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PRODUCTION OF ISOBUTANE AND ISOPENTANE BY DESTRUCTIVE HYDROGENATION OF PETROLEUM OILS

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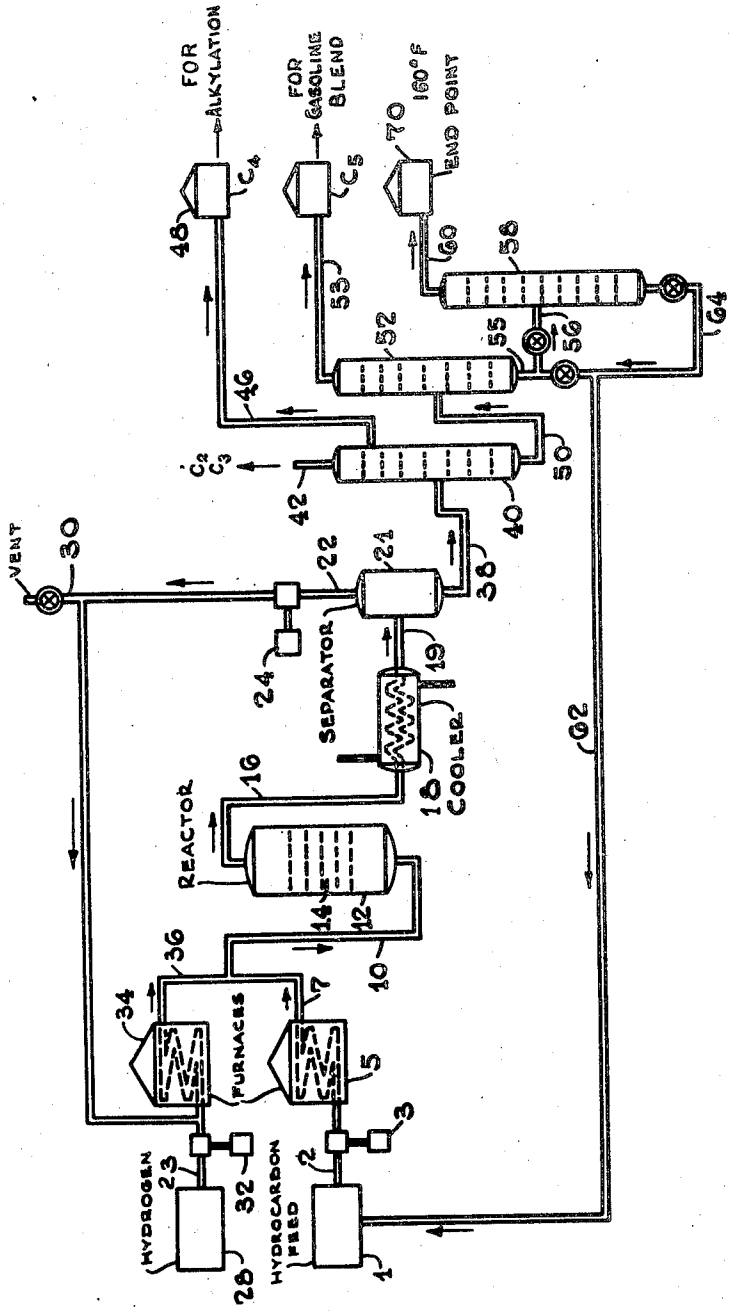

Fig. - 1.

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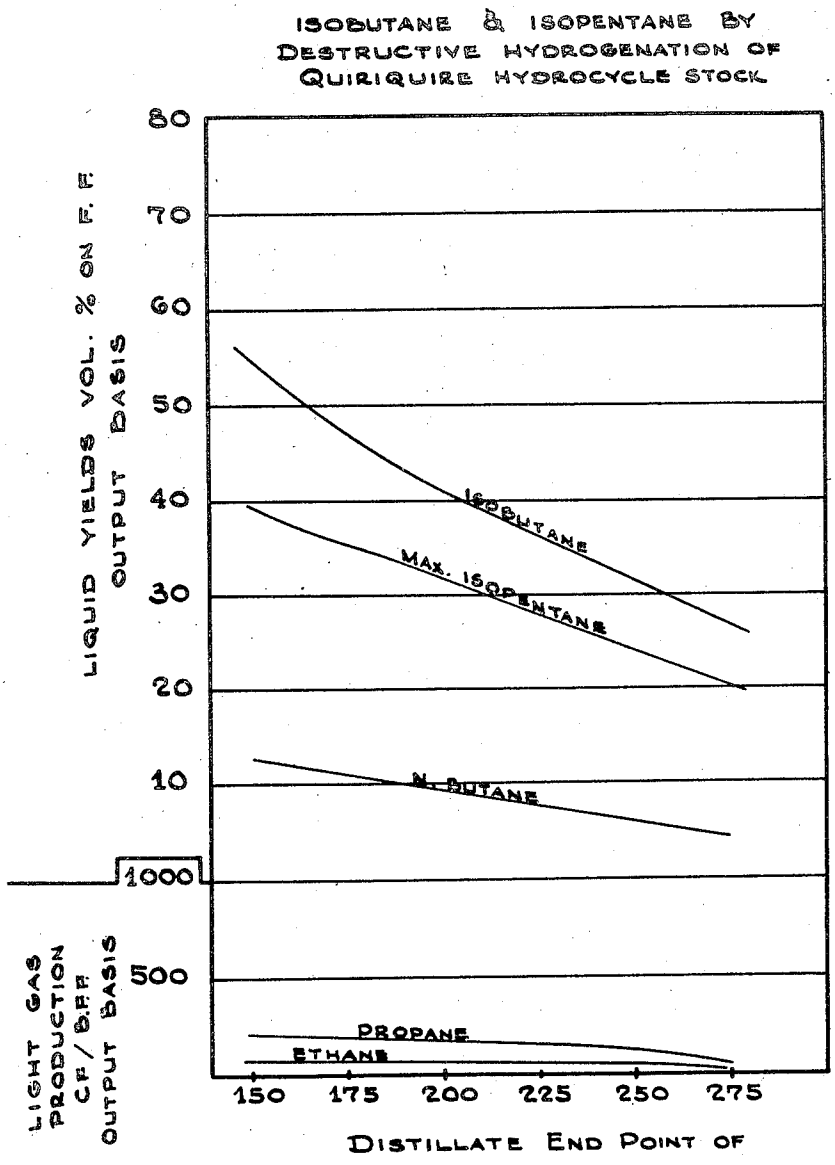

FIG. - 2

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PRODUCTION OF ISOBUTANE AND ISOPENTANE BY DESTRUCTIVE HYDROGENATION OF PETROLEUM OILS

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6 Claims. (Cl. 260—683.6)

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This invention is concerned with the production of low molecular weight hydrocarbons. More particularly, it relates to a destructive hydrogenation process employing a catalyst whereby large quantities of low molecular weight isoparaffins are produced.

An object of this invention is to provide a destructive hydrogenation process whereby large quantities of isobutane and isopentane may be obtained from a higher boiling petroleum feed stock.

A further object of my invention is to devise a process whereby not only are large quantities of isobutane and isopentane obtained but also high octane number aviation gasoline blending agents.

Recent technical advances in the art of producing high octane number gasoline have made necessary the consumption of large quantities of isoparaffins, particularly isobutane. This material is widely used in alkylation processes whereby aviation gasoline constituents are obtained. In the past, low molecular weight isoparaffins, particularly isobutane, were obtained as by-products in thermal or catalytic cracking processes or by the isomerization of the corresponding normal hydrocarbon. However, with the enormously increased demand for aviation gasoline, it is becoming more difficult for refiners to obtain adequate supplies of these valuable hydrocarbons.

A further object of this invention is, therefore, to provide producers of aviation gasoline with an additional process whereby further quantities of important raw materials employed in processes relating to the manufacture of aviation gasoline may be obtained.

I have now developed a process whereby predominant amounts of isobutane and isopentane can be produced from petroleum sources. Other light gases are also obtained, but these are found in rather small quantities. This process briefly comprises the destructive hydrogenation of a naphtha, gas oil or heavier hydrocarbon in the presence of a hydrogenation catalyst possessing isomerization activity in which the unconverted heavy products are continuously recycled to ultimate conversion to the desired products.

In one variation of my process, a naphtha charge stock is destructively hydrogenated to obtain hydrocarbons of relatively low molecular weights and heavier products which may be recycled through the catalyst or a selected portion of the latter hydrocarbons may be withdrawn from the system and utilized in aviation gasoline.

Further objects of the invention will be apparent from the following specification when considered together with the accompanying drawings in which:

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Figure 1 is a schematic drawing of the flow plan employed in the process;

Figure 2 is a graph showing the correlation of material yields in relation to the distillate endpoint of the recycled liquid product.

As shown in Figure 1, a hydrocarbon feed stock such as a naphtha or a gas oil having a gravity between 30–60° A. P. I. and a boiling range between about 100 and 700° F. is passed from tank 1 through pipe 2 by means of pump 3 to a preheating zone 5 where it is heated to a temperature between 500 and 600° F. It is then discharged into pipe 7 and mixed with preheated hydrogen and heated hydrocarbons is fed by means of pipe 10 to reactor 12 which contains a hydrogenation catalyst 14.

The catalysts employed may comprise various metals or compounds thereof such as the sulfides of nickel, cobalt, tungsten, and molybdenum, either alone or in admixture. For example, a suitable catalyst may comprise a mixture of nickel sulfide and tungsten sulfide. These metal sulfides may be impregnated on porous carriers or extending agents such as bauxite, acid activated clays containing bentonitic structures, synthetic or natural hydrosilicates of aluminum or magnesium, porcelain chips, charcoal, activated chars such as Nuchar, zeolites, silica gel, activated alumina and the like. I have preferred, however, to employ a catalyst comprising metallic nickel deposited on acid-activated clay since unexpectedly higher yields of isoparaffins are obtained with this catalyst than with the metal sulfide types.

This catalyst was prepared by treating Super Filtrol with 10% by weight of hydrofluoric acid, using a hydrofluoric acid solution having an HF content of about 10% for a period of about 0.5 to 1 hour. After washing several times with water, the material was impregnated with nickel nitrate, using enough of this salt to give about 10% Ni_2O_3 by weight on the catalyst. Following impregnation, the catalyst was heated to decompose the salt and the resulting oxide reduced with hydrogen.

While it is obvious that the hydrogenation catalyst may be any of several types which I have found to be effective also for isomerization, as mentioned heretofore, a catalyst comprising metallic nickel deposited on HF treated Super Filtrol is preferred. The conditions of hydrogenation are as follows:

Temperature, °F	600 to 800
Pressure, p. s. i. g	1,000 to 5,000
Feed rate, v/v./hr.[1]	0.5 to 5.0
Hydrogen recycle rate, CF/B[2]	5,000 to 10,000

[1] Volume of liquid feed per volume of catalyst per hour.
[2] Cubic feet per barrel of feed.

The products of hydrogenation are removed overhead from reactor 12 through line 16, passed

through cooler 18 and line 19 to high pressure separator 21. Light gases consisting of hydrogen and low molecular weight hydrocarbons such as methane, ethane and propane are removed overhead from separator 21 by way of pipe 22 and pump 24 and recycled to the system, although a portion thereof may be vented through pipe 30. Fresh hydrogen is withdrawn from storage holder 28 through line 23 and pump 32, mixed with recycle hydrogen, preheated in furnace 34 to a temperature below that maintained in the reactor 12 and discharged by means of pipe 36 into pipe 10 where it is mixed with the preheated hydrocarbon feed, and is then passed through the reaction zone.

The liquid hydrocarbon products which are separated in separator 21 are removed through line 38 to fractionator 40. Light hydrocarbons, particularly propane and small quantities of ethane, are removed as overhead through conduit 42 and may be suitably employed in other refinery processes. A side stream, containing hydrocarbons having 4 carbon atoms, is removed from tower 40 through pipe 46 and discharged into receiver 48. This fraction may be rectified by superfractionation in a separate distillation zone not shown in order to concentrate the isobutane present in the C_4 cut. The bottoms from tower 40 are removed through line 50 to a secondary fractionation tower 52 from which an overhead product is removed through line 53 which contains principally hydrocarbons having 5 carbon atoms. If desired, the isopentane constituent may be further concentrated by distillation means not shown since only conventional distillation means are required. The residue or bottoms from fractionator 52 may be removed through line 55 and either recycled directly to the process by way of pipes 55 and 62 or may alternatively be passed by way of line 56 to a third fractionating tower 58. In this modification, the function of tower 58 is to effect a separation between hydrocarbons boiling preferably below about 160° F. and heavier materials boiling above 160° F. The naphtha boiling up to about 160° F. is removed overhead through line 60 and passed into run-down tank 70, since I have found that this material is an excellent blending stock for preparing aviation gasolines of superior characteristics. The higher boiling hydrocarbon material is removed as bottoms by way of pipe 64 and recycled to the hydrogenation process for ultimate conversion to lighter hydrocarbons.

In a specific example, a stock obtained by hydrogenating Quiriquire crude oil to obtain a cycle stock having a gravity of 44.3° A. P. I., an initial boiling point of 293° F., and a final boiling point of 469° F. was destructively hydrogenated under the following conditions:

Average temperature, °F	700
Feed rate, v./v./hr	1.0
Recycle gas rate, CF/B	8,000
Pressure, p. s. i. g	3,000

Under these conditions, when recycling all material boiling above 158° F., 38.1 volume percent of isopentane on fresh feed and 52.2 volume percent of isobutane on fresh feed were obtained, along with 218 cubic feet of propane per barrel of fresh feed. As a result of detailed experiments, I have also found that it is possible to obtain high total yields of isobutane and isopentane by recycling hydrocarbons boiling up to about 225° F. As may be seen from Figure 2, much higher concentrations of isobutane and isopentane were realized by recycling materials having an initial boiling temperature of about 160° F. For example, it may be observed from Figure 2 that by decreasing the endpoint of the distillate from about 270° F. to 158° F., an increase in total C_4 production resulted from 33 to 65 volume percent based on fresh feed. Likewise, the total C_5 produced increased from about 23 to about 43% by volume on fresh feed. It will be noticed that the proportion of isobutane to n-butane remained approximately constant. As previously stated, the liquid yield of isobutane, calculated as volume percent on the fresh feed, was 52.2% when the distillate had an endpoint of 158° F., and under these same conditions the isopentane production amounted to 38%. This high production of isopentane I consider to be important since isopentane is utilized as a blending agent in gasoline of high octane number rating and not only provides volatility but also contributes to the high octane quality of the gasoline.

Substantial amounts of n-butane and n-pentane are formed in my process and these may advantageously be used as feed stocks to an isomerization process wherein further increments of the corresponding iso compounds can be obtained.

While I may recycle the total liquid product removed as bottom from fractionator 52 through lines 55 and 62, I prefer, however, to recycle only the heavier portions thereof boiling above about 160° F. It is also obvious that, should the supply of feed stock become limited, I would prefer to recycle all of the liquid material in order to obtain the maximum quantity of iso-C_4 and iso-C_5 hydrocarbons. In addition to these products, I have found that smaller quantities of ethane and propane are formed and these may be used for fuel purposes. In the case of propane, however, it may be subjected to a pyrolytic conversion treatment for the production of propylene and ethylene which may then be employed in alkylation processes.

I have determined that the A. S. T. M. octane number of the pentane-free distillate, having an endpoint of 158° F., produced in my process is 81.1 clear and, with 3 cc. lead tetraethyl per gallon added, is 97.5. Likewise, I have found that the A. S. T. M. octane number of a pentane-free distillate having an endpoint of 196° F. is 78.5 clear, and 94.2 with 3 cc. lead tetraethyl added. The A. S. T. M. octane number of a pentane-free distillate having an endpoint of 275° F. is only 75.5 clear, and 89.4 when containing 3 cc. of lead tetraethyl per gallon. It will be noted that, as the endpoint of the distillate increases, the octane number decreases and in one modification of my invention, I propose to limit the endpoint of the naphtha which I desire to include in aviation gasolines to about 160° F.

To recapitulate, I have devised an efficient process for producing significant quantities of low molecular weight isoparaffins, particularly isobutane and isopentane, as well as hydrocarbon components suitable for blending in aviation gasolines. Substantially, my invention in its preferred application comprises destructively hydrogenating a naphtha or light gas oil of suitably low sulfur content, preferably having a boiling point above about 100° F. and below about 800° F. with a catalyst comprising metallic nickel deposited on an activated clay base. Selected fractions of the product are obtained by fractional distillation procedures and, of these, I have found

that high concentrations of isoparaffins are present in the butane and pentane cuts. Preferably the isoparaffins produced have a molecular weight below about 115. In addition, I have found that the total product boiling above pentane may advantageously be recycled to ultimate conversion for the production of maximum amounts of the desired isoparaffins or else the lighter fraction may be diverted for inclusion in aviation gasoline while the bottoms are recycled with the fresh feed.

The character of the present invention and its novelty and utility in producing maximum amounts of isobutane and isopentane from higher boiling charging stocks can be seen from the preceding specification and examples given, although neither section is intended to limit unduly its general broad scope.

I claim as my invention:

1. The method of producing isobutane and isopentane, which comprises destructively hydrogenating petroleum hydrocarbons boiling above about 100° F. and below about 800° F., in the presence of hydrogen and of a catalyst containing an element selected from the class consisting of nickel, cobalt, tungsten and molybdenum having hydrogenating and isomerizing properties, removing the isobutane and isopentane, recycling hydrocarbons having a boiling range between about 160° F. and about 225° F. and continuing such recycling to obtain a maximum yield of isobutane and isopentane.

2. The method, according to claim 1, in which the catalyst comprises metallic nickel supported on an acid-activated clay.

3. The method, according to claim 1, in which the catalyst comprises metallic nickel supported on a clay base which has been activated by successive treatments with sulfuric acid and hydrofluoric acid.

4. The method of producing isobutane and isopentane, which comprises destructively hydrogenating a normally liquid petroleum distillate oil in the presence of hydrogen and of a catalyst comprising nickel supported on acid activated clay, at a temperature between about 600 and 800° F., and a pressure of about 1,000 to 5,000 pounds per square inch, employing a feed rate between 0.5 and 5.0 liquid volumes per volume of catalyst per hour, recycling hydrocarbons boiling in the range of about 160° F. to 225° F., and continuing such recycling to obtain a maximum yield of isobutane and isopentane.

5. In a process for the production of isoparaffins having a molecular weight below about 115, which comprises destructively hydrogenating normally liquid petroleum distillates at elevated temperatures and pressures in the presence of hydrogen in a reaction zone containing a supported hydrogenation catalyst containing an element selected from the class consisting of nickel, cobalt, tungsten and molybdenum, withdrawing the reaction products from the reaction zone, segregating the reaction products into a series of separate streams of consecutively higher boiling range, each of which said streams contains a substantial quantity of isoparaffinic constituents, and a higher boiling liquid fraction, the step of fractionating to obtain a higher boiling liquid fraction having a boiling range of about 160° F. to 225° F., and continuously recycling said fraction to the reaction zone for maximum conversion to isoparaffins.

6. In a process for the production of low molecular weight isoparaffins comprising passing a normally liquid petroleum distillate in the presence of hydrogen through a zone charged with a supported metallic hydrogenation catalyst containing an element selected from the class consisting of nickel, cobalt, tungsten and molybdenum and maintained under destructive heydrogenation conditions of pressure and temperature, removing the reaction products from the reaction zone and discharging them into a distillation zone, and fractionating the products thereof, the steps of separating a fraction rich in isobutane, a fraction rich in isopentane, a fraction boiling up to about 160° F., and a fraction having a boiling range between about 160° F. and 225° F., removing from the process the fractions respectively rich in isobutane, isopentane and hydrocarbons boiling up to about 160° F., and continuously recycling said fraction having a boiling range between about 160° F. and 225° F. for maximum conversion to isoparaffins.

ALEXIS VOORHIES, JR.

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