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DELEGATURA DE NUEVAS CREACIONES

SOLICITUD
FASE NACIONAL -PCT

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

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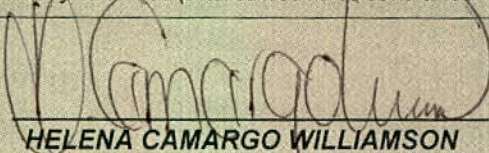
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22. BOGOTÁ D.C., FEBRERO 19 DE 2014

DIRECCIÓN DE NUEVAS CREACIONES
SOLICITUD FASE NACIONAL -PCT

1	TIPO DE SOLICITUD	☒ Patente de invención ☒ Capítulo I	☐ Patente de Modelo de Utilidad ☐ Capítulo II
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	PROCEDIMIENTO PARA LA ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE UNA CORRIENTE DE ETILENO		
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	☐ Los demás solicitantes y/o (demás) inventores se indican en una hoja a continuación.		

9	☐ REPRESENTANTE LEGAL ☒ APODERADO				
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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				
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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			Documentación Jurídica		
1. ☒ Descripción N° de folios:			9. ☒ Poderes, si fuera el caso.		
2. ☒ Reivindicaciones N° Reivindicaciones:			10. ☐ Documento que legalmente pruebe la cesión del inventor al solicitante o a su causante.		
3. ☒ Dibujos y/o figuras N° folios:			11. ☐ Copia del contrato de acceso de recursos genéticos o productos derivados, certificado o número de registro, si fuera el caso.		
4. ☒ Resumen.			12. ☐ Copia de la licencia o autorización de Conocimientos Tradicionales, certificado o número de registro, si fuera el caso.		
5. ☐ Certificado de depósito de material biológico si fuera el caso.			13. Reducción de tasas		
6. ☐ Listado de secuencias de nucleótidos y/o aminoácidos en forma digital si fuera el caso.			Micro, pequeñas o medianas empresas		
7. ☐ Arte final 12 x 12.			☐ Copia simple de la declaración de renta del año inmediatamente anterior, o en su defecto prueba documental idónea.		
8. ☐ Anexo formato digital.			☐ 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 PARA LA ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE
UNA CORRIENTE DE ETILENO**

Campo de la invención

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

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

Las olefinas pueden ser producidas por deshidratación del alcohol correspondiente. El etanol se puede obtener mediante fermentación de carbohidratos. Complementariamente a la materia orgánica 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 se pone después 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 luego 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 luego con agua) se envía después 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 para la 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, se hace después el fraccionamiento mediante un desetanizador y un desmetanizador.

El documento US 2005-0283038 A1 describe un procedimiento para la 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 70° F a aproximadamente 120° F (de 21 a 49° C), conteniendo dicha segunda corriente de efluente de vapor de aproximadamente un 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 luego 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 un 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 la 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 aldol 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 de la unidad. El tratamiento cáustico costoso con contenido significativo en polímeros de aceite rojo es también un problema importante así como también el tratamiento cáustico y la eliminación de desechos costosas. Además hay problemas de manipulación y eliminación de polímeros de aceite rojo.

Se ha descubierto ahora un procedimiento para la 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.

Breve sumario de la invención

La presente invención es, en una primera realización, un procedimiento para la eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

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

5 b) enviar dicha corriente (A) a un equipo depurador (también designado como desmetanizador) para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+, e

10 (i)

c) enviar dicha corriente de colas de la etapa b) a un desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+,

una corriente de cabezas que comprende esencialmente etileno y CO₂,

d) enviar dicha corriente de cabezas de la etapa c) a una zona de adsorción de CO₂ de

15 lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO₂,

o (ii)

c1) enviar dicha corriente de colas de la etapa b) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente esencialmente libre de CO₂, enviar después dicha corriente

a un desetanizador para producir

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

una corriente de cabezas que comprende esencialmente etileno esencialmente exento de CO₂.

El procedimiento anterior se denomina como realización 1.

25 En una segunda realización el desetanizador de la realización 1 se reemplaza con dos separadores C2.

Dicha segunda realización es un procedimiento para la eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

a) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno,

hasta un 1 % en peso de oxigenados, etano, CO, CO₂, H₂, CH₄ e hidrocarburos C₃+,

b) enviar dicha corriente (A) a un equipo depurador (también designado como desmetanizador) para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,

5 una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+, e

(i)

c) enviar dicha corriente de colas de la etapa b) a un separador C₂ primario para producir una corriente de colas que comprende esencialmente etano, oxigenados, hidrocarburos C₃+

10 y una porción de etileno,

una corriente de cabezas que comprende esencialmente etileno y CO₂,

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

e) enviar dicha corriente de colas de la etapa c) a un separador C₂ secundario para producir

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

una corriente de cabezas que comprende esencialmente etileno, reciclado opcionalmente a la zona de producción de la corriente (A)

o (ii)

20 c1) enviar dicha corriente de colas de la etapa b) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente esencialmente exenta de CO₂, enviar después dicha corriente a un separador C₂ primario para producir

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

25 una corriente de cabezas que comprende esencialmente etileno esencialmente exento de CO₂.

e1) enviar la corriente de colas de la etapa c1) a un separador C₂ secundario para producir

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

una corriente de cabezas que comprende esencialmente etileno, opcionalmente reciclado a la zona de producción de la corriente (A).

En una tercera realización el desmetanizador (equipo depurador) de la realización 1 es reemplazado por dos desmetanizadores.

Dicha tercera realización es un procedimiento para la 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 desmetanizador primario para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄ y una porción de etileno y etano,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+,

c) enviar dicha corriente de cabezas de la etapa b), opcionalmente a través de un compresor, a un desmetanizador secundario para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+, e

(i)

d) enviar dicha corriente de colas de la etapa b) y dicha corriente de colas de la etapa c) a un separador C₂ para producir

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

una corriente de cabezas que comprende esencialmente etileno y CO₂,

e) enviar dicha corriente de cabezas de la etapa b) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO₂,

o (ii)

d1) enviar dicha corriente de colas de la etapa b) y dicha corriente de colas de la etapa c) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente esencialmente libre

de CO₂, enviar luego dicha corriente a un separador C2 para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+, una corriente de cabezas que comprende esencialmente 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 poli(cloruros de vinilo) (PVC).

Descripción detallada de la invención

En lo que respecta a los contaminantes oxigenados también denominados 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 procedimiento de la invención.

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 procedimiento de la presente invención. La zona de secado de lecho fijo es en sí conocida.

En lo que respecta a la zona de adsorción de CO₂ de lecho fijo 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 aumentando 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, este es también designado como equipo depurador en la primera y segunda realizaciones y como un desmetanizador primario y secundario en la tercera realización. El fin de dicho desmetanizador es recuperar una corriente de cabezas que comprende esencialmente H₂, CH₄ y CO. De forma ventajosa se trata de una columna de destilación.

En lo que respecta a las condiciones de operación el desmetanizador 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 °C y una temperatura de colas en torno a 0 °C. El mismo desmetanizador que opera a 2100 kPa (21 barg) presenta una temperatura de cabezas de -30 °C una temperatura de colas en torno a -24 °C. 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.

En una realización la presión del separador C2 también designado como desetanizador 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. El separador C2/desetanizador es de forma ventajosa una columna de destilación.

En lo que respecta a la primera realización y al equipo depurador, este se trata de forma ventajosa de una columna de destilación. La corriente de cabezas es una mezcla esencialmente de CO, H₂ y CH₄. El desetanizador es de forma ventajosa una columna de destilación. La zona de adsorción de CO₂ de lecho fijo puede ser una adsorción de lecho fijo comercialmente disponible (TSA o PSA) como se describió anteriormente. Se recupera una corriente esencialmente exenta de CO₂.

En una realización el equipo depurador (desmetanizador) y el separador C2 / desetanizador se operan a la misma presión excepto la caída de presión entre el desmetanizador y el separador C2 / desetanizador para la transferencia de fluidos. De forma ventajosa la presión varía de 1500 a 4500 kPa (de 15 a 45 barg).

Se describe en la figura 1 un procedimiento de acuerdo con la primera realización, en la que 1 es el equipo depurador (desmetanizador), 2 y 3 los adsorbedores de CO₂ y 4 el desetanizador. En la parte superior del equipo depurador hay un condensador, un decantador que produce una fase líquida se envía como un reflujo a dicho equipo depurador y una fase gaseosa que es la corriente de cabezas, estos no se muestran en la figura 1. En las colas del equipo depurador hay un calderín no mostrado en la figura 1. El desetanizador tiene un equipamiento similar no mostrado en la figura 1. La corriente de etileno contaminada (A) que comprende esencialmente etileno, hasta un 1 % en peso de oxigenados, etano, CO, CO₂, H₂, CH₄ e hidrocarburos C₃+ se ha secado y enviado al equipo depurador 1 (también designado como un desmetanizador) para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,
una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+,
dicha corriente de colas del equipo depurador 1 se envía al desetanizador 4 para producir
una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+,
una corriente de cabezas que comprende esencialmente etileno y CO₂,
dicha corriente de cabezas del desetanizador 4 se envía a una zona de adsorción de CO₂ de lecho fijo 2 y 3 para recuperar una corriente de etileno esencialmente exenta de CO₂.

10 En un ejemplo específico la presión del equipo depurador varía de 1500 a 3000 kPa (de 15 a 30 barg) y la presión del desetanizador y de los adsorbedores de CO₂ es aproximadamente de 100 ó 200 kPa (1 ó 2 barg) menor de lo que corresponde a la caída de presión debida a conductos y equipamiento. En este intervalo de presión la temperatura en la parte superior del equipo depurador y después del condensador varía de -20 a -30 °C,
15 variando la temperatura en colas del equipo depurador de -15 a -25 °C, la temperatura en la parte superior del desetanizador y tras el condensador varía de -30 a -20 °C y la temperatura en colas del desetanizador varía de 75 a 85 °C.

Preferiblemente la presión del equipo depurador varía de 2000 a 2500 kPa (de 20 a 25 barg) y la presión del desetanizador y de los adsorbedores de CO₂ es aproximadamente
20 100 ó 200 kPa (1 ó 2 barg) menor de lo que corresponde a la caída de presión debida a conductos y equipamiento. En este intervalo de presión la temperatura en la parte superior del equipo depurador y después del condensador varía de -22 a -26 °C, la temperatura en colas del equipo depurador varía de -20 a -24 °C, la temperatura de la parte superior del desetanizador y después del condensador varía de -27 a -22 °C y la temperatura de colas del
25 desetanizador varía de 78 a 82 °C.

En otro ejemplo específico la presión del equipo depurador varía de 3500 a 4500 kPa (de 35 a 45 barg) y la presión del desetanizador y de los adsorbedores de CO₂ es aproximadamente de 1500 a 2500 kPa (de 15 a 25 barg) menos. De forma ventajosa la presión del desetanizador varía de 1500 a 2500 kPa (de 15 a 25 barg). En este intervalo de

presión la parte superior del equipo depurador se encuentra a una temperatura en el intervalo de -10 a 0 °C y condensa a una temperatura que varía de -35 a -45 °C, la temperatura en colas del equipo depurador varía de -5 a 5 °C, la temperatura en la parte superior del desetanizador varía de -25 a -35 °C, se condensa a una temperatura en el intervalo de -25 a -35 °C y la temperatura en colas del desetanizador varía de 75 a 85 °C.

Preferiblemente la presión del equipo depurador varía de 3800 a 4200 kPa (de 38 a 42 barg) y la presión del desetanizador y de los adsorbedores de CO2 varía de 1700 a 2200 kPa (de 17 a 22 barg). En este intervalo de presión la parte superior del equipo depurador se encuentra a una temperatura en el intervalo de -8 a -2 °C y condensa a una temperatura que varía de -38 a -42 °C, la temperatura en colas del equipo depurador varía de 0 a 5 °C, la temperatura en la parte superior del desetanizador varía de -28 a -32 °C, se condensa a una temperatura en el intervalo de -28 a -32 °C y la temperatura en colas del desetanizador varía de 78 a 82 °C.

En lo que respecta a la segunda realización y al desmetanizador, es de forma ventajosa una columna de destilación. Los separadores primarios y secundarios son cada uno de forma ventajosa una columna de destilación. La zona de adsorción de CO2 de lecho fijo se ha descrito ya anteriormente. Se recupera una corriente esencialmente exenta del CO2.

En una realización el desmetanizador y el separador C2 primario y secundario/desetanizador se operan a la misma presión excepto la caída de presión para la transferencia de fluidos. De forma ventajosa la presión varía de 1500 a 4500 kPa (de 15 a 45 barg).

Se describe en la figura 2 un procedimiento de acuerdo con la segunda realización, en la que 1 es el desmetanizador, 2 y 3 los adsorbedores de CO2, 4 el separador C2 primario y 5 el separador C2 secundario. En la parte superior del desmetanizador hay un condensador, un decantador que produce una fase líquida enviada como un reflujo de dicho desmetanizador y una fase gaseosa que es la corriente de cabezas, estas no se muestran en la figura 2. En colas del desmetanizador hay un calderín no mostrado en la figura 2. El separador C2 primario y el separador C2 secundario tienen cada uno un equipamiento

similar no mostrado en la figura 2.

La corriente de etileno (A) contaminada que comprende esencialmente etileno, hasta un 1 % en peso de oxigenados, etano, CO, CO₂, H₂, CH₄ e hidrocarburos C₃+ que se ha secado y enviado al desmetanizador 1

5 para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+,

dicha corriente de colas del desmetanizador 1 se envía al separador C2 primario 4 para

10 producir

una corriente de colas que comprende esencialmente etano, oxigenados, hidrocarburos C₃+ y una porción de etileno,

una corriente de cabezas que comprende esencialmente etileno y CO₂,

dicha corriente de cabezas del separador C2 primario 4 se envía a una zona de adsorción de

15 CO₂ de lecho fijo 2 y 3 para recuperar una corriente de etileno esencialmente exenta de CO₂,

la corriente de colas del separador C2 primario 4 se envía a un separador C2 secundario 5 para producir

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

una corriente de cabezas que comprende esencialmente etileno, opcionalmente reciclado a la zona de producción de corriente (A).

En un ejemplo específico la presión del desmetanizador varía de 3500 a 4500 kPa (de 35 a 45 barg) y la presión del separador C2 primario y de los adsorbedores de CO₂ es
25 aproximadamente 100 ó 200 kPa (1 ó 2 barg) menor de lo que corresponde a la caída de presión debida a conductos y equipamiento. La presión del separador C2 secundario varía de 1500 a 2500 kPa (de 15 a 25 barg). En estos intervalos de presión la parte superior del desmetanizador se encuentra a una temperatura en el intervalo de -10 a 0 °C, se condensa a una temperatura que varía de -35 a -45 °C, la temperatura en colas del desmetanizador varía

de -5 a 5 °C, la parte superior del separador C2 primario se encuentra en un intervalo de temperatura de -5 a 5 °C, se condensa en un intervalo de temperatura de -5 a 5 °C, la temperatura en colas del separador C2 primario varía de 75 a 85 °C, la parte superior del separador C2 secundario se encuentra en un intervalo de temperatura de -25 a -35 °C, se condensa en un intervalo de temperatura de -25 a -35 °C, y la temperatura en colas del separador C2 secundario varía de 75 a 85 °C.

Preferiblemente la presión del desmetanizador varía de 3800 a 4200 kPa (de 38 a 42 barg) y la presión del separador C2 primario y de los adsorbedores de CO₂ es aproximadamente 100 ó 200 kPa (1 ó 2 barg) menor de lo que corresponde a la caída de presión debida a conductos y equipamiento. La presión del separador C2 secundario varía de 1800 a 2200 kPa (de 18 a 22 barg). En estos intervalos de presión la parte superior del desmetanizador se encuentra a un intervalo de temperatura de -8 a -2 °C, se condensa a una temperatura que varía de -38 a -42 °C, la temperatura en colas del desmetanizador varía de 0 a 4 °C, la parte superior del separador C2 primario se encuentra en un intervalo de temperatura de -4 a 0 °C, se condensa en un intervalo de temperatura de -4 a 0 °C, la temperatura en colas del separador C2 primario varía de 78 a 82 °C, la parte superior del separador C2 secundario se encuentra en un intervalo de temperatura de -28 a -32 °C, se condensa en un intervalo de temperatura de -28 a -32 °C, y la temperatura en colas del separador C2 secundario varía de 78 a 82 °C.

En lo que se refiere a la tercera realización y el desmetanizador primario y secundario, se tratan cada uno de forma ventajosa de una columna de destilación. El separador C2 es de forma ventajosa una columna de destilación. La zona de adsorción de CO₂ de lecho fijo ya se ha descrito anteriormente. Se recupera una corriente esencialmente exenta de CO₂.

En una realización los desmetanizadores primario, secundario y el separador/desmetanizador C2 se operan a la misma presión excepto en la caída de presión para transferencia de fluidos. De forma ventajosa la presión varía de 1500 a 4500 kPa (de 15 a 45 barg).

Se describe en la figura 3 un procedimiento de acuerdo con la tercera realización en

la que 1 es el desmetanizador primario, 2 y 3 los adsorbedores de CO₂, 4 el desmetanizador secundario, 5 el separador C2 y 6 el compresor. En la parte superior del desmetanizador primario hay un condensador, un decantador que produce una fase líquida que se envía como un reflujo a dicho desmetanizador primario y una fase gaseosa que es la corriente de cabezas, no se muestran en la figura 3. La corriente de cabezas del desmetanizador primario se envía al compresor. En las colas del desmetanizador primario hay un calderín no mostrado en la figura 3. El desmetanizador secundario y el separador C2 tienen cada uno un equipamiento similar no mostrado en la figura 3.

La corriente de etileno (A) contaminada que comprende esencialmente etileno, hasta el 1 % en peso de oxigenados, etano, CO, CO₂, H₂, CH₄ e hidrocarburos C₃+ que ha sido secada se envía a un desmetanizador primario 1 para producir

una corriente de cabezas que comprende esencialmente CO, H₂, CH₄ y una porción de etileno y etano,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+,

la corriente de cabezas del desmetanizador 1 se envía por un compresor 6 a un desmetanizador secundario 4 para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+,

dicha corriente de colas del desmetanizador secundario 4 y dicha corriente de colas del desmetanizador primario 1 se envían a un separador C2 5 para producir

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

una corriente de cabezas que comprende esencialmente etileno y CO₂,

dicha corriente de cabezas del separador C2 5 se envía a una zona de adsorción de CO₂ de lecho fijo 2-3 para recuperar una corriente de etileno esencialmente exenta de CO₂.

En un ejemplo específico la presión del desmetanizador primario varía de 1500 a 2500 kPa (de 15 a 25 barg), la presión del desmetanizador secundario varía de 4000 a 5000

kPa (de 40 a 50 barg), la presión del separador C2 es esencialmente la misma presión que el desmetanizador primario excepto la caída de presión para transferencia de fluidos y varía de 1500 a 2500 kPa (de 15 a 25 barg) y la presión del adsorbedor de CO₂ es aproximadamente 100 ó 200 kPa (1 ó 2 barg) menor de lo que corresponde a la caída de presión debida a los conductos y equipo. En estos intervalos de presión la parte superior del desmetanizador primario se encuentra en un intervalo de temperatura de -25 a -35 °C, condensa a una temperatura que varía de -25 a -35 °C, la temperatura en colas del desmetanizador primario varía de -30 a -20 °C, la parte superior del desmetanizador secundario se encuentra en un intervalo de temperatura de -10 a 0 °C, se condensa a una temperatura que varía de -30 a -40 °C, la temperatura en colas del desmetanizador secundario varía de 0 a 10 °C, la parte superior del separador C2 se encuentra en un intervalo de temperatura de -25 a -35 °C, se condensa en un intervalo de temperatura de -25 a -35 °C, y la temperatura en colas del separador C2 varía de 75 a 85 °C.

Preferiblemente la presión del desmetanizador primario varía de 1800 a 2200 kPa (de 18 a 22 barg), la presión del desmetanizador secundario varía de 4300 a 4700 kPa (de 43 a 47 barg), la presión del separador C2 es esencialmente la misma presión que la del desmetanizador primario excepto la caída de presión para la transferencia de fluidos y varía de 1800 a 2200 kPa (de 18 a 22 barg) y la presión del adsorbedor de CO₂ es aproximadamente 100 ó 200 kPa (1 ó 2 barg) menor de lo que correspondiente a la caída de presión debida a conductos y equipamiento. En estos intervalos de presión la caída del desmetanizador primario se encuentra en un intervalo de temperatura de -25 a -31 °C, condensa a una temperatura que varía de -27 a -32 °C, la temperatura en colas del desmetanizador primario varía de -28 a -22 °C, la parte superior del desmetanizador secundario se encuentra en un intervalo de temperatura de -6 a -2 °C, condensa a una temperatura que varía de -30 a -35 °C, la temperatura en colas del desmetanizador secundario varía de 3 a 8 °C, la parte superior del separador C2 se encuentra en un intervalo de temperatura de -28 a -32 °C, se condensa en un intervalo de temperatura de -28 a -32 °C, y la temperatura en colas del separador C2 varía de 78 a 82 °C.

Ejemplos

Se opera el procedimiento de acuerdo con la figura 4. La figura 4 se deriva de la figura 1 por inserción de condensadores y calderines. Los resultados se encuentran en la siguiente tabla.

B° de corriente en la figura 4		1	2	3
		Alimentación del equipo depurador	Colas del equipo depurador	Purga del equipo depurador
Temperatura	°C	15	-20	-24
Presión	bar g	22	22	22
H2	kg/h	0,1		0,1
CO	kg/h	1		1
CO2	kg/h	1	1	
Etano	kg/h	5	5	
Etileno	kg/h	25091	25013	78
Acetaldehidos	kg/h	18	18	
C3+	kg/h	325	325	
Total	kg/h	25441,1	25362	79,1

Nº de corriente en la figura 4		4	5	6
		Colas del desetanizador	Destilado de vapor del desetanizador	Producto de etileno
Temperatura	°C	80	-24	20
Presión	bar g	21	21	20
H2	kg/h			
CO	kg/h			
CO2	kg/h		1	
Etano	kg/h		5	5
Etileno	kg/h	18	24995	24995
Acetaldehídos	kg/h	18		
C3+	kg/h	325		
Total	kg/h	361	25001	25000

REIVINDICACIONES

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

- 5 a) proporcionar una corriente de etileno (A) seca que comprende esencialmente etileno, hasta un 1 % en peso de oxigenados, etano, CO, CO₂, H₂, CH₄ e hidrocarburos C₃+,
b) enviar dicha corriente (A) a un equipo depurador (también designado como desmetanizador) para producir una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,
- 10 una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+, e
(i)
c) enviar dicha corriente de colas de la etapa b) a un desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+,
15 una corriente de cabezas que comprende esencialmente etileno y CO₂,
d) enviar dicha corriente de cabezas de la etapa c) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO₂,
o (ii)
c1) enviar dicha corriente de colas de la etapa b) a una zona de adsorción de CO₂ de lecho
20 fijo para recuperar una corriente esencialmente libre de CO₂, enviar después dicha corriente a un desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+,
una corriente de cabezas que comprende esencialmente etileno esencialmente exenta de CO₂.

25

2. Procedimiento de acuerdo con la reivindicación 1 en el que la zona de adsorción de CO₂ de lecho fijo se localiza a la entrada del desetanizador.

3. Procedimiento para la eliminación de contaminantes oxigenados de una corriente de

etileno que comprende:

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

b) enviar dicha corriente (A) a un equipo depurador (también designado como desmetanizador) para producir

una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+, e

(i)

c) enviar dicha corriente de colas de la etapa b) a un separador C2 primario para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+ y una porción de etileno,

una corriente de cabezas que comprende esencialmente etileno y CO₂,

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

e) enviar dicha corriente de colas de la etapa c) a un separador C2 secundario para producir una corriente de colas que comprende esencialmente etileno, oxigenados e hidrocarburos C₃+,

una corriente de cabezas que comprende esencialmente etileno, reciclado opcionalmente a la zona de producción de la corriente (A)

o (ii)

c1) enviar dicha corriente de colas de la etapa b) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente esencialmente libre de CO₂, enviar después dicha corriente a un separador C2 primario para producir

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

una corriente de cabezas que comprende esencialmente etileno esencialmente exento de CO₂.

e1) enviar la corriente de colas de la etapa c1) a un separador C2 secundario para producir

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

una corriente de cabezas que comprende esencialmente etileno, opcionalmente reciclado a la zona de producción de la corriente (A).

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4. Procedimiento de acuerdo con la reivindicación 3 en el que la zona de adsorción de CO2 de lecho fijo se localiza a la entrada del separador C2 primario.

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5. Procedimiento para la eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

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

b) enviar dicha corriente (A) a un desmetanizador primario para producir una corriente de cabezas que comprende esencialmente CO, H2 y CH4 y una porción de

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etileno y etano,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO2 e hidrocarburos C3+,

c) enviar dicha corriente de cabezas de la etapa b), opcionalmente a través de un compresor, a un desmetanizador secundario para producir

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una corriente de cabezas que comprende esencialmente CO, H2 y CH4,

una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO2 e hidrocarburos C3+, e

(i)

25

d) enviar dicha corriente de colas de la etapa b) y dicha corriente de colas de la etapa c) a un separador C2 para producir

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

una corriente de cabezas que comprende esencialmente etileno y CO2,

e) enviar dicha corriente de cabezas de la etapa d) a una zona de adsorción de CO2 de

lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO₂,

o (ii)

d1) enviar dicha corriente de colas de la etapa b) y dicha corriente de colas de la etapa c) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente esencialmente libre de CO₂, enviar después dicha corriente a un separador C2 para producir

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

una corriente de cabezas que comprende esencialmente etileno esencialmente exenta de CO₂.

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6. Procedimiento de acuerdo con la reivindicación 5, en el que la zona de adsorción de CO₂ de lecho fijo se localiza a la entrada del separador C2.

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

20

8. Procedimiento de acuerdo con la reivindicación 7, 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.

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9. Procedimiento de acuerdo con una cualquiera de las reivindicaciones 7 u 8, en el que la relación en peso de etano+CO+CO₂+H₂+CH₄+hidrocarburos C₃+ a etileno en (A) es menor de 5/95.

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

11. Procedimiento de acuerdo con una cualquiera de las reivindicaciones anteriores, en el

que la proporción de oxigenados en (A) es de hasta 3000 ppm en peso.

12. Procedimiento de acuerdo con la reivindicación 11, en el que la proporción de oxigenados en (A) es de hasta 2000 ppm en peso.

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

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

15. Procedimiento de acuerdo con la reivindicación 14, en el que la proporción de H₂ en (A) es de hasta 500 ppm en peso.

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

**PROCEDIMIENTO PARA LA ELIMINACIÓN DE CONTAMINANTES OXIGENADOS DE
UNA CORRIENTE DE ETILENO**

Resumen

La presente invención es, en una primera realización, un procedimiento para la eliminación de contaminantes oxigenados de una corriente de etileno que comprende:

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

b) enviar dicha corriente (A) a un equipo depurador (también designado como desmetanizador) para producir una corriente de cabezas que comprende esencialmente CO, H₂ y CH₄, una corriente de colas que comprende esencialmente etileno, oxigenados, etano, CO₂ e hidrocarburos C₃+, c) enviar dicha corriente de colas de la etapa b) a un desetanizador para producir una corriente de colas que comprende esencialmente etano, oxigenados e hidrocarburos C₃+, una corriente de cabezas que comprende esencialmente etileno y CO₂, d) enviar dicha corriente de cabezas de la etapa c) a una zona de adsorción de CO₂ de lecho fijo para recuperar una corriente de etileno esencialmente exenta de CO₂.

En otra realización la zona de adsorción de CO₂ puede estar localizada a la entrada del desetanizador. En otra realización el desmetanizador se reemplaza por dos desmetanizadores. En otra realización el desetanizador se reemplaza por dos separadores C₂.

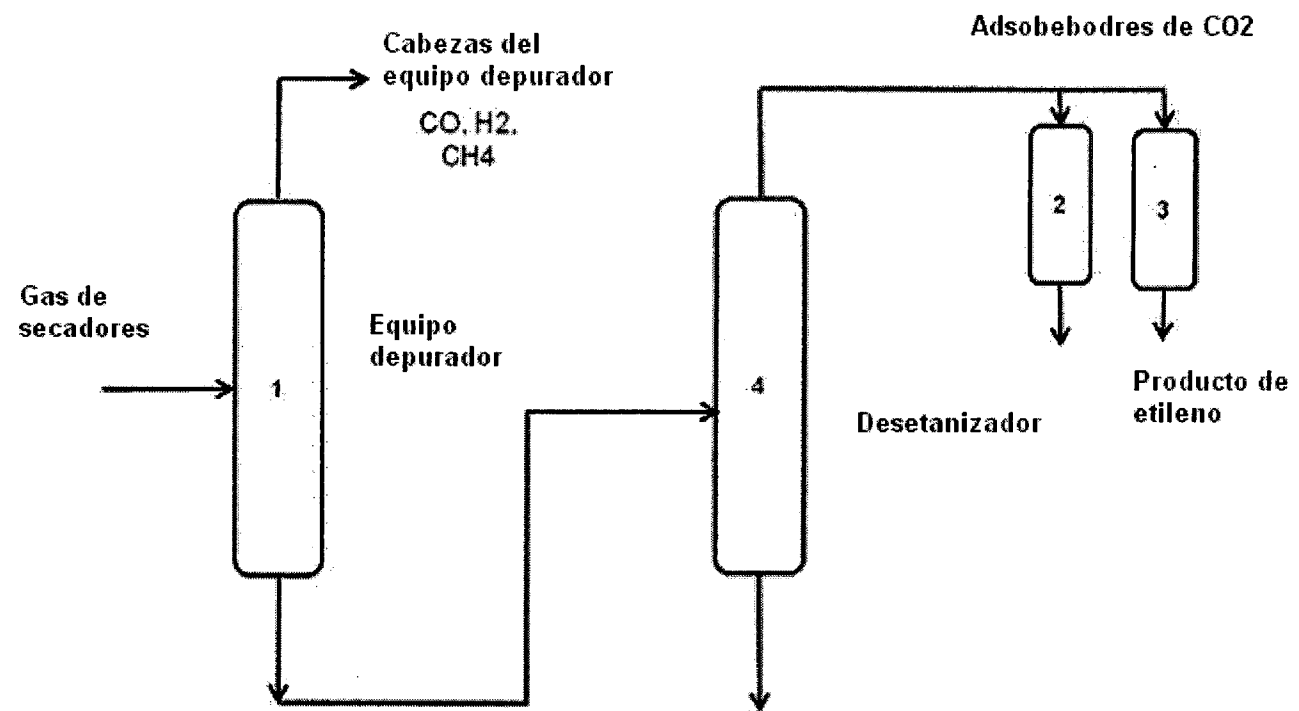


Fig 1

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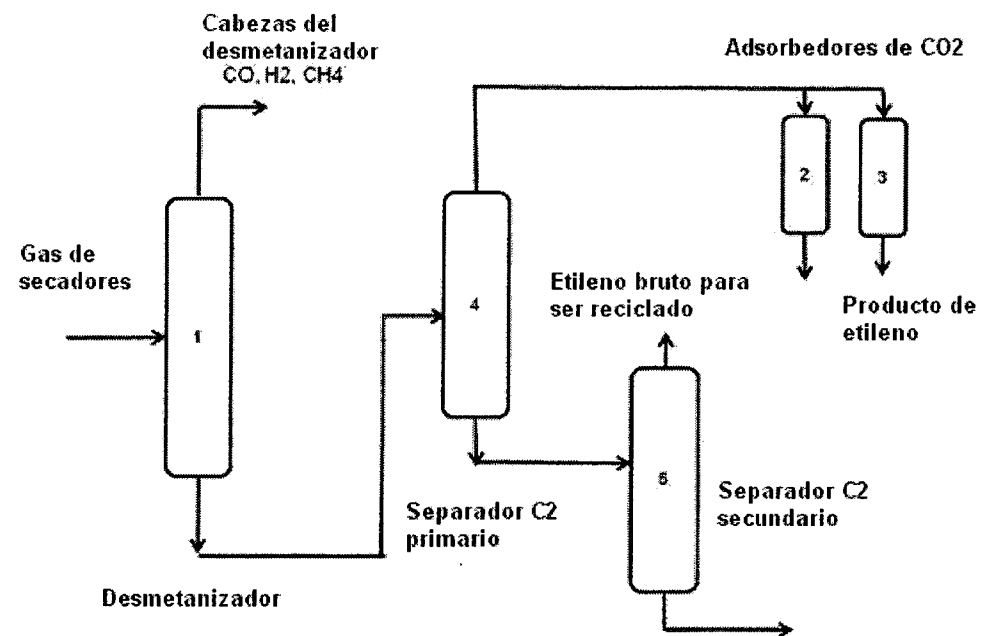


Fig 2

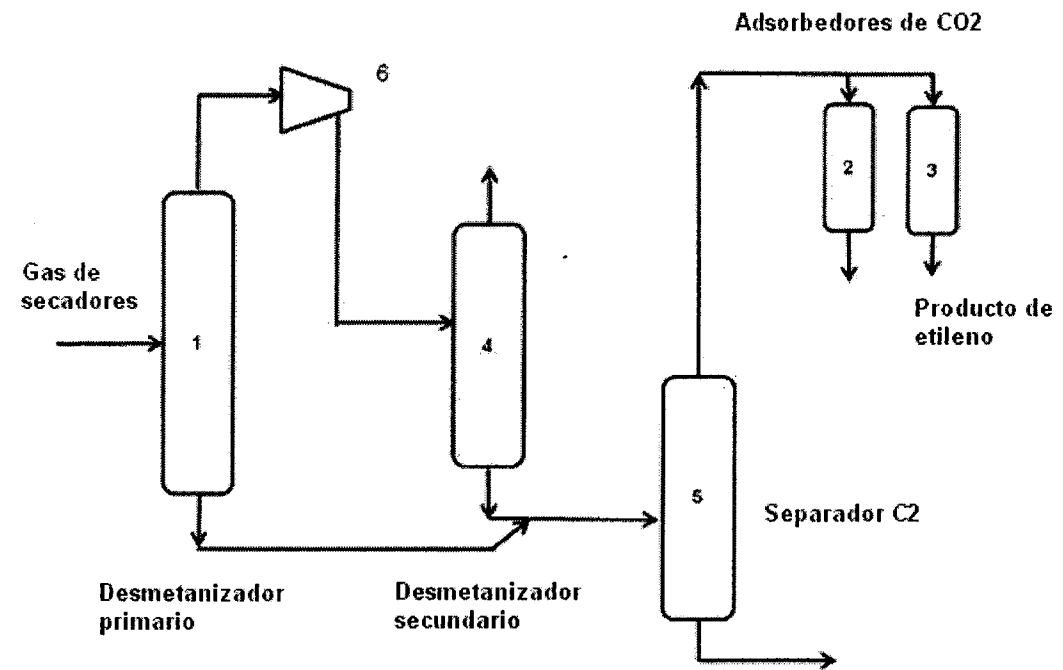
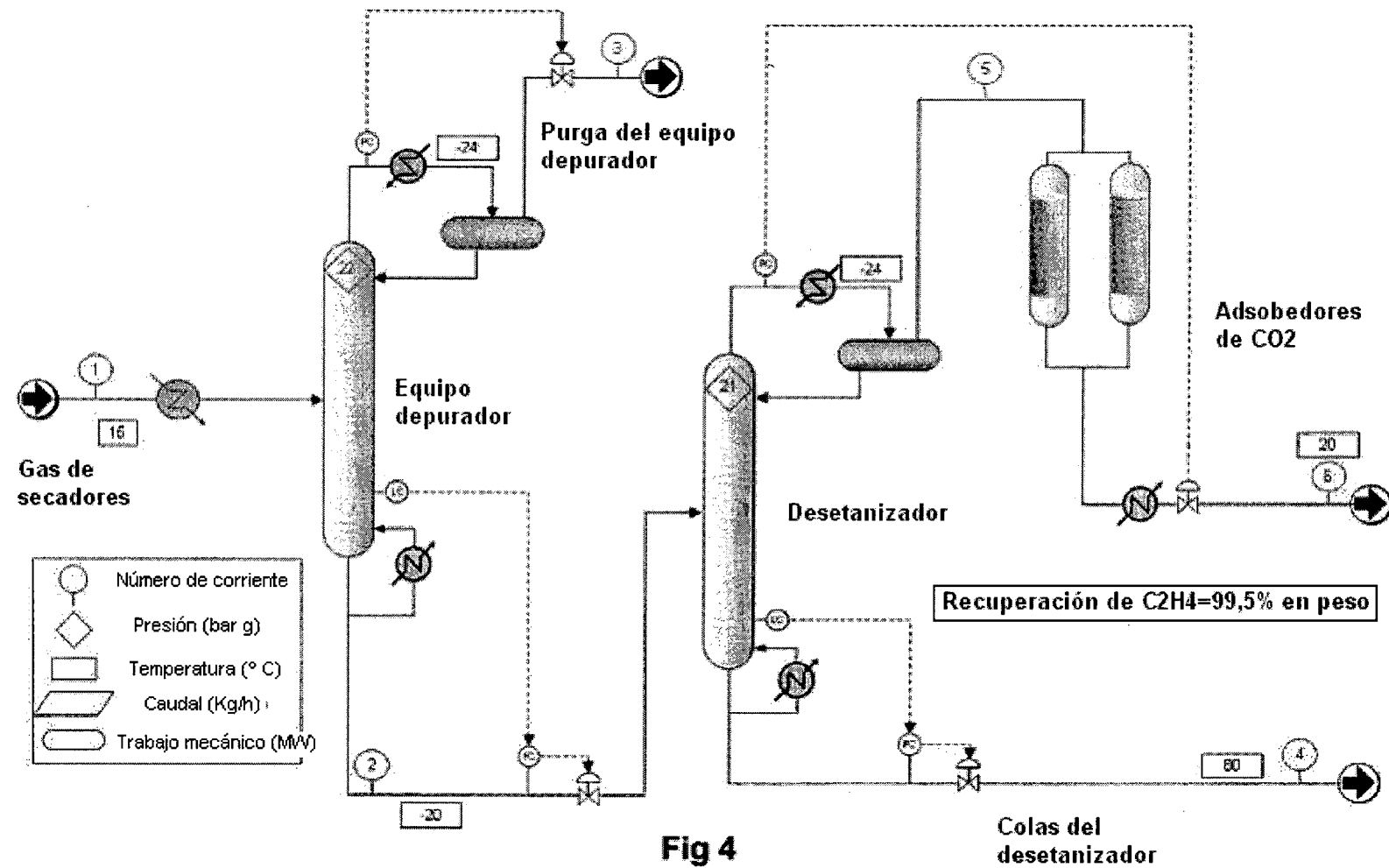


Fig 3

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

(57) Abstract: The present invention is, in a first embodiment, 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 stripper (also referred to as a demethanizer) to produce an overhead stream comprising essentially CO, H₂ and CH₄, a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, c) sending said bottom stream of step b) to a deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead stream consisting essentially of ethylene and CO₂, d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂. In another embodiment the CO₂ adsorption zone can be located at the inlet of the deethanizer. In another embodiment the demethanizer is replaced by two demethanizers. In another embodiment the the deethanizer is replaced by two C₂ splitters.

WO 2013/014002 A1

PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM AN
ETHYLENE STREAM

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[Field of the invention]

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

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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.

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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.

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[Background of the invention]

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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 +

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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

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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 CO₂-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.

[Brief summary of the invention]

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The present invention is, in a first embodiment, 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 stripper (also referred to as a demethanizer) to produce an overhead stream comprising essentially CO, H₂ and CH₄, a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, and
 - (i)
 - c) sending said bottom stream of step b) to a deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
 - d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂,
 - or (ii)
 - c1) sending said bottom stream of step b) to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, then sending said stream to a deethanizer to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
 - an overhead stream consisting essentially of ethylene essentially free of CO₂.

The above process is referred to as embodiment 1.

In a second embodiment the deethanizer of embodiment 1 is replaced by two C₂ splitters.

Said second embodiment is a process for removing oxygenated contaminants from an ethylene stream comprising :

- 210
- 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 stripper (also referred to as a demethanizer) to produce
- 5 an overhead stream comprising essentially CO, H₂ and CH₄,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, and
- (i)
- c) sending said bottom stream of step b) to a primary C₂ splitter to produce
- 10 a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,
an overhead stream consisting essentially of ethylene and CO₂,
- d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂,
- 15 e) sending the bottom stream of step c) to a secondary C₂ splitter to produce
a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
an overhead stream consisting essentially of ethylene, optionally recycled to the
- 20 production zone of stream (A),
- Or (ii)
- c1) sending said bottom stream of step b) to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, then sending said stream to a primary C₂ splitter to produce
- 25 a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,
an overhead stream consisting essentially of ethylene essentially free of CO₂,
- e1) sending the bottom stream of step c1) to a secondary C₂ splitter to produce
- 30 a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,

an overhead stream consisting essentially of ethylene, optionally recycled to the production zone of stream (A).

5 In a third embodiment the demethanizer (stripper) of embodiment 1 is replaced by two demethanizers.

Said third embodiment is a process for removing oxygenated contaminants from an ethylene stream comprising :

- 10 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 primary demethanizer to produce an overhead stream comprising essentially CO, H₂, CH₄ and a portion of ethylene and ethane,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and
15 C₃+ hydrocarbons,
- c) sending said overhead stream of step b), optionally through a compressor, to a secondary demethanizer to produce an overhead stream comprising essentially CO, H₂ and CH₄,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and
20 C₃+ hydrocarbons, and
- (i)
- d) sending said bottom stream of step b) and said bottom stream of step c) to a C₂ splitter to produce
a bottom stream comprising essentially ethane, oxygenates and C₃+
25 hydrocarbons,
an overhead stream consisting essentially of ethylene and CO₂,
- e) sending said overhead of step d) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂,
or (ii)
- 30 d1) sending said bottom stream of step b) and said bottom stream of step c) to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂,
then sending said stream to a C₂ splitter to produce

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a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons,
an overhead stream consisting essentially of ethylene essentially free of CO2.

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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.

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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.

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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.

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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.

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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.

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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,

d3

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).

5 [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
10 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
15 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
20 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
25 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
30 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

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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 process of the invention.

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 process of the present invention. The fixed bed drying zone is known in itself.

As regards the fixed bed CO₂ adsorption zone, 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 interpreted in the light of the further use of ethylene. Should ethylene is to be polymerized CO₂ has to be 1 ppm vol or less and preferably 0.5 ppm vol or less.

As regards the demethanizer, it is also referred to as a stripper in first and second embodiments and as a primary and secondary demethanizer in the third embodiment. The purpose of said demethanizer is to recover an overhead comprising essentially H₂, CH₄ and CO. It is advantageously a distillation column.

As regards the operating conditions, the demethanizer 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 essentially 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.

In an embodiment the pressure of the C2 splitter also referred to as a deethanizer 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. The C2 splitter/deethanizer is advantageously a distillation column.

As regards the first embodiment and the stripper, it is advantageously a distillation column. The overhead is a mixture of essentially CO, H2 and CH4. The deethanizer is advantageously a distillation column. The fixed bed CO2 adsorption zone can be an available commercial fixed bed adsorption (TSA or PSA) as described above. A stream essentially free of CO2 is recovered.

In an embodiment the stripper (demethanizer) and the C2 splitter /deethanizer are operating at the same pressure except the pressure drop between the demethanizer and the C2 splitter /deethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg.

A process according to the first embodiment is described on fig 1 wherein 1 is the stripper (demethanizer), 2 and 3 the CO2 adsorbers and 4 the deethanizer. On top of the stripper there are a condenser, a decanter producing a liquid phase sent as a reflux to said stripper and a gaseous phase which is the overhead, they are not shown on the fig 1. On the bottom of the stripper there is a reboiler not shown on fig 1. The deethanizer has a similar equipment not shown on fig 1. The contaminated ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO2, H2, CH4 and C3+ hydrocarbons has been dried and sent to the stripper 1 (also referred to as a demethanizer) to produce

an overhead stream comprising essentially CO, H2 and CH4,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO2 and C3+ hydrocarbons,

said bottom stream of the stripper 1 is sent to the deethanizer 4 to produce a bottom stream comprising essentially ethane, oxygenates and C3+ hydrocarbons,

an overhead stream consisting essentially of ethylene and CO₂,

- 5 said overhead of deethanizer 4 is sent to a fixed bed CO₂ adsorption zone 2 and 3 to recover an ethylene stream essentially free of CO₂.

In a specific example the pressure of the stripper ranges from 15 to 30 barg and the pressure of the deethanizer and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In
10 this range of pressure the temperature on top of stripper and after the condenser ranges from -20 to -30°C, the temperature on bottom of stripper ranges from -15 to -25°C, the temperature on top of deethanizer and after the condenser ranges from -30 to -20°C and the temperature on bottom of deethanizer ranges from 75 to 85°C.

15 Preferably the pressure of the stripper ranges from 20 to 25 barg and the pressure of the deethanizer and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In this range of pressure the temperature on top of stripper and after the condenser ranges from -22 to -26°C, the temperature on bottom of stripper ranges from -20 to -
20 24°C, the temperature on top of deethanizer and after the condenser ranges from -27 to -22°C and the temperature on bottom of deethanizer ranges from 78 to 82°C.

In another specific example the pressure of the stripper ranges from 35 to 45 barg and the pressure of the deethanizer and the CO₂ adsorbers is about
25 15 to 25 barg less. Advantageously the pressure of the deethanizer ranges from 15 to 25 barg. In this range of pressure the top of stripper is at a temperature in the range -10 to 0°C and condensed at a temperature ranging from -35 to -45°C, the temperature on bottom of stripper ranges from -5 to 5°C, the temperature on top of deethanizer ranges from -25 to -35°C, is condensed at a
30 temperature in the range -25 to -35°C and the temperature on bottom of deethanizer ranges from 75 to 85°C.

5 Preferably the pressure of the stripper ranges from 38 to 42 barg and the pressure of the deethanizer and the CO₂ adsorbers ranges from 17 to 22 barg. In this range of pressure the top of stripper is at a temperature in the range -8 to -2°C and condensed at a temperature ranging from -38 to -42°C, the temperature on bottom of stripper ranges from 0 to 5°C, the temperature on top of deethanizer ranges from -28 to -32°C, is condensed at a temperature in the range -28 to -32°C and the temperature on bottom of deethanizer ranges from 78 to 82°C.

10 **As regards the second embodiment** and the demethanizer, it is advantageously a distillation column. The primary and secondary splitters are each advantageously a distillation column. The fixed bed CO₂ adsorption zone has already been described above. A stream essentially free of CO₂ is recovered.

15 In an embodiment the demethanizer and the primary and secondary C₂ splitter /deethanizer are operating at the same pressure except the pressure drop for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg.

20 A process according to the second embodiment is described on fig 2 wherein 1 is the demethanizer, 2 and 3 the CO₂ adsorbers, 4 the primary C₂ splitter and 5 the secondary C₂ splitter. On top of the demethanizer there are a condenser, a decanter producing a liquid phase sent as a reflux to said demethanizer and a gaseous phase which is the overhead, they are not shown on the fig 2. On the bottom of the demethanizer there is a reboiler not shown on
25 fig 2. The primary C₂ splitter and the secondary C₂ splitter have each a similar equipment not shown on fig 2.

The contaminated ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons has been dried and sent to the demethanizer 1
30 to produce an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

said bottom stream of demethanizer 1 are sent to the primary C₂ splitter 4 to produce

5 a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,

an overhead stream consisting essentially of ethylene and CO₂,

said overhead of the primary C₂ splitter 4 is sent to a fixed bed CO₂ adsorption zone 2 and 3 to recover an ethylene stream essentially free of CO₂,

10 the bottom stream of the primary C₂ splitter 4 is sent to a secondary C₂ splitter 5 to produce

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

15 an overhead stream consisting essentially of ethylene, optionally recycled to the production zone of stream (A).

In a specific example the pressure of the demethanizer ranges from 35 to 45 barg and the pressure of the primary C₂ splitter and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. The pressure of the secondary C₂ splitter ranges from 15 to 25 barg. In these ranges of pressure the top of demethanizer is at a temperature in the range -10 to 0°C, is condensed at a temperature ranging from -35 to -45°C, the temperature on bottom of demethanizer ranges from -5 to 5°C, the top of the primary C₂ splitter is in a temperature range from -5 to 5°C, is condensed in a temperature range from -5 to 5°C, the temperature on bottom of primary C₂ splitter ranges from 75 to 85°C, the top of the secondary C₂ splitter is in a temperature range from -25 to -35°C, is condensed in a temperature range from -25 to -35°C and the temperature on bottom of secondary C₂ splitter ranges from 75 to 85°C.

30 Preferably the pressure of the demethanizer ranges from 38 to 42 barg and the pressure of the primary C₂ splitter and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. The pressure of the secondary C₂ splitter ranges from 18 to 22 barg. In these

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ranges of pressure the top of demethanizer is in a temperature range of -8°C to -2°C, is condensed at a temperature ranging from -38 to -42°C, the temperature on bottom of demethanizer ranges from 0 to 4°C, the top of primary C2 splitter is in a temperature range from -4 to 0°C, is condensed in a temperature range from -4 to 0°C, the temperature on bottom of primary C2 splitter ranges from 78 to 82°C, the top of the secondary C2 splitter is in a temperature range from -28 to -32°C, is condensed in a temperature range from -28 to -32°C, and the temperature on bottom of secondary C2 splitter ranges from 78 to 82°C.

10 **As regards the third embodiment** and the primary and secondary demethanizer, they are each advantageously a distillation column. The C2 splitter is advantageously a distillation column. The fixed bed CO₂ adsorption zone has already been described above. A stream essentially free of CO₂ is recovered.

15 In an embodiment the primary, the secondary demethanizers and the C2 splitter /demethanizer are operating at the same pressure except the pressure drop for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg.

20 A process according to the third embodiment is described on fig 3 wherein 1 is the primary demethanizer, 2 and 3 the CO₂ adsorbers, 4 the secondary demethanizer, 5 the C2 splitter and 6 the compressor. On top of the primary demethanizer there are a condenser, a decanter producing a liquid phase sent as a reflux to said primary demethanizer and a gaseous phase which is the overhead, they are not shown on the fig 3. The overhead of the primary demethanizer is sent to the compressor. On the bottom of the primary demethanizer there is a reboiler not shown on fig 3. The secondary demethanizer and the C2 splitter have each a similar equipment not shown on fig 3.

25 The contaminated ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons has been dried is sent to a primary demethanizer 1 to produce

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an overhead stream comprising essentially CO, H₂, CH₄ and a portion of ethylene and ethane,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

5 the overhead stream of demethanizer 1 is sent through a compressor 6 to a secondary demethanizer 4 to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

10 said bottom stream of secondary demethanizer 4 and said bottom stream of primary demethanizer 1 are sent to a C₂ splitter 5 to produce

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

an overhead stream consisting essentially of ethylene and CO₂,

15 said overhead of the C₂ splitter 5 is sent to a fixed bed CO₂ adsorption zone 2-3 to recover an ethylene stream essentially free of CO₂.

In a specific example the pressure of the primary demethanizer ranges from 15 to 25 barg, the pressure of the secondary demethanizer ranges from 40 to 50 barg, the pressure of the C₂ splitter is essentially at the same pressure as
20 the primary demethanizer except the pressure drop for transfer of fluids and ranges from 15 to 25 barg and the pressure of the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In these ranges of pressure the top of the primary demethanizer is in a temperature range of -25 to -35°C, condensed at a temperature ranging from -
25 25 to -35°C, the temperature in the bottom of the primary demethanizer ranges from -30 to -20°C, the top of the secondary demethanizer is in a temperature range of -10 to 0°C, is condensed at a temperature ranging from -30 to -40°C, the temperature in the bottom of the secondary demethanizer ranges from 0 to 10°C, the top of the C₂ splitter is in a temperature range from -25 to -35°C, is
30 condensed in a temperature range from -25 to -35°C, and the temperature in the bottom of the C₂ splitter ranges from 75 to 85°C.

Preferably the pressure of the primary demethanizer ranges from 18 to 22 barg, the pressure of the secondary demethanizer ranges from 43 to 47 barg, the pressure of the C2 splitter is essentially at the same pressure as the primary demethanizer except the pressure drop for transfer of fluids and ranges from 18 to 22 barg and the pressure of the CO2 adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In these ranges of pressure the top of the primary demethanizer is in a temperature range of -25 to -31°C, condensed at a temperature ranging from -27 to -32°C, the temperature in the bottom of the primary demethanizer ranges from -28 to -22°C, the top of the secondary demethanizer is in a temperature range of -6 to -2°C, condensed at a temperature ranging from -30 to -35°C, the temperature in the bottom of the secondary demethanizer ranges from 3 to 8°C, the top of the C2 splitter is in a temperature range from -28 to -32°C, is condensed in a temperature range from -28 to -32°C, and the temperature in the bottom of the C2 splitter ranges from 78 to 82°C.

[Examples]

The process according to fig 4 is operated. Fig 4 is derived from fig 1 by insertion of condensers and reboilers. The results are on the following table.

stream No on fig 4		1	2	3
		Stripper feed	Stripper bottoms	Stripper purge
Temperature	°C	15	-20	-24
Pressure	bar g	22	22	22
H2	kg/h	0.1		0.1
CO	kg/h	1		1
CO2	kg/h	1	1	
ethane	kg/h	5	5	
ethylene	kg/h	25091	25013	78
acetaldehydes	kg/h	18	18	
C3+	kg/h	325	325	
Total	kg/h	25441.1	25362	79.1

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stream No on fig 4		4	5	6
		Deethanizer bottoms	Deethanizer vapor distillate	Ethylene product
Temperature	°C	80	-24	20
Pressure	bar g	21	21	20
H2	kg/h			
CO	kg/h			
CO2	kg/h		1	
ethane	kg/h		5	5
ethylene	kg/h	18	24995	24995
acetaldehydes	kg/h	18		
C3+	kg/h	325		
Total	kg/h	361	25001	25000

CLAIMS

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

5 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 stripper (also referred to as a demethanizer) to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

10 a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, and

(i)

c) sending said bottom stream of step b) to a deethanizer to produce

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

an overhead stream consisting essentially of ethylene and CO₂,

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

or (ii)

20 c1) sending said bottom stream of step b) to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, then sending said stream to a deethanizer to produce

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

25 an overhead stream consisting essentially of ethylene essentially free of CO₂.

2 Process according to claim 1 wherein the fixed bed CO₂ adsorption zone is located at the inlet of the deethanizer.

30 3 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 stripper (also referred to as a demethanizer) to produce
- 5 an overhead stream comprising essentially CO, H₂ and CH₄,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, and
- (i)
- c) sending said bottom stream of step b) to a primary C₂ splitter to produce
- 10 a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,
an overhead stream consisting essentially of ethylene and CO₂,
- d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂,
- 15 e) sending the bottom stream of step c) to a secondary C₂ splitter to produce
a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
an overhead stream consisting essentially of ethylene, optionally recycled to the
- 20 production zone of stream (A),
Or (ii)
- c1) sending said bottom stream of step b) to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, then sending said stream to a primary C₂ splitter to produce
- 25 a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,
an overhead stream consisting essentially of ethylene essentially free of CO₂,
- e1) sending the bottom stream of step c1) to a secondary C₂ splitter to produce
- 30 a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,

an overhead stream consisting essentially of ethylene, optionally recycled to the production zone of stream (A).

5 4 Process according to claim 3 wherein the fixed bed CO₂ adsorption zone is located at the inlet of the primary C₂ splitter.

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

- 10 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 primary demethanizer to produce an overhead stream comprising essentially CO, H₂, CH₄ and a portion of ethylene and ethane,
15 a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,
 c) sending said overhead stream of step b), optionally through a compressor, to a secondary demethanizer to produce an overhead stream comprising essentially CO, H₂ and CH₄,
20 a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, and
 (i)
 d) sending said bottom stream of step b) and said bottom stream of step c) to a C₂ splitter to produce
25 a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
 an overhead stream consisting essentially of ethylene and CO₂,
 e) sending said overhead of step d) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂,
30 or (ii)

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d1) sending said bottom stream of step b) and said bottom stream of step c) to a fixed bed CO₂ adsorption zone to recover a stream essentially free of CO₂, then sending said stream to a C₂ splitter to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
5 an overhead stream consisting essentially of ethylene essentially free of CO₂.

6 Process according to claim 5 wherein the fixed bed CO₂
10 adsorption zone is located at the inlet of the C₂ splitter.

7 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.
15

8 Process according to claim 7 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.

9 Process according to any one of claims 7 or 8 wherein the weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene in (A) is less than 5/95.
20

10 Process according to any one of the preceding claims wherein the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.
25

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

12 Process according to claim 11 wherein the proportion of oxygenates in (A) is up to 2000 wppm.
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13 Process according to any one of the preceding claims wherein the proportion of H₂ in (A) is from 5 to 1000 wppm.

5 14 Process according to any one of the preceding claims wherein the proportion of H₂ in (A) is up to 800 wppm.

15 Process according to claim 14 wherein the proportion of H₂ in (A) is up to 500 wppm.

10 16 Process according to any one of the preceding claims wherein the dried ethylene stream (A) is originating from the dehydration of ethanol.

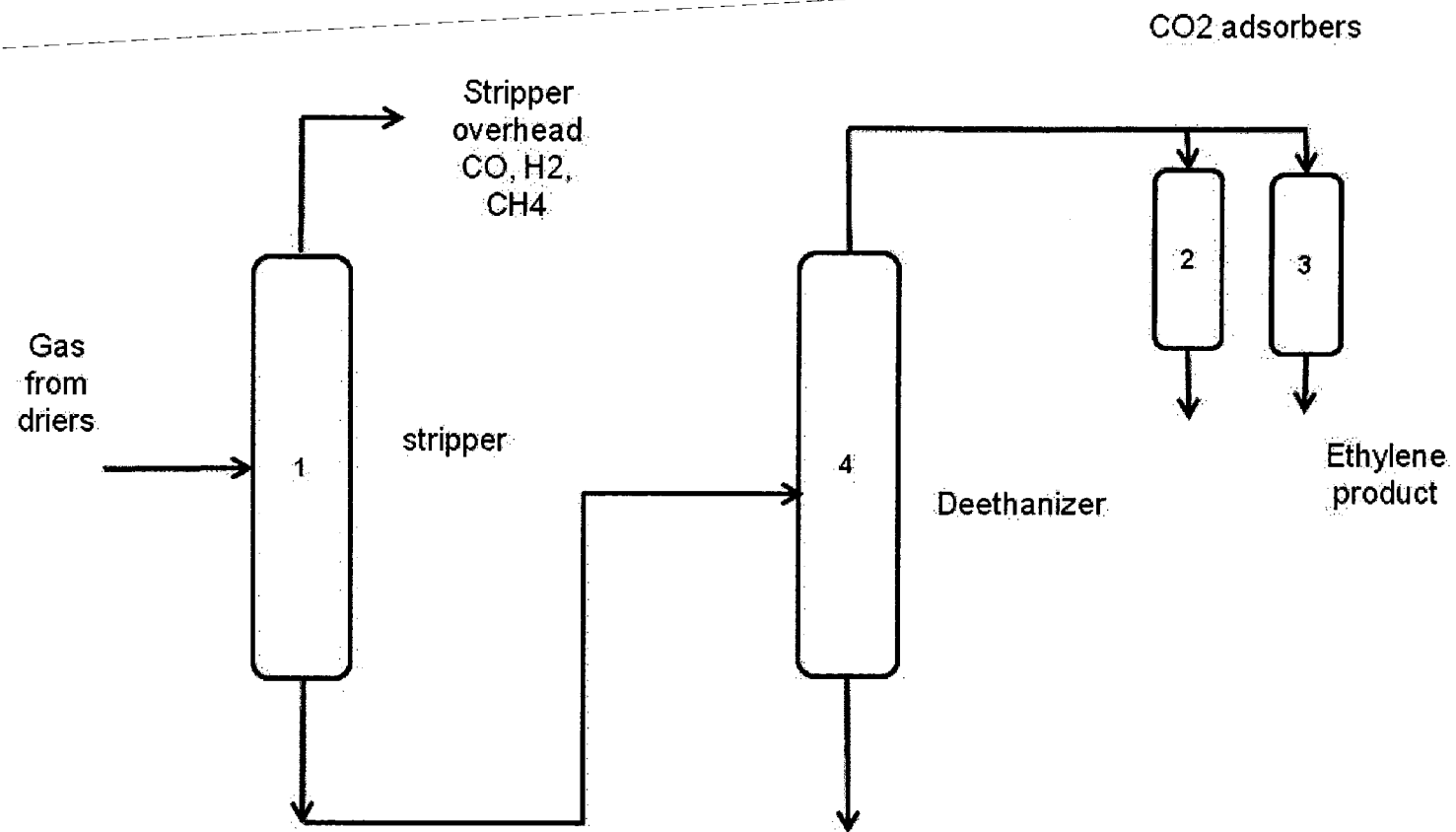


Fig 1

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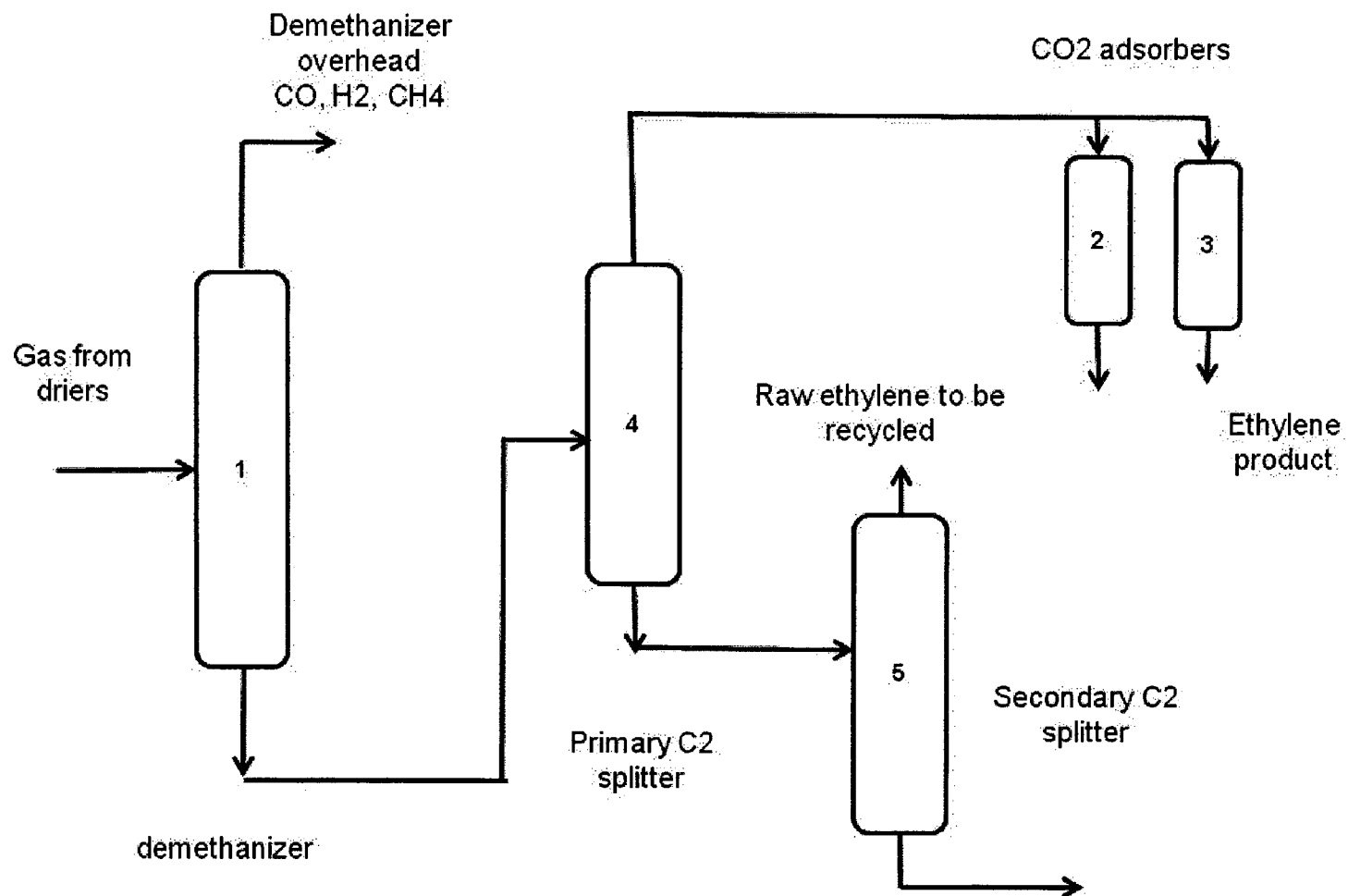


Fig 2

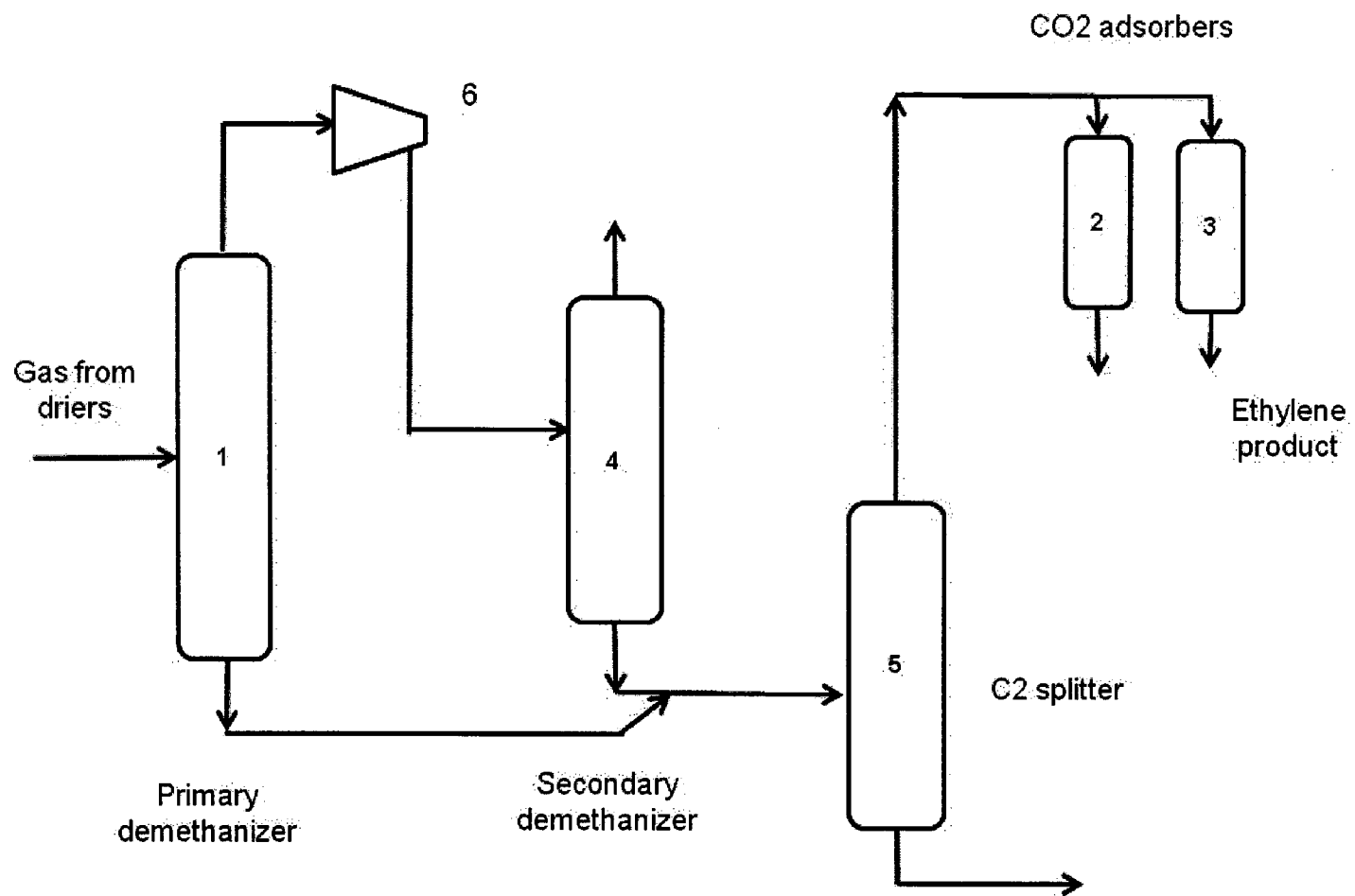


Fig 3

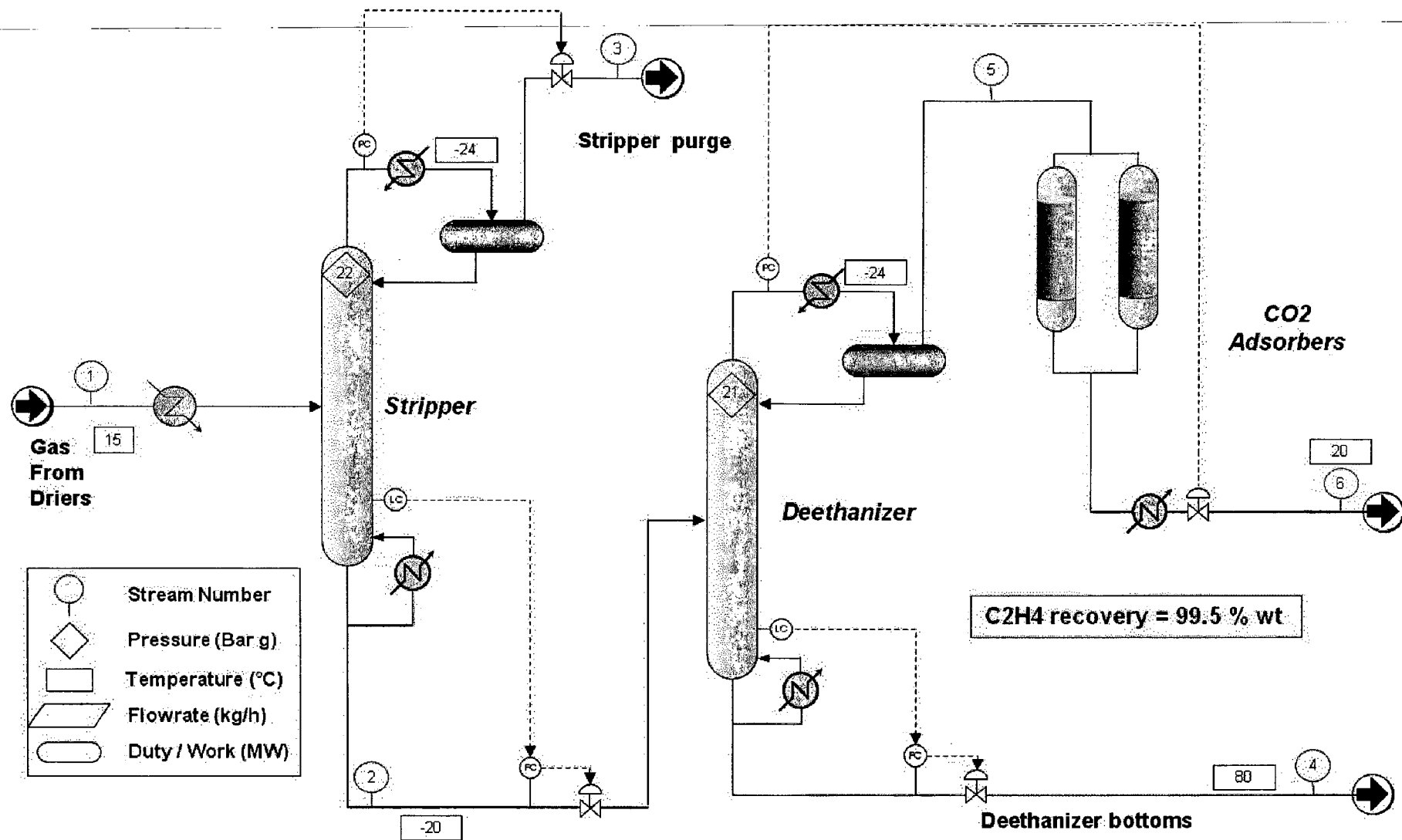


Fig 4

WO 2013/014002

PCT/EP2012/063754

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/063754

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C7/00 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, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/011404 A1 (EXXONMOBIL CHEM PATENTS INC [US]; VAN EGMOND COR [US]) 5 February 2004 (2004-02-05) page 23, paragraph 84 - page 39, paragraph 140 claim 1	1-16
Y	----- WO 2008/042613 A2 (UOP LLC [US]; SCHULTZ MICHAEL A [US]; TOWLER GAVIN P [US]; WEGERER DAV) 10 April 2008 (2008-04-10) paragraph [0015] paragraph [0081] paragraph [0087] - paragraph [0088] claims ----- -/--	1-16
☒ 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 20 September 2012		Date of mailing of the international search report 28/09/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Patteux, Claudine

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/063754

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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**DOCUMENT MADE AVAILABLE UNDER THE
PATENT COOPERATION TREATY (PCT)**

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Si aucun titre n'est indiqué se référer à la description.)

Process for removing oxygenated contaminants from an ethylene stream

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[Field of the invention]

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

5 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.

10 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]

25 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
5 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
10 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
15 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
20 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
25 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
30 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 CO₂-depleted stream is dried.

5

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.

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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.

[Brief summary of the invention]

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

25

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 stripper (also referred to as a demethanizer) to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

30

c) sending said bottom stream of step b) to a deethanizer to produce

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

an overhead stream consisting essentially of ethylene and CO₂.

d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

5 The above process is referred to as embodiment 1. In said process the fixed bed CO₂ adsorption zone can be at the inlet of the deethanizer.

In a second embodiment the deethanizer of embodiment 1 is replaced by two C₂ splitters.

10 Said second embodiment 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 stripper (also referred to as a demethanizer) to produce

15 an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

c) sending said bottom stream of step b) to a primary C₂ splitter to produce a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,

20 an overhead stream consisting essentially of ethylene and CO₂,

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

25 e) sending the bottom stream of step c) to a secondary C₂ splitter to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead stream consisting essentially of ethylene, optionally recycled to the production zone of stream (A).

In said process the fixed bed CO₂ adsorption zone can be at the inlet of the primary C₂ splitter.

30

In a third embodiment the demethanizer (stripper) of embodiment 1 is replaced by two demethanizers.

Said third embodiment 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,
- 5 b) sending said stream (A) to a primary demethanizer to produce an overhead stream comprising essentially CO, H₂, CH₄ and a portion of ethylene and ethane,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,
- 10 c) sending said overhead stream of step b), optionally through a compressor, to a secondary demethanizer to produce an overhead stream comprising essentially CO, H₂ and CH₄,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,
- 15 d) sending said bottom stream of step b) and said bottom stream of step c) to a C₂ splitter to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
an overhead stream consisting essentially of ethylene and CO₂,
- 20 e) sending said overhead of step d) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

In said process the fixed bed CO₂ adsorption zone can be at the inlet of the C₂ splitter.

25 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.

30 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.

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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 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, 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 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, 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 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 process of the invention.

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 process of the present invention. The fixed bed drying zone is known in itself.

As regards the fixed bed CO₂ adsorption zone, 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 or mixture thereof. A stream essentially free of CO₂ is recovered. Said fixed bed can be regenerated, during regeneration the desorption produces a stream which can be treated anywhere. "Essentially" has to be interpreted in the light of the further use of ethylene. Should ethylene is to be polymerized CO₂ has to be 1 ppm vol or less and preferably 0.5 ppm vol or less.

As regards the demethanizer, it is also referred to as a stripper in first and second embodiments and as a primary and secondary demethanizer in the third embodiment. The purpose of said demethanizer is to recover an overhead comprising essentially H₂, CH₄ and CO. It is advantageously a distillation column.

As regards the operating conditions, the demethanizer 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 essentially 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 H₂, CH₄ and CO in the ethylene stream (A) and mainly of the proportion of H₂.

In an embodiment the pressure of the C₂ splitter also referred to as a deethanizer 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 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+C₃+ hydrocarbons. The higher the proportion of oxygenates the higher the temperature. The higher the pressure the higher the temperature. The C₂ splitter/deethanizer is advantageously a distillation column.

As regards the first embodiment and the stripper, it is advantageously a distillation column. The overhead is a mixture essentially CO, H₂ and CH₄. The deethanizer is advantageously a distillation column. The fixed bed CO₂ adsorption zone can be an available commercial fixed bed adsorption (TSA or PSA) using molecular sieves or basic oxides or mixture thereof. A stream essentially free of CO₂ is recovered.

In an embodiment the demethanizer and the C₂ splitter /deethanizer are operating at the same pressure except the pressure drop between the demethanizer and the C₂ splitter /deethanizer for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg.

The first embodiment is described on fig 1 wherein 1 is the stripper, 2 and 3 the CO₂ adsorbers and 4 the deethanizer. The contaminated ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons has been dried and sent to the stripper 1 (also referred to as a demethanizer) to produce an overhead stream comprising essentially CO, H₂ and CH₄, a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons, said bottom stream of the stripper 1 is sent to the deethanizer 4 to produce a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead stream consisting essentially of ethylene and CO₂, said overhead of deethanizer 4 is sent to a fixed bed CO₂ adsorption zone 2 and 3 to recover an ethylene stream essentially free of CO₂.

In a specific example the pressure of the stripper ranges from 15 to 25 barg and the pressure of the deethanizer and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In this range of pressure the temperature on top of stripper ranges from -20 to -30°C, the temperature on bottom of stripper ranges from -15 to -25°C, the temperature on top of deethanizer ranges from -30 to -20°C and the temperature on bottom of deethanizer ranges from 75 to 85°C.

Preferably the pressure of the stripper ranges from 20 to 25 barg and the pressure of the deethanizer and the CO₂ adsorbers is about 1 or 2 barg less

corresponding to the pressure drop due to pipes and equipment. In this range of pressure, the temperature on top of stripper ranges from -22 to -26°C, the temperature on bottom of stripper ranges from -18 to -22°C, the temperature on top of deethanizer ranges from -27 to -22°C and the temperature on bottom of deethanizer ranges from 78 to 82°C.

In another specific example the pressure of the stripper ranges from 35 to 45 barg and the pressure of the deethanizer and the CO₂ adsorbers is about 15 to 25 barg less. Advantageously the pressure of the deethanizer ranges from 15 to 25 barg. In this range of pressure the top of stripper is condensed at a temperature ranging from -35 to -45°C, the temperature on bottom of stripper ranges from -5 to 5°C, the temperature on top of deethanizer ranges from -25 to -35°C and the temperature on bottom of deethanizer ranges from 75 to 85°C.

Preferably the pressure of the stripper ranges from 38 to 42 barg and the pressure of the deethanizer and the CO₂ adsorbers ranges from 17 to 22 barg. In this range of pressure the top of stripper is condensed at a temperature ranging from -38 to -42°C, the temperature on bottom of stripper ranges from 0 to 5°C, the temperature on top of deethanizer ranges from -28 to -32°C and the temperature on bottom of deethanizer ranges from 78 to 82°C.

As regards the second embodiment and the demethanizer, it is advantageously a distillation column. The primary and secondary splitters are each advantageously a distillation column. The fixed bed CO₂ adsorption zone has already been described above. A stream essentially free of CO₂ is recovered.

In an embodiment the demethanizer and the primary and secondary C₂ splitter /deethanizer are operating at the same pressure except the pressure drop for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg.

The second embodiment is described on fig 2 wherein 1 is the demethanizer, 2 and 3 the CO₂ adsorbers, 4 the primary C₂ splitter and 5 the secondary C₂ splitter. The contaminated ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃⁺ hydrocarbons has been dried and sent to the demethanizer 1 to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

said bottom stream of demethanizer 1 are sent to the primary C₂ splitter 4 to produce

5 a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,

an overhead stream consisting essentially of ethylene and CO₂,

said overhead of the primary C₂ splitter 4 is sent to a fixed bed CO₂ adsorption zone 2 and 3 to recover an ethylene stream essentially free of CO₂,

10 the bottom stream of the primary C₂ splitter 4 is sent to a secondary C₂ splitter 5 to produce

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

an overhead stream consisting essentially of ethylene, optionally recycled to the production zone of stream (A).

15 In a specific example the pressure of the demethanizer ranges from 35 to 45 barg and the pressure of the primary C₂ splitter and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. The pressure of the secondary C₂ splitter ranges from 15 to 25 barg. In these ranges of pressure the top of demethanizer is condensed at a temperature ranging from -35 to
20 -45°C, the temperature on bottom of demethanizer ranges from -5 to 5°C, the temperature on top of primary C₂ splitter ranges from -5 to 5°C, the temperature on bottom of primary C₂ splitter ranges from 75 to 85°C, the temperature on top of the secondary C₂ splitter ranges from -25 to -35°C and the temperature on bottom of secondary C₂ splitter ranges from 75 to 85°C.

25 Preferably the pressure of the demethanizer ranges from 38 to 42 barg and the pressure of the primary C₂ splitter and the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. The pressure of the secondary C₂ splitter ranges from 18 to 22 barg. In these ranges of pressure the top of demethanizer is condensed at a temperature ranging from -38 to -42°C,
30 the temperature on bottom of demethanizer ranges from 0 to 4°C, the temperature on top of primary C₂ splitter ranges from -4 to 0°C, the temperature on bottom of primary C₂ splitter ranges from 78 to 82°C, the temperature on top of the secondary C₂

splitter ranges from -28 to -32°C and the temperature on bottom of secondary C₂ splitter ranges from 78 to 82°C.

As regards the third embodiment and the primary and secondary demethanizer, they are each advantageously a distillation column. The C₂ splitter is advantageously a distillation column. The fixed bed CO₂ adsorption zone has already been described above. A stream essentially free of CO₂ is recovered.

In an embodiment the primary, the secondary demethanizers and the C₂ splitter /deethanizer are operating at the same pressure except the pressure drop for transfer of fluids. Advantageously the pressure is ranging from 15 to 45 barg.

The third embodiment is described on fig 3 wherein 1 is the primary demethanizer, 2 and 3 the CO₂ adsorbers, 4 the secondary demethanizer, 5 the C₂ splitter and 6 the compressor. The contaminated ethylene stream (A) comprising essentially ethylene, up to 1 w% oxygenates, ethane, CO, CO₂, H₂, CH₄ and C₃+ hydrocarbons has been dried is sent to a primary demethanizer 1 to produce an overhead stream comprising essentially CO, H₂, CH₄ and a portion of ethylene and ethane,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

the overhead stream of demethanizer 1 is sent through a compressor 6 to a secondary demethanizer 4 to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

said bottom stream of secondary demethanizer 4 and said bottom stream of primary demethanizer 1 are sent to a C₂ splitter 5 to produce

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

an overhead stream consisting essentially of ethylene and CO₂,

said overhead of the C₂ splitter 5 is sent to a fixed bed CO₂ adsorption zone 2-3 to recover an ethylene stream essentially free of CO₂.

In a specific example the pressure of the primary demethanizer ranges from 15 to 25 barg, the pressure of the secondary demethanizer ranges from 40 to 50

barg, the pressure of the C₂ splitter is essentially at the same pressure as the primary demethanizer except the pressure drop for transfer of fluids and ranges from 15 to 25 barg and the pressure of the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In these ranges of pressure the top of the primary demethanizer is condensed at a temperature ranging from -25 to -35°C, the temperature in the bottom of the primary demethanizer ranges from -30 to -20°C, the top of the secondary demethanizer is condensed at a temperature ranging from -30 to -40°C, the temperature in the bottom of the secondary demethanizer ranges from 0 to 10°C, the temperature on top of the C₂ splitter ranges from -25 to -35°C and the temperature in the bottom of the C₂ splitter ranges from 75 to 85°C.

Preferably the pressure of the primary demethanizer ranges from 18 to 22 barg, the pressure of the secondary demethanizer ranges from 43 to 47 barg, the pressure of the C₂ splitter is essentially at the same pressure as the primary demethanizer except the pressure drop for transfer of fluids and ranges from 18 to 22 barg and the pressure of the CO₂ adsorbers is about 1 or 2 barg less corresponding to the pressure drop due to pipes and equipment. In these ranges of pressure the top of the primary demethanizer is condensed at a temperature ranging from -27 to -31°C, the temperature in the bottom of the primary demethanizer ranges from -28 to -22°C, the top of the secondary demethanizer is condensed at a temperature ranging from -30 to -35°C, the temperature in the bottom of the secondary demethanizer ranges from 3 to 8°C, the temperature on top of the C₂ splitter ranges from -28 to -32°C and the temperature in the bottom of the C₂ splitter ranges from 78 to 82°C.

[Examples]

The process according to fig 4 is operated. Fig 4 is derived from fig 1 by insertion of condensers and reboilers. The results are on the following table.

stream No on fig 4		1	2	3
		Stripper feed	Stripper bottoms	Stripper purge
Temperature	°C	15	-20	-24
Pressure	bar g	22	22	22
H ₂	kg/h	0.1		0.1
CO	kg/h	1		1
CO ₂	kg/h	1	1	
ethane	kg/h	5	5	
ethylene	kg/h	25091	25013	78
acetaldehydes	kg/h	18	18	
C ₃ +	kg/h	325	325	
Total	kg/h	25441.1	25362	79.1

stream No on fig 4		4	5	6
		Deethanizer bottoms	Deethanizer vapor distillate	Ethylene product
Temperature	°C	80	-24	20
Pressure	bar g	21	21	20
H ₂	kg/h			
CO	kg/h			
CO ₂	kg/h		1	
ethane	kg/h		5	5
ethylene	kg/h	18	24995	24995
acetaldehydes	kg/h	18		
C ₃ +	kg/h	325		
Total	kg/h	361	25001	25000

CLAIMS

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

- 5 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 stripper (also referred to as a demethanizer) to produce
an overhead stream comprising essentially CO, H₂ and CH₄,
- 10 a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,
- c) sending said bottom stream of step b) to a deethanizer to produce
a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons,
an overhead stream consisting essentially of ethylene and CO₂,
- 15 d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

2 Process according to claim 1 wherein the fixed bed CO₂ adsorption zone is located at the inlet of the deethanizer.

3 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,
- 25 b) sending said stream (A) to a stripper (also referred to as a demethanizer) to produce
an overhead stream comprising essentially CO, H₂ and CH₄,
a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,
- 30 c) sending said bottom stream of step b) to a primary C₂ splitter to produce
a bottom stream comprising essentially ethane, oxygenates, C₃+ hydrocarbons and a portion of ethylene,

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an overhead stream consisting essentially of ethylene and CO₂,

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

e) sending the bottom stream of step c) to a secondary C₂ splitter to produce

5 a bottom stream comprising essentially ethane, oxygenates and C₃+ hydrocarbons, an overhead stream consisting essentially of ethylene, optionally recycled to the production zone of stream (A).

10 4 Process according to claim 3 wherein the fixed bed CO₂ adsorption zone is located at the inlet of the primary C₂ splitter.

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

15 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 primary demethanizer to produce an overhead stream comprising essentially CO, H₂, CH₄ and a portion of ethylene and ethane,

20 a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

c) sending said overhead stream of step b), optionally through a compressor, to a secondary demethanizer to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

25 a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

d) sending said bottom stream of step b) and said bottom stream of step c) to a C₂ splitter to produce

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

an overhead stream consisting essentially of ethylene and CO₂,

30 e) sending said overhead of step d) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

6 Process according to claim 5 wherein the fixed bed CO₂ adsorption zone can be at the inlet of the C₂ splitter.

5 7 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.

10 8 Process according to claim 7 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.

9 Process according to any one of claims 7 or 8 wherein the weight ratio of ethane+CO+CO₂+H₂+CH₄+C₃+ hydrocarbons to ethylene in (A) is less than 5/95.

15 10 Process according to any one of the preceding claims wherein the proportion of oxygenates in (A) is from 50 wppm to 7000 wppm.

20 11 Process according to any one of the preceding claims wherein wherein the proportion of oxygenates in (A) is up to 3000 wppm.

12 Process according to claim 11 wherein the proportion of oxygenates in (A) is up to 2000 wppm.

25 13 Process according to any one of the preceding claims wherein the proportion of H₂ in (A) is from 5 to 1000 wppm.

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

30 15 Process according to claim 14 wherein the proportion of H₂ in (A) is up to 500 wppm.

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PATENT

IFP Energies nouvelles et TOTAL Petrochemicals Research Feluy

**PROCESS FOR REMOVING OXYGENATED CONTAMINANTS FROM
AN ETHYLENE STREAM**

Inventors : Babua DAS, Manuela ARRATIA, Catherine BOUTROT

ABSTRACT

The present invention is, in a first embodiment, 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 stripper (also referred to as a demethanizer) to produce

an overhead stream comprising essentially CO, H₂ and CH₄,

a bottom stream comprising essentially ethylene, oxygenates, ethane, CO₂ and C₃+ hydrocarbons,

c) sending said bottom stream of step b) to a deethanizer to produce

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

an overhead stream consisting essentially of ethylene and CO₂,

d) sending said overhead of step c) to a fixed bed CO₂ adsorption zone to recover an ethylene stream essentially free of CO₂.

In another embodiment the demethanizer is replaced by two demethanizers.

In another embodiment the the deethanizer is replaced by two C₂ splitters

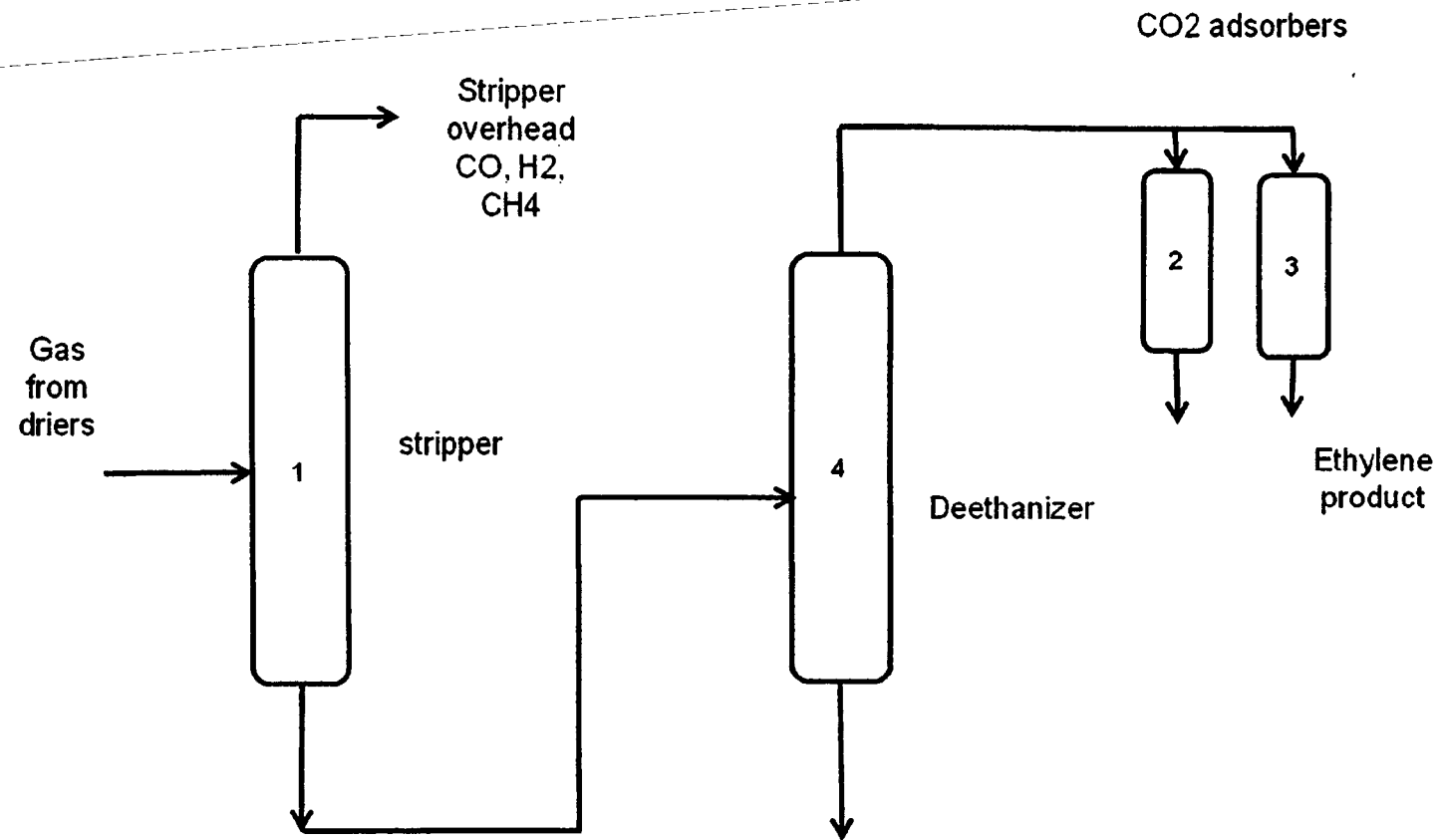


Fig 1

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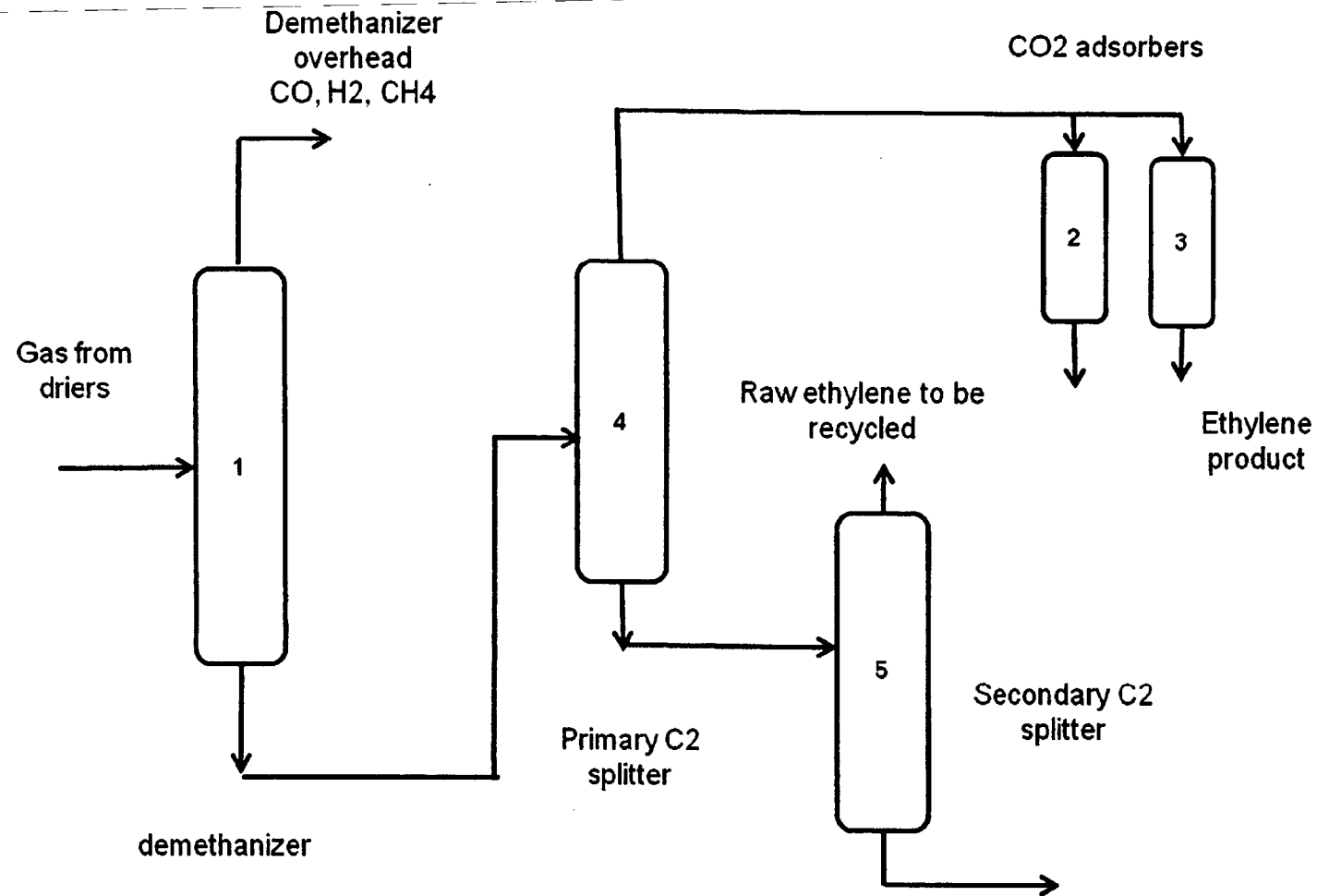


Fig 2

89-16

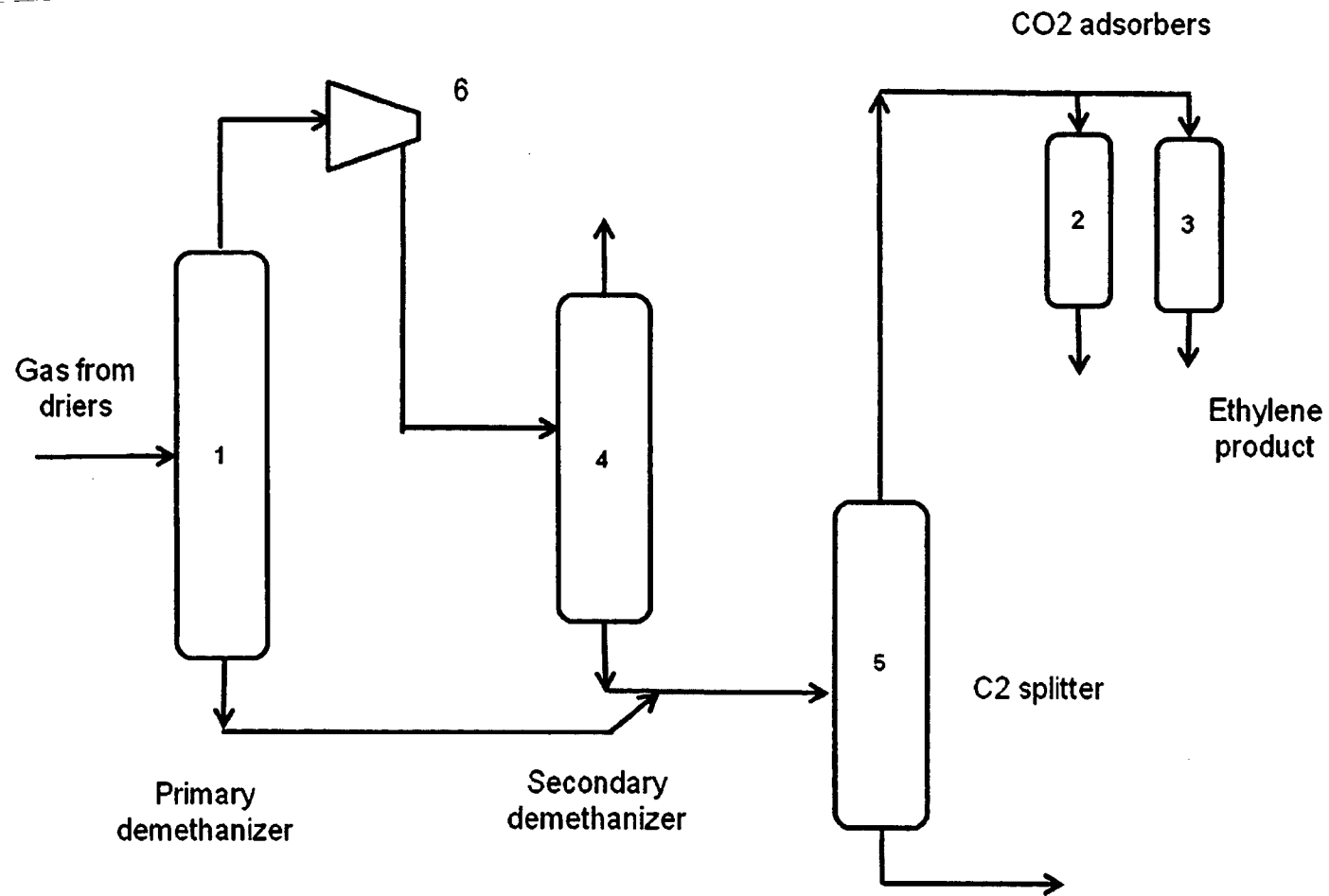


Fig 3

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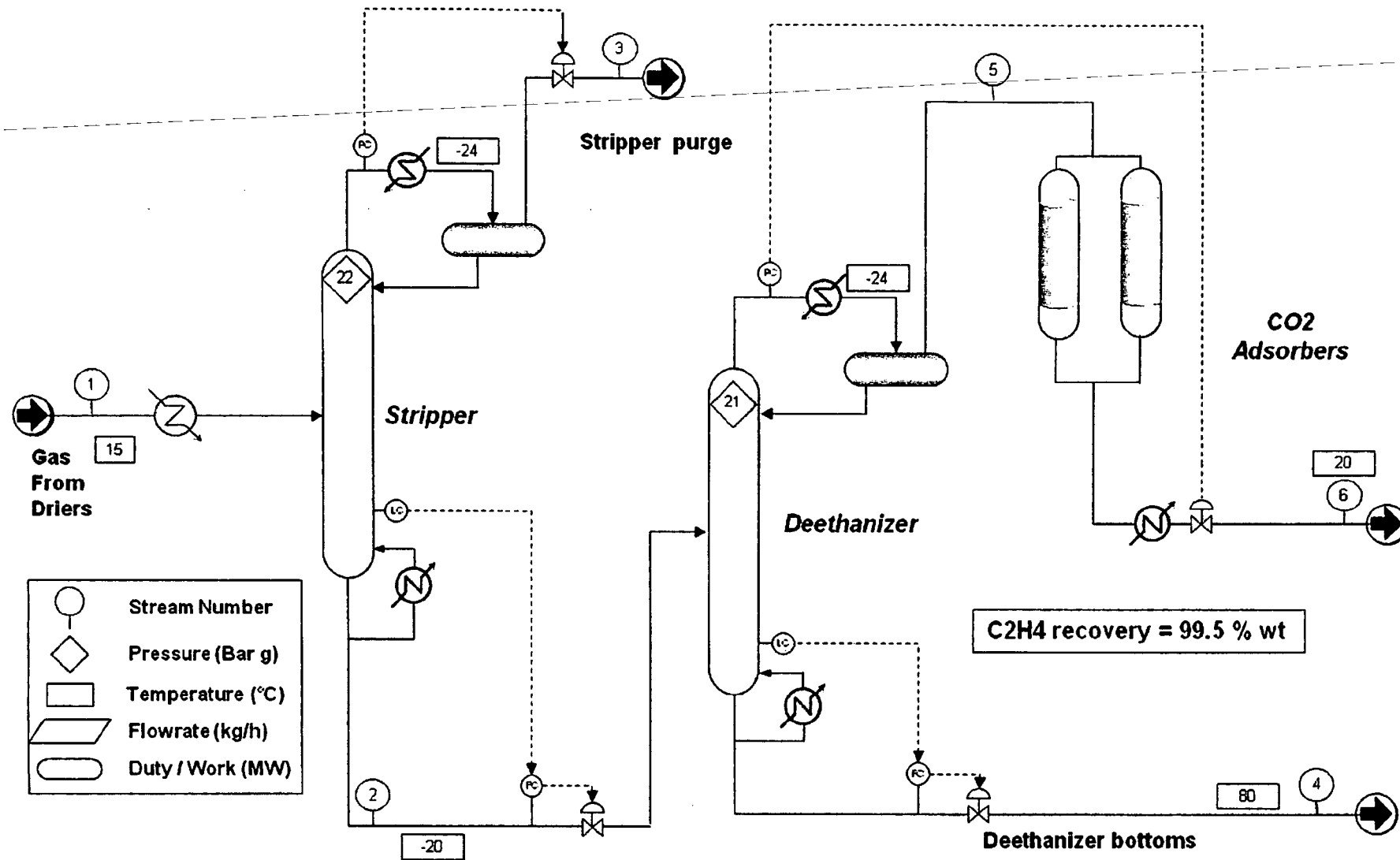


Fig 4

91

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) 08 August 2012 (08.08.2012)	
Applicant's or agent's file reference F-1299-WO	IMPORTANT NOTIFICATION
International application No. PCT/EP2012/063754	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.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
28 July 2011 (28.07.2011)	11290350.5	EP	06 August 2012 (06.08.2012)

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	Authorized officer Agnès Wittmann-Regis e-mail pt06.pct@wipo.int Telephone No. +41 22 338 74 06
Facsimile No. +41 22 338 89 70	

PATENT COOPERATION TREATY

PCT/EP2012/063754

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE

(PCT Rule 92bis.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)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference F-1299-WO	
International application No. PCT/EP2012/063754	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 Preliminary Examining Authority
☐ the International Searching Authority	☒ the designated Offices concerned
☐ the Authority(ies) specified for supplementary search	☐ the elected Offices concerned
	☐ other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Rochaix Thomas e-mail pt06.pct@wipo.int Telephone No. +41 22 338 74 06
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Facsimile No. +41 22 338 89 70

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800.176.089-2

-/-



Industria y Comercio

SUPERINTENDENCIA

RECIBO DE CAJA

No. 14 - 0019354

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 INVENCIÓN	515.000.00	515.000.00
			<u>\$515.000.00</u>

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

Responsable: _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 14-034851- -00000-0000

Fecha: 2014-02-19 14:59:04
Tra. 11 PATENTEIYII
Act. 411 PRESENTACIONDep. 2020 DIR.NUEVASCR
Eve: 378 FASENACIONALI
Folios: 96

Sede Centro: Carrera 13 No. 27 - 00 Pisos 3,4,5 y 10 Bogotá, D.C.- Colombia

Web: www.sic.gov.co e-mail: info@sic.gov.co Conmutador: (571) 5870000 Fax: (571) 5870284 Línea: 018000-910165 Call Center: (571) 6513240

, Febrero 19 de 2014 - 14:30:56

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800.176.089-2

- / -



Industria y Comercio

SUPERINTENDENCIA

RECIBO DE CAJA

No. 14 - 0019358

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
6 50005-01-01 SOLICITUDES	1607 REIVINDICACION PATENTE UNITARIA ADICIONAL A LAS 10 INIC	31.000.00	186.000.00
			\$186.000.00

SON: **CIENTO OCHENTA Y SEIS MIL PESOS MONEDA CORRIENTE***

Responsable: _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 14-034851- -00000-0000

Fecha: 2014-02-19 14:59:04 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 96

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Febrero 19 de 2014 - 14:30:56



No. 14-034851- -00000-0000

Fecha: 2014-02-19 14:59:04 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 96

PATENTE DE INVENCION ☐

MODELO DE UTIL

- ☐ 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 INVENCION 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 ☐