United States Patent Office

3,255,273
Patented June 7, 1966

3,255,273

HEPTENE MANUFACTURE PROCESS

William E. Catterall, Summit, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Apr. 30, 1965, Ser. No. 452,334
5 Claims. (Cl. 260—683.15)

This is a continuation-in-part of copending and now abandoned application Serial No. 164,389 filed January 4, 1962 which in turn was a continuation-in-part of Serial No. 781,423, filed December 19, 1958 and now abandoned.

This invention relates, in general, to an improved process for the manufacture of heptenes by copolymerization of C_3 olefins with C_4 olefins and, more particularly, relates to the use of isobutylene dimer available as a by-product from various refinery processes in addition to or in place of at least part of the C_4 olefins conventional used in this copolymerization process. In a preferred embodiment, the present invention relates to an optimum process for copolymerizing propylene with a substantial amount of isobutylene dimer and with a refinery C_4 unsaturate stream, for example, from catalytic cracking, to obtain heptenes.

The instant invention is especially advantageous inasmuch as isobutylene dimer is available in relatively large amounts as a by-product from various refinery processes. For example, in separating the various butylenes from streams containing a mixture thereof, it is customary to effect the removal of isobutylene either by simple sulfuric acid extraction or by sulfuric acid-catalyzed dimerization to diisobutylene, followed by distillation. Even in the former case, considerable quantities of diisobutylene are unavoidably formed. Conventionally, the dimer is disposed of by adding it to gasoline as a blending stock. Obviously, its dollar value as a gasoline component is not great and would be markedly enhanced were the dimer employed in the production of chemicals. The process of the present invention provides such a use for the production of chemicals.

It has now been found that the addition of a substantial amount of diisobutylene to the C_3–C_4 unsaturate feed stream utilized for conventional heptene polymerization processes surprisingly increases the yield of heptene. That is to say, when heptene is produced by passing propylene- and butylene-containing feeds over conventional polymerization catalysts, the addition of a substantial amount of diisobutylene to said streams in addition to or in place of at least part of the C_4 olefins enhances the yield of heptene, while providing numerous other advantages. Thus, in accordance with the present invention, when isobutylene streams are to be used in the production of C_7 olefins, it is unnecessary to remove diisobutylene therefrom prior to such use. Additionally, any C_7+ material either unreacted or formed during the copolymerization process can be recovered and used for gasoline blending. Hence, the present process provides a manner of utilizing diisobutylene which, economically, is attractive, inasmuch as that diisobutylene which is not upgraded by conversion to heptenes is not lost, but instead, serves a useful purpose.

It should also be noted that a dimer stream may be used which contains small amounts of trimer or higher polymers which usually are found in commercial dimer streams. In addition, prior to feeding the dimer stream

to the polymerization zone, it is preferred to remove the usual trace amounts of sulfuric acid esters present by conventional treatment such as redistillation, hot caustic treating, bauxite treating, etc.

The heptenes formed in the copolymerization process of the invention find utility commercially, for example, in the manufacture of isooctyl alcohol by the oxo process.

Since the present process is involved principally with the substitution of or addition to the feedstock in an otherwise conventional polymerization process whereby heptene is formed from C_3 and C_4 olefins, the process steps will be only generally and briefly described. Thus, polymerization is carried out with any of the known catalysts under conditions to obtain high yields of the desired C_7 material.

The propene-butene charging stock utilized with the isobutylene dimer may be of a wide variety of compositions, but preferably contains very little water. Both olefins and paraffins may be charged to the process in the C_4 and C_3 feed streams, although it is preferred that specifically isobutylene be used as the C_4 olefin to obtain maximum C_7 yields.

Some of the catalysts which may be used for the present polymerization are copper pyrophosphate and liquid phosphoric acid of 75 to 110 weight percent strength, used either in bulk or as a film on quartz chips. This phosphoric acid catalyst may also be used on kieselguhr, diatomaceous earth or silica, on which it is precalcined at about 400° to 500° F. The catalyst tends to lose activity by undergoing complete dehydration; therefore, a small amount of water or steam is added to the charging stock, e.g. to maintain the activity. The polymerization reaction is conducted under a pressure of 250 to 3000 p.s.i.g., preferably 500 to 1500, e.g. 1000 p.s.i.g., at temperatures of 280° to 550° F. preferably 350° to 450°, e.g. 400° F. Since the polymerization reaction is exothermic, heat is removed if necessary from the reaction zone to maintain these desired temperatures. Other polymerization catalysts may be used, with temperature and pressure conditions appropriate for the particular catalyst. For example, with a catalyst such as BF_3, lower temperatures and pressures than described above would be employed.

In accordance with the present invention, the proportion of dimer which is added to the C_3 olefin feed or to the C_3+C_4 olefin feed can vary within wide limits. Thus, even small amounts of dimer will increase the yield of C_7 olefin product to some extent. Consequently, the extreme lower limit on the amount of said dimer to be added depends upon practical, rather than theoretical considerations. Hence, the lower limit of dimer which is added to the reaction stream can broadly be stated as that amount which produces a sufficient increase in C_7 product to make such addition economically feasible. The present invention, therefore, contemplates the addition of dimer in amounts substantial enough to effect significant increase in the yield of C_7 olefin product. For the purposes of this invention, the amount of diisobutylene added to the olefin feed stream is always to be calculated as equivalent isobutylene.

As to the maximum amount, obviously some point is reached where the relative proportion of propylene becomes so low that the desired polymerization reaction is hindered. In its broad aspects, therefore, the invention contemplates the addition to the C_3 or C_3+C_4 feed streams of an amount of diisobutylene substantial enough

to significantly increase the yield of C_7 olefin product and not hinder the preparation of same.

Specifically, sufficient dimer to effect the desired results of the present invention constitutes amounts such as to provide a mole ratio of combined C_4 olefins and dimer (dimer being calculated as equivalent isobutylene) to C_3 of from about 0.15 to 3/1, preferably 0.3 to 3/1. Maximum yields of C_7 olefin product are attained when the mole ratio of C_3 to combined C_4 olefin and dimer is approximately 1.

It is to be understood, however, that the amount of dimer addition contemplated so as to effect especially advantageous yields in C_7 product is at least about 0.15 mole of dimer per mole of C_3 feed (see Table III hereinafter). Likewise, the invention contemplates use of no more than 3.0 moles of dimer per mole of C_3 feed. In view of the foregoing, it may be postulated that when a feed comprised essentially of C_3 olefin is utilized, the mole ratio of diisobutylene to C_3 olefin feed is within the range of about 0.15 to 3/1 (see Table I hereinafter), preferably 0.3 to 3/1.

It has also been found that dimer addition is somewhat more perfected when the C_4 olefin which is utilized with the C_3 olefin is substantially n-butene than when the C_4 olefin is mainly isobutylene.

When the catalyst is commercial kieselguhr-supported phosphoric acid (so-called solid phosphoric acid catalyst), feed rates used are in the range of 0.01 to 2.0 gallons of total feed per hour per pound of catalyst, preferably 0.05 to 0.50, e.g. 0.20 gallon per hour per pound of catalyst. Such feed rates exclude any coolant which may be injected throughout the reactor. Part or all of the dimer stream might also be used as the coolant. The monomer olefin content of the feed is generally 10 to 70 mole percent, preferably 20 to 50 mole percent, e.g. 40 mole percent. Propane and/or butanes, preferably butanes, may be recycled to dilute the fresh feed olefin to the desired olefin content to help maintain suitable reactor temperature control. Since dimer appears to undergo depolymerization to the monomer prior to reaction with propylene to produce C_7, and since such depolymerization absorbs heat, dimer addition may serve to reduce the requirement for paraffin recycle.

It is also contemplated in the present process that material in the effluent from the polymerization zone higher boiling than the C_7 material may be recycled to the process to increase the yield of C_7 material obtained.

The following data are presented to illustrate the excellent quality of diisobutylene as a feedstock in place of the conventional C_4 materials used in the prior art copolymerization to C_7 olefins processes. In Table I data are presented on C_7 yields where only dimer is added to propylene, and Table II presents data where also n-butene is used in addition to the dimer with the propylene.

TABLE I.—EFFECT OF DIMER ADDITION WITH PROPYLENE FEED

Run	A	B	C	D
Temperature, ° F	395	400	380	400
Pressure, p.s.i.g.	790	795	750	800
Total Feed Space Velocity, Gal./Hr./Lb. Catalyst	0.19	0.19	0.13	0.20
Monomer Feed Composition:				
Wt. percent Propylene	50	50	45	------
Wt. percent Saturates	50	50	55	------
Dimer Addition Rate, Wt. percent on Propylene Fed	162	244	0	[a]
Total Polymer Produced, Wt. percent on Propylene Fed	206	303	82	[b] 100
Propylene Conversion, percent	44	59	82	------
Ratio, C_8 in Product/C_8 Fed	0.31	0.42	------	0.58
Total Polymer Composition:[c]				
Wt. percent C_7	39.0	31.0	4.4	4.0
Wt. percent C_8	24.2	33.3	6.0	58.1

[a] Pure dimer fed, without propylene.
[b] Wt. percent on dimer fed.
[c] Analysis by low-voltage mass spectrometer.

TABLE II.—EFFECT OF DIMER ADDITION WITH PROPYLENE-n-BUTYLENE FEED

Run	E	F	G	H
Temperature, ° F	400	400	446	446
Pressure, p.s.i.g.	800	800	1,000	1,000
Total Feed Space Velocity, Gal./Hr./Lb. Catalyst	0.18	0.21	0.30	0.32
Monomer Feed Composition, Wt. Percent:				
Propylene	46.7	42.4	31.4	32.8
n-Butylene	7.6	9.0	7.9	0.3
Isobutylene	0.0	0.0	0.0	6.9
Saturates	45.7	48.6	60.7	60.0
Monomer Feed Composition, Mol Percent Total Butylenes on TotalOlefins	14	17	20	18
Dimer Addition Rate, Wt. Percent on Monomer Olefin Fed	20.0	23.4	0	0
Total Polymer Produced, Wt. Percent on Monomer Olefins Fed	81	123	86	92
Olefin Conversion, Wt. Percent:				
Propylene	60	100	91	92
n-Butylenes	100	100	79	------
Isobutylene	------	------	------	99
Total Monomer Olefins	67	100	88	94
Ratio, C_8 in Product/C_8 Fed	0.58	0.62	------	------
Total Polymer Composition:				
Wt. Percent C_7	30.2	29.0	13.7	24.3
Wt. Percent C_8	14.4	11.8	10.8	10.1

From this data it can be clearly seen that high yields of the C_7 material are obtained when using isobutylene dimer rather than the monomer as in the present process. It is considered that these results are unexpected since it would be supposed that the isobutylene dimer would polymerize with the olefins present to form higher boiling materials.

The excellent quality of the isobutylene dimer in place of the monomer as a feed can be seen from calculations based on Tables I and II which are given below in Table III.

TABLE III.—DIMER ADDITION AS EQUIVALENT TO, OR BETTER THAN ISOBUTYLENE ADDITION

Run	E	F
Feed Composition (100% Olefin Basis):		
Mol Percent Propylene	74.4	69.7
Mol Percent n-Butylene	12.0	14.8
Mol Percent Dimer (calculated as equivalent isobutylene)	13.6	15.5
Total	100.0	100.0
C_7 Yield, Wt. Percent on Total Polymer:		
Actual	30.2	29.0
Predicted (based on an equivalent amount of monomer being used instead of the dimer [1])	[2] 23–24	25–28

[1] Predicted by extrapolation and interpolation of C_7 yield data of Runs C, G and H.
[2] Actual run advantage may not be quite so large because actual Run E had rather low conversion (67%) which is known to enhance C_7 yield by limiting further polymerization of C_7 to C_{10} and C_{11}, etc.

What is claimed is:

1. In a process for preparing a C_7 olefin from a C_3 to C_4 hydrocarbon stream containing at least 20 mole percent olefin and consisting essentially of propylene and n-butylenes wherein said stream is contacted with a phosphoric acid catalyst at the rate of about 0.05 to 0.5 gallons per hour per pound of catalyst in a polymerization zone at temperatures of 280° to 550° F. and pressures of 250 to 3000 p.s.i.g. to produce said C_7 olefin, the improvement which consists of adding to said stream between about 0.15 to 3 moles of diisobutylene (calculated as equivalent isobutylene) per mole of propylene, thereby substantially increasing the yield of said C_7 olefin.

2. The process of claim **1** in which 0.3 to 3 moles of diisobutylene (calculated as equivalent isobutylene) per mole of propylene is added to said hydrocarbon stream.

3. The process of claim **1** in which the temperature is about 350° to 450° F.

4. The process of claim **1** in which the catalyst is phosphoric acid calcined on kieselguhr.

5. In a process for preparing a C_7 olefin from a C_3 hydrocarbon stream containing at least 20 mole percent olefin and consisting essentially of propylene, wherein said stream is contacted with a phosphoric acid catalyst at the rate of about 0.05 to 0.5 gallons per hour per pound

of catalyst in a polymerization zone at temperatures of 280° to 550° F. and pressures of 250 to 3000 p.s.i.g. to produce said C_7 olefin, the improvement which consists of adding to said stream between about 0.15 to 3 moles of diisobutylene (calculated as equivalent isobutylene) per mole of propylene, thereby substantially increasing the yield of said C_7 olefin.

References Cited by the Examiner

UNITED STATES PATENTS

2,116,157	5/1938	Morrell	260—683.15
2,182,617	12/1939	Michel	260—683.15
2,658,933	11/1953	May et al.	260—683.15
2,694,002	11/1954	Hays	260—683.15
2,695,326	11/1954	Lippincott et al.	260—683.15

OTHER REFERENCES

Ipatieff et al., "Industrial & Engineering Chemistry," vol. 37 (1945), pages 362–364.

PAUL M. COUGHLAN, *Primary Examiner.*