

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 June 2009 (11.06.2009)

PCT

(10) International Publication Number
WO 2009/073065 A1

(51) International Patent Classification:
C07C 2/28 (2006.01)

(21) International Application Number:
PCT/US2008/011816

(22) International Filing Date: 16 October 2008 (16.10.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/999,222 4 December 2007 (04.12.2007) US

(71) Applicant: **LYONDELL CHEMICAL TECHNOLOGY, L.P.** [US/US]; Two Greenville Crossing, 4001 Kennett Pike, Suite238, Greenville, Delaware 19807 (US).

(72) Inventors: **DUBNER, Walter, S.**; 210 Medford Road, Wilmington, Delaware 19803 (US). **RENAUDO, Christopher, P.**; 15707 Brookforest Drive, Houston, Texas 77059 (US). **LIN, Shaw-chan**; 1213 Anna Road, West Chester, Pennsylvania 19380 (US).

(74) Agents: **HAN, Yuanzhang** et al.; LyondellBasell Industries, 3801 West Chester Pike, Newtown Square, Pennsylvania 19073 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report*

(54) Title: DIISOBUTENE PROCESS

(57) Abstract: A process comprising reacting a feed comprising isobutene and a modifier in the presence of an acidic solid catalyst to produce diisobutene is disclosed. The amount of the modifier in the feed is reduced as the catalyst ages. Lower reaction temperature is maintained throughout the catalyst life, which is less likely to corrode the reactor. When an alcohol is used as a modifier, a lower reaction temperature causes lower degree of dehydration of the modifier, thus lower water concentration is maintained, which in turn reduces the likelihood of reactor corrosion.



WO 2009/073065 A1

DIISOBUTENE PROCESS

FIELD OF THE INVENTION

5 The invention is a process for making diisobutene from isobutene in the presence of an acidic solid catalyst. Diisobutene may be used as fuel blending components.

BACKGROUND OF THE INVENTION

10 The dimerization of olefins such as isobutene using an acidic solid catalyst is well-known in the art. For instance, U.S. Pat. No. 4,100,220 describes isobutene dimerization using a sulfonic acid resin catalyst and tert-butanol (tert-butyl alcohol, TBA) modifier. U.S. Pat. No. 4,447,668 discloses isobutene dimerization using sulfonic acid resin Amberlyst-15 with methyl tert-
15 butyl ether as solvent. U.S. Pat. No. 5,877,372 describes the dimerization of isobutene using a sulfonic acid resin catalyst, tert-butanol modifier, and isooctane diluent. U.S. Pat. No. 6,376,731 discloses the dimerization of isobutene in the presence of a C₃ or C₄ alkane and tert-butanol to promote selectivity to diisobutene.

20 The diisobutene produced may be used as such or may be hydrogenated to isooctane as described in U.S. Pat. No. 5,877,372 and U.S. Pat. No. 6,376,731. Diisobutene and isooctane are useful fuel blending components.

 Nearly all solid catalysts deactivate with time on stream. Often the reaction temperature needs to be raised as the catalyst deactivates so as to
25 maintain a constant product throughput. In an isobutene dimerization catalyzed by an acidic solid catalyst, small amounts of acid may leach into the reaction media, potentially corroding the reactor.

SUMMARY OF THE INVENTION

30 The invention is an isobutene dimerization process. The process comprises reacting a feed comprising isobutene and a modifier in the presence of an acidic solid catalyst, wherein the concentration of the modifier in the feed is reduced as the catalyst deactivates. Reactor throughput is maintained without raising reaction temperature, which could promote reactor corrosion.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows the net TBA (wt.%) in isobutene dimerization as a function of the reaction temperature, initial TBA concentration in the feed, and isobutene conversion.

5

DETAILED DESCRIPTION OF THE INVENTION

The invention is a process comprising reacting a feed comprising isobutene and a modifier in the presence of an acidic solid catalyst to produce diisobutene. Suitable solid catalysts include acidic ion-exchange resins, mixed
10 metal oxides (e.g., silica-alumina), acidic zeolites, acidic clays, and mixtures thereof.

Preferred catalysts are acidic ion-exchange resins. Acidic ion-exchange resins generally contain sulfonic acid or carboxylic acid groups. The acidic ion-exchange resin may contain protons and other cations (e.g., alkali metal,
15 alkaline earth metal, ammonium). Sulfonic acid resins, which are well known, are most preferred. Commercially available sulfonic acid resins include Amberlyst A-15, Amberlyst A-35, Amberlyst A-36 (available from Rohm & Haas Company), Purolite® C-275 (available from Purolite Corporation), and Dowex® 50 (available from Dow Chemical Company). Preferably the sulfonic acid resin
20 contains from 5 to 30 weight percent (wt.%) sulfur. The dimerization of isobutene using sulfonic acid resins is known in the art and has been described in U.S. Pat. Nos. 4,100,220, 4,447,668, 5,877,372 and 6,376,731.

The feed comprises isobutene. Isobutene in the feed may be from a number of sources. Suitable sources include isobutene-containing streams from
25 refining or steam cracking units, such as the refinery Cat B-B and Raffinate-1, or pure isobutene from TBA dehydration as described in U.S. Pat. Nos. 5,625,109, 3,510,538, 4,165,343, and 4,155,945. The production of TBA by the Oxirane process is well known, see, for example, U.S. Pat. No. 3,351,635. Cat B-B (sometimes known as Refinery B-B) is a C₄ stream (primarily butenes and
30 butanes) from the refining of crude oil by fluid catalytic cracking (FCC). Raffinate-1 is produced in steam cracking units after the selective separation or selective hydrogenation of 1,3-butadiene (see U.S. Pat. No. 6,586,649).

The amount of isobutene in the feed may range from approximately 5 wt.% to 99.5 wt.%. Preferably it contains at least 10 wt.% isobutene, more preferably, at least 50 wt.%.

The feed may comprise a diluent. A diluent is used as a heat sink to
5 reduce the temperature rise from the heat of the reaction. Typically, a C₁₋₁₀ paraffin (saturated hydrocarbon) is used. Suitable diluents include propane, butanes, pentanes, hexanes, heptanes, octanes, and mixtures thereof. For example, U.S. Pat. No. 5,877,372 discloses the oligomerization of isobutene in the presence of an isoalkane diluent. U.S. Pat. No. 6,376,731 discloses an
10 isobutene dimerization process in the presence of a C₃ or C₄ diluent. Preferably, the feed contains from 1 to 90 wt.% diluent, more preferably from 10 to 50 wt.% diluent.

The feed comprises a modifier. A modifier is a compound that moderates the catalyst activity and improves its selectivity. Generally the modifier is an
15 oxygenate (an organic molecule containing oxygen). Suitable oxygenates include alcohols, ethers, ketones, esters, phenols, and the like. Preferably, an alcohol is used. TBA is particularly preferred. The amount of modifier is preferably at least 0.5 wt.% relative to the feed, preferably from 1 to 15 wt.%, most preferably from 3 to 10 wt.%. Water may be used as a modifier, as water
20 can react with isobutene to form TBA under the reaction conditions.

A portion of the product stream may be recycled back to the reactor. Recycling helps to control the reaction temperature, as the recycled stream dilutes the feed and lowers the concentration of the isobutene in the reactor.

It is well known that activity of a catalyst often decreases as it is being
25 used in a chemical process. Causes of solid catalyst deactivation are basically threefold: chemical, mechanical, and thermal. Mechanisms of solid catalyst deactivation can be classified into five general modes: (1) chemical degradation including volatilization and leaching, (2) fouling, (3) mechanical degradation, (4) poisoning, and (5) thermal degradation. See Bartholomew, C. H. and Farrauto, R. J., Fundamentals of Industrial Catalytic Processes, second edition, John
30 Wiley & Sons (2006) pp. 260-287. In isobutene dimerizations catalyzed by acidic solid catalysts, the catalyst deactivation may be caused by leaching of acidic species from the catalyst, fouling of catalyst surface due to the formations of oligomers or polymers, attrition of the catalyst, poisoning of the acidic sites by

impurities (e.g., ammonia or amines), and thermal degradation of the catalyst. It is well known, for example, that sulfonic acid resins decompose at high temperature, producing sulfonic or sulfuric acids.

In the present process, the concentration of the modifier in the feed is adjusted as the catalyst deactivates. Optionally, the reactor temperature may be adjusted as well. Usually, in a continuous process, the temperature of the reactor is raised as the catalyst deactivates so as to maintain the flow rate and the conversion constant. Other strategies may be used to deal with the catalyst deactivation in a commercial plant, as described in Chem. Eng. J. 28 (1984) 13, which include: (1) varying throughput of the reactor feed while holding the reactor temperature and conversion constant; (2) allowing the conversion to fall while holding the reactor feed flow and the reactor temperature constant; (3) maintaining the fresh feed rate and the reactor temperature constant and let the recycle flow increase; (4) using a combination of parallel reactors so that one of reactors will be off-line, so the catalyst may be regenerated or replaced with fresh catalyst while the other reactors are operating; (5) continuous catalyst regeneration while maintaining throughput and the reactor temperature. Option (1) or (2) reduces the production rate as the catalyst deactivates. Option (3) may be limited by the equipment size (e.g., recycle pump, pressure drop across the bed, etc.). Option (4) requires additional reactors, thus greater capital investment. Option (5) can only be used in certain reactor types (e.g., fluidized-bed or slurry reactors) where a portion of the catalyst may be removed relatively easily from the reactor and the regenerated catalyst or fresh catalyst may be added to the reactor without shutting down the operation. Removing catalyst from a continuously operated reactor is a troublesome operation. In a fixed-bed process, such operation is extremely difficult to implement.

If an alcohol (e.g., TBA) is used as a modifier, a portion of the modifier may be dehydrated under the reaction conditions to produce water. For example, TBA is converted to isobutene and water. Water in the reaction media, particularly when it forms a separate phase and contains free acids leached from the catalyst, may corrode the reactor. The higher the reaction temperature, the more water forms, and the higher the risk of reactor corrosion. In such a case, lower reaction temperature is particularly beneficial.

The temperature of the dimerization partly depends on the type of catalyst used. The isobutene dimerization may be conducted at a temperature in the range of from 0 to 200°C, preferably from 20 to 150°C, most preferably from 50 to 120°C, and under a pressure sufficient to maintain the reactor content in liquid phase, preferably above 50 psig, e.g., from 50 to 500 psig.

The process may be performed in a batch, semi-batch, or a continuous mode. Preferably, the process is conducted in a continuous mode where the reactants continuously flow in the reactor and the products continuously flow out of the reactor (Smith, J. M., Chemical Engineering Kinetics, third edition, McGraw-Hill, Inc. (1981) pp. 25-33). The catalyst may be in a fixed bed or a slurry. A continuous fixed-bed process is particularly preferred.

The reaction products include diisobutene as well as some non-reacted isobutene and isobutene oligomers (e.g., triisobutenes, tetraisobutenes). Diisobutene and isobutene may be separated with conventional techniques (e.g., distillation). The isolated isobutene from the product stream may be recycled back to the dimerization.

The following examples illustrate the invention.

EXAMPLE 1-A

A 500-mL autoclave reactor is equipped with a feed line, a product line, a thermo well, and a stirrer. Purolite® CT 275 (Purolite Corporation, 20 g) is charged to the reactor. A feed consisting of 4.03 wt.% TBA and 95.97 wt.% isobutylene is continuously fed to the reactor. The product stream exits the reactor from the product line. The weight hourly space velocity is controlled at 2 h⁻¹. The reactor is heated with an electric heater and the temperature of the reaction is controlled at 150°F. The product stream is analyzed by an on-line gas chromatography (GC). The isobutylene conversion is 59%. The TBA concentration in the product stream is 4.33 wt.%. The results are listed in Table 1. The net TBA made by the reaction is 0.30 wt.%.

EXAMPLES 1-B TO 1-E

The procedure of Example 1 is repeated, except that the amounts of TBA and isobutylene fed to the reactor and the reaction temperature are different. The detailed reaction conditions and the results are shown in Table 1, and

graphed in Figure 1, where $\Delta\text{TBA} = \text{TBA wt.\% in product} - \text{TBA wt.\% in the feed}$. A positive value for ΔTBA indicates that TBA is made by the process from the reaction between isobutene and water present in the feed. A small amount of water is present in isobutene and TBA. A negative value for ΔTBA indicates that TBA is dehydrated to form isobutene and water in a 1:1 molar ratio.

Figure 1 shows that at constant TBA concentration in the feed, the higher the reaction temperature, the more TBA is converted to isobutene and water. In addition, higher temperature can cause the thermal decomposition of the catalyst. Thus in general, lower reaction temperature is preferred. Figure 1 also shows that at the same isobutene conversion, the lower the TBA concentration in the feed, the lower the reaction temperature required. According to the present invention, as the catalyst deactivates, the TBA is lowered so as to maintain the constant isobutene conversion.

15

EXAMPLE 2

A mixture of isobutene (flow rate = 100 g/h) and TBA (flow rate = 7 g/h) is fed to the top of a 0.8" ID tube reactor containing Purolite® CT-275 (washed with methanol and dried under vacuum at 120°C, 50 g). The reactor is under a pressure of 300 psig. The product exits the reactor from the bottom of the reactor. The temperature of the bed is slowly raised over a period of 48 h to 170°F to control the isobutene conversion to be about 60%. The conversion is maintained constant over 3600 h. The TBA flow rate is reduced as the catalyst deactivates over time. The expected diisobutene selectivity is about 94%. Diisobutene selectivity is defined as $2 \times (\text{moles of diisobutene formed}) / (\text{moles of isobutene reacted})$.

25

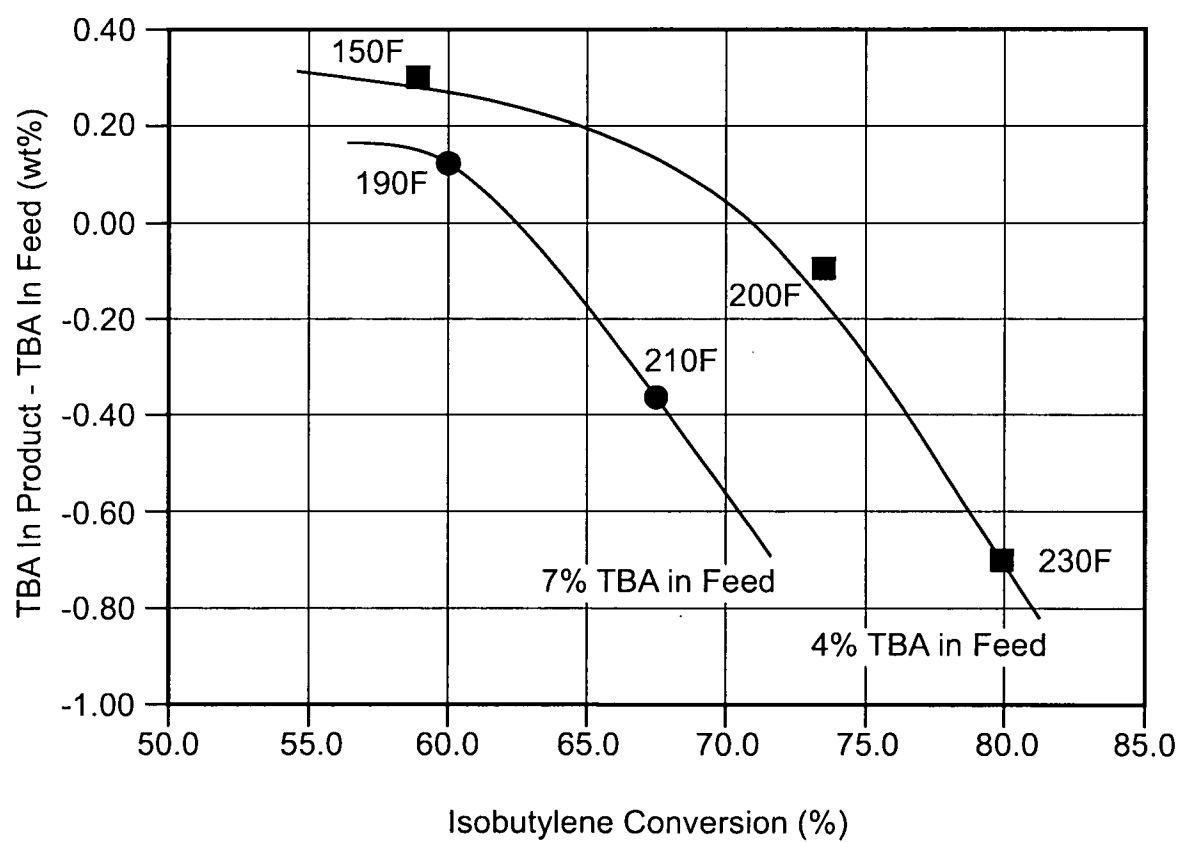
Table 1.

Example	Feed TBA (wt.%)	T (°F)	Isobutylene Conversion (%)	Product TBA (wt.%)	Δ TBA (wt.%)
1-A	4.03	150	59.0	4.33	0.30
1-B	4.03	200	73.5	3.93	-0.10
1-C	4.03	230	79.9	3.22	-0.81
1-D	7.22	190	60.1	7.34	0.12
1-E	7.06	210	67.6	6.69	-0.37

We claim:

1. A process comprising reacting a feed comprising isobutene and a modifier in the presence of an acidic solid catalyst to produce diisobutene, wherein the concentration of the modifier is reduced with time as the catalyst
5 deactivates.
2. The process of claim 1 wherein the feed contains at least 10 wt.% isobutene.
3. The process of claim 1 wherein the feed contains at least 50 wt.% isobutene.
- 10 4. The process of claim 1 wherein the feed contains a hydrocarbon diluent.
5. The process of claim 1 wherein the catalyst is an ion-exchange resin.
6. The process of claim 1 wherein the catalyst is a sulfonic acid ion-
15 exchange resin.
7. The process of claim 6 wherein the catalyst contains from 5 to 30 wt.% sulfur.
8. The process of claim 1 wherein the modifier is an oxygenate.
9. The process of claim 1 wherein the modifier is an alcohol.
- 20 10. The process of claim 1 wherein the modifier is tert-butanol (TBA).
11. The process of claim 10 wherein the amount of TBA is from 1 to 15 wt.% relative to the amount of the feed.
12. The process of claim 10 wherein the amount of TBA is from 3 to 10 wt.% relative to the amount of the feed.
- 25 13. The process of claim 1 performed at a temperature in the range of 50 to 120°C.
14. A fixed-bed process of claim 1.
15. A continuous process of claim 1.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/011816

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HONKELA, M.; KRAUSE A. OUTI: "Kinetic Modeling of the dimerisation of Isobutene" INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 43, no. 13, 19 May 2004 (2004-05-19), pages 3251-3260, XP002509497 page 3253; figure 4 page 3254, paragraph 2-4; figure 5 ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

9 January 2009

Date of mailing of the international search report

06/02/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Patteux, Claudine

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/011816

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HONKELA ET AL: "Comparison of ion-exchange resin catalysts in the dimerisation of isobutene" APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 295, no. 2, 9 November 2005 (2005-11-09), pages 216-223, XP005122274 ISSN: 0926-860X page 220, paragraph 2 -----	1-15
A	US 4 100 220 A (BOWMAN WILLIAM G ET AL) 11 July 1978 (1978-07-11) cited in the application the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2008/011816

Patent document
cited in search report

Publication
date

Patent family
member(s)

Publication
date

US 4100220

A

11-07-1978

NONE
