

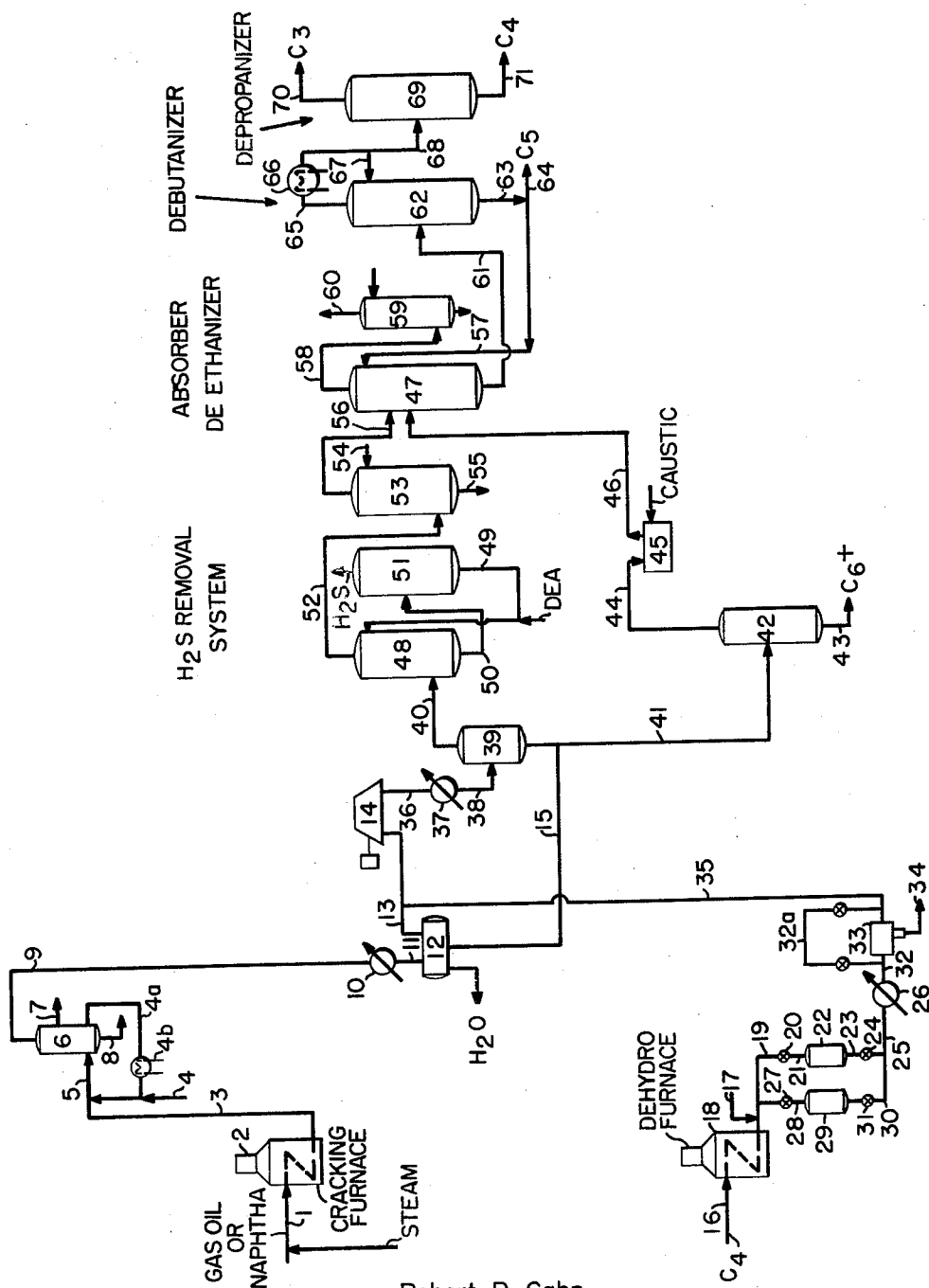
Oct. 27, 1964

R. P. CAHN ETAL

3,154,482

COMBINED STEAM CRACKER AND BUTENE DEHYDROGENATION LIGHT ENDS

Filed Nov. 2, 1959



Robert P. Cahn
Robert H. Johnston

Inventors

By *Peter H. Smolka* Patent Attorney

1

3,154,482

COMBINED STEAM CRACKER AND BUTENE
DEHYDROGENATION LIGHT ENDSRobert P. Cahn, Elizabeth, and Robert H. Johnston,
Whippany, N.J., assignors to Esso Research and Engi-
neering Company, a corporation of Delaware

Filed Nov. 2, 1959, Ser. No. 850,250

8 Claims. (Cl. 208-101)

The present invention relates to an improved system wherein butene dehydrogenation light ends are added to the light ends from a steam cracker and the combined stream is processed together in a single light ends system. This light ends system, due to the increase in the C_4/C_3 ratio of the total light ends processed, is operated with reduced lean oil requirements in a first absorber deethanizer and with a lower pressure operation of the following debutanizer tower.

In addition, by this combination processing of light ends large improvements are obtained in the butene dehydrogenation process. As is well known, most commercial butene dehydrogenation processes are cyclic involving at least two reactors, one of which is being regenerated while the other is onstream. Therefore, when the reactors are swung, usually every 30 minutes, there is a sudden variation in flow of process gases to the compressors utilized to compress the effluent from the reactor to the high pressures required for light ends fractionation. Thus, since the process is carried out cyclicly, handling these surges obtained periodically on the effluent gas stream during the swing to a freshly regenerated reactor requires more expensive and larger compressors than would otherwise be required. Additionally, these compressors suffer increased wear and, of course, have shorter lives due to these surges. Finally, the absorption and fractionation equipment downstream of the compressor is upset by these periodic surges, resulting in difficulties when lining out these facilities for smooth operation. By the present system, since the volume of the butene dehydrogenation light ends may be for example only approximately $\frac{1}{4}$ the volume of the light ends from the steam cracker, by combining these streams this surging is ironed out and smaller sized more efficient compressors which have longer lives may be used. Obviously also as a result, much smoother operation of the downstream equipment will be obtained.

Returning to the other advantages obtained by the present invention combination system, in conventional steam cracker light ends systems the debutanizer is operated at as low a pressure as is possible such as 150-170 p.s.i.g. in order to avoid excessive bottoms temperatures. Thus, too high a temperature would result in rapid fouling of the bottoms circuit in this tower. The pressure required in the debutanizer is set by the condensing temperature of the overhead. By combining the two light ends systems the debutanizer overhead product C_4/C_3 ratio is increased considerably, i.e., from 0.5-1.0 (e.g., 0.6) to 1.2-2 (e.g., 1.3) due to the large C_4 recycle from the dehydrogenation unit. Thus, the overhead may be condensed at a lower pressure in the order of 120-140 p.s.i.g. again using conventional cooling water in the overhead condenser and, of course, lower temperatures are thus obtained in the bottom of the tower. Thus, the design and operation of this tower is improved. It should be noted that the C_3/C_4 ratio in the steam cracker products is reasonably fixed at conventional conversion levels. Therefore, there is very little that can be done in the process itself to alleviate the problem of debutanizer tower pressure. Consequently, the addition of extraneous C_4 's, such as described in this case, is a real remedy to this problem.

2

With respect to the other previously mentioned improvement over conventional steam cracking light ends systems, the presence of the large amount of C_4 's in the light ends, above described, permits operation of the absorber deethanizer with smaller amounts of lean oil required. Thus, the amount of lean oil is decreased compared to the amount which would be expected to be obtained by merely combining two towers into a larger single tower, i.e., the sum of the lean oil rates required in the two separate towers. The order of this decrease in amount of lean oil required is about 5%. Actually, the lean oil required for the combined system is less than the lean oil for the absorber-deethanizer in the steam cracker light ends alone. Hence, the dehydrogenation effluent, due to its high C_4 content, actually lowers the lean oil requirements. This, of course, results in net savings in this column and in the following debutanizer and in reduced refrigeration required for both columns.

As a final improvement of the present combination system considerable savings are obtained due to the mere increased efficiency obtained in using a single light ends unit as compared to two smaller light ends units. Thus, for example, in distillation columns a rough rule of thumb is that costs are proportional roughly to the cost that would be expected for the size of the unit taken to the .6 power. As an example of such a calculation, assume the combination of a 10,000 bbl./day tower costing \$200,000 with a 2,000 bbl./day tower. Thus, by a simple proportion the 2,000 bbl./day tower alone would cost $(2/10)^{0.6} \times \$200,000$ or \$76,000 as compared to the 12,000 bbl./day tower which would cost $(12/10)^{0.6} \times \$20,000$, or \$221,000 for a net saving of \$55,000. Thus, this advantage is obtained gratis as an additional saving in the present invention and applies not only for all the towers in the light ends unit, but also for the compressor.

The present invention will be more clearly understood from a consideration of the accompanying diagrammatic illustration of a combination steam cracking and butene dehydrogenation unit.

Turning now to the figure, a gas oil or naphtha and steam specifically a gas oil boiling in the range of 350 to 700° F. is supplied through line 1 to a cracking furnace 2 operated at temperatures of 1300 to 1500° F. and pressures of 0 to 50 p.s.i.g. with residence times of 0.05 to 1 second wherein cracking is carried out to obtain predominantly olefins and diolefins. The effluent is passed at a temperature of 1300 to 1500° F., e.g., 1400° F., through line 3 and is quenched with a heavy oil supplied through line 4 to a temperature of 400-600° F., e.g., 450° F. before being supplied through line 5 to a distillation tower 6. In this distillation column gas oil is taken off from the middle of the column through line 7, tar is taken off from the bottom of the column through line 8 and the quench oil used in the process is taken off from the lower part of the column and is passed through line 4a and cooler 4b to line 4 as previously described. From the top of the column materials lighter than gas oil are passed through line 9 to cooler 10, where they are cooled to about 75-125° F. and wherein the lighter materials, mainly C_6 and lighter hydrocarbons, are separated overhead through line 13, and are passed to a 3-stage compressor 14, the heavier materials being separated as a liquid and passed through line 15 to further processing as will be described.

Turning now to the butene dehydrogenation unit, a butane-butene stream containing for example 70-95 mol percent, e.g., 80 mol percent butenes obtained from any of various refinery processes, is passed through line 16 in combination with some steam to a furnace 18 where it is heated to a temperature of about 1100° and is mixed with super-heated steam at 1000-1400° F., e.g.,

3

1300° F. from line 17 and is passed through line 19, valve 20 and line 21 to reactor 22 containing a fixed bed of a calcium nickel phosphate on alumina catalyst. Conditions and reactants are as follows:

CONDITIONS AND REACTANTS

Catalyst

The preferred catalyst comprises:

	General (Wt. percent)	Specific (Wt. percent)
Ni.....	4.3-5.5	5
Ca.....	27.8-32.0	30
PO ₄	49.0-60.5	57
Cr ₂ O ₃	1.0-8.0	6
Graphite.....	1.0-3.0	2

Reaction Conditions

	General	Specific
Space Velocity of n butenes, v./v./hr. ¹	75-200	120
Space Velocity of Steam, v./v./hr. ¹	1,400-4,000	2,300
Reactor Inlet Temperature, ° F.....	1,000-1,350	1,175
Temp. Drop Across Reactor, ° F.....	50-100	70
Reactor Outlet Pressure, p.s.i.a.....	15-30	20
n-Butylene Conversion, percent per pass.....	30-60	45
Selectivity to Butadiene, percent.....	75-95	85

¹ V./v./hr. = volume of gas at S.T.P./volume catalyst/hour.

The effluent from reactor 22 is passed through line 23 valve 24 and line 25 to cooler 26 where its temperature is reduced to 75-125° F., e.g., 100° F. About every 30 minutes it is necessary to regenerate catalyst whereupon reactor 22 is swung from the stream by closing valves 20 and 24 and opening valve 27 which passes vapors through line 28 to reactor 29, containing a fresh bed of catalyst and the effluent gases are passed through line 30 and valve 31 to line 25 previously described. Regeneration of the catalyst in the off stream reactor is obtained at temperatures of 1000 to 1250° F., e.g., 1100° F. utilizing steam by conventional means not shown, space velocity of the steam in regeneration being 500 to 1500, e.g., 900 v./v./hour. Alternatively to the use of the above described catalyst and reaction conditions obviously other catalysts and reaction conditions can also be used. For example, the following described catalyst, reaction conditions, and regeneration can be utilized.

Chromia-alumina catalyst, @ 1000-1200° F., e.g., 1150° F. inlet temperature, 1-15 p.s.i.a., e.g., 3 p.s.i.a.; onstream time 7-15 minutes, e.g., 10 minutes.

	Range	Example
W./w./h.....	0.5-1.5	1.1
Conversion ¹	25-30%	27%
Selectivity ¹	70-80%	76 mol %

¹ For feed of 81% n butenes, 19% n butane. Catalyst—20 wt. percent chromia on alumina.

Since the reactors operate under vacuum, a compression step on the reactor effluent, after quenching, is required, before it can be mixed with the steam cracker products at atmospheric pressure. The two comingled streams are then further compressed to absorber pressure.

The effluent stream from cooler 26 is passed through line 32 to a separator 33 for removal of water from the bottom of said separator through line 34 if the calcium nickel phosphate catalyst is used. The stream is thence passed through line 35 to join the steam cracker light ends effluent from separator 12 in line 13. Alternatively, if removal of water is not necessary the stream may be passed directly through line 32a to line 35.

The combined light ends from steam cracking and from butene dehydrogenation after compression in 3-stage compressor 14 are passed through line 36 to cooler 37 where their temperature is further reduced to about 75-125°

4

F., e.g., 100° F. The cooled stream is passed through line 38 to a further separator 39 wherein a predominantly C₃ and lighter hydrocarbon gaseous stream is passed overhead through line 40 to an absorber for removal of H₂S. From the bottom of separator 39 the heavier liquid materials are passed through line 41 to a naphtha splitter 42 wherein C₆ and heavier hydrocarbon materials are taken off as bottoms through line 43, the overhead material is passed through line 44 to a caustic scrubber 45 for removal of sulphur compounds and CO₂ and the scrubbed liquid is passed through line 46 to absorber deethanizer 47.

Returning to the predominantly C₃ and lighter hydrocarbon material in line 40, this material is passed to absorber tower 48 for removal of H₂S and CO₂ where it is contacted with diethanolamine supplied through line 49. The absorbed material and solvent are passed through line 50 to diethanolamine regenerator 51, regenerated material being supplied through line 49 back to the absorber as previously described. From the top of the absorber, light ends are passed through line 52 to caustic wash tower 53, supplied with caustic through line 54, spent caustic being removed through line 55, and the stream is then passed through line 56 to absorber deethanizer 47. This tower is supplied with a C₅ lean oil through line 57 and the C₂ and lighter hydrocarbon material is passed overhead through line 58 to sponge oil tower 59 wherein traces of C₅ lean oil are removed from the C₂ and lighter hydrocarbon gas taken overhead through line 60. From the bottom of the absorber deethanizer 47 C₃ and heavier hydrocarbon material is passed through line 61 to debutanizer tower 62, C₅ material being removed from the bottom of said tower through line 63 and passed in part through line 57 as previously described and in part being passed from the system through line 64. From the top of the tower C₄ and lighter hydrocarbon material is passed through line 65 to condenser 66 from which part of the stream is refluxed to the tower through line 67 and the remainder is passed through line 68 to depropanizer 69. Here the C₃ cut is separated overhead through line 70 and the C₄ cut is taken off as bottoms through line 71 to be passed to further processing including butadiene extraction not shown.

The present invention will additionally be understood from the following example illustrating the advantages of the present invention.

EXAMPLE

Steam Cracking

Feed, 7000 b./d., 350/700° F. gas oil
Products contain 1380 mols/hour C₃ and lighter hydrocarbons

Out of which propene+propane=280 mols/hr.

Also, we get C₄'s=157 mols/hr.

In an absorber-deethanizer operating at 325 p.s.i.g. and 60° F. top temperature, lean oil requirements would be 805 mols/hr. The debutanizer, when operating with 110° F. condensing temperature, will have to run at 170 p.s.i.g.

Butene Dehydrogenation

Feed 200 mols/hour C₄, containing 150 mols/hour n-butene. Catalyst, calcium nickel phosphate as above described.

At 45% conversion, the effluent contains 82.5 mols/hr. unconverted n-butenes.

The total reactor effluent will contain:

104 mols/hr. C₃ and lighter hydrocarbons (containing 6 mols/hr. propene).

220 mols/hr. C₄'s (butadiene, n-butenes, n-butane, etc.).

Where this feed is supplied to an absorber-depropanizer, operating at 325 p.s.i.g. and 60° F., 25 mols/hr. of lean oil is required.

5

By combining the two absorbers, the lean oil rate is only 795 mols/hr. or a saving of

$$\begin{array}{r} 805 \text{ mols/hr.} \\ + 25 \text{ mols/hr.} \\ \hline 830 \text{ mols/hr.} \\ 795 \text{ mols/hr.} \\ \hline 35 \text{ mols/hr.} \end{array}$$

or over 4%. In all cases above mols are lb. mols.

Also, the debutanizer operating on the mixed feed case can operate at 132 p.s.i.g., when running with 110° F. condensing temperature.

Corresponding debutanizer bottoms temperatures:

Tower pressure, p.s.i.g.:	Bottoms temp., ° F.
132 -----	281
170 -----	305

At 300° F., rapid fouling of reboilers, etc. is experienced. At 281° F. the rate of fouling is much slower.

Although a particular embodiment light ends system has been described the advantages described above will be obtained generally in all light ends systems. It is of course intended that this invention cover the processing of a combined stream of butene dehydrogenation light ends and steam cracking light ends in any of these systems.

It is to be understood that this invention is not limited to the specific example, which has been offered merely as an illustration, and that modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. An improved system for processing the light ends from a steam cracker and for processing the light ends from a butene dehydrogenation unit, which comprises combining the light ends from a steam cracker operated to produce mainly olefins and diolefins, said light ends comprising mainly C₆ and lighter hydrocarbons including C₃ hydrocarbons, with the effluent from a cyclic butene dehydrogenation unit, a fluctuation in the flow of product gases from the butene dehydrogenation effluent being obtained during the replacement of the reactor containing spent catalyst with a reactor containing freshly regenerated catalyst, passing the combined stream of vapors to a compressor wherein the pressure of the combined stream is raised to a high pressure of above about 150 p.s.i.g., and passing the high pressure stream to an absorption and fractionation light ends system for recovery of separate components from the stream.

2. The process of claim 1 in which the ratio of C₄ to C₃ components in the combined stream is in the range of 1.2 to 2/1.

3. The process of claim 1 in which the volume of the effluent from the butene dehydrogenation unit is about 5-50% of the volume of the light ends from the steam cracker.

4. The process of claim 1 in which the high pressure combined stream is passed to an absorber deethanizer operated using a C₅ lean oil stream, and the C₃ and

6

heavier hydrocarbons material from said absorber deethanizer is passed to a debutanizer operated at a pressure of below 140 p.s.i.g.

5. The process of claim 1 in which the high pressure combined stream is passed to an absorber deethanizer operated using a C₅ lean oil stream, the C₃ and heavier hydrocarbons material from said absorber deethanizer is passed to a debutanizer operated at a pressure of below 140 p.s.i.g. and a part of the C₅ bottom stream from the debutanizer is used as the C₅ lean oil in the absorber deethanizer.

6. The process of claim 1 in which butene dehydrogenation is carried out in the presence of steam and a calcium nickel phosphate catalyst and in which steam is condensed and removed from the effluent stream from the butene dehydrogenation unit before combining said stream with the light ends from the steam cracker.

7. The process of claim 1 in which butene dehydrogenation is carried out in the presence of a chromia alumina catalyst.

8. An improved system for processing the light ends from a steam cracker and for processing the light ends from a butene dehydrogenation unit, which comprises combining the light ends from a steam cracker operated to produce mainly olefins and diolefins, said light ends comprising mainly C₆ and lighter hydrocarbons including C₃ hydrocarbons, with the effluent from a cyclic butene dehydrogenation unit, said cyclic butene dehydrogenation being carried out in the presence of steam and a calcium nickel phosphate catalyst and a fluctuation in the flow of product gases from the unit being obtained during the replacement of the reactor containing spent catalyst with a reactor containing freshly regenerated catalyst, the volume of the effluent from the butene dehydrogenation unit being about 5-50% of the volume of the light ends from the steam cracker, compressing the combined stream of vapors to a high pressure of above about 150 p.s.i.g., passing the high pressure combined stream to an absorber deethanizer operated using a C₅ lean oil stream, passing C₃+ material from the bottom of said absorber deethanizer to a debutanizer operated at a pressure of below 140 p.s.i.g. and passing a part of the C₅ bottom stream from the debutanizer back to the absorber deethanizer to be used as the C₅ lean oil in said absorber deethanizer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,181,302	Keith et al.	Nov. 28, 1939
2,382,473	Frey	Aug. 14, 1945
2,391,555	De Simo et al.	Dec. 25, 1945
2,429,980	Allinson	Nov. 4, 1947
2,458,082	Kilpatrick	Jan. 4, 1949
2,745,889	Johnston et al.	May 15, 1956
2,750,435	Fetchin	June 12, 1956
2,831,041	Sieg et al.	Apr. 15, 1958
2,943,041	Johnston et al.	June 28, 1960
2,945,804	Hemminger	July 19, 1960
2,972,646	Cahn et al.	Feb. 21, 1961