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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

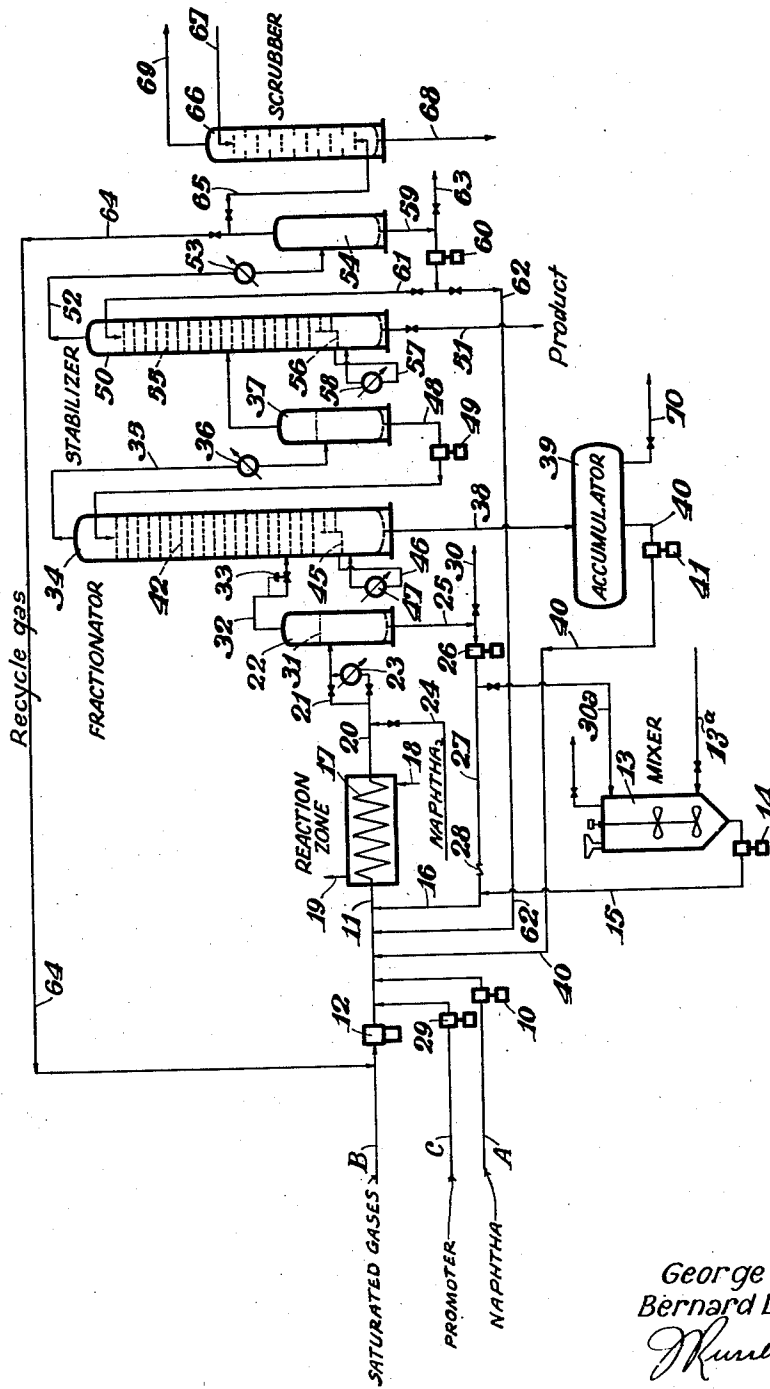


Fig. 1

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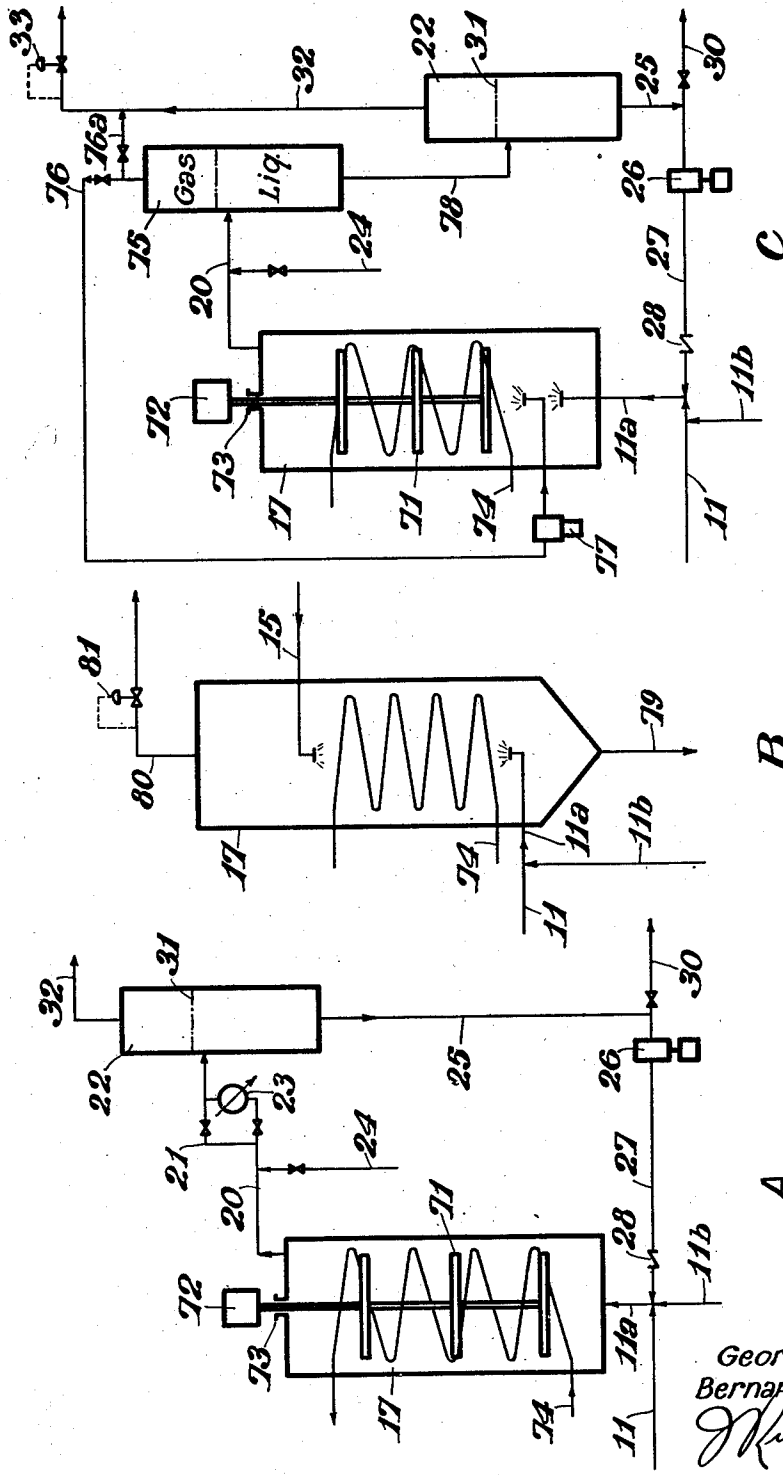


Fig. 2

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UNITED STATES PATENT OFFICE

2,220,092

CONVERSION OF HYDROCARBON PRODUCTS

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8 Claims. (Cl. 196—9)

This invention relates to the preparation of saturated branched-chain hydrocarbons including the saturated iso-hydrocarbons from an admixture of higher-boiling and lower-boiling aliphatic hydrocarbons with the aid of catalysts. In particular, our invention relates to the preparation of motor fuel products 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 paraffins 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 straight run naphtha, having a selected initial boiling point, and certain normally gaseous saturated hydrocarbons into branched-chain hydrocarbons having boiling points below or slightly overlapping the initial boiling point of the naphtha charged to the process. Examples of the paraffinic straight run naphthas are Mount Pleasant naphtha, Pennsylvania naphthas, Mid-Continent naphthas and the like. This conversion or branching of the hydrocarbons is effected without substantial formation of fixed gases such as hydrogen and methane. Following the conversion step the products are subjected, in one embodiment of our invention, to close fractionation in order to isolate a very substantial portion of the iso- and branched-chain paraffinic hydrocarbons produced in the process. A further description of the fractionating step as adapted to our conversion process will be set forth in detail hereinafter.

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.

One embodiment of our process will be described with reference to the conversion of saturated straight run petroleum naphtha having an initial boiling point above about 235° F. in the presence of an admixture of normally gaseous hydrocarbons such as propane, butane, and possibly some ethane. The straight run petroleum

naphtha containing C₃ and higher-boiling hydrocarbons, but substantially no hydrocarbons boiling below 235° F. enters the system through conduit A and is forced by pump 10 into the manifold 11. A mixture of saturated gases containing propane, butane, and some ethane enters the system through line B and is forced by compressor 12 into the manifold 11 where they are mixed with the other products therein. Also, a slurry or solution of aluminum chloride and 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 aluminum bromide. The naphtha, gases, 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. The reaction zone may be modified as shown by Figure 2. 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. a 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 200–4,000 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 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 reacted 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. Alternatively, we may use one of the reaction zones shown in Figure 2 and discussed hereinafter. By keeping the materials in the reaction

zone thoroughly mixed, the reaction time will be considerably reduced. By effecting the reaction of the hydrocarbon components in the vapor phase, the time of contact is still further reduced as indicated above.

As pointed out hereinafter, an aluminum chloride-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 chloride may be added to this aluminum chloride-hydrocarbon-complex and the admixture used as the catalyst in the reaction zone 17.

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 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 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. Oils heavier than the feed stock may be used as the quenching medium and the quenching step may be used with or without the assistance of the cooler 23. When a part or all of the feed naphtha is introduced through line 24 and used as a quenching medium, it returns to the reaction zone by the route of separator 22, line 38, accumulator tank 39 and line 40.

The 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 straight-chain hydrocarbons into branched-chain paraffins or iso-hydrocarbons. When the aluminum chloride complex is recycled and used as the catalyst, hydrogen chloride or other hydrogen halides may be introduced into the system through line C and 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 in the reaction zone 17 retards the formation of excessive amounts of aluminum chloride-hydrocarbon complex and thereby keeps the aluminum chloride in a highly reactive state for the purposes of our process. Intermittently or continuously all or a part of the aluminum chloride-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 may be operated at different temperatures and pressures, and it effects a sharp separation between the unreacted naphtha on the one hand and the saturated branched-chain or iso-hydrocarbons and added gases on the other. The hydrocarbon products withdrawn from the top of the fractionator 34 contain the added unreacted gases, branched-chain paraffinic hydrocarbons produced in the process and none or controlled amounts of the most volatile portion of the naphtha charged to the system. This overhead fraction from tower 34 is passed through line 35 to the cooler 36 and then introduced into the reflux drum 37. Of course, the hydrogen halide promoter will be in the overhead from tower 34. The 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 has an important bearing upon the successful and efficient operation of our process. In one embodiment of our invention, the overhead products from tower 34 may consist almost entirely of the unreacted feed gases and a fraction of branched-chain saturated hydrocarbons boiling below the initial boiling point of the naphtha charged to the system. For example, if the feed gases are an admixture of saturated C₂, C₃ and C₄ hydrocarbons and the feed naphtha has an initial boiling point within the range of 235 to 300° F., the overhead from tower 34 may consist almost entirely of unreacted feed gases and branched-chain saturated hydrocarbons boiling below the initial boiling point of the feed naphtha employed. Other naphthas used in our process may have initial boiling points ranging from 200° F. and higher. The feed gases may contain varying amounts of saturated C₂, C₃ and C₄ hydrocarbons, for example, the feed gases may contain only the saturated C₃ and C₄ hydrocarbons.

In the second embodiment of our invention, the end boiling point of the fraction taken overhead from fractionator 34 may overlap to a certain extent the initial boiling point of the feed naphtha. In this embodiment, the branched-chain saturated hydrocarbons will be admixed with the hydrocarbons in the front end of the feed naphtha. It is not desirable to permit a large amount of the hydrocarbons in the most volatile portion of the feed naphtha to pass overhead from tower 34 because they tend to reduce the amount of branched-chain saturated hydrocarbons con-

tained in the final motor fuel product separated from the process. If, in carrying out this embodiment of our invention, the feed gases are an admixture of saturated hydrocarbons and the feed naphtha has an initial boiling point within the range of 200-270° F., the overhead fraction from tower 34 may contain the unreacted feed gases and hydrocarbons boiling up to and overlapping the initial boiling point of the feed naphtha. For example, if the feed naphtha has an initial boiling point of about 200° F., 220° F., 235° F., or 265° F., the end boiling point of the overhead fraction from tower 34 may be above the initial boiling point of the naphtha used but below about 285° F. In most cases, the amount of branched-chain hydrocarbons in the overhead from tower 34 will be at least as high as 70% of the total paraffin hydrocarbons boiling above the C₄ gases.

In general, when fractionator 34 is operated so that the end boiling point of the overhead therefrom overlaps the initial boiling point of the feed naphtha, regardless of the initial boiling point of the feed naphtha, we prefer to fractionate to a degree defined by one of the following two methods. The first method is to cut the end boiling point of the overhead from tower 34 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 4 to 7% by volume. The second method is to operate tower 34 so that the temperature of the 95% point of the overhead fraction shall not exceed the temperature of the 5% point of the fraction withdrawn from the bottom of tower 34. The 5% and 95% points mentioned above refer to an A. S. T. M. distillation curve. By following either of these methods for determining the degree of fractionation in tower 34, we may recover a product from tower 50 which contains a very high percentage of saturated branched-chain hydrocarbons and which are very useful as high antiknock motor fuel per se or in combination with other gasoline fractions deficient in high antiknock hydrocarbons.

Bubble trays 42 are placed in the tower 34 to assist in the fractionation and it is desirable to use a large number of trays in order to effect the sharp fractionation between the products therein. A portion of the heavy products in the bottom of tower 34 are withdrawn from the 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.

A portion or all of 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. These higher boiling products consist mostly of the branched-chain saturated hydrocarbons produced in the process. In some instances, depending upon the fractionation effected in tower 34, controlled amounts of normally liquid straight-chain hydrocarbons will be present in the fraction of branched-chain saturated hydrocarbons. In addition, a portion, or substantially all, of the C₄ hydrocarbons in the stabilizer 50 may be removed from the bottom thereof along with the motor fuel fraction of branched-chain saturated hydrocarbons. This is particularly desirable when the

fraction of branched-chain hydrocarbons are to be blended with other hydrocarbon fractions such as debutanized cracked gasoline, polymerized gasolines or any motor fuel deficient in light ends because the C₄ hydrocarbons impart desirable volatility characteristics to motor fuels. The final product that is withdrawn from the bottom of stabilizer 50 through valved conduit 51 consists mostly of branched-chain paraffins, for example, the branched-chain pentanes, branched-chain hexanes, branched-chain heptanes and branched-chain octanes. 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) having initial and end boiling points intermediate the gases and naphtha charged to the system; (b) containing C₄ hydrocarbons such as butane and isobutane and having an end boiling point at or below the initial boiling point of the feed naphtha; (c) containing substantially no C₄ hydrocarbons and having an end boiling point that overlaps to a small extent the initial boiling point of the feed naphtha; and (d) containing some C₄ hydrocarbons and having an end boiling point that overlaps to a small extent the initial boiling point of the feed naphtha.

The unreacted gases, including all or controlled amounts of the C₄ hydrocarbons, pass from the top of stabilizer through line 52 to condenser 53 and thence to the reflux drum 54. 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 reintroduced into the tower. The heat added by the reboiler is sufficient to effect the desired fractionation in tower 50. It should be understood that other heating means may be used in the bottoms of towers 34 and 50 instead of the herein described reboilers.

A portion of the liquid hydrocarbons in reflux drum 54, consisting almost entirely of saturated hydrocarbons, is withdrawn through line 59 and passed by pump 60 through valved conduit 61 to the top of the stabilizer for use as reflux. A portion of this 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, a very substantial proportion of the gases introduced into reflux drum 54 will be liquefied and consequently can be recycled to the reaction zone very economically. If desired, the draw-off line 63 may be used to withdraw from the system a portion of the liquefied hydrocarbons in line 59.

The uncondensed gases in reflux drum 54 may be recycled to the inlet side of the system through valved conduit 64. Gases in line 64 consist predominantly of ethane and propane and relatively small amounts of butanes. Also, the gases recycled through line 64 contain a portion of the hydrogen chloride gas or hydrogen halide gas that passed along with the overhead products. A portion or all of the hydrocarbons withdrawn from the top of the reflux drum 54 may be passed through valved conduit 65 and introduced into the absorber 66 where the 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 from the bottom thereof through line 68 with the dissolved hydrogen chloride. The thus washed gases may be vented through line 69 and disposed of in any suitable manner.

It is apparent, therefore, that in the operation of our process only the liquefied fraction of hydrocarbons, consisting mostly of the butanes 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 or all of this liquefied fraction and all or a substantial part of the gases removed from the top of the reflux drum 54 may be recycled to the reaction zone. As another modification, the liquefied fraction of hydrocarbons withdrawn from the bottom of the reflux drum 54 and which is not used as reflux for stabilizer 50, may be withdrawn from the system through valved conduit 63; in this event, all or a substantial part of the hydrocarbons withdrawn from the top of the reflux drum are recycled to the reaction zone.

In carrying out any of the hereinbefore described embodiments of our process, the pressure and temperature of the products in separator 54 may be regulated so that the liquid product withdrawn through line 63 will consist mostly of butanes. In this case, the liquid products withdrawn from the bottom of separator 54 are not recycled but all or substantially all of the gases removed from the top of the separator 54 are preferably recycled. The butanes separated through line 63 may be blended with other motor fuel fractions such as those hereinbefore described.

In another modification of our process, the feed gases introduced through line B may consist largely of propane and butanes and the naphtha introduced through line A may have an initial boiling point above about 240° F. When these materials are used as a charging stock and subjected to the action of hydrogen chloride in the presence of the aluminum chloride-hydrocarbon complex, the fractionators 34 and 50 may be operated to give a product in line 51 which consists predominantly of branched-chain hydrocarbons containing 7 and 8 carbon atoms each. Relatively smaller amounts of branched-chain hydrocarbons containing 6, 5 and 4 carbon atoms each will also be present in this product. The unreacted propane and butanes and the entrained hydrogen chloride will be recycled to the inlet side of the system through lines 62 and/or 64.

The temperatures 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 100 pounds per square inch, a top temperature of about 400° F. and a bottom temperature of about 580° F., the products removed from the bottom thereof through line 38 will consist mostly of C₉ and higher molecular weight hydrocarbons whereas the products taken overhead from tower 34 will consist mostly of C₈ and lower molecular weight hydrocarbons. When tower 50 is operated at a pressure of about 90 pounds per square inch, a top temperature of about 140° F. and a bottom temperature of about 320° F., the products withdrawn through line 51 will consist largely of branched-chain paraffins containing from C₅ to C₈ carbon atoms each in the molecular and the hydrocarbons removed from the overhead of

tower 50 will consist mostly of C₄ and lighter hydrocarbons. The amount of hydrocarbons in the bottoms from tower 50 which are not branched-chain hydrocarbons will depend upon the degree of fractionation effected in tower 34.

In carrying out our herein described processes, the proportions of products charged to the reactor 17 may vary somewhat, for example, for one part by weight of naphtha charged to the reactor, the parts by weight of hydrocarbon gases, aluminum chloride and hydrogen halide may be from 0.1 to 1; 0.01 to 1; and 0.03 to 0.3 respectively. The proportions of ethane, propane and butanes in the feed gases may vary over a relatively wide range. For example, the composition of the gases charged to reactor 17 may contain from 15 to 40% by volume of ethane, 15 to 50% by volume of propane and 5 to 20% by volume of butanes. It should be understood that other proportions of these hydrocarbons may be used in the feed gases. In some cases, no ethane is charged to the system. The saturated hydrocarbon gases charged to the system may be derived from natural gas or separated from refinery gases. Methane does not assist in the reaction of producing branched-chain saturated hydrocarbons by our process and consequently should not be included in the feed gases.

In any of the modifications hereinbefore set forth, we may withdraw a part of the oil from accumulator tank 39 through valved conduit 70 instead of recycling it to the reaction zone.

The fractions of branched-chain paraffins produced by our process are particularly useful as aviation motor fuels.

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 the 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 71 which are mounted on the shaft driven by the motor 72. A packing is placed around the shaft at 73 to prevent the escape of gases and liquids from the reaction zone. A closed steam coil 74 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 before 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 75

rator 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 75 where the unreacted gases are withdrawn from the top thereof through valved conduit 76 and returned with the aid of the compressor 77 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 with the liquid feed naphtha and aluminum chloride catalyst on the other. The liquid products in the bottom of separator 75, including the aluminum halide-hydrocarbon complex as well as liquid hydrocarbon, are withdrawn from the bottom thereof through line 78 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 is 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 76a is provided for venting some of the gases in separator 75 into conduit 32 so that they will pass into the fractionating system as described in Figure 1.

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

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 11b. 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 74 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 79. 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 80 with the assistance of the pressure-reducing valve 81 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 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, at least one normally gaseous hydrocarbon having at least two carbon atoms per molecule, 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 heavier than methane 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, at least one normally gaseous hydrocarbon having at least three carbon atoms per molecule, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely heavier than ethane 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, at least one normally gaseous hydrocarbon having at least three carbon atoms per molecule, 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 heavier than ethane 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 hydrocarbons heavier than ethane 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, at least one normally gaseous hydrocarbon having at least three carbon atoms per molecule, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely heavier than ethane and substantially free of unsaturated hydrocarbons, at a temperature within the range from about 150° F. to about 600° 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, fractionating the remaining hydrocarbon products to produce said motor fuel fraction and a gaseous fraction consisting largely of hydrocarbons heavier than ethane 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 producing a motor fuel fraction rich in saturated branched-chain hydrocarbons and having a relatively high antiknock value, the steps comprising contacting in a reaction zone an admixture of a straight run petroleum fraction having an initial boiling point above about 200° F. and containing substantial amounts of straight-chain paraffin hydrocarbons, at least one normally gaseous hydrocarbon having at least three carbon atoms per molecule, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide

and their hydrocarbon complexes, and a hydrogen halide-affording promoter for said catalyst, the reacting hydrocarbon gases present being largely heavier than ethane 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 fraction 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.

7. The method of producing saturated branched-chain hydrocarbons suitable as motor fuel of the gasoline type which comprises heating in a reaction zone a flowing stream of an admixture of straight run petroleum naphtha having an initial boiling point above about 200° F. and containing substantial amounts of straight-chain paraffin hydrocarbons, substantially completely saturated normally gaseous hydrocarbons comprising mostly propane and butane, aluminum chloride and hydrogen chloride, at an elevated temperature and pressure sufficient to convert a part of the saturated hydrocarbon components therein into saturated branched-chain hydrocarbons suitable as motor fuel and without substantial formation of hydrogen and methane, withdrawing the products from the reaction zone and separating an aluminum chloride-hydrocarbon complex therefrom, fractionating the remaining hydrocarbon products of conversion into an overhead fraction containing said saturated branched-chain hydrocarbons and a bottom fraction to such a degree that the temperature of the 95% point of the overhead fraction does not exceed the temperature of the 5% point of the bottom fraction, and recycling at least a part of said bottom fraction to the reaction zone for further conversion.

8. In a process for producing a motor fuel fraction rich in saturated branched-chain hydrocarbons and having a relatively high antiknock value, the steps comprising contacting in a reaction zone an admixture of a straight run petroleum fraction having an initial boiling point above about 200° F. and containing substantial amounts of straight-chain paraffin hydrocarbons, at least one normally gaseous hydrocarbon having at least three carbon atoms per molecule, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a hydrogen halide-affording promoter for said catalyst, the reacting hydrocarbon gases present being largely heavier than ethane and substantially free of unsaturated hydrocarbons, at an elevated temperature within the range from about 150° F. to about 600° F. and under a pressure within the range from about 200 to about 4000 pounds per square inch, whereby a substantial part of the straight-chain paraffin hydrocarbons in said petroleum fraction is converted 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.

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