United States Patent Office 2,831,042
Patented Apr. 15, 1958

2,831,042

DEHYDROGENATION OF HYDROCARBONS

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No Drawing. Application September 30, 1955
Serial No. 537,871

8 Claims. (Cl. 260—680)

This invention relates to the catalytic dehydrogenation of paraffin hydrocarbons to produce olefins and diolefins and, more particularly, to an improved process for the production of olefins and diolefins from aliphatic paraffins containing from 3 to 5 carbon atoms per molecule. While the invention is applicable in its broadest aspects to the dehydrogenation of propane and the various butanes and pentanes, it finds particular utility in the conversion of n-butane and n-butene to butadiene. Accordingly, the invention will generally be described hereinafter as it relates to this reaction.

In the catalytic dehydrogenation of n-butane to n-butene and butadiene, two separate dehydrogenation equilibria must be satisfied and two different reaction rates are normally encountered. In general, it is found that at operating conditions where efficient and selective dehydrogenation of butane to butene is obtained, the yield of butadiene is low because of the limitation established by thermodynamic equilibrium. On the other hand, at conditions which would thermodynamically favor high yields of diolefin, the primary dehydrogenation of the paraffin to an olefin is far too severe, resulting in an unduly high yield of coke and cracked gases and poor dehydrogenation reaction selectivity.

Hence, though commercial processes have been developed and used in which a single catalyst and dehydrogenation reactor is employed for carrying out both the primary and secondary dehydrogenation reactions (i. e., the dehydrogenation of butane to butene and of the latter to butadiene), these processes must in general compromise in the selected process conditions between reaction selectivity and per pass yield of diolefin.

An alternative procedure for the production of diolefins by the dehydrogenation of the corresponding paraffins involves the separate dehydrogenation of butane and butene using somewhat different conditions for each dehydrogenation reaction. In the usual commercial operation, the butane is first dehydrogenated in the presence of a highly active dehydrogenation catalyst (e. g., chromium oxide on alumina) and at subatmospheric pressures, which results in a product containing unconverted butane, fairly high yields of butene, and much smaller amounts of butadiene, light gases, and heavy polymers. This first stage product is then quenched and passed into conventional facilities for recovering the mixed paraffin, olefin and diolefin fraction having the same molecular weight range as the feed, the light gases and heavy polymers being rejected. The recovered products (i. e., the C_4 hydrocarbons) are then passed into solvent extraction and extractive distillation zones wherein the butadiene and butene are separated from the butane component. The butenes are then passed, in mixture with 10 to 20 volumes of superheated steam, into a second dehydrogenation zone wherein a portion of them is converted to the corresponding diolefins. This second dehydrogenation reaction is normally carried out at a temperature somewhat higher than in the primary dehydrogenation and at atmospheric or superatmospheric pressures, in the presence of a water gas-active dehydrogenation catalyst. The effluent from the second dehydrogenation is then quenched and compressed, the unconverted olefins and the diolefins produced in the reaction are separated from the water, light gases and polymers, and are passed into a diolefin recovery zone. In this latter zone the diolefins are separated and recovered by solvent extraction (e. g., cuprous ammonium acetate) and the unconverted olefins are recycled to the second dehydrogenation reactor.

From the above brief description of a conventional commercial paraffin-olefin dehydrogenation, it is apparent that the separate dehydrogenation reactions require the use of difficult and relatively expensive separation and compression steps. Thus, the effluent from the first dehydrogenation reactor (the latter operating under subatmospheric pressures) must be quenched, compressed, the light gases and polymers removed, and then passed into diolefin and olefin recovery zones. The recovered olefins must then be preheated, mixed with large volumes of superheated steam, and the mixture passed into the second dehydrogenation zone which operates at pressures above that employed in the first-stage zone. From the second dehydrogenation zone the effluent must, in turn, be quenched, compressed, the water, light gases and polymers removed, and then passed to the diolefin recovery zone.

Accordingly, it is an object of the present invention to provide a two-stage process for the dehydrogenation of paraffins to olefins and diolefins, wherein high olefin yields and good process efficiencies are obtained and which eliminates various steps heretofore considered necessary. Another object is to provide a process for the dehydrogenation of aliphatic paraffins to the corresponding olefins and diolefins, and, further, for the dehydrogenation of n-butane to butene and butadiene.

The present invention is based on the discovery that substantial quantities of diolefins can be produced from aliphatic paraffin hydrocarbons containing 3 to 5 carbon atoms per molecule by first contacting the paraffinic hydrocarbon (alone or admixed with recycle olefin components) in a primary dehydrogenation zone with a dehydrogenation catalyst at a temperature of from about 1000° to 1200° F. and a pressure of from about 5 to 20 inches Hg absolute. The total effluent from the primary dehydrogenation zone is then admixed with from about 1 to 10 volumes of superheated steam per volume of hydrocarbon contained in the effluent, and the resulting mixture is then contacted in a secondary dehydrogenation zone at a temperature of from about 1050° to 1300° F. and at subatmospheric pressures substantially the same as those employed in the first dehydrogenation zone, with a water gas-active catalyst that is effective for olefin dehydrogenation in the presence of steam. The effluent from the secondary dehydrogenation zone can thereafter be conventionally quenched, the diolefin separately recovered, and the unreacted paraffins and olefins recycled to the primary dehydrogenation zone along with fresh paraffin feed.

From the above brief statement of the present invention, it is readily apparent that the production of diolefins from the corresponding paraffins can be effected in a manner considerably simpler than heretofore thought possible. Thus, in comparing the process flow of the present invention with that of the conventional two-stage commercial operation hereinbefore described, it can be seen that the present process eliminates (1) the quenching compression and paraffin-olefin-diolefin recovery operation upon the primary dehydrogenation zone effluent; (2) the costly olefin separation step in which the olefins are separated from the paraffins and diolefins produced in the first stage; and (3) the considerable preheating operation of the separated olefins prior to their passage with large volumes of superheated steam into the secondary dehydrogenation zone. A further advantage

of the present process over conventional operations is that the effluent from the first dehydrogenation zone passes in its entirety (along with added superheated steam) directly to the secondary dehydrogenation zone with no substantial change in pressure. In addition, it has been found that the subject process, by operating the secondary dehydrogenating step under subatmospheric pressure in series with the primary dehydrogenating step, requires substantially less superheated steam to be added to the second-stage reaction zone than previous processes, thereby further reducing equipment and operating costs.

According to one specific embodiment of the present invention, n-butane and a butane-butene recycle stream (described in more detail below) constitute the feed to a primary dehydrogenation zone. The feed is preheated to reaction temperature, which ranges from about 1000° to 1200° F., and preferably from about 1050° to 1125° F., and is then introduced into the primary dehydrogenation zone at a pressure of from about 5 to 20 inches of Hg absolute. The basic requirement of the primary dehydrogenation zone is that it provide a means for intimately contacting the feed with the catalyst under the conditions noted and to provide for control of the endothermic reaction and exothermic regeneration heats. Processes operating on a relatively short alternate reaction and regeneration cycle are conventionally employed. Therefore, any method of meeting this requirement is suitable for practicing the present invention. Multitubular reactors, the catalyst being disposed inside many long narrow tubes, and vessels containing catalyst beds are well known and have been successfully used on a commercial scale. The butane dehydrogenation reaction is conducted under the above specified temperature and pressure in the presence of any conventional dehydrogenating catalyst having a surface area of at least 20 $M.^2/g$. Representative catalysts falling into this category are those made up of chromium oxide deposited on activated aluminas, such as of the Bayer process, precipitated or gel types. The preferred catalysts are those containing from 5 to 30% chromium oxide deposited on such activated aluminas, or the catalysts described in U. S. Patent 2,706,741, or as described in my copending application Serial No. 518,919, filed June 29, 1955.

The total gaseous effluent from the primary dehydrogenation zone, consisting predominantly of unreacted butane and n-butenes, with smaller amounts of butadiene, hydrogen, propane, lighter gases, and heavy polymerization products, is then mixed with from about 1 to 10 volumes of superheated steam per volume of hydrocarbon contained in the effluent and passed into a secondary dehydrogenation zone. The mixing of the steam with the effluent from the primary dehydrogenation zone serves a twofold purpose: the first being that the steam acts as a diluent to the feed to the secondary dehydrogenation reactor, and, since the dehydrogenation reaction is favored by low partial pressures, the steam tends to lower the partial pressures of the reactants. Secondly, the major dehydrogenation reaction carried on in the secondary zone (generally, the dehydrogenation of n-butene to butadiene) is normally carried out at a higher temperature than the butane dehydrogenation reaction in the primary zone, and, therefore, the feed to the secondary reaction zone (the effluent of the primary zone) must be preheated. This is effected simply by adding superheated steam to the hot reaction product from the primary zone, thus providing the total feed to said secondary zone.

The secondary dehydrogenation step is conducted at a temperature of from about 1050° to 1300° F., and preferably from about 1100° to 1200° F., in the presence of a water gas-active dehydrogenation catalyst that is rendered effective and stable for long periods of operation in the presence of the steam previously admixed with the feed. On the other hand, catalysts effective for the dehydrogenation of paraffins are rendered almost completely ineffective for paraffin dehydrogenation by the addition of steam. Since the catalysts preferred for the dehydrogenation of paraffins are different than those preferred for the dehydrogenation of olefins, this water gas-active catalyst employed in the secondary zone differs from that (described above) employed in the first stage, or butane dehydrogenation zone. Among the catalysts suitable for use in the secondary dehydrogenation zone are the oxides or mixtures of the oxides of aluminum, iron, chromium and magnesium, usually promoted with potassium or other alkali metals in the form of the oxide, carbonate or similar salts. A nickel-calcium-phosphate catalyst composition has also been demonstrated to be effective for this reaction.

As noted hereinbefore, one of the advantages of the present invention lies in the fact that the pressure maintained in the secondary dehydrogenation zone can be essentially the same as that employed in the primary (paraffin) dehydrogenation zone, i. e., a pressure of from about 5 to 20 inches of mercury absolute. In the past, conventional two-stage units employed in the butane-butene-butadiene dehydrogenation reactions have employed subatmospheric pressure in the first stage (butane) and atmospheric pressure, or greater, in the second stage. I have found that both stages can operate successfully at virtually the same pressure (the only difference being the pressure drop through the lines and equipment between the two reaction zones), thereby providing considerable reduction in equipment and ease of operation over the previously operated two-stage process.

The effluent from the secondary dehydrogenation zone, comprising butane, butene, butadiene, hydrogen, propane and lighter gases and some heavy polymerization products, is then passed into conventional C_4 recovery facilities to separate and recover the total C_4 content of the effluent. Any means of accomplishing this is suitable for use in the present process. Normally, the effluent is quenched, compressed, and fed to a standard absorber-rectifier system for recovery of the mixed C_4 fraction from the total reaction product.

The separated C_4's, containing the unreacted butane, less butene and more butadiene than in the first-stage effluent, are then passed into a butadiene recovery zone. In this latter zone, the butadiene is recovered by any suitable method, such as by azeotropic distillation, solvent extraction, and complex or compound formation. At the present time, solvent extraction with a selective solvent such as copper ammonium acetate is the most well known and used butadiene recovery process. Following the butadiene removal, the remaining butane-butene mixture is preferably recycled to the primary dehydrogenation zone as a component of the feed.

The following example shows the results of operating the subject process for the dehydrogenation of n-butane to produce butadiene. Table I indicates the operating conditions and results obtained in the first-stage dehydrogenation zone and Table II shows those employed in the secondary dehydrogenation zone.

TABLE I

First-stage dehydrogenation

Catalyst—450 cc. Harshaw butadiene (18% Cr_2O_3, 82% Al_2O_3)	
Hydrocarbon feed rate, $ft.^3/hr.$ (90% C_4H_{10}, 10% C_4H_8)	4.0
Temperature, °F.	1050
Pressure, in. Hg abs	8
Product analysis, wt. percent of feed:	
CO_2 (as carbon)	1.0
Hydrogen	2.3
Light gases (C_3 and lighter)	5.5
C_4H_6	6.0
C_4H_8	28.0
C_4H_{10}	57.1

TABLE II

Second-stage dehydrogenation

	Feed from First Stage	Run No. 1	2	3	4	5
Hydrocarbon feed rate,[1] Ft.³/hr.		2.0	2.0	2.0	2.0	4.0
Hydrogen feed rate, Ft./³hr.		1.0	1.0	1.0	1.0	2.0
H_2O (Steam) feed rate, cc./hr.		400	400	400	400	400
Hours on Stream		0.5	10	20	1.5	1.5
Temperature, ° F.		1,190	1,190	1,190	1,240	1,240
Pressure, in. Hg Absolute		5.0	5.0	5.0	5.0	5.0
Catalyst 450 cc. Std. of Jersey 1707:						
Product Analysis, Wt. Percent Feed—						
CO_2 (as carbon)		1.9	2.5	3.0	4.2	3.5
Light gases (C_3 and lighter, including H_2)	7.9	10.6	12.6	14.7	20.4	16.6
C_4H_6	6.1	13.0	14.6	14.1	12.4	12.3
C_4H_8	28.3	15.8	13.5	12.2	9.6	12.8
C_4H_{10}	57.7	58.7	56.8	56.0	53.4	54.8
Incremental Production,[1] Weight Percent—						
C_4H_6		6.9	8.5	8.0	6.3	6.2
C_4H_8		−12.5	−14.8	−16.1	−18.7	−15.5
C_4H_{10}		+1.0	−0.9	−1.7	−4.3	−2.9

[1] Based upon the hydrocarbon content from the first-stage dehydrogenation zone as shown in Table I.

From the above tabulation of experimental results, it can be seen that the present process provides a simple, highly utilitarian means for producing high per pass yields of diolefins from the corresponding paraffins.

I claim:

1. A process for the dehydrogenation of an aliphatic paraffin hydrocarbon feed containing 3 to 5 carbon atoms per molecule to diolefin product, which comprises contacting said hydrocarbon feed in a primary dehydrogenation zone with a dehydrogenation catalyst at a temperature of from about 1000° to 1200° F. and a pressure of from about 5 to 20 inches Hg absolute, thereby converting an appreciable portion of said hydrocarbon feed to diolefin product; mixing the diolefin-containing hydrocarbon effluent from said dehydrogenation zone with from about 1 to 10 volumes of superheated steam per volume of hydrocarbon; and thereafter contacting the resulting mixture in a secondary dehydrogenation zone with a water gas-active dehydrogenation catalyst at a temperature of from about 1050° to 1300° F. and at a pressure substantially the same as that employed in the primary dehydrogenation zone; and recovering diolefin product from the effluent from said secondary zone.

2. The process of claim 1, wherein the temperature in the primary dehydrogenation zone is from about 1050° to 1125° F.

3. The process of claim 2, wherein the temperature in the secondary dehydrogenation zone is from about 1100° to 1200° F.

4. The process of claim 3, wherein the aliphatic hydrocarbon feed is n-butane.

5. A process for the dehydrogenation of an aliphatic paraffin hydrocarbon feed containing 3 to 5 carbon atoms per molecule to diolefin product, which comprises contacting said hydrocarbon feed in a primary dehydrogenation zone with a dehydrogenation catalyst comprising a major proportion of aluminum oxide and a minor proportion of chromium oxide at a temperature of from about 1000° to 1200° F. and a pressure of from about 5 to 20 inches Hg absolute, thereby converting an appreciable portion of said hydrocarbon feed to diolefin product; mixing the diolefin-containing hydrocarbon effluent from the primary dehydrogenation zone with from about 1 to 10 volumes of superheated steam per volume of hydrocarbon; contacting the resulting mixture in a secondary dehydrogenation zone with a water gas-active dehydrogenation catalyst at a temperature of from about 1050° to 1300° F. and a pressure of from about 5 to 20 inches Hg absolute; recovering a diolefinic product from the effluent of the secondary dehydrogenation zone and returning at least a portion of the remaining effluent from the secondary dehydrogenation zone to said primary dehydrogenation zone.

6. The process of claim 5, wherein the aliphatic paraffin is n-butane.

7. The process of claim 6, wherein the temperature in the primary dehydrogenation zone is from about 1050° to 1125° F.

8. The process of claim 7, wherein the temperature in the secondary dehydrogenation zone is from about 1100° to 1200° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,394,625	Matusak	Feb. 12, 1946
2,433,800	Watson	Dec. 30, 1947