21 and are introduced into the separator 22 where liquid phase separation is effected between the aluminum chloride-hydrocarbon complex on the one hand and the reacted and unreacted products on the other. Alternatively, the products in the transfer line may be passed through the cooler 23 before being introduced into the separator 22. The cooler is usually employed when the higher temperatures are used in the reactor 17. To assist further in the cooling of the products in the transfer line and thereby control the character of the reaction, all or a part of the naphtha feed stock may be used as a quenching medium and introduced into the transfer line through valved conduit 24. Also, oils heavier than the feed stock may be used as the quenching medium. The quenching step may be used with or without the assistance of the cooler 23.

An aluminum chloride-hydrocarbon complex settles to the lower part of the separator 22 in the form of a heavy liquid. This complex appears to be some kind of a loose combination between the aluminum chloride and a product of the aluminum chloride-hydrocarbon reactions. This solution is withdrawn from the bottom of the separator 22 through line 25 and passed by pump 26 through line 27 and check valve 28 to conduit 16 where it is returned to the reactor to serve as the catalyst for effecting the alteration of saturated chain hydrocarbons into branched-straight-chain paraffins or iso-hydrocarbons. When the aluminum chloride-hydrocarbon complex is recycled and used as the catalyst, hydrogen chloride or other hydrogen halides may be introduced into the system through line C with the aid of compressor 29 to serve as the promoter for the reaction. By recycling the aluminum chloride-hydrocarbon complex and adding small or large amounts of hydrogen chloride, as above described, only small amounts of the fresh catalyst need be added from time to time through line 15 to make up for losses. We have observed, however, that the presence of large amounts of hydrogen chloride or a promoter which liberates

a halogen acid in the presence of an aluminum halide retards the formation of excessive amounts of aluminum halide-hydrocarbon complex in the reaction zone and thereby keeps the aluminum halide in a highly reactive state for the purposes of our process. Intermittently or continuously all or a part of the aluminum halide-hydrocarbon complex may be withdrawn through valved conduit 30 and discarded or revived and re-used by introducing it into line 16. As another method of handling the aluminum chloride-hydrocarbon complex withdrawn from the bottom of separator 22, it may be passed through line 25, pump 26 and valved conduit 30a to the catalyst mixer 13 where small amounts of aluminum chloride are added thereto. This admixture is then passed from the bottom of the catalyst mixer 13 and introduced into line 16 as hereinbefore described. If desired, small amounts of hydrogen halides such as hydrogen chloride and hydrogen bromide may be added to the catalyst in the catalyst mixer 13 by means of valved line 13a or introduced into the system through line C. In the operation of our process we prefer to add the promoter to the process through conduit C rather than through the mixer 13.

The reacted and unreacted hydrocarbon products in separator 22 which are above the liquid level of the aluminum chloride-hydrocarbon complex as shown by line 31 are withdrawn through line 32 with the assistance of pressure regulator 33 and introduced into the fractionator 34. The pressure regulator 33 effects the desired reduction in pressure on the products before they enter the fractionator 34.

Fractionator 34 effects, as hereinafter indicated, the degree of fractionation desired. The temperature and pressure conditions, number of plates, and reflux ratio employed in the fractionator 34 may be varied to give the desired fractionation. The hydrocarbon products withdrawn from the top of the fractionator 34 contain the added unreacted propane, branched-chain paraffinic hydrocarbons produced in the process and controlled amounts of the naphthas charged to the system. This overhead fraction from tower 34 is passed through line 35 to the cooler 36 and thence into the reflux drum 37. Of course, the hydrogen halide promoter will be in the overhead from tower 34. The heavy hydrocarbon products in the bottom of fractionator 34 are withdrawn therefrom through line 38 and passed to the accumulator tank 39 where they may be recycled through conduit 40 with the aid of pump 41 to the inlet side of the system.

The degree of fractionation effected in tower 34 will determine to a large extent the composition of the final motor fuel product recovered from the bottom of tower 50. In one embodiment of our invention, the overhead products from tower 34 may consist of unreacted feed gas, and the fraction of hydrocarbons boiling within the gasoline range. For example, the overhead fraction from tower 34 may consist of the feed gas, and heavier hydrocarbons boiling up to about 390 to 430° F. In a second embodiment of our invention, the fractionator 34 may be operated so that end boiling point of the overhead will not exceed the end point of the motor fuel product desired. In either of these modifications, the low boiling constituents in the overhead from fractionator 34 are removed in the stabilizer 50 to give a high antiknock motor fuel

containing a large portion of branched-chain hydrocarbons.

In a third embodiment of our invention, the end boiling point of the fraction taken overhead from fractionator 34 may overlap only to a certain extent the initial boiling point of the feed naphtha charged to the system. In this embodiment, the branched-chain saturated hydrocarbons produced by the interaction of the hydrocarbon components in reactor 17 will be admixed with only a part of the hydrocarbons in the most volatile portion of the feed naphtha. For example, if the products charged to the reactor 17 consist of propane and a naphtha having an initial boiling point of about 200° F. and an end boiling point of about 460° F., the overhead from fractionator 34 may be cut at a point to exclude hydrocarbons boiling above about 390 to 410° F. Other naphthas may be used in this embodiment and the other embodiments of our invention, for example, straight run petroleum naphthas having initial boiling points within the range of 150-300° F. and end boiling points within the range of 440-500° F.

If desired, the fractionator 34 may be operated so that the end boiling point of the overhead therefrom does not overlap the initial boiling point of the feed naphtha to the extent indicated above. The end boiling point of the overhead from tower 34 may be cut at a point where the content of normally liquid straight-chain paraffins therein (excluding the gases, namely those boiling below 55° F.) will not exceed about 5 to 15% by volume. When the fractionator 34 is operated in this manner, the overhead therefrom will contain a very high concentration of saturated branched-chain hydrocarbons.

As a fourth modification of the method for operating fractionator 34, the end boiling point of the overhead therefrom may be cut at a point below the initial boiling point of the feed naphtha. For example, if the feed naphtha charged to the process, along with propane, has an initial boiling point within the range of 260 to 350° F., the end boiling point of the overhead fraction from tower 34 may be cut at a point slightly below the initial boiling point of the particular naphtha charged to the system.

The effect of the fractionation employed in tower 34 upon the final motor fuel product produced by our process will be discussed hereinafter in connection with the stabilizer 50.

Bubble trays 42 are placed in the tower 34 to assist in the fractionation. A portion of the heavy products in the bottom of tower 34 are withdrawn from trap-out plate 45, passed through line 46 to the reboiler 47 and then returned to the tower to supply heat for the fractionation of the products therein.

The liquefied products in the bottom of reflux drum 37 are recycled through line 48 with the aid of pump 49 to the top of the bubble tower or fractionator 34 and used as reflux. The overhead from the reflux drum is introduced into the stabilizer 50 where the desired fractionation is made between the normally gaseous hydrocarbons on the one hand and the higher boiling products on the other. The normally gaseous hydrocarbons in tower 50 consist almost entirely of the added unreacted propane and the isobutane produced by the catalytic reaction in the reaction zone 17. The product withdrawn from the bottom of stabilizer 50 through valved conduit 51 contains converted naphtha which has a much higher antiknock value than the original feed naphtha.

This increase in antiknock value is due, primarily, to the presence of branched-chain paraffins produced by the interaction of the feed naphtha and gases in reactor 17. These branched-chain paraffins are isobutane, branched-chain pentanes, branched-chain hexanes, branched-chain heptanes, branched-chain octanes and branched-chain paraffins containing 9 or more carbon atoms in the molecule. From the foregoing description of our process, it is apparent that the product removed from the bottom of tower 50 through valved conduit 51 contains a very large amount of branched-chain saturated hydrocarbons and, in addition, this fraction may be characterized as follows: (a) containing a substantial portion of the isobutane produced in the process and having an end point below or substantially equal to the end boiling point of the naphtha charged to the system; (b) containing a substantial portion of isobutane and having an end boiling point commensurate with that of commercial gasoline, that is, between 380 and 420° F.; (c) containing substantially no isobutane and having an end point below or substantially commensurate with the end boiling point of the feed naphtha; and (d) containing substantially no isobutane and having an end boiling point commensurate with that of commercial gasoline, that is, between 380 and 420° F. The high antiknock motor fuel products withdrawn through valved conduit 51 may be used as motor fuel as such or it may be blended with other hydrocarbon fractions such as debutanized cracked gasoline, polymerized gasolines or any motor fuel deficient in anti-detonating components. It is particularly desirable to blend the product referred to in (d) above with a motor fuel such as cracked gasoline or polymerized gasoline that already contains a sufficient amount of light ends to give a desired vapor pressure but which is deficient in high antiknock components such as the branched-chain paraffins. Also, it is particularly advantageous to blend the product referred to in (b) above with a partly debutanized or completely debutanized cracked gasoline to give a high antiknock motor fuel of desired volatility. The motor fuels produced by our process which have an end boiling point of about 390° F. or lower are particularly desirable as aviation motor fuel because of their anti-detonating and volatility characteristics, and high heating value.

The unreacted propane passes from the top of the stabilizer through line 52 to condenser 53 and thence into the reflux drum 54. If the isobutane produced in the reaction zone 17 is not removed from the bottom of tower 50 along with the high antiknock motor fuel fraction, it will pass overhead along with the propane. Bubble trays 55 or other fractionating means are placed in the stabilizer 50 to assist in the fractionation therein. A portion of the product in the bottom of the stabilizer may be withdrawn from trap-out plate 56 and passed through line 57 to the reboiler or heating means 58 and thence introduced into the bottom of the stabilizer. The heat added by the reboiler is usually sufficient to effect the desired fractionation in tower 50. It should be understood that other heating means may be used in the bottom of towers 34 and 50 instead of, or in combination with the herein described reboilers.

A portion of the liquid hydrocarbons in reflux drum 54 is withdrawn through line 59 and passed by pump 60 through valved conduit 61 to the top of the stabilizer for use as reflux. If desired, a cooling coil may be placed in the top of tower 50

to condense a part of the vapors therein for use as reflux. A portion of the liquefied hydrocarbon product in line 59 may be passed through valved conduit 62 and introduced into the manifold 11 for further use in the process of converting straight-chain paraffins into branched-chain paraffins. By employing an efficient cooler at 53, substantially all of the products in reflux drum 54 will be in the liquid phase and the portion thereof that is not used as reflux may be recycled through line 62 to the reactor 17—thereby avoiding the necessity of compressing the gases that are removed from the overhead of drum 54. As previously stated, the halogen-containing promoter which is employed in the reaction zone 17 will pass along with the overhead from towers 34 and 50 and consequently a substantial portion of this promoter will be present in the products recycled from drum 54 to the reactor 17. If desired, the draw-off line 63 may be used to withdraw from the system a portion of the liquefied hydrocarbon product in line 59.

The uncondensed gas in reflux drum 54, assuming that all of the products in drum 54 are not recycled in the liquid phase as previously indicated, is recycled to the inlet side of the system through valved conduit 64. Also, a portion of the hydrogen halide promoter used in the process will pass along with this overhead product. If desired, all of the hydrocarbons withdrawn from the top of reflux drum 54 may be passed through valved conduit 65 and introduced into the absorber 66 where the hydrogen halide such as hydrogen chloride is separated from these gases. Water, hydrochloric acid or any other suitable solvent may be introduced into the top of the absorber through line 67 and withdrawn through the bottom thereof through line 68 with the dissolved promoter. The thus washed gases may be returned to the recycled gas line through valved conduit 69. From time to time a small portion of these gases may be vented through valved conduit 70 in order to prevent inert gases from building up in the system. By removing the halide promoter and any free halogen that may be present in these gases, corrosion of the compressor 12 is avoided.

It is apparent, therefore, that in the operation of our process only the liquefied fraction of hydrocarbons, containing the isobutane and propane, withdrawn from the bottom of reflux drum 54 may be recycled through line 62 to the reaction zone. Alternatively, or in combination with this step, a portion of or all of the liquefied fraction and all or a substantial part of the gases removed from the top of reflux drum 54 may be recycled to the reaction zone. In carrying out any of the hereinbefore described embodiments of our process, the pressure and temperature maintained in separator 54 may be regulated so that the liquid product withdrawn through line 63 will consist largely of isobutane. Of course, when it is desired to remove substantially all of the isobutane from the liquid products in separator 54 the liquid products in the bottom of separator 54 may be passed to a fractionator (not shown) whereby a sharp fractionation is made between propane on the one hand and isobutane on the other. When the separator 54 or the fractionator (not shown) are used to make a sharp separation between the propane fraction and isobutane, the liquid products from the bottom of separator 54 or the fractionator (not shown) are not recycled but all or substantially all of the gases removed

from the top of the separator 54 or the fractionator are recycled.

As another embodiment of our process, the feed gases introduced through line B may consist almost entirely of propane and the naphtha introduced through line A may have an initial boiling point above about 260° F. When these materials are used as the charging stock and subjected to the action of aluminum chloride or the aluminum chloride-hydrocarbon complex while in the presence of a promoter such as hydrogen chloride, hydrogen bromide, carbon tetrachloride and the like, the fractionators 34 and 50 may be operated to give a product in line 51 which boils below 260° F. and which consist predominantly of branched-chain hydrocarbons containing from 4 to 8 carbon atoms each in the molecule. In this case the stabilizer 50 may be operated so that only the branched-chain hydrocarbons containing from 5 to 8 carbon atoms are withdrawn from the bottom thereof through line 51 and the propane and isobutane recycled by any of the methods hereinbefore described.

The temperature employed in the tops and bottoms of towers 34 and 50 as well as the pressures maintained therein may be varied in order to effect the desired type of fractionation. When tower 34 is operated at a pressure of about 210 pounds per square inch, a top temperature of about 440° F. and a bottom temperature of about 600° F., the products withdrawn from the bottom thereof through line 38 will consist mostly of hydrocarbons boiling above about 410 to 430° F. whereas the products taken overhead from tower 34 will consist mostly of the lower molecular weight hydrocarbons. When tower 50 is operated at a pressure of about 200 pounds per square inch, a top temperature of about 200° F. and a bottom temperature of about 500° F., the products withdrawn through line 51 will be substantially free of propane and isobutane, however, if tower 50 is operated at a pressure of about 200 pounds per square inch, a top temperature of about 110° F. and a bottom temperature of about 400° F., a substantial portion of isobutane produced by the process will be retained in the product withdrawn from the bottom of the tower.

In carrying out our herein described process, the portions of products charged to the reaction chamber 17 may vary somewhat. For example, for one part by weight of naphtha charged to the reactor, the parts by weight of gas, catalyst and promoter may be from 0.1 to 1; 0.01 to 1; and 0.03 to 0.3 respectively. The proportion of gas referred to above applies to the use of propane per se or the admixture of propane and isobutane.

In any of the modifications hereinbefore set forth, we may withdraw a part of the oil from accumulator tank 39 through valved conduit 71 instead of recycling it to the reaction zone. Alternatively, a once-through operation may be used wherein the heavy products in the accumulator tank 39 are not recycled. However, in this once-through conversion of the naphtha we do recycle the gases by any of the methods hereinbefore described.

As stated hereinbefore, Figure 2 shows some of the modified forms of the reaction zone which may be used to effect intimate liquid phase contact as well as vapor phase contact between the hydrocarbon reactants and catalysts. In describing the three modifications of the reaction zone, the same numerals will be used, whenever possible, as are used on Figure 1.

Modification A illustrates the use of a mixer mounted within the reaction zone 17. This modification is used preferably for liquid phase operations. The feed naphtha, gases, catalyst and promoter enter the reactor 17 through the manifold 11 and pass into the reactor through line 11a. If desired, a part or all of the catalyst and/or promoter may be added to the reactor through line 11b. As the hydrocarbon, catalyst and promoter pass up through the reactor, they are thoroughly mixed by the revolving blades 72 which are mounted on the shaft driven by the motor 73. A packing is placed around the shaft at 74 to prevent the escape of gases and liquids from the reaction zone. A closed steam coil 75 is placed inside the reactor to provide the necessary heat for the reaction, however, the products in line 11 may be heated by any conventional means before entering the reactor 17. The converted products pass from the reaction zone through the transfer line 20, valved conduit 21 and are introduced into the separator 22 where liquid phase separation is effected between the aluminum halide-hydrocarbon complex on the one hand and the reacted and unreacted products on the other. Alternatively, the products in the transfer line may be passed to the cooler 23 being introduced into the separator 22. The feed stock may be introduced through valved conduit 24. The aluminum halide-hydrocarbon complex is withdrawn from the lower part of the separator 22 and passed by line 25, pump 26, line 27 and check valve 28 to the inlet of the reaction zone. Intermittently or continuously all or a part of the aluminum halide-hydrocarbon complex may be withdrawn through valved conduit 30 and treated as hereinbefore described. The reacted and unreacted hydrocarbon products in separator 22 which are above the liquid level of the complex as shown by line 31 are withdrawn through line 32 with the assistance of pressure regulator 33 and introduced into the fractionator 34. In brief, this modification of the reaction zone is very easily adapted to the process hereinbefore described with reference to Figure 1.

Modification C illustrates the use of a mixer mounted within the reaction zone, similar to that shown in modification A, with the improvement of permitting the recycling of gases within the reaction zone before the reacted and unreacted products are passed to the fractionating system. The reacted products pass from the top of the reaction zone through line 20 and are introduced into separator 76 where the unreacted gases are withdrawn from the top thereof through valved conduit 77 and returned with the aid of the compressor 78 to the bottom of the reactor 17. This step of recycling the unreacted gases in combination with the turbo-mixer provides an excellent way of obtaining thorough contact between the gases and promoter on the one hand and the liquid feed naphtha and aluminum chloride catalyst on the other. The liquid products in the bottom of separator 76, including the aluminum halide-hydrocarbon complex as well as liquid hydrocarbons, are withdrawn from the bottom thereof through line 79 and introduced into the separator 22. The separation effected in separator 22 and the method of handling the aluminum halide-hydrocarbon complex and hydrocarbon products are the same as described with reference to modification A and also Figure 1. To prevent the building up of unreacted hydrocarbons within reaction zone 17, a valved by-pass 77a is provided for venting some of the gases in

separator 76 into conduit 32 so that they will pass into the fractionating system as described in Figure 1.

In either of the above two modifications, we may use a turbo-mixer in the place of the mixing device shown.

Modification B illustrates the use of a vapor phase reaction chamber. The feed naphtha, gases and promoter enter the reactor 17 through the manifold 11 and pass into the reactor through line 11a. If desired, a part or all of the promoter may be added to the reactor through line 11b. The products in line 11a are sprayed or atomized into the bottom of the reaction zone 17. We prefer to heat the hydrocarbons in manifold 11 before they enter zone 17 so that they will vaporize when introduced therein. A closed steam coil 75 is provided in the chamber to maintain the desired temperature therein. The catalyst comprising a mineral oil slurry of the aluminum halide is sprayed into the top of the chamber 17 through conduit 15. This slurry of catalyst may be prepared in the mixer as shown by Figure 1. The counter-current contact between the descending catalyst and ascending hydrocarbon vapors and promoter insures intimate contact between the products in the reaction zone 17. The aluminum halide-hydrocarbon complex falls to the bottom of the chamber 17 and is withdrawn through line 80. If desired, the liquid level of the aluminum halide-hydrocarbon complex or catalyst solution in zone 17 may be permitted to rise a short distance above the level of the nozzle on line 11a so that the feed products in line 11 will be atomized into the liquid catalyst or catalyst slurry. This complex or liquid catalyst may be recycled directly to line 15 or it may be mixed with additional quantities of the aluminum halide and/or promoter and returned to line 15. The reacted and unreacted hydrocarbon constituents in zone 17 are withdrawn from the top thereof through line 81 with the assistance of the pressure-reducing valve 82 and introduced into the fractionator 34 as shown in Figure 1.

The pressure and temperature conditions maintained in modifications A, B and C of the reaction zone may be the same as those described in connection with Figure 1. Also, it has already been pointed out that the time of contact may vary over a relatively wide range and that thorough mixing or agitation of the constituents in the reaction zone 17 materially shortens this time of contact.

While we have described our invention with reference to specific examples by way of illustration, it is apparent that other modifications may be employed.

We claim:

1. In a process for converting substantial amounts of the straight-chain paraffin hydrocarbons in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial

part of the straight-chain paraffin hydrocarbons in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

2. In a process for converting substantial amounts of the straight-chain paraffin hydrocarbons in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at a temperature within the range from about 150° F. to about 600° F. and under superatmospheric pressure, whereby substantially no hydrogen and methane are formed, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

3. The process of claim 2 wherein said temperature is in the range from about 200° F. to about 500° F. and said pressure is in the range from about 200 to about 4000 pounds per square inch.

4. In a continuous process for converting substantial amounts of the straight-chain paraffin hydrocarbons in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain paraffin hydrocarbons in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating therefrom an aluminum halide-hydrocarbon complex, fractionating the remaining hydrocarbon products to produce said motor fuel fraction and a gaseous fraction consisting largely of propane and substantially free of unsaturated hydrocarbons, and recycling at least a portion of said gaseous fraction to said reaction zone.

5. In a continuous process for converting substantial amounts of the straight-chain paraffin hydrocarbons in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at a tempera-

ture within the range from about 150° F. to about 600° F. and under superatmospheric pressure, whereby substantially no hydrogen and methane are formed, withdrawing the products from said reaction zone and separating therefrom an aluminum chloride-hydrocarbon complex, fractionating the remaining hydrocarbon products to product said motor fuel fraction and a gaseous fraction consisting largely of propane and substantially free of unsaturated hydrocarbons, and recycling at least a portion of said gaseous fraction to said reaction zone.

6. In a process for converting substantial amounts of the straight-chain paraffin hydrocarbons in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at a temperature within the range from about 200° F. to about 500° F. and under a pressure in the range from about 200 to about 4000 pounds per square inch, whereby substantially no hydrogen and methane are formed, withdrawing the products from said reaction zone and separating therefrom an aluminum chloride-hydrocarbon complex, subjecting the remaining hydrocarbon products to stabilization, whereby substantially all of the isobutane is removed from said hydrocarbon products, and said motor fuel fraction and a gaseous fraction consisting largely of propane and isobutane and substantially free of unsaturated hydrocarbons are produced, and recycling at least a portion of said gaseous fraction to said reaction zone.

7. In a continuous process for converting straight-run petroleum naphtha containing substantial amounts of straight-chain paraffin hydrocarbons and a fraction of substantially completely saturated gases containing at least 85% of propane into a motor fuel product containing relatively large amounts of saturated branched-chain hydrocarbons, the steps comprising contacting in a reaction zone an admixture of said straight-run petroleum naphtha, said fraction of saturated hydrocarbon gases containing at least 85% propane, an aluminum halide and a halogen promoter, at an elevated temperature and pressure sufficient to convert a part of the hydrocarbon components therein into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from the reaction zone and separating therefrom an aluminum halide-hydrocarbon complex, subjecting the remaining hydrocarbon products to stabilization, thus removing from said remaining hydrocarbon products substantially all of the normally gaseous hydrocarbons and thereby forming a motor fuel product of lower vapor pressure than commercial gasoline but containing relatively large amounts of branched-chain hydrocarbons and recycling at least a portion of the normally gaseous hydrocarbons separated by the stabilization to the reaction zone for further use.

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