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54. TÍTULO PROCEDIMIENTO PARA LA PRODUCCION EN FASE CONDENSADA A PARTIR DE
UNO O MAS REACTANTES EN FASE GASEOSA.

51. CLASIFICACIÓN INTERNACIONAL C10G 2/00

71. SOLICITANTE BP EXPLORATION OPERATING COMPANY LIMITED.

DOMICILIO MIDDLESEX, GRAN BRETAÑA.

74. APODERADO DILIA RODRIGUEZ D'ALEMAN

22. BOGOTÁ, D. C., _____



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Patente de Invención

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Capítulo I

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Capítulo II

2

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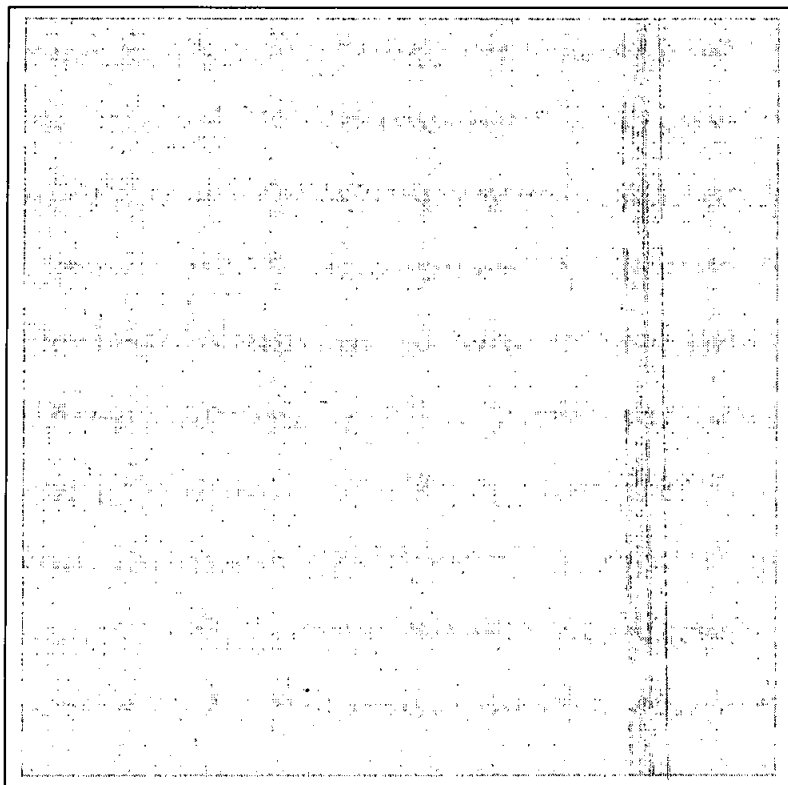
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- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Documento que acredite la existencia y representación legal cuando el solicitante sea persona jurídica
- ☐ Poderes si fuese el caso
- ☐ Documento de cesión del inventor al solicitante o a su causante
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- ☒ Copia de la solicitud internacional (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
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11 FIGURA CARACTERISTICA



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***** CONSIGNACION *****

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***** CONCEPTO *****

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1	50005-01-01	SOLICITUDES	
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RESUMEN

Un procedimiento para la producción de al menos un producto en fase condensada a partir de uno o más reactantes en fase gaseosa en presencia de un catalizador sólido que tiene uno o más componentes catalíticos, en donde el catalizador sólido tiene dos o más regiones en las que es diferente el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos.

**PROCEDIMIENTO PARA LA PRODUCCION DE UN PRODUCTO EN
FASE CONDENSADA A PARTIR DE UNO O MAS REACTANTES EN FASE
GASEOSA**

Esta invención está relacionada con el campo de la catálisis heterogénea y, más concretamente, con un procedimiento mejorado para convertir uno o más reactantes en fase gaseosa a un producto en fase condensada en presencia de un catalizador sólido.

La síntesis de Fischer-Tropsch es una reacción conocida para la producción de hidrocarburos a partir de singas (una mezcla de monóxido de carbono e hidrógeno), en donde el singas se pone en contacto con un catalizador heterogéneo para producir una mezcla de hidrocarburos. El singas se produce habitualmente mediante procedimientos tales como reformado con vapor de agua de carbón o gas natural, o bien a partir de la oxidación parcial de gas natural, y se puede producir también a partir de biomasa. Una de las aplicaciones de la síntesis de Fischer-Tropsch es la producción de líquidos hidrocarbonados y/o ceras que se pueden emplear como combustibles, o en la producción de combustibles, a través de procedimientos tal como el hidrocracking.

Durante los procedimientos catalizados de forma heterogénea para la síntesis de Fischer-Tropsch de hidrocarburos, pueden condensar los hidrocarburos producto, que son líquidos o sólidos bajo las condiciones de reacción, sobre las superficies del catalizador, lo cual inhibe el contacto del singas reactante con la superficie del catalizador y da lugar a una menor conversión de los reactantes.

Los reactores de diámetro variable han sido descritos hasta ahora para controlar las temperaturas de reacción en procedimientos que involucran reactantes y productos que se encuentran en fase gaseosa bajo las condiciones de reacción. Así, la

WO 03/011449 describe un aparato en donde el área en sección transversal de un lecho de catalizador sólido se incrementa a lo largo de su eje longitudinal mediante el uso de insertos conformados que portan material de transferencia de calor, y la DE 2 929 300 describe un reactor de diámetro variable para controlar la temperatura del catalizador en reacciones endotérmicas o exotérmicas, en donde la forma de los insertos que portan material de transferencia de calor se varía a lo largo de su longitud. Sin embargo, los procedimientos allí descritos no producen productos que se encuentran en una fase condensada bajo las condiciones de reacción y, por tanto, no enfocan la cuestión del recubrimiento del catalizador sólido con producto en fase condensada.

De acuerdo con la presente invención, se proporciona un procedimiento para la producción de un producto en fase condensada a partir de uno o más reactantes en fase gaseosa, cuyo procedimiento comprende alimentar uno o más reactantes al interior de un reactor, en cuyo reactor tales uno o más reactantes reaccionan en fase gaseosa en presencia de un catalizador sólido que tiene uno o más componentes catalíticos para producir al menos un producto en fase condensada, caracterizado porque el catalizador sólido tiene dos o más regiones en donde el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos es diferente.

En la presente invención, el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos del catalizador sólido es diferente dentro de dos o más regiones del catalizador sólido. Por el hecho de disponer diferentes tiempos de contacto dentro de cada región, las conversiones de tales uno o más reactantes en fase gaseosa a producto en fase condensada pueden ser optimizadas al mantener la reacción de al menos un producto en fase condensada a

tales uno o más componentes catalíticos (referida de aquí en adelante como la relación de producto en fase condensada a componente catalítico) en cada región dentro de un intervalo predeterminado de valores.

El intervalo predeterminado de valores para la relación de producto en fase condensada a componente catalítico puede estar basada, por ejemplo, en resultados de observaciones experimentales o en modelos teóricos. El intervalo se elegirá habitualmente de manera que se optimice la eficiencia del procedimiento, por ejemplo manteniendo bajas relaciones de producto en fase condensada a componente catalítico en regiones en donde se presenta una baja conversión de reactantes, o manteniendo altas relaciones de producto a componente catalítico cuando se requieran conversiones reducidas. El intervalo de valores para la reacción dependerá de la variabilidad de la concentración de producto en fase condensada dentro de cada región del catalizador.

Por ejemplo, en regiones del catalizador sólido en donde la cantidad de producto en fase condensada es elevada, entonces el recubrimiento del catalizador por el producto o productos en fase condensada será también elevado dando ello lugar a bajas conversiones de reactantes. Por tanto, las conversiones de reactantes se pueden mejorar aumentando el tiempo de contacto entre tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos dentro de esa región del catalizador sólido. Por el contrario, en regiones del catalizador sólido en donde está presente una baja cantidad de producto en fase condensada, la relación de producto en fase condensada a componente catalítico será baja, por lo que el recubrimiento del catalizador será bajo, y las conversiones pueden ser altas. En consecuencia, mediante la reducción del tiempo de contacto, se pueden conseguir conversiones reducidas.

En modalidades preferidas de la presente invención, el tiempo de contacto de

tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos en cada región del catalizador sólido, se puede variar por el hecho de disponer de regiones del catalizador sólido con diferentes concentraciones de componentes catalíticos y/o regiones del catalizador sólido con área en sección transversal y volumen diferentes.

De este modo, en una modalidad de la invención, el catalizador sólido comprende regiones que tienen diferentes concentraciones de tales uno o más componentes catalíticos. El área en sección transversal y/o el volumen del catalizador sólido pueden ser los mismos en diferentes regiones del catalizador sólido con el fin de conseguir un tiempo de contacto diferente entre tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos allí presentes. De este modo, un catalizador sólido que presenta dos o más regiones del mismo área en sección transversal y volumen, pero con una concentración diferente de tales uno o más componentes catalíticos, tendrá un tiempo de contacto diferente de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos. Por tanto, se puede emplear un catalizador sólido que tiene dos o más regiones con diferentes concentraciones de tales uno o más componentes catalíticos, para mantener de manera independiente la relación de tales uno o más productos en fase condensada a tales uno o más componentes catalíticos en cada región dentro de un intervalo predeterminado de valores.

Además, o alternatively, dos o más regiones del catalizador sólido tienen un área en sección transversal y volumen diferentes lo cual se traduce en una diferente velocidad espacial de los reactantes en fase gaseosa dentro de las diferentes regiones del catalizador sólido. La concentración de tales uno o más componentes catalíticos dentro de cada región del catalizador sólido puede ser la misma o

diferente, de manera que es diferente el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos en las dos o más regiones del catalizador sólido. Con preferencia, la concentración de tales uno o más componentes catalíticos dentro de cada región del catalizador sólido es uniforme por todo el catalizador sólido, lo cual puede reducir la complejidad de la carga del catalizador al interior de un reactor.

Por el hecho de incrementar el área en sección transversal y el volumen del catalizador sólido en regiones en donde las conversiones de reactantes son bajas, la relación de producto en fase condensada a componente catalítico desciende consecuentemente, dando ello como resultado un menor recubrimiento del catalizador y conversiones mejoradas de los reactantes. Por el contrario, por el hecho de disponer de un área en sección transversal y un volumen reducidos, se puede conseguir un mayor recubrimiento de tales uno o más componentes catalíticos por el producto en fase condensada, lo cual puede reducir las conversiones de reactantes en dicha región. Este último caso puede ser ventajoso, por ejemplo, para reacciones exotérmicas en donde el grado de exotermia dentro de una región del catalizador sólido se reduce preferentemente con el fin de evitar daños en el catalizador o la desactivación de este último. Por tales medios, se puede emplear un catalizador sólido que presenta dos o más regiones de área en sección transversal y volumen diferentes, para mantener de manera independiente la relación de al menos un producto en fase condensada a tales uno o más reactantes en fase gaseosa en cada región dentro de un intervalo predeterminado de valores.

Otra ventaja de esta modalidad de la presente invención es que el catalizador sólido puede ser distribuido dentro de un reactor de manera que pueden estar presentes volúmenes más elevados de catalizador en regiones en donde se desean

menores relaciones de producto o productos en fase condensada a tales uno o más componentes catalíticos, y pueden estar presentes volúmenes más bajos de catalizador en regiones en donde se requieren relaciones más elevadas, lo cual mejora la utilización del catalizador sólido. El área en sección transversal del catalizador sólido puede variar de forma continua entre las regiones de área en sección transversal y volumen presentes, o alternatively puede variar de un modo separado y escalonado, de manera que cada región del lecho de catalizador quede definida como un cambio gradual y distinto del área en sección transversal.

El catalizador sólido puede comprender, por ejemplo, un inserto conformado, tal como un monolito, un lecho de materiales fibrosos o una malla, o bien un lecho de partículas sólidas tales como esferas, perlas, gránulos o extruidos. Con preferencia, el catalizador sólido comprende partículas catalíticas empacadas, dado que las partículas se pueden insertar fácilmente en el reactor, de manera que las mismas se adaptan a las variaciones de diámetro allí existentes.

El catalizador sólido comprende uno o más componentes catalíticos que catalizan la conversión de tales uno o más reactantes en fase gaseosa a por lo menos un producto en fase condensada. Puede existir un solo componente catalítico, por ejemplo un metal de transición o compuesto de un metal de transición, o bien puede existir más de un componente catalítico, tales como co-catalizadores adicionales o promotores catalíticos. Tales uno o más componentes catalíticos pueden estar soportados o sin soportar.

La concentración de tales uno o más componentes catalíticos dentro de una región de catalizador sólido se puede variar, por ejemplo, mezclando partículas catalíticamente inertes con partículas que comprenden tales uno o más componentes catalíticos. Alternativa o adicionalmente, cuando tales uno o más componentes

catalíticos se encuentran sobre un soporte, entonces las diferentes regiones del catalizador sólido pueden comprender regiones que tienen diferentes cargas de tales uno o más componentes catalíticos sobre el soporte.

El reactor puede comprender uno o más insertos. En una modalidad preferida de la invención, el reactor comprende uno o más insertos dispuestos longitudinalmente y que presentan dos o más regiones con área en sección transversal y volumen variables. El catalizador sólido puede estar dentro de tales uno o más insertos, o bien en el espacio del reactor entre tales uno o más insertos y las paredes interiores del reactor. Dependiendo de dónde esté situado el catalizador, los insertos o la región libre de catalizador entre los insertos y las paredes interiores del reactor pueden emplearse para soportar un medio de intercambio de calor con el fin de controlar la temperatura dentro del reactor. El medio de intercambio de calor puede fluir en corriente paralela con respecto al flujo de tales uno o más reactantes gaseosos, o puede fluir en contracorriente con respecto al flujo de tales uno o más reactantes gaseosos.

En el transcurso de la reacción, se forman uno o más productos, al menos uno de los cuales se encuentra en la fase condensada bajo las condiciones de reacción. La invención resulta particularmente adecuada para procedimientos en donde los productos están en fase líquida bajo las condiciones de reacción, dado que los productos líquidos se separan más fácilmente de un catalizador sólido en comparación con los productos de tipo céreo u otros productos sólidos.

En una modalidad de la presente invención, se alimentan en corrientes paralelas dos reactantes en fase gaseosa al interior de un reactor y se pasan sobre un lecho de catalizador fijo que tiene una concentración uniforme de componentes catalíticos, en donde los reactantes en fase gaseosa reaccionan para producir un

producto en fase líquida. En el punto inicial de contacto de los dos reactantes en fase gaseosa con el lecho del catalizador sólido, la concentración de producto en fase líquida es baja. La concentración del producto en fase líquida aumenta a medida que procede la reacción y llega a ser más concentrada a medida que los reactantes en fase gaseosa pasan a lo largo del lecho de catalizador sólido. Esto puede causar un mayor grado de recubrimiento del catalizador sólido por el producto en fase líquida en regiones aguas abajo del catalizador sólido, en relación a la dirección de flujo de los reactantes en fase gaseosa. Por el hecho de disponer de un área en sección transversal y un volumen incrementados del catalizador sólido en regiones aguas abajo, se reduce la relación de producto líquido a tales uno o más componentes catalíticos, conduciendo ello a un menor recubrimiento del catalizador y también a un mayor tiempo de contacto de los reactantes en fase gaseosa con el catalizador sólido dentro de dichas regiones. El resultado es una mejora en las conversiones de reactantes en las regiones de área en sección transversal y volumen más grandes.

En una modalidad alternativa de la invención, el área en sección transversal y el volumen del catalizador sólido se reducen en una región adyacente al punto inicial de contacto con tales uno o más reactantes en fase gaseosa. Esta modalidad podría ser ventajosa, por ejemplo, en reacciones en donde existe un retardo entre el contacto inicial de tales uno o más reactantes con el catalizador sólido y el inicio de una reacción exotérmica. De este modo, inicialmente es ventajoso disponer una velocidad de flujo lenta de los reactantes sobre el catalizador sólido con el fin de aumentar el tiempo de contacto de los reactantes con tales uno o más componentes catalíticos, y para promover el inicio de la reacción. Una vez iniciada la reacción y a medida que aumenta la velocidad de reacción, el calor generado por la exotermia puede causar potencialmente daños en el catalizador o la desactivación de este último, pudiendo

dar ello como resultado una menor selectividad al producto deseado y una menor vida de servicio del catalizador. Por tanto, a través de la reducción del área en sección transversal y volumen de una región adyacente aguas abajo del catalizador sólido, se incrementa la velocidad de flujo de los reactantes sobre el catalizador, lo cual reduce el tiempo de contacto de los reactantes con el catalizador sólido, pudiendo ello dar como resultado menores conversiones de reactantes y una menor velocidad de reacción. Además, al reducir el área en sección transversal y el volumen, se puede aumentar la relación de productos en fase condensada a tales uno o más componentes catalíticos, lo cual actúa además para reducir la conversión de tales uno o más reactantes en fase gaseosa. Opcionalmente, las regiones del catalizador sólido situadas más aguas abajo pueden presentar un área en sección transversal y un volumen incrementados, con el fin de mejorar las conversiones en aquellos casos en los que de otro modo podría presentarse un mayor recubrimiento del catalizador sólido por el producto líquido. Alternativamente, las regiones del catalizador sólido situadas más aguas abajo pueden tener un área en sección transversal y un volumen incluso más bajos.

El catalizador sólido puede comprender espacios de separación o porciones que están libres de catalizador. Por ejemplo, en modalidades de la invención en donde el catalizador sólido comprende partículas y las diferentes regiones del catalizador sólido tienen diferentes concentraciones de componente o componentes catalíticos, las diferentes regiones del catalizador pueden estar separadas por rejillas con el fin de prevenir la mezcla cruzada de las partículas en las diferentes regiones. En dichas modalidades, el volumen entre las rejillas puede no estar completamente relleno con catalizador y partículas inertes, por ejemplo como resultado de la sedimentación de las partículas.

Cuando existe más de un reactante gaseoso, los reactantes se pueden alimentar al interior del reactor por separado o previamente mezclados. Los mismos pueden inicialmente entrar en contacto con el catalizador sólido en la misma porción del catalizador sólido, o bien se pueden añadir en diferentes porciones del catalizador sólido. El punto inicial de contacto de tales uno o más reactantes con el catalizador sólido es el punto en el cual todos los reactantes entran inicialmente en contacto entre sí en fase gaseosa y en presencia del catalizador sólido. Con preferencia, tales uno o más reactantes gaseosos fluyen en corrientes paralelas sobre el catalizador sólido.

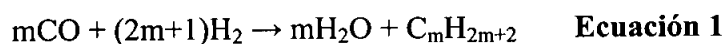
Tales uno o más reactantes en fase gaseosa se pueden alimentar al interior del reactor en fase gaseosa o, alternativamente, como una fase condensada que se vaporiza dentro del reactor, de manera que la misma entra en contacto con el catalizador sólido en la fase gaseosa.

El procedimiento de la presente invención puede comprender opcionalmente una pluralidad de reactores dispuestos en serie, de manera que cualquier composición extraída del primer reactor se alimenta a un segundo reactor y la composición extraída del segundo reactor se alimenta a un tercer reactor y así sucesivamente. En esta modalidad, la composición extraída de cada reactor comprende producto en fase condensada y reactantes sin reaccionar. Opcionalmente, al menos parte del producto en fase condensada se extrae en un punto entre los reactores y se alimenta, por ejemplo, a una sección de purificación. En dicha modalidad, cada reactor comprende catalizador sólido y al menos el primer reactor contendrá catalizador sólido con dos o más regiones en donde es diferente el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos, como anteriormente se ha descrito aquí.

La corriente o corrientes que contienen producto, extraídas de tales uno o más

reactores, se alimentan habitualmente a una zona de purificación, en donde se separan los reactantes sin reaccionar y los subproductos indeseables, y opcionalmente se reciclan al reactor o a cualquiera de tales uno o más reactores.

La presente invención es adecuada para utilizarse en la producción catalizada de forma heterogénea de hidrocarburos a partir de singas mediante la síntesis de Fischer-Tropsch, por ejemplo en la producción de un combustible diesel o de aviación o un precursor del mismo. La síntesis de Fischer-Tropsch de hidrocarburos a partir de singas puede ser representada por la ecuación 1:



El procedimiento dará lugar habitualmente a un producto que comprende hidrocarburos con un intervalo de números de átomos de carbono que dependerá, inter alia, de la relación $\text{CO}:\text{H}_2$ del singas, de las condiciones de procesado y del catalizador. Los hidrocarburos o mezclas de los mismos son preferentemente líquidos bajo las condiciones de reacción. Con preferencia, el número de hidrocarburos se encuentra predominantemente en el intervalo en donde el valor de “m” en la ecuación 1 es mayor de 5.

La relación en volumen de hidrógeno a monóxido de carbono ($\text{H}_2:\text{CO}$) en el singas reactante es con preferencia del orden de 0,5:1 a 5:1, más preferentemente de 1:1 a 3:1 y con suma preferencia de 1,8:1 a 2,2:1. Tales uno o más reactantes gaseosos pueden también comprender otros componentes gaseosos, tales como nitrógeno, dióxido de carbono, agua, metano y otros hidrocarburos ligeros saturados y/o insaturados, estando presentes preferentemente cada uno de ellos en una concentración menor de 30% en volumen.

La temperatura de la reacción de Fischer-Tropsch es con preferencia del orden de 100 a 400° C, más preferentemente de 150 a 350° C y con suma preferencia

de 150 a 250° C. La presión es con preferencia del orden de 1 a 100 bares (de 0,1 a 10 MPa), más preferentemente de 5 a 75 bares (de 0,5 a 7,5 MPa) y con suma preferencia de 10 a 40 bares (de 1,0 a 4,0 MPa).

Tales uno o más reactantes gaseosos pueden también comprender materiales reciclados extraídos de cualquier punto del procedimiento, tales como reactantes sin reaccionar separados del producto hidrocarbonado durante la purificación.

El singas se pasa normalmente sobre el lecho de catalizador a una velocidad espacial horaria de gas (GHSV) del orden de 100 a 10.000 h⁻¹ (volúmenes de gas convertidos a temperatura y presión normales), con preferencia del orden de 250 a 5.000 h⁻¹, tal como de 250 a 3.000 h⁻¹ y más preferentemente de 250 a 2.000 h⁻¹.

El catalizador es habitualmente un catalizador de lecho fijo en partículas que comprende un metal activo para la catálisis de Fischer-Tropsch. Los metales preferidos se eligen entre uno o más de cobalto, hierro, rutenio, níquel, molibdeno, tungsteno y renio, con preferencia cobalto y/o hierro, incluso más preferentemente cobalto. Con preferencia, el metal está soportado, por ejemplo sobre un soporte que comprende uno o más de sílice, alúmina, sílice/alúmina, titania, zirconia, ceria u óxido de zinc. Preferentemente, el soporte es alúmina y/u óxido de zinc, más preferentemente óxido de zinc. Con suma preferencia, el catalizador comprende cobalto sobre un soporte de óxido de zinc. Composiciones catalíticas adecuadas para los procesos de Fischer-Tropsch, y en la presente invención, se describen, por ejemplo, en EP-A-0 261 870 y EP-A-0 209 980.

La invención será ilustrada ahora con referencia a las figuras, en donde:

La figura 1 es una representación esquemática de secciones longitudinales de dos reactores en donde se resalta la concentración de producto en fase condensada en tres regiones diferentes de dos reactores diferentes que contienen el mismo

catalizador sólido.

La figura 2 es una representación esquemática de una sección longitudinal de un reactor de acuerdo con la presente invención que comprende insertos rellenos de catalizador.

La figura 3 muestra una serie de secciones transversales a través del reactor ilustrado en la figura 2.

La figura 1 ilustra la diferencia de concentración de un producto en fase condensada en tres regiones de un reactor A con un catalizador sólido que tiene regiones de área en sección transversal y volumen constantes, y concentración uniforme de tales uno o más componentes catalíticos, y un reactor B con catalizador sólido que tiene el mismo catalizador sólido, pero con regiones de área en sección transversal y volumen diferentes. Por tanto, el catalizador sólido del reactor A se encuentra al margen de la presente invención, mientras que el del reactor B está de acuerdo con la presente invención. Se alimentan dos reactantes 1 y 2 en corrientes paralelas y descendientemente al interior de cada reactor y reaccionan en la fase gaseosa en presencia del catalizador sólido (no mostrado) para producir producto en fase condensada 4. La concentración del producto en fase condensada 3 dentro del reactor viene representada por el grado de sombreado, en donde el sombreado claro representa una baja concentración de producto en fase condensada y el sombreado fuerte representa una alta concentración de producto en fase condensada. En el reactor A, el volumen de cada región del catalizador sólido es el mismo. A medida que aumenta la concentración de producto desde la Región 1 a la Región 3, el resultado es un incremento de la relación de producto en fase condensada a tales uno o más componentes catalíticos en las respectivas regiones. En el reactor B, la relación se mantiene constante en todas las tres regiones del catalizador sólido

mediante el incremento del área en sección transversal y del volumen en regiones consecutivas. De este modo, las conversiones de reactantes en las tres regiones del catalizador sólido en el reactor B son optimizadas a través de la reducción del grado de recubrimiento del catalizador por el producto en fase condensada mediante la reducción de la relación de producto en fase condensada a tales uno o más componentes catalíticos.

La figura 2 muestra un reactor 11 con una pluralidad de insertos 12 que contienen partículas de catalizador de Fischer-Tropsch 18. Se alimenta refrigerante al interior del espacio del reactor entre los insertos 13 a través de la entrada 14 y se extrae a través de la salida 15. El singas 16 se alimenta al interior de los insertos que contienen catalizador a través de la entrada 17 y entra en contacto con el catalizador sólido 18 dentro de los insertos. Los productos hidrocarbonados en fase condensada y los reactantes sin reaccionar se extraen de los insertos que contienen catalizador a través de la salida 19. El diámetro de los insertos aumenta progresivamente desde la parte superior de los lechos de catalizador sólido, en donde los gases reactantes entran primeramente en contacto con el catalizador, a la parte inferior de los lechos de catalizador sólido, formando regiones discretas del lecho de catalizador sólido con diferente área en sección transversal. El volumen de los lechos de catalizador sólido aumenta a medida que lo hace el área en sección transversal.

La figura 3 ilustra cuatro secciones transversales del reactor 11 de la figura 1, a través de los planos A-A', B-B', C-C' y D-D'. Los insertos 12 y el área de sección transversal de los lechos de catalizador sólido 18 allí presentes, tienen diferentes diámetros Z a diferentes profundidades. El espacio 13 entre los insertos está relleno de refrigerante.

REIVINDICACIONES

1.- Procedimiento para la producción de un producto en fase condensada a partir de uno o más reactantes en fase gaseosa, cuyo procedimiento comprende alimentar uno o más reactantes al interior de un reactor, en cuyo reactor tales uno o más reactantes reaccionan en fase gaseosa en presencia de un catalizador sólido que tiene uno o más componentes catalíticos para producir al menos un producto en fase condensada, caracterizado porque el catalizador sólido tiene dos o más regiones en donde el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos es diferente.

2.- Procedimiento según la reivindicación 1, caracterizado porque cada región del catalizador sólido tiene diferentes concentraciones de tales uno o más componentes catalíticos.

3.- Procedimiento según la reivindicación 1 o 2, caracterizado porque las dos o más regiones del catalizador sólido tiene un área en sección transversal y un volumen diferentes.

4.- Procedimiento según cualquiera de las reivindicación 1 a 3, caracterizado porque el catalizador sólido comprende partículas tales como esferas, perlas, gránulos o extruidos.

5.- Procedimiento según cualquiera de las reivindicaciones 1 a 4, caracterizado porque el catalizador sólido comprende un soporte seleccionado entre uno o más de sílice, alúmina, sílice/alúmina, titania, zirconia, ceria u óxido de zinc.

6.- Procedimiento según cualquiera de las reivindicaciones 1 a 5, caracterizado porque el componente o componentes catalíticos consisten en un metal activo para la síntesis de Fischer-Tropsch seleccionado entre uno o más de cobalto, hierro, rutenio, níquel, molibdeno, tungsteno y renio.

7.- Procedimiento según cualquiera de las reivindicaciones 1 a 6, caracterizado porque el singas es un reactante y el producto o productos en fase condensada comprenden una mezcla de hidrocarburos que son líquidos bajo las condiciones de reacción.

8.- Procedimiento según cualquiera de las reivindicaciones 1 a 7, caracterizado porque el reactor comprende uno o más insertos.

9.- Procedimiento según la reivindicación 8, caracterizado porque tales uno o más insertos contienen el catalizador sólido y el espacio entre los insertos está rodeado por un medio de transferencia de calor.

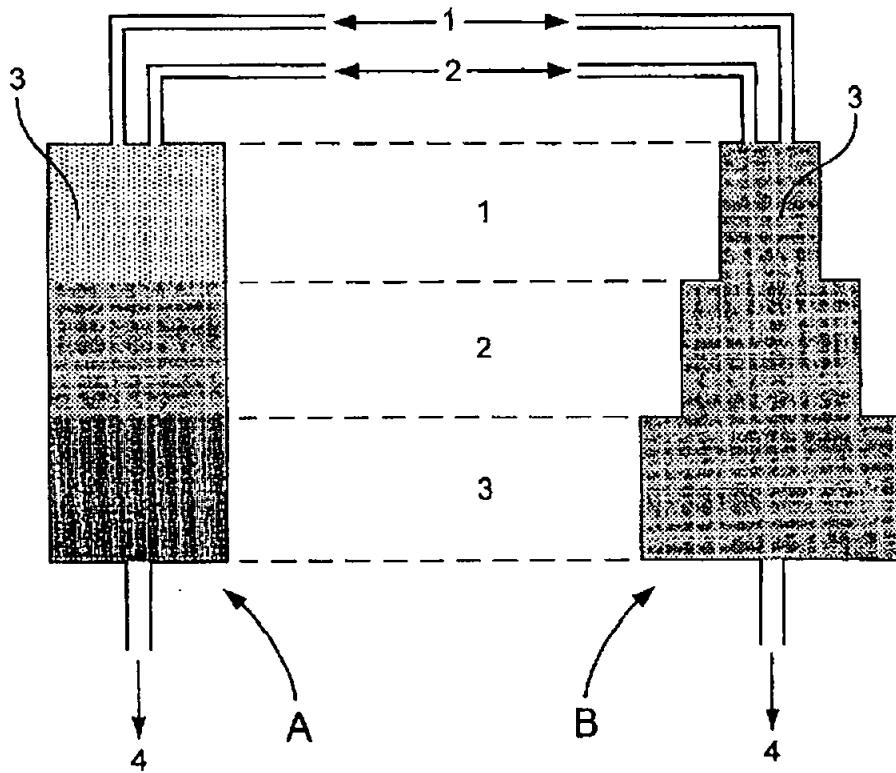
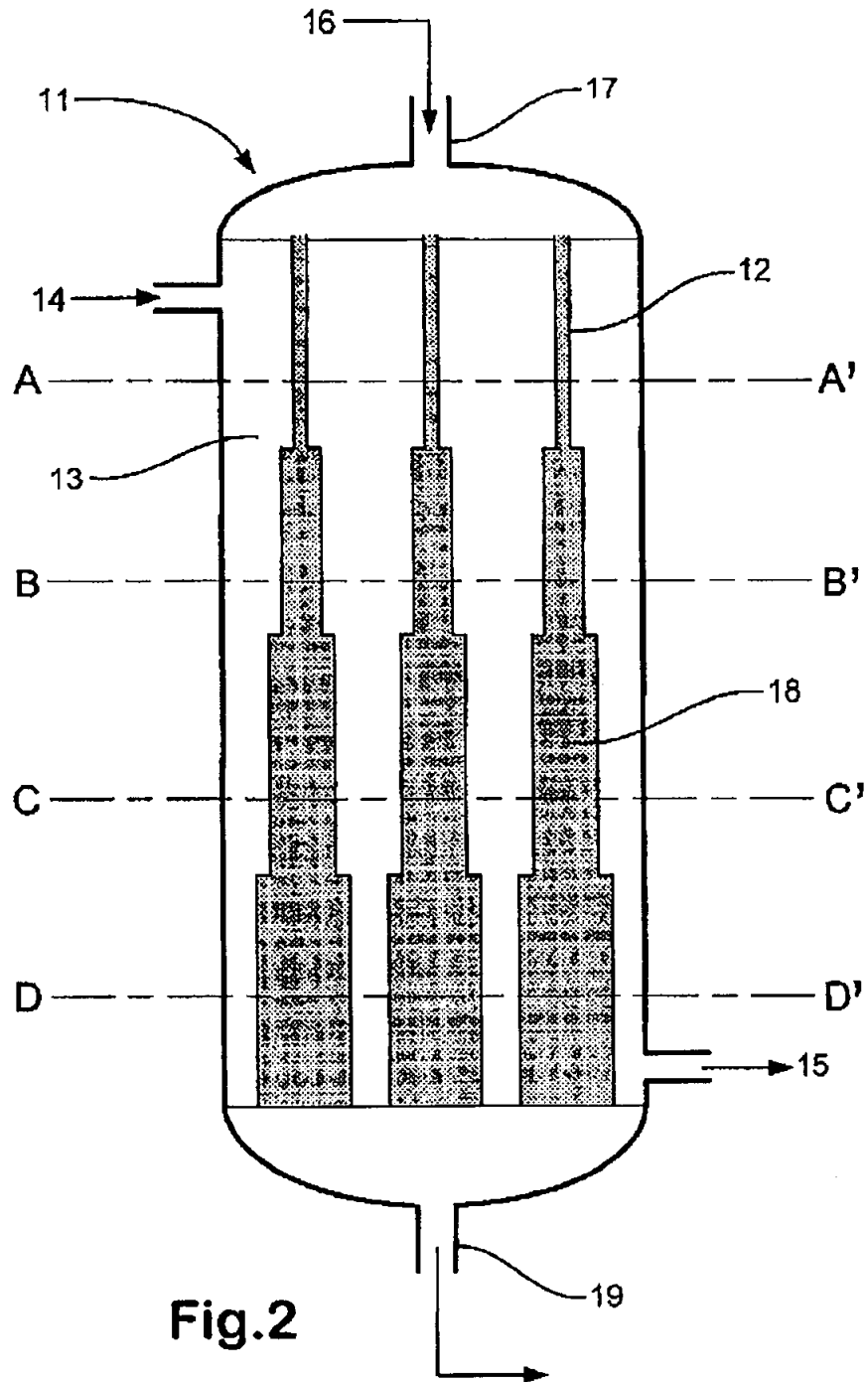


Fig.1



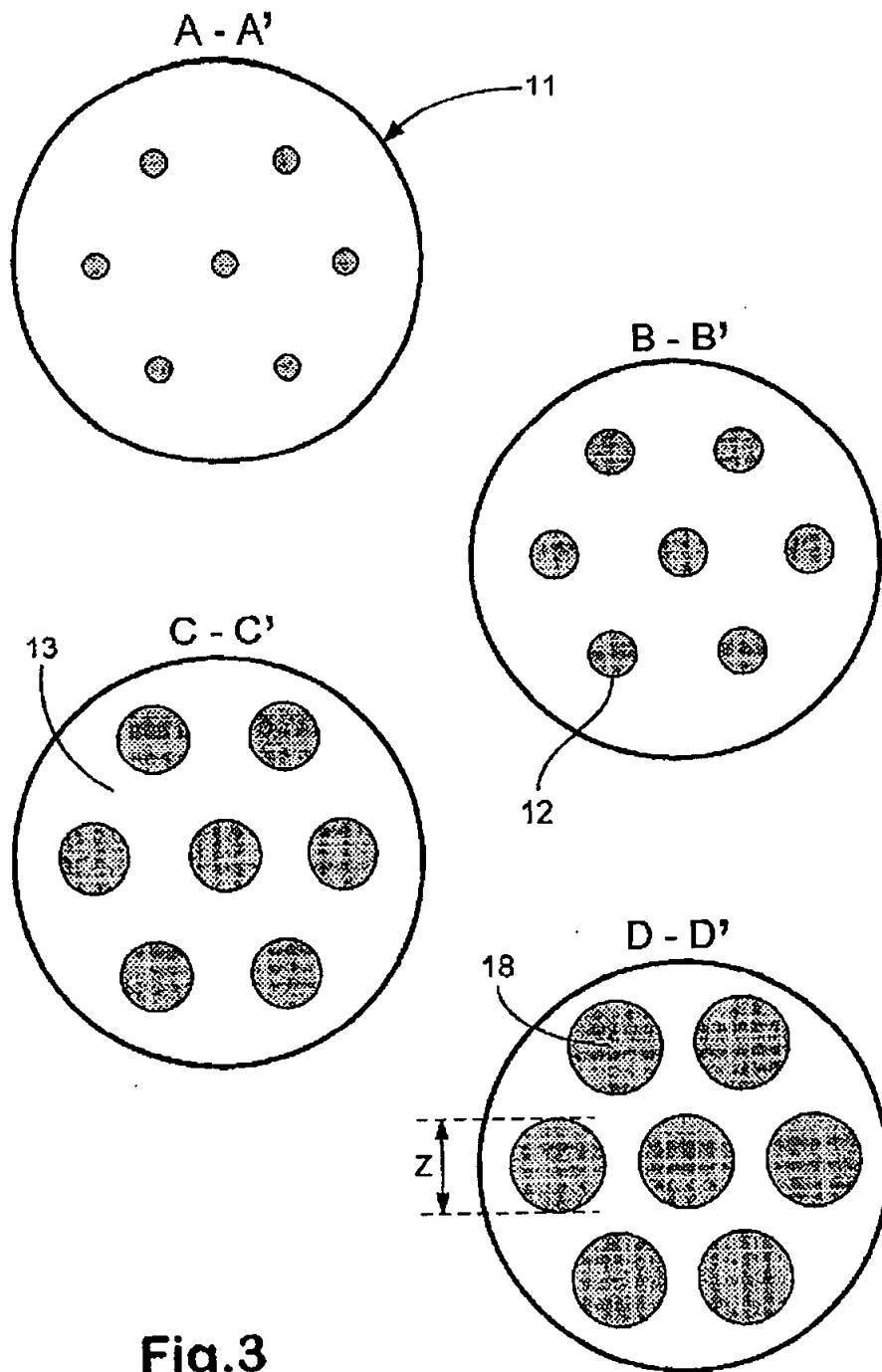


Fig.3

*Inicialmente presentadas en
fase internacional.*

REIVINDICACIONES

1.- Procedimiento para la producción de un producto en fase condensada a partir de uno o más reactantes en fase gaseosa, cuyo procedimiento comprende alimentar uno o más reactantes al interior de un reactor, en cuyo reactor tales uno o más reactantes reaccionan en fase gaseosa en presencia de un catalizador sólido que tiene uno o más componentes catalíticos para producir al menos un producto en fase condensada, caracterizado porque el catalizador sólido tiene dos o más regiones en donde el tiempo de contacto de tales uno o más reactantes en fase gaseosa con tales uno o más componentes catalíticos es diferente.

2.- Procedimiento según la reivindicación 1, caracterizado porque cada región del catalizador sólido tiene diferentes concentraciones de tales uno o más componentes catalíticos.

3.- Procedimiento según la reivindicación 1 o 2, caracterizado porque las dos o más regiones del catalizador sólido tiene un área en sección transversal y un volumen diferentes.

4.- Procedimiento según cualquiera de las reivindicación 1 a 3, caracterizado porque el catalizador sólido comprende partículas tales como esferas, perlas, gránulos o extruidos.

5.- Procedimiento según cualquiera de las reivindicaciones 1 a 4, caracterizado porque el catalizador sólido comprende un soporte seleccionado entre uno o más de sílice, alúmina, sílice/alúmina, titania, zirconia, ceria u óxido de zinc.

6.- Procedimiento según cualquiera de las reivindicaciones 1 a 5, caracterizado porque el componente o componentes catalíticos consisten en un metal activo para la síntesis de Fischer-Tropsch seleccionado entre uno o más de cobalto, hierro, rutenio, níquel, molibdeno, tungsteno y renio.

7.- Procedimiento según cualquiera de las reivindicaciones 1 a 6, caracterizado porque el singas es un reactante y el producto o productos en fase condensada comprenden una mezcla de hidrocarburos que son líquidos bajo las

condiciones de reacción.

8.- Procedimiento según cualquiera de las reivindicaciones 1 a 7, caracterizado porque el reactor comprende uno o más insertos.

9.- Procedimiento según la reivindicación 8, caracterizado porque tales uno o más insertos contienen el catalizador sólido y el espacio entre los insertos está rodeado por un medio de transferencia de calor.

10.- Uso de un catalizador sólido que comprende uno o más componentes catalíticos y que tiene dos o más regiones con diferentes concentraciones de tales uno o más componentes catalíticos, en un procedimiento para la producción de al menos un producto en fase condensada a partir de uno o más reactantes en fase gaseosa, para mantener independientemente la relación de tales uno o más productos en fase condensada a tales uno o más componentes catalíticos en las dos o más regiones del catalizador sólido dentro de un intervalo predeterminado de valores.

11.- Uso de un catalizador sólido según la reivindicación 10, caracterizado porque el procedimiento es un procedimiento según la reivindicación 2 o según cualquiera de las reivindicaciones 3 a 9 cuando estas dependen de la reivindicación 3.

12.- Uso de un catalizador sólido que comprende uno o más componentes catalíticos y que tienen dos o más regiones de área en sección transversal y volumen diferentes, en un procedimiento para la producción de al menos un producto en fase condensada a partir de uno o más reactantes en fase gaseosa, para mantener independientemente la relación de tales uno o más productos en fase condensada a tales uno o más componentes catalíticos en cada región del catalizador sólido dentro de un intervalo predeterminado de valores.

13.- Uso de un catalizador sólido según la reivindicación 12, caracterizado porque el procedimiento es un procedimiento según la reivindicación 3 o según cualquiera de las reivindicaciones 4 a 9 cuando estas dependen de la reivindicación 3.

bp

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International Preliminary Examining
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Germany

13th July 2007

PAT/RO/aw/024/10309

BY FACSIMILE

Dear Sirs

International Application No. PCT/GB2006/004359
BP Exploration Operating Company Limited
BP Case No. BPX 10309

This is with reference to the Written Opinion of the International Searching Authority dated 21st February 2007 in relation to the above-identified PCT application, and to the enclosed Demand for International Preliminary Examination.

Amendments

Pursuant to Article 34 PCT, the Applicant wishes to amend the claims by deleting claims 10 to 13.

A marked-up copy of the claims showing the amendments is enclosed, together with a replacement set of claims in which the amendments have been incorporated.

Novelty

In the Written Opinion, it is stated that claim 1 lacks novelty over GB 2 132 111 (D1).

The Applicant disagrees.

Claim 1 of the present application relates to a process for the production of a condensed-phase product from one or more gas-phase reactants over a

Contd/

solid catalyst having one or more catalyst components, in which the catalyst comprises two or more regions in which the contact time of the gas-phase reactants with the one or more catalyst components is different.

D1 relates to a process for the methanisation of syngas over a catalyst in a variable diameter reactor. There is no disclosure in D1 of the production of condensed-phase product. The products are methane, steam and fuel gases (page 1 lines 24-25), none of which would be in a condensed phase under the conditions of the disclosed methanisation reaction.

Claim 1, and claims dependent thereon, is therefore novel over D1.

Inventive Step

D1 is taken to represent the closest prior art for the assessment of inventive step, as it relates to a reaction in which one or more gas-phase reactants are contacted with a solid catalyst in which the catalyst comprises two or more regions in which the contact time of the gas-phase reactants with the catalyst is different.

A difference between claim 1 and D1 is that claim 1 relates to a process in which there is a condensed-phase product.

In processes where condensed-phase products are produced, the solid catalyst becomes covered in condensed-phase product, which reduces reactant conversions (as discussed at page 1 lines 14-18 of the present application).

The objective technical problem to be solved can therefore be formulated as to reduce the extent of coverage of solid catalyst components by condensed phase product.

The present invention solves this problem by operating the process such that the contact time of the one or more gas-phase reactants with one or more components of the catalyst is different in two or more regions of the solid catalyst. This enables the extent of catalyst coverage in different regions to be controlled, which enables reactant conversions to be improved, as described for example at page 2 lines 18-26.

D1 relates to the conversion of gas-phase reactants to produce gas-phase products, and is silent on products being in the condensed phase. It is therefore also silent on the subject of catalyst coverage by condensed-phase product, and contains no relevant teaching on this subject.

Therefore, there is no teaching in D1 of the effects of condensed phase product on coverage of the solid catalyst, and hence the art-skilled person would not look to D1 to solve the objective technical problem as defined above.

Claim 1, and claims dependent thereon, is therefore inventive over D1.

Other objections

The Examiner states that claim 1 does not define the matter for which protection is sought.

The Applicant disagrees, and submits that the result to be achieved is to reduce coverage of the catalyst components by the condensed-phase product. The invention of claim 1 achieves this result by operating the process such that the contact time between the one or more gas-phase reactants with catalyst components is different in two or more regions of the catalyst.

The art-skilled person is taught a number of ways to practice the invention, for example at page 2 line 3 to page 3 line 32 and in the examples at page 8 line 26 to page 9 line 2.

Claims 2 and 3, for example, relate to specific embodiments of the invention, in which claim 2 relates to a solid catalyst having two or more regions with different concentrations of catalyst components, and claim 3 relating to the solid catalyst having two or more regions with different cross-sectional area and volume.

The Applicant therefore believes that the invention of claim 1 is clearly defined, and comprises all the technical features necessary for the art-skilled person to understand the scope of protection and to practice the invention.

By the deletion of claims 10 to 13, the Examiner's objections relating to these claims are considered to be no longer applicable.

The Applicant believes that the claims of the present application conform to the requirements of Articles 6, 33(2), 33(3) and 33(4) PCT, and a positive International Preliminary Report on Patentability is respectfully requested. Should the Examining Division believe otherwise, an opportunity to respond to any further objections is requested, pursuant to Rule 66.4 PCT

Yours faithfully



Dr Richard Oldroyd_
Global Patents & Technology Law (Central)



Eric Dekezel
GA No.36478

Encs

BP

Richard Oldroyd

BP International Limited. Global Patents & Technology Law (Central).
(Derecho Global de Patentes y Tecnología)
Bldg 200, 1st Floor, Chertsey Road.

Autoridad Internacional Examinadora Preliminar
Oficina Europea de Patentes
Dirección General 2
Erhardtstrasse 27 D-80298 Munchen 2. Alemania

13 de julio de 2007.

PAT/RO/aw/024/10309

Por fax:

Apreciados señores:

Solicitud Internacional No. PCT/GB2008/004359
BP Exploration Operating Company Limited
Caso BP No. BPX 10309

Nos referimos a la Opinión Escrita de la Autoridad Internacional de Búsqueda fechada el 21 de febrero de 2007 con relación a la solicitud PCT anteriormente mencionada y a la demanda adjunta para Examen Internacional Preliminar.

Enmiendas:

De acuerdo con el Artículo 34 PCT, el Solicitante desea enmendar las reclamaciones eliminándolas de la 10 a la 13.

Se adjunta una copia marcada de las reclamaciones, que muestra las enmiendas junto con una serie de reclamaciones de reemplazo en las cuales han sido incorporadas las enmiendas.



Novedad:

En la Opinión Escrita se establece que a la reclamación 1 le falta novedad sobre GB 2 132 111 (D1).

El solicitante no está de acuerdo.

La reclamación 1 de la presente solicitud se refiere a un proceso para la producción de un producto de fase condensada de uno o más reactantes de fase de gas sobre un catalizador sólido que tiene uno o más componentes catalizadores, en el cual es diferente el tiempo de contacto de los reactantes de fase de gas con uno o más de los componentes del catalizador.

D1 se refiere a un proceso para la metanización de gas de síntesis sobre un catalizador en un reactor de diámetro variable. No hay revelación en D1 de la producción del producto de fase condensada. Los productos son metano, vapor y gases combustibles (página 1, líneas 24-25), ninguno de los cuales estaría en una fase condensada de acuerdo con las condiciones de la reacción revelada de metanización.

La reclamación 1 y las reclamaciones que dependen de ella es por lo tanto novedad sobre D1.

Paso inventivo.

D1 se toma para representar el arte previo más cercano para la evaluación del paso inventivo, puesto que se relaciona con una



Traductor Oficial

JORGE E. SIERRA REYES

Matr. No. 376 - 1993 Minjusticia

reacción en la cual uno o más reactivos de la fase de gas están contactados con un catalizador sólido en el cual el catalizador abarca dos o más regiones en las cuales es diferente el tiempo de contacto de los reactantes de la fase de gas con el catalizador.

Una diferencia entre la reclamación 1 y D1 es que la reclamación 1 se relaciona con un proceso en el cual hay un producto de fase condensada.

En los procesos donde se originan productos de fase condensada, el catalizador sólido queda cubierto en el producto de fase condensada, lo cual reduce las conversiones de reactantes (como se estableció en la página 1 líneas 14-18 de la presente solicitud).

El problema técnico objetivo que debe resolverse puede por lo tanto formularse como reducir la extensión del cubrimiento de los componentes del catalizador sólido por el producto de fase condensada.

El presente invento resuelve este problema realizando el proceso de forma que el tiempo de contacto de uno o más de los reactantes de la fase de gas con uno o más componentes del catalizador sea diferente en dos o más regiones del catalizador sólido. Esto permite que la extensión del cubrimiento del catalizador se controle en diferentes regiones, lo cual permite que se mejoren las conversiones del reactante, como se describe por ejemplo en la página 2, líneas 18-26.



D1 se relaciona con la conversión de los reactantes de la fase de gas para originar productos de fase de gas y es poco notorio en productos que estén en la fase condensada. Por lo tanto también es poco notorio en el asunto del cubrimiento del catalizador por el producto en fase condensada y no contiene ninguna enseñanza de importancia sobre este asunto.

Por lo tanto, no hay enseñanza D1 de los efectos del producto de fase condensada sobre el cubrimiento del catalizador sólido y de ahí que la persona hábil en el arte no observaría el D1 resolver el problema técnico objetivo como se define anteriormente.

La reclamación 1 y las reclamaciones que dependen de la misma es por lo tanto inventiva sobre D1.

Otras objeciones.

El Examinador establece que la reclamación no define el asunto para el cual se busca protección.

El Solicitante no está acuerdo y propone que el resultado que se logre debe reducir el cubrimiento de los componentes del catalizador por el producto de la fase condensada. La invención de la reclamación 1 logra este resultado realizando el proceso de forma tal que el tiempo de contacto entre uno o más de los reactantes de la fase de gas con los componentes del catalizador sea diferente en una o más regiones del catalizador.



A la persona adiestrada en el arte se le enseñe una serie de formas de realizar el invento, por ejemplo, en la página 2, línea 3 hasta la página 3, línea 32, y en los ejemplos de la página 8, línea 26 hasta la página 9, línea 2.

Las reclamaciones 2 y 3, por ejemplo, se relacionan con encarnaciones del invento, en las cuales la reclamación 2 se relaciona con un catalizador sólido que tiene 2 o más regiones con concentraciones diferentes de componentes de catalizador, y la reclamación 3 se relaciona con el catalizador sólido que tiene 2 o más regiones con diferente área y volumen de sección cruzada.

Por lo tanto el Solicitante cree que la invención de la reclamación 1 está claramente definida y abarca todas las características técnicas necesarias para que la persona adiestrada en el arte entienda el alcance de la protección y se ejercite en el invento.

Por la supresión de las reclamaciones 10 a 13, las objeciones del Examinador con relación a dichas reclamaciones ya no se consideran aplicables.

El Solicitante cree que las reclamaciones de la presente solicitud se ciñen a las exigencias de los Artículos 6, 33(2), 33(3) y 33(4) PCT y se solicita respetuosamente un positivo Informe Preliminar Internacional sobre Patentabilidad. Si la División Examinadora lo cree de otra



manera, se solicita una oportunidad para responder a cualquier objeción adicional, de acuerdo con la Regla 66.4 PCT.

De ustedes cordialmente,

(Firmado) Dr. Richard Oldroyd

Global Patents & Technology Law (Central)

(Firmado) Eric Dekezel

GA No. 36478

Certificación:

Certifico que la presente es una traducción verdadera y completa del documento adjunto:

Título: "bp Richard Oldroyd – Carta"

Fecha: 26 de junio de 2008.

Traductor: Jorge Enrique Sierra Reyes.

Licencia No. 376 de 1993, del Ministerio de Justicia.

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Documento No. 11-321



Traductor Oficial

JORGE E. SIERRA REYES

Licencia 376 - 1993 Minjusticia

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) BPX 10309

Box No. I TITLE OF INVENTION
PROCESS FOR PRODUCING CONDENSED-PHASE PRODUCT FROM ONE OR MORE GAS-PHASE REACTANTS

Box No. II APPLICANT ☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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Chertsey Road
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Telephone No.

Facsimile No.

Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

☐ all designated States

☒ all designated States except the United States of America

☐ the United States of America only

☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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United Kingdom

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

NL

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

☐ all designated States

☐ all designated States except the United States of America

☒ the United States of America only

☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

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☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents. However,

- ☐ DE Germany is not designated for any kind of national protection
☐ JP Japan is not designated for any kind of national protection
☐ KR Republic of Korea is not designated for any kind of national protection
☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application. See the Notes to Box No. V as to the consequences of such national law provisions in these States).

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1) 19 December 2005	05257795.4		EP	
item (2)				
item (3)				

- ☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

- ☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)).

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / .EP.....

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

		Number of declarations
☐ Box No. VIII (i)	Declaration as to the identity of the inventor	:
☒ Box No. VIII (ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	: 1
☐ Box No. VIII (iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	:
☒ Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)	: 1
☐ Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	:

Box No. VIII (ii) DECLARATION: ENTITLEMENT TO APPLY FOR AND BE GRANTED A PATENT

The declaration must conform to the standardized wording provided for in Section 212; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (ii). If this Box is not used, this sheet should not be included in the request.

Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4.17(ii) and 51 bis.1(a)(ii)), in a case where the declaration under Rule 4.17(iv) is not appropriate:

In relation to this International Application, BP EXPLORATION OPERATING COMPANY LIMITED is entitled to apply for and be granted a patent by virtue of the following:

BP EXPLORATION OPERATING COMPANY LIMITED is entitled by virtue of a contract of employment with the inventor, GAEMERS, Sander

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (ii)".

Box No. VIII (iv) DECLARATION: INVENTORSHIP (only for the purposes of the designation of the United States of America)
The declaration must conform to the following standardized wording provided for in Section 214; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (iv). If this Box is not used, this sheet should not be included in the request.

**Declaration of inventorship (Rules 4.17(iv) and 51bis.1(a)(iv))
 for the purposes of the designation of the United States of America:**

I hereby declare that I believe I am the original, first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought.

This declaration is directed to the international application of which it forms a part (if filing declaration with application).

This declaration is directed to international application No. PCT/..... (if furnishing declaration pursuant to Rule 26ter).

I hereby declare that my residence, mailing address, and citizenship are as stated next to my name.

I hereby state that I have reviewed and understand the contents of the above-identified international application, including the claims of said application. I have identified in the request of said application, in compliance with PCT Rule 4.10, any claim to foreign priority, and I have identified below, under the heading "Prior Applications," by application number, country or Member of the World Trade Organization, day, month and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international application designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed.

Prior Applications:

I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation-in-part application.

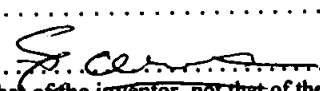
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name: GAEMERS, Sander

Residence: Elstead, Surrey, United Kingdom
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Citizenship: Dutch

Inventor's Signature:  Date: 27 Nov 2006
 (The signature must be that of the inventor, not that of the agent)

Name:

Residence: ..
 (city and either US state, if applicable, or country)

Mailing Address:

Citizenship:

Inventor's Signature: Date:
 (The signature must be that of the inventor, not that of the agent)

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iv)".

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:		This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):		Number of items
(a) on paper, the following number of sheets:				
request (including declaration sheets)	5	1. ☒ fee calculation sheet		1
description (excluding sequence listing and/or tables related thereto)	9	2. ☒ original separate power of attorney		1
claims	2	3. ☐ original general power of attorney		
abstract	1	4. ☒ copy of general power of attorney; reference number, if any:		1
drawings	3	5. ☐ statement explaining lack of signature		
Sub-total number of sheets	20	6. ☐ priority document(s) identified in Box No. VI as item(s):		
sequence listing		7. ☐ translation of international application into (language):		
tables related thereto		8. ☐ separate indications concerning deposited microorganism or other biological material		
(for both, actual number of sheets if filed on paper, whether or not also filed in electronic form; see (c) below)		9. ☐ sequence listing in electronic form (indicate type and number of carriers)		
Total number of sheets	20	(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)		
(b) ☐ only in electronic form (Section 801(a)(i))		(ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter		
(i) ☐ sequence listing		(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column		
(ii) ☐ tables related thereto		10. ☐ tables in electronic form related to sequence listing (indicate type and number of carriers)		
(c) ☐ also in electronic form (Section 801(a)(ii))		(i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application)		
(i) ☐ sequence listing		(ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater)		
(ii) ☐ tables related thereto		(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column		
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the		11. ☐ other (specify):		
☐ sequence listing:				
☐ tables related thereto:				
(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)				
Figure of the drawings which should accompany the abstract: 2		Language of filing of the international application: English		

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

for BP EXPLORATION OPERATING COMPANY LIMITED -

DEKEZEL, Eric

For receiving Office use only		2. Drawings: ☐ received: ☐ not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid	

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING
AVAILABILITY OF THE PUBLICATION
OF THE INTERNATIONAL APPLICATION

To:

DEKEZEL, Eric
BP International Limited
Patents & Agreements
Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LN
ROYAUME-UNI

- 5 JUL 2007

IMPORTANT NOTICE

Date of mailing (day/month/year)
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19 December 2005 (19.12.2005)

Applicant

BP EXPLORATION OPERATING COMPANY LIMITED et al

The applicant is hereby notified that the International Bureau:

☒ has published the above-indicated international application on 28 June 2007 (28.06.2007) under
No. WO 2007/071903☐ has republished the above-indicated international application on under
No. WOFor an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48)
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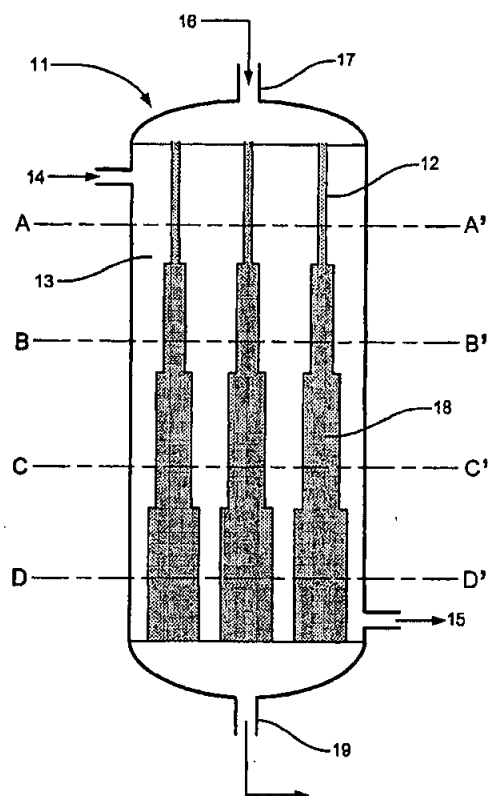
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[Continued on next page]

(54) Title: PROCESS FOR PRODUCING CONDENSED-PHASE PRODUCT FROM ONE OR MORE GAS-PHASE REACTANTS



(57) Abstract: A process for producing at least one condensed-phase product from one or more gas-phase reactants in the presence of a solid catalyst having one or more catalyst components, wherein the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different.

WO 2007/071903 A1



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *with international search report*

PROCESS FOR PRODUCING CONDENSED-PHASE PRODUCT FROM ONE OR MORE GAS-PHASE REACTANTS

This invention relates to the field of heterogeneous catalysis, more specifically to an improved process for converting one or more gas-phase reactants into a condensed-phase product in the presence of a solid catalyst.

Fischer-Tropsch synthesis is a known reaction for the production of hydrocarbons from syngas (a mixture of carbon monoxide and hydrogen), wherein syngas is contacted with a heterogeneous catalyst to produce a mixture of hydrocarbons. Syngas is typically produced by processes such as steam reforming of coal or natural gas, or from the partial oxidation of natural gas, and it may also be produced from biomass. One application of Fischer-Tropsch synthesis is in the production of hydrocarbon liquids and/or waxes that may be used as fuels or in the production of fuels through processes such as hydrocracking.

During heterogeneously catalysed processes for Fischer-Tropsch synthesis of hydrocarbons, product hydrocarbons that are liquid or solid under reaction conditions can condense on the catalyst surface, which inhibits contact of the syngas reactant with the catalyst surface and results in reduced conversion of reactants.

Variable diameter reactors have hitherto been described for controlling reaction temperatures in processes involving reactants and products that are in the gas-phase under reaction conditions. Thus, WO 03/011449 describes an apparatus in which the cross-sectional area of a solid catalyst bed is increased along its longitudinal axis by use of shaped inserts carrying heat transfer material, and DE 2 929 300 describes a variable diameter reactor for controlling the temperature of catalyst in endothermic or exothermic reactions in which the shape of inserts carrying heat-transfer material is varied along their length. However, the processes described therein do not produce products that are in a condensed-phase under reaction conditions, and hence do not address the issue of coverage of the solid catalyst with condensed-phase product.

According to the present invention, there is provided a process for the production of a condensed-phase product from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product, characterised in that the

solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different.

In the present invention, the contact time of the one or more gas-phase reactants with the one or more catalyst components of the solid catalyst is different within two or more regions of the solid catalyst. By having different contact times within each region, the conversions of the one or more gas-phase reactants into condensed-phase product can be optimised by maintaining the ratio of the at least one condensed-phase product to the one or more catalyst components (henceforth termed the condensed-phase product to catalyst component ratio) in each region to within a pre-determined range of values.

The predetermined range of values for the condensed-phase product to catalyst component ratio may be based, for example, on results from experimental observations or on theoretical models. The range will typically be selected so as to optimise the efficiency of the process, for example by maintaining low condensed-phase product to catalyst component ratios in regions where there is low reactant conversion, or by maintaining high product to catalyst component ratios where reduced conversions are required. The range of values for the ratio will depend on the variability of the condensed-phase product concentration within each region of the catalyst.

For example, in regions of the solid catalyst in which the quantity of condensed-phase product is high, then the coverage of catalyst by the at least one condensed-phase product will be also be high resulting in low reactant conversions. The reactant conversions can therefore be improved by increasing the contact time between the one or more gas-phase reactants with the one or more catalyst components within that region of the solid catalyst. Conversely, in regions of the solid catalyst in which there is a low quantity of condensed-phase product, the condensed-phase product to catalyst component ratio will be low, hence the catalyst coverage will be low, and the conversions can be high. Therefore, by reducing the contact time, reduced conversions can be achieved.

In preferred embodiments of the present invention, the contact time of the one or more gas-phase reactants with the one or more catalyst components in each region of the solid catalyst may be varied by having regions of the solid catalyst with different concentrations of catalyst components and/or regions of the solid catalyst with different cross-sectional area and volume.

Thus, in one embodiment of the invention, the solid catalyst comprises regions

having different concentrations of the one or more catalyst components. The cross-sectional area and/or the volume of the solid catalyst may be the same in different regions of the solid catalyst in order to achieve a different contact time between the one or more gas-phase reactants with the one or more catalyst components therein. Thus, a solid catalyst having two or more regions of the same cross-sectional area and volume, but with a different concentration of the one or more catalyst components, will have a different contact time of the one or more gas-phase reactants with the one or more catalyst components. Thus, a solid catalyst having two or more regions with different concentrations of the one or more catalyst components may be used to maintain independently the ratio of the at least one condensed-phase product to the one or more catalyst components in each region to within a pre-determined range of values.

Additionally, or alternatively, two or more regions of the solid catalyst have a different cross-sectional area and volume which results in a different space velocity of the gas-phase reactants within the different regions of the solid catalyst. The concentration of the one or more catalyst components within each region of the solid catalyst may be the same or different, such that the contact time of the one or more gas-phase reactants with the one or more catalyst components in the two or more regions of the solid catalyst is different. Preferably, the concentration of the one or more catalyst components within each region of the solid catalyst is uniform throughout the solid catalyst, which can reduce the complexity of the loading of the catalyst into a reactor.

By having increased cross-sectional area and volume of solid catalyst in regions where reactant conversions are low, the condensed-phase product to catalyst component ratio is consequently decreased, resulting in decreased catalyst coverage and improved reactant conversions. Conversely, by having a reduced cross-sectional area and volume, an increased coverage of the one or more catalyst components by condensed-phase product can be achieved, which can reduce reactant conversions in that region. This latter case may be advantageous, for example, for exothermic reactions where the extent of exotherm within a region of the solid catalyst is preferably reduced in order to avoid damage to or deactivation of the catalyst. By such means, a solid catalyst having two or more regions of different cross-sectional area and volume may be used to maintain independently the ratio of the at least one condensed-phase product to the one or more gas-phase reactants in each region to within a predetermined range of values.

A further advantage of this embodiment of the present invention is that the solid catalyst can be distributed within a reactor so that higher volumes of catalyst can be present in regions where reduced ratios of the at least one condensed-phase product to the one or more catalyst components are desired, and lower volumes of catalyst can be present in regions where higher ratios are required, which improves utilisation of the solid catalyst. The cross-sectional area of the solid catalyst may vary continuously between the regions of different cross-sectional area and volume, or alternatively may vary in a discrete, stepped way, such that each region of the catalyst bed is defined by a distinct step change in cross-sectional area.

The solid catalyst may comprise, for example, a shaped insert, such as a monolith, a bed of fibrous materials or mesh, or a bed of solid particles such as spheres, beads, granules or extrudates. Preferably, the solid catalyst comprises packed catalyst particles, as the particles can readily be inserted into the reactor so that they adapt to the variations in diameter therein.

The solid catalyst comprises one or more catalyst components which catalyse the conversion of the one or more gas-phase reactants to at least one condensed-phase product. There may be a single catalyst component, for example a transition metal or transition metal compound, or there may be more than one catalyst component, such as additional co-catalysts or catalyst promoters. The one or more catalyst components may be supported or unsupported.

The concentration of the one or more catalyst components within a region of solid catalyst may be varied, for example, by mixing catalytically inert particles with particles comprising the one or more catalyst components. Alternatively or additionally, where the one or more catalyst components are on a support, then different regions of the solid catalyst may comprise regions having different loadings of the one or more catalyst components on the support.

The reactor may comprise one or more inserts. In a preferred embodiment of the invention, the reactor comprises one or more longitudinally disposed inserts having two or more regions with variable cross-sectional area and volume. The solid catalyst may either be within the one or more inserts, or in the reactor space between the one or more inserts and the inner walls of the reactor. Depending on where the catalyst is situated, either the inserts or the catalyst-free region between the inserts and the inner walls of the reactor may

be used to carry a heat-exchange medium in order to control the temperature within the reactor. The heat-exchange medium can flow either co-currently in relation to the flow of the one or more gaseous reactants, or counter to the flow of the one or more gaseous reactants.

5 During the course of the reaction, one or more products are formed, at least one of which is in the condensed-phase under the reaction conditions. The invention is particularly suited for processes in which the products are liquid-phase under the reaction conditions, as liquid products are more easily separated from a solid catalyst compared to wax-like products or other solid products.

10 In one embodiment of the present invention, two gas-phase reactants are co-currently fed into a reactor, and are passed over a fixed catalyst bed having a uniform concentration of catalyst components, wherein the gas-phase reactants react to produce a liquid-phase product. At the initial point of contact of the two gas-phase reactants with the solid catalyst bed, the concentration of liquid-phase product is low. The concentration of the
15 liquid-phase product increases as the reaction proceeds, and becomes more concentrated as the gas-phase reactants pass along the solid catalyst bed. This can cause a greater extent of coverage of the solid catalyst by liquid-phase product in downstream regions of the solid catalyst, in relation to the direction of flow of gas-phase reactants. By having an increased cross-sectional area and volume of the solid catalyst in downstream regions, the ratio of
20 liquid product to the one or more catalyst components is reduced, leading to less coverage of the catalyst and also an increased contact time of the gas-phase reactants with the solid catalyst within those regions. The result is an improvement in reactant conversions in the regions of higher cross-sectional area and volume.

In an alternative embodiment of the invention, the cross sectional area and volume of
25 the solid catalyst is reduced in a region adjacent to the initial point of contact with the one or more gas-phase reactants. This embodiment could be advantageous, for example, in reactions where there is a delay between initial contact of the one or more reactants with the solid catalyst and the onset of an exothermic reaction. Thus, initially, it is advantageous to have a slow flow rate of reactants over the solid catalyst in order to
30 increase the contact time of reactants with the one or more catalyst components, and to promote initiation of the reaction. Once the reaction has initiated, and the rate of reaction increases, the heat generated by the exotherm can potentially cause damage or deactivation

of the catalyst, and can result in reduced selectivity to desired product and reduced catalyst lifetime. Therefore, by reducing the cross-sectional area and volume of an adjacent downstream region of the solid catalyst, the flow rate of reactants over the catalyst is increased, which reduces the contact time of the reactants with the solid catalyst, which can
5 result in reduced reactant conversions and reaction rate. Additionally, by reducing the cross-sectional area and volume, the ratio of condensed-phase product to the one or more catalyst components can be increased, which further acts to reduce the conversion of the one or more gas-phase reactants. Optionally, regions of the solid catalyst further downstream may have an increased cross-sectional area and volume in order to improve
10 conversions where increased coverage of the solid catalyst by the liquid product could otherwise occur. Alternatively, regions of the solid catalyst further downstream may have an even lower cross-sectional area and volume.

The solid catalyst may comprise gaps, or portions that are free of catalyst. For example, in embodiments of the invention in which the solid catalyst comprises particles,
15 and the different regions of the solid catalyst have different concentrations of catalyst component(s), the different catalyst regions may be separated by grids in order to prevent cross-mixing of the particles in the different regions. In such embodiments, the volume between the grids may not be completely filled with catalyst and inert particles, for example as a result of settling of the particles.

20 Where there is more than one gaseous reactant, the reactants may be fed into the reactor either separately or pre-mixed. They may initially all contact the solid catalyst at the same portion of the solid catalyst, or they may be added at different positions of the solid catalyst. The initial point of contact of the one or more reactants with the solid catalyst is the point at which all the reactants initially contact each other in the gas-phase
25 and in the presence of the solid catalyst. Preferably, the one or more gaseous reactants flow co-currently over the solid catalyst.

The one or more gas-phase reactants may be fed into the reactor in the gas-phase, or alternatively as a condensed phase which vapourises within the reactor so that it contacts the solid catalyst in the gas-phase.

30 The process of the present invention may optionally comprise a plurality of reactors arranged in series, such that any composition removed from the first reactor is fed to a second reactor, and composition removed from the second reactor is fed to a third reactor

and so on. In this embodiment, the composition removed from each reactor comprises condensed-phase product and unreacted reactants. Optionally, at least some of the condensed-phase product is removed at a point between the reactors and fed, for example, to a purification section. In such an embodiment, each reactor comprises solid catalyst, and at least the first reactor will have solid catalyst with two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different, as hitherto described.

The one or more product-containing streams removed from the one or more reactors are typically fed to a purification zone, wherein unreacted reactants and undesirable by-products are removed and optionally recycled to the reactor, or any one or more of the reactors.

The present invention is suitable for use in the heterogeneously catalysed production of hydrocarbons from syngas by Fischer-Tropsch synthesis, for example in the production of a diesel or aviation fuel or precursor thereof. Fischer-Tropsch synthesis of hydrocarbons from syngas may be represented by equation 1:



The process will typically result in a product comprising hydrocarbons with a range of carbon numbers, which will depend, *inter alia*, on the CO : H₂ ratio of the syngas, the processing conditions and on the catalyst. The hydrocarbons or mixtures thereof are preferably liquid under the reaction conditions. Preferably, the hydrocarbon number is predominantly in the range where the value "m" from equation 1 is greater than 5.

The volume ratio of hydrogen to carbon monoxide (H₂:CO) in the syngas reactant is preferably in the range of from 0.5:1 to 5:1, more preferably from 1:1 to 3:1, and most preferably 1.8:1 to 2.2:1. The one or more gaseous reactants may also comprise other gaseous components, such as nitrogen, carbon dioxide, water, methane and other saturated and/or unsaturated light hydrocarbons, each preferably being present at a concentration of less than 30% by volume.

The temperature of the Fischer-Tropsch reaction is preferably in the range from 100 to 400°C, more preferably from 150 to 350°C, and most preferably from 150 to 250°C. The pressure is preferably in the range from 1 to 100 bar (from 0.1 to 10 MPa), more

preferably from 5 to 75 bar (from 0.5 to 7.5MPa), and most preferably from 10 to 40 bar (from 1.0 to 4.0 MPa).

The one or more gaseous reactants may also comprise recycled materials extracted from elsewhere in the process, such as unreacted reactants separated from the hydrocarbon product during purification.

The syngas is typically passed over the catalyst bed at a gas hourly space velocity (GHSV) in the range from 100 to 10000 h⁻¹ (gas volumes converted to standard temperature and pressure), preferably from 250 to 5000 h⁻¹, such as from 250 to 3000 h⁻¹ and more preferably from 250 to 2000 h⁻¹.

The catalyst is typically a particulate fixed-bed catalyst, and comprises a metal active for Fischer-Tropsch catalysis. Preferred metals are selected from one or more of cobalt, iron, ruthenium, nickel, molybdenum, tungsten, and rhenium, preferably cobalt and/or iron, even more preferably cobalt. Preferably, the metal is supported, for example on a support comprising one or more of silica, alumina, silica/alumina, titania, zirconia, ceria or zinc oxide. Preferably, the support is alumina and/or zinc oxide, more preferably zinc oxide. Most preferably, the catalyst comprises cobalt on a zinc oxide support. Catalyst compositions suitable for Fischer-Tropsch processes, and in the present invention, are described, for example, in EP-A-0 261 870 and EP-A-0 209 980.

The invention will now be illustrated with reference to the Figures, in which;

Figure 1 is a schematic representation of longitudinal sections of two reactors highlighting the concentration of condensed-phase product in three different regions of two different reactors containing the same solid catalyst;

Figure 2 is a schematic representation of a longitudinal section of a reactor according to the present invention comprising catalyst-filled inserts;

Figure 3 shows a series of cross-sections through the reactor illustrated in Figure 2.

Figure 1 illustrates the difference in the concentration of a condensed-phase product in three regions of a reactor A with a solid catalyst having regions of constant cross-sectional area and volume, and uniform concentration of the one or more catalyst components, and a reactor B with solid catalyst having the same solid catalyst, but with regions of different cross-sectional area and volume. The solid catalyst of reactor A is therefore not in accordance with the present invention, while that of reactor B is in accordance with the present invention. Two reactants 1 and 2 are co-currently and

downwardly fed into each reactor, and react in the gas-phase in the presence of the solid catalyst (not shown) to produce condensed-phase product 4. The concentration of the condensed-phase product 3 within the reactor is represented by the degree of shading, wherein light shading represents a low concentration of condensed-phase product and heavy shading represents a high concentration of condensed-phase product. In reactor A, the volume of each region of the solid catalyst is the same. As the product concentration increases from Region 1 to Region 3, the result is an increasing ratio of condensed-phase product to one or more catalyst components in the respective regions. In reactor B, the ratio is maintained constant in all three regions of the solid catalyst by increasing the cross-sectional area and volume in consecutive regions. Thus, reactant conversions in the three regions of solid catalyst in reactor B are optimised by reducing the extent of coverage of the catalyst by the condensed-phase product by reducing the ratio of condensed-phase product to the one or more catalyst components.

Figure 2 shows a reactor 11 with a plurality of inserts 12 which contain particles of Fischer-Tropsch catalyst 18. Coolant is fed into the reactor space between the inserts 13 through inlet 14 and removed through outlet 15. Syngas 16 is fed into the catalyst-containing inserts through inlet 17, and contacted with the solid catalyst 18 within the inserts. Condensed-phase hydrocarbon products and unreacted reactants are removed from the catalyst-containing inserts through outlet 19. The diameter of the inserts progressively increases from the top of the solid catalyst beds, where the reactant gases first come into contact with the catalyst, to the bottom of the solid catalyst beds, forming discrete regions of the solid catalyst bed with different cross-sectional area. The volume of the solid catalyst beds increases with increased cross-sectional area.

Figure 3 illustrates four cross-sections of the reactor 11 of Figure 1, through planes A-A', B-B', C-C' and D-D'. The inserts 12, and the cross-sectional area of the solid catalyst beds 18 therein, have different diameters, Z, at different depths. The space 13 between the inserts is filled with coolant.

Claims:

1. A process for the production of a condensed-phase product from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in
5 which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product, characterised in that the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different.
- 10 2. A process as claimed in claim 1, in which each region of the solid catalyst has different concentrations of the one or more catalyst components.
3. A process as claimed in claim 1 or claim 2, in which the two or more regions of the solid catalyst have a different cross-sectional area and volume.
4. A process as claimed in any one of claims 1 to 3, in which the solid catalyst,
15 comprises particles such as spheres, beads, granules or extrudates.
5. A process as claimed in any one of claims 1 to 4, in which the solid catalyst comprises a support selected from one or more of silica, alumina, silica/alumina, titania, zirconia, ceria or zinc oxide.
6. A process as claimed in any one of claims 1 to 5, in which at least one catalyst
20 component is a metal active for Fischer-Tropsch synthesis selected from one or more of cobalt, iron, ruthenium, nickel, molybdenum, tungsten, and rhenium.
7. A process as claimed in any one of claims 1 to 6, in which syngas is a reactant, and the at least one condensed-phase product comprises a mixture of hydrocarbons that is liquid under the reaction conditions.
- 25 8. A process as claimed in any one of claims 1 to 7, in which the reactor comprises one or more inserts.
9. A process as claimed in claim 8, in which the one or more inserts contain the solid catalyst and the space between the inserts is surrounded by a heat-transfer medium.
10. The use of a solid catalyst comprising one or more catalyst components and having
30 two or more regions with different concentrations of the one or more catalyst components in a process for the production of at least one condensed-phase product from one or more gas-phase reactants to maintain independently the ratio of the at least one condensed-phase

product to the one or more catalyst components in the two or more regions of the solid catalyst within a predetermined range of values.

11. Use of a solid catalyst as claimed in claim 10, in which the process is a process according to claim 2 or any one of claims 3 to 9 when dependent on claim 3.

5 12. The use of a solid catalyst comprising one or more catalyst components and having two or more regions of different cross-sectional area and volume in a process for the production of at least one condensed-phase product from one or more gas-phase reactants to maintain independently the ratio of the at least one condensed-phase product to the one or more catalyst components in each region of the solid catalyst within a predetermined
10 range of values.

13. Use of a solid catalyst as claimed in claim 12, in which the process is a process according to claim 3 or any one of claims 4 to 9 when dependent on claim 3.

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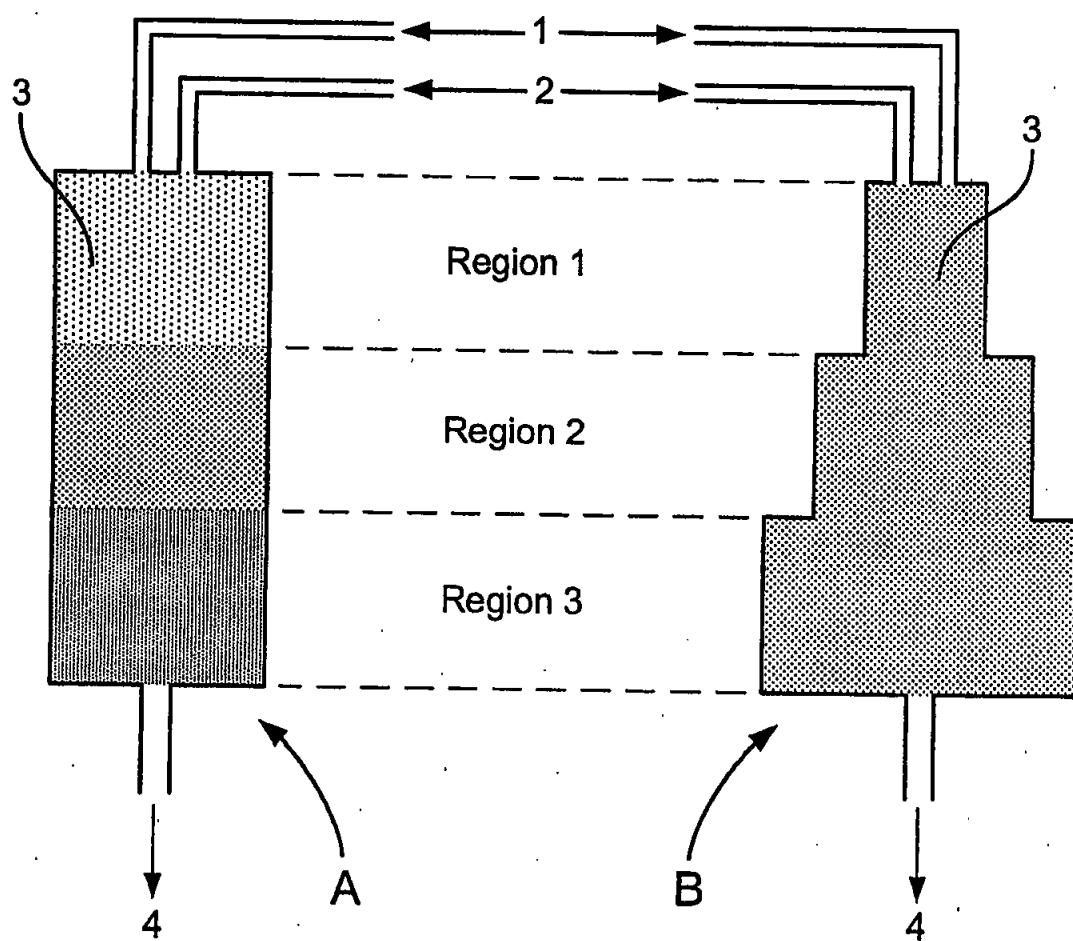


Fig.1

2/3

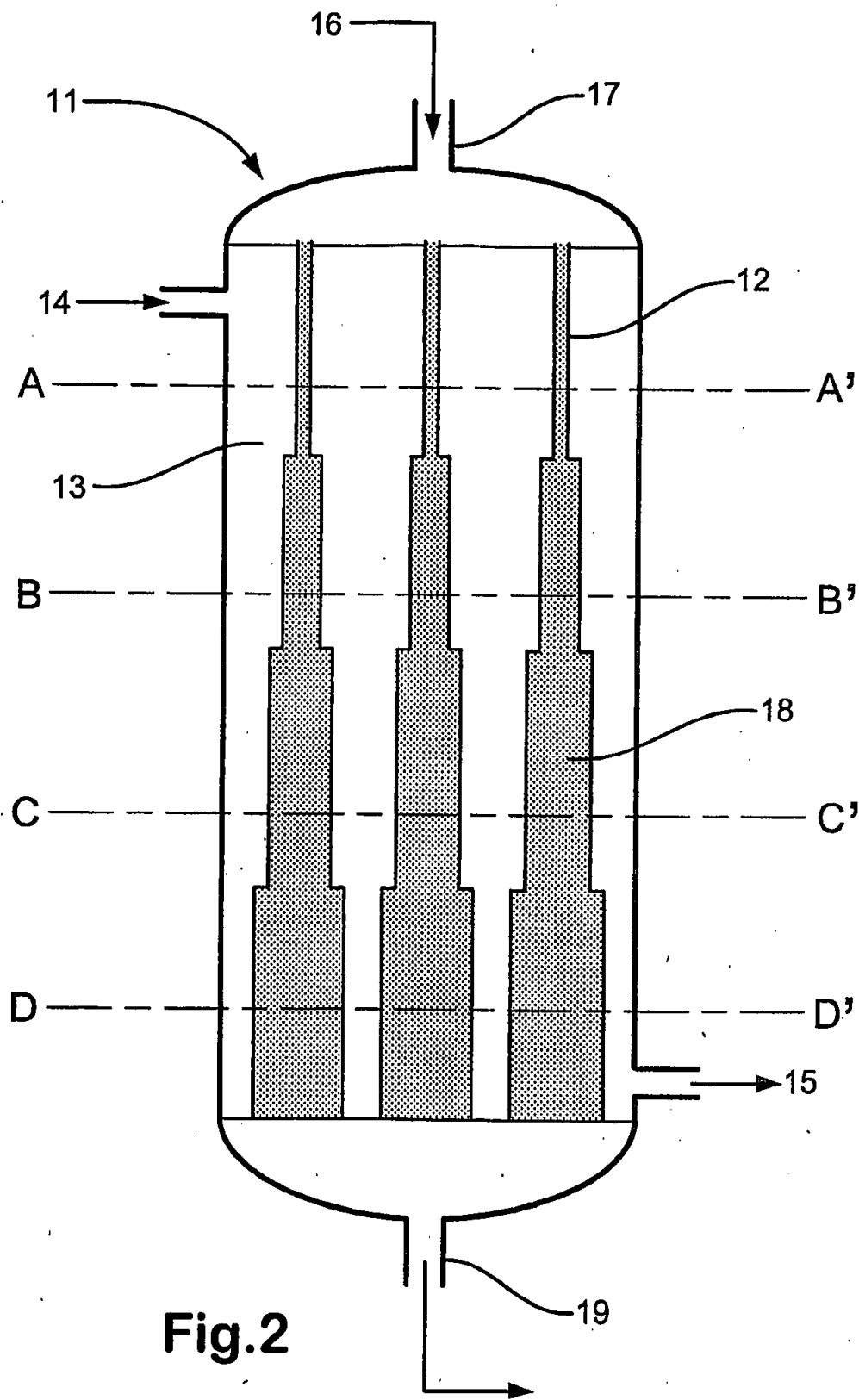


Fig.2

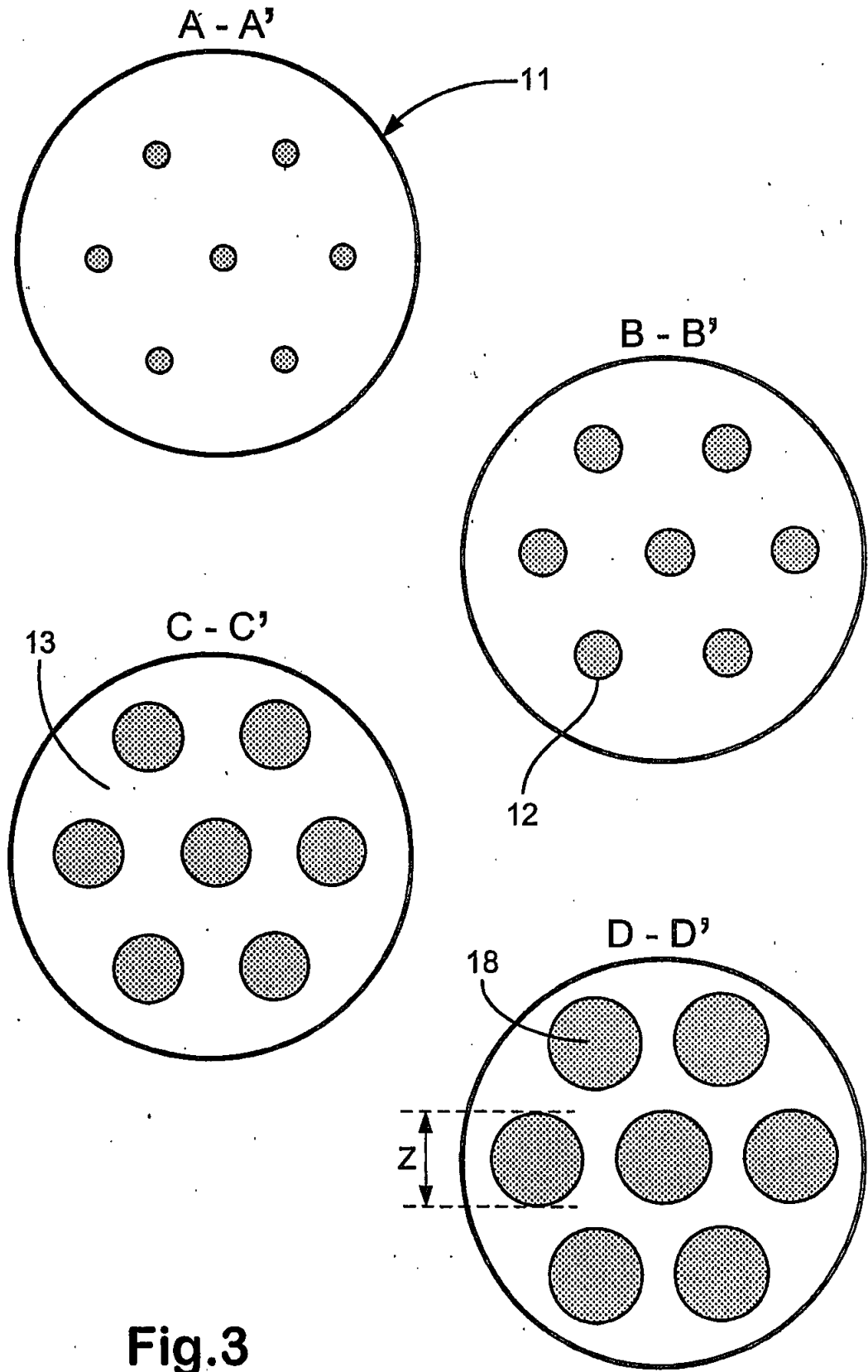


Fig.3

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/004359

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G2/00 B01J8/04 B01J23/75

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G B01J

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 132 111 A (* KERNFORSCHUNGSANLAGE JULICH GESELLSCHAFT MIT BESCHRANKTER HAFTUNG; *) 4 July 1984 (1984-07-04) the whole document	1-4, 7-13
Y	-----	5, 6
X	DE 29 29 300 A1 (LINDE AG) 29 January 1981 (1981-01-29) cited in the application	1, 3, 4, 7-9, 12, 13
Y	the whole document	5, 6
Y	EP 0 261 870 A (THE BRITISH PETROLEUM COMPANY P.L.C) 30 March 1988 (1988-03-30) cited in the application the whole document	5, 6

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

* Special categories of cited documents:

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

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

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

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

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

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

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

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

8 document member of the same patent family

Date of the actual completion of the International search

14 February 2007

Date of mailing of the international search report

21/02/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5518 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cagnoli, Michele

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2006/004359

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2132111	A	04-07-1984	CA 1214318 A1	25-11-1986
			DE 3247821 A1	27-09-1984
			FR 2538265 A1	29-06-1984
			JP 59133293 A	31-07-1984
DE 2929300	A1	29-01-1981	AT 379760 B	25-02-1986
			AT 595479 A	15-07-1985
EP 0261870	A	30-03-1988	AU 605506 B2	17-01-1991
			AU 7848887 A	31-03-1988
			CA 1307782 C	22-09-1992
			CN 87106596 A	13-04-1988
			CN 1052844 A	10-07-1991
			DE 3764754 D1	11-10-1990
			JP 2573965 B2	22-01-1997
			JP 63141644 A	14-06-1988
			NO 873958 A	28-03-1988
			NZ 221823 A	28-08-1990
			US 4826800 A	02-05-1989
			US 5023277 A	11-06-1991
			ZA 8707162 A	30-05-1989

PATENT COOPERATION TREATY

AMP
EDK

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

BP INTERNATIONAL LIMITED
Attn. Dekezel, Eric
Patents & Agreements
Chertsey Road, Sunbury-on-Thames
Middlesex, TW16 7LN
GRANDE BRETAGNE

Received in PAT

22 FEB 2007

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Date of mailing
(day/month/year)

21/02/2007

Applicant's or agent's file reference

BPX 10309

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/GB2006/004359

International filing date

(day/month/year)

22/11/2006

Applicant

BP EXPLORATION OPERATING COMPANY LIMITED

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the International Search Report.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 338.82.70

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.
3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.
- ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Reminders

Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until **30 months** from the priority date (in some Offices even later); otherwise, the applicant must, within **20 months** from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Nadia Rousseau

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Volume I/A, Annexes B1 and B2).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, Volume I/A, paragraph 296).

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference BPX 10309	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/GB2006/004359	International filing date (day/month/year) 22/11/2006	(Earliest) Priority Date (day/month/year) 19/12/2005
Applicant BP EXPLORATION OPERATING COMPANY LIMITED		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of:

- ☒ the international application in the language in which it was filed
☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box No. II)

3. ☐ **Unity of invention is lacking** (see Box No. III)

4. With regard to the **title**,

- ☒ the text is approved as submitted by the applicant
☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant
☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,

- a. the figure of the **drawings** to be published with the abstract is Figure No. 2
☒ as suggested by the applicant
☐ as selected by this Authority, because the applicant failed to suggest a figure
☐ as selected by this Authority, because this figure better characterizes the invention
- b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/004359A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G2/00 B01J8/04 B01J23/75

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G B01J

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 132 111 A (* KERNFORSCHUNGSANLAGE JULICH GESELLSCHAFT MIT BESCHRANKTER HAFTUNG; *) 4 July 1984 (1984-07-04)	1-4, 7-13
Y	the whole document	5, 6
X	DE 29 29 300 A1 (LINDE AG) 29 January 1981 (1981-01-29)	1, 3, 4, 7-9, 12, 13
Y	cited in the application	5, 6
Y	the whole document	5, 6
Y	EP 0 261 870 A (THE BRITISH PETROLEUM COMPANY P.L.C) 30 March 1988 (1988-03-30)	5, 6
	cited in the application	
	the whole document	

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

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

14 February 2007

Date of mailing of the international search report

21/02/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cagnoli, Michele

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2006/004359

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
GB 2132111	A	04-07-1984	CA	1214318 A1	25-11-1986
			DE	3247821 A1	27-09-1984
			FR	2538265 A1	29-06-1984
			JP	59133293 A	31-07-1984
DE 2929300	A1	29-01-1981	AT	379760 B	25-02-1986
			AT	595479 A	15-07-1985
EP 0261870	A	30-03-1988	AU	605506 B2	17-01-1991
			AU	7848887 A	31-03-1988
			CA	1307782 C	22-09-1992
			CN	87106596 A	13-04-1988
			CN	1052844 A	10-07-1991
			DE	3764754 D1	11-10-1990
			JP	2573965 B2	22-01-1997
			JP	63141644 A	14-06-1988
			NO	873958 A	28-03-1988
			NZ	221823 A	28-08-1990
			US	4826800 A	02-05-1989
			US	5023277 A	11-06-1991
			ZA	8707162 A	30-05-1989

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/GB2006/004359

International filing date (day/month/year)
22.11.2006

Priority date (day/month/year)
19.12.2005

International Patent Classification (IPC) or both national classification and IPC
INV. C10G2/00 B01J8/04 B01J23/75

Applicant
BP EXPLORATION OPERATING COMPANY LIMITED

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1 (a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Date of completion of
this opinion

see form
PCT/ISA/210

Authorized Officer

Cagnoli, Michele

Telephone No. +49 89 2399-7576



Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:
 - ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b. format of material:
 - ☐ on paper
 - ☐ in electronic form
 - c. time of filing/furnishing:
 - ☐ contained in the international application as filed.
 - ☐ filed together with the international application in electronic form.
 - ☐ furnished subsequently to this Authority for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2006/004359

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	5,6
	No: Claims	1-4,7-13
Inventive step (IS)	Yes: Claims	
	No: Claims	1-13
Industrial applicability (IA)	Yes: Claims	1-13
	No: Claims	

2. Citations and explanations

see separate sheet

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure:

D1: GB-A-2132111

1. The subject-matter of claim 1 is not new in the sense of Article 33(2) PCT, and therefore the requirements of Article 33 PCT are not met.
 - 1.1. Document D1, which is considered to represent the most relevant state of the art, discloses (see page 1, lines 5-7 and 36-56, page 2, lines 18-32, claims 1 and 2, and figure 1) a process having all the features of claim 1, namely:
"A process for the production of a condensed-phase product from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product (the reactions for methanising synthesis gas produce higher hydrocarbons as by products, that are in condensed-phase), wherein the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with one or more catalyst components is different".
2. The same reasoning applies mutatis-mutandis to the subject-matter of claim 10 and of claim 12 (see for example claim 1 and 2 respectively) that therefore are also not new in the sense of Art. 33(2) PCT.
3. Dependent claims 2 to 9, 11 and 13 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT with respect to novelty or inventive step, because their additional features are either anticipated by D1 or rendered obvious by the available prior art.
4. The present application does not meet the requirements of Art 6 PCT in that claims 1, 10 and 12 do not define the matter for which protection is sought.
The claims attempt to define the subject-matter in terms of the result to be achieved, without providing the technical features necessary for achieving this result.

5. Although claims 1, 10 and 12 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and/or in respect of the terminology used for the features of that subject-matter (a process in which a catalyst is used, as in claim 1, and the use of a catalyst in a process, as in claims 10 and 12, appears to be the same).

The aforementioned claims therefore lack conciseness and as such do not meet the requirements of Article 6 PCT.

PATENT COOPERATION TREATY

AMP
EDIC

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:		Received in PAT 30 JUL 2007		NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY (PCT Rules 59.3(e) and 61.1(b), first sentence and Administrative Instructions, Section 601(a))	
DEKEZEL, Eric BP INTERNATIONAL LIMITED Global Patents & Technology Law (Central) Chertsey Road Sunbury-on-Thames Middlesex TW16 7BP GRANDE BRETAGNE				Date of mailing (day/month/year) 25-07-2007	
Applicant's or agent's file reference BPX 10309			IMPORTANT NOTIFICATION		
International application No.	International filing date (day/month/year)	Priority date (day/month/year)			
PCT/GB2006/004359	22 November 2006 (22-11-2006)	19 December 2005 (19-12-2005)			
Applicant BP EXPLORATION OPERATING COMPANY LIMITED et al.					

1. The applicant is hereby **notified** that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

16 July 2007 (16-07-2007)

2. This date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

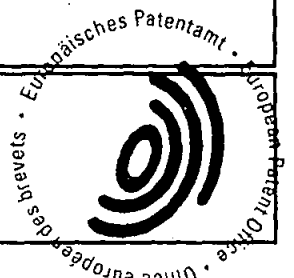
3. ☐ **ATTENTION:** That date of receipt is **after** the expiration of 19 months from the priority date. Consequently, in respect of some Offices, the demand does not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)) and the acts for entry into the national phase must therefore be performed within 20 months from the priority date (or later in some Offices). However, in respect of some other Offices, the time limit of 30 months (or later) may nevertheless apply. See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0 Fax: (+49-89) 2399-4465	Authorized officer Velez, Maria de Lurdes Tel: 2615
--	---

Form PCT/IPEA/402 (April 2002; reprint January 2004)



TRATADO DE COOPERACION EN MATERIA DE PATENTES

De: AUTORIDAD INTERNACIONAL DE EXAMINACIÓN PRELIMINAR

A: See form PCT/ISA/220	PCT OPINION ESCRITA (PCT Regla 43bis.1)	
	Fecha de Envío (día/mes/año) ver formato PCT/ISA/210 (segunda hoja)	
	RESPUESTA VENCE dentro de 2 meses contados desde la fecha de envío	
Referencia del solicitante o agente Ver formato PCT/ISA/220	Fecha de presentación internacional (día/mes/año)	Fecha de prioridad (día/mes/año)
Solicitud Internacional No. PCT/GB2006/004359	22.11.2006	19.12.2005
Clasificación Internacional de Patentes (IPC) o clasificación nacional e IPC INV. C10G2/00 B01J8/04 B01J23/75		
Solicitante BP EXPLORATION OPERATING COMPANY LIMITED		

1. Este opinión contiene indicaciones relacionadas con los siguientes puntos:
- I. X Base de la opinion
 - II. Prioridad
 - III. El no-establecimiento de opinión en relación con la novedad, nivel inventivo y aplicación industrial
 - IV. Falta de unidad de invención
 - V. X Declaración motivada conforme a la Regla 43bis.1 (a)(i) con relación a la novedad, nivel inventivo o aplicación industrial; citaciones y explicaciones que soportan dicha declaración
 - VI. Ciertos documentos citados
 - VII. Ciertos defectos en la solicitud internacional
 - VIII. Ciertas observaciones en la solicitud internacional

2. SIGUIENTE ACCIÓN

Si una solicitud de examen preliminar internacional es hecha, esta opinión será usualmente considerada como una opinión escrita de la autoridad del examen preliminar internacional. Sin embargo, esto no aplica si el solicitante escoge otra autoridad como IPEA y la escogida IPEA ha notificado a la oficina internacional bajo la regla 66.1 bis (b) que opiniones escritas de la autoridad de búsqueda internacional no serán considerados.

En esta opinión, como se indica arriba, será considerada como una opinión escrita de la IPEA, el solicitante es invitado a presentar a la IPEA una respuesta escrita junto con, si fuera apropiado, modificaciones antes de la expiración de tres meses desde la fecha de envío del formato PCT/ISA/220 o antes de la expiración de 22 meses de la fecha de prioridad, cualquiera que expire con posterioridad.

Para opciones adicionales, ver formato PCT/ISA/220.

3. Para opciones adicionales ver notas de la formato PCT/ISA/220.

Nombre y dirección de la autoridad encargada del examen preliminar internacional: Oficina de Patentes Europea D-80298 Munich Tel: +49 89 2399 - 0 Tx: 523656. epmu d Fax: +49 89 2399 - 4465	Fecha de finalización de esta opinión ver formato PCT/ISA/210	Oficial Autorizado/ Examinador Cagnoli, Michele Tel No. +49 89 2399-7576
---	--	---

I. BASE DEL INFORME

1. En relación con el **idioma**, esta opinión ha sido establecida con base en la solicitud internacional como fue presentada, a menos que se indique lo contrario en este ítem.

___ Esta opinión fue establecida con base en la traducción de la lengua original al siguiente idioma ___, que es el idioma de traducción prescrito para los presupuestos de la búsqueda internacional. (bajo las reglas 12. 3 y 23.1 (b)).

2. Respecto a cualquier secuencia **nucleótido y/o aminoácido** revelado en la solicitud internacional, el examen preliminar internacional fue llevado a cabo con base en la lista de secuencias:

a. tipo de material

___ lista de secuencias.

___ tabla relacionada con la lista de secuencias.

b. formato del material.

___ en formato escrito.

___ en formato de computador leíble.

c. tiempo de presentación

___ contenido en la solicitud internacional como fue presentado.

___ presentado con la solicitud internacional en computador y leíble a computador.

___ allegado subsiguientemente a esta autoridad para los propósitos de la búsqueda.

3. ___ En adición, en caso de que haya mas de una copia o versión de la lista de secuencias o/y tabla relacionada presentada, las requeridas opiniones relacionadas con que la información en la subsiguiente o adicionales copias son idénticas de aquellas de la solicitud como fue presentada y que no van mas allá de la solicitud como fue presentada, fueron proporcionadas.

4. Comentarios adicionales:

V. Declaración motivada conforme a la Regla 43bis.1 (a)(i) con relación a la novedad, nivel inventivo o aplicación industrial; citas y explicaciones que sustentan dicha declaración**1. Declaración**

Novedad (N) SI: Reivindicaciones 5,6
 NO: Reivindicaciones 1-4,7-13

Nivel inventivo (IS) SI: Reivindicaciones
 NO: Reivindicaciones 1-13

Aplicación Industrial (IA) SI: Reivindicaciones 1-13
 NO: Reivindicaciones

2. Citas y explicaciones**Ver hoja separada**

Se hace referencia a los siguientes documentos:

D1: GB-A-2 132 111

D2: DE-A-29 29 300

D3: EP-A-0 261 870

1. La materia objeto de la reivindicación 1 no es nueva en el sentido del Artículo 33(2) PCT, y por lo tanto no se reúnen los requerimientos del Artículo 33 PCT.

- 1.1. El documento D1 el cual se considera que representa el estado más relevante del Arte, divulga (ver página 1, líneas 5-7 y 36-56, página, 2 líneas 18-32, reivindicaciones 1 y 2 y figura 1) un proceso que tiene todas las características de la reivindicación 1, a saber:

"Un proceso para la producción de un producto en fase condensada (en el caso de D1 el producto condensado es agua, el principal sub-producto de la metanación e hidrocarburos más altos) a partir de uno o más reactivos en fase gaseosa, proceso que comprende alimentar uno o más reactivos en un reactor, reactor en el que reaccionan uno o más reactivos en fase gaseosa en presencia de un catalizador sólido que tiene uno o más componentes catalizadores para producir por lo menos

un producto en fase condensada (las reacciones de metanación por gas de síntesis produce agua e hidrocarburos más altos como sub-productos, los cuales después de salir del reactor son llevados normalmente a condiciones de sus fases condensadas) en donde el catalizador sólido tiene dos o más regiones en las que es diferente el tiempo de contacto de uno o más reactivos en fase gaseosa con uno o más componentes catalizadores "

1.2. El proceso de la reivindicación 1 tampoco es nuevo a la vista del documento D2, el cual divulga las mismas etapas de proceso y se dirige hacia la producción de metanol y amoniaco (éste último esta normalmente en fase líquida, por lo que también tiene que ser considerado una producto en fase condensada)

2. Las reivindicaciones dependientes 2 a 9 no parecen contener ninguna característica adicional que, en combinación con las características de cualquiera de las reivindicación a las que ellas se refieren, reúnan los requerimientos del PCT con respecto a la novedad o nivel inventivo, puesto que sus características adicionales son anticipadas por D1-D3 o resultan obvias por lo disponible en el arte previo.

3. La presente solicitud no reúne los requerimientos del Art. 6 PCT puesto que la reivindicación 1 no define la materia para la cual se solicita protección.

La reivindicación pretende definir la materia objeto en términos del resultado a ser alcanzado, sin proporcionar las características técnicas necesarias para alcanzar éste resultado.

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ _____

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty.

For International Preliminary Examining Authority use only	
Identification of IPEA	Date of receipt of DEMAND
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION	
Applicant's or agent's file reference BPX 10309	
International application No. PCT/GB2006/004359	International filing date (day/month/year) 22 November 2006
(Earliest) Priority date (day/month/year) 19 December 2005	
Title of invention PROCESS FOR PRODUCING CONDENSED-PHASE PRODUCT FROM ONE OR MORE GAS-PHASE REACTANTS	
Box No. II APPLICANT(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
BP EXPLORATION OPERATING COMPANY LIMITED Chertsey Road Sunbury-on-Thames Middlesex, TW16 7BP United Kingdom	
Telephone No.	
Facsimile No.	
Applicant's registration No. with the Office	
State (that is, country) of nationality: GB	State (that is, country) of residence: GB
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
GAEMERS, Sander 1 Westbrook Green Cottages Westbrook Hill Elstead Surrey, GU8 6LH United Kingdom	
State (that is, country) of nationality: NL	State (that is, country) of residence: GB
☐ Further applicants are indicated on a continuation sheet.	

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCEThe following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*DEKEZEL, Eric
BP INTERNATIONAL LIMITED
Global Patents and Technology Law (Central)
Chertsey Road, Sunbury-on-Thames,
Middlesex, TW16 7LN, United Kingdom

Telephone No.

01932 763201

Facsimile No.

01932 762388

Agent's registration No. with the Office

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.**Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION****Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filedthe description ☒ as originally filed☐ as amended under Article 34the claims ☐ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☒ as amended under Article 34the drawings ☒ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ Where the IPEA wishes to start the international preliminary examination at the same time as the international search in accordance with Rule 69.1(b), the applicant requests the IPEA to postpone the start of the international preliminary examination until the expiration of the applicable time limit under Rule 69.1(d).4. ☐ The applicant expressly wishes the international preliminary examination to start earlier than at the expiration of the applicable time limit under Rule 54bis.1(a).

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English☒ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☐ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**

The filing of this demand constitutes the election of all Contracting States which are designated and are bound by Chapter II of the PCT.

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | | |
|--|---|-------|--------|
| 1. translation of international application | : | _____ | sheets |
| 2. amendments under Article 34 | : | 1 | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | _____ | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | _____ | sheets |
| 5. letter | : | 5 | sheets |
| 6. other (<i>specify</i>) | : | _____ | sheets |

For International Preliminary
Examining Authority use only

received not received

- | | |
|--------------------------|--------------------------|
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in electronic form |
| 3. ☐ original general power of attorney | 7. ☐ tables in electronic form related to a sequence listing |
| 4. ☐ copy of general power of attorney; reference number, if any: | 8. ☐ other (<i>specify</i>): |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).


DEKEZEL, Eric
Authorised Representative

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the time limit of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

6. ☐ The date of receipt of the demand is AFTER the expiration of the time limit under Rule 54bis.1(a) and item 7 or 8, below, does not apply.

7. ☐ The date of receipt of the demand is WITHIN the time limit under Rule 54bis.1(a) as extended by virtue of Rule 80.5.

8. ☐ Although the date of receipt of the demand is after the expiration of the time limit under Rule 54bis.1(a), the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/GB2006/004359 Applicant's or agent's file reference BPX 10309	For International Preliminary Examining Authority use only Date stamp of the IPEA								
Applicant BP EXPLORATION OPERATING COMPANY LIMITED et al									
CALCULATION OF PRESCRIBED FEES <table style="width: 100%;"><tr><td style="width: 50%;">1. Preliminary examination fee</td><td style="width: 50%; text-align: right;">EUR 1595-00 P</td></tr><tr><td>2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)</td><td style="text-align: right;">EUR 129-00 H</td></tr><tr><td>3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box</td><td style="text-align: right; border: 1px solid black; padding: 5px;">EUR 1,724-00</td></tr><tr><td></td><td style="text-align: right; border: 1px solid black; padding: 2px;">TOTAL</td></tr></table>		1. Preliminary examination fee	EUR 1595-00 P	2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)	EUR 129-00 H	3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	EUR 1,724-00		TOTAL
1. Preliminary examination fee	EUR 1595-00 P								
2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>)	EUR 129-00 H								
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	EUR 1,724-00								
	TOTAL								
MODE OF PAYMENT (Not all modes of payment may be available at all IPEAs) <table style="width: 100%;"><tr><td>☒ authorization to charge deposit account with the IPEA (see below)</td><td>☐ cash</td></tr><tr><td>☐ cheque</td><td>☐ revenue stamps</td></tr><tr><td>☐ postal money order</td><td>☐ coupons</td></tr><tr><td>☐ bank draft</td><td>☐ other (specify):</td></tr></table>		☒ authorization to charge deposit account with the IPEA (see below)	☐ cash	☐ cheque	☐ revenue stamps	☐ postal money order	☐ coupons	☐ bank draft	☐ other (specify):
☒ authorization to charge deposit account with the IPEA (see below)	☐ cash								
☐ cheque	☐ revenue stamps								
☐ postal money order	☐ coupons								
☐ bank draft	☐ other (specify):								
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all IPEAs) <table style="width: 100%;"><tr><td style="width: 50%; vertical-align: top;">☒ Authorization to charge the total fees indicated above. ☐ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.</td><td style="width: 50%; vertical-align: top;">IPEA/ <u>EP</u> Deposit Account No.: <u>28050129 BP Int Ltd</u> Date: <u>12th July 2007</u> Name: <u>Anne Perry</u> Signature: <u><i>A. M. Perry</i></u></td></tr></table>		☒ Authorization to charge the total fees indicated above. ☐ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	IPEA/ <u>EP</u> Deposit Account No.: <u>28050129 BP Int Ltd</u> Date: <u>12th July 2007</u> Name: <u>Anne Perry</u> Signature: <u><i>A. M. Perry</i></u>						
☒ Authorization to charge the total fees indicated above. ☐ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	IPEA/ <u>EP</u> Deposit Account No.: <u>28050129 BP Int Ltd</u> Date: <u>12th July 2007</u> Name: <u>Anne Perry</u> Signature: <u><i>A. M. Perry</i></u>								

AMP
EOK

From the INTERNATIONAL BUREAU

PCT

Received in PAT

19 APR 2007

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

To:

DEKEZEL, Eric
BP International Limited
Patents & Agreements
Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LN
ROYAUME-UNI

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 06 April 2007 (06.04.2007)	
Applicant's or agent's file reference BPX 10309	IMPORTANT NOTIFICATION
International application No. PCT/GB2006/004359	International filing date (day/month/year) 22 November 2006 (22.11.2006)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 19 December 2005 (19.12.2005)
Applicant BP EXPLORATION OPERATING COMPANY LIMITED et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt 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 a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit 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.
- (If applicable) An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or 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)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), 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.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
19 December 2005 (19.12.2005) ✓	05257795.4 ✓	EP ✓	19 March 2007 (19.03.2007)

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

Authorized officer

Nora Lindner

Facsimile No. +41 22 338 82 70

Facsimile No. +41 22 338 82 70
Telephone No. +41 22 338 74 02

Form PCT/IB/304 (October 2005)

1/C7J3J8OD0

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Reference is made to the following documents:

D1: GB-A-2 132 111

D2: DE-A-29 29 300

D3: EP-A-0 261 870

1. The subject-matter of claim 1 is not new in the sense of Article 33(2) PCT, and therefore the requirements of Article 33 PCT are not met.
 - 1.1. Document D1, which is considered to represent the most relevant state of the art, discloses (see page 1, lines 5-7 and 36-56, page 2, lines 18-32, claims 1 and 2, and figure 1) a process having all the features of claim 1, namely:

"A process for the production of a condensed-phase product (in the case of D1 the condensed product is water, the principal byproduct of the methanation and higher hydrocarbons) from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product (the reactions for methanising synthesis gas produce water and higher hydrocarbons as by products, which after exiting the reactor are normally brought to conditions of their condensed-phase), wherein the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with one or more catalyst components is different".
 - 1.2. The process of claim 1 is also not new in view of document D2, which discloses the same process steps and is directed towards production of methanol and ammonia (this latter is normally in liquid phase, so that it has to be considered also a product in the condensed phase)
2. Dependent claims 2 to 9 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT with respect to novelty or inventive step, because their additional features are either anticipated by D1-D3 or rendered obvious by the available prior art.

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/GB2006/004359

3. The present application does not meet the requirements of Art 6 PCT in that claim 1 does not define the matter for which protection is sought.
The claim attempts to define the subject-matter in terms of the result to be achieved, without providing the technical features necessary for achieving this result.

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Claims:

1. A process for the production of a condensed-phase product from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in
5 which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product, characterised in that the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different.
- 10 2. A process as claimed in claim 1, in which each region of the solid catalyst has different concentrations of the one or more catalyst components.
3. A process as claimed in claim 1 or claim 2, in which the two or more regions of the solid catalyst have a different cross-sectional area and volume.
4. A process as claimed in any one of claims 1 to 3, in which the solid catalyst
15 comprises particles such as spheres, beads, granules or extrudates.
5. A process as claimed in any one of claims 1 to 4, in which the solid catalyst comprises a support selected from one or more of silica, alumina, silica/alumina, titania, zirconia, ceria or zinc oxide.
6. A process as claimed in any one of claims 1 to 5, in which at least one catalyst
20 component is a metal active for Fischer-Tropsch synthesis selected from one or more of cobalt, iron, ruthenium, nickel, molybdenum, tungsten, and rhenium.
7. A process as claimed in any one of claims 1 to 6, in which syngas is a reactant, and the at least one condensed-phase product comprises a mixture of hydrocarbons that is liquid under the reaction conditions.
- 25 8. A process as claimed in any one of claims 1 to 7, in which the reactor comprises one or more inserts.
9. A process as claimed in claim 8, in which the one or more inserts contain the solid catalyst and the space between the inserts is surrounded by a heat-transfer medium.

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EUROPEAN PATENT APPLICATION

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⑤④ **Syngas conversion catalyst, its production and use thereof.**

⑤⑦ A composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons, which composition comprises as essential components (i) cobalt either as the elemental metal, the oxide or a compound thermally decomposable to the elemental metal and/or oxide and (ii) zinc in the form of the oxide or a compound thermally decomposable to the oxide.

EP 0 261 870 A1

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SYNGAS CONVERSION CATALYST, ITS PRODUCTION AND USE THEREOF

The present invention relates to a composition for use after reductive activation as a catalyst in the conversion of gaseous mixtures principally comprising carbon monoxide and hydrogen, hereinafter to be referred to as synthesis gas, to hydrocarbons, in particular to hydrocarbons in the C₅-C₈ range, to processes for producing the catalyst and to a process utilising the catalyst in the conversion of synthesis gas to the aforesaid hydrocarbons.

The conversion of synthesis gas into hydrocarbons by the Fischer-Tropsch process has been known for many years but the process has only achieved commercial significance in countries such as South Africa where unique economic factors prevail. The growing importance of alternative energy sources such as coal and natural gas has focussed renewed interest in the Fischer-Tropsch process as one of the more attractive direct and environmentally acceptable routes to high quality transportation fuels.

Many metals, for example cobalt, nickel, iron, molybdenum, tungsten, thorium, ruthenium, rhenium and platinum are known to be catalytically active, either alone or in combination, in the conversion of synthesis gas into hydrocarbons and oxygenated derivatives thereof. Of the aforesaid metals, cobalt, nickel and iron have been studied most extensively. Generally, the metals are used in combination with a support material, of which the most common are alumina, silica and carbon.

The use of cobalt as a catalytically active metal in combination with a support has been described in, for example, EP-A-127220, EP-A-142887, GB-A-2146350, GB-A-2130113 and GB-A-2125062. EP-A-127220, for example discloses the use of a catalyst comprising (i) 3-60 pbw cobalt, (ii) 0.1-100 pbw zirconium, titanium, ruthenium or chromium, per 100 pbw silica, alumina or silica-alumina, (iii) the catalyst having been prepared by kneading and/or impregnation.

Our own published European application No 0209980 (BP Case No. 6131) describes the use in the conversion of synthesis gas to hydrocarbons of a catalyst having a composition represented by the formula:

$\text{Co}_a\text{A}_b\text{La}_c\text{CeO}_x$
wherein A is an alkali metal

a is greater than zero and up to 25% w/w,

b is in the range from zero to 5% w/w,

c is in the range from zero to 15% w/w,

x is a number such that the valence requirements of the other elements for oxygen is satisfied, and the remainder of the composition, subject to the requirement for x, is cerium,

the percentages w/w being based on the total weight of the composition.

We have now found that compositions containing cobalt and zinc oxide as essential components are, after reductive activation, active as catalysts in the conversion of synthesis gas to hydrocarbons. Moreover, in contrast to many prior art cobalt-containing catalysts, as typified by the aforesaid European application publication No. 0209980, such catalysts are more selective to hydrocarbons in the C₅-C₈ range and, in fact can be very selective to a waxy hydrocarbon product.

Accordingly, the present invention provides a composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons, which composition comprises as essential components (i) cobalt either as the elemental metal, the oxide or a compound thermally decomposable to the elemental metal and/or oxide and (ii) zinc in the form of the oxide or a compound thermally decomposable to the oxide.

Suitably the composition may contain up to 70%, preferably up to 40% cobalt, the remainder of the composition being zinc and oxygen, the percentages being based on an atomic basis.

The composition may also contain in elemental or oxide form one or more of the metals (M) chromium, nickel, iron, molybdenum, tungsten, zirconium, gallium, thorium, lanthanum, cerium, ruthenium, rhenium, palladium or platinum, suitably in an amount up to 15% w/w.

Useful compositions, after thermal decomposition may suitably be represented by the formula:-

$\text{Co}_a\text{M}_b\text{Zn}_c\text{O}_x$ (I)

wherein M is as above,

a is greater than zero and up to 70% w/w,

b is from zero to 15% w/w,

c is greater than zero, and

x is a number such that the valence requirements of the other elements for oxygen is satisfied.

The composition may suitably be unsupported or supported, suitably on a conventional refractory support material, for example silica, alumina, silica/alumina, zirconia, titania, or the like.

The composition may be prepared by a variety of methods including impregnation, precipitation or gelation. A suitable method, for example, comprises impregnation zinc oxide with a compound of cobalt thermally decomposable to the oxide. Any suitable impregnation technique including the incipient wetness technique or the excess solution technique, both of which are well-known in the art, may be employed. The incipient wetness technique is so-called because it requires that the volume of impregnating solution be predetermined so as to provide the minimum volume of solution necessary to just wet the entire surface of the support, with no excess liquid. The excess solution technique as the name implies, requires an excess of the impregnating solution, the solvent being thereafter removed, usually by evaporation.

The impregnation solution may suitably be either an aqueous solution or a nonaqueous, organic solution of the thermally decomposable cobalt compound. Suitable nonaqueous organic solvents include, for example, alcohols, ketones, liquid paraffinic hydrocarbons and ethers. Alternatively, aqueous organic solutions, for example an aqueous alcoholic solution, of the thermally decomposable cobalt compound may be employed.

Suitable soluble compounds include for example the nitrate, acetate or acetylacetonate, preferably the nitrate. It is preferred to avoid the use of the halides because these have been found to be detrimental.

It is preferred to produce the composition by precipitation, either by coprecipitation of the metals cobalt and zinc in the form of insoluble thermally decomposable compounds thereof or by precipitation of an insoluble thermally decomposable compound of cobalt in the presence of zinc oxide.

A particularly preferred process for producing a composition comprises the steps of:

(I) precipitating at a temperature in the range from 0 to 100°C the metals cobalt and zinc in the form of insoluble thermally decomposable compounds thereof using a precipitant comprising ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, a tetraalkylammonium hydroxide or an organic amine, and

(II) recovering the precipitate obtained in step (I).

Step I of the aforesaid process may be accomplished in a variety of ways, some being better than others in terms of the activity of the final catalyst. Thus, an embodiment (A) comprises bringing together in solution at a temperature below 50°C soluble salts of the metals cobalt and zinc and a precipitant comprising ammonium hydroxide, carbonate, or bicarbonate, a tetraalkylammonium hydroxide or an organic amine. Alternatively, an embodiment (B) comprises bringing together in a substantially cobalt-free solution a soluble zinc salt with a precipitant so as to precipitate a zinc compound and thereafter in the presence of the precipitated zinc compound bringing together a solution of a soluble cobalt salt with a precipitant so as to precipitate an insoluble thermally decomposable cobalt compound. After precipitation of the zinc compound, the solution of the soluble cobalt salt may suitably be added to the precipitated zinc compound without any intervening treatment, such as for example filtration, prior to precipitating the cobalt compound. Alternatively, the precipitated zinc compound may be separated, washed and re-dispersed prior to precipitating the cobalt compound. Many variants on the aforesaid embodiments (A) and (B) are possible, for example instead of adding the precipitant to the salts, the salts may be added to the precipitant.

Addition of the precipitant causes the initially low pH of the mixture to rise. It is desirable in the preparation of catalysts according to the invention that the final pH of the mixture is greater than 6, preferably in the range from 7 to 10. The precipitant may be added until a pH in the aforesaid range is achieved, whereupon the addition of further precipitant may be discontinued, thereby arresting the rise in the pH. In order to improve the homogeneity of the catalyst it is preferred to agitate the mixture during precipitation, suitably by mechanical stirring.

In a particularly preferred alternative process for the production of a composition of the formula (I) steps (I) and (II) of the aforesaid process are replaced by the steps (I') and (II') as follows:

(I') bringing together in solution at a temperature below the boiling point of the solution soluble compounds of cobalt and zinc and a precipitant comprising either ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, a tetraalkylammonium hydroxide or an organic amine so as to form a precipitate, the cobalt, zinc and precipitant being brought together at a rate such that a substantially constant pH in the range from 6 to 9 is maintained, and

(II') recovering the precipitate so-obtained.

Steps (I') and (II') may be effected either batchwise or continuously.

Step (I') of the aforesaid process may suitably be accomplished by continuously feeding simultaneously to a precipitation zone and mixing therein a solution of a soluble compound of cobalt and zinc and a solution of the precipitant, the solution of the precipitant being fed at such a rate as to maintain the pH of the mixture substantially constant within the range from 6 to 9. The precipitation zone may suitably take the

form of a vessel provided with means for separately introducing a solution of a soluble compound of cobalt and zinc and a solution of the precipitant so arranged as to mix the solutions, agitation means, pH measuring means and means for continuously withdrawing the precipitate, for example an overflow pipe. Instead of the solution of the precipitant a solid precipitant may be employed.

5 Continuous operation in the manner of step (I') and (II') facilitates the production of the composition on a commercial scale.

Any soluble salt of cobalt and zinc may be employed. Suitable salts include, for example, carboxylates, chlorides and nitrates. In contrast with impregnation methods, chlorides are equally effective in precipitation methods for preparing the catalyst.

10 It is preferred to use aqueous solutions of the salts, though aqueous alcoholic solutions for example may be employed if desired.

As regards the precipitant, in addition to ammonium carbonate, ammonium bicarbonate and ammonium hydroxide, tetraalkylammonium hydroxides and organic amines may also be used. The alkyl group of the tetraalkylammonium hydroxide may suitably be a C₁ to C₄ alkyl group. A suitable organic amine is 15 cyclohexylamine. Experiments have shown that the use of alkali metal precipitants lead to very much inferior catalysts. It is therefore preferred to avoid the presence of alkali metals in the catalyst composition. Compositions free from alkali metal may suitably be produced using as the precipitant either ammonium carbonate or ammonium bicarbonate, even more preferably ammonium bicarbonate. Ammonium carbonate may suitably be used in a commercially available form, which comprises a mixture of ammonium 20 bicarbonate and ammonium carbamate. Instead of using a pre-formed carbonate or bicarbonate it is possible to use the precursors of these salts, for example a soluble salt and carbon dioxide.

Precipitation whether it be under rising pH or constant pH conditions is preferably carried out at a temperature below 50°C, even more preferably at a temperature below 30°C. It will usually be found convenient to operate at room temperature, for example 15 to 25°C.

25 Step (I) or Step (I') may be carried out in an atmosphere of carbon dioxide.

In step (II) of the process the precipitate obtained in step (I) is recovered. This may suitably be accomplished by filtration but other methods for separating solids from liquids, for example centrifugation, may be employed. After recovery, it is preferred to wash the precipitate, suitably with water, so as to remove unwanted residual soluble matter. Thereafter, the precipitate may be dried, suitably at an elevated 30 temperature below 200°C, for example about 150°C.

Additional metals may also be introduced, if desired, at any stage in the production of the composition, for example during the precipitation step or by post-impregnation.

Irrespective of whether the composition is prepared by impregnation, precipitation or coprecipitation or by any other method, it is preferred to carry out one or more additional steps before the composition is 35 used as a catalyst. Thus it is preferred to roast the composition, suitably by heating it in, for example, a stream of gas such as nitrogen or air at a temperature suitably in the range from 250 to 600°C. In this manner the composition may be converted into a composition of the formula (I).

It is also necessary to reductively activate the composition, suitably by contact at elevated temperature with a reducing gas, for example hydrogen, which may be diluted with nitrogen. Typically, the conditions 40 employed during the reductive activation step may suitably be a pressure in the range from 1 to 100 bar and a temperature in the range from 150 to 500°C for a period of up to 24 hours or longer. Whilst it is preferred to effect the reductive activation step as a discrete step prior to use as a catalyst for the conversion of synthesis gas, it may be incorporated into the synthesis gas conversion process.

In another aspect the present invention also provides a process for the conversion of synthesis gas to 45 hydrocarbons which process comprises contacting synthesis gas under conditions of elevated temperature and atmospheric or elevated pressure with a reductively activated catalyst composition as hereinbefore described.

As is well known in the art synthesis gas principally comprises carbon monoxide and hydrogen and possibly also minor amounts of carbon dioxide, nitrogen and other inert gases depending upon its origin 50 and degree of purity. Methods of preparing synthesis gas are established in the art and usually involve the partial oxidation of a carbonaceous substance, e.g. coal. Alternatively, synthesis gas may be prepared, for example by the catalytic steam reforming of methane. For the purpose of the present invention the carbon monoxide to hydrogen ratio may suitably be in the range from 2:1 to 1:6. Whilst the ratio of the carbon monoxide to hydrogen in the synthesis gas produced by the aforesaid processes may differ from these 55 ranges, it may be altered appropriately by the addition of either carbon monoxide or hydrogen, or may be adjusted by the so-called shift reaction well known to those skilled in the art.

The elevated temperature may suitably be in the range from 160 to 350°C, preferably from 200 to 250°C. The pressure may suitably be in the range from 0 to 100 bar, preferably from 10 to 50 bar. The GHSV for continuous operation may suitably be in the range from 100 to 25000h⁻¹.

The process may be carried out batchwise or continuously in a fixed bed, fluidised bed or slurry phase reactor.

It is an advantage of the process of the present invention that it can be operated in a manner whereby the carbon dioxide make is low and, unexpectedly in view of the nature of the catalyst, the oxygenates make is very low. Surprisingly also, the process can be very selective to hydrocarbons in the C₅-C₈ range and particularly to wax range hydrocarbons. In contrast it has been observed that similarly prepared ruthenium/zinc oxide catalysts are almost inactive and iron/zinc oxide catalysts produce very light hydrocarbons in low selectivities. The catalyst composition of the present invention therefore provides a route to gasoline range hydrocarbons involving the production of wax range hydrocarbons and subsequent cracking and upgrading of this product.

In a modification of the process of the present invention the catalyst of formula (I) may incorporate a suitable porometallosilicate. The porometallosilicate may suitably be an aluminosilicate zeolite, preferably an aluminosilicate zeolite having a high (that is greater than 10:1) silica to alumina ratio. Suitable aluminosilicate zeolites include, but are by no means restricted to zeolite MFI-type, as described in for example US Patent No. 3702886.

In a further more preferred modification, the process of the invention may include a further step in which the product, or at least a portion thereof, obtained by contacting synthesis gas with the catalyst of formula (I) is up-graded by, for example, oligomerisation of lower olefins present therein to higher hydrocarbons in the manner described in, for example, US-A-4544792, US-A-4520215 and US-A-4504693; hydrocracking in the manner described in, for example GB-A-2146350; cracking and isomerisation of heavy by-products in the manner described in, for example, US-A-4423265 and up-grading in the manner described in, for example AU-A-8321809 and GB-A-2021145.

The invention will now be further illustrated by the following Examples. In the Examples CO conversion is defined as moles of CO used/moles of CO fed x 100 and carbon selectivity as moles of CO attributed to a particular product/moles of CO converted x 100.

Example 1 Co:Zn = 1:2

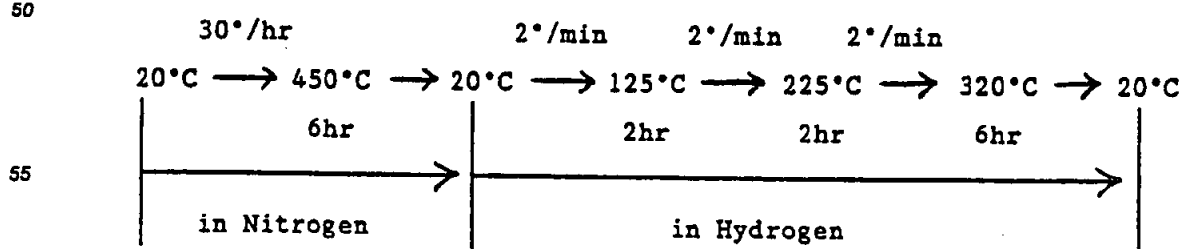
A. Catalyst Preparation

Ammonium bicarbonate (215 g, 2.72 mol) was dissolved in distilled water (2 dm³) and stirred vigorously at room temperature. To this solution was added a solution containing Cobaltous nitrate (50.0 g, 0.17 mol) and zinc nitrate (102.2 g, 0.34 mol) dissolved in 1 dm³ of distilled water. The rate of addition of the metal salts solution was approximately 12 cm³/min. The pH of the bicarbonate solution remained reasonably constant during the addition (ca pH 7.5 - 8.0). The resulting fine precipitate remained suspended in the stirred solution throughout the addition period. The precipitate was collected and dried on a filter bed.

Residual matter was washed from the precipitated cake by suspending it in 500 cm³ of distilled water, stirring the suspension vigorously and again filtering to dryness. The washing procedure was repeated a second time before the precipitated cake was dried in an oven at 150°C for 16 hours.

B. Catalyst Pretreatment

The oven dried cake was heated under an atmosphere of flowing nitrogen and then hydrogen according to the following temperature programme:



The resulting catalyst was opened to air before storing in a bottle.

C. Catalyst Testing

The catalyst was pressed to 6 tons and the resulting pellets crushed and sieved to BSS 18-25 mesh. It was mixed with an equal volume of carborundum (BSS 18-25 mesh) and loaded into a fixed bed reactor. A stream of hydrogen was passed over the catalyst bed which was given the following overnight heating programme:

$10^{\circ}\text{C} \xrightarrow{2^{\circ}\text{C/min}} 150^{\circ}\text{C} \xrightarrow{1^{\circ}\text{C/min}} 225^{\circ}\text{C} \xrightarrow{14\text{ hr}} 225^{\circ}\text{C}$

The bed temperature was reduced to 170°C before introducing syngas ($\text{H}_2/\text{CO} = 2$) and pressurising to 30 bar. The syngas flow rate was adjusted to give the required bed GHSV and the temperature was increased until syngas conversion occurred.

Example 2 Co:Zn = 1:1

The method used in Example 1 was repeated except that 75.0g (0.25 mol) of cobaltous nitrate, 76.7 g (0.25 mol) of zinc nitrate and 270 g (3.42 mol) of ammonium bicarbonate were used.

Example 3 Co:Zn = 2:1

The method used in Example 1 was repeated except that 100 g (0.34 mol) of cobaltous nitrate, 51.1 g (0.17 mol) of zinc nitrate and 270 g (3.42 mol) of ammonium bicarbonate were used.

Example 4 Co:Zn = 1:3

The method used in Example 1 was repeated except that 37.5 g (0.13 mol) of cobaltous nitrate and 115.0 g (0.39 mol) of zinc nitrate were used.

Example 5 Co:Zn = 1:4

The method used in Example 1 was repeated except that 30.0 g (0.10 mol) of cobaltous nitrate and 122.6 g (0.41 mol) of zinc nitrate were used.

Example 6 Co:Zn = 1:5

The method used in Example 1 was repeated except that 25.0 g (0.086 mol) of cobaltous nitrate, 127.8 g (0.43 mol) of zinc nitrate and 235 g (2.97 mol) of ammonium bicarbonate were used.

Example 7 Co:Zn = 1:2 from cobaltous chloride

The method used in Example 1 was repeated except that 40.9 g (0.17 mol) of cobaltous chloride and 102.2 g (0.34 mol) of zinc nitrate were dissolved in 0.75 dm^3 of distilled water. The base solution contained 300 g (3.80 mol) of ammonium bicarbonate dissolved in 2 dm^3 of distilled water.

Example 8 Co:Zn = 1:2 from cobaltous acetate

The method used in Example 1 was repeated except that 42.8 g (0.17 mol) of cobaltous acetate and 102.2g (0.34 mol) of zinc nitrate were dissolved in 0.75 dm³ of distilled water. The base solution contained 300 g (3.80 mol) of ammonium bicarbonate dissolved in 2 dm³ of distilled water.

Example 9 Co:Zn = 1:2 precipitated by Cyclohexylamine

The method used in Example 1 was repeated except that 50.0 g (0.17 mol) of cobaltous nitrate and 102.2 g (0.34 mol) of zinc nitrate were dissolved in 0.75 dm³ of distilled water. The base solution contained 418 g (4.31 mol) of cyclohexylamine mixed with 2.5 dm³ of distilled water.

Example 10 Co:Zn:Cr = 4:7:1

The method used in Example 1 was repeated except that 17.2 g (0.04 mol) of chromium (III) nitrate was added to a solution already containing 50.0 g (0.17 mol) of cobaltous nitrate and 89.25 g (0.30 mol) of zinc nitrate dissolved in 0.75 dm³ of distilled water. The base solution contained 450 g (5.70 mol) of ammonium bicarbonate dissolved in 3 dm³ of distilled water.

Example 11 Co:Zn:Zr = 4:7:1

The method used in Example 1 was repeated except that 12.22 g (0.04 mol) of zirconyl nitrate was added to a solution already containing 50.0 g (0.17 mol) of cobaltous nitrate and 89.25 g (0.30 mol) of zinc nitrate dissolved in 1.0 dm³ of distilled water. The base solution contained 330 g (4.18 mol) of ammonium bicarbonate dissolved in 2 dm³ of distilled water.

Example 12 Co:Zn:Ga = 4:7:1

The method used in Example 1 was repeated except that 15.59 g (0.04 mol) of gallium nitrate was added to a solution already containing 50.0 g (0.17 mol) of cobaltous nitrate and 89.25 g (0.30 mol) of zinc nitrate dissolved in 0.75 dm³ of distilled water. The base solution contained 450 g (5.70 mol) of ammonium bicarbonate dissolved in 3 dm³ of distilled water.

Example 13 Co:Zn:Ru = 1:2:0.0054

The method used in Example 1 was repeated except that 0.224 g (0.92 mol) of ruthenium chloride was added to a solution already containing 50.0 g (0.17 mol) of cobaltous nitrate and 102.2 g (0.34 mol) of zinc nitrate dissolved in 0.75 dm³ of distilled water. The base solution contained 450 g (5.70 mol) of ammonium bicarbonate dissolved in 3 dm³ of distilled water.

Example 14 Co:Zn = 1:4 by continuous coprecipitation

Ammonium bicarbonate (770 g, 9.75 mol) was dissolved in 7 dm³ of distilled water. A second solution was prepared by dissolving cobaltous nitrate (85.7 g, 0.29 mol) and zinc nitrate (350.0 g, 1.16 mol) in 2.86 dm³ of distilled water. These solutions were separately pumped into a stirred reactor vessel (500 cm³) where precipitation occurred. The rate of addition of the nitrate and bicarbonate solutions was 32 and 83 cm³/minute respectively. The resulting precipitate/slurry was pumped out of the reactor vessel at a rate of 115 cm³/min directly onto a filter bed. The pH in the precipitation vessel remained between 7.35 and 7.40 during the addition period (90 minutes). The precipitated cake was washed free of residual matter by

suspending it in 2 dm³ of distilled water which was vigorously stirred. The resulting suspension was then filtered to dryness. The washing procedure was repeated a second time before the precipitated cake was dried in an oven at 150°C for 16 hours. The catalyst was given the same pretreatment as described in Example 1.

Example 15 Co:Zn = 1:15 by impregnation

Cobaltous nitrate (18.3 g, 62 mol) was dissolved in 80 cm³ of AnalaR acetone. This solution was slowly added to ZnO (70 g) with continuous stirring until a consistent paste was formed. A further 20 cm³ of acetone was used to ensure that all of the cobalt was washed onto the zinc oxide. With continuous stirring/kneading, the paste was dried over a steam bath until a uniform powder was formed. The powder was left in an oven at 150°C overnight. The catalyst was given the same pretreatment as described in Example 1.

Example 16 Co:Zn = 1:2 tested with zeolite H-MFI

The method used in Example 1 was repeated and 5 cm³ of the finished catalyst (BSS 18-25 mesh) was mixed with 5 cm³ of carborundum (BSS 18-25 mesh). This was loaded into a fixed-bed reactor with a further 7 cm³ of carborundum loaded downstream of the FT bed. A bed of H-MFI zeolite (10 cm³, BSS 18-25 mesh) was then positioned downstream of both the FT bed and carborundum spacer. A temperature of 233°C was applied to the FT bed and 321°C to the zeolite bed. The waxy hydrocarbon product, CO₂ and water from the FT bed, along with unreacted synthesis gas, were all fed over the zeolite. The wax product was upgraded to LPG and a liquid C₅⁺ product.

The results of Examples 1 to 16 are given in the accompanying Table.

TABLE
Results for Syngas to Hydrocarbon Conversion

H₂:CO = 2:1
Pressure = 30 bar

Example	T/°C	Bed GHSV	% CO Conversion	% Carbon Molar Selectivity			
				CO ₂	CH ₄	C ₃ ⁺	oxygenates
1	216	2500	64.2	0.5	9.1	89.6	0.1
1	206	1250	70.1	0.5	8.3	90.5	0.1
2	240	2500	68.0	2.8	20.5	74.1	0.4
3	216	2500	53.9	1.6	12.8	83.1	0.4
4	252	2500	56.2	2.0	19.3	75.9	0.4
5	232	2500	60.7	1.2	16.2	81.2	0.1
6	259	2500	55.2	2.6	27.6	66.6	0.2
7	246	2500	60.9	1.2	14.6	82.0	0.8
8	240	2500	52.7	1.2	14.1	82.7	0.7
9	202	2500	43.0	0.3	8.0	90.4	0.3
10	233	2500	58.1	1.3	15.5	81.6	0.4
11	218	2500	55.1	0.8	11.0	86.9	0.4
12	218	2500	48.9	0.6	15.5	82.2	0.4
13	219	2500	64.2	0.8	9.1	88.9	0.4
14	209	1250	56.5	0.5	6.3	91.8	0.7
15	238	2500	42.5	0.9	18.5	76.9	1.4
16	233*	2500	50.6	1.9	12.1	84.8*	0.04
Comp Test 1	325	2500	67.0	33.3	23.1	31.0	1.4
Comp Test 2	350	2500	<5.0	#	#	#	#

* FT bed at 233°C, zeolite bed at 321°C, the C₃⁺ selectivity of 84.8% was 46.3% LPG and 38.5% of a liquid C₅⁺ product.

In view of the very low conversion the product was not analysed.

COMPARISON TEST 1

Iron Catalyst Preparation

Ammonium bicarbonate (225 g, 2.85 mol) was dissolved in distilled water (2 dm³) and stirred vigorously at room temperature. To this solution was added a solution containing ferric nitrate (123.6 g, 0.30 mol) and zinc nitrate (24.0 g, 0.08 mol) dissolved in 1 dm³ of distilled water. The rate of addition of the metal salts solution was approximately 12 cm³/min. The remainder of the preparation was the same as described for the cobalt catalyst in Example 1.

B. Catalyst Pretreatment

The procedure of Example 1 was repeated.

C. Catalyst Testing

The procedure of Example 1 was repeated.
The results are presented in the Table.

COMPARISON TEST 2

1% Ru/ZnO

A. Preparation

Ammonium bicarbonate (154 g, 1.95 mol) was dissolved in distilled water (2 dm³) and stirred vigorously at room temperature. To this solution was added a solution containing ruthenium chloride (0.65 g, ca 2.5 mmol) and zinc nitrate (92.7 g, 0.31 mol) dissolved in 750 cm³ of distilled water. The rate of addition of the metal salts solution was approximately 12 cm³/min. The remainder of the preparation was the same as described for Example 1.

B. Catalyst Pretreatment

The procedure of Example 1 was repeated.

C. Catalyst Testing

The procedure of Example 1 was repeated.
The results are presented in the Table.

Comparison Tests 1 and 2 are not in accordance with the present invention and are included only for the purpose of comparison.

Claims

1 A composition for use after reductive activation as a catalyst in the conversion of synthesis gas to hydrocarbons, which composition comprises as essential components (i) cobalt either as the elemental metal, the oxide or a compound thermally decomposable to the elemental metal and/or oxide and (ii) zinc in the form of the oxide or a compound thermally decomposable to the oxide.

2 A composition according to claim 1 additionally containing in elemental or oxide form one or more of the metals (M) nickel, iron, molybdenum, tungsten, zirconium, gallium, thorium, lanthanum, cerium, ruthenium, rhenium, palladium or platinum.

3 A composition, which after thermal decomposition of thermally decomposable compounds, is represented by the formula:



wherein M is one or more of the metals nickel, iron, molybdenum, tungsten, zirconium, gallium, thorium, lanthanum, cerium, ruthenium, rhenium, palladium or platinum.

a is greater than zero and up to 70% w/w,

b is from zero to 15% w/w,

c is greater than zero, and

x is a number such that the valence requirements of the other elements for oxygen is satisfied.

4 A process for preparing the catalyst composition of claim 1 which process comprises impregnating zinc oxide with a compound of cobalt thermally decomposable to the oxide.

5 A process for preparing the catalyst composition of claim 1 which process comprises the steps of:

(I) precipitating at a temperature in the range from 0 to 100°C the metals cobalt and zinc in the form of insoluble thermally decomposable compounds thereof using a precipitant comprising ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, a tetraalkylammonium hydroxide or an organic amine, and

(II) recovering the precipitate obtained in step (I).

6 A process for the production of the catalyst composition of claim 1 which process comprises the steps of:

(I') bringing together in solution at a temperature below the boiling point of the solution soluble compounds of cobalt and zinc and a precipitant comprising either ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, a tetraalkylammonium hydroxide or an organic amine so as to form a precipitate, the cobalt, zinc and precipitant being brought together at a rate such that a substantially constant pH in the range from 6 to 9 is maintained, and

(II') recovering the precipitate so-obtained.

7 A process according to either claim 5 or claim 6 wherein the precipitant is either ammonium carbonate or ammonium bicarbonate.

8 A process according to any one of claims 5 to 7 wherein precipitation is carried out at a temperature below 30°C.

9 A process according to any one of claims 4 to 8 wherein the composition is converted to a composition having the formula (I) by heating at a temperature in the range from 250 to 600°C in a stream of nitrogen or air.

10 A process according to any one of the preceding claims wherein the composition is reductively activated by contact with a reducing gas at a temperature in the range from 150 to 500°C and a pressure in the range from 1 to 100 bar for a period of up to 24 hours or longer.

11 A process for the conversion of synthesis gas to hydrocarbons which process comprises contacting synthesis gas under conditions of elevated temperature and atmospheric or elevated pressure with the reductively activated catalyst composition of claim 1.

12 A process according to claim 11 wherein the elevated temperature is in the range from 160 to 350°C and the pressure is in the range from 0 to 100 bar.

13 A process according to claim 12 wherein the elevated temperature is in the range from 200 to 250°C and the pressure is in the range from 10 to 50 bar.

14 A process according to any one of claims 11 to 13 including the further step of up-grading the hydrocarbon product, or at least a portion thereof, by oligomerisation of lower olefins present therein to higher hydrocarbons.

15 A process according to any one of claims 11 to 13 including the further step of hydrocracking the hydrocarbon product, or at least a portion thereof.

16 A process according to any one of claims 11 to 13 including the further step of cracking and isomerising the hydrocarbon product, or at least a portion thereof.

17 A process according to any one of claims 11 to 13 including the further step of up-grading the hydrocarbon product, or at least a portion thereof.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	US-A-4 107 091 (KHERA) * Abstract; columns 5,6,7; claims 1-5 *	1-13	B 01 J 23/80 B 01 J 23/84
Y	DE-A-2 625 541 (BASF) * Claim; pages 4,5 *	1-13	B 01 J 23/89 C 07 C 1/04
A	EP-A-0 055 512 (STANDARD OIL)		
A	EP-A-0 153 780 (SHELL)		
D,A	GB-A-2 125 062 (SHELL)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			B 01 J C 07 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-12-1987	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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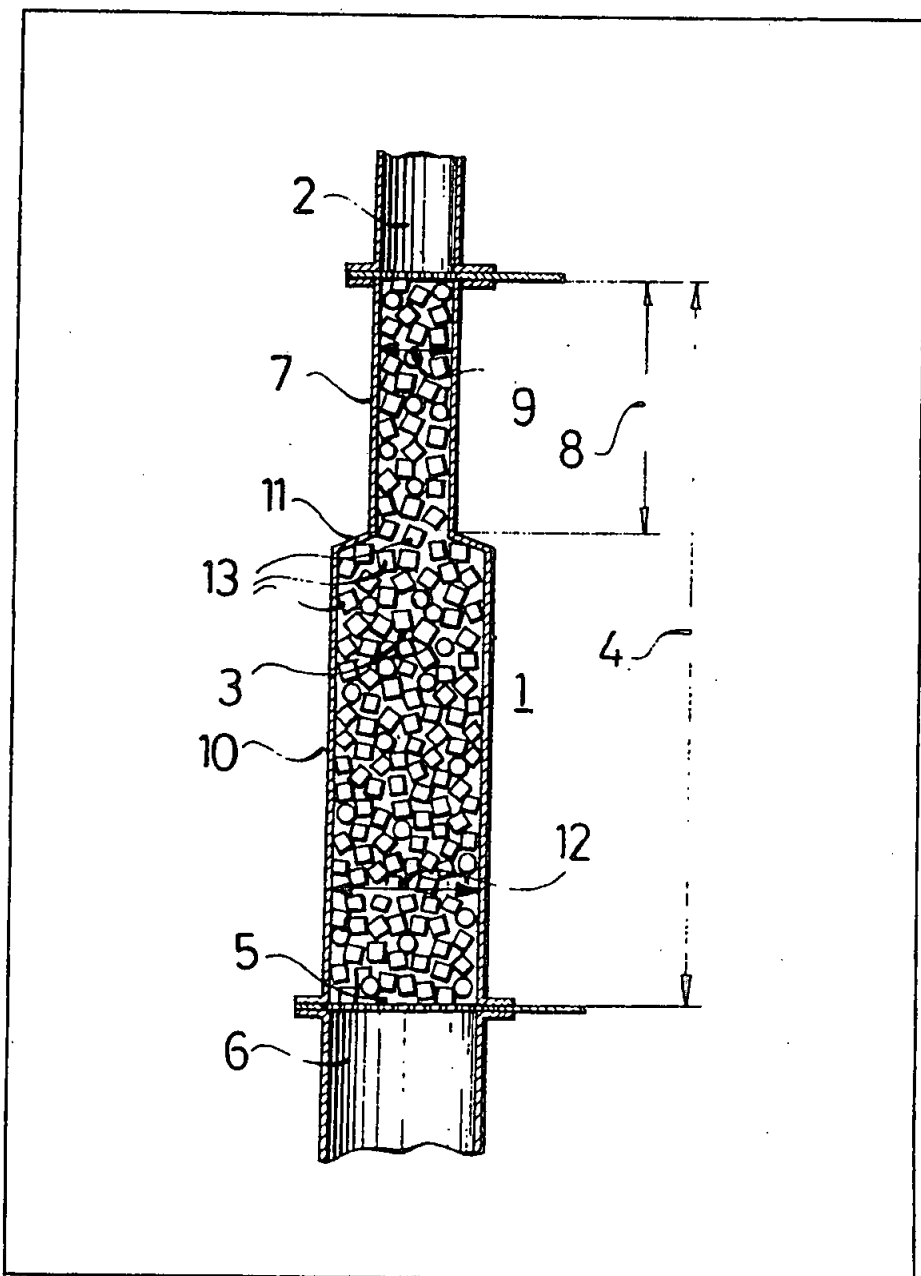
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(54) Reaction tube for an exothermic heterogeneously catalysed gas reaction

(57) A reaction tube (1) for carrying out reaction between components of a reaction gas is filled with solid catalyst particles (3). The tube is subdivided into two successive sections, and in the upstream section (7) the ratio of the hydraulic tube diameter to the "equivalent diameter" of the catalyst particles (a dimension equal to the diameter of a

sphere of corresponding volume) is smaller than the corresponding ratio for the downstream section (10) of the reaction tube. Additionally the upstream section (7) cooled, and is given a length such that the gas in it after reaching a maximum permissible reaction temperature can be cooled sufficiently prior to entering the downstream section (10) that the temperature in the downstream section remains

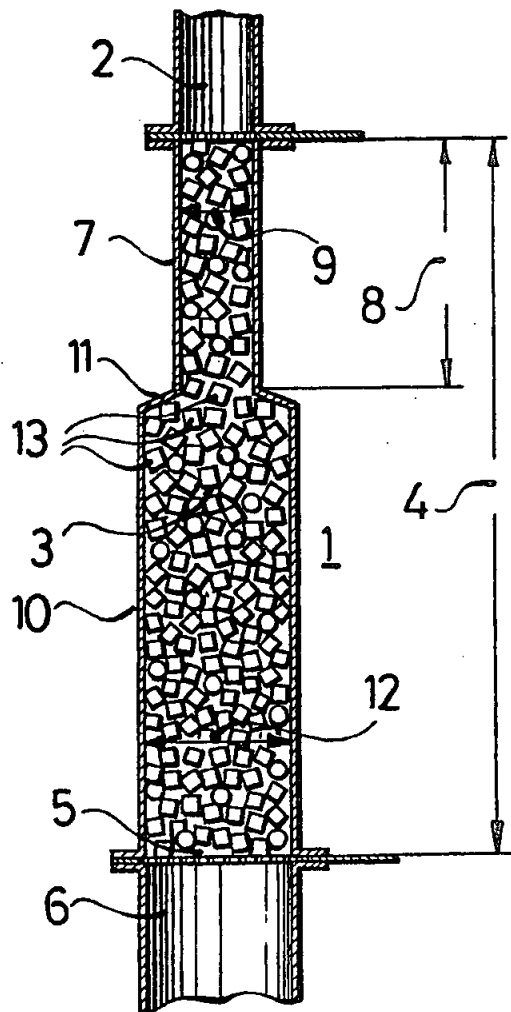
(57) continued overleaf...



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below the maximum permissible temperature. The hydraulic tube diameter may be varied by mixing filler bodies with the catalyst.

The reaction tube is especially suited to a methanation reaction performed on a synthesis gas containing carbon monoxide, carbon dioxide and hydrogen.



SPECIFICATION

Reaction tube for an exothermic, heterogeneously catalysed gas reaction

- 5 The invention relates to a reaction tube for an exothermic reaction between gaseous components of a reaction gas. In particular, although not exclusively, the reaction tube may be used for methanising a synthesis gas containing carbon monoxide, carbon dioxide and hydrogen. The reaction tube contains a solid catalyst which forms a bed through which the reaction gas reacting on the solid catalyst can flow and which is cooled from the outside. The reaction tube has an inlet connection for the supply of reaction gas and is connected at its outlet to a gas duct through which the gaseous product is discharged. The catalyst can be a loose fill or heap of catalyst particles, such as obtained by tipping into the tube. 10
- In the case of exothermic gas reactions in which solid catalysts are employed, it must be ensured on the one hand that the heat of reaction does not inadmissibly overheat the solid catalyst. The rate at which the heat of reaction is liberated depends, not only upon the state of the reaction gas, but also upon the quality and the volume of the catalyst which actively participates in the course of the reaction. The heating-up of the catalyst is counteracted by external cooling of the reaction tube. On the other hand, the reaction product which is extracted as a gaseous product, should be in a predetermined thermodynamic equilibrium when extracted from the reaction tube. The length of the reaction tube and the pressure loss in it must be kept within acceptable structural and economic limits. The steps which must be taken in order to fulfil these 15 conditions are, at least in part, diametrically opposed. 20
- For methanising gases rich in carbon oxides, it is known to carry out the reaction using reaction tubes which are filled with solid catalyst and which have a constant tube diameter. Methanisation is applied to gases substantially comprising hydrogen H_2 , carbon monoxide CO , carbon dioxide CO_2 , and methane CH_4 . The methanisation produces, for example, fuel gases which are used as a substitute for gases obtainable from natural sources, or gases which serve as energy vehicles in a long-distance energy circuit, such as that described, for example, in DT-PS 1 298 233 or DT-AS 1 601 001. In methanisation, the CH_4 content of the gas is increased by exothermic reactions 25
- $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ $\Delta H^\circ_{298 K} = -206 \text{ kJ/mole}$
 $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$ $\Delta H^\circ_{298 K} = -165 \text{ kJ/mole}$ 30
- proceeding on solid catalysts. The gas formed can be fed directly into the natural-gas network after separating off the water produced in the reaction, or it is again reformed with steam in the long-distance energy circuit. The heat generated in the reaction tube is carried away to a coolant (see, for example, DE-OS 25 29 316, DE-OS 29 49 588). 35
- With reaction tubes of constant diameter, it has not hitherto been possible to satisfy at the same time all the aforesaid conditions for the performance of the process even when using qualitatively different catalyst materials. When using more than one catalyst material in the reaction tube so that the different catalyst materials are successively traversed by the reacting gas, considerable disadvantages arise in the performance of the process. In particular there are disadvantages arising from the varying ageing of the individual layers of catalyst and the resultant changes in the maximum temperature in the catalyst bed. 40
- The object of the invention is to conduct the reaction with the use of a solid catalyst of predetermined quality, in such a way that, with limited pressure loss, overheating of the solid catalyst can be avoided on the one hand, while on the other hand there is made available at a predetermined temperature a gas mixture which is in thermodynamic equilibrium. 45
- For this purpose the present invention provides a reaction tube for an exothermic reaction between gaseous components of a reaction gas, notably for methanising a synthesis gas containing carbon monoxide, carbon dioxide and hydrogen, the reaction tube containing a solid catalyst which forms a bed through which the reaction gas reacting on the solid catalyst can flow and which is cooled from the outside, 50 the said reaction tube having an inlet union for the supply of reaction gas and being connected at its outlet to a gas duct through which a product gas is discharged, characterised in that the reaction tube is divided at least into two successive tube sections, of which the first tube section, upstream as seen in the direction of flow of the reaction gas has a hydraulic tube diameter which is smaller in relation to the "equivalent diameter" of solid catalyst particles present in this tube section than is the hydraulic diameter of the succeeding second tube section in relation to the equivalent diameter of solid catalyst particles present in the 55 second, downstream tube section.
- There is here meant by "hydraulic tube diameter" a diameter which is equal to the diameter of a cylindrical pipeline and which is given by the relation:
- 60 $d_h = 4 f/U$ 60
 where:
 f = free cross-sectional area of flow of the pipeline
 U = circumference of the free cross-sectional area of flow. 65

By "equivalent diameter", there is to be understood a diameter of a sphere equal to the volume of a particle of catalyst. The equivalent diameter d_g is calculated, starting from the sphere volume

$$V_k = \frac{1}{6} \pi \cdot d_g^3$$

5 in accordance with the relation:

$$d_g = \sqrt[3]{6 \cdot V_p / \pi}$$

10 V_p = particle volume.

This ratio of hydraulic tube diameter to equivalent diameter serves to take account of the fact that on the one hand, the dissipation of the heat of reaction is enhanced with decreasing hydraulic diameter, while on the other hand the ratio of geometrical surface to volume of the particles of catalyst influences the yield of the reaction. The calculation of the hydraulic tube diameter in the determination of this ratio is based solely upon the geometrical data of the tube section when it is empty, i.e. not filled with catalyst particles. The dimensions of the catalyst particles are disregarded for calculating the tube diameter.

According to a further feature of the invention, the first, upstream, tube section is designed with such a length that the reaction gas in this tube section can be cooled, after reaching a maximum permissible reaction temperature and until it passes into the second, downstream tube section, to such a temperature that the temperature of the reaction gas in the second tube section remains below the maximum permissible temperature. This proceeds, with advantage, from recognition that the danger of overheating of the solid catalyst exists essentially in the region of the inlet of the reaction tube. Therefore, particular care is taken to ensure that there is a considerable dissipation of heat in this region. In the succeeding, second tube section, the desired thermodynamic equilibrium is established at a predetermined temperature. This subdivision of the reaction tube into two tube sections which are individually adapted to the course of the reaction results in relatively short reaction tubes and low pressure loss.

In a further development of the reaction tube, the upstream tube section contains, in addition to the particles of solid catalyst, space-filling bodies which reduce the hydraulic diameter of the tube and are catalytically inert in the exothermic reaction. In fixing the ratio of the hydraulic tube diameter to the equivalent diameter of the particles, it is necessary to take account of the displacement bodies only in the determination of the hydraulic tube diameter. The equivalent diameter of the particles remains unaffected by the dimensions of the displacement bodies.

Preferably, the upstream tube section has a smaller tube diameter than the succeeding downstream tube section. It would also be possible to use reaction tubes which widen conically as seen in the direction of flow of the reaction gas. For increasing the cooling action, the upstream tube section could also be subdivided into a number of individual tubes in which case the hydraulic tube diameter will be defined by the sum of the hydraulic diameters of these individual tubes.

In the following, the invention is more particularly explained by a description of exemplary embodiments. The drawing diagrammatically illustrates a reaction tube comprising two tube sections having different diameters.

There is illustrated in the drawing a reaction tube 1 to which an exothermically reacting reaction gas can be fed by way of its inlet 2. The reaction tube 1 is filled with a solid catalyst bed 3 which promotes the reaction of the components of the reaction gas, and it is cooled over its entire length 4 from the outside. In the illustrated embodiment, the reaction tube 1 is surrounded by a pressure vessel, not illustrated in the drawing, which is filled with water under pressure. In taking up the heat evolved in the reaction, the water boils. The gaseous product withdrawn from the outlet 5 by way of a gas duct 6.

The reaction gas first flows through an upstream tube section 7 having a length 8. This first tube section has a smaller internal diameter 9 than the succeeding second tube section 10 downstream in the direction of flow of the reaction gas) of the reaction tube 1. In the transition portion 11, the reaction tube 1 widens from the diameter 9 to a diameter 12. In the illustrated embodiment, both tube sections 7 and 10 are of cylindrical form. In this case, the hydraulic tube diameters of these tube sections correspond to the internal tube diameters 9 and 12.

Solid catalyst particles 13, which all consisting of the same catalyst material, are provided in the two tube sections 7 and 10 of the reaction tube. The quantity of heat developed per catalyst mass during the reaction when a particular catalyst material is employed is known for each individual stage of the reaction. For a given throughput of a reaction gas having a particular composition and for a given solid catalyst volume, the ratio of hydraulic tube diameter to equivalent diameter in the upstream tube section 7 is selected so that, with a constant water temperature in the pressure vessel surrounding the reaction tube 1, the catalyst temperature does not exceed a maximum permissible temperature appropriate for the material of the solid catalyst. On entering the first tube section 7, the reaction gas rapidly reacts with a considerable evolution of heat. After the maximum temperature has been reached, the rate of transformation of the components decreases again and the velocity of the reaction is considerably reduced.

The ratio of hydraulic tube diameter to equivalent diameter acquires a higher value in the downstream tube section 10 than in the upstream tube section 7. The ratio is made such that as short a length of tube as

possible is sufficient to set up the desired thermodynamic equilibrium at a preset temperature for the product gas. The length of the upstream tube section 7 is made such that the reaction gas is cooled to such a temperature before passing into the downstream tube section 10 that the reaction gas does not exceed the maximum permissible temperature even in the downstream tube section, from which a smaller quantity of heat per unit time can be transferred to the water boiling in the pressure vessel.

Instead of being constructed as a single tube as in the illustrated embodiment, the upstream tube section 7 of the reaction tube 1 may be formed of a number of individual tubes which lead into the downstream tube section 10 at the transition portion 11 of the reaction tube. The individual tubes are filled with solid catalyst particles as in the illustrated embodiment and are washed by the boiling water in the pressure vessel for the purpose of cooling. For determining the ratio of hydraulic tube diameter to equivalent diameter in this case, the sum of the hydraulic tube diameters of all the individual tubes must be taken as the hydraulic tube diameter of the upstream tube section. It is also possible to employ, for reducing the hydraulic tube diameter, space-filling bodies which have catalytically inert properties for the reaction.

For methanising a synthesis gas having a gas composition of 10% CH₄, 9% CO, 10% CO₂, 67% H₂ and 4% N₂ in a reaction tube 1 comprising two tube sections 7 and 10, a water pressure of 100 bar was established in the pressure vessel. At this pressure, the boiling point of water is 311°C. The reaction tube 1 was filled with solid catalyst particles consisting of a ceramic catalyst material suitable for high-temperature methanisation, which had a nickel base (Haldor Topsoe A/S, catalyst material MCR-2x). The catalyst particles, which were of cylindrical shape, had a mean diameter and a mean height of 4.3 mm each. This gives a value of about 4.9 mm for the equivalent diameter d_g. The maximum permissible operating temperature for this catalyst material is 700°C. If the reaction gas entering the upstream tube section 7 at a temperature of 300°C and having the composition indicated in the foregoing reacted without cooling, a temperature of about 780°C would be attained as adiabatic limit temperature in the reaction tube 1. For the desired product gas quality, the escaping product gas must be set to a thermodynamic equilibrium temperature between 311° and a maximum of 370°C.

Under these boundary conditions, with a throughput of 1.8 km/reaction gas per hour and with known data for the reaction kinetics of the catalyst MCR-2x, the reaction tube 1 having a total length of 8m was designed with a length of 3m and a diameter of 25 mm in its first, upstream tube section 7, and with a diameter of 50 mm in its second, downstream tube section 10.

For catalyst particles of the same catalyst material as in example above, but with a mean diameter and a mean height of 8 mm each for a throughput of 6.7 km/reaction gas per hour, the reaction tube 1 had the following dimensions: upstream tube section 7, length 3 m, diameter 50 mm; downstream tube section 10, length 5 m, diameter 70 mm. The length of the whole reaction tube 1 was thus 8 m.

With the same catalyst material and under the same boundary conditions in the cooling of the reaction tube 1 as in the preceding examples, a reaction tube was designed for a throughput of 9 km/reaction gas per hour, for two different particle sizes of the solid catalyst. In the upstream tube section 7 of the reaction tube 1, cylindrical solid catalyst particles having a mean diameter and a mean height of 8 mm each were employed, and the downstream tube section 10 was filled with solid catalyst particles having a mean diameter and a mean height of 4.3 mm each. In this case, the upstream tube section 7 had a length of 3 m and a diameter of 50 mm, and the downstream tube section 10 had a diameter of 70 mm. The total length of the reaction tube was less than 7 m. With this form of the reaction tube 1, it was possible to obtain, despite the considerably higher throughput of the escaping product gas, a composition corresponding to the thermodynamic equilibrium of the synthesis gas in the temperature range between 311° and 370°C.

CLAIMS

1. Reaction tube for an exothermic reaction between gaseous components of a reaction gas, which tube contains solid catalyst forming a bed through which the reaction gas reacting on the solid catalyst can flow, and which is cooled from the outside, the reaction tube having an inlet connection for the supply of reaction gas, and an outlet connection to a gas duct for discharge of product gas, characterised in that the reaction tube is subdivided into two successive tube sections, of which the upstream section has a ratio of hydraulic tube diameter of the "equivalent diameter" of the solid catalyst particles in this tube section which is smaller than the ratio of the hydraulic diameter of the downstream section while the said upstream section has a length such that the reaction gas in the upstream tube section can be cooled after reaching a maximum permissible reaction temperature, and between these and entering the downstream section, sufficiently that the temperature of the reaction gas in the downstream tube section remains below the maximum permissible temperature.

2. A reaction tube according to claim 1 wherein in addition to solid catalyst particles the upstream tube section contains space-filling bodies which are catalytically inert toward the exothermic reaction, but reduce the hydraulic tube diameter.

3. A reaction tube according to claim 1 or claim 2 wherein the upstream tube section comprises a plurality of individual tubes.

4. A reaction tube according to claim 1 or claim 2 wherein the upstream tube section comprises a plurality of individual tubes, arranged so that all deliver into a common downstream tube, with the ratio of the total hydraulic tube diameter of the tubes of the upstream section to the solid catalyst particles therein

being less than the ratio of the hydraulic tube diameter of the downstream tube section to the catalyst particles in the downstream tube section.

5. A reaction tube according to any one of the preceding claims containing a solid catalyst for methanising a synthesis gas containing carbon monoxide, carbon dioxide and hydrogen.

5 6. A reaction tube substantially as described herein with reference to the accompanying drawing.

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7. A methanation plant incorporating a reaction tube to any one of the preceding claims.

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Unionspriorität:

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Bezeichnung:

Reaktor zur Durchführung katalytischer endothermer oder exothermer Reaktionen

71

Anmelder:

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72

Erfinder:

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7/80

(H 1142)

H 79/56
Pa/Vo
17.7.1979

Patentansprüche

1. Reaktor zur Durchführung katalytischer endothermer oder exothermer Reaktionen mit einem von reagierenden Fluiden durchströmten und mit Katalysatormaterial gefüllten Reaktionsraum, der in Wärmekontakt mit einem Wärme abgebenden oder aufnehmenden Fluid steht, dadurch gekennzeichnet, daß die Querschnittsfläche des Reaktionsraums sich entlang des Strömungswegs der reagierenden Fluide in Abhängigkeit von der zur Reaktion erforderlichen oder bei der Reaktion frei werdenden Wärmemenge ändert.
2. Reaktor nach Anspruch 1, dadurch gekennzeichnet, daß der Reaktionsraum im wesentlichen aus Rohren (5, 13, 14, 15) besteht und die Rohre in mehrere Abschnitte mit unterschiedlichen Durchmessern unterteilt sind.
3. Reaktor nach Anspruch 1, dadurch gekennzeichnet, daß der Reaktionsraum im wesentlichen aus Rohren (12) besteht und die Rohre (12) entlang des Strömungswegs sich kontinuierlich ändernde Durchmesser aufweisen.

Form. 5729 7.78

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1 4. Reaktor nach Anspruch 1, dadurch gekennzeichnet, daß
 der Reaktionsraum von in das Katalysatormaterial ein-
 5 gebrachten Hemden (17) mit entlang des Strömungswegs
 sich verändernden Durchmessern begrenzt ist und inner-
 halb der Hemden (17) Rohre (16) für das Wärme abgeben-
 de oder aufnehmende Fluid angeordnet sind.

10 5. Reaktor nach einem der Ansprüche 1 bis 4, dadurch ge-
 kennzeichnet, daß ein Teil des Reaktionsraums eine vom
 restlichen Reaktionsraum abweichende Querschnittsver-
 teilung entlang des Strömungswegs aufweist und alter-
 nativ oder zusätzlich zum restlichen Reaktionsraum mit
 den Zuführungseinrichtungen der reagierenden Fluide
 15 verbindbar ist.

6. Reaktor nach einem der Ansprüche 2, 3 oder 5, dadurch
 gekennzeichnet, daß benachbarte Rohre (5) bezüglich
 der Strömungsrichtung antiparallel angeordnet sind.

20 7. Reaktor nach einem der Ansprüche 2, 3, 5 oder 6, da-
 durch gekennzeichnet, daß mindestens zwei der Rohre
 (13, 14) innerhalb des Reaktors zu einem Rohr (15)
 vereinigt sind.

25 8. Reaktor nach einem der Ansprüche 2, 3, 5, 6 oder 7, da-
 durch gekennzeichnet, daß für jeden Durchmesser D_1
 (in mm) eines Rohres (5, 12, 13, 14, 15) folgende Be-
 ziehung zu der durch den Durchmesser D_1 strömenden Gas-
 30 menge pro Zeiteinheit V (in Nm^3/h) besteht:

$$D_1 = p \cdot v^q,$$

wobei p , q Konstante sind.

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17.7.1979

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Reaktor zur Durchführung katalytischer
endothermer oder exothermer Reaktionen

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Die Erfindung betrifft einen Reaktor zur Durchführung katalytischer, endothermer oder exothermer Reaktionen mit einem von reagierenden Fluiden durchströmten und mit Katalysatormaterial gefüllten Reaktionsraum, der in Wärmekontakt mit einem Wärme abgebenden oder auf-

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nehmenden Fluid steht.

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Viele reaktionskinetische Vorgänge, wie beispielsweise die Methanolsynthese oder die Ammoniaksynthese, spielen sich in Anwesenheit von Katalysatoren ab. Abhängig von den herrschenden Betriebs- und Reaktionsbedingungen, von den Katalysatoren und den geometrischen Verhältnissen in dem Reaktor, stellen sich bei den Reaktionen Gaszusammensetzungen ein, die dem Gleichgewichtszustand mehr oder weniger nahe kommen. Häufig laufen in den Reaktoren auch

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mehrere Reaktionen mit unterschiedlicher Reaktionsgeschwindigkeit und Reaktionsenthalpie gleichzeitig ab. Die im Reaktor auftretenden Temperaturbereiche sind vielfach wegen der Mindestansprangtemperatur des Katalysators und/oder wegen der Bildung unerwünschter Zwischenprodukte

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nach unten, wegen des jeweils erwünschten Annäherungs-

- 1 grades an das Gleichgewicht und auch aus Gründen der Wirtschaftlichkeit und der Werkstoffe einschließlich des Katalysators, nach oben begrenzt. In jedem Fall ist die Herstellung eines erwünschten Temperaturverlaufs im Reaktor eine wichtige Bedingung für seine Auslegung.

So ist beispielsweise in der Zeitschrift "Chemtech", Juli 1973, Seiten 430 bis 435, ein Methanolreaktor der eingangs genannten Art beschrieben, bei dem der Katalysator im Inneren von Rohren angeordnet ist, die von reagierenden Gasen durchströmt sind. Die bei der Reaktion entstehende Wärme wird von verdampfendem Kühlwasser (Kühlfluid), das im Außenraum um die Rohre strömt, abgeführt. Das in der zitierten Literaturstelle gezeigte Temperaturprofil für einen solchen Reaktor ergibt, ausgehend von einer Gaseinlaßtemperatur, die unterhalb der Temperatur des Kühlfluids liegt, bedingt durch die katalytisch ausgelöste Reaktion, eine Erwärmung bis zu einem Höchstwert, der etwa 11° über der Kühlfluidtemperatur liegt und, bedingt durch die geringer werdende Reaktionswärme und den Wärmeübergang an das Kühlfluid, eine anschließende Abkühlung bis zur Gasaustrittstemperatur, die einige Grad über der Temperatur des Kühlfluids liegt.

- 25 Im beschriebenen Reaktor wird zunächst vom Gas und vom Katalysator noch Wärme aus dem Kühlmittel aufgenommen. Würde die Eingangstemperatur der Gase höher gewählt werden, würde auch die Höchsttemperatur im Reaktor nach oben verschoben werden, was aber wegen einer möglichen Schädigung des Katalysators, wegen der Gleichgewichtsbedingungen und aus wirtschaftlichen Gründen nur begrenzt möglich ist.

Der vorliegenden Erfindung liegt daher die Aufgabe zugrunde, einen Reaktor der eingangs genannten Art zu entwickeln, der sich durch eine besonders gute Anpassung des tatsächlichen

- 1 Temperaturverlaufs an den für die Reaktion günstigsten Wert auszeichnet und der mit vertretbarem finanziellen und technischen Aufwand herstellbar ist.
- 5 Diese Aufgabe wird erfindungsgemäß dadurch gelöst, daß die Querschnittsfläche des Reaktionsraums sich entlang des Strömungswegs der reagierenden Fluide in Abhängigkeit von der zur Reaktion erforderlichen oder bei der Reaktion frei werdenden Wärmemenge ändert.
- 10 Der Querschnitt ist dem Verlauf der theoretisch optimalen Temperatur im Reaktor angepaßt, und zwar ist in Abschnitten, in denen große Wärmemengen freigesetzt (bei exothermen Reaktionen) oder benötigt werden (bei endothermen Reaktionen),
15 der Querschnitt des Reaktionsraums möglichst klein und umgekehrt in Abschnitten, in denen kleine Wärmemengen freigesetzt oder benötigt werden, der Querschnitt möglichst groß gewählt. Dies bedeutet im ersten Fall ein großes Verhältnis von mit dem Wärme zu- oder abführenden Fluid in Berührung stehender Wandfläche zu Katalysatorvolumen und damit
20 ein besonders hohes Maß an Wärmeübertragungsvermögen vom Katalysator oder auf den Katalysator, während das Verhältnis Oberfläche zu Katalysatorvolumen im zweiten Fall klein ist und somit nur ein geringer Wärmeaustausch stattfindet.
- 25 Durch den Gegenstand der vorliegenden Erfindung ist es auf überraschend einfache Weise gelungen, den Temperaturverlauf in dem Reaktor den jeweiligen Gegebenheiten einer Reaktion möglichst optimal anzupassen. Große Wärmemengen werden an
30 denjenigen Stellen im Reaktor den reagierenden Fluiden zugeführt oder entzogen, an denen diese Wärme tatsächlich benötigt oder erzeugt wird, während an anderen Stellen, an denen wenig Reaktionswärme benötigt oder erzeugt wird, durch die erfindungsgemäße Ausbildung des Reaktors ein
35 wesentlich geringerer Wärmeaustausch stattfindet.

1 Der Erfindungsgegenstand ist sowohl für Einphasensysteme
(gasförmige Reaktionspartner) als auch für Zweiphasen-
systeme (gasförmige und flüssige Reaktionspartner) sowie
für Festbettkatalysatoren und Fließbettkatalysatoren ge-
5 eignet.

Es hat sich als vorteilhaft erwiesen, daß der Reaktionsraum
im wesentlichen aus Rohren besteht und die Rohre in mehrere
Abschnitte mit unterschiedlichen Durchmessern unterteilt
10 sind. Bei dieser Ausführungsform, bei der das Katalysator-
material im Inneren der Rohre angeordnet ist, sind die Rohre
parallel von den reagierenden Fluiden durchströmt. Im Außen-
raum um die Rohre ist ein Wärme abgebendes oder aufnehmendes
Fluid geführt, je nachdem, ob es sich um eine endotherme
15 oder eine exotherme Reaktion handelt. Selbstverständlich
können neben den Durchmessern der einzelnen Rohrabschnitte
auch deren Längen unterschiedlich groß gewählt sein, um
auf diese Weise den Gegebenheiten im Reaktor noch besser
Rechnung zu tragen.

20 Bei einer anderen vorteilhaften Ausführungsform des Erfin-
dungsgegenstandes, bei der der Reaktionsraum ebenfalls im
wesentlichen aus Rohren besteht, weisen die Rohre entlang
des Strömungswegs der reagierenden Fluide sich kontinuier-
25 lich ändernde Durchmesser auf.

Bei einer weiteren vorteilhaften Ausführungsform des Erfin-
dungsgegenstandes ist der Reaktionsraum von in das Kataly-
satormaterial eingebrachten Hemden mit entlang des Strö-
30 mungswegs der reagierenden Fluide sich ändernden Durchmes-
sern begrenzt und sind innerhalb der Hemden Rohre für das
Wärme abgebende oder aufnehmende Fluid angeordnet. Der
Strömungsquerschnitt für die Fluide ist je nach Anordnung
der Hemden mehr oder weniger verengt. Das Katalysatorma-
35 terial innerhalb der Hemden ist von den Rohren durchdrungen.

Bei Über- oder Unterlastbetrieb des Reaktors muß die Gleichgewichtseinstellung nach anderen Gesichtspunkten als im Normalbetrieb erfolgen, da sich die Fluidgeschwindigkeiten, die Reaktionsenthalpien und auch die umgesetzten Fluidmengen ändern. Selbst wenn also der Reaktor beim Normalbetrieb möglichst optimal an die Reaktion angepaßt ist, kann es sein, daß bei einem Über- oder Unterlastbetrieb weniger günstige Anpassungsbedingungen im Reaktor herrschen. Aus diesem Grund wird in Weiterbildung des Erfindungsgegenstandes vorgeschlagen, daß ein Teil des Reaktionsraums eine vom restlichen Reaktionsraum abweichende Querschnittsverteilung entlang des Strömungswegs aufweist und alternativ oder zusätzlich zum restlichen Reaktionsraum mit den Zuführungseinrichtungen der reagierenden Fluide verbindbar ist.

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- 1 Unterlastbetrieb vorgesehenen Fluidmengen und Fluidströmungsgeschwindigkeiten einen möglichst optimalen Temperaturverlauf ergibt.
- 5 Bei einer vorteilhaften Ausbildung des erfindungsgemäßen Reaktors sind benachbarte Rohre bezüglich der Strömungsrichtung antiparallel angeordnet. Dieser Aufbau erweist sich dann als vorteilhaft, wenn bei antiparalleler Anordnung komplementäre Rohrabschnitte aufeinandertreffen, so daß bei-
- 10 spielsweise neben einem Abschnitt mit großem Durchmesser beim antiparallel angeordneten Rohr ein Abschnitt mit kleinem Durchmesser zu liegen kommt. Auf diese Weise ist das Bauvolumen des Reaktors erheblich reduziert.
- 15 Bei einer zweckmäßigen Modifikation des Erfindungsgegenstandes sind mindestens zwei der Rohre innerhalb des Reaktors zu einem Rohr vereinigt.

Für den erfindungsgemäßen Reaktor ergibt sich für jeden Durchmesser D_1 (in mm) eines Rohres zu der durch den Durchmesser D_1 strömenden Gasmenge pro Zeiteinheit V (in Nm^3/h):

$$D_1 = p \cdot V^q$$

wobei p , q Konstante sind. Für p , q ergeben sich z.B. für einen Methanolsynthesereaktor die Zahlenwerte $15 \leq p \leq 25$

25 und $0,12 \leq q \leq 0,22$.

Der erfindungsgemäße Reaktor ist insbesondere für eine Ammoniaksynthese oder für eine Methanolsynthese geeignet, ohne jedoch auf diese Verwendungen beschränkt zu sein.

- 30 Weitere Einzelheiten der vorliegenden Erfindung werden anhand von schematisch dargestellten Ausführungsbeispielen beschrieben.

35

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1 Hierbei zeigen die Figuren 1 bis 6 verschiedene Ausführungs-
formen des erfindungsgemäßen Reaktors.

In sämtlichen Figuren ist mit 1 ein erfindungsgemäßer Reaktor
5 bezeichnet, der in einem Mantel 2 untergebracht ist. Der
Reaktor 1 ist nach Art eines Rohrwärmetauschers aufgebaut
und weist zwei voneinander getrennte Strömungsräume auf.

In den Figuren 1 bis 5 ist der eine Strömungsraum 4 von
10 mehreren Rohren 5 gebildet, die im Mantel 2 angeordnet und
an ihren beiden Enden in Rohrplatten 6 eingeschweißt sind.
Die Rohrenden stehen auf beiden Seiten mit Sammelräumen 7a,
7b in Verbindung, über die die reagierenden Fluide gemäß
Pfeilen 8, 9 zu- und abgeführt werden. Der andere Strömungs-
15 raum 3, der von dem Mantel 2 begrenzt ist, dient zur Führung
eines Wärme zuführenden oder abführenden Fluids, das gemäß
Pfeilen 10, 11 zu- und abgeführt wird. Die Rohre 5 sind mit
einem Katalysatormaterial gefüllt. Erfindungsgemäß ändert
sich der Durchmesser der Rohre 5 entlang des Strömungswegs
20 der reagierenden Fluide, und zwar sind die Durchmesser so
gewählt, daß an allen Stellen des Reaktionsraums ein mög-
lichst idealer Gleichgewichtszustand und/oder günstige Wärme-
übertragungsverhältnisse herrschen, d.h. an den Stellen, an
denen viel Wärme entsteht, oder zur Reaktion benötigt wird
25 (je nachdem ob die ablaufende Reaktion exotherm oder endo-
therm ist), weisen die Rohre kleine Durchmesser auf, um das
Reaktionsvolumen relativ zu der mit dem mantelseitig geführ-
ten Fluid in Verbindung stehenden Oberfläche zu verkleinern
und umgekehrt.

30

So zeigt z.B. Figur 1 eine Anordnung, die eine gute Anpassung
an ein erwünschtes Temperaturprofil liefert.

Für den in Figur 2 dargestellten Reaktor, der beispielsweise
35 für die Methanolsynthese verwendet wird, sind im folgenden
einige repräsentative Zahlenbeispiele zusammengestellt.

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- 1 Gaszusammensetzung beim Eintritt
in den Reaktor 17 % CO, 73 % H₂
Gasmenge pro Rohr 5 % CO₂, 5 % inert
Gaseintrittstemperatur V = 200 Nm³/h
245° C
- 5 Eintrittstemperatur des Kühlwassers 230° C
Durchmesser erster Rohrabschnitt 45 mm
Durchmesser zweiter Rohrabschnitt 52 mm
Durchmesser dritter Rohrabschnitt 45 mm
Länge erster Rohrabschnitt 2,5 m
- 10 Länge zweiter Rohrabschnitt 1,5 m
Länge dritter Rohrabschnitt 4,0 m
Raumgeschwindigkeit erster Abschnitt 40 000 bis 50 000 V/V_{Kat}
Raumgeschwindigkeit zweiter Abschnitt 55 000 bis 70 000 V/V_{Kat}
Raumgeschwindigkeit dritter Abschnitt 30 000 bis 40 000 V/V_{Kat}
- 15 mit V_{Kat} (in m³) Volumen des Katalysatormaterials.

Etwas allgemeiner ausgedrückt gilt für einen derartigen Reaktor für die Methanolsynthese, daß die Zahl der Rohrabschnitte zwischen 2 und 5 liegt und vorzugsweise 3 beträgt,
20 daß die Durchmesser D_i der Rohrabschnitte zwischen 20 und 100 mm betragen und daß für die Durchmesser D_i (in mm) und für die Gasmenge pro Rohr V (in Nm³/h) die Bedingung

$$D_i = (15 \dots 25) \cdot V^{0,12 \dots 0,22}$$

25 eingehalten werden sollte.

Figur 3 zeigt einen Reaktor, bei dem benachbarte Rohre 5 antiparallel bezüglich der Strömungsrichtung der reagierenden
30 Fluide angeordnet sind. Diese Anordnung ist immer dann sinnvoll, wenn dadurch neben Rohrabschnitten mit großen Durchmessern solche mit kleinen Durchmessern und umgekehrt zu liegen kommen. Auf diese Weise wird Platz eingespart und der Reaktor kann kleiner gebaut werden.

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- 1 Figur 4 zeigt einen Reaktor, bei dem sich der Durchmesser der Rohre 12 entlang des Strömungswegs der reagierenden Fluide kontinuierlich ändert.
- 5 In Figur 5 ist ein Ausschnitt eines Reaktors dargestellt, bei dem zwei Rohre 13, 14 zu einem Rohr 15 vereinigt sind. Diese Bauart stellt eine weitere Variationsmöglichkeit zur gleichzeitigen Optimierung von Reaktionsgleichgewicht und Bauvolumen dar.
- 10
- Figur 6 zeigt eine abgewandelte Bauform eines Reaktors. Hierbei ist der Katalysator nicht in Rohren, sondern im gesamten Innenraum des Mantels 2 angeordnet. Das Wärme zuführende oder abführende Fluid ist in Rohren 16 geführt, die innerhalb von Hemden 17 verlaufen. Pfeile 8, 9 geben die Strömungsrichtung der reagierenden Fluide, Pfeile 10, 11 die Strömungsrichtung des Wärme zuführenden oder abführenden Fluids an. Die Hemden 17 sind in das Katalysatormaterial eingelegt und begrenzen den Strömungsweg der reagierenden
- 20 Fluide seitlich. Sie verengen und erweitern den Strömungsquerschnitt je nach den gegebenen Anforderungen. Die Querschnittsänderungen entlang des Strömungswegs können kontinuierlich oder in Stufen erfolgen.

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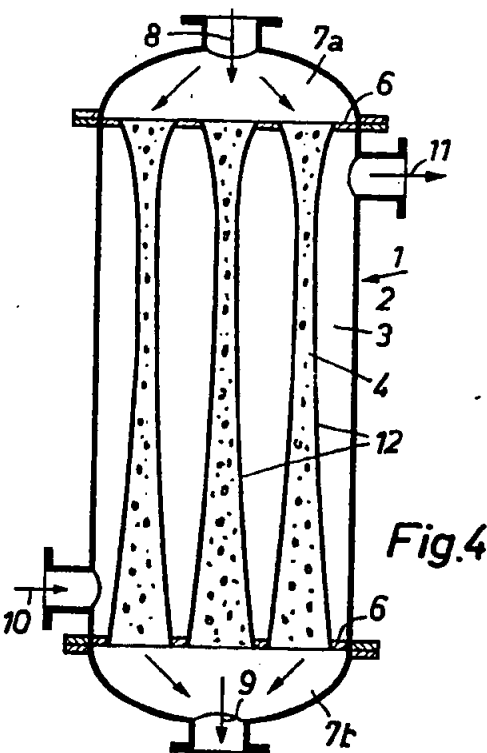
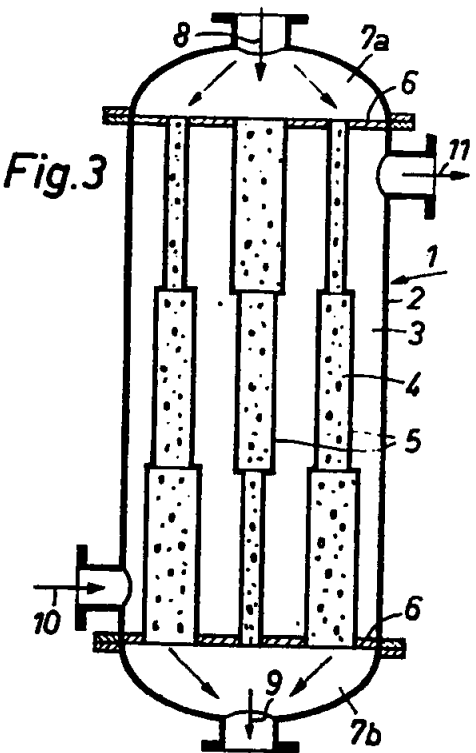
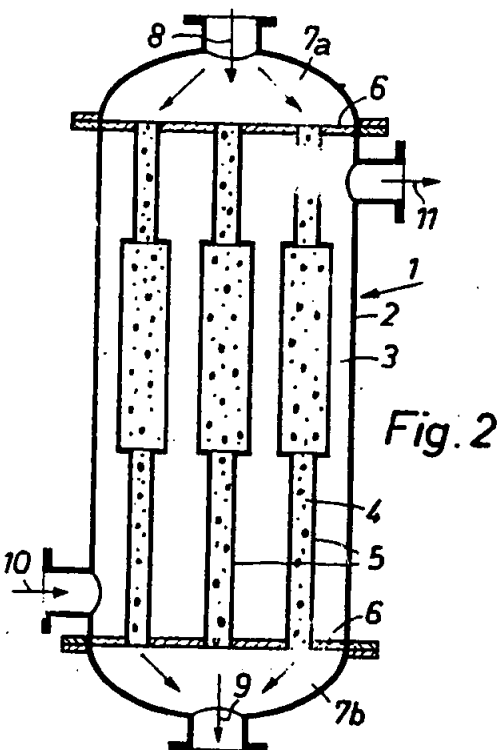
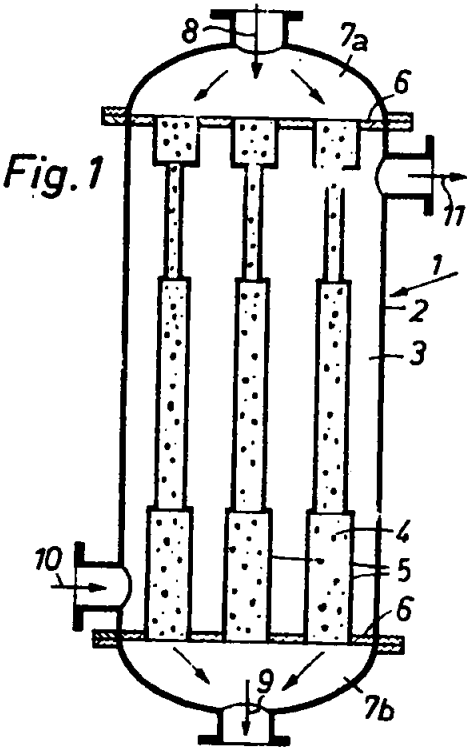
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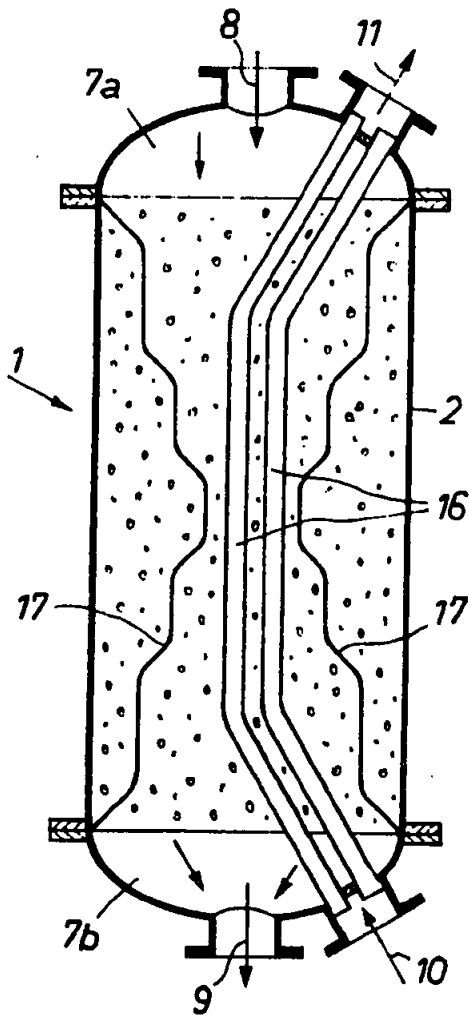


Fig. 6

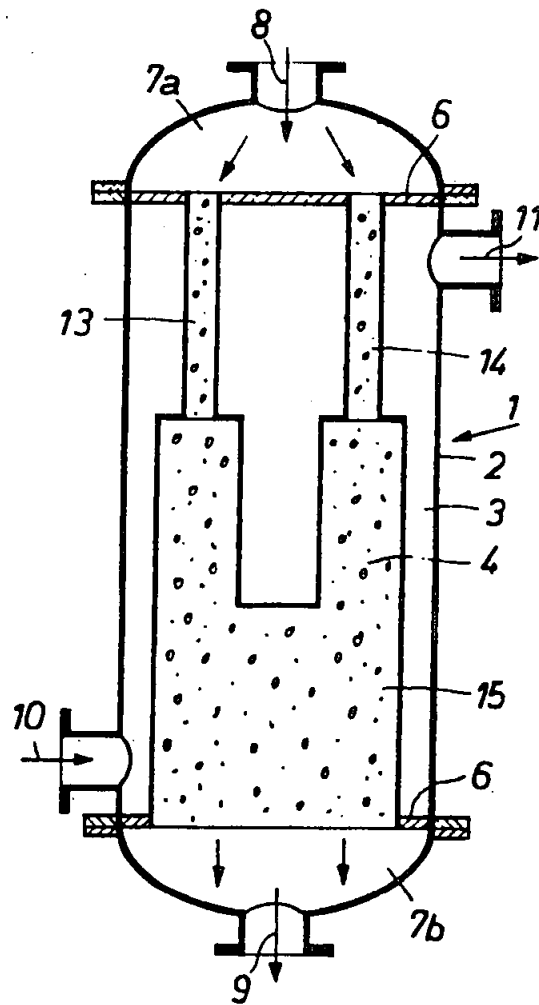


Fig. 5

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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: BP INTERNATIONAL LIMITED Global Patents & Technology Law (Central) Chertsey Road Sunbury on Thames Middlesex TW16 7LN GRANDE BRETAGNE		Received in PAT - 4 APR 2008		PCT NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (PCT Rule 71.1)	
			Date of mailing (day/month/year) 01.04.2008		
Applicant's or agent's file reference BPX 10309			IMPORTANT NOTIFICATION		
International application No. PCT/GB2006/004359		International filing date (day/month/year) 22.11.2006		Priority date (day/month/year) 19.12.2005	
Applicant BP EXPLORATION OPERATING COMPANY LIMITED					
- The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application. - A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices. - Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices. REMINDER The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301). Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned. For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide. The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.					
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465			Authorized Officer Smith, Kirstine Tel. +49 89 2399-6173		

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BPX 10309		FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/GB2006/004359		International filing date (day/month/year) 22.11.2006		Priority date (day/month/year) 19.12.2005
International Patent Classification (IPC) or national classification and IPC INV. C10G2/00				
Applicant BP EXPLORATION OPERATING COMPANY LIMITED				
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>5</u> sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. ☒ sent to the applicant and to the International Bureau a total of <u>1</u> sheets, as follows: ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. b. ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).				
4. This report contains indications relating to the following items: ☒ Box No. I Basis of the report ☐ Box No. II Priority ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability ☐ Box No. IV Lack of unity of invention ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement ☐ Box No. VI Certain documents cited ☐ Box No. VII Certain defects in the international application ☐ Box No. VIII Certain observations on the international application				
Date of submission of the demand 2007-07-16		Date of completion of this report 01.04.2008		
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Cagnoli, Michele Telephone No. +49 89 2399-7576 		

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/GB2006/004359

Box No. I Basis of the report

1. With regard to the **language**, this report is based on

- ☒ the international application in the language in which it was filed
- ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3(a) and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4(a))
 - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-9 as originally filed

Claims, Numbers

1-9 received on 16.07.2007 with letter of 13.07.2007

Drawings, Sheets

1/3-3/3 as originally filed

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

5. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 70.2 (e)).

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/GB2006/004359

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	<u>1-4,7-9</u>
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-9</u>
Industrial applicability (IA)	Yes: Claims	<u>1-9</u>
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Claims:

1. A process for the production of a condensed-phase product from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in
5 which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product, characterised in that the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different.
- 10 2. A process as claimed in claim 1, in which each region of the solid catalyst has different concentrations of the one or more catalyst components.
3. A process as claimed in claim 1 or claim 2, in which the two or more regions of the solid catalyst have a different cross-sectional area and volume.
4. A process as claimed in any one of claims 1 to 3, in which the solid catalyst
15 comprises particles such as spheres, beads, granules or extrudates.
5. A process as claimed in any one of claims 1 to 4, in which the solid catalyst comprises a support selected from one or more of silica, alumina, silica/alumina, titania, zirconia, ceria or zinc oxide.
6. A process as claimed in any one of claims 1 to 5, in which at least one catalyst
20 component is a metal active for Fischer-Tropsch synthesis selected from one or more of cobalt, iron, ruthenium, nickel, molybdenum, tungsten, and rhenium.
7. A process as claimed in any one of claims 1 to 6, in which syngas is a reactant, and the at least one condensed-phase product comprises a mixture of hydrocarbons that is liquid under the reaction conditions.
- 25 8. A process as claimed in any one of claims 1 to 7, in which the reactor comprises one or more inserts.
9. A process as claimed in claim 8, in which the one or more inserts contain the solid catalyst and the space between the inserts is surrounded by a heat-transfer medium.

Claims:

1. A process for the production of a condensed-phase product from one or more gas-phase reactants, which process comprises feeding one or more reactants into a reactor, in which reactor the one or more reactants react in the gas-phase in the presence of a solid catalyst having one or more catalyst components to produce at least one condensed-phase product, characterised in that the solid catalyst has two or more regions in which the contact time of the one or more gas-phase reactants with the one or more catalyst components is different.
2. A process as claimed in claim 1, in which each region of the solid catalyst has different concentrations of the one or more catalyst components.
3. A process as claimed in claim 1 or claim 2, in which the two or more regions of the solid catalyst have a different cross-sectional area and volume.
4. A process as claimed in any one of claims 1 to 3, in which the solid catalyst comprises particles such as spheres, beads, granules or extrudates.
5. A process as claimed in any one of claims 1 to 4, in which the solid catalyst comprises a support selected from one or more of silica, alumina, silica/alumina, titania, zirconia, ceria or zinc oxide.
6. A process as claimed in any one of claims 1 to 5, in which at least one catalyst component is a metal active for Fischer-Tropsch synthesis selected from one or more of cobalt, iron, ruthenium, nickel, molybdenum, tungsten, and rhenium.
7. A process as claimed in any one of claims 1 to 6, in which syngas is a reactant, and the at least one condensed-phase product comprises a mixture of hydrocarbons that is liquid under the reaction conditions.
8. A process as claimed in any one of claims 1 to 7, in which the reactor comprises one or more inserts.
9. A process as claimed in claim 8, in which the one or more inserts contain the solid catalyst and the space between the inserts is surrounded by a heat-transfer medium.
- ~~10. The use of a solid catalyst comprising one or more catalyst components and having two or more regions with different concentrations of the one or more catalyst components in a process for the production of at least one condensed phase product from one or more gas phase reactants to maintain independently the ratio of the at least one condensed phase~~

product to the one or more catalyst components in the two or more regions of the solid catalyst within a predetermined range of values.

11. Use of a solid catalyst as claimed in claim 10, in which the process is a process according to claim 2 or any one of claims 3 to 9 when dependent on claim 3.

12. The use of a solid catalyst comprising one or more catalyst components and having two or more regions of different cross-sectional area and volume in a process for the production of at least one condensed phase product from one or more gas phase reactants to maintain independently the ratio of the at least one condensed phase product to the one or more catalyst components in each region of the solid catalyst within a predetermined range of values.

13. Use of a solid catalyst as claimed in claim 12, in which the process is a process according to claim 3 or any one of claims 4 to 9 when dependent on claim 3.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 08-074999- -00000-0000

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Act. 411 PRESENTACION Folios: 123



Industria y Comercio
SUPERINTENDENCIA

**REQUISITOS MINIMOS PARA ADMISION A TRAMITE
PCT**

PATENTE DE INVENCION ☒

MODELO DE UTILIDAD ☐

- ◆ Indicación de que se solicita la concesión de 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 ☒

COMPLETA ☒

INCOMPLETA ☐

DISEÑO INDUSTRIAL ☐

- ◆ Indicación de que se solicita el registro de 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 ☐

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

COMPLETA ☐

INCOMPLETA ☐

SRP

Firma Responsable

Fecha Julio 21-07

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
RODRIGUEZ D^a ALEMAN DILIA MARIA

REFERENCIA	Radicación No.	8 74999
	Solicitud internacional	PCT/GB2006/004359
	Fecha inicio fase nacional	19/07/2008
	Trámite	11
	Evento	379
	Actuación	430
	Oficio No.	10875

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

1. La solicitud no contiene el poder debidamente otorgado, con el lleno de los requisitos exigidos por los artículos 63 y subsiguientes del Código de Procedimiento Civil. Adicionalmente, deberá presentar el documento que acredita la existencia y representación legal de la sociedad solicitante, cuando ésta fuere persona jurídica.

2. La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante, conforme a lo establecido por el artículo 26 literal k) de la Decisión 486 de la Comisión de la Comunidad Andina. Cuando se trate de documentos otorgados en el extranjero, estos deberán legalizarse de conformidad con lo dispuesto por los artículos 259 y 260 del Código de Procedimiento Civil. Cuando se trate de las declaraciones a que hace referencia la Regla 4.17 ii) del Tratado de Cooperación en Materia de Patentes PCT., el alcance de las tales declaraciones se determinará según indiquen claramente una cesión de derechos del inventor al solicitante o su causante, de conformidad con lo dispuesto en el numeral 5.2.15 del Capítulo Quinto, Título X de la Circular Única de Superintendencia de Industria y Comercio.

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

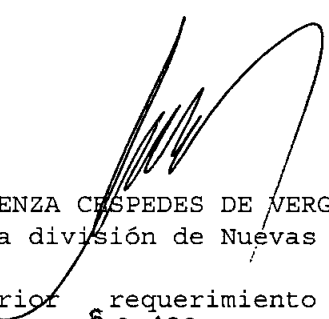
Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Unica No.10 de 2001.

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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Radicación No.: 8 74999



ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de
fecha 29 AGO. 2008
jfernand