POSSE
HERRERA
RUIZ

9.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

012

No. 14-034844- -00000-0000

Fecha: 2014-02-19 14:57:07 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 86

Industria y Comercio
SUPERINTENDENCIA

DELEGATURA DE NUEVAS CREACIONES

SOLICITUD
FASE NACIONAL -PCT

21. EXPEDIENTE No. _____

54. TITULO: PROCEDIMIENTO DE ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE UNA CORRIENTE DE ETILENO

51. CLASIFICACION INTERNACIONAL:

C07C 7/00 (2006.01) C07C 7/04 (2006.01)
C07C 7/12 (2006.01) C07C 11/04 (2006.01

71. SOLICITANTE:

1. TOTAL RESEARCH & TECHNOLOGY FELUY
2. IFP ENERGIES NOUVELLES

DOMICILIO:
1. Zone Industrielle C, B-7181 Seneffe BELGICA
2. 1 & 4 avenue de Bois Préau, F-92852 Rueil Malmaison FRANCIA

74. APODERADO: HELENA CAMARGO WILLIAMSON

22. BOGOTÁ D.C., FEBRERO 19 DE 2014

Industria y Comercio
SUPERINTENDENCIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO — adicación
No. 14-034844- -00000-0000
Fecha: 2014-02-19 14:57:07 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 86

DIRECCIÓN DE N
SOLICITUD FASE NACIONAL –PCT

1	TIPO DE SOLICITUD	[X] Patente de invención [X] Capítulo I	[ ] Patente de Modelo de Utilidad [ ] Capitulo II

2 DATOS SOLICITUD INTERNACIONAL PCT (86)

Solicitud Internacional No.	PCT/EP2012/063755	Fecha	13/07/2012
Publicación Internacional No.	WO 2013/014003 A1	Fecha	31/01/2013

3 TÍTULO DE LA INVENCIÓN (200 caracteres o espacios máximos)

PROCEDIMIENTO DE ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE UNA CORRIENTE DE ETILENO

4 CLASIFICACIÓN INTERNACIONAL (CIP)

C07C 7/00 (2006.01) *C07C 7/04* (2006.01) *C07C 7/12* (2006.01) *C07C 11/04* (2006.01)

SOLICITANTE (S) Esta persona también es inventor. Para datos adicionales utilizar hoja de información complementaria

APELLIDOS O RAZÓN SOCIAL	NOMBRE	IDENTIFICACIÓN	TIPO
1. TOTAL RESEARCH & TECHNOLOGY FELUY 2. IFP ENERGIES NOUVELLES			

6 DATOS DEL SOLICITANTE

1. DIRECCIÓN: Zone Industrielle C, B-7181
No. TELÉFONO:
CIUDAD: Seneffe
CORREO ELECTRÓNICO:
DEPARTAMENTO/ESTADO:
NACIONALIDAD O LUGAR DE CONSTITUCIÓN: BELGICA

2. DIRECCIÓN: 1 & 4 avenue de Bois Préau, F-92852
No. TELÉFONO:
CIUDAD: Rueil Malmaison
CORREO ELECTRÓNICO:
DEPARTAMENTO/ESTADO:
NACIONALIDAD O LUGAR DE CONSTITUCIÓN: FRANCIA

7 INVENTOR (ES) Para datos adicionales utilizar hoja de información complementaria

APELLIDOS	NOMBRES	NACIONALIDAD
1. DAS	Babua	INDIA
2. ARRIATA	Manuela	VENEZUELA
3. BOUTROT	Catherine	FRANCIA

DIRECCIÓN DE CORREO ELECTRÓNICO:

8 DATOS INVENTOR (ES)

PAÍS RESIDENCIA	DEPARTAMENTO/ESTADO	CIUDAD	DIRECCIÓN
1. BELGICA		1. Evere	1. Avenue Henri Dunantlaan 40, B-1140
2. FRANCIA		2. Paris	2. 35 rue Saint Georges, F-75009
3. FRANCIA		3. Chatou	3. 9 avenue Paul Doumer, F-78400

OTRO(S) SOLICITANTE(S) Y/O (OTRO(S)) INVENTOR(ES)

[ ] Los demás solicitantes y/o (demás) inventores se indican en una hoja a continuación.

9	☐ REPRESENTANTE LEGAL ☒ APODERADO		
APELLIDOS	NOMBRES	IDENTIFICACIÓN	
CAMARGO WILLIAMSON	HELENA	C.C 35.455.268 de Bogota	T.P 76985

DIRECCIÓN	CARRERA 7 Nº 71 – 52, TORRE A, PISO 5	No. TELÉFONO	3257300
CIUDAD	BOGOTÁ	CORREO ELECTRÓNICO	helena.camargo@phrlegal.com
PAÍS	COLOMBIA	No. RADICACIÓN DE PROTOCOLO DE PODER GENERAL	

10 DECLARACIONES DE PRIORIDAD ☒ SI ☐ NO

(33) PAÍS DE ORIGEN	CÓDIGO PAÍS	(31) NÚMERO	(32) FECHA (AAAA/MM/DD)
1. COMUNIDAD EUROPEA		11290349.7	28/07/2011

11 DECLARACIÓN SOBRE USO DE RECURSOS GENÉTICOS O BIOLÓGICOS

Declaro que el objeto de la presente solicitud de patente fue obtenido a partir de recursos genéticos o biológicos de los que cualquiera de los países miembros de la Comunidad Andina es país de origen.

☐ SI ☒ NO

12 DECLARACIÓN SOBRE USO DE CONOCIMIENTOS TRADICIONALES

Declaro que el objeto de la presente solicitud de patente fue obtenido a partir de conocimientos tradicionales de comunidades indígenas, afroamericanas o locales de países miembros de la Comunidad Andina.

☐ SI ☒ NO

13 REDUCCIÓN DE TASAS

Declaro que carezco de medios económicos para presentar la solicitud de patente.

☐ SI ☒ NO

Micro, pequeñas y medianas empresas ☐
Universidades públicas o privadas ☐
Entidades sin ánimo de lucro ☐

Debe aportar los documentos que se indican en el numeral 17 de anexos

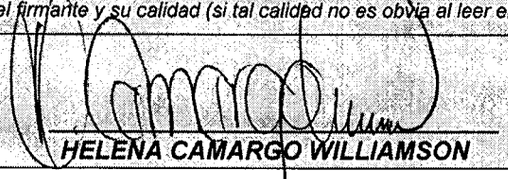
14 AUTORIZACIÓN DE NOTIFICACIÓN EN LÍNEA ☒ SI ☐ NO

Manifiesto que he leído y entendido perfectamente los términos y condiciones de uso de medios electrónicos para las notificaciones en línea a través de Internet de los actos administrativos proferidos por la Superintendencia de Industria y Comercio que deben ser notificados personalmente y, en consecuencia, autorizo el servicio de notificación a través de internet.

15	COMPROBANTE DE PAGO O PAGO ELECTRÓNICO	N°	Fecha

16 FIRMA DEL SOLICITANTE, DEL APODERADO O DEL REPRESENTANTE LEGAL

Junto a cada firma, indicar el nombre del firmante y su calidad (si tal calidad no es obvia al leer el petitorio)



HELENA CAMARGO WILLIAMSON

17 ANEXOS

Documentación Técnica
Solicitud Internacional en castellano

1. ☒ Descripción N° de folios:
2. ☒ Reivindicaciones N° Reivindicaciones:
3. ☒ Dibujos y/o figuras N° folios:
4. ☒ Resumen.
5. ☐ Certificado de depósito de material biológico si fuera el caso.
6. ☐ Listado de secuencias de nucleótidos y/o aminoácidos en forma digital si fuera el caso.
7. ☐ Arte final 12 x 12.
8. ☐ Anexo formato digital.

Documentación Jurídica

9. ☒ Poderes, si fuera el caso,
10. ☐ Documento que legalmente pruebe la cesión del inventor al solicitante o a su causante.
11. ☐ Copia del contrato de acceso de recursos genéticos o productos derivados, *certificado o número de registro, si fuera el caso.*
12. ☐ Copia de la licencia o autorización de Conocimientos Tradicionales, certificado o número de registro, si fuera el caso.
13. **Reducción de tasas**

Micro, pequeñas o medinas empresas
☐ Copia simple de la declaración de renta del año inmediatamente anterior, o en su defecto prueba documental idónea.
☐ Documento de constancia de cumplimiento con lo establecido en la ley 905 de 2004.

Universidades públicas o privadas
☐ Copia acto de reconocimiento institucional emitido por el Ministerio de Educación

Entidades sin ánimo de lucro
☐ Copia de registro vigente en Cámara de comercio.
☐ Hoja de información complementaria.
☐ Otros, especificar

14. ☒ Comprobante de pago de la tasa de presentación de la solicitud.
15. ☐ Comprobante de pago por reivindicación de prioridad.
16. ☒ Comprobante de pago de la tasa por concepto de excedente de palabras en la publicación.
17. ☒ Comprobante de pago por reivindicación adicional a 10.

PROCEDIMIENTO DE ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE UNA CORRIENTE DE ETILENO

Campo de la invención

La presente invención es un procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno.

Las olefinas son producidas tradicionalmente a partir de componentes del petróleo mediante procesos de craqueo catalítico o con vapor. Estos procesos de craqueo, especialmente el craqueo con vapor, producen olefina(s) ligera(s), tales como etileno y/o propileno, a partir de diversos componentes de hidrocarburos. El etileno y el propileno son importantes productos petroquímicos básicos útiles en una variedad de procesos de fabricación de plásticos y otros compuestos químicos. El suministro limitado y el coste creciente del crudo han promovido la búsqueda de procesos alternativos de producción de productos de hidrocarburos.

Las olefinas pueden ser producidas por deshidratación del alcohol correspondiente. El etanol se puede obtener mediante fermentación de carbohidratos. Compuesta por la materia orgánica procedente de organismos vivos, la biomasa es la fuente de energía renovable líder en el mundo. El efluente producido por la deshidratación de etanol comprende esencialmente etanol no transformado, agua, etileno, acetaldehído. El acetaldehído puede provocar problemas en operaciones de recuperación de etileno. Puede comprender también cantidades muy pequeñas de etano, CO, CO2, H2, CH4 e hidrocarburos C3+. La relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos C3+ a etileno es la mayoría de las veces menor de 20/80.

Antecedentes de la invención

El documento US 20030098281 A1 describe un procedimiento de control de concentraciones de agua y/o oxigenados de una corriente de olefina. El procedimiento incluye poner en contacto la corriente de olefina con un absorbente líquido. El absorbente líquido se selecciona del grupo constituido por un poliol, amina, amida, nitrilo, compuesto que contiene nitrógeno heterocíclico y mezclas de los mismos. Se condensa una corriente

gaseosa que comprende esencialmente vapor, etileno, propileno y menos de 2 % en peso de oxigenados en una torre de desactivación. Las cabezas de dicha torre de desactivación se lava con una solución cáustica para eliminar CO2 y a continuación se pone en contacto con el absorbente líquido para eliminar los oxigenados.

El documento WO 03 020670 A1 proporciona un procedimiento para eliminar componentes oxigenados tales como acetaldehído, CO2 y/o agua de una corriente de olefina. Esto explica que es deseable eliminar tales componentes oxigenados, ya que estos pueden envenenar catalizadores que se usan para procesar posteriormente la composición de olefina. Adicionalmente la presencia de ciertos compuestos oxigenados, tales como acetaldehído, puede provocar el fallo en otras unidades de purificación de olefinas, por ejemplo, unidades de tratamiento de gas ácido. El procedimiento comprende proporcionar una corriente de olefina que contiene etileno, propileno, olefinas C4+ y acetaldehído. La corriente de olefina se separa en una primera fracción y una segunda fracción, en la que la primera fracción comprende al menos una mayor parte del etileno y/o propileno presentes en la corriente de olefina, y la segunda fracción comprende al menos una mayor parte de las olefinas C4+ y acetaldehído presente en la corriente de olefina. La primera fracción se trata a continuación con gas ácido mediante hidróxido de sodio o hidróxido de potasio. La corriente de olefina se separa por destilación, preferiblemente, la destilación es destilación extractiva usando un extractante. El extractante preferido es una composición polar que presenta un punto de ebullición medio de al menos 38 °C a 1 atm. El metanol es un tipo de extractante preferido.

El documento WO 03 020672 A1 describe el procedimiento de eliminación de dimetiléter de una corriente que contiene etileno y/o propileno. La corriente de olefina se pasa a una columna de absorción de agua, se usa metanol como el absorbente de agua. El metanol y el agua introducida, así como también algunos hidrocarburos oxigenados, se recuperan como la corriente de colas de dicha columna de absorción de agua, se recupera una olefina por cabezas y se envía a una columna de destilación. La columna de destilación separa etileno y propileno, así como también componentes de menor punto de ebullición del dimetiléter y de componentes de mayor punto de ebullición, incluyendo

componentes C4+ y metanol que queda del lavado de metanol. Se añade más metanol a la columna de destilación para reducir la formación de clatrato y/o agua libre en la columna de destilación. La corriente que contiene etileno y propileno sale de la columna de destilación como cabezas y los componentes de mayor punto de ebullición que incluyen el dimetiléter y componentes C4+ salen de la columna de destilación como las colas. Etileno y propileno fluyen a una columna de lavado cáustica.

El documento WO 03 033438 A1 describe un procedimiento para el procesamiento de una corriente de olefina que contiene oxigenados y agua, que comprende: proporcionar una corriente de olefina que contiene oxigenados y agua; deshidratar la corriente de olefina; comprimir la corriente de olefina deshidratada; lavar la corriente de olefina con metanol para eliminar al menos una parte del oxigenado de la corriente de olefina; poner en contacto la corriente de olefina lavada con metanol con agua; y fraccionamiento de la corriente de olefina en contacto con agua. La corriente de olefina recuperada (lavada con metanol y a continuación con agua) se envía a continuación a un lavado con álcali y a una etapa de secado. La corriente de olefina que contiene oxigenados y agua es el efluente de un procedimiento MTO.

El documento US 6.444.869 describe un procedimiento de producción de etileno partiendo de una corriente efluente para conversión de oxigenado. La corriente de efluente de conversión de oxigenado comprende hidrógeno, metano, etileno, etano, propileno, propano y olefinas C4+. Este efluente se comprime, se trata para eliminar oxigenados, se pasa a una zona de eliminación de dióxido de carbono en la que se absorbe el dióxido de carbono poniendo en contacto una solución cáustica o poniendo en contacto una solución de amina en combinación con una solución cáustica de una forma convencional para eliminar el dióxido de carbono, se seca, a continuación se hace el fraccionamiento mediante un desetanizador y un desmetanizador.

El documento US 2005-0283038 A1 describe un procedimiento de producción de una corriente de olefinas partiendo de una primera corriente de efluente de vapor de una reacción de conversión de oxigenado a olefina, comprendiendo dicha primera corriente de efluente de vapor olefinas C2 y C3, hidrocarburos C4 y compuestos carbonilo C2 a C6. En

el procedimiento, la temperatura y presión de la corriente de efluente de vapor se ajustan para producir una segunda corriente de efluente de vapor que presenta una presión que varía de aproximadamente 100 psig a aproximadamente 350 psig (de 790 a 2514 kPa) y una temperatura que varía de aproximadamente 70º F a aproximadamente 120º F (de 21 a 49° C), conteniendo dicha segunda corriente de efluente de vapor de aproximadamente 50 % en peso o más de hidrocarburos C4 basado en el peso total de hidrocarburos C4 en la primera corriente de efluente de vapor. La segunda corriente de efluente de vapor se lava a continuación con una corriente que contiene alcohol líquido para producir una tercera corriente de efluente de vapor, después de lo cual la tercera corriente de efluente de vapor se lava con agua líquida para proporcionar una cuarta corriente de efluente de vapor que comprende las olefinas C2 y C3 y aproximadamente de 1,0 % en peso o menos de compuestos de carbonilo C2 a C6. En una realización de un procedimiento de recuperación de este tipo, al menos parte de la cuarta corriente de efluente de vapor se pone en contacto con un componente básico, tal como componente cáustico o una amina, para eliminar la masa del dióxido de carbono del mismo (eliminando de este modo "gas ácido" de la cuarta corriente de efluente de vapor), después de esto se seca la corriente sin CO2.

La desventaja principal de las técnicas anteriores es el fallo del limpiador cáustico. El gas de entrada al limpiador cáustico contiene oxigenados reactivos como aldehídos y cetonas. Estos aldehídos reaccionan en la reacción de condensación de alcohol en el ambiente de la torre cáustica formando polímeros de aceite rojo en cantidad significativa. Esto provoca el fallo significativo relativo a la torre cáustica lo que incide en el tiempo de paso por la unidad. El tratamiento cáustico consumido con contenido significativo en polímeros de aceite rojo es también un problema importante así como también el tratamiento cáustico consumido y la eliminación de desechos. Además hay problemas de manipulación y eliminación de polímeros de aceite rojo.

Se ha descubierto ahora un procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno en la que no hay lavado cáustico para eliminar el CO2 y tampoco columna de lavado para eliminar los oxigenados. Los oxigenados son

compuestos orgánicos constituidos por carbono, oxígeno e hidrógeno.

Breve sumario de la invención

La presente invención es un procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

a) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno, hasta 1 % en peso de oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+,

b) enviar dicha corriente (A) a un separador C2 / desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+, una corriente de cabezas que comprende el resto de componentes,

c) enviar dicha corriente de cabezas a una zona de adsorción de CO2 de lecho fijo para recuperar una corriente esencialmente exenta de CO2,

d) enviar dicha corriente esencialmente exenta de CO2 a un desmetanizador / equipo depurador de CO para recuperar una corriente de cabezas que comprende H2, CH4 y CO, etileno líquido en las colas.

En otra realización la etapa de eliminación de CO2 se puede realizar en el etileno recuperado. En dicha realización la presente invención es un procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

a1) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno, hasta 1 % en peso de oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+,

b1) enviar dicha corriente (A) a un separador C2 / desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+,

una corriente de cabezas que comprende el resto de componentes,

c1) enviar dicha corriente de cabezas a un desmetanizador / equipo depurador de CO para recuperar una corriente de cabezas que comprende H2, CH4 y CO,

etileno líquido que comprende CO2 en las colas,

d1) enviar dicho etileno que comprende CO2 a una zona de adsorción de CO2 de lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO2.

En una realización la relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos

C3+ a etileno en (A) es menor de 10/90.

En una realización la relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos C3+ a etileno en (A) es menor de 10/90 y superior a 0,1/99,9.

En una realización la relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos C3+ a etileno en (A) es menor de 5/95.

En una realización la proporción de oxigenados en (A) va de 50 ppm en peso a 7000 ppm en peso.

En una realización la proporción de oxigenados en (A) es de hasta 3000 ppm en peso.

En una realización la proporción de oxigenados en (A) es de hasta 2000 ppm en peso.

En una realización la proporción de H2 en (A) es de 5 a 1000 ppm en peso.

En una realización la proporción de H2 en (A) es de hasta 800 ppm en peso.

En una realización la proporción de H2 en (A) es de hasta 500 ppm en peso.

De forma ventajosa "corriente de etileno seca" en la etapa a) significa un contenido en agua menor de 5 ppm en peso, de forma ventajosa menos de 3 ppm en peso y preferiblemente menos de 1 ppm en peso.

En una realización cuando la corriente de etileno (A) seca se ha preparado mediante deshidratación de etanol dicha corriente (A) no contiene sustancialmente acetileno.

El etileno tratado de acuerdo con esta invención es particularmente adecuado para uso como alimentación para la producción de alfa-olefinas, etilbenceno/estireno, óxido de etileno/etilenglicol, dicloruro de etileno y polímeros correspondientes, como homo- o copolímeros de polietileno (PE, EPR, EPDM etc.), poliestireno (PS), copolímeros de estireno con butadieno, isopreno, acrilonitrilo o combinaciones (SBS, SIS, SBR, ABS, SAN), poliésteres (PET) y policloruros de vinilo (PVC).

Descripción detallada de la invención

En lo que respecta a los contaminantes oxigenados también denominados como oxigenados, se puede citar etanol, alcoholes C3; éteres tales como dietiléter y

metiletiléter; ácidos carboxílicos tales como ácido acético; aldehídos tales como acetaldehído; cetonas tales como acetona; y ésteres tales como metilésteres. Contaminantes oxigenados particularmente problemáticos en una deshidratación de alcohol son aldehídos.

En lo que respecta a la corriente de etileno (A) de la etapa a), esta puede originarse de la deshidratación de etanol. Dicha deshidratación puede hacerse en uno o más reactores de deshidratación de etanol. En lo que respecta a la deshidratación del alcohol, se describe este procedimiento en los documentos WO-2009-098262, WO-2009-098267, WO-2009-098268 y WO-2009-098269 cuyo contenido se incorpora a la presente solicitud. La presente invención es muy eficiente para la purificación de etileno producido por deshidratación de etanol.

La salida de dicho reactor de deshidratación comprende esencialmente etileno y vapor así como también cantidades menores de oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+. "Cantidades menores" significa que la relación en peso de etano +CO+CO2+H2+CH4+hidrocarburos C3+ a etileno es menor de 20/80 y la mayoría de las veces menor de 10/90.

Dicha salida del reactor de deshidratación se enfría inicialmente, de forma típica en una torre de desactivación que usa agua como el medio de desactivación. En la torre de desactivación la mayor parte del agua contenida en la salida del reactor de deshidratación se condensa y se elimina de las colas de la torre como una corriente de colas de agua líquida. Una parte de dicha corriente de colas de agua se enfría en un intercambiador de calor y se recicla como medio de desactivación a la parte superior de la columna de desactivación. La parte de la corriente de colas de agua que no se recicla como medio de desactivación puede contener una parte de los oxigenados y en su caso la mayor parte del etanol no transformado. Dicha corriente puede ser tratada en una columna de depuración para recuperar una corriente de agua pura. Se eliminan etileno, oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+ de la parte superior de la torre de desactivación a una presión típica tal como 100 a 1600 kPa (1 a 16 barg) absolutos y se designan como la corriente de etileno contaminada. De forma ventajosa dicha corriente de

etileno contaminada se comprime sucesivamente y se enfría en una o más etapas para eliminar la mayor parte del agua, se alimenta adicionalmente a una zona de secado de lecho fijo y finalmente al separador C2/desetanizador de la etapa b).

En las etapas de compresión previas el agua recuperada contiene una parte de los contaminantes oxigenados e hidrocarburos disueltos. La corriente de hidrocarburos contaminada se puede enfriar también antes de la primera etapa de compresión y recuperar agua. En una realización el agua recuperada tras cada enfriamiento va a una etapa de compresión y tras enfriamiento, si procede, antes de la primera etapa de compresión, se envía a una columna de depuración para producir una corriente de cabezas que comprende esencialmente contaminantes oxigenados e hidrocarburos y una corriente de colas esencialmente de agua pura. De forma opcional la corriente de cabezas se quema para destruir los contaminantes oxigenados y recuperar calor.

Tras las etapas de compresión la corriente de etileno contaminada se alimenta adicionalmente a una zona de secado de lecho fijo y finalmente al separador C2/desetanizador de la etapa b). La zona de secado de lecho fijo es en sí conocida.

En lo que respecta al separador C2/desetanizador de la etapa b), este es de forma ventajosa una columna de destilación. La corriente de cabezas es una mezcla de etileno, CO, CO2, H2 y CH4.

En lo que respecta a la zona de adsorción de CO2 de lecho fijo de la etapa c) esta puede ser cualquier componente capaz de eliminar CO2 de forma selectiva. A modo de ejemplo se trata de una adsorción en lecho fijo comercialmente disponible (PSA para adsorción regulable por presión o TSA para adsorción regulable por temperatura) que usa tamices moleculares u óxidos básicos, óxidos básicos soportados, carbones de gran área superficial, componentes marco organometálicos (MOF) o mezclas de los mismos. Los tamices moleculares son preferiblemente zeolitas de bajo contenido en sílice, que presentan 8 (entre las que está zeolita A) o 12 (entre las que está zeolita X) miembros de anillo e intercambiadas con cationes alcalinos, alcalinotérreos o lantánidos. Otros tamices moleculares son silicatos de titanio cristalinos (materiales de la familia de ETS). Óxidos básicos soportados son preferiblemente óxidos alcalinos, alcalinotérreos o lantánidos

soportados sobre carbonos, aluminio, sílice, circonio o titanio de gran área superficial. La eliminación de CO2 puede llevarse a cabo con una corriente de líquido o con una corriente de etileno gaseoso en función de la presión y temperatura. Se recupera una corriente esencialmente exenta de CO2. Debido a que solo tienen que ser eliminadas cantidades traza de CO2 del etileno, el ciclo de proceso preferido es del tipo de adsorción por regulación térmica (TSA). Dicho adsorbente de lecho fijo, una vez saturado con CO2, puede ser regenerado, durante la regeneración la desorción produce una corriente que pueden ser tratada en cualquier lugar. En un ciclo de proceso de TSA la regeneración se realiza mientras se arrastra el adsorbente saturado con un gas inerte aumentado la temperatura hasta que tiene lugar la desorción del CO2. Eventualmente el adsorbente saturado puede ser reemplazado por nuevo adsorbente y el adsorbente saturado bien puede ser acondicionado o regenerado ex situ para uso posterior. "Esencialmente" tiene que considerarse a la luz del uso posterior de etileno. Si el etileno se tiene que polimerizar el CO2 tiene que ser 1 ppm en volumen o menos y preferiblemente 0,5 ppm en volumen o menos.

En lo que respecta al desmetanizador, su fin es recuperar una corriente de cabezas que comprende esencialmente H2, CH4 y CO y etileno líquido en las colas. De forma ventajosa se trata de una columna de destilación.

En lo que respecta a las condiciones de operación, el desmetanizador de la etapa d) tiene que estar a una presión suficientemente alta para operar a temperaturas que no sean demasiado bajas. Un desmetanizador para recuperar una corriente de cabezas que comprende H2, CH4 y CO y esencialmente etileno líquido en colas que opera a 4000 kPa (40 barg) presenta una temperatura de cabezas en torno a 0 a -10 ºC y una temperatura de colas en torno a 0 ºC. El mismo desmetanizador que opera a 2100 kPa (21 barg) presenta una temperatura de cabezas de -30 ºC una temperatura de colas en torno a -24 ºC.

Estas temperaturas y presiones son una función de la proporción de H2, CH4 y CO en la corriente de etileno (A) y principalmente de la proporción de H2. La proporción de H2, CH4 y CO en la corriente de etileno (A) y principalmente la proporción de H2 controla

también la presión y temperatura del separador C2 / desetanizador localizado aguas arriba de dicho desmetanizador.

En una realización la presión de la etapa b) se selecciona para tener una temperatura de las colas del separador C2/desetanizador tal que no haya oligomerización o polimerización de los oxigenados. A modo de ejemplo dicha temperatura no debería superar 150 °C y de forma ventajosa no superar 100 °C. Esta temperatura es función de la presión y de la proporción de oxigenados en la mezcla de oxigenados+etano+hidrocarburos C3+. Cuanto mayor sea la proporción de oxigenados mayor será la temperatura. Cuanto mayor sea la presión mayor será la temperatura.

En una realización el separador C2 / desetanizador y el desmetanizador se operan a la misma presión excepto la caída de presión entre el separador C2 / desetanizador y el desmetanizador para la trasferencia de fluidos. De forma ventajosa la presión varía de 1500 a 4500 kPa (de 15 a 45 barg). En esta realización la corriente de etileno contaminada que viene de la columna de desactivación se comprime de forma ventajosa en dos a cuatro fases de compresión en serie (en función de la presión del reactor de deshidratación), se envía a los secadores y finalmente al desetanizador separador C2.

Dicha realización se describe en la figura 1 en la que (1) es el desetanizador separador C2, (2) y (3) los adsorbedores de CO2 y (4) el desmetanizador / equipo depurador de CO. La corriente de etileno contaminada de la columna de desactivación se ha secado y enviado al desetanizador separador C2 (1) para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+ y una corriente de cabezas que comprende etileno, CO, CO2, H2 y CH4 (no se muestran condensador, decantador y reflujo del desetanizador separador C2, el calderín del desetanizador separador C2 no se muestra). Dicha corriente de cabezas se envía a los adsorbedores de CO2 (2) y (3) para recuperar una corriente esencialmente exenta de CO2 y a continuación al desmetanizador / equipo depurador de CO (4) para recuperar una corriente de cabezas que comprende H2, CH4 y CO y etileno líquido en colas. El condensador, decantador y reflujo del desmetanizador / equipo depurador de CO no se muestran, el calderín del desmetanizador / equipo depurador de CO no se muestra.

En un ejemplo específico de acuerdo con la figura 1 la presión del separador C2 / desetanizador está en torno a 1500 a 2500 kPa (de 15 a 25 barg), la parte superior de dicho separador / desetanizador está a una temperatura en torno a -20 ºC a -30 ºC, condensa a una temperatura en el intervalo de -20 ºC a -30 ºC, la temperatura en colas de dicho separador / desetanizador está en torno a 70 a 90 ºC, la presión del desmetanizador / equipo depurador de CO en torno a 1500 a 2500 kPa (de 15 a 25 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -15 ºC a -35 ºC, se condensa a una temperatura en torno a -15 a -35 ºC y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -15 ºC a -35 ºC.

De forma ventajosa la presión del separador C2 / desetanizador está en torno a 1800 a 2500 kPa (de 18 a 25 barg), la parte superior de dicho separador / desetanizador está a una temperatura en torno a -18 ºC a -28 ºC, condensa a una temperatura en el intervalo de -18 ºC a -28 ºC, la temperatura en colas de dicho separador / desetanizador está en torno a 75 a 85 ºC, la presión del desmetanizador / equipo depurador de CO está en torno a 1800 a 2500 kPa (18 a 25 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -20 ºC a -30 ºC, se condensa a una temperatura en torno a -20 a -30 ºC y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -20 ºC a -30 ºC.

En una realización al presión del separador C2 / desetanizador es menor que la presión del desmenatizador / equipo depurador de CO. De forma ventajosa la presión del separador C2 / desetanizador varía de 1500 a 2500 (de 15 a 25 barg) y de forma simultánea la diferencia de presión entre el desmetazinador / equipo depurador de CO y el separador C2 / desetanizador varía de 1000 a 2500 kPa (de 10 a 25 barg). En esta realización la corriente de etileno contaminada que viene de la columna de desactivación se comprime de forma ventajosa en dos a tres etapas de compresión en serie, se envía a los secadores y finalmente al desetanizador separador C2. A continuación, la corriente de cabezas del desetanizador separador C2 se comprime y se envía a través de los adsorbedores de CO2 al desmetanizador / equipo depurador de CO. De forma opcional la corriente esencialmente libre de CO2 que abandona la zona de adsorción de CO2 de

lecho fijo se enfría, se envía a un decantador para producir una fase líquida enviada como un reflujo al separador C2 / desetanizador y se envía una fase gaseosa al desmetanizador / equipo depurador de CO.

Dicha realización se describe en la figura 2. La corriente de etileno contaminada de la columna de desactivación ha sido secada y enviada a una presión en torno a 1500 a 2500 kPa (de 15 a 25 barg) al desetanizador separador C2 (1) para producir una corriente de colas (el calderín no se muestra) que comprende esencialmente etano, oxigenados e hidrocarburos C3+ y una corriente de cabezas que comprende etileno, CO, CO2, H2 y CH4. Dicha corriente de cabezas (parte superior del desetanizador separador C2) se envía al compresor (6) para aumentar la presión con 1000 a 2500 kPa (de 10 a 25 barg) sobre la presión del separador C2 / desetanizador, opcionalmente enfriada (el enfriador no se muestra) y se envía a los absorbedores de CO2 (2) y (3) para recuperar una corriente esencialmente exenta de CO2. A continuación, dicha corriente exenta de CO2 se enfría (el enfriador no se muestra) y se envía al decantador (5) para producir una fase líquida enviada como un reflujo al desetanizador separador C2 (1) y una fase gaseosa enviada al desmetanizador / equipo depurador de CO (4). Dicho desmetanizador / equipo depurador (4) produce una corriente de cabezas (el condensador, decantador y reflujo no se muestran) que comprende H2, CH4 y CO y etileno líquido en colas (el calderín no se muestra).

De forma alternativa, el condensador y decantador (5) pueden ser instalados entre la salida superior del separador C2 / desetanizador (1) y el compresor (6). La fase líquida producida se envía como un reflujo al separador C2 / desetanizador (1) mientras que la fase gaseosa se envía al compresor (6). En otras palabras la corriente de etileno contaminada de la columna de desactivación ha sido secada y enviada al desetanizador separador C2 (1) para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+ y una corriente de cabezas que comprende etielno, CO, CO2, H2 y CH4. Dicha corriente de cabezas, la salida superior del separador C2 / desetanizador (1), se condensa, se envía a un decantador para lograr una fase fase líquida enviada como un reflujo al separador C2 / desetanizador (1) y una fase gaseosa se

envía al compresor (6). A continuación, la corriente comprimida se envía a los adsorbedores de CO2 (2) y (3) para recuperar una corriente esencialmente exenta de CO2 y a continuación al desmetanizador / equipo depurador de CO (4) para recuperar una corriente de cabezas que comprende H2, CH4 y CO y etileno líquido en las colas.

En un ejemplo específico de acuerdo con la figura 2 la presión del separador / desetanizador está en torno a 1500 a 2500 kPa (de 15 a 25 barg), la temperatura en la parte superior de dicho separador / desetanizador está en torno a -25 ºC a -35 ºC, la temperatura en colas de dicho separador / desetanizador en torno a 70 a 90 ºC, la presión del desmetanizador / equipo depurador de CO en torno a 3500 a 4500 kPa (de 35 a 45 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -10 ºC a 10 ºC, se condensa a una temperatura en torno a -35 a -45 ºC y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -10 ºC a -10 ºC.

De forma ventajosa la presión del separador / desetanizador está en torno a 1800 a 2000 kPa (18 a 20 barg), la temperatura en la parte superior de dicho separador / desetanizador está en torno a -28 ºC a -32 ºC, la temperatura de colas de dicho separador / desetanizador en torno a 78 a 82 ºC, la presión del desmetanizador / equipo depurador de CO en torno a 3800 a 4200 kPa (de 38 a 42 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -5 ºC a 5 ºC, se condensa a una temperatura en torno a -38 a -42 ºC y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -2 a 2 ºC.

En lo que respecta a la otra realización en la que la etapa de eliminación de CO2 se realiza sobre el etileno recuperado, opera de una forma similar a lo explicado anteriormente en donde la etapa de eliminación de CO2 está antes del desmetanizador / equipo depurador de CO.

En una realización el separador C2 / desetanizador y el desmetanizador se operan a la misma presión excepto la caída de presión entre el separador C2 / desetanizador y el desmetanizador para la trasferencia de fluidos. De forma ventajosa la presión varía de 1500 a 4500 kPa (de 15 a 45 barg). En esta realización la corriente de etileno contaminada que viene de la columna de desactivación se comprime de forma ventajosa

en dos a cuatro fases de compresión en serie (en función de la presión del reactor de deshidratación), se envía a los secadores y finalmente al desetanizador separador C2.

Dicha realización se describe en la figura 3 en la que (1) es el desetanizador separador C2, (2) y (3) los adsorbedores de CO2 y (4) el desmetanizador / equipo depurador de CO. La corriente de etileno contaminada de la columna de desactivación ha sido secada y enviada al desetanizador separador C2 (1) para producir una corriente de colas (el calderín no se muestra) que comprende esencialmente etano, oxigenados e hidrocarburos C3+ y una corriente de cabezas (el condensador, el decantador y el reflujo no se muestran) que comprende etileno, CO, CO2, H2 y CH4. Dicha corriente de cabezas se envía al desmetanizador / equipo depurador de CO (4) para recuperar una corriente de cabezas (el condensador, el decantador y el reflujo no se muestran) que comprende H2, CH4 y CO y etileno líquido que comprende CO2 en colas (el calderín no se muestra). Dicho etileno que comprende CO2 se envía a una zona de adsorción de CO2 de lecho fijo, los adsorbedores de CO2 (2) y (3), para recuperar una corriente de etileno esencialmente exenta de CO2.

En un ejemplo específico de acuerdo con la figura 3 la presión del separador C2 / desetanizador está en torno a 1500 a 2500 kPa (de 15 a 25 barg), la parte superior de dicho separador / desetanizador está a una temperatura en torno a -20 °C a -30 °C, condensa a una temperatura en el intervalo de -20 °C a -30 °C, la temperatura en colas de dicho separador / desetanizador está en torno a 70 a 90 °C, la presión del desmetanizador / equipo depurador de CO en torno a 1500 a 2500 kPa (de 15 a 25 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -15 °C a -35 °C, se condensa a una temperatura en torno a -15 a -35 °C y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -15 °C a -35 °C.

De forma ventajosa la presión del separador C2 / desetanizador está en torno a 1800 a 2500 kPa (de 18 a 25 barg), la parte superior de dicho separador / desetanizador está a una temperatura en torno a -18 °C a -28 °C, condensa a una temperatura en el intervalo de -18 °C a -28 °C, la temperatura en colas de dicho separador / desetanizador está en torno a 75 a 85 °C, la presión del desmetanizador / equipo depurador de CO está

en torno a 1800 a 2500 kPa (18 a 25 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -20 °C a -30 °C, se condensa a una temperatura en torno a -20 a -30 °C y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -20 °C a -30 °C.

En una realización la presión del separador C2 / desetanizador es menor que la presión del desmenatizador / equipo depurador de CO. De forma ventajosa la presión del separador C2 / desetanizador varía de 1500 a 2500 (de 15 a 25 barg) y de forma simultánea la diferencia de presión entre el desmetazinador / equipo depurador de CO y el separador C2 / desetanizador varía de 1000 a 2500 kPa (de 10 a 25 barg). En esta realización la corriente de etileno contaminada que viene de la columna de desactivación se comprime de forma ventajosa en dos a tres etapas de compresión en serie, se envía a los secadores y finalmente al desetanizador separador C2. A continuación, la corriente de cabezas del desetanizador separador C2 se comprime y se envía al desmetanizador / equipo depurador de CO.

Dicha realización se describe en la figura 4. Adicionalmente a la figura 3 hay equipo adicional: un compresor (6). La corriente de etileno contaminada de la columna de desactivación ha sido secada y enviada a una presión en torno de 1500 a 2500 kPa (15 a 25 barg) al desetanizador separador C2 (1) para producir una corriente de colas (el calderín no se muestra) que comprende esencialmente etano, oxigenados e hidrocarburos C3+ y una corriente de cabezas que comprende etileno, CO, CO2, H2 y CH4. Dicha corriente de cabezas se condensa, se envía a un decantador para conseguir una fase líquida se envía como un reflujo a (1) y se envía una fase gaseosa al compresor (6). Dicho condensador, decantador y reflujo no se muestran). El compresor (6) aumenta la presión con 1000 a 2500 kPa (de 10 a 25 barg) por encima de la presión de separador C2 /desetanizador, y la corriente comprimida se envía al desmetanizador / separador de CO (4). Dicho desmetanizador / equipo depurador de CO (4) produce una corriente de cabezas (el condensador, el decantador y el reflujo no se muestran) que comprende H2, CH4 y CO y en las colas etileno líquido que comprende CO2 (el calderín no se muestra). Dicho etileno que comprende CO2 se envía a una zona de adsorción de CO2 de lecho

fijo, los adsorbedores de CO2 (2) y (3), para recuperar una corriente de etileno esencialmente exenta de CO2.

En un ejemplo específico de acuerdo con la figura 4 la presión del separador / desetanizador está en torno a 1500 a 2500 kPa (de 15 a 25 barg), la parte superior de dicho separador / desetanizador está a una temperatura en torno a -25 °C a -35 °C, condensa a una temperatura en el intervalo de -25 °C a -35 °C, la temperatura en colas de dicho separador / desetanizador está en torno a 70 a 90 °C, la presión del desmetanizador / equipo depurador de CO en torno a 3500 a 4500 kPa (de 35 a 45 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -10 °C a 10 °C, se condensa a una temperatura en torno a -35 a -45 °C y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -10 °C a 10 °C.

De forma ventajosa la presión del separador / desetanizador está en torno a 1800 a 2000 kPa (18 a 20 barg), la parte superior de dicho separador / desetanizador está a una temperatura en torno a -28 °C a -32 °C, la temperatura de colas de dicho separador / desetanizador en torno a 78 a 82 °C, la presión del desmetanizador / equipo depurador de CO en torno a 3800 a 4200 kPa (de 38 a 42 barg), la parte superior del desmetanizador / equipo depurador de CO está en torno a -5 °C a 5 °C, se condensa a una temperatura en torno a -38 a -42 °C y la temperatura en colas del desmetanizador / equipo depurador de CO está en torno a -2 a 2 °C.

Ejemplo

Se opera el procedimiento de acuerdo con la figura 5. La figura 5 se deriva de la figura 2 por cambio de la posición del condensador y decantador (5), estos se localizan entre la salida del separador C2 / desetanizador y el compresor. Los resultados se encuentran en la siguiente tabla.

N.º de corriente en la figura 5		1	2	3
		Alimentación del separador	Colas del separador C2	Destilado de vapor del

		C2		separador C2
Temperatura	ºC	15	80	-30
Presión	bar g	20	19	19
H2	kg/h	8		8
CO	kg/h	1		1
CO2	kg/h	1		1
Etano	kg/h	23	11	12
Etileno	kg/h	25108	30	25078
Aceltaldehídos	kg/h	150	150	
C3+	kg/h	715	715	
Total	kg/h	26006	906	25100

N.º de corriente en la figura 5		4	6	5
		Alimentación del desetanizador	Purga del desetanizador	Producto de etileno
Temperatura	ºC	-2	-40	20
Presión	bar g	40	40	20
H2	kg/h	8	8	
CO	kg/h	1	1	
CO2	kg/h			
Etano	kg/h	12		12
Etileno	kg/h	25078	90	24988
Aceltaldehídos	kg/h			
C3+	kg/h			
Total	kg/h	25099	99	25000

REIVINDICACIONES

1. Procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

a) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno, hasta 1 % en peso de oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+,

b) enviar dicha corriente (A) a un separador C2 / desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+, una corriente de cabezas que comprende el resto de componentes,

c) enviar dicha corriente de cabezas a una zona de adsorción de CO2 de lecho fijo para recuperar una corriente esencialmente exenta de CO2,

d) enviar dicha corriente esencialmente exenta de CO2 a un desmetanizador / equipo depurador de CO para recuperar una corriente de cabezas que comprende H2, CH4 y CO, etileno líquido en las colas.

2. Procedimiento de acuerdo con la reivindicación 1, en el que el separador C2 / desetanizador y el desmetanizador se operan a la misma presión, excepto la caída de presión entre el separador C2 / desetanizador y el desmetanizador para la transferencia de fluidos, y dicha presión varía de 1500 kPa a 4500 kPa.

3. Procedimiento de acuerdo con la reivindicación 1, en el que la presión del separador C2 / desetanizador es menor que la presión del desmetanizador / equipo depurador de CO, variando la presión del separador C2 / desetanizador de 1500 a 2500 kPa y simultáneamente la diferencia de presión entre el desmetanizador / equipo depurador de CO y el separador C2 / desetanizador varía de 1000 kPa ó 2500 kPa.

4. Procedimiento de acuerdo con la reivindicación 3, en el que la corriente de cabezas, la salida superior, del separador C2 / desetanizador, se condensa, se envía a un decantador para lograr enviar una fase líquida como reflujo a dicho separador C2 / desetanizador y se

envía una fase gaseosa a un compresor, a continuación la corriente comprimida se envía a la zona de adsorción de CO2.

5. Procedimiento de acuerdo con la reivindicación 3, en el que la corriente de cabezas, la salida superior, del separador C2 / desetanizador, se envía a un compresor, enfriado opcionalmente y se envía a la zona de adsorción de CO2 para recuperar una corriente esencialmente exenta de CO2, a continuación dicha corriente exenta de CO2 se enfría y se envía a un decantador para producir una fase líquida enviada como un reflujo al separador C2 / desetanizador y se envía una fase gaseosa al desmetanizador / equipo depurador de CO.

6. Procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

a1) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno, hasta 1 % en peso de oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+,

b) enviar dicha corriente (A) a un separador C2 / desetanizador para producir

una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+,

una corriente de cabezas que comprende el resto de componentes,

c1) enviar dicha corriente de cabezas a un desmetanizador / equipo depurador de CO para recuperar una corriente de cabezas que comprende H2, CH4 y CO,

etileno líquido que comprende CO2 en las colas,

d1) enviar dicho etileno que comprende CO2 a una zona de adsorción de CO2 de lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO2.

7. Procedimiento de acuerdo con la reivindicación 6, en el que el separador C2 / desetanizador y el desmetanizador se operan a la misma presión, excepto la caída de presión entre el separador C2 / desetanizador y el desmetanizador para la transferencia de fluidos, y dicha presión varía de 1500 kPa a 4500 kPa.

8. Procedimiento de acuerdo con la reivindicación 6, en el que la presión del separador C2 / desetanizador es menor que la presión del desmetanizador / equipo depurador de CO, variando la presión del separador C2 / desetanizador de 1500 a 2500 kPa y simultáneamente la diferencia de presión entre el desmetanizador / equipo depurador de CO y el separador C2 / desetanizador varía de 1000 kPa ó 2500 kPa.

9. Procedimiento de acuerdo con una cualquiera de las reivindicaciones 6 a 8, en el que la corriente de cabezas, la salida superior, del separador C2 / desetanizador, se condensa, se envía a un decantador para lograr enviar una fase líquida como reflujo a dicho separador C2 / desetanizador y se envía una fase gaseosa a un compresor, a continuación la corriente del compresor se envía al desmetanizador / equipo de depuración de CO.

10. Procedimiento de acuerdo con una cualquiera de las reivindicaciones precedentes, en el que la relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos C3+ a etileno en (A) es menor de 10/90.

11. Procedimiento de acuerdo con la reivindicación 10, en el que la relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos C3+ a etileno en (A) es menor de 10/90 y se superior a 0,1/99,9.

12. Procedimiento de acuerdo con una cualquiera de las reivindicaciones 1 a 9 o reivindicación 11, en el que la relación en peso de etano+CO+CO2+H2+CH4+hidrocarburos C3+ a etileno en (A) es menor de 5/95.

13. Procedimiento de acuerdo con una cualquiera de las reivindicaciones precedentes, en el que la proporción de oxigenados en (A) es de 50 ppm en peso a 7000 ppm en peso.

14. Procedimiento de acuerdo con una cualquiera de las reivindicaciones precedentes, en el que la proporción de oxigenados en (A) es de hasta 3000 ppm en peso.

15. Procedimiento de acuerdo con la reivindicación 14, en el que la proporción de oxigenados en (A) es de hasta 2000 ppm en peso.

16. Procedimiento de acuerdo con una cualquiera de las reivindicaciones precedentes, en el que la proporción de H2 en (A) es de 5 a 1000 ppm en peso.

17. Procedimiento de acuerdo con una cualquiera de las reivindicaciones precedentes, en el que la proporción de H2 en (A) es de hasta 800 ppm en peso.

18. Procedimiento de acuerdo con la reivindicación 17, en el que la proporción de H2 en (A) es de hasta 500 ppm en peso.

19. Procedimiento de acuerdo con una cualquiera de las reivindicaciones precedentes, en el que la corriente de etileno (A) seca se origina de la deshidratación de etanol.

PROCEDIMIENTO DE ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE UNA CORRIENTE DE ETILENO

Resumen

La presente invención es un procedimiento de eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

a) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno, hasta 1 % en peso de oxigenados, etano, CO, CO2, H2, CH4 e hidrocarburos C3+,

b) enviar dicha corriente (A) a un separador C2 / desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C3+, una corriente de cabezas que comprende el resto de componentes, c) enviar dicha corriente de cabezas a una zona de adsorción de CO2 de lecho fijo para recuperar una corriente esencialmente exenta de CO2, d) enviar dicha corriente esencialmente exenta de CO2 a un desmetanizador / equipo depurador de CO para recuperar una corriente de cabezas que comprende H2, CH4 y CO, etileno líquido en las colas. En otra realización la etapa de eliminación de CO2 se puede realizar en el etileno recuperado.

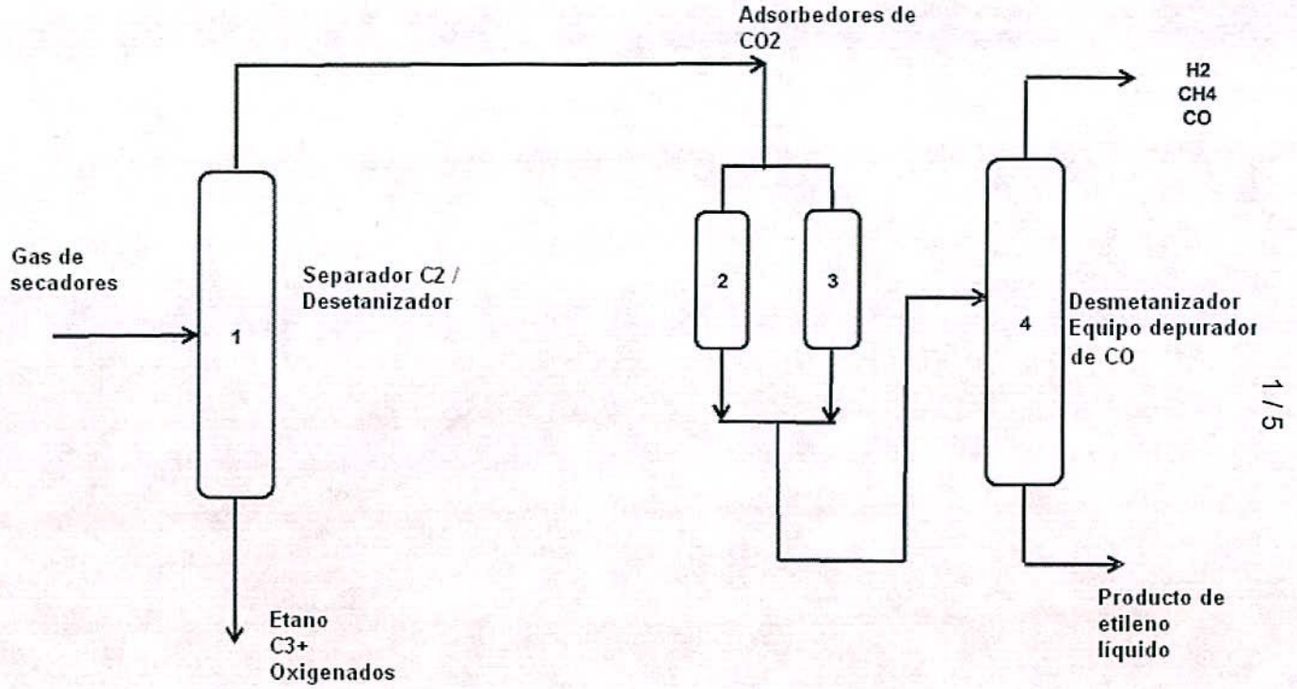

Adsorbedores de CO2
H2
CH4
CO
Gas de secadores
1
Separador C2 / Desetanizador
2
3
4
Desmetanizador Equipo depurador de CO
Etano
C3+
Oxigenados
Producto de etileno líquido

Fig 1

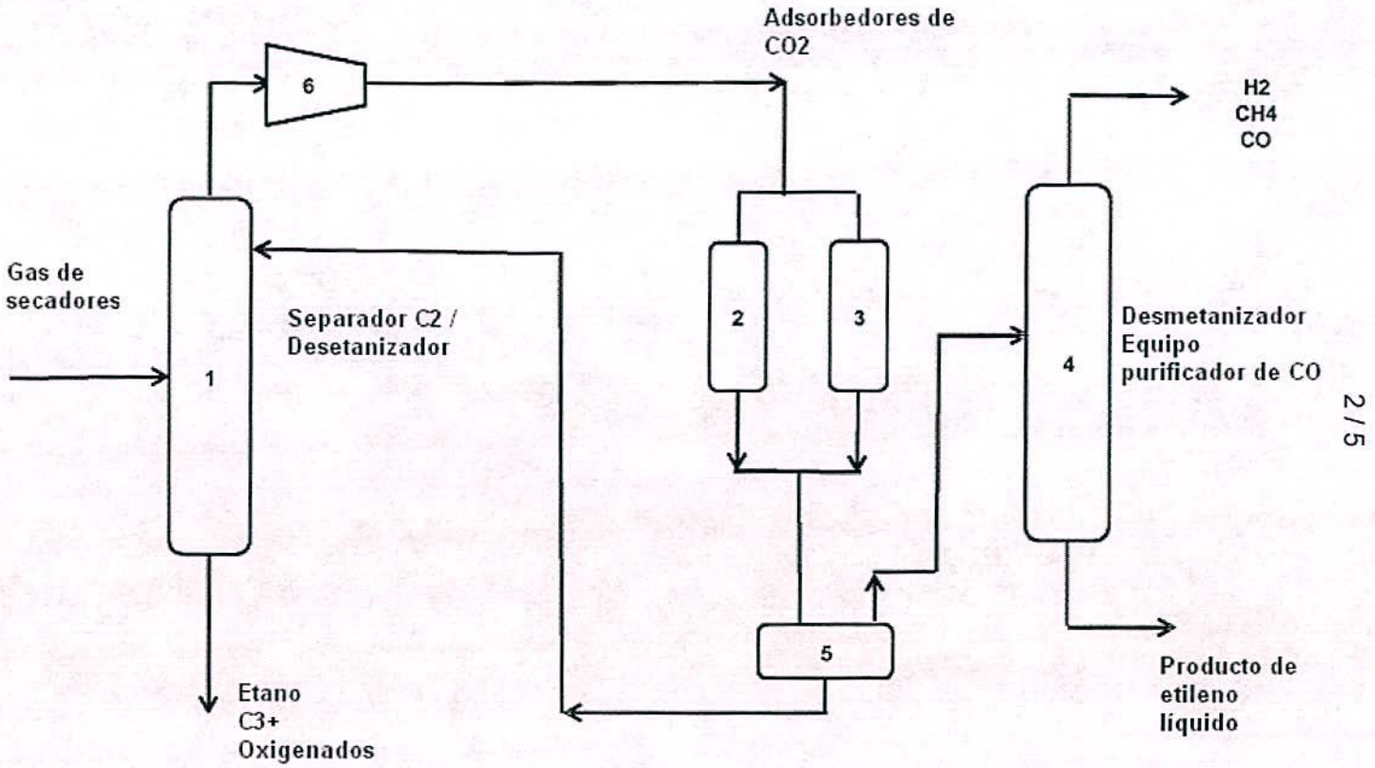

Adsorbedores de CO2
6
H2
CH4
CO
Gas de secadores
Separador C2 / Desetanizador
2
3
4
Desmetanizador Equipo purificador de CO
1
5
Etano
C3+
Oxigenados
Producto de etileno líquido

Fig 2

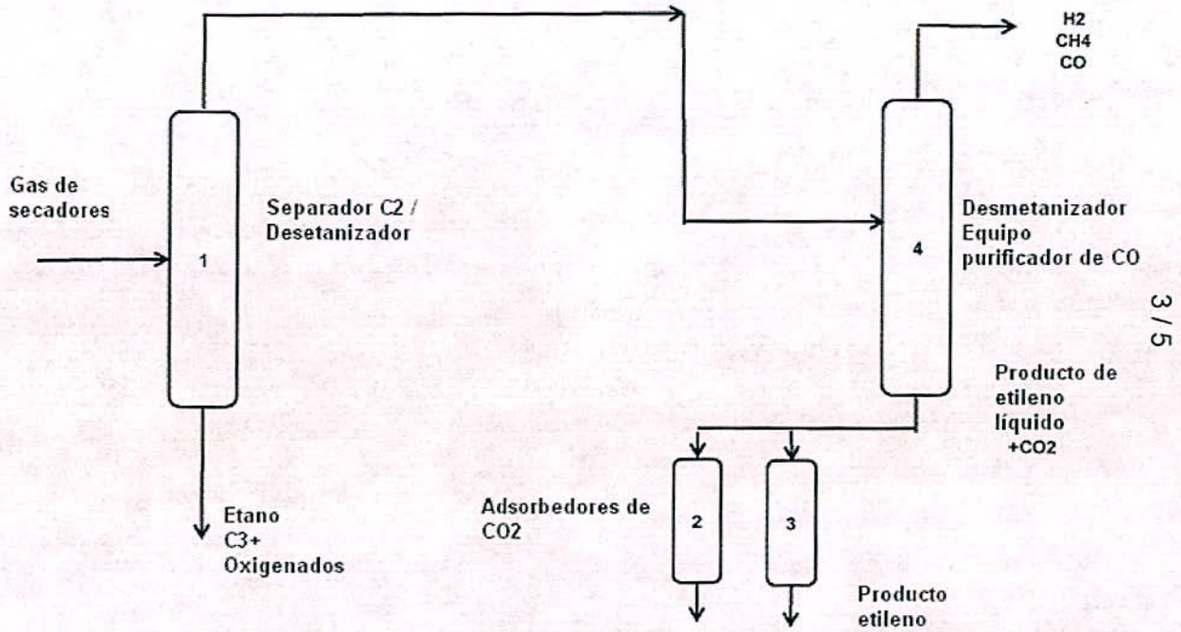

Gas de
secadores
1
Separador C2 /
Desetanizador
Etano
C3+
Oxigenados
H2
CH4
CO
4
Desmetanizador
Equipo
purificador de CO
Producto de
etileno
líquido
+CO2
Adsorbedores de
CO2
2
3
Producto
etileno

Fig 3

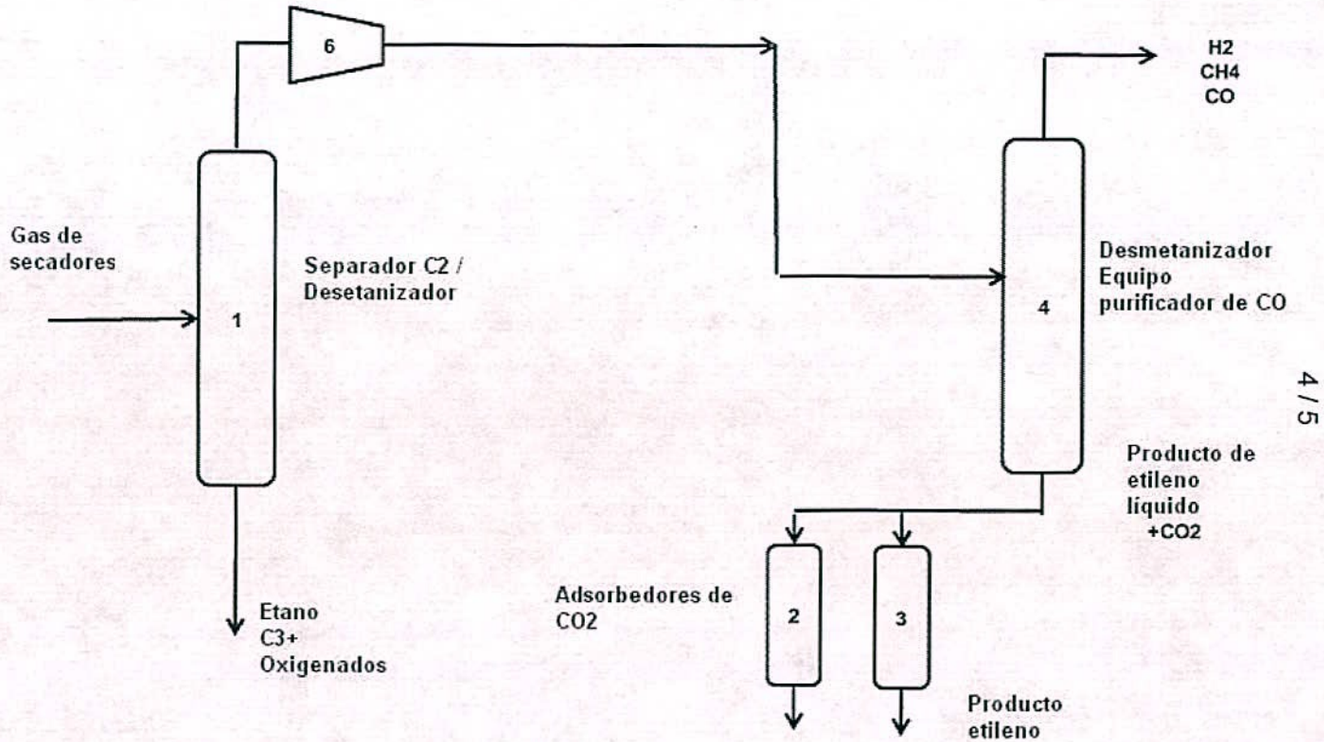

6
H2
CH4
CO
Gas de
secadores
1
Separador C2 /
Desetanizador
4
Desmetanizador
Equipo
purificador de CO
Producto de
etileno
líquido
+CO2
Adsorbedores de
CO2
2
3
Etano
C3+
Oxigenados
Producto
etileno

Fig 4

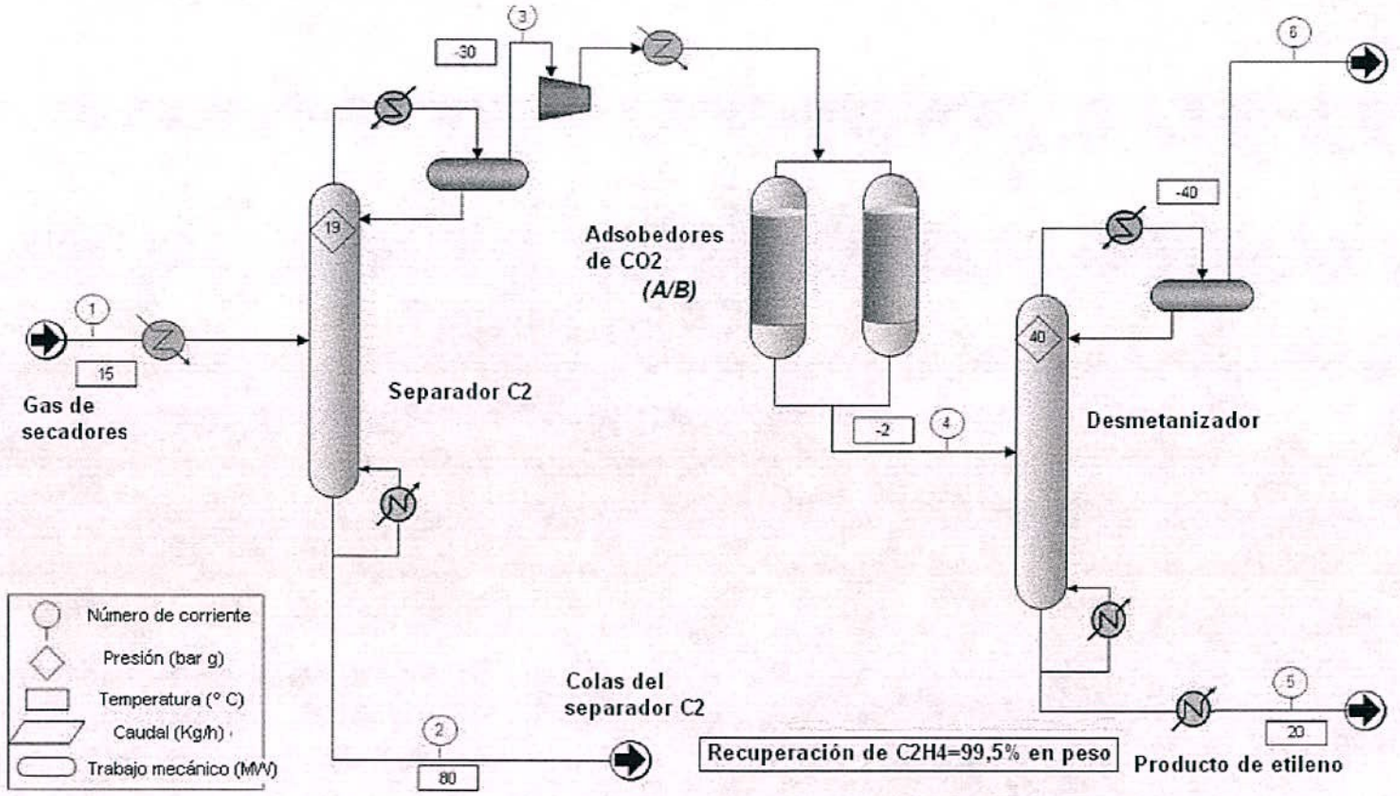

-30
3
19
Adsobedores
de CO2
(A/B)
6
-40
1
15
Gas de
secadores
Separador C2
40
Desmetanizador
-2
4
Número de corriente
Presión (bar g)
Temperatura (° C)
Caudal (Kg/h)
Trabajo mecánico (MW)
Colas del
separador C2
2
80
5
20
Recuperación de C2H4=99,5% en peso
Producto de etileno

Fig 5

30

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 January 2013 (31.01.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/014003 A1

(51) International Patent Classification:
C07C 7/00 (2006.01) *C07C 7/12* (2006.01)
C07C 7/04 (2006.01) *C07C 11/04* (2006.01)

(21) International Application Number:
PCT/EP2012/063755

(22) International Filing Date:
13 July 2012 (13.07.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11290349.7 28 July 2011 (28.07.2011) EP

(71) Applicants *(for all designated States except US)*: **TOTAL RESEARCH & TECHNOLOGY FELUY** [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE). **IFP ENERGIES NOUVELLES** [FR/FR]; 1 & 4 avenue de Bois Préau, F-92852 Rueil Malmaison (FR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **DAS, Babua** [IN/BE]; Avenue Henri Dunantlaan 40, B-1140 Evere (BE). **ARRIATA, Manuela** [VE/FR]; 35 rue Saint Georges, F-75009 Paris (FR). **BOUTROT, Catherine** [FR/FR]; 9 avenue Paul Doumer, F-78400 Chatou (FR).

(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, 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, 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, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, ML, MR, NE, SN, TD, TG).

Published:

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

WO 2013/014003 A1

(54) **Title**: PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN ETHYLENE STREAM

(57) **Abstract**: The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising : a)providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons, b)sending said stream (A) to a C2 splitter/deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons, an overhead comprising the remaining components, c)sending said overhead to a fixed bed CO2 adsorption zone to recover a stream essentially free of CO2, d)sending said stream essentially free of CO2 to a demethanizer/CO stripper to recover an overhead comprising H2, CH4 and CO, liquid ethylene at the bottoms. In another embodiment the CO2 removal step can be made on the recovered ethylene.

PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN ETHYLENE STREAM

[Field of the invention]

The present invention is a process for removing oxygenated contaminants from an ethylene stream.

Olefins are traditionally produced from petroleum feedstocks by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s), such as ethylene and/or propylene, from a variety of hydrocarbon feedstock. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds. The limited supply and increasing cost of crude oil has prompted the search for alternative processes for producing hydrocarbon products.

Olefins can be produced by dehydration of the corresponding alcohol. Ethanol can be obtained by fermentation of carbohydrates. Made up of organic matter from living organisms, biomass is the world's leading renewable energy source. The effluent produced by the ethanol dehydration comprises essentially unconverted ethanol, water, ethylene, acetaldehyde. Acetaldehyde may cause problems in ethylene recovery operations. It may comprise also very small amounts of ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons. The weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene is most of time less than 20/80.

[Background of the invention]

US 20030098281 A1 describes a method of controlling water and/or oxygenate concentrations of an olefin stream. The method includes contacting the olefin stream with a liquid absorbent. The liquid absorbent is selected from the group consisting of a polyol, amine, amide, nitrile, heterocyclic nitrogen

containing compound, and mixtures thereof. A gaseous stream comprising essentially steam, ethylene, propylene and less than 2 w% of oxygenates is condensed in a quench tower. The overhead of said quench tower is washed with a caustic solution to remove CO2 and then contacted with the liquid absorbent to remove the oxygenates.

WO 03 020670 A1 provides a method for removing oxygenated components such as acetaldehyde, CO2 and/or water from an olefin stream. It explains it is desirable to remove such oxygenated components, since they may poison catalysts that are used to further process olefin composition. In addition, the presence of certain oxygenated compounds, such as acetaldehyde, can cause fouling in other olefin purification units, e.g., acid gas treating units. The method comprises providing an olefin stream containing ethylene, propylene, C4+ olefins and acetaldehyde. The olefin stream is separated into a first fraction and a second fraction, wherein the first fraction comprises at least a majority of the ethylene and/or propylene present in the olefin stream, and the second fraction comprises at least a majority of the C4+ olefins and acetaldehyde present in the olefin stream. The first fraction is then acid gas treated by sodium hydroxide or potassium hydroxide. The olefin stream is separated by distillation, preferably, the distillation is extractive distillation using an extractant. The preferred extractant is a polar composition having an average boiling point of at least 38°C at 1 atm. Methanol is one type of preferred extractant.

WO 03 020672 A1 describes method of removing dimethyl ether from an ethylene and/or propylene containing stream. The olefin stream is passed to a water absorption column, methanol is used as the water absorbent. Methanol and entrained water, as well as some oxygenated hydrocarbon, is recovered as the bottoms stream of said water absorption column, an overhead olefin is recovered and sent to a distillation column. The distillation column separates ethylene and propylene, as well as lighter boiling point components from the dimethyl ether and heavier boiling point components, including C4+ components and methanol remaining from the methanol wash. Additional

methanol is added to the distillation column to reduce clathrate and/or free water formation in the distillation column. The ethylene and propylene containing stream exits the distillation column as overhead and the heavier boiling point components which include the dimethyl ether and C4+ components exit the distillation column as the bottoms. Ethylene and propylene then flow to a caustic wash column.

WO 03 033438 A1 describes a method for processing an olefin stream containing oxygenates and water, comprising: providing an olefin stream containing oxygenates and water; dewatering the olefin stream; compressing the dewatered olefin stream; washing the olefin stream with methanol to remove at least a portion of the oxygenate from the olefin stream; contacting the methanol washed olefin stream with water; and fractionating the water contacted olefin stream. The recovered olefin stream (washed with methanol and then with water) is further sent to an alkali wash and a drying step. The olefin stream containing oxygenates and water is the effluent of an MTO process.

US 6,444,869 describes a process for the production of ethylene from an oxygenate conversion effluent stream. The oxygenate conversion effluent stream comprises hydrogen, methane, ethylene, ethane, propylene, propane and C4+ olefins. This effluent is compressed, treated to remove oxygenates, passed to a carbon dioxide removal zone wherein carbon dioxide is absorbed by contacting a caustic solution or by contacting an amine solution in combination with a caustic solution in a conventional manner to remove the carbon dioxide, dried, then fractionation is made through a deethanizer and a demethanizer.

US 2005-0283038 A1 described a process for producing an olefins stream from a first vapor effluent stream from an oxygenate to olefin conversion reaction, said first vapor effluent stream comprising C2 and C3 olefins, C4 hydrocarbons, and C2 to C6 carbonyl compounds. In the process, the

temperature and pressure of the first vapor effluent stream are adjusted to produce a second vapor effluent stream having a pressure ranging from about 100 psig to about 350 psig (790 to 2514 kPa) and a temperature ranging from about 70° F. to about 120° F. (21 to 49° C.), said second vapor effluent stream containing about 50 wt. % or more C4 hydrocarbons based upon the total weight of C4 hydrocarbons in the first vapor effluent stream. The second vapor effluent stream is then washed with a liquid alcohol-containing stream to produce a third vapor effluent stream, whereafter the third vapor effluent stream is washed with liquid water to provide a fourth vapor effluent stream comprising the C2 and C3 olefins and about 1.0 wt. % or less C2 to C6 carbonyl compounds. In one embodiment of such a recovery process, at least part of the fourth vapor effluent stream is contacted with a basic component, such as caustic or an amine, to remove the bulk of the carbon dioxide therefrom (thus removing "acid gas" from the fourth vapor effluent stream), whereafter the CO_2-depleted stream is dried.

The main drawback of the above prior arts is the fouling of the caustic scrubber. The inlet gas to the caustic scrubber contains reactive oxygenates like aldehydes and ketones. These aldehydes react in the aldol condensation reaction in the caustic tower environment to form significant red oil polymers. This causes significant fouling concerns in the caustic tower which impact the unit run length. The spent caustic treatment with significant red oil polymer content is also an important concern as well as the spent caustic treatment and disposal issues. In addition there are the handling and disposal issues of red oil polymers.

It has now been discovered a process for removing oxygenated contaminants from an ethylene stream wherein there is no caustic wash to remove the CO2 and no wash column to remove the oxygenates. Oxygenates are organic compounds consisting of carbon, oxygen and hydrogen.

[Brief summary of the invention]

The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons,

b) sending said stream (A) to a C2 splitter/deethanizer to produce

a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons,

an overhead comprising the remaining components,

c) sending said overhead to a fixed bed CO2 adsorption zone to recover a stream essentially free of CO2,

d) sending said stream essentially free of CO2 to a demethanizer/CO stripper to recover an overhead comprising H2, CH4 and CO,

liquid ethylene at the bottoms.

In another embodiment the CO2 removal step can be made on the recovered ethylene. In said embodiment the present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

a1) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons,

b1) sending said stream (A) to a C2 splitter/deethanizer to produce

a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons,

an overhead comprising the remaining components,

c1) sending said overhead stream to a demethanizer/CO stripper to recover an overhead comprising H2, CH4 and CO,

liquid ethylene comprising CO2 at the bottoms.

d1) sending said ethylene comprising CO2 to a fixed bed CO2 adsorption zone to recover an ethylene stream essentially free of CO2.

In an embodiment the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene in (A) is less than 10/90.

In an embodiment the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene in (A) is less than 10/90 and above 0.1/99.9.

In an embodiment the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene in (A) is less than 5/95.

In an embodiment the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

In an embodiment the proportion of oxygenates in (A) is up to 3000 wppm.

In an embodiment the proportion of oxygenates in (A) is up to 2000 wppm.

In an embodiment the proportion of H2 in (A) is from 5 to 1000 wppm.

In an embodiment the proportion of H2 in (A) is up to 800 wppm.

In an embodiment the proportion of H2 in (A) is up to 500 wppm.

Advantageously "dried ethylene stream" at step a) means a water content less than 5 wppm, advantageously less than 3wppm and preferably less than 1 wppm.

In an embodiment when the dried ethylene stream (A) has been made by ethanol dehydration said stream (A) contains substantially no acetylene.

Ethylene treated in accordance with this invention is particularly suitable for use as feedstock for making alpha-olefins, ethylbenzene/styrene, ethyleneoxide/ethyleneglycol, ethylenedichloride and corresponding polymers, like polyethylene homo or copolymer (PE, EPR, EPDM etc), polystyrene (PS), styrene copolymers with butadiene, isoprene, acrylonitrile or combinations (SBS, SIS, SBR, ABS, SAN), polyesters (PET) and polyvinylchlorides (PVC)

[Detailed description of the invention]

As regards the oxygenated contaminants, also referred to as oxygenates, one can cite ethanol, C3 alcohols; ethers such as diethylether and methyl ethyl ether; carboxylic acids such as acetic acid; aldehydes such as acetaldehyde; ketones such as acetone; and esters such as methyl esters. Particularly problematic oxygenate contaminants in an alcohol dehydration are aldehydes.

As regards the ethylene stream (A) of step a), it can be originating from the dehydration of ethanol. Said dehydration can be made in one or more ethanol dehydration reactors. As regards alcohol dehydration, such process is described in WO-2009-098262, WO-2009-098267, WO-2009-098268 and WO-2009-098269 the content of which is incorporated in the present application. The present invention is very efficient for the purification of ethylene produced by dehydration of ethanol.

The outlet of said dehydration reactor comprises essentially ethylene and steam as well as minor amounts of oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons. "Minor amounts" means the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene is less than 20/80 and most of time less than 10/90.

Said outlet of dehydration reactor is initially cooled, typically in a quench tower employing water as the quench medium. In the quench tower, most of the water contained in the outlet of dehydration reactor is condensed and is removed from the bottom of the tower as a liquid water bottom stream. A part of said water bottom stream is cooled in a heat exchanger and recycled as quenching medium to the top of the quench column. The part of the water bottom stream which is not recycled as quenching medium may contain a part of the oxygenates and mostly unconverted ethanol if any. Said stream can be treated in a stripping column to recover a pure water stream. Ethylene, oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons are removed from the top of the quench tower at a pressure typically such as 1 to 16 bars absolute and are referred to as the contaminated ethylene stream.

Advantageously said contaminated ethylene stream is successively compressed and cooled in one or more steps to remove the major part of water, further fed to a fixed bed drying zone and finally to the C2 splitter/deethanizer of step b).

In the previous compression steps the recovered water contains a part of the oxygenated contaminants and hydrocarbons dissolved. The contaminated hydrocarbon stream can also be cooled before the first compression step and water recovered. In an embodiment the water recovered upon each cooling further to a compression step and upon cooling, if any, before the first compression step is sent to a stripping column to produce an overhead stream comprising essentially oxygenated contaminants and hydrocarbons and an essentially pure water bottoms stream. Optionally the overhead stream is burned to destroy the oxygenated contaminants and recover heat.

After the compression steps the contaminated ethylene stream is further fed to a fixed bed drying zone and finally to the C2 splitter/deethanizer of step b). The fixed bed drying zone is known in itself.

As regards the C2 splitter/deethanizer of step b), it is advantageously a distillation column. The overhead is a mixture of ethylene, CO, CO2, H2 and CH4.

As regards the fixed bed CO2 adsorption zone of step c), it can be any component capable to selectively remove CO2. By way of example it is an available commercial fixed bed adsorption (PSA for pressure swing adsorption or TSA for temperature swing adsorption) using molecular sieves or basic oxides, supported basic oxides, high surface area carbons, organo-metallic framework components (MOF's) or mixture thereof. The molecular sieves are preferably low silica zeolites, having 8 (among which zeolite A) or 12 membered (among which zeolite X) rings and exchanged with alkali, alkaline earth or lanthanide cations. Other molecular sieves are crystalline titanosilicates (ETS family materials). Supported basic oxides are preferably, alkali, alkaline earth or

lanthanide oxides supported on high surface area carbons, alumina, silica, zirconia or titania. The removal of CO2 can be carried out with a liquid stream or with a gaseous ethylene stream depending on the pressure and temperature. A stream essentially free of CO2 is recovered. As only trace amounts of CO2 have to be removed from the ethylene, the preferred process cycle is of the thermal swing adsorption (TSA) type. Said fixed bed adsorbent, once saturated with CO2, can be regenerated, during regeneration the desorption produces a stream which can be treated anywhere. In a TSA process cycle, the regeneration is done while sweeping the saturated adsorbent with an inert gas by increasing the temperature until desorption of the CO2 occurs. Eventually the saturated adsorbent can be replaced by new adsorbent and the saturated adsorbent either be disposed of or regenerated ex-situ for further use. "Essentially" has to be interpretated in the light of the further use of ethylene. Should ethylene to be polymerized CO2 has to be 1 ppm vol or less and preferably 0.5 ppm vol or less.

As regards the demethanizer, purpose is to recover an overhead comprising H2, CH4 and CO and liquid ethylene at the bottoms. It is advantageously a distillation column.

As regards the operating conditions, The demethanizer of step d) has to be at a pressure high enough to operate at temperatures which are not too low. A demethanizer to recover an overhead comprising H2, CH4 and CO and liquid ethylene at the bottoms operating at 40 barg has an overhead temperature of around 0 to -10°C and a bottom temperature of around 0°C. The same demethanizer operating at 21 barg has an overhead temperature of -30°C and a bottom temperature of around -24°C.

These temperatures and pressures are a function of the proportion of H2, CH4 and CO in the ethylene stream (A) and mainly of the proportion of H2. The proportion of H2, CH4 and CO in the ethylene stream (A) and mainly the proportion of H2 governs also the pressure and temperature of the C2 splitter/deethanizer located upstream said demethanizer.

In an embodiment the pressure of step b) is selected to have a temperature of the C2 splitter/deethanizer bottoms such as there is no oligomerization or polymerization of the oxygenates. By way of example said temperature should not exceed 150°C and advantageously not exceed 100°C. This temperature is function of the pressure and of the proportion of oxygenates in the mixture of oxygenates+ethane+C3+ hydrocarbons. The higher the proportion of oxygenates the higher the temperature. The higher the pressure the higher the temperature.

In an embodiment the C2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C2 splitter /deethanizer and the demethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to four compression stages in series (depending on dehydration reactor pressure), sent to the driers and finally to the C2 splitter deethanizer.

Said embodiment is described on fig 1 wherein (1) is the C2 splitter deethanizer, (2) and (3) the CO2 adsorbers and (4) the demethanizer/CO stripper. The contaminated ethylene stream from the quench column has been dried and sent to the C2 splitter deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO2, H2 and CH4 (condenser, decanter and reflux of C2 splitter deethanizer are not shown, reboiler of C2 splitter deethanizer is not shown). Said overhead is sent to the CO2 adsorbers (2) and (3) to recover a stream essentially free of CO2 and then to the demethanizer/CO stripper (4) to recover an overhead comprising H2, CH4 and CO and liquid ethylene at the bottoms. Condenser, decanter and reflux of the demethanizer/CO stripper are not shown, reboiler of the demethanizer/CO stripper is not shown.

In a specific example according to fig 1 the pressure of the C2 splitter/deethanizer is around 15 to 25 barg, the top of said splitter/deethanizer is at a temperature around -20°C to -30°C, condensed at a temperature in the range -20°C to -30°C, the temperature on bottoms of said splitter/deethanizer is around 70 to 90°C, the pressure of the demethanizer/CO stripper around 15 to 25 barg, the top of the demethanizer/CO stripper is around -15°C to -35°C, is condensed at a temperature around -15 to -35°C and the temperature on bottoms of the demethanizer/CO stripper is around -15°C to -35°C.

Advantageously the pressure of the C2 splitter/deethanizer is around 18 to 25 barg, the top of said splitter/deethanizer is at a temperature around -18°C to -28°C, condensed at a temperature in the range -18°C to -28°C, the temperature on bottoms of said splitter/deethanizer is around 75 to 85°C, the pressure of the demethanizer/CO stripper around 18 to 25 barg, the top of the demethanizer/CO stripper is around -20°C to -30°C, is condensed at a temperature around -20 to -30°C and the temperature on bottoms of the demethanizer/CO stripper is around -20°C to -30°C.

In an embodiment the pressure of the C2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper. Advantageously the pressure of the C2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C2 splitter /deethanizer is ranging from 10 to 25 barg In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to three compression stages in series, sent to the driers and finally to the C2 splitter deethanizer. Then the overhead of the C2 splitter deethanizer is compressed and sent through the CO2 adsorbers to the demethanizer/CO stripper. Optionally the essentially CO2 free stream leaving the fixed bed CO2 adsorption zone is cooled, sent to a decanter to produce a liquid phase sent as a reflux to the C2 splitter/deethanizer and a gaseous phase sent to the demethanizer/CO stripper.

Said embodiment is described on fig 2. The contaminated ethylene stream from the quench column has been dried and sent at a pressure around

15 to 25 barg to the C2 splitter deethanizer (1) to produce a bottom stream (the reboiler is not shown) comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO2, H2 and CH4. Said overhead (top of the the C2 splitter deethanizer) is sent to the compressor (6) to increase the pressure with 10 to 25 barg over the C2 splitter /deethanizer pressure, optionally cooled (the cooler is not shown) and sent to the CO2 adsorbers (2) and (3) to recover a stream essentially free of CO2. Then said CO2 free stream is cooled (the cooler is not shown) and sent to the decanter (5) to produce a liquid phase sent as a reflux to the C2 splitter deethanizer (1) and a gaseous phase sent to the demethanizer/CO stripper (4). Said demethanizer/CO stripper (4) produces an overhead (the condenser, decanter and reflux are not shown) comprising H2, CH4 and CO and liquid ethylene at the bottoms (the reboiler is not shown).

Alternatively, the condenser and decanter (5) can be installed between the top outlet of the C2 splitter/deethaniser (1) and the compressor (6). The produced liquid phase is sent as a reflux to the C2 splitter/deethaniser (1) while the gaseous phase is sent to the compressor (6). In other words the contaminated ethylene stream from the quench column has been dried and sent to the C2 splitter deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO2, H2 and CH4 Said overhead, the top outlet of the C2 splitter/deethaniser (1), is condensed, sent to a decanter to get a liquid phase sent as a reflux to the C2 splitter/deethaniser (1) and a gaseous phase sent to the compressor (6). Then the compressed stream is sent to the CO2 adsorbers (2) and (3) to recover a stream essentially free of CO2 and then to the demethanizer/CO stripper (4) to recover an overhead comprising H2, CH4 and CO and liquid ethylene at the bottoms.

In a specific example according to fig 2 the pressure of the splitter/deethanizer is around 15 to 25 barg, the temperature on top of said splitter/deethanizer around -25°C to -35°C, the temperature on bottoms of said splitter/deethanizer around 70 to 90°C, the pressure of the demethanizer/CO stripper around 35 to 45 barg, the top of the demethanizer/CO stripper is around

-10°C to 10°C, is condensed at a temperature around -35 to -45°C and the temperature on bottoms of the demethanizer/CO stripper is around -10 to 10°C.

Advantageously the pressure of the splitter/deethanizer is around 18 to 20 barg, the temperature on top of said splitter/deethanizer around -28°C to -32°C, the temperature on bottoms of said splitter/deethanizer around 78 to 82°C, the pressure of the demethanizer/CO stripper around 38 to 42 barg, the top of the demethanizer/CO stripper is around -5°C to 5°C, is condensed at a temperature around -38 to -42°C and the temperature on bottoms of the demethanizer/CO stripper is around -2 to 2°C.

As regards the other embodiment wherein the CO2 removal step is made on the recovered ethylene, it works in a similar way as explained above in which the CO2 removal step is before the demethanizer/CO stripper.

In an embodiment the C2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C2 splitter /deethanizer and the demethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to four compression stages in series (depending on dehydration reactor pressure), sent to the driers and finally to the C2 splitter deethanizer.

Said embodiment is described on fig 3 wherein (1) is the C2 splitter deethanizer, (2) and (3) the CO2 adsorbers and (4) the demethanizer/CO stripper. The contaminated ethylene stream from the quench column has been dried and sent to the C2 splitter deethanizer (1) to produce a bottom stream (the reboiler is not shown) comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead (the condenser, the decanter and the reflux are not shown) comprising ethylene, CO, CO2, H2 and CH4. Said overhead is sent the demethanizer/CO stripper (4) to recover an overhead (the condenser, the decanter and the reflux are not shown) comprising H2, CH4 and CO and liquid ethylene comprising CO2 at the bottoms (the reboiler is not shown). Said

ethylene comprising CO2 is sent to a fixed bed CO2 adsorption zone, the CO2 adsorbers (2) and (3) to recover an ethylene stream essentially free of CO2.

In a specific example according to fig 3 the pressure of the C2 splitter/deethanizer is around 15 to 25 barg, the top of said splitter/deethanizer is at a temperature around -20°C to -30°C, condensed at a temperature in the range -20°C to -30°C, the temperature on bottoms of said splitter/deethanizer is around 70 to 90°C, the pressure of the demethanizer/CO stripper around 15 to 25 barg, the top of the demethanizer/CO stripper is around -15°C to -35°C, is condensed at a temperature around -15 to -35°C and the temperature on bottoms of the demethanizer/CO stripper is around -15°C to -35°C.

Advantageously the pressure of the C2 splitter/deethanizer is around 18 to 25 barg, the top of said splitter/deethanizer is at a temperature around -18°C to -28°C, condensed at a temperature in the range -18°C to -28°C, the temperature on bottoms of said splitter/deethanizer is around 75 to 85°C, the pressure of the demethanizer/CO stripper around 18 to 25 barg, the top of the demethanizer/CO stripper is around -20°C to -30°C, is condensed at a temperature around -20 to -30°C and the temperature on bottoms of the demethanizer/CO stripper is around -20°C to -30°C.

In an embodiment the pressure of the C2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper. Advantageously the pressure of the C2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C2 splitter /deethanizer is ranging from 10 to 25 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in two to three compression stages in series, sent to the driers and finally to the C2 splitter deethanizer. Then the overhead of the C2 splitter deethanizer is compressed and sent to the demethanizer/CO stripper.

Said embodiment is described on fig 4. In addition to fig 3 there are additional equipment : a compressor (6). The contaminated ethylene stream

from the quench column has been dried and sent at a pressure around 15 to 25 barg to the C2 splitter deethanizer (1) to produce a bottom stream (the reboiler is not shown) comprising essentially ethane, oxygenates and C3+ hydrocarbons and an overhead comprising ethylene, CO, CO2, H2 and CH4. Said overhead is condensed, sent to a decanter to get a liquid phase sent as a reflux to (1) and a gaseous phase sent to the compressor (6). Said condenser, decanter and reflux are not shown). The compressor (6) increases the pressure with 10 to 25 barg over the C2 splitter /deethanizer pressure, and the compressed stream is sent to the demethanizer/CO stripper (4). Said demethanizer/CO stripper (4) produces an overhead (the condenser, the decanter and the reflux are not shown) comprising H2, CH4 and CO and at the bottom liquid ethylene comprising CO2 (the reboiler is not shown). Said ethylene comprising CO2 is sent to a fixed bed CO2 adsorption zone, the CO2 adsorbers (2) and (3) to recover an ethylene stream essentially free of CO2.

In a specific example according to fig 4 the pressure of the splitter/deethanizer is around 15 to 25 barg, the top of said splitter/deethanizer is at a temperature around -25°C to -35°C, condensed at a temperature in the range -25°C to -35°C, the temperature on bottoms of said splitter/deethanizer is around 70 to 90°C, the pressure of the demethanizer/CO stripper around 35 to 45 barg, the top of the demethanizer/CO stripper is around -10°C to 10°C, is condensed at a temperature around -35 to -45°C and the temperature on bottoms of the demethanizer/CO stripper is around -10 to 10°C.

Advantageously the pressure of the splitter/deethanizer is around 18 to 20 barg, the top of said splitter/deethanizer is at a temperature around -28°C to -32°C, the temperature on bottoms of said splitter/deethanizer around 78 to 82°C, the pressure of the demethanizer/CO stripper around 38 to 42 barg, the top of the demethanizer/CO stripper is around -5°C to 5°C, is condensed at a temperature around -38 to -42°C and the temperature on bottoms of the demethanizer/CO stripper is around -2 to 2°C.

[Example]

The process according to fig 5 is operated. Fig 5 is derived from fig 2 by changing the position of the condenser and decanter (5), they are located between the outlet of the C2 splitter/deethaniser and the compressor. The results are on the following table.

stream No on fig 5		1	2	3
		C2 splitter feed	C2 splitter bottoms	C2 splitter vapor distillat
Temperature	°C	15	80	-30
Pressure	bar g	20	19	19
H2	kg/h	8		8
CO	kg/h	1		1
CO2	kg/h	1		1
ethane	kg/h	23	11	12
ethylene	kg/h	25108	30	25078
acetaldehydes	kg/h	150	150	
C3+	kg/h	715	715	
Total	kg/h	26006	906	25100

stream No on fig 5		4	6	5
		Demethanizer feed	Demethanizer purge	Ethylene product
Temperature	°C	-2	-40	20
Pressure	bar g	40	40	20
H2	kg/h	8	8	
CO	kg/h	1	1	
CO2	kg/h			
ethane	kg/h	12		12
ethylene	kg/h	25078	90	24988
acetaldehydes	kg/h			
C3+	kg/h			
Total	kg/h	25099	99	25000

CLAIMS

1 Process for removing oxygenated contaminants from an ethylene stream comprising :

a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons,

b) sending said stream (A) to a C2 splitter/deethanizer to produce

a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons,

an overhead comprising the remaining components,

c) sending said overhead to a fixed bed CO2 adsorption zone to recover a stream essentially free of CO2,

d) sending said stream essentially free of CO2 to a demethanizer/CO stripper to recover an overhead comprising H2, CH4 and CO,

liquid ethylene at the bottoms.

2 Process according to claim 1 wherein the C2 splitter /deethanizer and the demethanizer are operating at the same pressure, except the pressure drop between the C2 splitter /deethanizer and the demethanizer for transfer of fluids, and said pressure is ranging from 15 to 45 barg.

3 Process according to claim 1 wherein the pressure of the C2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper, the pressure of the C2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C2 splitter /deethanizer is ranging from 10 to 25 barg.

4 Process according to claim 3 wherein the overhead, the top outlet, of the C2 splitter/deethaniser, is condensed, sent to a decanter to get a liquid phase sent as a reflux to said C2 splitter/deethaniser and a gaseous phase sent

to a compressor, then the compressed stream is sent to the CO2 adsorption zone.

5 Process according to claim 3 wherein the overhead, the top outlet, of the C2 splitter/deethaniser, is sent to a compressor, optionally cooled and sent to the CO2 adsorption zone to recover a stream essentially free of CO2, then said CO2 free stream is cooled and sent to a decanter to produce a liquid phase sent as a reflux to the C2 splitter deethanizer and a gaseous phase sent to the demethanizer/CO stripper.

6 Process for removing oxygenated contaminants from an ethylene stream comprising :

a1) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons,

b1) sending said stream (A) to a C2 splitter/deethanizer to produce

a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons,

an overhead comprising the remaining components,

c1) sending said overhead stream to a demethanizer/CO stripper to recover an overhead comprising H2, CH4 and CO,

liquid ethylene comprising CO2 at the bottoms.

d1) sending said ethylene comprising CO2 to a fixed bed CO2 adsorption zone to recover an ethylene stream essentially free of CO2.

7 Process according to claim 6 wherein the C2 splitter /deethanizer and the demethanizer are operating at the same pressure, except the pressure drop between the C2 splitter /deethanizer and the demethanizer for transfer of fluids, and said pressure is ranging from 15 to 45 barg.

8 Process according to claim 6 wherein the pressure of the C2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper, the pressure of the C2 splitter /deethanizer is ranging from 15 to 25 barg and

simultaneously the pressure difference between the demethanizer/CO stripper and the C2 splitter /deethanizer is ranging from 10 o 25 barg.

9 Process according to any one of claims 6 to 8 wherein the overhead, the top outlet, of the C2 splitter/deethaniser, is condensed, sent to a decanter to get a liquid phase sent as a reflux to said C2 splitter/deethaniser and a gaseous phase sent to a compressor, then the compressed stream is sent to the demethanizer/CO stripper.

10 Process according to any one of the preceding claims wherein the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene in (A) is less than 10/90.

11 Process according to claim 10 wherein the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene in (A) is less than 10/90 and above 0.1/99.9.

12 Process according to any one of claims 1 to 9 or claim 11 wherein the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene in (A) is less than 5/95.

13 Process according to any one of the preceding claims wherein the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

14 Process according to any one of the preceding claims wherein wherein the proportion of oxygenates in (A) is up to 3000 wppm.

15 Process according to claim 14 wherein the proportion of oxygenates in (A) is up to 2000 wppm.

16 Process according to any one of the preceding claims wherein the proportion of H2 in (A) is from 5 to 1000 wppm.

17 Process according to any one of the preceding claims wherein the proportion of H2 in (A) is up to 800 wppm.

18 Process according to claim 17 wherein the proportion of H2 in (A) is up to 500 wppm.

19 Process according to any one of the preceding claims wherein the dried ethylene stream (A) is originating from the dehydration of ethanol.

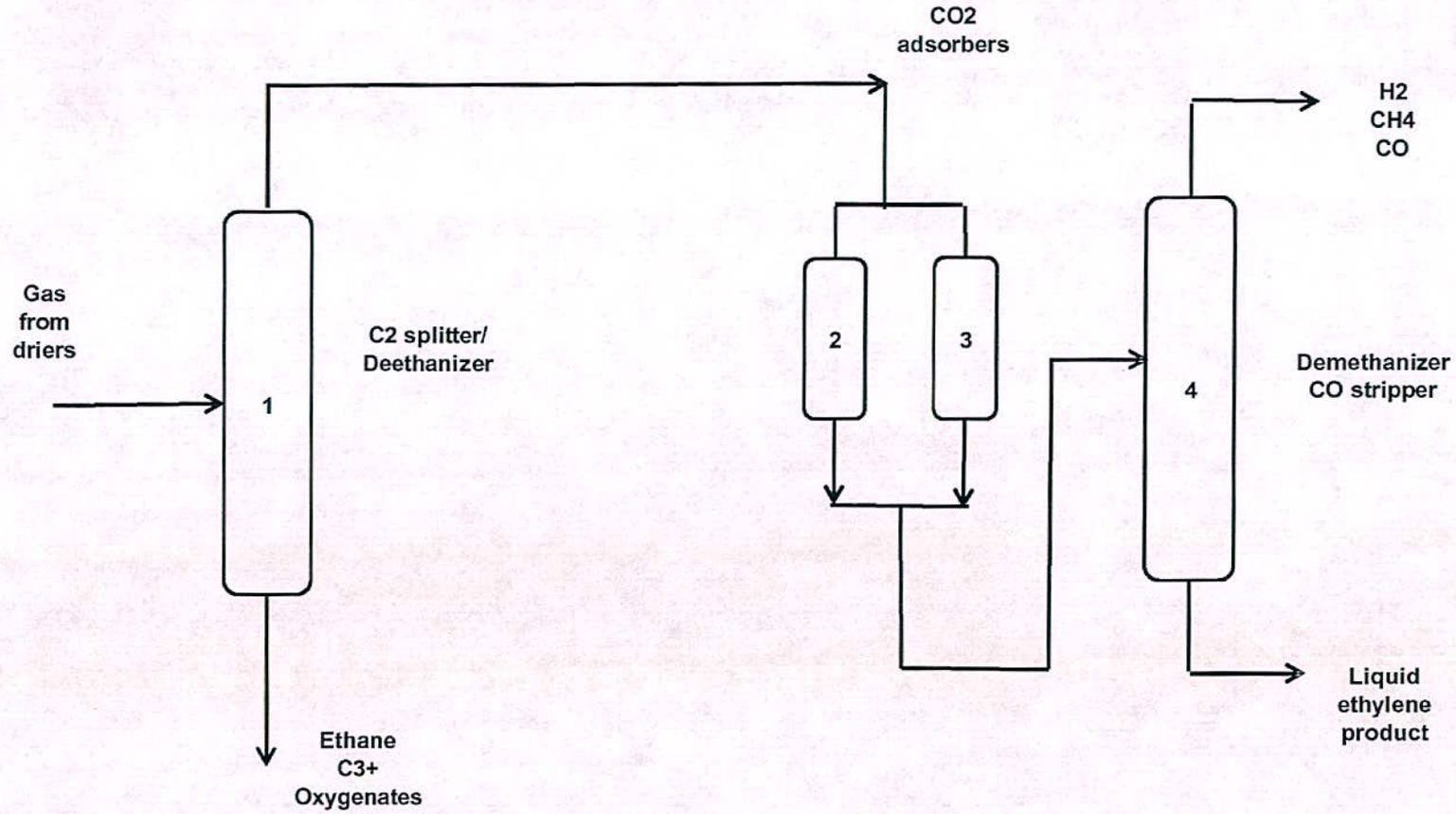

CO2
adsorbers
H2
CH4
CO
Gas
from
driers
C2 splitter/
Deethanizer
1
2
3
4
Demethanizer
CO stripper
Liquid
ethylene
product
Ethane
C3+
Oxygenates

Fig 1

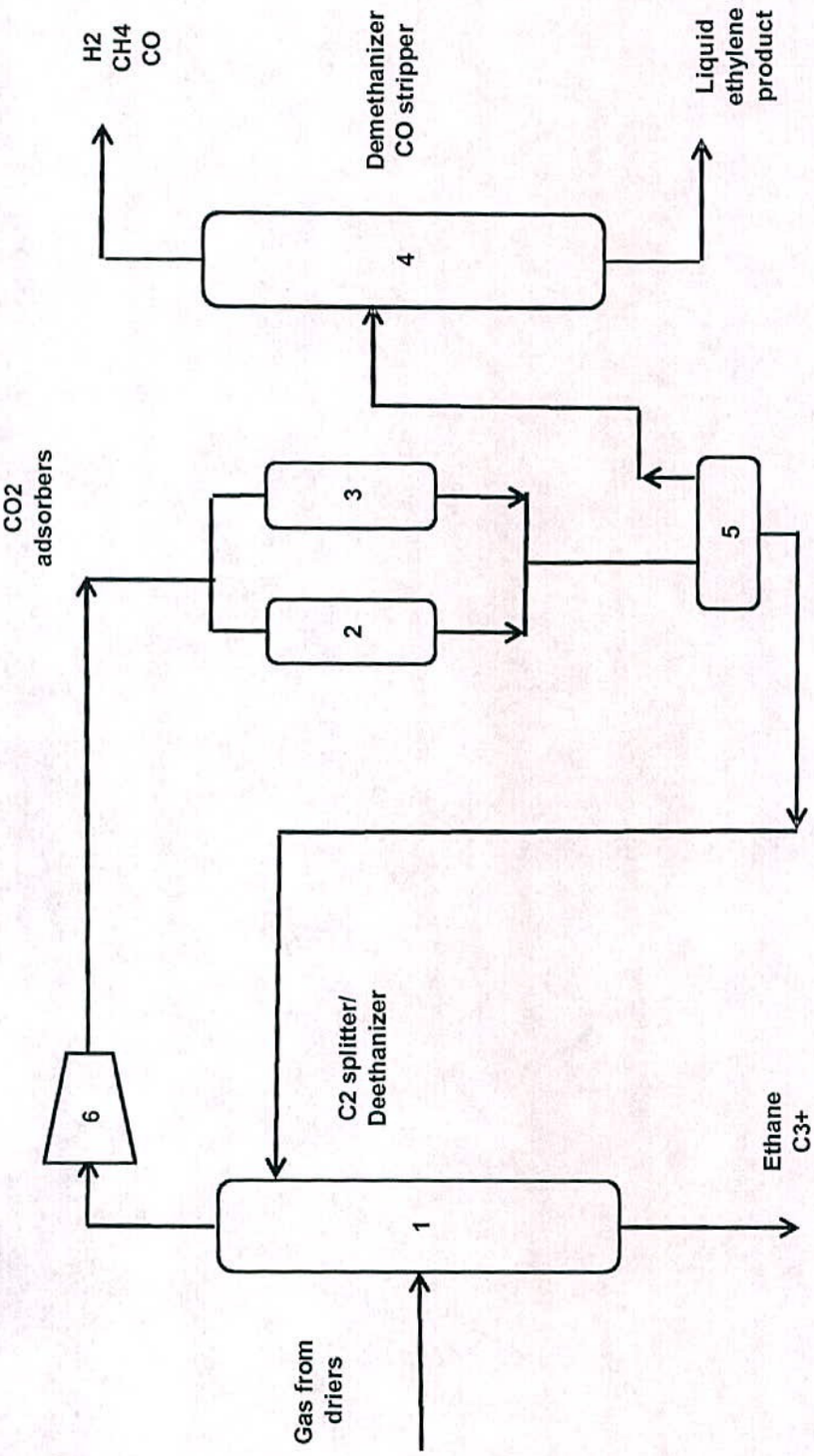

H2
CH4
CO
Demethanizer
CO stripper
Liquid
ethylene
product
4
CO2
adsorbers
3
2
5
6
C2 splitter/
Deethanizer
1
Ethane
C3+
Oxygenates
Gas from
driers

Fig 2

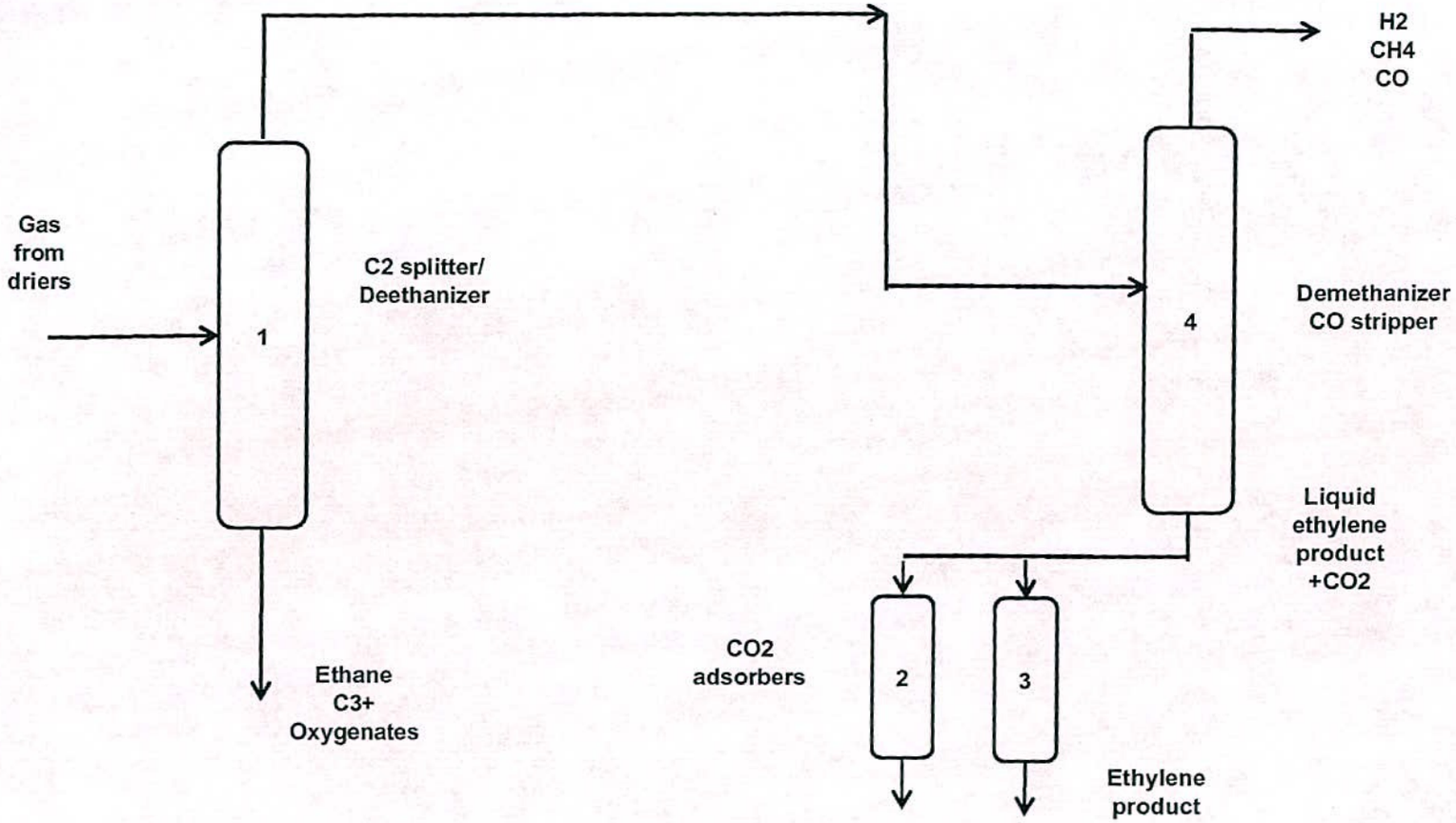

Gas
from
driers
1
C2 splitter/
Deethanizer
Ethane
C3+
Oxygenates
H2
CH4
CO
4
Demethanizer
CO stripper
Liquid
ethylene
product
+CO2
CO2
adsorbers
2
3
Ethylene
product

Fig 3

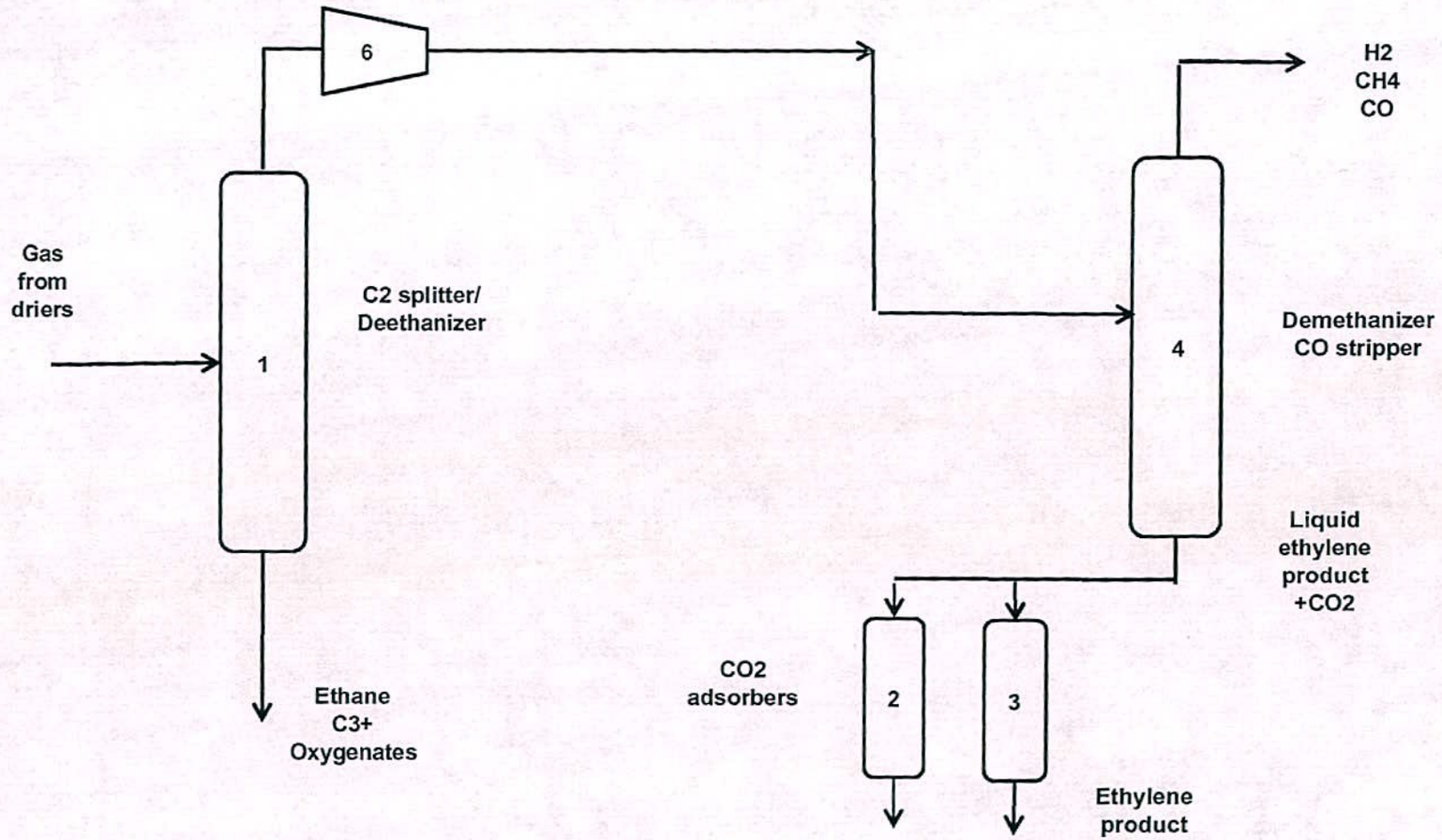

6
H2
CH4
CO
Gas
from
driers
C2 splitter/
Deethanizer
1
4
Demethanizer
CO stripper
Liquid
ethylene
product
+CO2
CO2
adsorbers
2
3
Ethane
C3+
Oxygenates
Ethylene
product

Fig 4

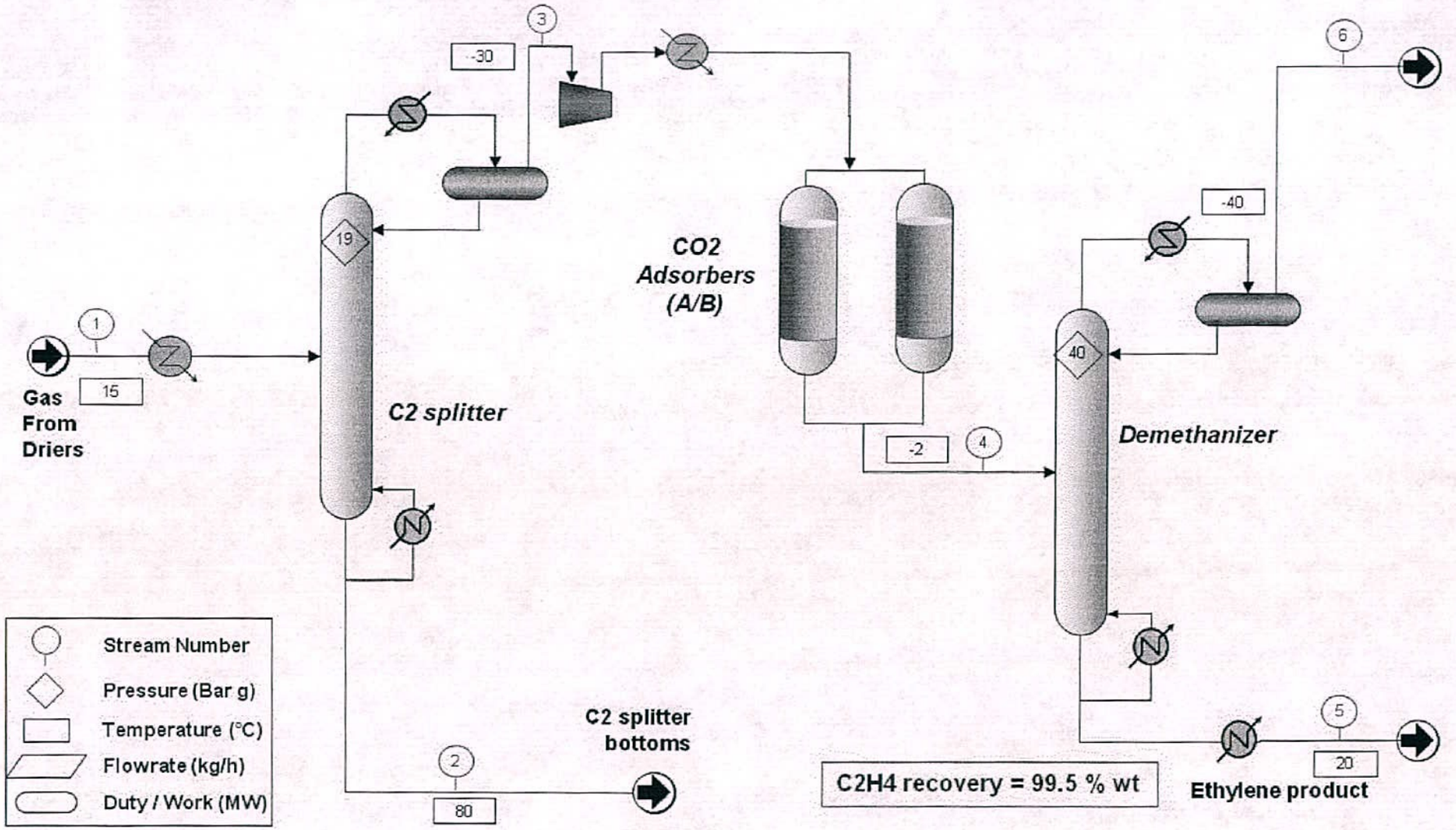

Gas From Driers
1
15
C2 splitter
19
3
-30
CO2 Adsorbers (A/B)
-2
4
Demethanizer
40
6
-40
5
20
Ethylene product
C2H4 recovery = 99.5 % wt
C2 splitter bottoms
2
80
Stream Number
Pressure (Bar g)
Temperature (°C)
Flowrate (kg/h)
Duty / Work (MW)

Fig 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/063755

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C7/00 C07C7/04 C07C7/12 C07C11/04
ADD.

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 practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/25174 A1 (UOP LLC [US]; SENETAR JOHN J [US]; MILLER LAWRENCE W [US]; CHENG LINDA) 12 April 2001 (2001-04-12) claims	1-19

☐ 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
5 September 2012	14/09/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	O'Sullivan, Paul

57

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/063755

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0125174 A1	12-04-2001	AU 7825600 A	10-05-2001
		EG 22225 A	31-10-2002
		NO 20004985 A	05-04-2001
		US 6303841 B1	16-10-2001
		US 2002007101 A1	17-01-2002
		WO 0125174 A1	12-04-2001

58

WIPO
WORLD
INTELLECTUAL PROPERTY
ORGANIZATION

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:		**PCT/EP2012/063755**
International filing date:		**13 July 2012 (13.07.2012)**
Document type:		**Certified copy of priority document**
Document details:	Country/Office:	**EP**
	Number:	**11290349.7**
	Filing date:	**28 July 2011 (28.07.2011)**
Date of receipt at the International Bureau:		**13 August 2012 (13.08.2012)**

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-*bis*)

34, chemin des Colombettes
1211 Geneva 20, Switzerland
www.wipo.int

Europäisches Patentamt
European Patent Office
Office européen des brevets

Bescheinigung	Certificate	Attestation
Die angehefteten Unterlagen stimmen mit der als ursprünglich eingereicht geltenden Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.	The attached documents are exact copies of the text in which the European patent application described on the following page is deemed to have been filed.	Les documents joints à la présente attestation sont conformes au texte, considéré comme initialement déposé, de la demande de brevet européen qui est spécifiée à la page suivante.

Patentanmeldung Nr.	**Patent application No.**	**Demande de brevet n°**
	11290349.7 / EP11290349	

The organization code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP11290349.

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le President de l'Office européen des brevets
p.o.

U. Ingmann

SN03715

66

Anmeldung Nr:
Application no.: 11290349.7
Demande no :

Anmeldetag:
Date of filing: 28.07.11
Date de dépôt :

Anmelder / Applicant(s) / Demandeur(s):

IFP
1-4 Avenue de Bois Préau
92852 Rueil-Malmaison Cédex/FR

Total Petrochemicals Research Feluy
1.8 zone industrielle C
7181 Seneffe (Feluy)/BE

Bezeichnung der Erfindung / Title of the invention / Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

A process for removing oxygenated contaminants from an ethylene stream

In Anspruch genommene Priorität(en) / Priority(Priorities) claimed / Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen / State/Date/File no. / Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation / International Patent Classification / Classification internationale de brevets:

C07C7/00

Am Anmeldetag benannte Vertragstaaten / Contracting States designated at date of filing / Etats contractants désignées lors du dépôt:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Bemerkungen:
Remarks:
Remarques:

The applicant's name at the date of filing of the application was as follows:

IFP Energies nouvelles - Rueil Malmaison Cedex/FR

The registration of the changes has taken effect on 27.07.2012.

[Field of the invention]

The present invention is a process for removing oxygenated contaminants from an ethylene stream.

Olefins are traditionally produced from petroleum feedstocks by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s), such as ethylene and/or propylene, from a variety of hydrocarbon feedstock. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds. The limited supply and increasing cost of crude oil has prompted the search for alternative processes for producing hydrocarbon products.

Olefins can be produced by dehydration of the corresponding alcohol. Ethanol can be obtained by fermentation of carbohydrates. Made up of organic matter from living organisms, biomass is the world's leading renewable energy source. The effluent produced by the ethanol dehydration comprises essentially unconverted ethanol, water, ethylene, acetaldehyde. Acetaldehyde may cause problems in ethylene recovery operations. It may comprise also very small amounts of ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons. The weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene is most of time less than 20/80

[Background of the invention]

US 20030098281 A1 describes a method of controlling water and/or oxygenate concentrations of an olefin stream. The method includes contacting the olefin stream with a liquid absorbent. The liquid absorbent is selected from the group consisting of a polyol, amine, amide, nitrile, heterocyclic nitrogen containing compound, and mixtures thereof. A gaseous stream comprising essentially steam, ethylene, propylene and less than 2 w% of oxygenates is condensed in a quench tower. The overhead of said quench tower is washed with a caustic solution to remove CO_2 and then contacted with the liquid absorbent to remove the oxygenates.

WO 03 020670 A1 provides a method for removing oxygenated components such as acetaldehyde, CO_2 and/or water from an olefin stream. It explains it is desirable to remove such oxygenated components, since they may poison catalysts that are used to further process olefin composition. In addition, the presence of certain

oxygenated compounds, such as acetaldehyde, can cause fouling in other olefin purification units, e.g., acid gas treating units. The method comprises providing an olefin stream containing ethylene, propylene, C_4+ olefins and acetaldehyde. The olefin stream is separated into a first fraction and a second fraction, wherein the first fraction comprises at least a majority of the ethylene and/or propylene present in the olefin stream, and the second fraction comprises at least a majority of the C_4+ olefins and acetaldehyde present in the olefin stream. The first fraction is then acid gas treated by sodium hydroxide or potassium hydroxide. The olefin stream is separated by distillation, preferably, the distillation is extractive distillation using an extractant. The preferred extractant is a polar composition having an average boiling point of at least 38°C at 1 atm. Methanol is one type of preferred extractant.

WO 03 020672 A1 describes method of removing dimethyl ether from an ethylene and/or propylene containing stream. The olefin stream is passed to a water absorption column, methanol is used as the water absorbent. Methanol and entrained water, as well as some oxygenated hydrocarbon, is recovered as the bottoms stream of said water absorption column, an overhead olefin is recovered and sent to a distillation column. The distillation column separates ethylene and propylene, as well as lighter boiling point components from the dimethyl ether and heavier boiling point components, including C_4 + components and methanol remaining from the methanol wash. Additional methanol is added to the distillation column to reduce clathrate and/or free water formation in the distillation column. The ethylene and propylene containing stream exits the distillation column as overhead and the heavier boiling point components which include the dimethyl ether and C_4 + components exit the distillation column as the bottoms. Ethylene and propylene then flow to a caustic wash column.

WO 03 033438 A1 describes a method for processing an olefin stream containing oxygenates and water, comprising: providing an olefin stream containing oxygenates and water; dewatering the olefin stream; compressing the dewatered olefin stream; washing the olefin stream with methanol to remove at least a portion of the oxygenate from the olefin stream; contacting the methanol washed olefin stream with water; and fractionating the water contacted olefin stream. The revovered olefin stream (washed with methanol and then with water) is further sent to an alkali wash and a drying step. The olefin stream containing oxygenates and water is the effluent of an MTO process.

US 6,444,869 describes a process for the production of ethylene from an oxygenate conversion effluent stream. The oxygenate conversion effluent stream comprises hydrogen, methane, ethylene, ethane, propylene, propane and C_4+ olefins. This effluent is compressed, treated to remove oxygenates, passed to a carbon dioxide removal zone wherein carbon dioxide is absorbed by contacting a caustic solution or by contacting an amine solution in combination with a caustic solution in a conventional manner to remove the carbon dioxide, dried, then fractionation is made through a deethanizer and a demethanizer.

US 2005-0283038 A1 described a process for producing an olefins stream from a first vapor effluent stream from an oxygenate to olefin conversion reaction, said first vapor effluent stream comprising C_2 and C_3 olefins, C_4 hydrocarbons, and C_2 to C_6 carbonyl compounds. In the process, the temperature and pressure of the first vapor effluent stream are adjusted to produce a second vapor effluent stream having a pressure ranging from about 100 psig to about 350 psig (790 to 2514 kPa) and a temperature ranging from about 70° F. to about 120° F. (21 to 49° C.), said second vapor effluent stream containing about 50 wt. % or more C_4 hydrocarbons based upon the total weight of C_4 hydrocarbons in the first vapor effluent stream. The second vapor effluent stream is then washed with a liquid alcohol-containing stream to produce a third vapor effluent stream, whereafter the third vapor effluent stream is washed with liquid water to provide a fourth vapor effluent stream comprising the C_2 and C_3 olefins and about 1.0 wt. % or less C_2 to C_6 carbonyl compounds. In one embodiment of such a recovery process, at least part of the fourth vapor effluent stream is contacted with a basic component, such as caustic or an amine, to remove the bulk of the carbon dioxide therefrom (thus removing "acid gas" from the fourth vapor effluent stream), whereafter the CO_2-depleted stream is dried.

The main drawback of the above prior arts is the fouling of the caustic scrubber. The inlet gas to the caustic scrubber contains reactive oxygenates like aldehydes and ketones. These aldehydes react in the aldol condensation reaction in the caustic tower environment to form significant red oil polymers. This causes significant fouling concerns in the caustic tower which impact the unit run length. The spent caustic treatment with significant red oil polymer content is also an important concern as well as the spent caustic treatment and disposal issues. In addition there are the handling and disposal issues of red oil polymers.

It has now been discovered a process for removing oxygenated contaminants from an ethylene stream wherein there is no caustic wash to remove the CO_2 and no wash column to remove the oxygenates.

[Brief summary of the invention]

The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons,

b) sending said stream (A) to a C_2 splitter/deethanizer to produce
a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons,
an overhead comprising the remaining components,

c) sending said overhead to a fixed bed CO_2 adsorption zone to recover a stream essentially free of CO_2,

d) sending said stream essentially free of CO_2 to a demethanizer/CO stripper to recover an overhead comprising H_2, CH_4 and CO,
liquid ethylene at the bottoms.

In another embodiment the CO_2 removal step can be made on the recovered ethylene. In said embodiment the present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

a1) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons,

b1) sending said stream (A) to a C_2 splitter/deethanizer to produce
a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons,
an overhead comprising the remaining components,

c1) sending said overhead stream to a demethanizer/CO stripper to recover an overhead comprising H_2, CH_4 and CO,
liquid ethylene comprising CO_2 at the bottoms.

d1) sending said ethylene comprising CO_2 to a fixed bed CO_2 adsorption zone to recover an ethylene stream essentially free of CO_2.

In an embodiment the weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene in (A) is less than 10/90.

In an embodiment the weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene in (A) is less than 10/90 and above 0.1/99.9.

In an embodiment the weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene in (A) is less than 5/95.

In an embodiment the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

In an embodiment the proportion of oxygenates in (A) is up to 3000 wppm.

In an embodiment the proportion of oxygenates in (A) is up to 2000 wppm.

In an embodiment the proportion of H_2 in (A) is from 5 to 1000 wppm.

In an embodiment the proportion of H_2 in (A) is up to 800 wppm.

In an embodiment the proportion of H_2 in (A) is up to 500 wppm.

Advantageously "dried ethylene stream" at step a) means a water content less than 5 wppm, advantageously less than 3wppm and preferably less than 1 wppm.

In an embodiment when the dried ethylene stream (A) has been made by ethanol dehydration said stream (A) contains no acetylene and no diolefines.

Ethylene treated in accordance with this invention is particularly suitable for use as feedstock for making polyethylene homo or copolymer.

[Detailed description of the invention]

As regards the oxygenated contaminants one can cite ethanol, C_3 alcohols; ethers such as diethylether and methyl ethyl ether; carboxylic acids such as acetic acid; aldehydes such as acetaldehyde; ketones such as acetone; and esters such as methyl esters. Particularly problematic oxygenate contaminants in an alcohol dehydration are aldehydes.

As regards the ethylene stream (A) of step a), it can be originating from an ethanol dehydration reactor. As regards alcohol dehydration, such process is described in WO-2009-098262, WO-2009-098267, WO-2009-098268 and WO-2009-098269 the

content of which is incorporated in the present application. The present invention is very efficient for the purification of ethylene produced by dehydration of ethanol.

The outlet of said dehydration reactor comprises essentially ethylene and steam as well as minor amounts of oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons. "Minor amounts" means the weight ratio of ethane+CO+CO2+H2+CH4+C3+ hydrocarbons to ethylene is less than 20/80 and most of time less than 10/90.

Said outlet of dehydration reactor is initially cooled, typically in a quench tower employing water as the quench medium. In the quench tower, most of the water contained in the outlet of dehydration reactor is condensed and is removed from the bottom of the tower as a liquid water bottom stream. A part of said water bottom stream is cooled in a heat exchanger and recycled as quenching medium to the top of the quench column. The part of the water bottom stream which is not recycled as quenching medium may contain a part of the oxygenates and mostly unconverted ethanol if any. Said stream can be treated in a stripping column to recover a pure water stream. Ethylene, oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons are removed from the top of the quench tower at a pressure typically such as 1 to 3 bars absolute and are referred to as the contaminated ethylene stream. Advantageously said contaminated ethylene stream is successively compressed and cooled in one or more steps to remove the major part of water, further fed to a fixed bed drying zone and finally to the C_2 splitter/deethanizer of step b).

In the previous compression steps the recovered water contains a part of the oxygenated contaminants and hydrocarbons dissolved. The contaminated hydrocarbon stream can also be cooled before the first compression step and water recovered. In an embodiment the water recovered upon each cooling further to a compression step and upon cooling, if any, before the first compression step is sent to a stripping column to produce an overhead stream comprising essentially oxygenated contaminants and hydrocarbons and an essentially pure water bottoms stream. Optionally the overhead stream is burned to destroy the oxygenated contaminants and recover heat.

After the compression steps the contaminated ethylene stream is further fed to a fixed bed drying zone and finally to the C_2 splitter/deethanizer of step b). The fixed bed drying zone is known in itself.

As regards the C_2 splitter/deethanizer of step b), it is advantageously a distillation column. The overhead is a mixture of ethylene, CO, CO_2, H_2 and CH_4.

As regards the fixed bed CO_2 adsorption zone of step c), it can be any component capable to selectively remove CO_2. By way of example it is an available commercial fixed bed adsorption (PSA for pressure swing adsorption or TSA for temperature swing adsorption) using molecular sieves or basic oxides or mixture thereof. A stream essentially free of CO_2 is recovered. Said fixed bed can be regenerated, during regeneration the desorption produces a stream which can be treated anywhere. "Essentially" has to be interpretated in the light of the further use of ethylene. Should ethylene is to be polymerized CO_2 has to be 1 ppm vol or less and preferably 0.5 ppm vol or less.

As regards the demethanizer, purpose is to recover an overhead comprising H_2, CH_4 and CO and liquid ethylene at the bottoms. It is advantageously a distillation column.

As regards the operating conditions, The demethanizer of step d) has to be at a pressure high enough to operate at temperatures which are not too low. A demethanizer to recover an overhead comprising H_2, CH_4 and CO and liquid ethylene at the bottoms operating at 40 barg has an overhead temperature of around -40°C and a bottom temperature of around 0°C. The same demethanizer operating at 21 barg has an overhead temperature of -30°C and a bottom temperature of around -24°C. These temperatures and pressures are a function of the proportion of H_2, CH_4 and CO in the ethylene stream (A) and mainly of the proportion of H_2. The proportion of H_2, CH_4 and CO in the ethylene stream (A) and mainly the proportion of H_2 governs also the pressure and temperature of the C_2 splitter/deethanizer located upstream said demethanizer.

In an embodiment the pressure of step b) is selected to have a temperature of the C_2 splitter/deethanizer bottoms such as there is no oligomerization or polymerization of the oxygenates. By way of example said temperature should not exceed 100°C and advantageously not exceed 85°C. This temperature is function of the pressure and of the proportion of oxygenates in the mixture of

oxygenates+ethane+C_3+ hydrocarbons. The higher the proportion of oxygenates the higher the temperature. The higher the pressure the higher the temperature.

In an embodiment the C_2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C_2 splitter /deethanizer and the demethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in four compression stages in series, sent to the driers and finally to the C_2 splitter deethanizer.

Said embodiment is described on fig 1 wherein (1) is the C_2 splitter deethanizer, (2) and (3) the CO_2 adsorbers and (4) the demethanizer/CO stripper. The contaminated ethylene stream from the quench column has been dried and sent to the C_2 splitter deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons and an overhead comprising ethylene, CO, CO_2, H_2 and CH_4 (reflux of C_2 splitter deethanizer is not shown). Said overhead is sent to the CO_2 adsorbers (2) and (3) to recover a stream essentially free of CO_2 and then to the demethanizer/CO stripper (4) to recover an overhead comprising H_2, CH_4 and CO and liquid ethylene at the bottoms.

In an embodiment the pressure of the C_2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper. Advantageously the pressure of the C_2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C_2 splitter /deethanizer is ranging from 15 to 25 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in three compression stages in series, sent to the driers and finally to the C_2 splitter deethanizer. Then the overhead of the C_2 splitter deethanizer is compressed and sent through the CO_2 adsorbers to the demethanizer/CO stripper. Optionally the essentially CO_2 free stream leaving the fixed bed CO_2 adsorption zone is cooled, sent to a decanter to produce a liquid phase sent as a reflux to the C_2 splitter/deethanizer and a gaseous phase sent to the demethanizer/CO stripper. Advantage of this option is to avoid a condenser on top of the C_2 splitter/deethanizer and a reflux pump.

Said embodiment is described on fig 2. In addition to fig 1 there are additional equipment : a compressor (6) and a decanter (5). The contaminated ethylene stream from the quench column has been dried and sent at a pressure around 15 to 25 barg to

the C_2 splitter deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons and an overhead comprising ethylene, CO, CO_2, H_2 and CH_4. Said overhead is sent to the compressor (6) to increase the pressure of 15 to 25 barg over the C_2 splitter /deethanizer pressure, cooled (the cooler is not shown) and sent to the CO_2 adsorbers (2) and (3) to recover a stream essentially free of CO_2. Then said CO_2 free stream is cooled (the cooler is not shown) and sent to the decanter (5) to produce a liquid phase sent as a reflux to the C_2 splitter deethanizer (1) and a gaseous phase sent to the demethanizer/CO stripper (4). Said demethanizer/CO stripper (4) produces an overhead comprising H_2, CH_4 and CO and liquid ethylene at the bottoms.

In a specific example according to fig 2 the pressure of the splitter/deethanizer is around 15 to 25 barg, the temperature on top of said splitter/deethanizer around -25°C to -35°C, the temperature on bottoms of said splitter/deethanizer around 70 to 90°C, the pressure of the demethanizer/CO stripper around 35 to 45 barg, the top of the demethanizer/CO stripper is condensed at a temperature around -35 to -45°C and the temperature on bottoms of the demethanizer/CO stripper is around -10 to 10°C.

Advantageously the pressure of the splitter/deethanizer is around 18 to 20 barg, the temperature on top of said splitter/deethanizer around -28°C to -32°C, the temperature on bottoms of said splitter/deethanizer around 78 to 82°C, the pressure of the demethanizer/CO stripper around 38 to 42 barg, the top of the demethanizer/CO stripper is condensed at a temperature around -38 to -42°C and the temperature on bottoms of the demethanizer/CO stripper is around -2 to 2°C.

As regards the other embodiment wherein the CO_2 removal step is made on the recovered ethylene, it works in a similar way as explained above in which the CO_2 removal step is before the demethanizer/CO stripper.

In an embodiment the C_2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C_2 splitter /deethanizer and the demethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in four compression stages in series, sent to the driers and finally to the C_2 splitter deethanizer.

Said embodiment is described on fig 3 wherein (1) is the C_2 splitter deethanizer, (2) and (3) the CO_2 adsorbers and (4) the demethanizer/CO stripper. The contaminated ethylene stream from the quench column has been dried and sent to the C_2 splitter

deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons and an overhead comprising ethylene, CO, CO_2, H_2 and CH_4. Said overhead is sent the demethanizer/CO stripper (4) to recover an overhead comprising H_2, CH_4 and CO and liquid ethylene comprising CO_2 at the bottoms. Said ethylene comprising CO_2 is sent to a fixed bed CO_2 adsorption zone, the CO_2 adsorbers (2) and (3) to recover an ethylene stream essentially free of CO_2.

In an embodiment the pressure of the C_2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper. Advantageously the pressure of the C_2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C_2 splitter /deethanizer is ranging from 15 to 25 barg. In this embodiment the contaminated ethylene stream coming from the quench column is advantageously compressed in three compression stages in series, sent to the driers and finally to the C_2 splitter deethanizer. Then the overhead of the C_2 splitter deethanizer is compressed and sent to the demethanizer/CO stripper.

Said embodiment is described on fig 4. In addition to fig 3 there are additional equipment : a compressor (6). The contaminated ethylene stream from the quench column has been dried and sent at a pressure around 15 to 25 barg to the C_2 splitter deethanizer (1) to produce a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons and an overhead comprising ethylene, CO, CO_2, H_2 and CH_4. Said overhead is sent to the compressor (6) to increase the pressure of 15 to 25 barg over the C_2 splitter /deethanizer pressure, and then to the demethanizer/CO stripper (4). Said demethanizer/CO stripper (4) produces an overhead comprising H_2, CH_4 and CO and liquid ethylene comprising CO_2 at the bottoms. Said ethylene comprising CO_2 is sent to a fixed bed CO_2 adsorption zone, the CO_2 adsorbers (2) and (3) to recover an ethylene stream essentially free of CO_2.

In a specific example according to fig 4 the pressure of the splitter/deethanizer is around 15 to 25 barg, the temperature on top of said splitter/deethanizer around -25°C to -35°C, the temperature on bottoms of said splitter/deethanizer around 70 to 90°C, the pressure of the demethanizer/CO stripper around 35 to 45 barg, the top of the demethanizer/CO stripper is condensed at a temperature around -35 to -45°C and the temperature on bottoms of the demethanizer/CO stripper is around -10 to 10°C.

Advantageously the pressure of the splitter/deethanizer is around 18 to 20 barg, the temperature on top of said splitter/deethanizer around -28°C to -32°C, the

temperature on bottoms of said splitter/deethanizer around 78 to 82°C, the pressure of the demethanizer/CO stripper around 38 to 42 barg, the top of the demethanizer/CO stripper is condensed at a temperature around -38 to -42°C and the temperature on bottoms of the demethanizer/CO stripper is around -2 to 2°C.

[Example]

The process according to fig 5 is operated. Fig 5 is derived from fig 4 by changing the position of the CO_2 adsorbers, they are located a the inlet of the demethanizer instead of the bottom of said demethanizer. The results are on the following table.

stream No on fig 5		1	2	3
		C2 splitter feed	C2 splitter bottoms	C2 splitter vapor distillat
Temperature	°C	15	80	-30
Pressure	bar g	20	19	19
H_2	kg/h	8		8
CO	kg/h	1		1
CO_2	kg/h	1		1
ethane	kg/h	23	11	12
ethylene	kg/h	25108	30	25078
acetaldehydes	kg/h	150	150	
C_3+	kg/h	715	715	
Total	kg/h	26006	906	25100

stream No on fig 5		4	6	5
		Demethanizer feed	Demethanizer purge	Ethylene product
Temperature	°C	-2	-40	20
Pressure	bar g	40	40	20
H_2	kg/h	8	8	
CO	kg/h	1	1	
CO_2	kg/h			
ethane	kg/h	12		12
ethylene	kg/h	25078	90	24988
acetaldehydes	kg/h			
C_3+	kg/h			
Total	kg/h	25099	99	25000

CLAIMS

1 Process for removing oxygenated contaminants from an ethylene stream comprising :

a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons,

b) sending said stream (A) to a C_2 splitter/deethanizer to produce
a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons,
an overhead comprising the remaining components,

c) sending said overhead to a fixed bed CO_2 adsorption zone to recover a stream essentially free of CO_2,

d) sending said stream essentially free of CO_2 to a demethanizer/CO stripper to recover an overhead comprising H_2, CH_4 and CO,
liquid ethylene at the bottoms.

2 Process according to claim 1 wherein the C_2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C_2 splitter /deethanizer and the demethanizer for transfer of fluids and said pressure is ranging from 15 to 45 barg.

3 Process according to claim 1 wherein the pressure of the C_2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper, the pressure of the C_2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C_2 splitter /deethanizer is ranging from 15 to 25 barg.

4 Process according to any one of the preceding claims wherein the overhead of the C_2 splitter deethanizer is compressed and sent through the CO_2 adsorbers to the demethanizer/CO stripper.

5 Process according to claim 4 wherein the essentially CO_2 free stream leaving the fixed bed CO_2 adsorption zone is cooled, sent to a decanter to produce a liquid phase sent as a reflux to the C_2 splitter deethanizer and a gaseous phase sent to the demethanizer/CO stripper.

6 Process for removing oxygenated contaminants from an ethylene stream comprising :

a1) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons,

b1) sending said stream (A) to a C_2 splitter/deethanizer to produce
a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons,
an overhead comprising the remaining components,

c1) sending said overhead stream to a demethanizer/CO stripper to recover an overhead comprising H_2, CH_4 and CO,
liquid ethylene comprising CO_2 at the bottoms.

d1) sending said ethylene comprising CO_2 to a fixed bed CO_2 adsorption zone to recover an ethylene stream essentially free of CO_2.

7 Process according to claim 6 wherein the C_2 splitter /deethanizer and the demethanizer are operating at the same pressure except the pressure drop between the C_2 splitter /deethanizer and the demethanizer for transfer of fluids and said pressure is ranging from 15 to 45 barg.

8 Process according to claim 6 wherein the pressure of the C_2 splitter /deethanizer is lower than the pressure of the demethanizer/CO stripper, the pressure of the C_2 splitter /deethanizer is ranging from 15 to 25 barg and simultaneously the pressure difference between the demethanizer/CO stripper and the C_2 splitter /deethanizer is ranging from 15 to 25 barg.

9 Process according to any one of claims 6 to 8 wherein the overhead of the C_2 splitter deethanizer is compressed and sent to the demethanizer/CO stripper.

10 Process according to any one of the preceding claims wherein the weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene in (A) is less than 10/90.

11 Process according to claim 10 wherein the weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene in (A) is less than 10/90 and above 0.1/99.9.

12 Process according to any one of claims 1 to 9 or claim 11 wherein the weight ratio of ethane+CO+CO_2+H_2+CH_4+C_3+ hydrocarbons to ethylene in (A) is less than 5/95.

13 Process according to any one of the preceding claims wherein the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

14 Process according to any one of the preceding claims wherein wherein the proportion of oxygenates in (A) is up to 3000 wppm.

15 Process according to claim 14 wherein the proportion of oxygenates in (A) is up to 2000 wppm.

16 Process according to any one of the preceding claims wherein the proportion of H_2 in (A) is from 5 to 1000 wppm.

17 Process according to any one of the preceding claims wherein the proportion of H_2 in (A) is up to 800 wppm.

18 Process according to claim 17 wherein the proportion of H_2 in (A) is up to 500 wppm.

PATENT

IFP Energies nouvelles et TOTAL Petrochemicals Research Feluy

A PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN ETHYLENE STREAM

Inventors : Babua DAS, Manuela ARRATIA, Catherine BOUTROT

ABSTRACT

The present invention is a process for removing oxygenated contaminants from an ethylene stream comprising :

a) providing a dried ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO_2, H_2, CH_4 and C_3+ hydrocarbons,

b) sending said stream (A) to a C_2 splitter/deethanizer to produce
a bottom stream comprising essentially ethane, oxygenates and C_3+ hydrocarbons,
an overhead comprising the remaining components,

c) sending said overhead to a fixed bed CO_2 adsorption zone to recover a stream essentially free of CO_2,

d) sending said stream essentially free of CO_2 to a demethanizer/CO stripper to recover an overhead comprising H_2, CH_4 and CO,
liquid ethylene at the bottoms.

In another embodiment the CO_2 removal step can be made on the recovered ethylene.

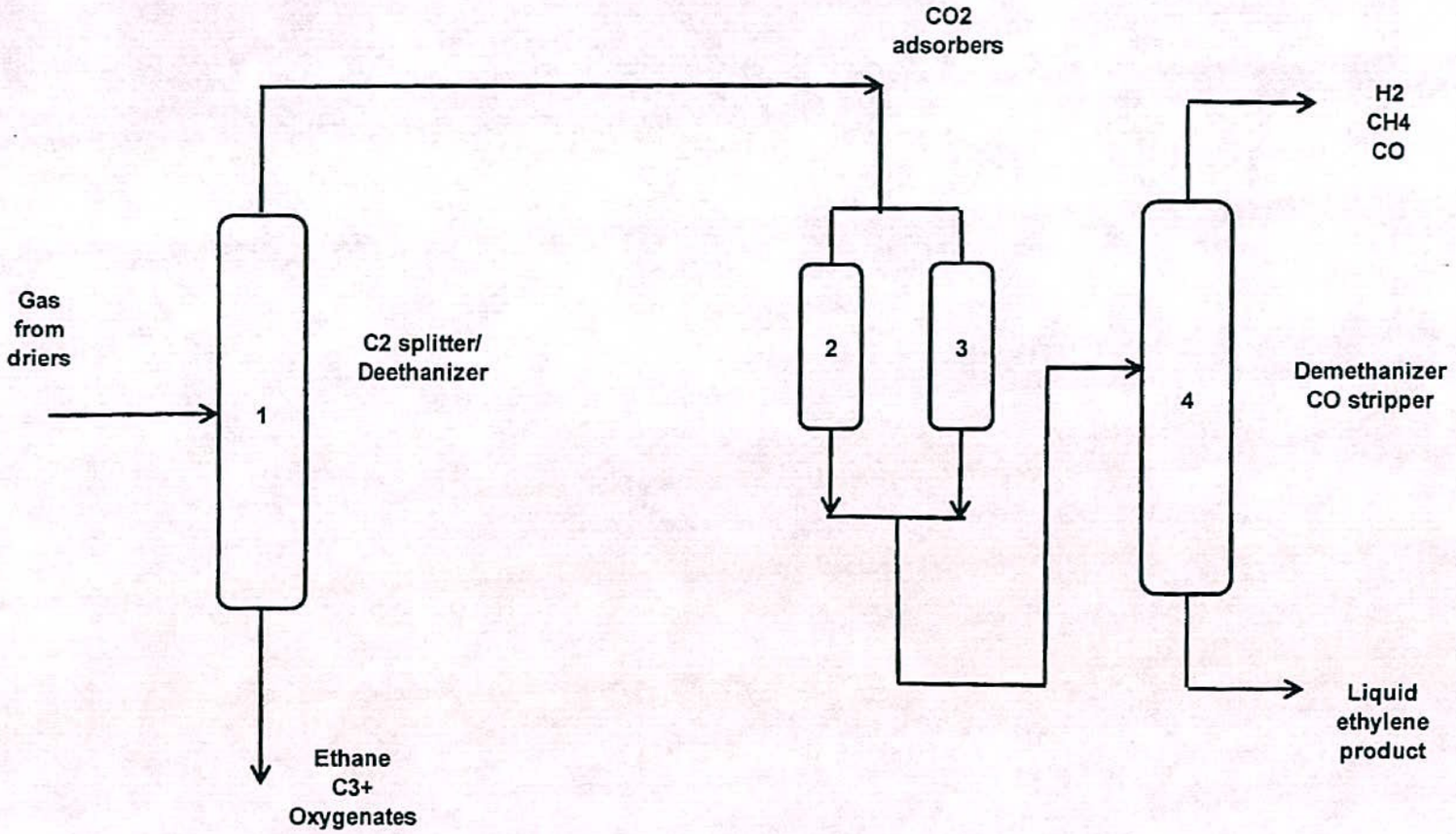

CO2
adsorbers
H2
CH4
CO
Gas
from
driers
C2 splitter/
Deethanizer
1
2
3
4
Demethanizer
CO stripper
Liquid
ethylene
product
Ethane
C3+
Oxygenates

Fig 1

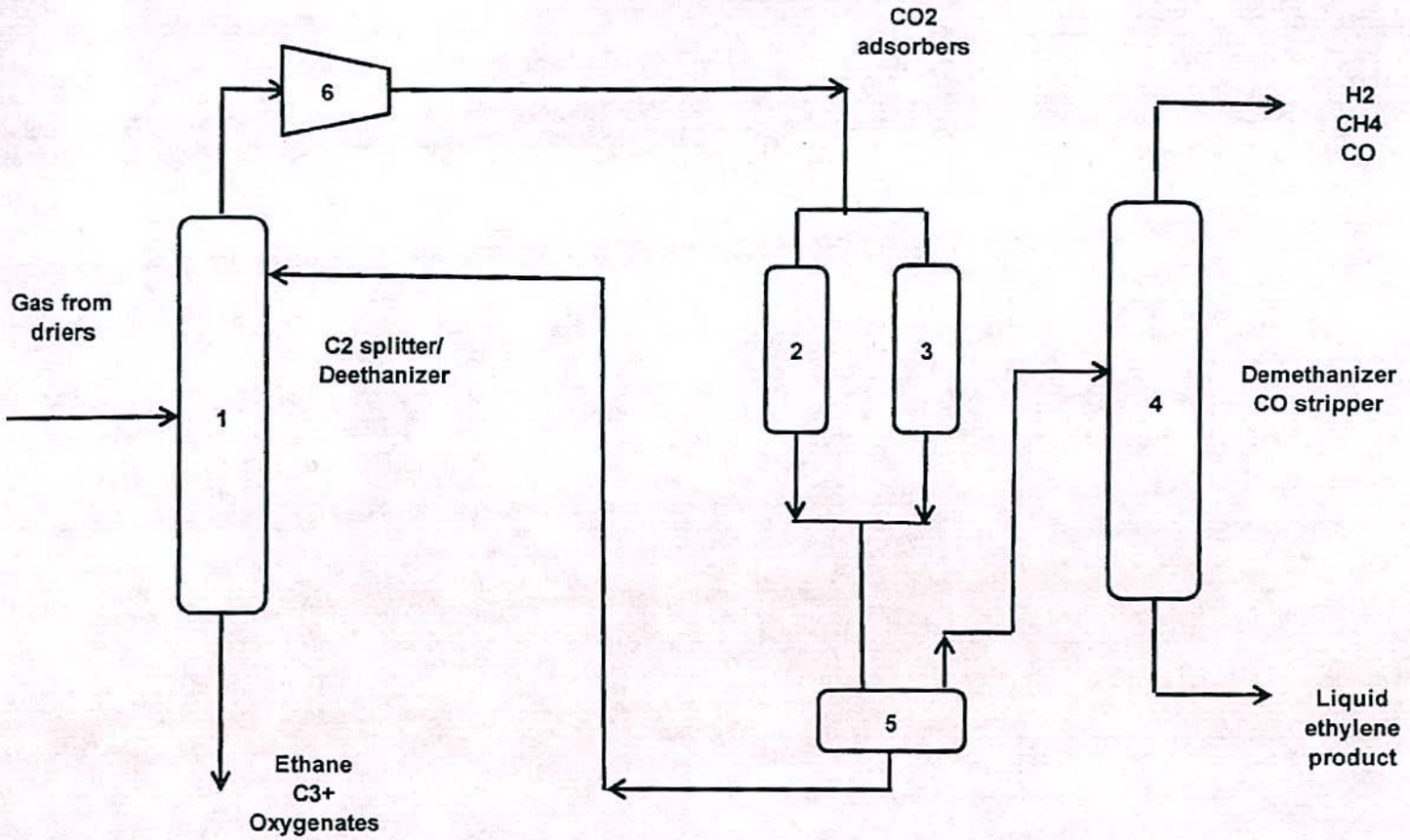

CO2
adsorbers
6
H2
CH4
CO
Gas from
driers
C2 splitter/
Deethanizer
2
3
4
Demethanizer
CO stripper
1
5
Liquid
ethylene
product
Ethane
C3+
Oxygenates

Fig 2

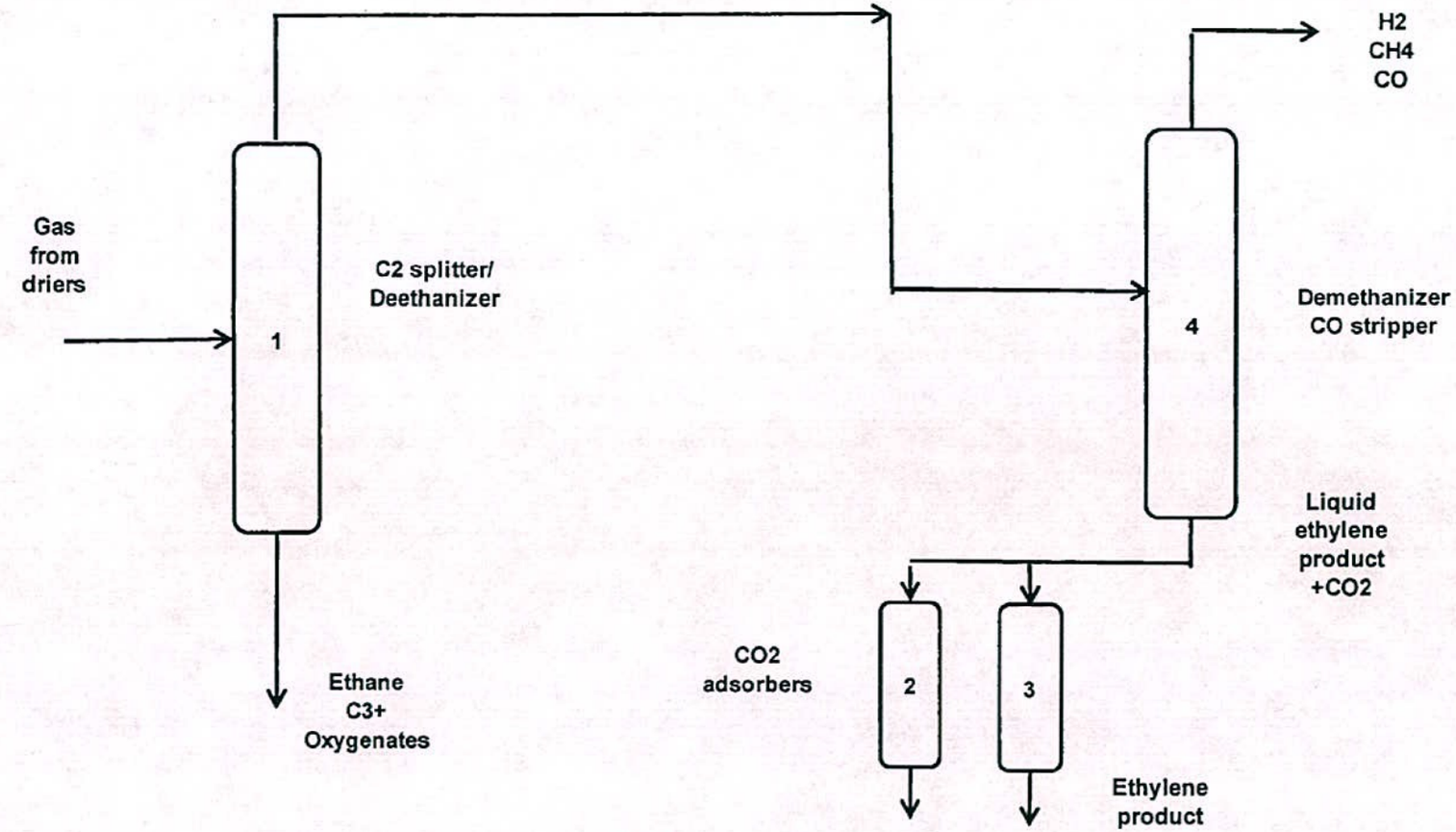

Gas
from
driers
1
C2 splitter/
Deethanizer
Ethane
C3+
Oxygenates
H2
CH4
CO
4
Demethanizer
CO stripper
Liquid
ethylene
product
+CO2
CO2
adsorbers
2
3
Ethylene
product

Fig 3

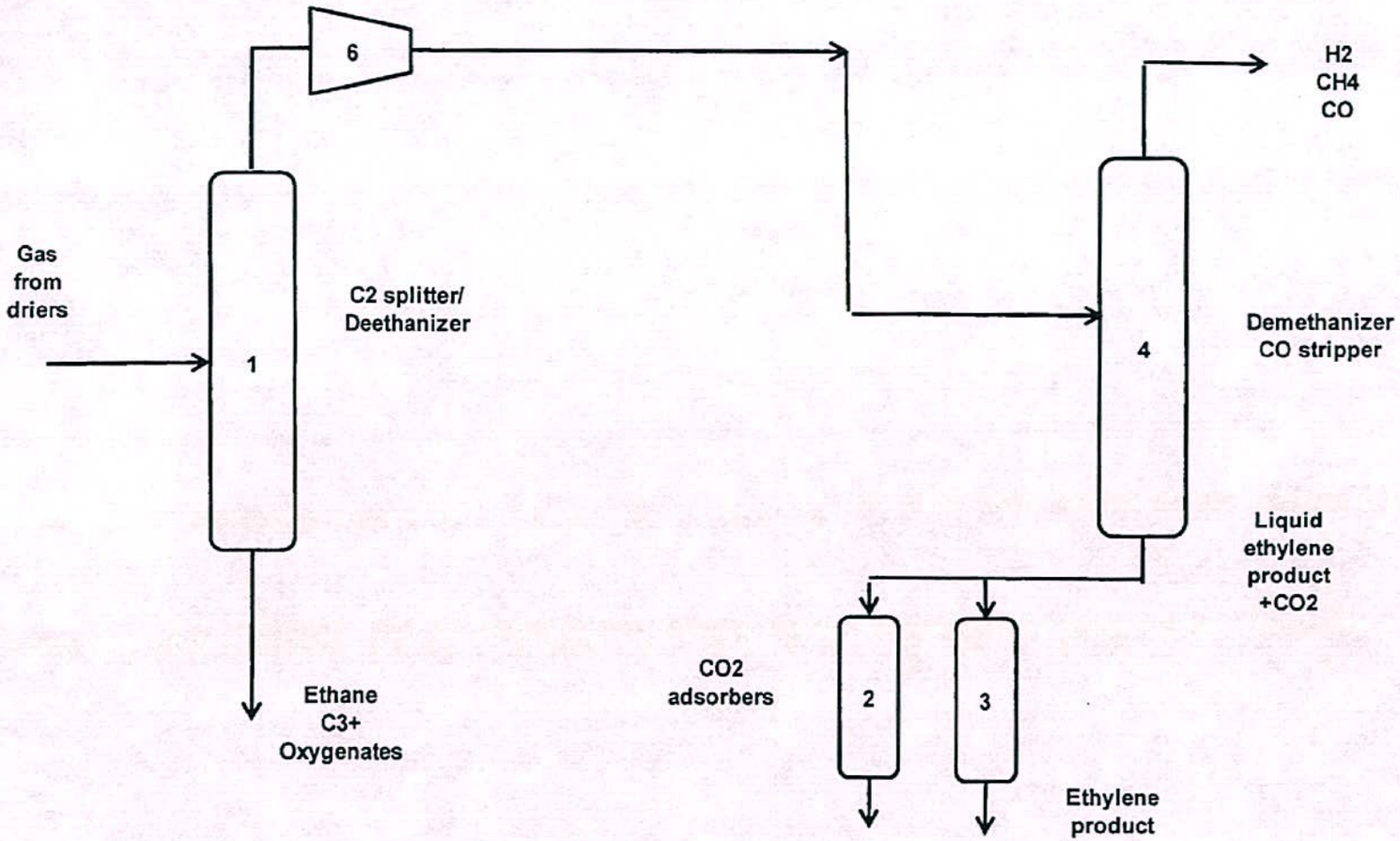

6
H2
CH4
CO
Gas
from
driers
C2 splitter/
Deethanizer
1
4
Demethanizer
CO stripper
Liquid
ethylene
product
+CO2
CO2
adsorbers
2
3
Ethane
C3+
Oxygenates
Ethylene
product

Fig 4

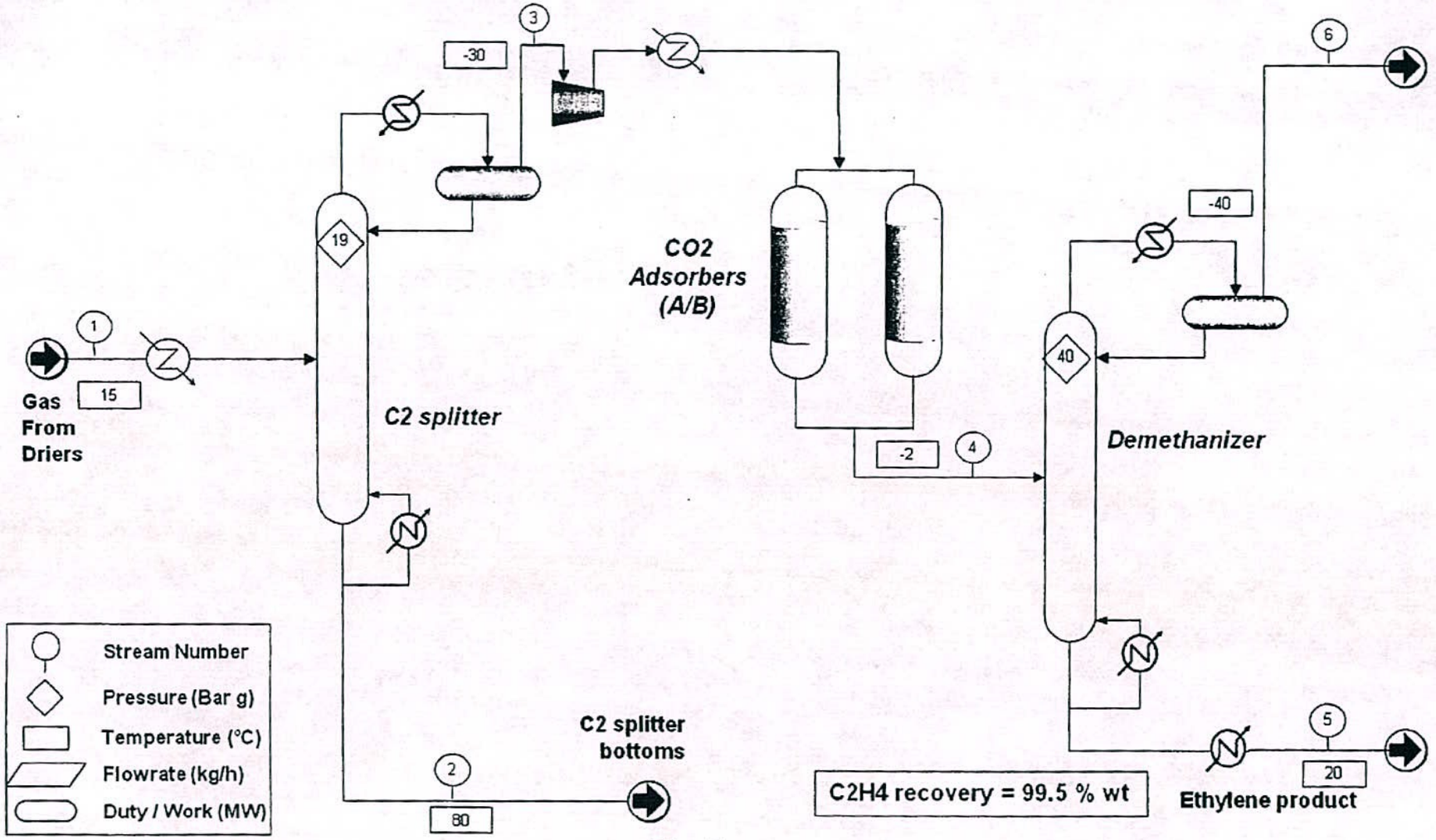

3
-30
6
19
CO2
Adsorbers
(A/B)
-40
1
15
Gas
From
Driers
C2 splitter
40
Demethanizer
-2
4
Stream Number
Pressure (Bar g)
Temperature (°C)
Flowrate (kg/h)
Duty / Work (MW)
C2 splitter
bottoms
5
20
2
80
C2H4 recovery = 99.5 % wt
Ethylene product

Fig 5

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION, OBTENTION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

TOTAL PETROCHEMICALS RESEARCH FELUY
Zone Industrielle C
B-7181 Seneffe (Feluy)
BELGIQUE

Date of mailing *(day/month/year)* 16 August 2012 (16.08.2012)	
Applicant's or agent's file reference F-1300-WO	**IMPORTANT NOTIFICATION**
International application No. PCT/EP2012/063755	International filing date *(day/month/year)* 13 July 2012 (13.07.2012)
International publication date *(day/month/year)* **Not yet published**	Priority date *(day/month/year)* 28 July 2011 (28.07.2011)
Applicant TOTAL PETROCHEMICALS RESEARCH FELUY et al	

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-*bis*)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
28 July 2011 (28.07.2011)	11290349.7	EP	13 August 2012 (13.08.2012)

The letters "NR" denote a priority document which, on the date of mailing of this Form, had not yet been received or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-*bis*). Where the applicant has failed to either submit, request to prepare and transmit, or to request the International Bureau to obtain the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

An asterisk "*" next to a date of receipt, denotes a priority document submitted or transmitted to or obtained by the International Bureau but not in compliance with Rule 17.1(a), (b) or (b-*bis*) (the priority document was received after the time limit prescribed in Rule 17.1(a); the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b) or the request to the International Bureau to obtain the priority document was made after the applicable time limit under Rule 17.1(b-*bis*)). Even though the priority document was not furnished in compliance with Rule 17.1(a), (b) or (b-*bis*), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 70

Authorized officer
Agnès Wittmann-Regis
e-mail pt06.pct@wipo.int
Telephone No. +41 22 338 74 06

42

PATENT COOPERATION TREATY PCT/EP2012/063755

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

TOTAL RESEARCH & TECHNOLOGY FELUY
Zone Industrielle C
B-7181 Seneffe
BELGIQUE

Date of mailing *(day/month/year)*
23 August 2012 (23.08.2012)

Applicant's or agent's file reference
F-1300-WO

IMPORTANT NOTIFICATION

International application No.
PCT/EP2012/063755

International filing date *(day/month/year)*
13 July 2012 (13.07.2012)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address
TOTAL PETROCHEMICALS RESEARCH FELUY
Zone Industrielle C
B-7181 Seneffe (Feluy)
Belgium

State of Nationality: BE
State of Residence: BE
Telephone No.:
Facsimile No.:
E-mail address:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address
TOTAL RESEARCH & TECHNOLOGY FELUY
Zone Industrielle C
B-7181 Seneffe
Belgium

State of Nationality: BE
State of Residence: BE
Telephone No.:
Facsimile No.:
E-mail address:
☐ Notifications by e-mail authorized

3. Further observations, if necessary:
The above change has also been recorded in respect of the address for correspondence, as indicated in the addressee box at the top of this form.

4. A copy of this notification has been sent to:

☒ the receiving Office
☒ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☐ the International Preliminary Examining Authority
☐ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer
Blanc Veronique
e-mail pt06.pct@wipo.int
Telephone No. +41 22 338 74 06

PATENT COOPERATION TREATY PCT/EP2012/063755

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

TOTAL RESEARCH & TECHNOLOGY FELUY
Zone Industrielle C
B-7181 Seneffe
BELGIQUE

Date of mailing *(day/month/year)*
14 January 2014 (14.01.2014)

Applicant's or agent's file reference
F-1300-WO

IMPORTANT NOTIFICATION

International application No.
PCT/EP2012/063755

International filing date *(day/month/year)*
13 July 2012 (13.07.2012)

1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address
ARRIATA, Manuela
35 rue Saint Georges
F-75009 Paris
France

State of Nationality: VE
State of Residence: FR
Telephone No.:
Facsimile No.:
E-mail address:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address
ARRATIA, Manuela
35 rue Saint Georges
F-75009 Paris
France

State of Nationality: VE
State of Residence: FR
Telephone No.:
Facsimile No.:
E-mail address:
☐ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☐ the International Preliminary Examining Authority
☒ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 89 70

Authorized officer
Rochaix Thomas
e-mail pt06.pct@wipo.int
Telephone No. +41 22 338 74 06

84

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -

Industria y Comercio
SUPERINTENDENCIA

RECIBO DE CAJA

No. 14 - 0019353

Bogotá D.C., Febrero 19 de 2014 - 14:30:55

RECIBIDO DE : POSSE HERRERA & RUIZ S.A NI 830.122.196 RE

*** Soporte del Pago ***

TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR PAGO
RECIBO DE CA	999999999	17317	13/02/2014		52.000.00
CONSIGNACION	BANCO DE BOGOTA	062754387	650554800	13/02/2014	2.520.000.00

*** Conceptos Pagados ***

CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE INVENCION	515.000.00	515.000.00
				$515.000.00

==========

SON: **QUINIENTOSQUINCE MIL PESOS MONEDA CORRIENTE***

Responsable: _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 14-034844- -00000-0000
Fecha: 2014-02-19 14:57:07 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 86

85

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -

Industria y Comercio
SUPERINTENDENCIA

RECIBO DE CAJA

No. 14 - 0019357

Bogotá D.C., Febrero 19 de 2014 - 14:30:55

RECIBIDO DE : POSSE HERRERA & RUIZ S.A NI 830.122.196 RE

*** Soporte del Pago ***

TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR.PAGO
RECIBO DE CA	999999999	17317	13/02/2014		52.000.00
CONSIGNACION	BANCO DE BOGOTA	062754387	650554800	13/02/2014	2.520.000.00

*** Conceptos Pagados ***

CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
9	50005-01-01 SOLICITUDES	1607 REIVINDICACION PATENTE UNITARIA ADICIONAL A LAS 10 INIC	31.000.00	279.000.00
				$279.000.00

==========

SON: **DOSCIENTOS SETENTA Y NUEVE MIL PESOS MONEDA CORRIENTE***

Responsable: _____
-*****-

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 14-034844- -00000-0000

Fecha: 2014-02-19 14:57:07 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 86

(36)

Industria y Comercio
SUPERINTENDENCIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 14-034844- -00000-0000

Fecha: 2014-02-19 14:57:07 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 86

PATENTE DE INVENCIÓN ☐ **MODELO DE U**

- ☐ Indicación que se solicita una patente.
- ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
- ☐ Descripción de la invención
- ☐ Dibujos de ser estos pertinentes
- ☐ Comprobante de pago de las tasas establecidas (De ser el caso formato de descuento)

Completa ☐ Incompleta ☐

PATENTE DE INVENCIÓN PCT ☐ **MODELO DE UTILIDAD PCT** ☐ **Art.33 Decisión 486/00, Circular Única**

- ☐ Indicación que se solicita una PCT
- ☐ Copia de la solicitud en español, tal como fue presentada inicialmente (capítulo descriptivo, reivindicatorio, resumen)
- ☐ Dibujos de ser estos pertinentes
- ☐ Comprobante de pago de las tasas establecidas (de ser el caso formato de descuento)

Completa ☐ Incompleta ☐

DISEÑO INDUSTRIAL ☐ **(Art. 119 Decisión 486/00)**

- ☐ Indicación que se solicita Diseño industrial
- ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
- ☐ Representación gráfica y fotográfica del Diseño industrial o muestra del material que incorpora el diseño
- ☐ Comprobante de pago de las tasas establecidas

Completa ☐ Incompleta ☐

ESQUEMA DE TRAZADO ☐ **(Art. 92 Decisión 486/00)**

- ☐ Indicación que se solicita un esquema de trazado
- ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
- ☐ Representación gráfica de un esquema de trazado
- ☐ Comprobante de pago de las tasas establecidas

Completa ☐ Incompleta ☐