

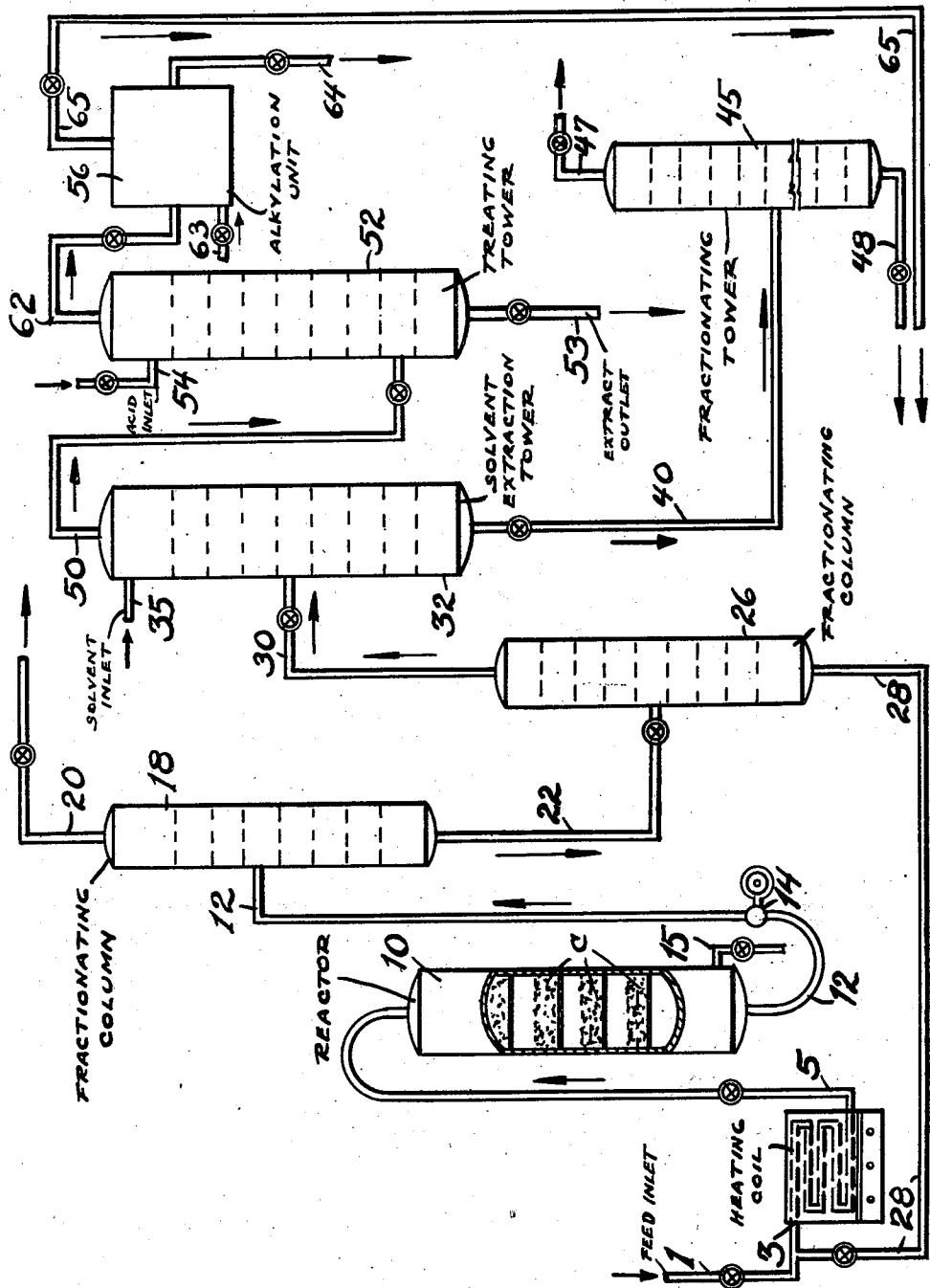
Dec. 18, 1945.

C. A. HILLMAN ET AL

2,391,160

REFINING OPERATION

Filed May 2, 1942



Charles A. Hillman Inventors
Donald L. Campbell

By J. Small Attorney

UNITED STATES PATENT OFFICE

2,391,160

REFINING OPERATION

Charles A. Hillman, Sea Girt, and Donald L. Campbell, Short Hills, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application May 2, 1942, Serial No. 441,518

1 Claim. (Cl. 260-680)

The present invention relates to a combined dehydrogenation of saturated hydrocarbons to form valuable di-olefins such as butadiene, together with the alkylation of mono-olefins also formed with iso-paraffins to form alkylates boiling within the gasoline range and having a high octane rating.

The process of polymerizing butadiene alone or with other materials to form a rubber substitute or synthetic rubber is known. To produce this rubber substitute or similar synthetic rubbers by polymerizing di-olefins obviously requires considerable quantities of the said di-olefins if the synthetic rubbers are to be produced in large quantities. The production of di-olefins in normal refinery practice is insufficient to supply the demands for large scale synthetic rubber production using di-olefins as starting materials, and in our present invention, we have devised means for producing di-olefins such as butadiene from saturated hydrocarbons available in refinery practice or as field "butane," according to an improved method which includes a single stage catalytic dehydrogenation of normal butane followed by a precise fractionation of reaction products to recover a fraction consisting primarily of butadiene, iso-butane, iso-butene, and butene-1, which fraction is thereafter subjected to solvent extraction to form an extract containing essentially only butadiene and a raffinate containing the remainder of the said fraction, which raffinate may be alkylated employing supplementary or extraneous iso-butane to form an aviation gasoline. Said supplementary iso-butane may be obtained by fractionation of the source material from which the above mentioned normal butane is obtained.

One object of the present invention is to dehydrogenate a hydrocarbon fraction containing normal butane to form substantial quantities of butadiene, and in order to reduce the amount of material recycled to the dehydrogenation zone, the reaction products after extraction of the formed butadiene are alkylated so that principally normal butane and normal butenes are recycled to the dehydrogenation zone.

A more specific object of the present invention includes precisely fractionating reaction products from a single stage dehydrogenation of normal butane to separate and recycle to the dehydrogenation stage, a fraction containing normal butane and butene-2.

A further object of our invention is to recover a quantity of isobutene by liquid extraction of the reaction products remaining after removal of

butadiene and regeneration of the iso-butylene from the extract.

Other and further objects of our invention will appear from the following more detailed description and claim.

In order to afford a better understanding of our invention reference is made to the accompanying drawing in which we have shown diagrammatically a form and arrangement of apparatus elements in which our invention may be carried into practical effect.

We shall now set forth a specific example illustrating our invention, and in so doing will refer to the drawing.

Referring therefore in detail to the drawing, 1 represents a charging line for normal butane. This butane is charged to a furnace 3 where it is heated to a temperature of 1330° F. and thereafter withdrawn through line 5 and discharged into a reactor 10 containing catalyst C composed of 4-6% chromic oxide on alumina and preferably supported on spaced foraminous trays. The conditions maintained within the reactor 10 are the following:

Temperature-----Average 1230° F.
Pressure-----Average 95 mm. Hg absolute
Contact time-----1/4 second

Due to the fact that the reaction is endothermic and the reactor is substantially adiabatic, the furnace outlet temperature will be somewhat higher than the average temperature in reactor 10). Alternatively heat may be supplied to the reactor.

The reaction products are withdrawn from reactor 10 through line 12 and then discharged into a compressor 14 where the gases are compressed to a pressure of about 600 lbs./sq. in. whereupon they are withdrawn and discharged into a fractionator 18 from which C₃ and lighter hydrocarbons are withdrawn overhead through line 20, while the heavy bottoms comprising C₄ and heavier hydrocarbons are withdrawn through line 22 and discharged into a second fractionator 26 where the C₄ hydrocarbons are carefully fractionated to recover a normal butane and a butene-2 fraction which is recovered through line 28 and recycled to charging line 1. The overhead fraction containing butadiene, iso-butane, iso-butene, and butene-1, together with small quantities of normal butane and butene-2, is withdrawn through line 30 and thence discharged into an extraction tower 32. The solvent, preferably methyl amine, is discharged into tower 32 through line 35, and this solvent dissolves out

butadiene, and the extract thus formed is withdrawn through line 40. The extract is then discharged into a fractionating column 45 from which the butadiene is recovered through line 47, while the methyl amine is recovered through line 48 and recycled to line 35 leading into solvent extraction zone 32. Further details of this process, such as water extraction of solvent from the raffinate and extract, are not shown because the process is well known.

The raffinate formed in solvent extraction zone 32 is withdrawn through line 50, and this material containing iso-butane as well as butenes, particularly iso-butene, is discharged into an alkylation system 56 where it may be alkylated under known conditions, such as with sulfuric acid. However, before discharging the materials in line 50 into the alkylation unit 56, it is preferable to treat the same with sulfuric acid to cause extraction of the iso-butene therein contained. To this end therefore, the materials are discharged into a second treating tower 52 where they are treated with diluted sulfuric acid (about 65%) introduced into said tower through line 54 where at about 65° F. it extracts the isobutene. The material freed from isobutene is withdrawn from treating tower 52 through line 62 and discharged into alkylation plant 56. The isobutene-sulfuric acid extract is withdrawn through line 53.

The details of the sulfuric acid alkylation are well known to the art and need not be set forth at length here. It will be understood, of course, that instead of using sulfuric acid any alkylation catalyst, such as hydrogen fluoride, phosphoric acid, etc., may be used and the known expedients such as employing an excess of iso-paraffin over olefin in a reaction zone may be employed. Supplementary or extraneous isobutane is preferably discharged into the alkylation system through line 63 in order to maintain the proper excess of iso-paraffin over olefin so that high yields and high quality products may be obtained. The alkylate is withdrawn through line 64 and delivered to finishing equipment to produce a salable aviation gasoline. The alkylation reaction is carried out by so proportioning the iso-paraffin to olefin that substantially all of the iso-paraffin and olefin are converted to an alkylate, leaving only normal paraffins. These normal paraffins are withdrawn from the alkylation system through line 65 and recycled to the charging line 1 containing fresh feed.

In the previous description, obviously many modifications of the process may be made without departing from the spirit thereof. For instance, instead of using a stationary catalyst, it is within the purview of our invention to employ a powdered catalyst which is suspended in the reaction vapors undergoing dehydrogenation. This type of operation has many advantages in that continuity of operation may be easily obtained, since the suspension of reaction vapors may be withdrawn from the reaction zone and passed through separating devices where the catalyst may be separated from the vapors, regenerated and returned to the reaction zone. In the modification shown in the drawing, it will be necessary periodically to discontinue the dehydrogenation reaction carried out in reactor 10 to regenerate the catalyst to remove coke. This regeneration may be readily accomplished by forcing an oxygen-containing gas under combustion conditions throughout the reactor to cause combustion and burning of the coke or carbonaceous deposits formed on the catalyst. However,

as stated, where the catalyst flows through the reaction zone in the form of a suspension or fluidized mass of catalyst intermixed with the reaction vapors, the catalyst after separation from the reaction vapors may be suspended in air or the like and regenerated and thereafter returned to the reaction zone, thus maintaining the aforementioned continuity of operation. Also, since the dehydrogenation of butane is a reaction which requires careful temperature control in order to produce maximum yields of the desired products such as butadiene, it may be necessary to quench the reaction in 10 by means of a quenching medium, such as cold butane gas, or even liquefied normal butane which may be charged into the reactor through line 15 or into line 12.

To recapitulate, our present invention involves a process for producing butadiene by dehydrogenating normal butane catalytically with a one-stage operation, and the process is characterized by the advantage that the reaction products are carefully fractionated to remove unreacted normal butane and butene-2, and thereafter solvent extracting to remove butadiene and to form a recycle fraction. However, we propose to alkylate the recycled product to remove olefins and iso-paraffins so that the recycled product contains substantially only normal butane. Obviously, this alkylation step in our process has the decided advantage of cutting down the equipment necessary to carry out the dehydrogenation, for the recycle gases contain substantially only normal butane which is the desired starting material for dehydrogenation to produce butadiene. Consequently, our process is one which may be operated with less equipment and utilities than heretofore accomplished. In the prior art with which we are aware, the entire C₄ cut of the product after separation of butadiene was recycled to the reaction zone, and this product included iso-butane, iso-butene, butene-1, and other products. Not only do we require less equipment and consume less steam and other utilities in our process, but in reactor 10 we form less coke for a given conversion and, consequently, reactor 10 may be operated for a longer period of time without regeneration of catalyst than has been heretofore possible.

It will be understood that the several fractionating columns shown in the accompanying drawing are of conventional design and are provided with the usual reboiling and reflux equipment.

Many modifications of our invention not specifically mentioned herein will readily suggest themselves to those familiar with this art. For example, the conditions maintained within the reactor for dehydrogenating normal butane may be varied over a wide range say from 1000° to 1400° F. temperature, from 25 mm. Hg absolute to atmospheric pressure and from 0.05 to 2 seconds contact time. Also various catalysts may be used with some of which steam may be used as a diluent to give 25 mm. Hg absolute to atmospheric partial pressure for the reactants in the reactor while the total pressure in the reactor is superatmospheric.

By carrying out this process we obtain yields of 25 to 50 mols of butadiene per 100 mols of normal butane fresh feed to the system including the butadiene obtained from the processing of the recycle streams described above. In addition there would be produced 10 to 25 mols of mono-olefins including iso-butene, butene-1 and nonrecycled butene-2 and 4 to 12 mols of iso-butane per 100 mols of normal butane fresh feed

to the system including the amounts obtained from the processing of the recycle streams described above. Instead of using chromic oxide on alumina, activated or hydrated, we may use the oxides of vanadium, molybdenum, tungsten or in fact the oxides of the metals of the IV, V, VI, and VIII groups of the periodic system supported on alumina or some other known support.

As an alternative iso-butene may be extracted from the feed to the alkylation plant by contacting weak sulfuric acid with the liquid stream of C₄ hydrocarbons and the iso-butene regenerated from the extract liquid phase by means well known in the art. The raffinate would contain substantially all the iso-butane and butene-1 made in the dehydrogenation of the normal butane. This raffinate would be suitable for feed to the alkylation process above described. The iso-butene removed would be valuable as a feed to a polymerization process for making butyl rubber or Vistanex. In the case of the manufacture of butyl rubber a small portion of the butadiene made from the combination process would also serve as a minor feed component in the preparation of the butyl rubber.

As another alternative the C₄ hydrocarbons from which butadiene has been extracted may be processed through a selective catalytic polymerization process which removes the iso-butene and a portion of the butene-1 to make a polymer which can be hydrogenated to give a component for high octane aviation gasoline. The raffinate from the polymerization could then be fed to the alkylation process.

It is our intention to include in the scope of the attached claim all of the matter specifically described herein and all that included by necessary implication, except that matter excluded by the terms of said claim.

What we claim is:

A continuous process for manufacturing butadiene from normal butane which comprises heating the butane to dehydrogenation temperatures, discharging the heated butane into a dehydrogenation zone where it is permitted to remain in contact with a catalyst, consisting of chromic oxide supported on alumina, for a period of time of from about 0.05 to 2 seconds, at a temperature range from about 1000° F. to 1400° F., and at an average 95 mm. mercury absolute pressure, withdrawing the reaction products from the reaction zone, separating a portion of the butane and butene-2 from the reaction products by fractionation, recycling said separated butane and butene-2 to the dehydrogenation zone, treating the remainder of the C₄ cut of the reaction products with methyl amine to remove butadiene extracting iso-butene with sulfuric acid from the reaction products remaining after butadiene removal, subjecting the residual mixture to alkylation conditions in the presence of an alkylation catalyst whereby iso-butane and butenes are converted to alkylate, separating the alkylate from the normal butane and recycling the latter to the dehydrogenation zone.

CHARLES A. HILLMAN.
DONALD L. CAMPBELL.