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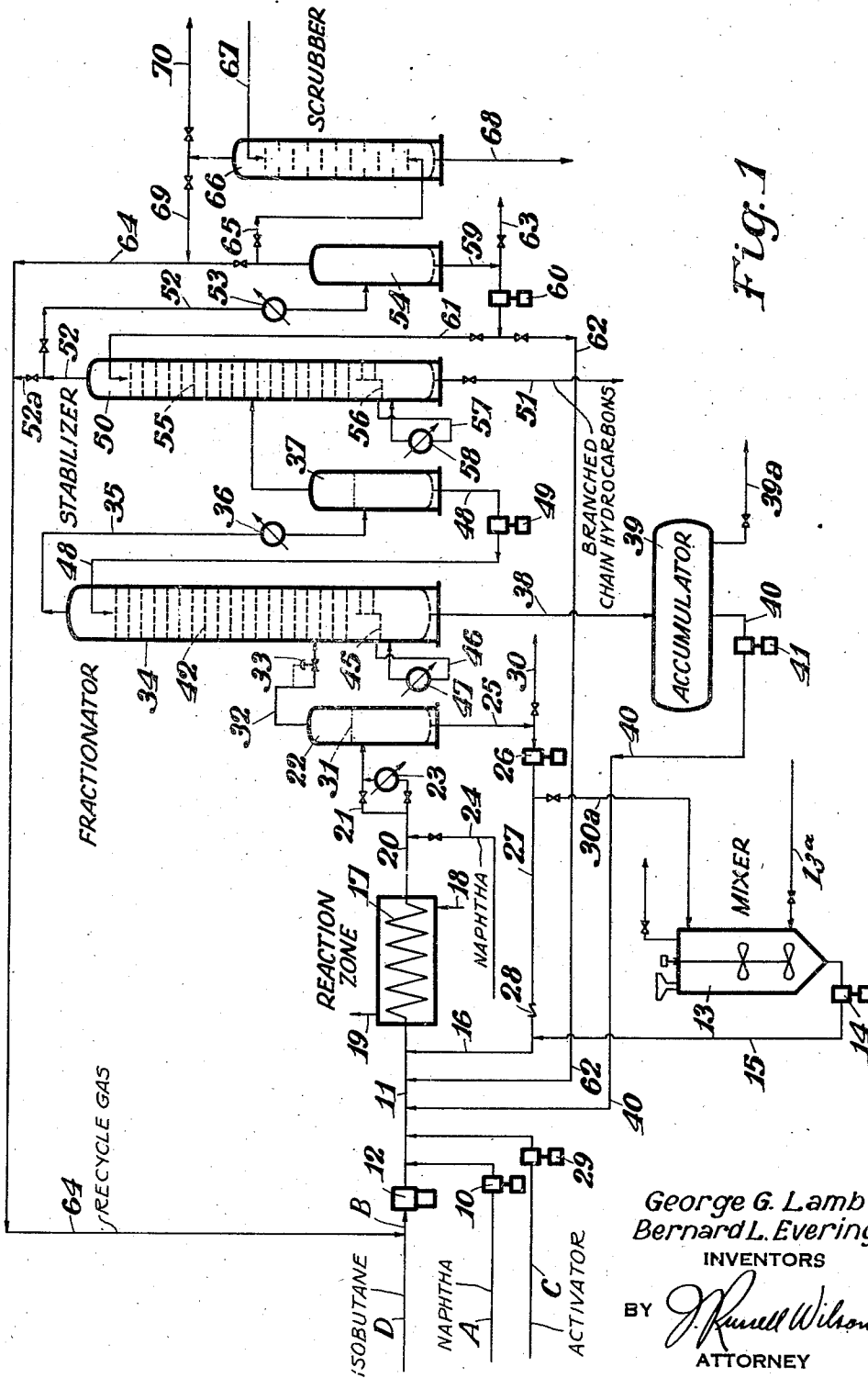
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2,220,090

CONVERSION OF HYDROCARBON PRODUCTS

Filed Nov. 24, 1937

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

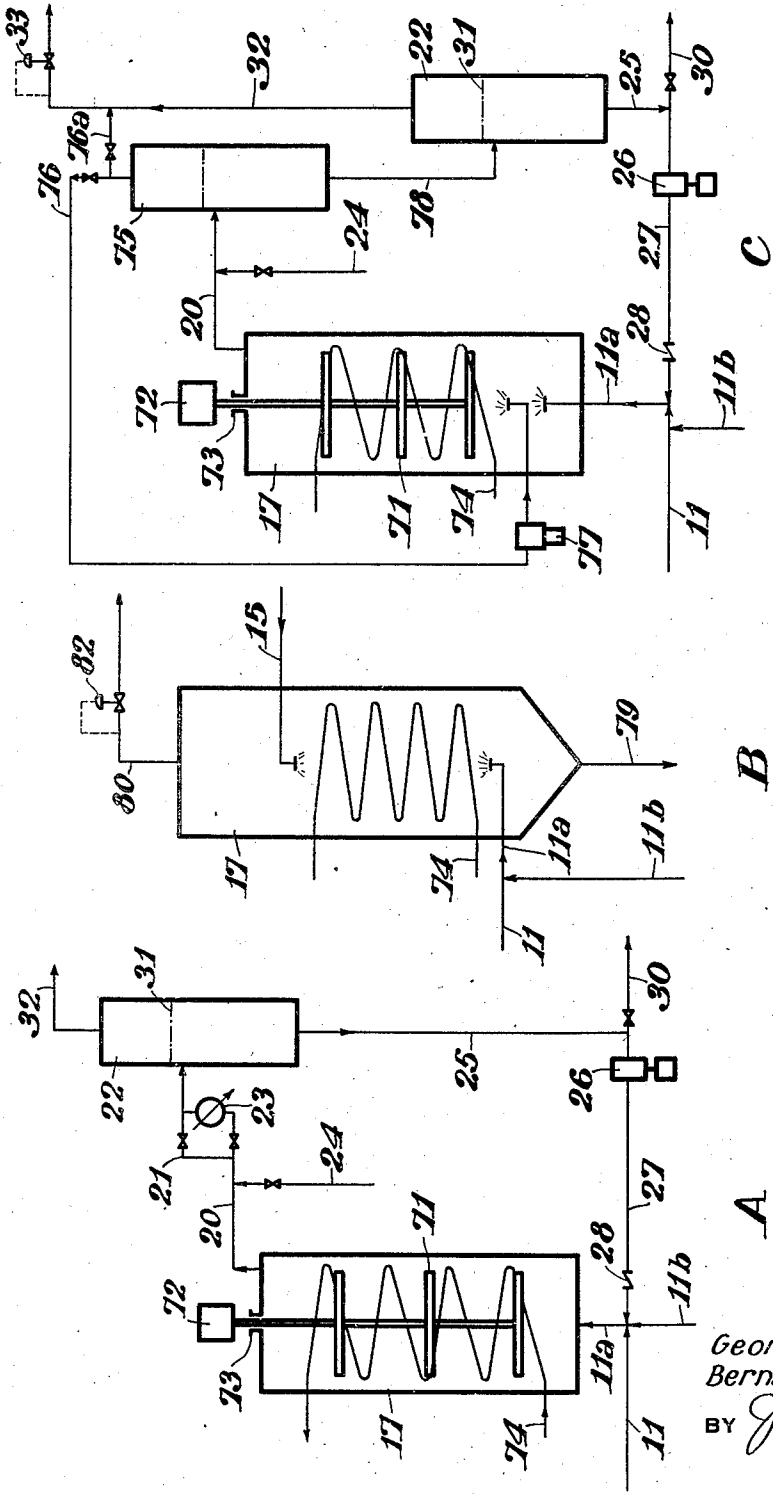


Fig. 2

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## UNITED STATES PATENT OFFICE

2,220,090

## CONVERSION OF HYDROCARBON PRODUCTS

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6 Claims. (Cl. 196—9)

This invention relates to the preparation of a high antiknock motor fuel from an admixture of isobutane and straight-run petroleum naphtha with the aid of catalysts. In particular, our invention relates to the preparation of a motor fuel product containing relatively large quantities of normally liquid 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 react straight run petroleum naphtha or saturated petroleum naphtha with isobutane prepared in situ to produce a motor fuel product 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 naphtha and the like. This conversion of the admixture of hydrocarbons into normally liquid branched-chain saturated 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. The drawings, particularly Figure 1, attached to and forming a part of the specification are diagrammatic illustrations 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 a petroleum naphtha that has an initial boiling point within the range of 150-200° F. and an end boiling point ranging

from 360 to 420° F., however, our process may be used with petroleum naphthas that have initial boiling points above about 60° F. and end boiling points within the range of 400-500° F. The straight run petroleum naphtha enters the system through conduit A and is forced by pump 10 into the manifold 11. Isobutane 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. We prefer to use in our process the isobutane produced in the reaction zone of our process and the isobutane so produced is introduced into line E through the recycled gas conduit 64. If desired, however, isobutane from an extraneous source may be introduced into the system through line D. 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 manifold 11 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 250-475° 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 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 about 6000 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 about 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 naphtha is mostly in the vapor phase, the reaction may be effected in a shorter period of time, from 5 to 300 seconds. Of course, longer periods of time may be used if desired. 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 of the hydrocarbon components in zone 17. Alternatively, the commercial type of pipe still may be used as the heating zone. Also, mixing means may be used in the reaction zone to effect better contact between the naphtha and catalyst and halide promoter. Figure 2 shows three modified forms of the reaction zone wherein means are provided for thoroughly agitating or mixing the reactants. By keeping the materials in the reaction zone thoroughly mixed, the reaction time will be considerably reduced.

As pointed out hereinafter, an aluminum halide-hydrocarbon complex, in the form of a solution, is formed in the reaction zone and it may be used as the catalyst in 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. When aluminum chloride is used as the catalyst this complex is referred to as aluminum chloride-hydrocarbon complex.

During the digestion of the straight run petroleum naphtha with aluminum chloride and a promoter or aluminum halide-hydrocarbon complex and promoter in reaction zone 17, a part of the naphtha is converted into isobutane which reacts with the other constituents therein to produce normally liquid branched-chain hydrocarbons such as 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. The isobutane which does not react with the other constituents in reaction zone 17 is recovered by the fractionation and stabilization steps hereinafter described and returned to the reaction zone for further use. 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. 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 ap-

pears 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-chain paraffins or iso-paraffins. 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 this 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 capable of liberating a halogen acid in the reaction zone 17 retards the formation of excessive amounts of aluminum halide-hydrocarbon complex 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 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 under varying conditions and it effects, as hereinafter indicated, the desired degree of fractionation. The temperature and pressure conditions, number of plates and reflux ratio used in tower 34 may be varied to effect the desired fractionation. The hydrocarbon products withdrawn from the top of fractionator 34 contain the unreacted isobutane and the motor fuel product containing large quantities of normally liquid branched-chain saturated hydrocarbons. The overhead fraction from tower 34 is passed through line 35 to the cooler 36 and then introduced into the reflux drum 37. Of course, a substantial part of 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. These heavy hydrocarbon products withdrawn from the bottom of tower 34 are usually the heavy ends of the naphtha feed stock. For example, if the feed naphtha has an end boiling point of about 420° F. or above and the overhead from fractionator 34 is cut at a point to exclude hydrocarbons boiling above about 400° F., it is apparent that the bottom products from tower 34 will consist mostly of these heavy ends of the feed naphtha. Also, if any such heavy hydrocarbon products are produced by the reaction in zone 17, they will also be withdrawn from the bottom of tower 34. A part or all of these hydrocarbon products in accumulator tank 39 may be recycled to the inlet side of the system and used as a part of the charging stock. The valved conduit 39a may be used to withdraw the hydrocarbon products from the accumulator tank.

The degree of fractionation effected in tower 34 will determine the end boiling point and, to a certain extent, the composition of the final motor fuel product recovered from the bottom of tower or stabilizer 50. In one embodiment of our invention the overhead products from tower 34 may consist of unreacted isobutane and a fraction of hydrocarbons boiling within the gasoline range. For example, the overhead in tower 34 may consist of isobutane and a motor fuel product containing large quantities of normally liquid branched-chain hydrocarbons boiling up to about 380 to 420° F. Alternatively, the overhead from fractionator 34 may be cut to give a hydrocarbon product that does not exceed the end point of the particular motor fuel product desired. In either of these modifications, the low boiling constituents, consisting almost entirely of isobutane, in the overhead from fractionator 34 are removed therefrom in the stabilizer 50 to give a high antiknock motor fuel product containing a large portion of normally liquid branched-chain hydrocarbons. However, a portion of the isobutane may be left in the final motor fuel product as disclosed hereinafter.

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 by the above examples. The end boiling point of the overhead from fractionator 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 10% 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. When operating fractionator 34 according to this modification, the initial boiling point of the naphtha charged to the system should be at least as high as 200° F. and preferably within the range of 200-320° F.

As another 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 has an initial boiling point within the range of 260-350° 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. In this modification of the process, the overhead from tower 34 consists almost entirely of branched-chain hydrocarbons.

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 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, consisting almost entirely of isobutane on the one hand and the higher boiling products on the other. The fraction of normally gaseous hydrocarbons in tower 50 consists almost entirely of isobutane produced by the catalytic action of the aluminum chloride and promoter or aluminum halide-hydrocarbon complex and promoter upon the feed naphtha 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 isobutane in reactor 17. These branched-chain paraffins are 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 boiling 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 commercial gasoline, that is, between 380 and 420° F.; (c) containing substantially no isobutane and having an end boiling 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 product withdrawn through conduit 51 may be used as a motor fuel as such or it may be blended with other hydrocarbon fractions such as debutanized cracked gasoline, polymerized gasoline 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. The motor fuel products produced by our process are particularly useful as aviation fuel because of their high anti-knock value and desired volatility characteristics, and high heating value.

5 The unreacted isobutane passes from the top of the stabilizer through line 52 and may be passed through valved conduit 52a directly to the recycled gas line and returned to the reaction zone with the aid of compressor 12. In this modification of the process, cooling coils, not shown, may be placed in the top of tower 50 to condense a part of the vapors therein for use as reflux. This unreacted gas from the top of stabilizer 50  
10 may be passed through line 52 to condenser 53 and thence into the reflux drum 54. Bubble trays 55 or other fractionating means are placed in stabilizer 50 to assist in the fractionation therein. A portion of the product in the bottom of the stabilizer may be withdrawn from the trap-out plate 56 and passed through line 57 to the reboiler or heating means 58 and then 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.

30 A portion of the liquefied hydrocarbon product 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. Of course, a cooling coil may be used in the top of tower 50 along with the use of this reflux. The remaining 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 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  
45 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 hydrogen halide 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  
50 be used to withdraw from the system a portion of the liquefied hydrocarbon product in line 59.

The uncondensed gases in reflux drum 54, assuming that all of the products in drum 54 are not recycled in the liquid phase, is recycled to the inlet side of the system through valved conduit  
60 64 or the recycled gas line. 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  
70 line 68 with the dissolved promoter. The thus washed gases may be returned to the recycled gas line 64 through valved conduit 69 and 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.  
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By removing the halide promoter and any free halogen that may be present in these gases, corrosion of the compressor 12 may be considerably minimized.

It is apparent, therefore, that in the operation 5 of our process only the liquefied fraction of hydrocarbons, consisting almost entirely of isobutane withdrawn from the bottom of reflux drum 54, may be recycled through line 62 to the reaction zone. Alternatively, or in combination with  
10 this step, a portion of or all of the liquefied fraction and all or a substantial part of the gases removed from the top or reflux drum 54 may be recycled to the reaction zone. It is apparent, therefore, that the isobutane may be recycled in the  
15 liquid or gaseous phase.

As another modification of our process, the hydrocarbon components introduced into the reactor 17 may consist almost entirely of isobutane and straight run petroleum naphtha having an  
20 initial boiling point of about 260-270° F. When these materials are reacted with the aid of aluminum chloride or the aluminum halide-hydrocarbon complexes while in the presence of a promoter such as hydrogen chloride, hydrogen bromide, carbon tetrachloride and the like, the fractionators  
25 34 and 50 may be operated to give a product in line 51 which boils below 260-270° F. and which consists predominantly of branched-chain hydrocarbons containing from 4 to 8 carbon atoms each  
30 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  
35 line 51 and the 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 fractionation. When tower 34 is  
40 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  
45 above about 410-430° F. whereas the products taken overhead from tower 34 will consist mostly of lower molecular weight hydrocarbons. When tower 50 is operated at a pressure of about 200 pounds per square inch, a top temperature of  
50 about 200° F. and a bottom temperature of about 500° F., the products withdrawn through line 51 will be substantially free from isobutane, however, if tower 50 is operated at a pressure of about 200 pounds per square inch, a top temperature  
55 of about 110° F. and a bottom temperature of about 400° F., a substantial portion of the isobutane produced in the process will be retained in the product withdrawn from the bottom of the tower.  
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In carrying out our herein described process, the proportions of products charged to the reaction zone 17 may vary somewhat. For example, for one part by weight of naphtha charged to the reaction zone, the parts by weight of isobutane,  
65 catalyst and promoter may be from 0.1 to 1; 0.01 to 1; and 0.03 to 0.3 respectively.

In any of the modifications hereinbefore set forth, we may withdraw a part of the oil from accumulator tank 39 through valved conduit 39a in-  
70 stead 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  
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the isobutane by one 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, isobutane, 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 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 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 isobutane is 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 gas 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 75, including the aluminum halide-hydrocarbon complex as well as liquid hydro-

carbons, 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 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 76a is provided for venting some of the gas in separator 75 into conduit 32 so that they will pass into the fractionating system as described in Figure 1.

In place of the mixing device 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, isobutane, 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 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 thru 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 thru 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 30 with the assistance of the pressure-reducing valve 32 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, isobutane, 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 isobutane 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 branch-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, isobutane, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely isobutane 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 anti-knock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, isobutane, 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 isobutane 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 isobutane 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, isobutane, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely isobutane 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 therefrom an aluminum chloride-hydrocarbon complex, fractionating the remaining hydrocarbon products to produce said motor fuel fraction and a gaseous fraction consisting largely of isobutane 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, isobutane, aluminum chloride and a hydrogen halide, the reacting hydrocarbon gases present being largely isobutane 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 isobutane and substantially free of unsaturated hydrocarbons are produced, and recycling at least a portion of said gaseous fraction to said reaction zone.

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