(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 December 2014 (31.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/209463 A1

(51) International Patent Classification:
*C10G 21/00* (2006.01)

(21) International Application Number:
PCT/US2014/032956

(22) International Filing Date:
4 April 2014 (04.04.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/927,748 26 June 2013 (26.06.2013) US

(71) Applicant: **UOP LLC** [US/US]; 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) Inventors: **KRUPA, Steven L.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **FOLEY, Timothy D.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(74) Agent: **GOODING, Arthur E.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

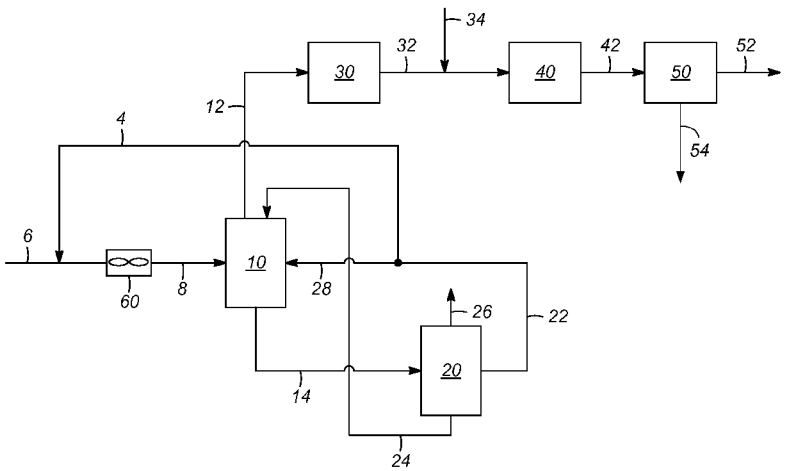
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

**Published**:

— *with international search report (Art. 21(3))*

(54) Title: CRUDE BUTADIENE PRE-TREATMENT FOR REMOVAL OF HIGH FURAN CONTENT




(57) Abstract: A process is presented for the purification of 1,3 butadiene. The process is for treating a butadiene stream from an oxidative dehydrogenation unit, where a butane stream is dehydrogenated, generating a butadiene rich stream. The butadiene rich stream is fractionated and passed through a butadiene recovery unit. Additional C4 compounds recovered from the fractionation bottoms stream are further processed for increasing yields of butadiene.

WO 2014/209463 A1

# CRUDE BUTADIENE PRE-TREATMENT FOR REMOVAL OF HIGH FURAN CONTENT

## STATEMENT OF PRIORITY

**[0001]** This application claims priority to U.S. Application No. 13/927,748 which was filed on June 26, 2013, the contents of which are hereby incorporated by reference in its entirety.

## FIELD OF THE INVENTION

**[0002]** The field of the invention relates to the dehydrogenation of hydrocarbons. Specifically, the invention relates to the purification process of a crude butadiene stream in the recovery of products from the dehydrogenation of light hydrocarbons using an oxidative dehydrogenation process.

## BACKGROUND OF THE INVENTION

**[0003]** 1,3-Butadiene is an important monomer for the production of high molecular weight polymers. It is used extensively in the production of tires and other products in the automotive industry. It is also used extensively in the production of synthetic rubbers, such as styrene-butadiene rubber, nitrile-butadiene rubber, and styrene-butadiene latex. Polymer grade butadiene requires a high purity, and needs to be essentially free of active chemicals such as acetylenes, carbonyls, and contaminants such as sulfur and other heavy components. As used, hereinafter, the term butadiene will be used to refer to 1,3-butadiene.

**[0004]** Butadiene is usually a by-product recovered from the stream cracking of naphtha during the production of ethylene and propylene. Naphtha cracking, either through stream or catalytic cracking, produces a range of products, and is not optimized for the production of chemicals such as butadiene. Another route for the production of butadiene is through catalytic oxidative dehydrogenation of n-butane, which yields a higher concentration of butadiene, but also yields some undesirable side products that must be removed.

## SUMMARY OF THE INVENTION

**[0005]** The present invention provides a process for the removal of heterocyclic oxygenates from a hydrocarbon stream, where the heterocyclic oxygenates, and other oxygenates that are not sufficiently removable with a wash system that removes oxygenates such as aldehydes and ketones. The wash system is a bisulfite wash that will remove many of the oxygenates generated that are soluble in the bisulfite solution. The process is useful for the production of butadienes. Butadienes can be generated by oxidative dehydrogenation with a relatively high concentration, but also generates furan.

**[0006]** The process includes mixing the butadiene stream from the oxidative dehydrogenation process with a solvent to generate a mixed process stream. The mixed process stream forms a first process stream and is passed to an extraction unit with additional solvent for the removal of oxygenates, and in particular furan into the solvent. Water is passed to the extraction unit to facilitate the separation of the butadiene and solvent mixture into an aqueous phase and a non-aqueous phase. The non-aqueous phase forms a second process stream having a reduced oxygenate content, and the aqueous phase forms a third process stream with a high oxygenate content. The second process stream is passed for further processing to generate a purified 1,3-butadiene stream. The further processing includes a wash to remove residual aldehydes and ketones, and passing the washed second process stream to a selective hydrogenation unit for the selective hydrogenation of acetylenes to generate a fourth stream having reduced acetylenes content. The fourth process stream is passed to a 1,3-butadiene separation unit.

**[0007]** The third process stream is passed to a solvent recovery unit, where the oxygenates are separated from the third process stream and removed from the system. The solvent and water are recovered in the solvent recovery unit and recycled to the extraction unit. A preferred solvent is methanol.

**[0008]** Other objects, advantages and applications of the present invention will become apparent to those skilled in the art from the following detailed description and drawings.

## BRIEF DESCRIPTION OF THE DRAWING

**[0009]** The Figure is a process for the production of polymer grade 1,3-butadiene.

## DETAILED DESCRIPTION OF THE INVENTION

**[0010]** The production of butadiene can be performed with oxidative dehydrogenation of n-butane. The oxidative dehydrogenation process provides an attractive route for the production of butadiene as there are lower concentrations of undesirable compounds that need to be removed, such as isobutylene or isobutane. This reduces separation costs due to fewer similar boiling point compounds. The oxidative dehydrogenation process generates a crude butadiene stream having a high concentration of 1,3 butadiene, but also a high concentration of oxygenates relative to a typical steam cracker crude C4 stream.

**[0011]** The oxidative dehydrogenation process has some selectivity for the production of isobutylene. The isobutylene is removed to produce a purified butadiene process stream. Removal of the isobutylene is usually performed with an (methyl tertiary butyl ether) MTBE unit in a C4 complex. The removal of isobutylene can also be performed with an equivalent unit for the production of ETBE, or other similar processes. A major contaminant in the crude butadiene stream is furan, which can be as high as 2500 ppm by weight of the stream. The furan needs to be reduced to a safe level to protect downstream catalysts, including before the butadiene stream reaches the MTBE unit, but is not removed in a sodium bisulfate wash. The crude butadiene stream requires additional processing to remove heterocyclic oxygenate compounds generated by the oxidative dehydrogenation process. In particular, the heterocyclic oxygenate compounds includes furan, as the furan creates increased complexity and equipment and processing costs associated with the methanol recovery section in the MTBE unit. The furan also needs to be removed to prevent any furan contamination in the MTBE product stream. The furan contamination would render the MTBE product unstable which can result in peroxide formation and require the addition of inhibitors that are normally not required. Therefore, in order to meet MTBE product specifications, the furan needs to be reduced to a level that minimizes cost for the MTBE unit. Furan also can create problems with the butadiene extraction unit where furan can accumulate in the circulating solvent. Without removal of the furan, there is additional increased complexity and cost associated with the butadiene extraction unit, as the butadiene extraction solvent needs to maintain an operational level of purity. The buildup of furan in the solvent would require the treatment of the extraction solvent.

**[0012]** The present process provides a method of removal of the furan to very low levels to meet downstream process specifications. The process, as shown in the Figure, includes mixing a crude butadiene stream 6 with a solvent stream 4 to generate a first process stream 8. The first process stream 8 is passed to an extraction unit 10 to generate a second process stream 12 having a reduced oxygenate content, and a third process stream 14 having an increased, or high, oxygenate content. The second stream 12 is passed to a selective hydrogenation unit 40 to generate a fourth process stream 42 with a reduced acetylenes content. The fourth process stream 42 is passed to a 1,3-butadiene separation unit 50 to recover a purified 1,3-butadiene product stream 52. The separation unit 50 generates a raffinate stream 54, called Raffinate-1, containing the remaining C4s in the process stream 42.

**[0013]** The acetylenes include any acetylenes generated by the oxidative dehydrogenation process, and include acetylene, vinyl acetylene, methyl acetylene and ethyl acetylene. Other acetylenes that are generated would be expected to also be selectively hydrogenated in the selective hydrogenation unit, or have been seen to be in concentrations low enough to not be a concern for this process.

**[0014]** The second process stream 12 will contain some oxygenates, typically aldehydes and the like, that are not removed in the extraction unit 10. The second process stream 12 can be further passed through a wash unit 30, prior to passing the second process stream 12 to the selective hydrogenation unit 40. An oxygenate depleted stream 32 is generated and passed with a hydrogen stream 34 to the selective hydrogenation unit 40. The wash unit 30 comprises a sodium bisulfate wash unit to remove residual aldehydes and ketones not removed by the extraction unit 10.

**[0015]** The extraction unit 10 is preferably liquid-liquid extraction column, wherein the furan is soluble in the solvent. A solvent for use in the extraction distillation column 10 is an alcohol. A preferred alcohol is methanol. The extraction distillation includes passing a solvent stream 28 to the extraction unit 10. A water stream 24 is passed to the extraction unit 10. The water is a co-solvent to force splitting out of a separate aqueous phase and to avoid a high methanol content in the crude butadiene stream 12 leaving the extraction unit 10. The water and solvent contacting the crude butadiene stream removes the heterocyclic oxygenates, and in particular furan. Additional oxygenates are also removed. The third

process stream 14 is withdrawn from the extraction unit 10 and passed to a solvent recovery unit 20.

**[0016]** The solvent recovery unit 20 generates a bottoms stream 24 comprising water. The water is recycled to the extraction unit for reuse. The solvent recovery unit 20 also generates an intermediate stream 22 comprising the solvent, which is split into two portions. A first portion is passed to be mixed with the crude butadiene stream, and a second portion is passed to the extraction unit 10. The solvent recovery unit 20 generates an overhead stream 26 comprising oxygenates, including furan, that have been removed from the crude butadiene stream. In the instant case, the solvent of choice is methanol. When another solvent is chosen, the solvent recovery unit can be configured to accommodate that solvent, including having the solvent passed out with the bottoms stream, and the bottoms stream passed to a separate distillation column for the separation of water and solvent.

**[0017]** The extraction unit 10 and the solvent recovery unit 20 provide for a closed loop system with respect to the water and methanol. The water and methanol cycle between the two units and under ideal operating conditions no new solvent needs to be added. Makeup solvent can be added due to normal losses during operation.

**[0018]** The process can further include passing the 1,3-butadiene stream with the oxygenates removed to an extractive distillation column to generate an overhead stream comprising the remaining C4s and a bottoms stream comprising 1,3-butadiene. Additional processing can separate out 1-butene from the remaining C4s, as 1-butene is a commercially valuable product. The bottoms stream includes an extractive solvent and the bottoms stream is passed to another distillation column for separating the 1,3-butadiene from the extractive solvent. The extractive solvent is in then recycled to the extractive distillation column for separating 1,3-butadiene from the mixture.

**[0019]** In general, the crude butadiene stream has a high butadiene content. The process includes mixing the crude butadiene stream with a solvent. The mixing can be done with a static mixer or other type of mixer to provide a well mixed mixture passed to a counter-current liquid-liquid extractor. More solvent and water are added to insure the absorption of the heterocyclic oxygenates, including furan, into the solvent mixture and to force phase separation of an aqueous phase, with the aqueous phase containing the oxygenates removed from the butadiene stream.

**[0020]** In one embodiment, if the extraction of the furan is sufficient from the mixing of the solvent with the butadiene stream, the a mixer-settler system can be used rather than the counter-current extractor. The mixed stream is passed to a mixing-settling unit, where additional solvent and water are passed to the mixing-settling unit. The water generates an aqueous phase comprising the furan, and a non-aqueous phase comprising C4 hydrocarbon compounds without furan is generated. The non-aqueous phase is passed to a wash unit using sodium bisulfate to remove aldehydes and ketones to generate an oxygenate free C4 stream. The oxygenate free C4 stream is then passed to a 1,3-butadiene purification unit to generate a purified 1,3-butadiene stream.

**[0021]** The aqueous phase is passed to a solvent recovery distillation column to recover the solvent and water for reuse. The water and solvent are in a closed loop with no need for continuous addition of solvent or water. The use of methanol as the solvent is preferred.

**[0022]** While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

## SPECIFIC EMBODIMENTS

**[0023]** While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

**[0024]** A first embodiment of the invention is a process for the purification of a crude butadiene stream, comprising mixing the crude butadiene stream with a solvent to generate a first process stream; passing the first process stream to an extraction unit to generate a second process stream with reduced oxygenate content and a third process stream with a high oxygenate content; passing the second process stream to a selective hydrogenation unit to generate a fourth process stream with reduced acetylenes content; and passing the fourth process stream to a 1,3-butadiene separation unit. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the solvent is methanol. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph

further comprising adding more solvent to the extraction unit adding water to the extraction unit; and withdrawing the third process stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising passing the third process stream to a fractionation column to generate a bottoms stream comprising water, an intermediate stream comprising solvent, and an overhead stream comprising furan. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising passing the bottoms stream to the extraction unit; and passing the intermediate stream to the extraction unit. The process of claims 1 further comprising passing the second process stream to a wash unit to remove residual oxygenates and generate an oxygenate depleted second process stream; and passing the oxygenate depleted second process stream to the selective hydrogenation unit. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the wash unit comprises a sodium bisulfate wash unit for removing residual aldehydes and ketones. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the crude butadiene stream comprises heterocyclic oxygenate compounds. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the heterocyclic oxygenate compounds include furan. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the extraction unit is an extractive distillation column.

**[0025]** A second embodiment of the invention is a process for the purification of 1,3-butadiene, comprising passing a crude butadiene stream, wherein the crude butadiene stream comprises heterocyclic oxygenates, to a mixer; passing a solvent to the mixer to generate a first process stream comprising crude butadiene and solvent; passing the first process stream to an extraction unit to generate a second process stream comprising 1,3-butadiene and having a reduced oxygenate content, and a third process stream comprising oxygenates; passing the second process stream to a wash unit to generate an oxygenate depleted second process stream; passing the oxygenate depleted second process stream to a selective hydrogenation unit to generate a fourth process stream; passing the third process stream to a

fractionation column to generate an overhead stream comprising heterocyclic oxygenate compounds, an intermediate stream comprising solvent, and a bottoms stream comprising water; passing the bottoms stream to the extraction unit; splitting the intermediate stream into a first portion and a second portion; passing the first portion comprising solvent to the mixer; passing the second portion comprising solvent to the extraction unit; and passing the fourth process stream to a 1,3-butadiene separation unit to generate a purified 1,3-butadiene stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the generation of the purified 1,3-butadiene stream comprises passing the fourth process stream to an extractive distillation column to generate an overhead stream comprising C4s, and a bottoms stream comprising 1,3-butadiene and an extractive solvent; and passing the bottoms stream to a butadiene distillation column to generate an overhead stream comprising 1,3-butadiene and a bottoms stream comprising the extractive solvent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the heterocyclic oxygenate compound comprises furan. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the wash unit comprises a sodium bisulfate wash unit. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the solvent comprises an alcohol. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the solvent comprises methanol.

**[0026]** A third embodiment of the invention is a process for the removal of furan from a crude butadiene stream, comprising mixing the crude butadiene stream with a solvent in a mixer to generate a mixed stream; passing the mixed stream to a liquid-liquid separation unit; passing water to liquid-liquid separation unit, to generate a two phase system with an aqueous phase comprising water, solvent and furan, and a non-aqueous phase comprising C4 compounds, wherein the liquid-liquid separation unit is selected from the group consisting of a counter-current extraction column and a mixer-settler; and drawing off the aqueous phase to recover the solvent and water. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein

the solvent is methanol. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph further comprising passing the aqueous phase to an distillation column to generate an overhead stream comprising furan, an intermediate stream comprising solvent, and a bottoms stream comprising water; and passing the bottoms stream to the liquid-liquid separation unit; and passing the intermediate stream to the mixer. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein the intermediate stream is split into a first portion and a second portion, and further comprising passing the first portion to the mixer; and passing the second portion to the liquid-liquid separation unit.

**[0027]** Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

**[0028]** In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS:

1. A process for the purification of a crude butadiene stream, comprising:

mixing the crude butadiene stream with a solvent to generate a first process stream;

passing the first process stream to an extraction unit to generate a second process stream with reduced oxygenate content and a third process stream with a high oxygenate content;

passing the second process stream to a selective hydrogenation unit to generate a fourth process stream with reduced acetylenes content; and

passing the fourth process stream to a 1,3-butadiene separation unit.

2. The process of claim 1 wherein the solvent is methanol.

3. The process of claim 1 further comprising:

adding more solvent to the extraction unit:

adding water to the extraction unit; and

withdrawing the third process stream.

4. The process of claim 3 further comprising:

passing the third process stream to a fractionation column to generate a bottoms stream comprising water, an intermediate stream comprising solvent, and an overhead stream comprising furan.

5. The process of claim 4 further comprising:

passing the bottoms stream to the extraction unit; and

passing the intermediate stream to the extraction unit.

6. The process of claims 1 further comprising:

passing the second process stream to a wash unit to remove residual oxygenates and generate an oxygenate depleted second process stream; and

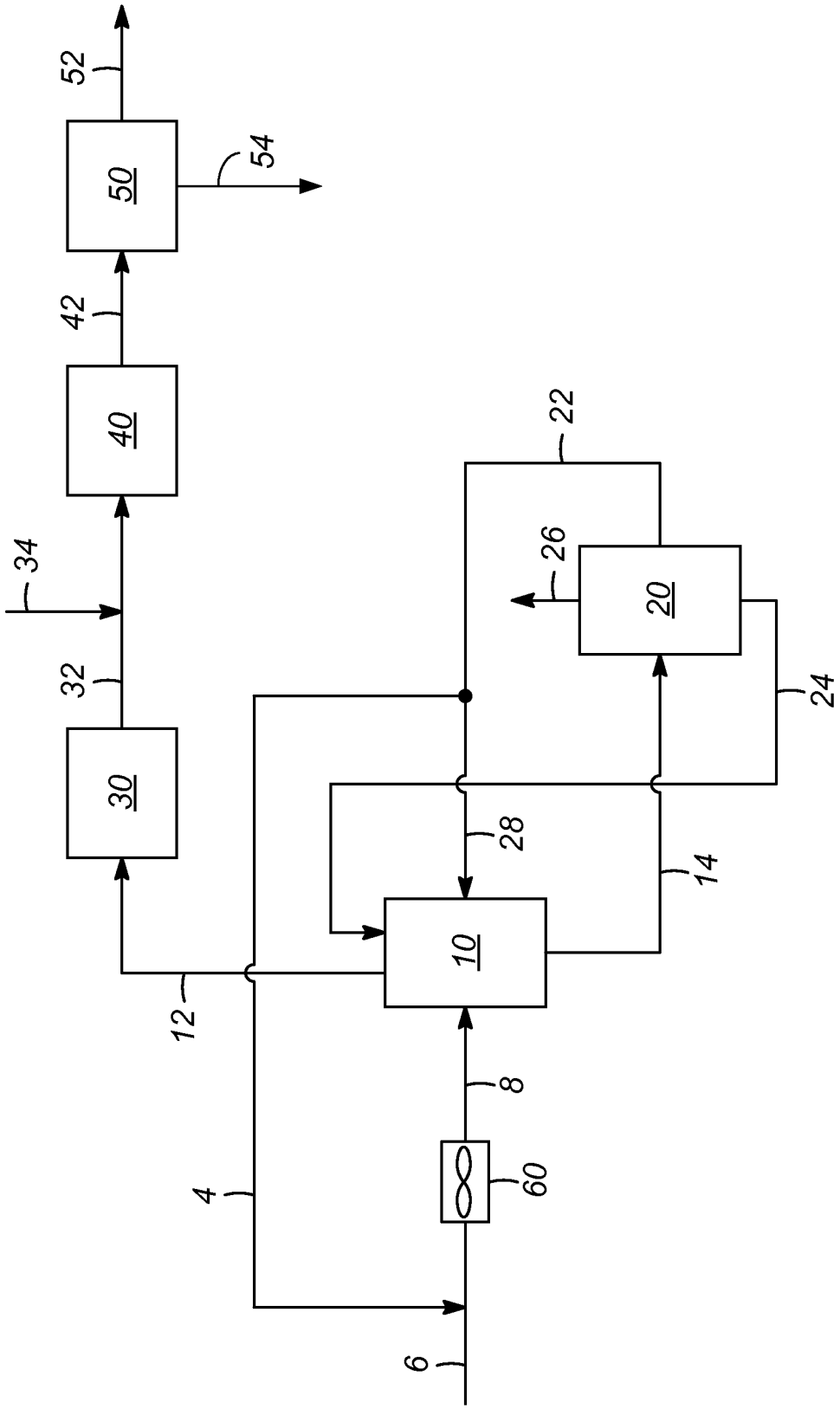
passing the oxygenate depleted second process stream to the selective hydrogenation unit.

7. The process of claim 6 wherein the wash unit comprises a sodium bisulfate wash unit for removing residual aldehydes and ketones.

8. The process of claim 1 wherein the crude butadiene stream comprises heterocyclic oxygenate compounds.

9. The process of claim 8 wherein the heterocyclic oxygenate compounds include furan.

10. The process of claim 1 wherein the extraction unit is an extractive distillation column.


52
50
54
42
40
34
32
30
22
26
20
24
28
14
10
12
8
60
4
6

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/US2014/032956**

**A. CLASSIFICATION OF SUBJECT MATTER**

**C10G 21/00(2006.01)i**

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)
C10G 21/00; C07C 7/10; C07C 7/00; C10G 45/32; C07C 7/04; B01D 3/00; C07C ; C10G 65/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: crude butadiene, purification, solvent extraction, methanol, water, hydrogenation, oxygenate, acetylene, aldehyde, ketone, furan

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 2004-080928 A2 (SASOL TECHNOLOGY (PROPRIETAY) LIMITED) 23 September 2004<br>See abstract; page 7, line 28-page 9, line 8; claims 1-6, 8, 9; figure 3. | 1-10 |
| A | US 4090923 A (HASKELL, D. M. et al.) 23 May 1978<br>See abstract; column 2, line 29-column 3, line 15; claim 1; figure. | 1-10 |
| A | US 6395953 B1 (KOGA, T. et al.) 28 May 2002<br>See abstract; column 4, lines 9-36; column 5, line 16-column 7, line 18; claims 1, 3; figure 1. | 1-10 |
| A | US 6093285 A (FERNALD, D. T. et al.) 25 July 2000<br>See abstract; column 2, line 50-column 3, line 4; column 4, line 4-column 5, line 4; claims 1, 2; figure 1. | 1-10 |
| A | US 4686317 A (QUANN, R. J. et al.) 11 August 1987<br>See abstract; column 4, line 22-column 5, line 45; claims 1-4; figure. | 1-10 |
| A | KR 10-2010-0009009 A (SK ENERGY CO., LTD.) 27 January 2010<br>See abstract; paragraphs [0011]-[0013], [0027]-[0042]; claims 1, 13; figure 1. | 1-10 |

☐ 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 application or patent 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
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 04 September 2014 (04.09.2014) | **12 September 2014 (12.09.2014)** |


Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
LEE, Dong Wook
Telephone No. +82-42-481-8163

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.
**PCT/US2014/032956**

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 2004-080928 A2 | 23/09/2004 | AU 2004-220263 A1 | 23/09/2004 |
| | | AU 2004-220263 B2 | 27/08/2009 |
| | | AU 2004-220264 A1 | 23/09/2004 |
| | | AU 2004-220265 A1 | 23/09/2004 |
| | | AU 2004-220265 B2 | 18/06/2009 |
| | | AU 2004-220290 A1 | 23/09/2004 |
| | | AU 2004-220290 B2 | 02/04/2009 |
| | | CA 2518544 A1 | 23/09/2004 |
| | | CA 2518544 C | 09/08/2011 |
| | | CA 2518597 A1 | 23/09/2004 |
| | | CA 2518597 C | 17/01/2012 |
| | | CN 100345803 C0 | 31/10/2007 |
| | | CN 100575320 C | 30/12/2009 |
| | | CN 1759082 A | 12/04/2006 |
| | | CN 1759082 C0 | 23/04/2008 |
| | | CN 1764618 A | 26/04/2006 |
| | | CN 1764619 A | 26/04/2006 |
| | | CN 1764619 C0 | 26/04/2006 |
| | | CN 1826303 A | 30/08/2006 |
| | | CN 1826303 C0 | 27/08/2008 |
| | | EA 007843 B1 | 27/02/2007 |
| | | EG 24947 A | 13/02/2011 |
| | | EP 1601634 A2 | 07/12/2005 |
| | | EP 1601634 B1 | 25/11/2009 |
| | | EP 1603853 A2 | 14/12/2005 |
| | | EP 1603853 B1 | 15/07/2009 |
| | | JP 04484866 B2 | 16/06/2010 |
| | | JP 04484867 B2 | 16/06/2010 |
| | | JP 2006-519836 A | 31/08/2006 |
| | | JP 2006-519837 A | 31/08/2006 |
| | | KR 10-1063517 B1 | 08/09/2011 |
| | | KR 10-1079345 B1 | 04/11/2011 |
| | | US 2006-0211907 A1 | 21/09/2006 |
| | | US 2006-0258894 A1 | 16/11/2006 |
| | | US 2007-0038007 A1 | 15/02/2007 |
| | | US 2007-0066859 A1 | 22/03/2007 |
| | | US 7465846 B2 | 16/12/2008 |
| | | US 7737312 B2 | 15/06/2010 |
| | | US 7863492 B2 | 04/01/2011 |
| | | WO 2004-080926 A2 | 23/09/2004 |
| | | WO 2004-080926 A3 | 13/01/2005 |
| | | WO 2004-080927 A2 | 23/09/2004 |
| | | WO 2004-080927 A3 | 11/11/2004 |
| | | WO 2004-080928 A3 | 11/11/2004 |
| | | WO 2004-080929 A2 | 23/09/2004 |
| | | WO 2004-080929 A3 | 11/11/2004 |
| US 4090923 A | 23/05/1978 | None | |

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.
**PCT/US2014/032956**

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 6395953 B1 | 28/05/2002 | CN 1147567 C0 | 28/04/2004 |
| | | CN 1250466 A0 | 12/04/2000 |
| | | DE 69834482 D1 | 14/06/2006 |
| | | DE 69834482 T2 | 03/05/2007 |
| | | EP 0969074 A1 | 05/01/2000 |
| | | EP 0969074 A4 | 24/05/2000 |
| | | EP 0969074 B1 | 10/05/2006 |
| | | ES 2262225 T3 | 16/11/2006 |
| | | ID 22877 A | 16/12/1999 |
| | | JP 03941151 B2 | 04/07/2007 |
| | | JP 10-251660 A | 22/09/1998 |
| | | JP 10-251661 A | 22/09/1998 |
| | | KR 10-0542782 B1 | 11/01/2006 |
| | | US 2002-0052533 A1 | 02/05/2002 |
| | | WO 98-40448 A1 | 17/09/1998 |
| US 06093285 A | 25/07/2000 | None | |
| US 4686317 A | 11/08/1987 | ZA 8608851 A | 27/07/1988 |
| KR 10-2010-0009009 A | 27/01/2010 | CN 101755216 A | 23/06/2010 |
| | | CN 101755216 B | 10/10/2012 |
| | | CN 101821361 A | 01/09/2010 |
| | | EP 2310474 A1 | 20/04/2011 |
| | | JP 05327485 B2 | 30/10/2013 |
| | | JP 2011-528655 A | 24/11/2011 |
| | | TW 200912323 A | 16/03/2009 |
| | | TW I394953 B | 01/05/2013 |
| | | US 2010-0137664 A1 | 03/06/2010 |
| | | US 2010-0219852 A1 | 02/09/2010 |
| | | US 8149008 B2 | 03/04/2012 |
| | | WO 2009-011365 A1 | 22/01/2009 |
| | | WO 2010-008109 A1 | 21/01/2010 |