PETITORIO

Industria y Comercio
SUPERINTENDENCIA

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL ~~18-0~~ 2005-09-18

1) SOLICITUD DE:

☒ Patente de invención ☐ Patente de Modelo de Utilidad

☐ Capitulo I. ☒ Capitulo II.

2) SOLICITANTE (71)	**Nombre: INNOVENE EUROPE LIMITED** **Dirección: Cherstsey Road Sunbury on Thames Middlesex TW 16 7 BP Reino Unido** **Nacionalidad o domicilio: Thames Middlesex TW, Reino Unido** **Lugar de constitución: Reino Unido**	**IDENTIFICACIÓN** **C.C.** ☐ **NIT:** ☐ **C.E.** ☐ **OTRO** ☐ **Cual** _____ **NÚMERO**_____
	Teléfono: Fax: **E. Mail:**	
3) REPRESENTANTE O APODERADO	Nombre: DILIA MARÍA RODRÍGUEZ D´ALEMAN Dirección: Carrera 11 N°. 86-53 Piso 6 Bogotá D.C. Teléfono: 6181088 Fax: 6350824 E. Mail: info@clarkemodet.com.co	**IDENTIFICACIÓN** **C.C.** ☒ **NIT:** ☐ **C.E.** ☐ **OTRO** ☐ **NÚMERO:** 41.654.882 **TP:** 20824 CSJ
4) INVENTOR (ES) (72)	**Nombre: 1. COLMAN, Dereck, Alan; 2. MATTHEWMAN, Michael, John, Alexander; 3. REID, Ian, Allan, Beattie; 4. WILLIAMS, Vaughan, Clifford; 5. WOODFIN, William, Terence** **Dirección: 1. 21 Knoll Road, Fleet, Hampshire GU51 4 PR, Gran Bretaña; 2. 25 Old Pasture Road, Frimley, Surrey GU 16 8SA, Gran Bretaña; 3. 12 Crowthorne Close, Southfields, London SW 18 5 RX, Gran Bretaña; 4. 88 Shaftesbury Crescent, Laleham, Staines, Middlesex TW 18 1 QW, Gran Bretaña; 5. Chalk Cottage, Chapel Street, North Waltham, Hampshire RG25 2BZ, Gran Bretaña.** **Nacionalidad o Domicilio: Todos los anteriores, Ingleses**	

5) PCT (86)
Solicitud Internacional No. PCT/GB2004/000488 Fecha: Febrero 6, 2004
Publicación Internacional No. WO 2004/074222 A1 Fecha: Septiembre 2, 2004

6)Título (54) REACTOR DE CRACKING AUTO-TERMICO

7) Clasificación Internacional: C07C 5/48, 11/02, B01J 19/26

8) PRIORIDAD SI ☒ NO ☐	**33) País de Origen**	**(32) Fecha**	**(31) Número de Solicitud**
	Gran Bretaña	**Feb. 18, 2003**	**0303723.1**
	Gran Bretaña	**Dic. 22, 2003**	**0329710.8**

9) Comprobante de pago N°. 05-57.169 Fecha: Agosto 1, 2005

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina

SUPERINDUSTRIA Y COMERCIO
Radicacion : 05078164 00000000 Folios: 112
Fecha (AMD): 2005-08-08 16:20:58
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 57,169
FECHA : AGOSTO 1 DE 2005

***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMBCONSIGNACION		BANCO POPULAR	050-00110-6	35422048	01/08/2005	3,365,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	443,000.00
		TOTAL : $	443,000.00

SON: CUATROCIENTOS CUARENTA Y TRES MIL PESOS

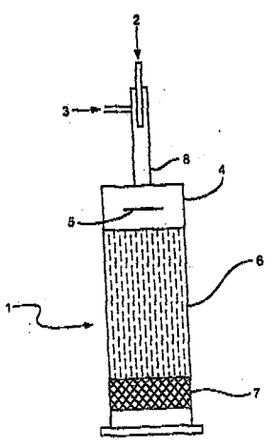
RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

10) ANEXOS

- [x] Comprobante de pago de la tasa de presentación de la solicitud
- [ ] Comprobante de pago por reivindicación de prioridad
- [ ] Documento que acredita la existencia y representación legal cuando el solicitante sea persona Jurídica
- [ ] Poderes, si fuera el caso
- [ ] Documento de cesión del inventor al solicitante o a su causante
- [ ] Declaraciones
- [x] Copia de la solicitud Internacional. (Resumen, descripción, reivindicación, Dibujos).
- [x] Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicación, Dibujos)
- [x] Copia del examen preliminar efectuado por la IPEA
- [ ] De ser el caso, copia del contrato de acceso
- [ ] De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas
- [ ] De ser el caso, certificado de depósito del material biológico
- [x] Arte final 12 x 12 y 6 x 6 cm
- [ ] De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionados parcial o totalmente con la invención de esta solicitud.
- [x] Otros:
  1. Solicitud PCT
  2. Notificación de la presentación de la prioridad
  3. PCT Capítulo II
  4. Notificación del cambio de dirección del solicitante
  5. Notificación del cambio de solicitante
  6. Países designados
  7. Notificación de la transmisión de la búsqueda
  8. Reporte de búsqueda

11) FIGURA CARACTERÍSTICA:



12) Solicitud concesión de la patente,

NOMBRE: DILIA RODRÍGUEZ D'ALEMAN

FIRMA:

C.C. 41.654.882 de Bogota **TP** 20824 CSJ

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina

p-687661

PATENT COOPERATION TREATY

AMP
AK

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING TRANSMITTAL OF COPY OF INTERNATIONAL APPLICATION AS PUBLISHED OR REPUBLISHED

- 6 SEP 2004

To:

HYMERS, Ronald, Robson
BP International Limited
Patents & Agreements
Chertsey Road
Sunbury on Thames
Middlesex TW16 7LN
ROYAUME-UNI

Date of mailing *(day/month/year)*
02 September 2004 (02.09.2004)

Applicant's or agent's file reference
9983

IMPORTANT NOTICE

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB2004/000488	06 February 2004 (06.02.2004)	18 February 2003 (18.02.2003)

Applicant
BP CHEMICALS LIMITED et al

The International Bureau transmits herewith the following documents:

Copy

☑ copy of the international application as published by the International Bureau on 02 September 2004 (02.09.2004) under No. WO 2004/074222

☐ copy of international application as republished by the International Bureau on under No. WO
For an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48) or (88) *(as the case may be)* on the front page of the attached document.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.+41 22 740 14 35	Authorized officer Nora Lindner Facsimile No.+41 22 338 89 65

Form PCT/IB/311 (January 2004)

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 September 2004 (02.09.2004)

PCT

(10) International Publication Number
WO 2004/074222 A1

(51) International Patent Classification[7]: C07C 5/48, 11/02, B01J 19/26

(21) International Application Number: PCT/GB2004/000488

(22) International Filing Date: 6 February 2004 (06.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0303723.1 18 February 2003 (18.02.2003) GB
0329710.8 22 December 2003 (22.12.2003) GB

(71) Applicant (*for all designated States except US*): **BP CHEMICALS LIMITED** [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **COLMAN, Derek, Alan** [GB/GB]; 21 Knoll Road, Fleet, Hampshire GU51 4PR (GB). **MATTHEWMAN, Michael, John, Alexander** [GB/GB]; 25 Old Pasture Road, Frimley, Surrey GU16 8SA (GB). **REID, Ian, Allan, Beattie** [GB/GB]; 12 Crowthorne Close, Southfields, London SW18 5RX (GB). **WILLIAMS, Vaughan, Clifford** [GB/GB]; 88 Shaftesbury Crescent, Laleham, Staines, Middlesex TW18 1QW (GB). **WOODFIN, William, Terence** [GB/GB]; Chalk Cottage, Chapel Street, North Waltham, Hampshire RG25 2BZ (GB).

(74) Agent: **HYMERS, Ronald, Robson**; BP International Limited, Patents & Agreements, Chertsey Road, Sunbury on Thames, Middlesex TW16 7LN (GB).

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

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

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.

(54) Title: AUTO THERMAL CRACKING REACTOR

(57) Abstract: The present invention provides a reactor design that enables an auto-thermal cracking process to be conducted at any suitable pressure wherein the gaseous reactants are preheated separately before mixing and then presented to the reaction zone in a uniformly distributed manner. In particular, the present invention relates to apparatus for reacting a first and second gaseous reactant to form a gaseous product wherein the apparatus comprises at least one first supply means for the first gaseous reactant, at least one second supply means for the second gaseous reactant, a resistance zone and a reaction zone, preferably comprising a catalyst, wherein the first supply means comprises a plurality of first outlets for delivery of the first gaseous reactant, and the second supply means comprises a plurality of second outlets for delivery of the second gaseous reactant, the resistance zone is porous, the reaction zone is positioned downstream of the resistance zone with respect to the flow of the first and second gaseous reactants and wherein the first supply means and the second supply means are arranged such that the first gas and the second gas are contacted in an essentially parallel manner and mixed prior to contacting the resistance zone. The present invention also provides a process for the production of a mono-olefin utilizing said apparatus.

WO 2004/074222 A1

AUTO THERMAL CRACKING REACTOR

The present invention relates to a reactor suitable for the production of olefins by auto-thermal cracking.

Auto-thermal cracking is a known process for the production of olefins. An example of such a process is described in EP-A- 0 332 289. In this process, a hydrocarbon and an oxygen-containing gas are contacted with a catalyst, which is capable of supporting combustion beyond the fuel rich limit of flammability. The hydrocarbon is partially combusted, and the heat produced is used to drive the dehydrogenation of the hydrocarbon feed into olefins.

In the auto-thermal cracking process the hydrocarbon and the oxygen-containing gas may be uniformly mixed and preheated prior to contacting the catalyst. However mixing and preheating the hydrocarbon and oxygen-containing gas becomes problematic if it is desired to carry out the process at elevated pressure due to flammability constraints. Thus, it becomes desirable to reduce the time between forming the mixture of hot gaseous reactants and contacting the mixture with the catalyst.

The present invention provides a reactor design that enables an auto-thermal cracking process to be conducted at any suitable pressure wherein the gaseous reactants are preheated separately before mixing and then presented to the reaction zone in a uniformly distributed manner.

Accordingly the present invention provides apparatus for reacting a first gaseous reactant with a second gaseous reactant to form a gaseous product,

wherein the apparatus comprises at least one first supply means for the first gaseous reactant, at least one second supply means for the second gaseous reactant, a resistance zone and a reaction zone, preferably comprising a catalyst, and

wherein the first supply means comprises a plurality of first outlets for delivery of the first gaseous reactant, and the second supply means comprises a plurality of second outlets for delivery of the second gaseous reactant,

the resistance zone is porous, is positioned downstream of the first and second supply means with respect to the flow of the first and second gaseous reactants and is in fluid communication with the first and second supply means,

the reaction zone is positioned downstream of the resistance zone with respect to the flow of the first and second gaseous reactants and is in fluid communication with the resistance zone, and

wherein the first supply means and the second supply means are arranged such that the first gas and the second gas are contacted in an essentially parallel manner and mixed prior to contacting the resistance zone.

Preferably, the first supply means comprises at least one first inlet for supplying a first gaseous reactant to at least one first manifold and a plurality of first outlets exiting the first manifold for delivery of the first gaseous reactant, and the second supply means comprises at least one second inlet for supplying a second gaseous reactant to at least one second manifold and a plurality of second outlets exiting the second manifold for delivery of the second gaseous reactant.

The apparatus suitably comprises at least 100, preferably at least 500, most preferably at least 1000, first and second outlets per metre squared of the transverse cross section of the reaction zone.

The first and second supply means are arranged such that the first and second gas are contacted in an essentially parallel manner. By "essentially parallel manner" is meant that the first and second gas, when they are brought into contact, are both flowing in essentially the same direction, such as axially, rather than flowing in opposite or tangential relative directions. Contacting the gases in an essentially parallel manner, rather than, for example, in a tangential manner, provides reduced turbulence in the region where the gases first contact (where mixing is not yet complete, and the compositions of gases present can vary significantly).

Turbulence can increase the residence time of mixed gas in the reactor, which increases the risk of flammability problems arising. In some cases, contacting the gases in a perpendicular manner can lead to regions of low flow, or even stagnant regions, containing flammable gas mixtures close to the contacting region. Contacting the gases

in an essentially parallel manner according to the present invention reduces the potential for regions of low flow mixed gas, reducing the potential for flammability problems.

In a first embodiment of the invention the contacting/mixing arrangement is provided by positioning one supply means within the other and providing at least a portion of the supply means located within the other with suitable openings such that one gaseous reactant can pass through the openings and contact the other gaseous reactant.

Preferably, the first embodiment of the invention provides apparatus wherein

the first supply means comprises at least one first inlet for supplying a first gaseous reactant to at least one first manifold and a plurality of injection tubes exiting said first manifold for delivery of the first gaseous reactant, and the second supply means comprises at least one second inlet for supplying a second gaseous reactant to at least one second manifold and a plurality of conduits exiting said second manifold for delivery of the second gaseous reactant,

wherein the second manifold is positioned downstream of the first manifold with respect to the flow of the first gaseous reactant,

the resistance zone is porous, is positioned downstream of the second manifold with respect to the flow of the first and second gaseous reactants and is in fluid communication with the conduits exiting the second manifold,

the reaction zone is positioned downstream of the resistance zone with respect to the flow of the first and second gaseous reactants and is in fluid communication with the resistance zone, and

wherein each conduit comprises an upstream end exiting the second manifold and a downstream end in fluid communication with the resistance zone and wherein the injection tubes exiting the first manifold are arranged such that they extend through the second manifold and project axially into the upstream end of the conduits.

Advantageously the apparatus of the first embodiment usually comprises a first cooling zone contacting the downstream end of the plurality of conduits exiting the second manifold arranged such that the downstream end of the plurality of conduits are cooled. This ensures that the gaseous reactants are prevented from reacting until they enter the reaction zone.

Furthermore the apparatus of the first embodiment usually comprises a product cooling zone downstream of the reaction zone such that the gaseous products can be

cooled upon exiting the reaction zone.

In the first embodiment of the invention, preferably, the first manifold is a first chamber and the second manifold is a second chamber and the injection tubes exiting the first chamber form a plurality of elongated passageways extending through the second chamber into the upstream end of the plurality of conduits exiting the second manifold.

The volumes of the first and second chambers are not especially critical. However, in a preferred embodiment, the volumes of the first and second chambers are adapted to be relatively small for safety reasons. Typically when the reactor diameter is 600 mm the volume of the first chamber is usually between 5-100 litres, preferably between 10-40 litres and more preferably between 15-25 litres e.g. 22 litres. The volume of these chambers will be proportional to the cross-sectional area of the reactor (i.e. diameter squared)

Typically when the reactor diameter is 600 mm the volume of the second chamber is usually between 20-200 litres, preferably between 30-100 litres and more preferably between 40-80 litres e.g. 50 litres.

The apparatus of the first embodiment usually comprises an equal number of injection tubes and conduits, each injection tube projecting into a corresponding conduit. Preferably the apparatus comprises at least 100, preferably at least 500, most preferably at least 1000 injection tubes per metre squared of the transverse cross section of the reaction zone.

So as to allow the injection tubes to project into the conduits the external diameter of the injection tubes where they project into the conduits is less than the internal diameter of the conduits. The exact external diameter is not critical to the invention, but usually the injection tubes have an external diameter of between 2.0 to 5.0mm, e.g. 4.0mm. The injection tubes have a length sufficient to extend through the second chamber (i.e. typically greater than 170 mm).

At the end of each of the plurality of injection tubes remote from the manifold, the first gaseous reactant can exit the tubes through a suitable opening, preferably a nozzle, and which has a diameter less than the external diameter of the injection tube, preferably between 0.5 to 3.0mm, such as between 1.0 to 2.0mm. The nozzle, when present, preferably has a diameter less than the internal diameter of the injection tube other than at the nozzle, hence providing a restriction that assists in obtaining even flow

rates from all injection tubes, without providing the pressure drop characteristics that would be obtained if the internal diameter of the injection tube was this size for a significant length of the injection tube.

Usually the conduits have an internal diameter of between 1 to 10mm, preferably between 2 to 8mm e.g. 7mm and a length of between 50 to 500mm, preferably between 100 to 300mm e.g. 210mm. The conduits may be arranged in a symmetrical configuration such as in a triangular or square configuration.

The ratio of the inner diameter of the conduits to the diameter of the opening, e.g. nozzle, of the injection tubes is suitably in the range 2:1 to 10:1, for example, in the range 3:1 to 5:1.

Where the injection tubes of the first supply means extend through the manifold of the second supply means, each injection tube may be provided with an outer tube, around the injection tube (which forms an inner tube within said outer tube). The outer tube provides thermal insulation from the second gaseous reactant when this is at a different temperature than the first gaseous reactant (which passes along the inside of the inner tube).

In a further preferred embodiment, suitable flow restrictors are also provided between the outer surface of the injection tubes and the inner surface of the conduits, at a location at or close to where the injection tubes enter the conduits at the upstream end of the conduits (i.e. close to the second manifold). These flow restrictors may be located on the injection tubes and/or on the conduits, and, by providing resistance, they assist in obtaining even flow rates of the second gaseous reactant into each conduit. These flow restrictors should be located remote from the exits of the first injection tubes such that the velocity of the second gaseous reactant, which has a maximum velocity in the conduit when passing through or past the flow restrictors, has reduced (from that maximum) when mixed with the first gaseous reactant. Preferably the pressure drop of the flow passing these restrictions is of similar order as the pressure drop of the first gaseous reactant through the nozzles or other restrictions at the end of the injection tubes (such as 1 bar and 0.5 bar respectively). This ensures that the proportions of the reactants entering the reaction zone remain similar when there are small fluctuations in pressures in the reaction zone or in the feeds. For optimum yields, the tolerance on the nozzle diameters and the flow restrictors for the second gaseous reactant should be such that the concentration of the gaseous mixture varies by no more than 5%.

Typically, between 5-40mm, preferably between 10-30mm, and most preferably between 15-25mm e.g. 20mm of the length of the injection tube projects axially into the conduit.

Wherein the apparatus of the first embodiment comprises a first cooling zone the first cooling zone is preferably provided by contacting a cooling fluid with the external surface area of the downstream end of the conduits. Typically, 10-20% of the external surface area of the conduit may be contacted with the cooling fluid.

In a second embodiment of the present invention, the contacting/mixing arrangement is provided by a first supply means comprising at least one first inlet for supplying a first gaseous reactant to at least one first manifold and a plurality of first injection tubes exiting said first manifold for delivery of the first gaseous reactant, and a second supply means comprising at least one second inlet for supplying a second gaseous reactant to at least one second manifold and a plurality of second injection tubes exiting said second manifold for delivery of the second gaseous reactant, wherein each injection tube has an exit at the end remote from the manifold and which has a cross-sectional opening of $1mm^2$ or less, and wherein the exits from the first and second injection tubes are in an intermixed configuration.

By intermixed, as used herein, is meant that the exits of the plurality of first injection tubes are dispersed amongst the exits of the plurality of second injection tubes and/or vice versa. Thus, for example, where there are more first injection tubes than second injection tubes, the exits of the second injection tubes will be dispersed amongst the exits of the first injection tubes and the optimal configuration for the exits for the second injection tubes will be such that each second injection tube will have the exit of at least one first injection tube as its nearest neighbour.

Suitably, there are at least 10000 first and second injection tubes in total per square metre. The use of said number of intermixed tubes provides rapid mixing at the outlets of said tubes.

For optimal delivery of the first and second gaseous reactants to the resistance zone, the exits from the injection tubes of the second embodiment should all be located in an essentially planar configuration.

The exits of the first injection tubes may be arranged in a symmetrical configuration, such as in a triangular, square, rectangular or hexagonal configuration and/or the exits of the second injection tubes may be arranged in a symmetrical

configuration, such as in a triangular, square, rectangular or hexagonal configuration.

In this second embodiment, the exits may be any suitable shape in cross-section, such as triangular, rectangular, square, hexagonal, D-shaped, oval or circular.

Mixing of the gases becomes more rapid as the number of tubes is increased and the cross-sectional opening of the exits of the tubes is decreased.

Thus in a preferred aspect of the second embodiment of the present invention, each injection tube has an exit at the end remote from the manifold which has a cross-sectional opening of 0.5mm^2 or less. More preferably the exits have a cross-sectional opening of 0.2 mm^2 or less, such as 0.1mm^2 or less. Suitably, the exits have a cross-sectional opening of 0.004mm^2 or more.

The exits for the injection tubes for one reactant may vary in size and shape but are preferably the same. Similarly, the exits for the second gaseous reactant may be different to, or may be the same size and shape as the exits for the first gaseous reactant.

Most preferably, the exits are D-shaped, such as semi-circular, with a cross-sectional opening of between 0.01mm^2 and 0.05mm^2.

The apparatus of this second embodiment may comprise an equal number of first and second injection tubes for delivery of said first and second gaseous reactants respectively. Alternatively, the relative number of injection tubes for delivery of each gaseous reactant may be different, for example, the relative number of injection tubes for delivery of each gaseous reactant may be in proportion to the relative amount of each gaseous reactant to be delivered. However, the relationship between the numbers of tubes is not critical to the invention, and, for example, the velocities of the first and second gaseous reactants exiting the respective injection tubes may be, and preferably are, different. In particular, the use of differing flow rates for each of the first and second gaseous reactants allows different ratios of said first and second gaseous reactants to be achieved utilizing a fixed number of injection tubes for each reactant.

Preferably, one of the reactants, more preferably the reactant with lowest molecular mass, exits one set of the injection tubes with a higher velocity than the other reactant exits the other injection tubes. For example, the size and number of the injection tubes for one reactant may be such that the ratio of the exit velocities is at least 10:1 for example the exit velocity of one reactant is at least 100 m/s while the number and size of the injection tubes for the other reactant may be such that the exit velocity is less than 10 m/s. The mean velocity of the combined flows having exited the injection

tubes may be of the order of 3 m/s.

As the cross-sectional opening of the exit tubes decreases, so the number of first and second injection tubes per unit area of the transverse cross-section of the reaction zone can increase. Thus, the apparatus of the second embodiment may comprise at least 100000, for example at least 1000000, such as 4000000 injection tubes (total of first and second injection tubes) per square metre of the transverse cross section of the reaction zone.

Similarly, the distance between one exit and its nearest neighbour will also decrease as the cross-sectional opening of the exit tubes decreases and the number of first and second injection tubes increases. Thus, the distance between one exit and its nearest neighbour in this second embodiment may be less than 2000 microns, such as less than 1000 microns and preferably in the range 100 to 500 microns. The distance between neighbouring tubes is preferably of similar dimension to the exits themselves, such as in the range from one half to twice the maximum dimension across the opening of the exit.

By using the intermixed arrangement of the first and second injection tubes with relatively small exit holes according to the second embodiment of the present invention, for delivery of the first and second gaseous reactants respectively, rapid mixing of the first and second gaseous reactants is achieved. Typically, by using an intermixed arrangement of the first and second injection tubes with exits with a cross-sectional opening of 0.5mm^2 or less, adequate mixing may be achieved in a distance of less than 5mm from the exits of the injection tubes, allowing the gases to be mixed and contacted with the resistance zone in a short space, and, hence, within a short period of time.

The apparatus of the second embodiment usually comprises a product cooling zone downstream of the reaction zone, such that the gaseous products can be cooled upon exiting the reaction zone.

Preferably, in the second embodiment of the invention, the first manifold comprises a first chamber and the second manifold comprises a second chamber, with the respective first and second gaseous components exiting therefrom and into a plurality of first and second injection tubes. The injection tubes with exits with a cross-sectional opening of 1 mm^2 or less are preferably formed as passageways in a diffusion bonded block. Diffusion bonded blocks formed by diffusion bonding of layers of etched metal structures are known for heat exchange uses, and are described generally, for

example, in "Industrial Microchannel Devices – Where are we Today ?"; Pua, L.M. and Rumbold, S.O.; First International Conferences on Microchannels and Minichannels, Rochester, NY, April 2003.

The use of diffusion bonding techniques in the present invention allows a plurality of passageways to be formed connecting the first and second chambers respectively to a plurality of first and second exits, the exits being in an intermixed configuration, as required for forming the injection tubes of the second embodiment of the present invention.

As with the first embodiment, the volume of the first and second chambers are not especially critical, but, preferably, the volume of the first and second chambers in the second embodiment are adapted to be relatively small for safety reasons.

After mixing according to the process of the present invention, either by the apparatus of the first or second embodiment, or otherwise, the mixed first and second gaseous reactants are contacted with a resistance zone positioned downstream of first and second supply means.

The resistance zone is porous. The permeability of the porous resistance zone ensures dispersion of the fluid reactants as they pass through the zone. The fluids move through a network of channels laterally as well as axially (axially being the general direction of flow of the reactants through the resistance zone), and leave the resistance zone substantially uniformly distributed over the cross-sectional area of the resistance zone.

Preferably, the resistance zone is as permeable laterally as it is axially. More preferably the resistance zone has a permeability which is substantially the same in any direction, such as having a permeability in any direction which is from 0.2 to 5 times the permeability in any other direction.

Methods are known for determining the permeability of porous media. The pressure gradient or pressure drop per unit length through the resistance zone may be defined using the inertial resistance coefficient where the pressure gradient equals the product of the inertial resistance coefficient and the dynamic pressure. The dynamic pressure is half the product of the fluid density and the square of the superficial velocity and has units of pressure. The inertial resistance coefficient has units of reciprocal length. The resistance zone usually has an average inertial resistance coefficient (i.e. averaged over all directions) of between 500-10000 /metre (/m), preferably between

2000-4000 /m and advantageously between 2500-3500 /m e.g. 3250 /m.

The resistance zone may be formed of a porous metal structure, but preferably the porous material is a non metal e.g. a ceramic material. Suitable ceramic materials include lithium aluminium silicate (LAS), alumina (α-Al_2O_3), yttria stabilised zirconia, alumina titanate, niascon, and calcium zirconyl phosphate. A preferred porous material is gamma alumina.

The distance of the resistance zone from the ends of the conduits in the first embodiment and the exit of the tubes in the second embodiment is preferably less than 20 mm, more preferably between 1 and 10 mm, more preferably between 1.5 and 5 mm, such as 2 mm.

Wherein the reaction zone comprises a supported catalyst preferably the porous material in the resistance zone may be the same as the porous material used as the catalyst support. The porous material may be in the form of spheres, other granular shapes or ceramic foams. The reaction zone may comprise a supported catalyst in the form of a monolith providing a continuous multichannel structure.

For the porous material in the resistance zone, advantageously at least 70%, preferably at least 80% and advantageously at least 90% of the pores have a pore width of less than 5.0mm e.g. usually between 0.1-3.0mm, preferably between 0.2-2.0mm and most preferably between 0.5-1.5mm.

Typically the resistance zone has between 10-60 pores per square inch, preferably between 20-50 pores per square inch and most preferably between 30-45 pores per square inch.

Usually the depth of the resistance zone is between 5-100mm but is preferably 10-50mm.

Usually the reaction zone has a depth of between 10-200mm but is preferably 20-100mm e.g. 60mm. Preferably the reaction zone comprises a catalyst.

(The depth of the resistance zone and the reaction zone are measured in the direction of flow of the reactant gases. In general, the preferred depths are defined by the flow rate of the reactant gases, since this determines the contact time, and, as with other dimensions measured in the direction of gas flow, are, for most practical purposes, independent of reactor cross-section.)

When a catalyst is employed suitably the catalyst is a supported platinum group metal. Preferably, the metal is either platinum or palladium, or a mixture thereof.

Although a wide range of support materials are available, it is preferred to use alumina as the support. The support material may be in the form of spheres, other granular shapes or ceramic foams. Preferably, the support is a monolith which is a continuous multichannel ceramic structure, frequently of a honeycomb appearance. A preferred support for the catalytically active metals is a gamma alumina. The support is loaded with a mixture of platinum and palladium by conventional methods well known to those skilled in the art. The resulting compound is then heat treated to 1200°C before use. catalyst promoters may also be loaded onto the support. Suitable promoters include copper and tin.

The catalyst is usually held in place in the reactor in a suitable holder, such as a catalyst basket. Preferably, to prevent gas by-passing the catalyst between the catalyst and the holder, any space between the catalyst and the holder is filled with a suitable sealing material. Suitable sealing materials include man made mineral wools e.g. ceramic wool, which can be wrapped around the edges of the catalyst in the holder. In addition the catalyst may be coated around the edge with a material similar to the main catalyst support material, such as alumina, to aid this sealing.

The apparatus may comprise a product cooling zone downstream of the reaction zone, such that the gaseous products can be cooled upon exiting the reaction zone. The product cooling zone may be provided by one or more injection nozzles that are capable of injecting a condensate into the product stream exiting the reaction zone.

Preferably the first and second manifolds, the injection tubes, the conduits (if present), the housing for the resistance zone and the reaction zone are metallic e.g. steel. Where pure oxygen is employed as a gaseous reactant it may be necessary to make or coat some or all of any part of the apparatus that may contact the oxygen from/with an alloy that resists reaction with oxygen. Reaction with oxygen is more likely when the temperature of the oxygen is high and/or the oxygen is at high velocity. Suitable alloys include monel.

Immediately downstream of the reaction zone, where the temperature of the products from the reaction is high, the preferred material of construction is a high nickel alloy, such as Inconel, Incaloy, Hastelloy or Paralloy. The metal may be formed into shape by one or more of the following techniques: static casting, rotational casting, forging, machining and welding.

The apparatus may comprise a suitable thermal sleeve to reduce thermal stresses

on the apparatus immediately downstream of the reaction zone. Thermal stresses can occur where relatively rapid changes in temperature, either a rapid increase or decrease, occur inside an apparatus, for example, at start-up or shut-down. The inner surface of the wall of the apparatus heats or cools rapidly, but the outer surface heats or cools more slowly providing stress across the wall (the wall being relatively thick, for example, to cope with the pressure differential between the inside of and the outside of the apparatus). The use of a sleeve of thin material, which may be of a similar material to the wall of the apparatus, as a thermal sleeve inside the apparatus reduces the rate of temperature change that impacts the inner surface of the wall, and hence reduces the thermal stress.

The apparatus is advantageously employed to partially oxidize a gaseous feedstock. Preferably the first gaseous reactant is an oxygen containing gas and the second gaseous reactant is a gaseous paraffinic hydrocarbon.

The present invention also provides a process for the production of a mono-olefin utilizing the apparatus previously described.

Thus, utilizing the apparatus of the first embodiment, the invention provides a process for the production of a mono-olefin said process comprising

passing an oxygen containing gas into a first manifold and injecting the oxygen-containing gas via a plurality of injection tubes into a plurality of conduits,

passing gaseous paraffinic hydrocarbon via a second manifold into the plurality of conduits wherein the gaseous paraffinic hydrocarbon is contacted in an essentially parallel manner and mixed with the oxygen-containing gas,

passing the gaseous mixture to a reaction zone via a porous resistance zone, and

partially combusting in the reaction zone the gaseous mixture, preferably in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability, to produce the mono-olefin.

Utilizing the apparatus of the second embodiment, the invention provides a process for the production of a mono-olefin said process comprising

passing an oxygen containing gas from at least one first inlet via at least one first manifold to a plurality of first injection tubes and passing a gaseous paraffinic hydrocarbon from at least one second inlet via at least one second manifold to a plurality of second injection tubes, wherein each injection tube has an exit at the end remote from the manifold and which has a cross-sectional opening of 1mm^2 or less, and

wherein the exits from the first and second injection tubes are co-located in an intermixed configuration,

passing the gaseous mixture to a reaction zone via a porous resistance zone, and

partially combusting in the reaction zone the gaseous mixture, preferably in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability, to produce the mono-olefin.

Preferred processes for the production of a mono-olefin utilize apparatus with the preferred features as previously described. Thus, for example, the preferred apparatus for a process utilizing the apparatus of the second embodiment is such that each injection tube has an exit at the end remote from the manifold which has a cross-sectional opening of 0.5mm^2 or less. More preferably the exits have a cross-sectional opening of 0.2 mm^2 or less, such as 0.1mm^2 or less.

In the process for the production of a mono-olefin from a feedstock comprising a gaseous paraffinic hydrocarbon, the paraffinic hydrocarbon may suitably be ethane, propane or butane. The paraffinic hydrocarbon may be substantially pure or may be in admixture with other hydrocarbons and optionally other materials, for example methane, nitrogen, carbon monoxide, carbon dioxide, steam or hydrogen. A paraffinic hydrocarbon-containing fraction such as naphtha, gas oil, vacuum gas oil, or mixtures thereof, may be employed. A suitable feedstock is a mixture of gaseous paraffinic hydrocarbons, principally comprising ethane, resulting from the separation of methane from natural gas. A preferred feedstock is a paraffinic hydrocarbon principally comprising ethane which provides a product principally comprising ethylene as the mono-olefin.

As the oxygen-containing gas there may suitably be used either oxygen or air. It is preferred to use oxygen, optionally diluted with an inert gas, for example nitrogen. The ratio of the gaseous paraffinic hydrocarbon to the oxygen-containing gas mixture is usually from 5 to 20 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas for complete combustion to carbon dioxide and water. The preferred composition is from 5 to 10 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas.

Although the apparatus can be used at any pressure e.g. between 0-100barg it is particularly useful at elevated pressure. The pressure at the first and second inlets is preferably between 10-50barg, most preferably between 20-40barg, and advantageously between 25-35barg e.g. 30barg.

The oxygen containing gas may be fed at ambient temperature, but is usually preheated to 50 to 150°C, preferably 80-120°C e.g. 100°C. The oxygen containing gas is injected into the conduits or from the exits of the plurality of injection tubes at a velocity to prevent the possibility of a flame stabilizing on the exits of the injection tubes. Especially in the first embodiment of the present invention, the injection tubes may end in a suitable nozzle to increase the exit velocity The exit velocity is typically greater than 30m/s, preferably greater than 50m/s, and advantageously greater than 70m/s.

The gaseous paraffinic hydrocarbon is usually preheated to 100 to 400°C, preferably 150-350°C e.g. 300°C and passed into the conduits or from the plurality of second injection tubes wherein it is intimately mixed with the oxygen containing gas. The gaseous paraffinic hydrocarbon enters the conduits or exits the plurality of second injection tubes at a velocity typically greater than 5m/s, preferably greater than 15m/s, and advantageously greater than 20m/s.

In the first embodiment, the velocity of the oxygen containing gas exiting the injection tubes and the velocity of the gaseous paraffinic hydrocarbon passing into the conduits preferably has the ratio of at least 1.5:1, preferably at least 3:1 and most preferably less than 6:1, such as 4:1. This ratio ensures rapid mixing.

In the second embodiment, the ratio of the velocity of the oxygen containing gas exiting the first injection tubes and the velocity of the gaseous paraffinic hydrocarbon exiting the second injection tubes will depend on the relative ratios of numbers of first and second injection tubes, their relative sizes and the desired oxygen to paraffinic hydrocarbon ratio, but preferably the ratio is at least 0.1:1, preferably at least 1:1 and most preferably at least 5:1. Typically, the exit velocity of the oxygen containing gas is at least 50m/s, especially at least 100 m/s. For example, the size and number of the injection tubes for the oxygen containing gas may be such that the exit velocity is at least 100 m/s while the number and size of the injection tubes for the gaseous paraffinic hydrocarbon may be such that the exit velocity is less than 10 m/s, and the mean velocity of the combined flows having exited the injection tubes may be of the order of 3 m/s.

The temperature of the gaseous mixture is usually between 100 to 400°C, preferably 100 to 300°C e.g. 200°C. In addition to passing the gaseous paraffinic hydrocarbon to the conduits or second injection tubes, other gases may also be passed to

the conduits or second injection tubes e.g. hydrogen, carbon monoxide and/or carbon dioxide.

In the first embodiment, the gas mixture may be cooled by the first cooling zone wherein a coolant, such as water, is passed around the external surface area of the downstream end of the conduits. The cooling of the downstream end of the conduits prevents local heating of the conduit which eliminates the tendency for any "flame creep back" in the event of a stable flame being formed at the exit of the conduits.

The temperature of the coolant is typically between 20-200°C, and preferably between 80-120°C e.g. 100°C. The coolant flow rate is manipulated such that the coolant temperature increase is less than 100°C, preferably less than 50°C, and most preferably less than 30°C.

The first cooling zone reduces the temperature of the gaseous mixture by at least 10°C, preferably by at least 20°C, and most preferably by at least 30°C.

In both embodiments the gaseous mixture is usually passed to the resistance zone at a mean cross-section velocity between 1.0-10.0m/s, preferably between 2.0-6.0m/s and most preferably between 2.5–3.5m/s.

The gaseous mixture is usually passed to the reaction zone at a velocity between 1.0-10.0m/s, preferably between 2.0-6.0m/s and most preferably between 2.5–3.5m/s.

The pressure drop through the resistance zone is typically between 0.01-0.2bar, and preferably between 0.05- 0.1bar e.g. 0.08bar.

The temperature in the reaction zone is usually greater than 500°C, for example greater than 650°C, typically greater than 750°C, and preferably greater than 800°C. The upper temperature limit may suitably be up to 1200°C, for example up to 1100°C, preferably up to 1000°C.

The products exit the reaction zone at a temperature greater than 800°C e.g. greater than 900°C and at a pressure usually between 10-50barg, most preferably between 20-40barg, and advantageously between 25-35barg e.g. 30barg.

Preferably the products are rapidly cooled in a product cooling zone. This ensures a high olefinic yield because the product cooling step slows down the rate of reaction in the gaseous product stream thus preventing further reactions taking place.

Advantageously the gaseous product stream is cooled by injecting a condensate into the gaseous product stream, preferably at multiple points, such that the vaporisation

of the condensate cools the gaseous product stream.

The condensate may be a gas or a liquid. When the condensate is gas it is preferably an inert gas. Preferably the condensate is a liquid e.g. water.

Injecting the condensate at high pressure and high temperature ensures that a large proportion of the condensate instantaneously vaporizes at the reactor pressure and therefore provides a very rapid temperature drop in the gaseous product stream. Consequently the condensate, such as water, is usually injected at a pressure higher than the pressure of the gaseous product stream, such as 100 barg and is usually injected at a temperature of between 100-400°C and preferably between 200-350°C e.g. 300°C.

Preferably the temperature of the gaseous product stream is reduced to 800°C preferably to 600°C within 60mS preferably 40mS and advantageously 20mS from exiting the reaction zone.

The present invention will now be illustrated with the aid of figures, wherein:
Figure 1 represents an apparatus according to the first embodiment of the present invention,
Figure 2a represents schematically a section of an intermixed configuration of first and second injection tubes for an apparatus according to the second embodiment of the present invention, and
Figure 2b represents schematically a side view of an apparatus according to the second embodiment of the present invention.

In Figure 1 an oxygen containing gas is passed via a first inlet (1) into a first chamber (2) and then into a plurality of injection tubes (3). A gaseous paraffinic hydrocarbon is passed via second inlet (4) into a second chamber (5) and then into the plurality of conduits (6). The oxygen containing gas is injected via injection tubes (3) into the conduits (6) wherein the gaseous paraffinic hydrocarbon is mixed with the oxygen-containing gas.

The gaseous mixture is then passed to the resistance zone (7) wherein the momentum is taken from the gaseous mixture such that it is passed in a uniform manner to the reaction zone (8) which comprises a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability. The gaseous reactants are converted in the reaction zone (8) to provide a product stream comprising olefins.

Prior to passing the gaseous mixture to the resistance zone (7) a first cooling zone (9) contacting the downstream end of the plurality of conduits is used to reduce the

temperature of the gaseous mixture.

Finally the product stream comprising olefins is passed to a product cooling zone (10) to reduce the temperature of the product stream prior to recovery.

In Figure 2a, a series of first injection tubes (23), shown by open circles, are arranged in a triangular configuration. The exits of the first injection tubes are dispersed amongst the exits of a plurality of second injection tubes (26), which are arranged in a rectangular configuration. In the overall arrangement (the Figure shows just a section) there are approximately twice as many second injection tubes as first injection tubes in this configuration.

In Figure 2b an oxygen containing gas is passed into a first chamber (22) and then into the plurality of first injection tubes (23). A gaseous paraffinic hydrocarbon is passed into a second chamber (25) and then into the plurality of second injection tubes (26). The oxygen containing gas and gaseous paraffinic hydrocarbon exit the respective injection tubes and rapidly mix.

The gaseous mixture is then passed to the resistance zone (27) wherein the velocity of the gaseous mixture is smoothed (momentum is taken from the gaseous mixture) such that it is passed in a uniform manner to a reaction zone (28) which comprises a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability. The gaseous reactants are converted in the reaction zone (28) to provide a product stream comprising olefins.

Finally the product stream comprising olefins is passed to a product cooling zone (not shown) to reduce the temperature of the product stream prior to recovery.

Claims:

1. Apparatus for reacting a first gaseous reactant with a second gaseous reactant to form a gaseous product, wherein the apparatus comprises at least one first supply means for the first gaseous reactant, at least one second supply means for the second gaseous reactant, a resistance zone and a reaction zone, preferably comprising a catalyst,

wherein the first supply means comprises a plurality of first outlets for delivery of the first gaseous reactant, and the second supply means comprises a plurality of second outlets for delivery of the second gaseous reactant,

wherein the resistance zone is porous, is positioned downstream of the first and second supply means with respect to the flow of the first and second gaseous reactants and is in fluid communication with the first and second supply means,

the reaction zone is positioned downstream of the resistance zone with respect to the flow of the first and second gaseous reactants and is fluid communication with the resistance zone, and

wherein the first supply means and the second supply means are arranged such that the first gas and the second gas are contacted in an essentially parallel manner and mixed prior to contacting the resistance zone.

2. The apparatus according to claim 1, which comprises at least 100, preferably at least 500, most preferably at least 1000, first and second outlets per metre squared of the transverse cross section of the reaction zone.

3. The apparatus according to claim 1 or claim 2, wherein the first supply means comprises at least one first inlet for supplying a first gaseous reactant to at least one first manifold and a plurality of injection tubes exiting said first manifold for delivery of the first gaseous reactant, and the second supply means comprises at least one second inlet

for supplying a second gaseous reactant to at least one second manifold and a plurality of conduits exiting said second manifold for delivery of the second gaseous reactant,

wherein the second manifold is positioned downstream of the first manifold with respect to the flow of the first gaseous reactant, and

the resistance zone is porous, is positioned downstream of the second manifold with respect to the flow of the first and second gaseous reactants and is in fluid communication with the conduits exiting the second manifold,

the reaction zone is positioned downstream of the resistance zone with respect to the flow of the first and second gaseous reactants and is in fluid communication with the resistance zone, and

wherein each conduit comprises an upstream end exiting the second manifold and a downstream end in fluid communication with the resistance zone and wherein the injection tubes exiting the first manifold are arranged such that they extend through the second manifold and project axially into the upstream end of the conduits.

4. The apparatus according to claim 3, which also comprises a first cooling zone contacting the downstream end of the plurality of conduits exiting the second manifold arranged such that the downstream end of the plurality of conduits are cooled.

5. The apparatus according to claim 3 or claim 4, wherein the first manifold is a first chamber and the second manifold is a second chamber and the injection tubes exiting the first chamber form a plurality of elongated passageways extending through the second chamber into the upstream end of the plurality of conduits exiting the second manifold.

6. The apparatus according to any one of claims 3 to 5, wherein the injection tubes end in a nozzle which provides a restriction at the opening, and which preferably has an internal diameter in the range between 0.5 to 3.0mm, such as between 1.0 to 2.0mm.

7. The apparatus according to any one of claims 3 to 6, wherein flow restrictors are provided between the outer surface of the injection tubes and the inner surface of the conduits, at a location at or close to where the injection tubes enter the conduits at the upstream end of the conduits.

8. The apparatus according to claim 1 or claim 2, wherein the first supply means comprises at least one first inlet for supplying a first gaseous reactant to at least one first manifold and a plurality of first injection tubes exiting said first manifold for delivery of the first gaseous reactant, and the second supply means comprising at least one second

inlet for supplying a second gaseous reactant to at least one second manifold and a plurality of second injection tubes exiting said second manifold for delivery of the second gaseous reactant,

wherein each injection tube has an exit at the end remote from the manifold and which has a cross-sectional opening of 1mm^2 or less, and

wherein the exits from the first and second injection tubes are co-located in an intermixed configuration.

9. The apparatus according to claim 8, wherein there are at least 10000 first and second injection tubes in total per square metre.

10. The apparatus according to claim 8 or claim 9, wherein the exits from the injection tubes are all located in an essentially planar configuration.

11. The apparatus according to any one of claims 8 to 10, wherein each injection tube has an exit at the end remote from the manifold which has a cross-sectional opening of 0.5mm^2 or less, more preferably 0.2 mm^2 or less, such as 0.1mm^2 or less.

12. The apparatus according to any one of claims 8 to 11, wherein the injection tubes are formed as passageways in a diffusion bonded block.

13. The apparatus according to any one of the preceding claims which comprises a product cooling zone downstream of the reaction zone, such that the gaseous products can be cooled upon exiting the reaction zone.

14. The apparatus according to any one of the preceding claims, wherein the resistance zone has an average inertial pressure gradient coefficient of between 1000-5000/m, preferably between 2000-4000/m, such as between 2500-3500/m.

15. A process for the production of a mono-olefin utilizing the apparatus as claimed in claim 1 or claim 2, which process comprises

passing an oxygen containing gas into a first supply means and passing gaseous paraffinic hydrocarbon into a second supply means, such that the gaseous paraffinic hydrocarbon is contacted in an essentially parallel manner and mixed with the oxygen-containing gas

passing the gaseous mixture to a reaction zone via a porous resistance zone and

partially combusting in the reaction zone the gaseous mixture, preferably in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability, to produce the mono-olefin.

16. A process for the production of a mono-olefin utilizing the apparatus as claimed in

any one of claims 3 to 7, which process comprises

passing an oxygen containing gas into a first manifold and injecting the oxygen-containing gas via a plurality of injection tubes into a plurality of conduits,

passing gaseous paraffinic hydrocarbon via a second manifold into the plurality of conduits wherein the gaseous paraffinic hydrocarbon is contacted in an essentially parallel manner and mixed with the oxygen-containing gas

passing the gaseous mixture to a reaction zone via a porous resistance zone and

partially combusting in the reaction zone the gaseous mixture, preferably in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability, to produce the mono-olefin.

17. A process for the production of a mono-olefin utilizing the apparatus as claimed in any one of claims 8 to 12, which process comprises

passing an oxygen containing gas from at least one first inlet via at least one first manifold to a plurality of first injection tubes and passing a gaseous paraffinic hydrocarbon from at least one second inlet via at least one second manifold to a plurality of second injection tubes, wherein each injection tube has an exit at the end remote from the manifold and which has a cross-sectional opening of $1mm^2$ or less, and wherein the exits from the first and second injection tubes are co-located in an intermixed configuration,

passing the gaseous mixture to a reaction zone via a porous resistance zone and

partially combusting in the reaction zone the gaseous mixture, preferably in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability, to produce the mono-olefin.

18. A process as claimed in any one of claims 15 to 17, wherein the gaseous paraffinic hydrocarbon is ethane, propane or butane, optionally in admixture with other hydrocarbons and optionally with other materials, for example methane, nitrogen, carbon monoxide, carbon dioxide, steam or hydrogen.

19. A process as claimed in any one of claims 15 to 18, wherein the ratio of the gaseous paraffinic hydrocarbon to the oxygen-containing gas mixture is from 5 to 20 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas for complete combustion to carbon dioxide and water, preferably from 5 to 10 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas.

20. A process as claimed in any one of claims 15 to 19, wherein the pressure at the

first and second inlets is preferably between 10-50barg, most preferably between 20-40barg, and advantageously between 25-35barg.

21. A process as claimed in any one of claims 15 to 20, wherein the gaseous product stream from the reaction zone is rapidly cooled in a product cooling zone, preferably by injecting a condensate into the gaseous product stream at multiple points such that the vaporisation of the condensate cools the gaseous product stream.

Fig.1

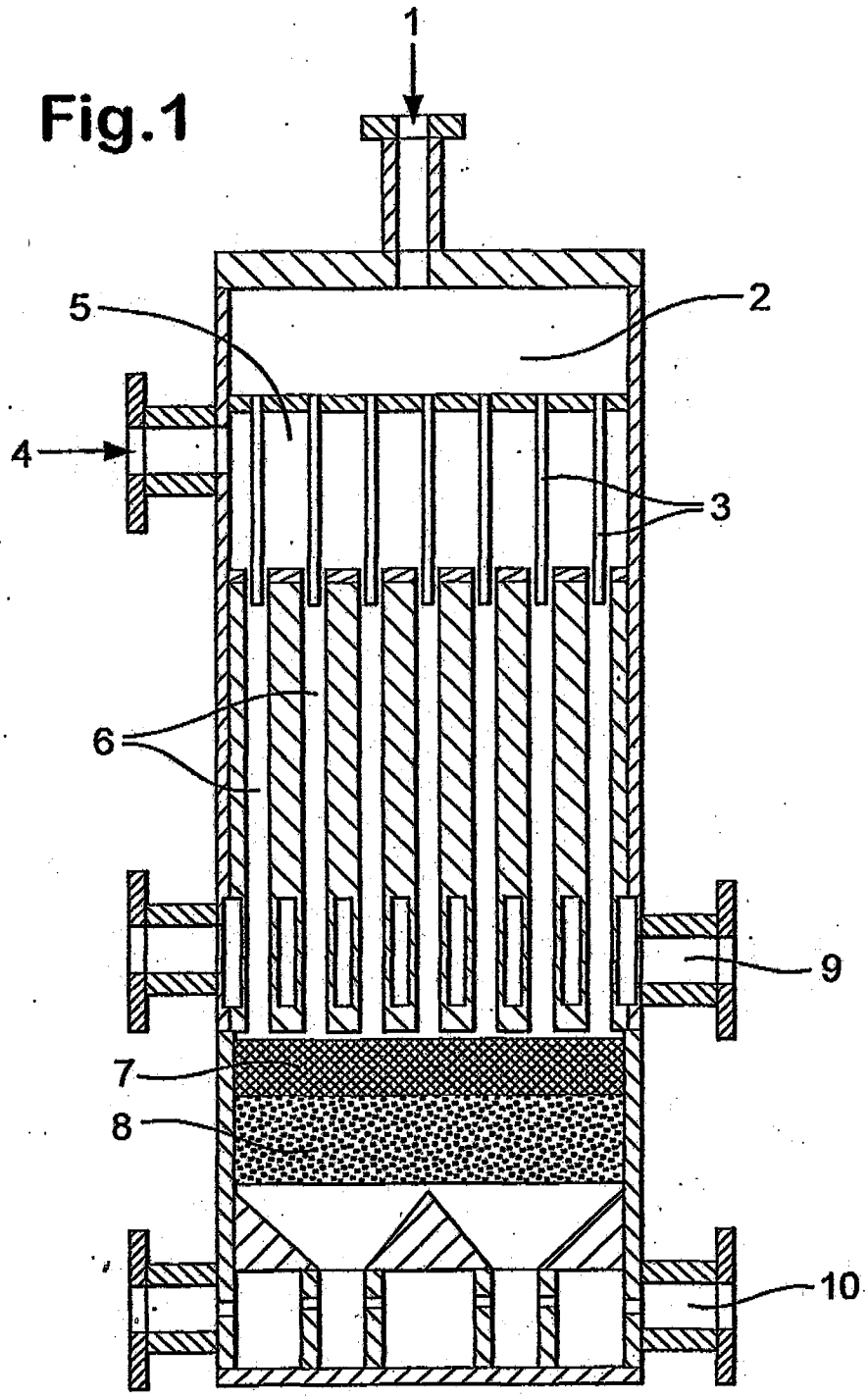


Fig.2a

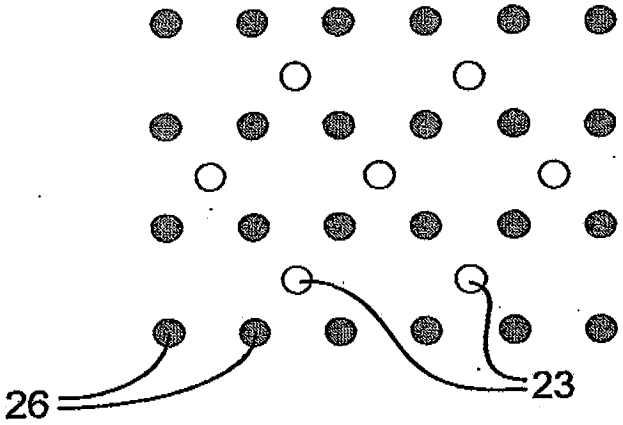
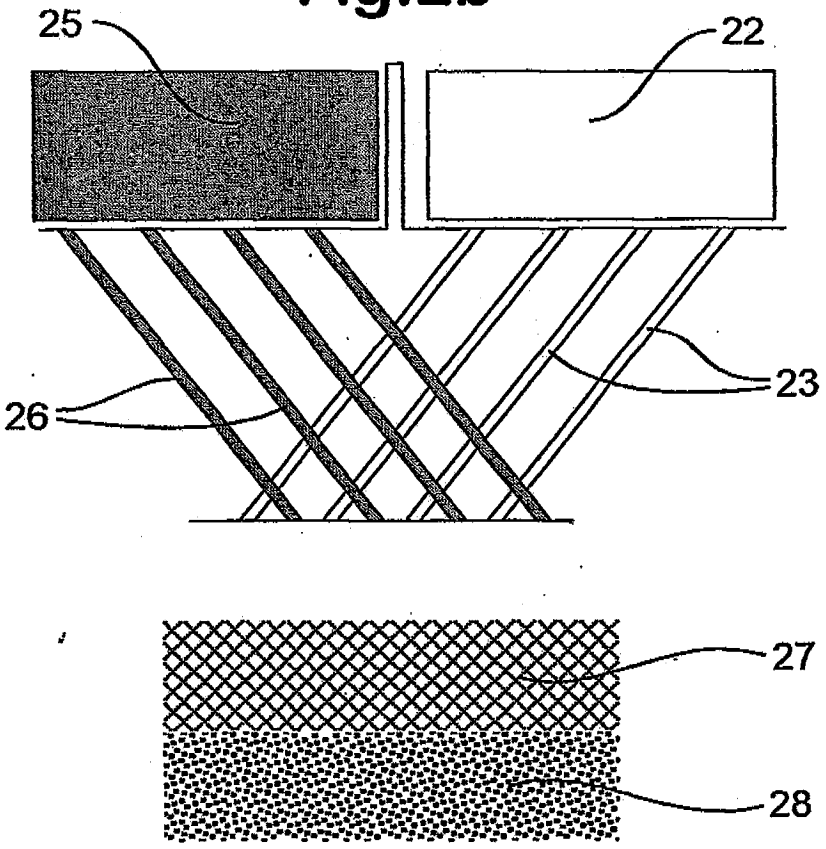


Fig.2b



INTERNATIONAL SEARCH REPORT

PCT/GB2004/000488

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C5/48 C07C11/02 B01J19/26

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)
IPC 7 C07C 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, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/83405 A (COLMAN DEREK ALAN ;HESKETH TREVOR JOHN (GB); WOODFIN WILLIAM TEREN) 8 November 2001 (2001-11-08) page 6, line 6 - page 7, line 21; page 11, line 33 - page 13, line 12; page 16, lines 28-31; figure 1; table 1	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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	Date of mailing of the international search report
11 May 2004	24/05/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Kleidernigg, O

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB2004/000488

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0183405 A	08-11-2001	AU 9519001 A	12-11-2001
		BR 0110586 A	01-04-2003
		CA 2407831 A1	08-11-2001
		CN 1440373 T	03-09-2003
		EP 1278711 A1	29-01-2003
		WO 0183405 A1	08-11-2001
		JP 2003531876 T	28-10-2003
		NO 20025218 A	31-10-2002
		ZA 200208620 A	03-06-2003

REACTOR DE CRACKING AUTO-TERMICO

La presente invención se refiere a un reactor adecuado para la producción de olefinas mediante cracking auto-térmico.

El cracking auto-térmico es un procedimiento conocido para la producción de olefinas. Un ejemplo de dicho procedimiento se describe en EP-A-0 332 289. En este procedimiento, un hidrocarburo y un gas que contiene oxígeno se ponen en contacto con un catalizador, el cual es capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible. El hidrocarburo es quemado parcialmente y el calor producido es utilizado para impulsar la deshidrogenación de la alimentación hidrocarbonada a olefinas.

En el procedimiento de cracking auto-térmico, el hidrocarburo y el gas que contiene oxígeno se pueden mezclar y precalentar uniformemente antes de entrar en contacto con el catalizador. Sin embargo, la mezcla y el precalentamiento del hidrocarburo y del gas que contiene oxígeno es una operación que llega a ser problemática en el caso de que se desee llevar a cabo el procedimiento a presión elevada debido a limitaciones de inflamabilidad. De este modo, llega a ser conveniente reducir el tiempo entre la formación de la mezcla de reactantes gaseosos calientes y el contacto de la mezcla con el catalizador.

La presente invención proporciona un diseño de reactor que permite llevar a cabo un procedimiento de cracking auto-térmico a cualquier presión adecuada, en donde los reactantes gaseosos se precalientan por separado antes de mezclarlos y luego se ofrecen a la zona de reacción de una manera uniformemente distribuida.

En consecuencia, la presente invención proporciona un aparato para hacer reaccionar un primer reactante gaseoso con un segundo reactante gaseoso para formar un producto gaseoso,

en donde el aparato comprende al menos un primer medio de suministro para el primer reactante gaseoso, al menos un segundo medio de suministro para el segundo reactante gaseoso, una zona de resistencia y una zona de reacción, que preferentemente comprende un catalizador, y

en donde el primer medio de suministro comprende una pluralidad de primeras salidas para el suministro del primer reactante gaseoso y el segundo medio de suministro comprende una pluralidad de segundas salidas para el suministro del segundo reactante gaseoso,

la zona de resistencia es porosa, está situada aguas abajo de los primero y segundo medios de suministro con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con los primero y segundo medios de suministro,

la zona de reacción está situada aguas abajo de la zona de resistencia con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con la zona de resistencia, y

en donde el primer medio de suministro y el segundo medio de suministro están dispuestos de manera que el primer gas y el segundo gas se ponen en contacto de una forma esencialmente paralela y se mezclan antes de entrar en contacto con la zona de resistencia.

Preferentemente, el primer medio de suministro comprende al menos una primera entrada para suministrar un primer reactante gaseoso a por lo menos un primer colector y una pluralidad de primeras salidas que salen del primer colector para suministrar el primer reactante gaseoso, y el segundo medio de suministro comprende al menos una segunda entrada para suministrar un segundo reactante gaseoso a por lo menos un segundo colector y una pluralidad de segundas salidas que

salen del segundo colector para suministrar el segundo reactante gaseoso.

El aparato comprende adecuadamente al menos 100, preferentemente al menos 500, más preferentemente al menos 1.000, de dichas primeras y segundas salidas por metro cuadrado de sección transversal de la zona de reacción.

Los primero y segundo medios de suministro están dispuestos de manera que el primer gas y el segundo gas se ponen en contacto de una forma esencialmente paralela. Por la expresión "de una forma esencialmente paralela" se quiere dar a entender que el primer gas y el segundo gas, cuando se ponen en contacto, fluyen ambos esencialmente en la misma dirección, tal como axialmente, en lugar de fluir en direcciones opuestas o tangenciales entre sí. El contacto de los gases de una forma esencialmente paralela, en lugar, por ejemplo, de una forma tangencial, proporciona una menor turbulencia en la región en donde los gases entran en contacto por primera vez (en donde la mezcla todavía no es completa y las composiciones de los gases presentes pueden variar de manera importante).

La turbulencia puede aumentar el tiempo de residencia del gas mezclado en el reactor, lo cual aumenta el riesgo de que surjan problemas de inflamabilidad. En algunos casos, el contacto de los gases de una forma perpendicular puede conducir a regiones de bajo flujo o incluso a regiones muertas, que contienen mezclas gaseosas inflamables próximas a la región de contacto. El contacto de los gases de una forma esencialmente paralela según la presente invención reduce el potencial de presencia de regiones de bajo flujo de gas mezclado, reduciendo ello el potencial de que surjan problemas de inflamabilidad.

En una primera modalidad de la invención, la disposición de contacto/mezcla se consigue situando un medio de suministro dentro del otro y proporcionando al menos una porción del medio de suministro situada dentro del otro con aberturas

adecuadas, de manera que uno de los reactantes gaseosos pueda pasar a través de las aberturas y entrar en contacto con el otro reactante gaseoso.

Preferentemente, la primera modalidad de la invención proporciona un aparato en donde

el primer medio de suministro comprende al menos una primera entrada para suministrar un primer reactante gaseoso a por lo menos un primer colector y una pluralidad de tubos de inyección que salen de dicho primer colector para suministrar el primer reactante gaseoso, y el segundo medio de suministro comprende al menos una segunda entrada para suministrar un segundo reactante gaseoso a por lo menos un segundo colector y una pluralidad de conductos que salen de dicho segundo colector para suministrar el segundo reactante gaseoso,

en donde el segundo colector está situado aguas abajo del primer colector con respecto al flujo del primer reactante gaseoso,

la zona de resistencia es porosa, está situada aguas abajo del segundo colector con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con los conductos que salen del segundo colector,

la zona de reacción está situada aguas abajo de la zona de resistencia con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con la zona de resistencia, y

en donde cada conducto comprende un extremo aguas arriba que sale del segundo colector y un extremo aguas abajo en comunicación fluídica con la zona de resistencia y en donde los tubos de inyección que salen del primer colector están dispuestos de manera que los mismos se extienden a través del segundo colector y se proyectan axialmente al interior del extremo aguas arriba de los conductos.

Convenientemente, el aparato de la primera modalidad comprende

normalmente una primera zona de enfriamiento que entra en contacto con el extremo aguas abajo de la pluralidad de conductos que salen del segundo colector, dispuesta de manera que se enfría el extremo aguas abajo de la pluralidad de conductos. Esto asegura que los reactantes gaseosos no puedan reaccionar hasta que los mismos entran en la zona de reacción.

Por otro lado, el aparato de la primera modalidad comprende normalmente una zona de enfriamiento de los productos aguas abajo de la zona de reacción, de manera que los productos gaseosos pueden ser enfriados tras salir de la zona de reacción.

En la primera modalidad de la invención, preferentemente, el primer colector es una primera cámara y el segundo colector es una segunda cámara y los tubos de inyección que salen de la primera cámara forman una pluralidad de pasadizos alargados que se extienden a través de la segunda cámara al interior del extremo aguas arriba de la pluralidad de conductos que salen del segundo colector.

Los volúmenes de las primera y segunda cámaras no son especialmente críticos. Sin embargo, en una modalidad preferida, los volúmenes de las primera y segunda cámaras están adaptados para que sean relativamente pequeños por motivos de seguridad. Generalmente, cuando el diámetro del reactor es de 600 mm, el volumen de la primera cámara es normalmente de 5-100 litros, preferentemente de 10-40 litros y más preferentemente de 15-25 litros, por ejemplo 22 litros. El volumen de estas cámaras será proporcional al área en sección transversal del reactor (es decir, el diámetro al cuadrado).

Generalmente, cuando el diámetro del reactor es de 600 mm, el volumen de la segunda cámara es normalmente de 20-200 litros, preferentemente de 30-100 litros y más preferentemente de 40-80 litros, por ejemplo, 50 litros.

El aparato de la primera modalidad comprende normalmente un número igual de tubos de inyección y de conductos, proyectándose cada tubo de inyección al interior del correspondiente conducto. Preferentemente, el aparato comprende al menos 100, preferentemente al menos 500, más preferentemente al menos 1.000 tubos de inyección por metro cuadrado de la sección transversal de la zona de reacción.

Para que los tubos de inyección puedan proyectarse al interior de los conductos, el diámetro externo de los tubos de inyección, en donde los mismos se proyectan al interior de los conductos, es menor que el diámetro interno de los conductos. El diámetro externo exacto no resulta crítico para la invención, pero normalmente los tubos de inyección tienen un diámetro externo entre 2 y 5 mm, por ejemplo, 4 mm. Los tubos de inyección tienen una longitud suficiente para extenderse a través de la segunda cámara (es decir, generalmente mayor de 170 mm).

En el extremo de cada uno de la pluralidad de tubos de inyección, distantes del colector, el primer reactante gaseoso puede salir de los tubos a través de una abertura adecuada, preferentemente una tobera, y que tiene un diámetro menor que el diámetro externo del tubo de inyección, preferentemente entre 0,5 y 3 mm, tal como entre 1 y 2 mm. La tobera, cuando está presente, tiene preferentemente un diámetro menor que el diámetro interno del tubo de inyección distinto al de la tobera, proporcionando por tanto una restricción que ayuda a conseguir velocidades de flujo uniformes desde todos los tubos de inyección, sin proporcionar la caída de presión característica que se obtendría en el caso de que el diámetro interno del tubo de inyección fuese de esta dimensión en una longitud importante del tubo de inyección.

Normalmente, los conductos tienen un diámetro interno entre 1 y 10 mm, preferentemente entre 2 y 8 mm, por ejemplo 7 mm, y una longitud entre 50 y 500

mm, preferentemente entre 100 y 300 mm, por ejemplo 210 mm. Los conductos pueden estar dispuestos según una configuración simétrica, tal como en una configuración triangular o cuadrada.

La relación del diámetro interior de los conductos al diámetro de la abertura, por ejemplo la tobera, de los tubos de inyección es adecuadamente del orden de 2:1 a 10:1, por ejemplo, del orden de 3:1 a 5:1.

Cuando los tubos de inyección del primer medio de suministro se extienden a través del colector del segundo medio de suministro, cada tubo de inyección puede estar provisto de un tubo exterior, alrededor del tubo de inyección (el cual forma un tubo interior dentro de dicho tubo exterior). El tubo exterior proporciona aislamiento térmico respecto del segundo reactante gaseoso cuando este se encuentra a una temperatura diferente de la del primer reactante gaseoso (el cual pasa por dentro del tubo interior).

En otra modalidad preferida, están previstos también restrictores del flujo adecuados entre la superficie exterior de los tubos de inyección y la superficie interior de los conductos, en una posición en o cerca del punto en donde los tubos de inyección entran en los conductos en el extremo aguas arriba de los conductos (es decir, cerca del segundo colector). Dichos restrictores del flujo pueden estar situados en los tubos de inyección y/o en los conductos y, al proporcionar resistencia, los mismos ayudan a conseguir velocidades de flujo uniformes del segundo reactante gaseoso al interior de cada conducto. Dichos restrictores del flujo deberán estar situados lejos de las salidas de los primeros tubos de inyección, de manera que la velocidad del segundo reactante gaseoso, que presenta una velocidad máxima en el conducto cuando pasa a través o a lo largo de los restrictores del flujo, se reduzca (respecto del valor máximo) cuando se mezcla con el primer reactante gaseoso.

Preferentemente, la caída de presión del flujo que pasa por estos restrictores es de un orden similar a la caída de presión del primer reactante gaseoso a través de las toberas u otras restricciones existentes en el extremo de los tubos de inyección (tal como 1 bar y 0,5 bares, respectivamente). Esto asegura que las proporciones de los reactantes que entran en la zona de reacción permanezcan en valores similares cuando existan pequeñas fluctuaciones de presión en la zona de reacción o en las alimentaciones. Para conseguir rendimientos óptimos, la tolerancia en los diámetros de la tobera y de los restrictores de flujo para el segundo reactante gaseoso deberá ser tal que la concentración de la mezcla gaseosa no varíe en más de 5%.

Normalmente, al interior del conducto se proyecta axialmente una longitud del tubo de inyección de 5-40 mm, preferentemente de 10-30 mm y más preferentemente de 15-25 mm, por ejemplo, 20 mm.

Cuando el aparato de la primera modalidad comprende una primera zona de enfriamiento, la primera zona de enfriamiento se proporciona preferentemente mediante el contacto de un fluido de enfriamiento con el área superficial externa del extremo aguas debajo de los conductos. Generalmente, con el fluido de enfriamiento puede entrar en contacto del 10 a 20% del área superficial externa del conducto.

En una segunda modalidad de la presente invención, la disposición de contacto/mezcla se consigue mediante un primer medio de suministro que comprende al menos una primera entrada para suministrar un primer reactante gaseoso a por lo menos un primer colector y una pluralidad de primeros tubos de inyección que salen de dicho primer colector para suministrar el primer reactante gaseoso, y un segundo medio de suministro que comprende al menos una segunda entrada para suministrar un segundo reactante gaseoso a por lo menos un segundo colector y una pluralidad de segundos tubos de inyección que salen de dicho segundo

colector para suministrar el segundo reactante gaseoso, en donde cada tubo de inyección tiene una salida en el extremo distante del colector y que tiene una abertura con una sección transversal de 1 mm^2 o menos, y en donde las salidas de los primeros y segundos tubos de inyección se encuentran en una configuración entremezclada.

Por el término "entremezclada" tal como aquí se emplea, se quiere dar a entender que las salidas de la pluralidad de primeros tubos de inyección están dispersas entre las salidas de la pluralidad de segundos tubos de inyección y/o viceversa. Así, por ejemplo, cuando existen más primeros tubos de inyección que segundos tubos de inyección, las salidas de los segundos tubos de inyección estarán dispersas entre las salidas de los primeros tubos de inyección y la configuración óptima para las salidas de los segundos tubos de inyección será tal que cada segundo tubo de inyección tendrá la salida de al menos un primer tubo de inyección como su vecina más próxima.

Adecuadamente, existen en total al menos 10.000 primeros y segundos tubos de inyección por metro cuadrado. El uso de dicho número de tubos entremezclados da lugar a una rápida mezcla en las salidas de dichos tubos.

Para el suministro óptimo de los primero y segundo reactantes gaseosos a la zona de resistencia, las salidas de los tubos de inyección de la segunda modalidad deberán estar situadas todas ellas según una configuración esencialmente plana.

Las salidas de los primeros tubos de inyección pueden estar dispuestas en una configuración simétrica, tal como en una configuración triangular, cuadrada, rectangular o hexagonal, y/o las salidas de los segundos tubos de inyección pueden estar dispuestas en una configuración simétrica, tal como en una configuración triangular, cuadrada, rectangular o hexagonal.

En esta segunda modalidad, las salidas pueden tener cualquier forma adecuada en sección transversal, tal como triangular, rectangular, cuadrada, hexagonal, en forma de D, ovalada o circular.

La mezcla de los gases llega a ser más rápida a medida que aumenta el número de tubos y disminuye la abertura en sección transversal de las salidas de los tubos.

De este modo, en un aspecto preferido de la segunda modalidad de la presente invención, cada tubo de inyección tiene una salida en el extremo distante del colector que tiene una abertura en sección transversal de 0,5 mm^2 o menos. Más preferentemente, las salidas tienen una abertura en sección transversal de 0,2 mm^2 o menos, tal como de 0,1 mm^2 o menos. Adecuadamente, las salidas tienen una abertura en sección transversal de 0,004 mm^2 o más.

Las salidas de los tubos de inyección para uno de los reactantes pueden variar en cuanto a tamaño y forma, pero preferentemente son iguales. Similarmente, las salidas para el segundo reactante gaseoso pueden ser diferentes de las salidas para el primer reactante gaseoso, o bien pueden ser de la misma configuración y tamaño que estas últimas.

Con suma preferencia, las salidas tienen forma de D, tal como una forma semi-circular, con una abertura en sección transversal comprendida entre 0,01 mm^2 y 0,05 mm^2.

El aparato de esta segunda modalidad puede comprender un número igual de primeros y segundos tubos de inyección para el suministro de dichos primero y segundo reactantes gaseosos, respectivamente. Alternativamente, el número relativo de tubos de inyección para el suministro de cada reactante gaseoso puede ser diferente, por ejemplo, el número relativo de tubos de inyección para suministrar

cada reactante gaseoso puede estar en proporción a la cantidad relativa de cada reactante gaseoso que ha de ser suministrado. Sin embargo, la relación entre los números de los tubos no resulta crítica para esta invención y, por ejemplo, las velocidades de los primero y segundo reactantes gaseoso que salen de los respectivos tubos de inyección pueden ser diferentes y preferentemente lo son. En particular, el uso de diferentes velocidades de flujo para cada uno de dichos primero y segundo reactantes gaseosos, permite conseguir diferentes relaciones de dichos primero y segundo reactantes gaseosos utilizando un número fijo de tubos de inyección para cada reactante.

Preferentemente, uno de los reactantes, más preferentemente el reactante con peso molecular más bajo, sale de uno de los conjuntos de tubos de inyección a una velocidad más alta que la velocidad a la cual sale el otro reactante de los otros tubos de inyección. Por ejemplo, el tamaño y el número de los tubos de inyección para uno de los reactantes pueden ser tales que la relación de las velocidades de salida es de al menos 10:1, por ejemplo, la velocidad de salida de uno de los reactantes es de al menos 100 m/s, mientras que el número y el tamaño de los tubos de inyección para el otro reactante pueden ser tales que la velocidad de salida es menor de 10 m/s. La velocidad media de los flujos combinados que han salido de los tubos de inyección puede ser del orden de 3 m/s.

A medida que disminuye la abertura en sección transversal de los tubos de salida, puede aumentar el número de primeros y segundos tubos de inyección por unidad de área de la sección transversal de la zona de reacción. Así, el aparato de la segunda modalidad puede comprender al menos 100.000, por ejemplo al menos 1.000.000, tal como 4.000.000 de tubos de inyección (total de los primeros y segundos tubos de inyección) por metro cuadrado de sección transversal de la zona

comprende una primera cámara y el segundo colector comprende una segunda cámara, en donde los respectivos primero y segundo componentes gaseosos salen de las mismas y se dirigen al interior de una pluralidad de primeros y segundos tubos de inyección. Los tubos de inyección con salidas con una abertura en sección transversal de 1 mm^2 o menos, están formados preferentemente como pasadizos en un bloque aglomerado por difusión. Los bloques aglomerados por difusión, formados mediante la aglomeración por difusión de capas de estructuras metálicas mordentadas, son ya conocidos por utilizarse en operaciones de intercambio de calor, y se describen en términos generales, por ejemplo, en "Industrial Microchannel Devices – Where are we Today?"; Pua, L.M. y Rumbold, S.O.; First International Conferences on Microchannels and Minichannels, Rochester, NY, Abril 2003.

El uso de técnicas de aglomeración por difusión en la presente invención permite formar una pluralidad de pasadizos que conectan las primera y segunda cámaras respectivamente a una pluralidad de primeras y segundas salidas, encontrándose las salidas en una configuración entremezclada, como se requiere para la formación de los tubos de inyección de la segunda modalidad de la presente invención.

Como en el caso de la primera modalidad, el volumen de dichas primera y segunda cámaras no resulta especialmente crítico pero, preferentemente, el volumen de dichas primera y segunda cámaras en la segunda modalidad se adapta para que sea relativamente pequeño por motivos de seguridad.

Después de la operación de mezcla de acuerdo con el procedimiento de la presente invención mediante el aparato de la primera o segunda modalidad, o bien de cualquier otra forma, los primero y segundo reactantes gaseosos mezclados se ponen en contacto con una zona de resistencia situada aguas abajo de dichos primero y

segundo medios de suministro.

La zona de resistencia es porosa. La permeabilidad de la zona de resistencia porosa asegura la dispersión de los reactantes fluidos a medida que estos pasan a través de la zona. Los fluidos se mueven a través de una red de canales lateralmente, así como axialmente (siendo la dirección axial la dirección general de flujo de los reactantes a través de la zona de resistencia) y abandonan la zona de resistencia distribuidos de un modo sustancialmente uniforme por el área en sección transversal de la zona de resistencia.

Preferentemente, la zona de resistencia es permeable tanto lateralmente como axialmente. Más preferentemente, la zona de resistencia tiene una permeabilidad que es sustancialmente la misma en cualquier dirección, teniendo por ejemplo una permeabilidad en cualquier dirección que es de 0,2 a 5 veces la permeabilidad en cualquier otra dirección.

Se conocen ya métodos para determinar la permeabilidad de medios porosos. Se puede definir el gradiente de presión o la caída de presión por unidad de longitud a través de la zona de resistencia, usando el coeficiente de resistencia inercial en donde el gradiente de presión es igual al producto del coeficiente de resistencia inercial y de la presión dinámica. La presión dinámica es la mitad del producto de la densidad del fluido y del cuadrado de la velocidad superficial y tiene unidades de presión. El coeficiente de resistencia inercial tiene unidades de longitud recíproca. La zona de resistencia tiene normalmente un coeficiente de resistencia inercial medio (es decir, el valor medio en todas las direcciones) de 500-10.000/metro (/m), preferentemente de 2.000-4.000/m y convenientemente de 2.500-3.500/m, por ejemplo 3.250/m.

La zona de resistencia puede estar formada por una estructura metálica

porosa, pero preferentemente el material poroso es un material no metálico, por ejemplo, un material cerámico. Materiales cerámicos adecuados incluyen silicato de litio-aluminio (LAS), alúmina (α-Al_2O_3), zirconia estabilizada con itria, titanato de alúmina, niascon y zirconilfosfato de calcio. Un material poroso preferido es gamma-alúmina.

La distancia de la zona de resistencia desde los extremos de los conductos en la primera modalidad y desde la salida de los tubos en la segunda modalidad, es preferentemente menor de 20 mm, más preferentemente entre 1 y 10 mm y muy particularmente entre 1,5 y 5 mm, tal como 2 mm.

Cuando la zona de reacción comprende un catalizador soportado, preferentemente el material poroso de la zona de resistencia puede ser el mismo que el material poroso usado como soporte del catalizador. El material poroso puede estar en forma de esferas, pudiendo tener también otras formas granuladas o de espumas cerámicas. La zona de reacción puede comprender un catalizador soportado en forma de un monolito que proporciona una estructura de múltiples canales continuos.

Para el material poroso de la zona de resistencia, convenientemente al menos el 70%, con preferencia al menos el 80% y ventajosamente al menos el 90% de los poros tienen un ancho de poros menor de 0,5 mm, por ejemplo, normalmente de 0,1-3 mm, con preferencia de 0,2-2 mm y más preferentemente de 0,5-1,5 mm.

Normalmente, la zona de resistencia tiene 10-60 poros por 6,45 cm^2, con preferencia 20-50 poros por 6,45 cm^2 y más preferentemente 30-45 poros por 6,45 cm^2.

Generalmente, la profundidad de la zona de resistencia es de 5-100 mm, preferentemente de 10-540 mm.

Normalmente, la zona de reacción tiene una profundidad de 10-200 mm, con

preferencia de 20-100 mm, por ejemplo, 60 mm. Preferentemente, la zona de reacción comprende un catalizador.

(La profundidad de la zona de resistencia y de la zona de reacción se mide en la dirección de flujo de los gases reactantes. En general, las profundidades preferidas se definen por la velocidad de flujo de los gases reactantes, puesto que ello determina el tiempo de contacto y, como ocurre con otras dimensiones medidas en la dirección del flujo de gas, son, para la mayoría de fines prácticos, independientes de la sección transversal del reactor).

Cuando se emplea un catalizador, convenientemente el catalizador es un metal del grupo del platino soportado. Preferentemente, el metal es platino o paladio o bien una mezcla de ambos. Aunque se dispone de una amplia variedad de materiales de soporte, es preferible usar alúmina como soporte. El material de soporte puede estar en forma de esferas, o bien en otras formas granuladas o de espumas cerámicas. Preferentemente, el soporte es un monolito que consiste en una estructura cerámica de múltiples canales continuos, frecuentemente con una apariencia alveolar. Un soporte preferido para los metales catalíticamente activos es una gamma-alúmina. El soporte se carga con una mezcla de platino de paladio por métodos convencionales bien conocidos para los expertos en la materia. El compuesto resultante se trata entonces térmicamente a 1.200° C antes de su uso. Sobre el soporte se pueden cargar también promotores catalíticos. Promotores adecuados incluyen cobre y estaño.

El catalizador se mantiene normalmente en su sitio en el reactor utilizando un retenedor adecuado, tal como un cesto de catalizador. Preferentemente, para evitar que el gas se desvíe del catalizador entre el catalizador y el cesto, cualquier espacio existente entre el catalizador y el retenedor se rellena con un material de obturación

adecuado. Materiales de obturación adecuados incluyen lanas minerales artificiales, por ejemplo lana cerámica, que se pueden envolver alrededor de los bordes del catalizador en el retenedor. Además, el catalizador puede ser revestido alrededor de los bordes con un material similar al material de soporte principal del catalizador, tal como alúmina, para facilitar dicha obturación.

El aparato puede comprender una zona de enfriamiento de los productos aguas abajo de la zona de reacción, de manera que los productos gaseosos puedan ser enfriados tras salir de la zona de reacción. La zona de enfriamiento de los productos puede ser proporcionada por una o más toberas de inyección capaces de inyectar un condensado en la corriente de productos que sale de la zona de reacción.

Preferentemente, los primero y segundo colectores, los tubos de inyección, los conductos (si están presentes), el alojamiento para la zona de resistencia y la zona de reacción son metálicos, por ejemplo de acero. Cuando se emplea oxígeno puro como un reactante gaseoso, puede ser necesario fabricar o revestir parte o la totalidad de cualquier parte del aparato que puede estar en contacto con el oxígeno, empleando una aleación que resista la reacción con oxígeno. La reacción con oxígeno es más probable que ocurra cuando la temperatura del oxígeno es alta y/o cuando el oxígeno se encuentra a elevada velocidad. Aleaciones adecuadas incluyen monel.

Inmediatamente aguas abajo de la zona de reacción, en donde la temperatura de los productos de la reacción es elevada, el material de construcción preferido es una aleación de alto contenido en níquel, tal como Inconel, Incaloy, Hastelloy o Paralloy. El metal puede ser configurado a la forma deseada mediante una o más de las siguientes técnicas: colada estática, colada centrífuga, forjado, mecanizado y soldadura.

El aparato puede comprender una camisa térmica adecuada para reducir

tensiones térmicas sobre el aparato inmediatamente aguas abajo de la zona de reacción. Las tensiones térmicas pueden presentarse cuando ocurren cambios relativamente rápidos en la temperatura, bien un incremento rápido o un descenso rápido, en el interior del aparato, por ejemplo, en la puesta en marcha o en la parada. La superficie interior de la pared del aparato se calienta o se enfría rápidamente, pero la superficie exterior se calienta o se enfría más lentamente, proporcionando ello tensión térmica de un lado a otro de la pared (siendo la pared relativamente gruesa, por ejemplo, para competir con la diferencia de presión entre el interior y el exterior del aparato). El uso de una camisa de material fino, que puede ser de un material similar al de la pared del aparato, como una camisa térmica dentro del aparato reduce la velocidad de cambio de temperatura que impacta en la superficie interior de la pared y, por tanto, reduce la tensión térmica.

El aparato se emplea convenientemente para oxidar de forma parcial un material de alimentación gaseoso. Con preferencia, el primer reactante gaseoso es un gas que contiene oxígeno y el segundo reactante gaseoso es un hidrocarburo parafínico gaseoso.

La presente invención proporciona también un procedimiento para la producción de una mono-olefina empleando el aparato anteriormente descrito.

De este modo, utilizando el aparato de la primera modalidad, la invención proporciona un procedimiento para la producción de una mono-olefina, comprendiendo dicho procedimiento:

pasar un gas que contiene oxígeno al interior de un primer colector e inyectar el gas que contiene oxígeno por vía de una pluralidad de tubos de inyección al interior de una pluralidad de conductos,

pasar un hidrocarburo parafínico gaseoso por vía de un segundo colector al

interior de la pluralidad de conductos, en donde el hidrocarburo parafínico gaseoso se pone en contacto de una forma esencialmente paralela y se mezcla con el gas que contiene oxígeno,

pasar la mezcla gaseosa a una zona de reacción por vía de una zona de resistencia porosa y

quemar parcialmente la mezcla gaseosa en la zona de reacción, preferentemente en presencia de un catalizador que es capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir la mono-olefina.

Empleando el aparato de la segunda modalidad, la invención proporciona un procedimiento para la producción de una mono-olefina, comprendiendo dicho procedimiento:

pasar un gas que contiene oxígeno desde al menos una primera entrada por vía de al menos un primer colector a una pluralidad de primeros tubos de inyección y pasar un hidrocarburo parafínico gaseoso desde al menos una segunda entrada por vía de al menos un segundo colector a una pluralidad de segundos tubos de inyección, en donde cada tubo de inyección tiene una salida en el extremo distante del colector y que tiene una abertura en sección transversal de 1 mm^2 o menos, y en donde las salidas de los primeros y segundos tubos de inyección están situadas de manera conjunta según una configuración entremezclada,

pasar la mezcla gaseosa a una zona de reacción por vía de una zona de resistencia porosa y

quemar parcialmente la mezcla gaseosa en la zona de reacción, preferentemente en presencia de un catalizador que es capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir

la mono-olefina.

Los procedimientos preferidos para la producción de una mono-olefina utilizan un aparato con las características preferidas como las descritas anteriormente. Así, por ejemplo, el aparato preferido para un procedimiento que utiliza el aparato de la segunda modalidad es tal que cada tubo de inyección tiene una salida en el extremo distante del colector que tiene una abertura en sección transversal de 0,5 mm^2 o menos. Más preferentemente, las salidas tienen una abertura en sección transversal de 0,2 mm^2 o menos, tal como 0,1 mm^2 o menos.

En el procedimiento para la producción de una mono-olefina a partir de un material de alimentación que comprende un hidrocarburo parafínico gaseoso, el hidrocarburo parafínico puede ser adecuadamente etano, propano o butano. El hidrocarburo parafínico puede ser sustancialmente puro o puede estar en mezcla con otros hidrocarburos y opcionalmente otros materiales, por ejemplo, metano, nitrógeno, monóxido de carbono, dióxido de carbono, vapor de agua o hidrógeno. Se puede emplear una fracción que contiene hidrocarburos parafínicos tal como nafta, gasóleo, gasóleo de vacío o mezclas de los mismos. Un material de alimentación adecuado es una mezcla de hidrocarburos parafínicos gaseosos, comprendiendo principalmente etano, resultante de la separación de metano de gas natural. Un material de alimentación preferido es un hidrocarburo parafínico que comprende principalmente etano y que proporciona un producto que comprende principalmente etileno como la mono-olefina.

Como gas que contiene oxígeno se puede emplear adecuadamente oxígeno o aire. Es preferible usar oxígeno, opcionalmente diluido con un gas inerte, por ejemplo nitrógeno. La relación del hidrocarburo parafínico gaseoso a la mezcla de gas que contiene oxígeno es normalmente de 5 a 20 veces la relación estequiométrica

de hidrocarburo a gas que contiene oxígeno para la combustión completa a dióxido de carbono y agua. La composición preferida es de 5 a 10 veces la relación estequiométrica de hidrocarburo a gas que contiene oxígeno.

Aunque el aparato se puede emplear a cualquier presión, por ejemplo entre 0-100 barg, resulta particularmente útil a presión elevada. La presión en las primeras y segundas entradas es con preferencia entre 10-50 barg, más preferentemente entre 20-40 barg y convenientemente entre 25-35 barg, por ejemplo 30 barg.

El gas que contiene oxígeno se puede alimentar a temperatura ambiente, pero normalmente se precalienta a 50-150° C, preferentemente 80-120° C, por ejemplo, 100° C. El gas que contiene oxígeno se inyecta en los conductos o desde las salidas de la pluralidad de tubos de inyección a una velocidad que impida la posibilidad de la estabilización de una llama en las salidas de los tubos de inyección. Especialmente en la primera modalidad de la presente invención, los tubos de inyección pueden terminar en una tobera adecuada para aumentar la velocidad de salida. La velocidad de salida es generalmente mayor de 30 m/s, con preferencia mayor de 50 m/s, y convenientemente mayor de 70 m/s.

El hidrocarburo parafínico gaseoso se precalienta normalmente a 100-400° C, preferentemente 150-350° C, por ejemplo 300° C, y se pasa al interior de los conductos o desde la pluralidad de segundos tubos de inyección en donde se mezcla íntimamente con el gas que contiene oxígeno. El hidrocarburo parafínico gaseoso entra en los conductos o sale de la pluralidad de segundos tubos de inyección a una velocidad generalmente mayor de 5 m/s, con preferencia mayor de 15 m/s y convenientemente mayor de 20 m/s.

En la primera modalidad, la velocidad del gas que contiene oxígeno que sale de los tubos de inyección y la velocidad del hidrocarburo parafínico gaseoso que

pasa al interior de los conductos, tienen preferentemente una relación de al menos 1,5:1, con preferencia de al menos 3:1 y más preferentemente menor de 6:1, tal como 4:1. Esta relación asegura una mezcla rápida.

En la segunda modalidad, la relación de la velocidad del gas que contiene oxígeno que sale de los primeros tubos de inyección y la velocidad del hidrocarburo parafínico gaseoso que sale de los segundos tubos de inyección dependerá de las relaciones relativas de los números de primeros y segundos tubos de inyección, de sus tamaños relativos y de la relación oxígeno/hidrocarburo parafínico deseada, pero preferentemente la relación es de al menos 0,1:1, con preferencia de al menos 1:1 y más preferentemente de al menos 5:1. Normalmente, la velocidad de salida del gas que contiene oxígeno es de al menos 50 m/s, especialmente de al menos 100 m/s. Por ejemplo, el tamaño y el número de los números de inyección para el gas que contiene oxígeno pueden ser tales que la velocidad de salida es de al menos 100 m/s, mientras que el número y el tamaño de los tubos de inyección para el hidrocarburo parafínico gaseoso pueden ser tales que la velocidad de salida es menor de 10 m/s, y la velocidad media de los flujos combinados que salen de los tubos de inyección puede ser del orden de 3 m/s.

La temperatura de la mezcla gaseosa se encuentra normalmente entre 100 y 400° C, con preferencia entre 100 y 300° C, por ejemplo 200° C. Además de pasar el hidrocarburo parafínico gaseoso a los conductos o segundos tubos de inyección, se pueden pasar también otros gases a los conductos o segundos tubos de inyección, por ejemplo, hidrógeno, monóxido de carbono y/o dióxido de carbono.

En la primera modalidad, la mezcla gaseosa puede ser enfriada por la primera zona de enfriamiento en donde se pasa un refrigerante, tal como agua, alrededor del área superficial externa del extremo aguas abajo de los conductos. El enfriamiento

del extremo aguas abajo de los conductos impide el calentamiento local del conducto lo cual elimina la tendencia a cualquier "arrastre de la llama hacia atrás" en el caso de que se forme una llama estable en la salida de los conductos.

La temperatura del refrigerante es normalmente de 20-200° C, con preferencia de 80-120° C, por ejemplo 100° C. La velocidad de flujo del refrigerante se manipula de manera que el incremento de temperatura del refrigerante sea menor de 100° C, con preferencia menor de 50° C y más preferentemente menor de 30° C.

La primera zona de enfriamiento reduce la temperatura de la mezcla gaseosa en al menos 10° C, con preferencia en al menos 20° C y más preferentemente en al menos 30° C.

En ambas modalidades, la mezcla gaseosa se pasa normalmente a la zona de resistencia a una velocidad media en sección transversal de 1-10 m/s, con preferencia de 2-6 m/s y más preferentemente de 2,5-3,5 m/s.

La mezcla gaseosa se pasa normalmente a la zona de reacción a una velocidad de 1-10 m/s, con preferencia de 2-6 m/s y más preferentemente de 2,5-3,5 m/s.

La caída de presión a través de la zona de resistencia es normalmente de 0,01-0,2 bar, preferentemente de 0,05-0,1 bar, por ejemplo, 0,08 bar.

La temperatura en la zona de reacción es generalmente mayor de 500° C, por ejemplo mayor de 650° C, habitualmente mayor de 750° C y preferentemente mayor de 800° C. El límite superior de temperatura puede ser adecuadamente de hasta 1.200° C, por ejemplo de hasta 1.100° C, preferentemente de hasta 1.000° C.

Los productos salen de la zona de reacción a una temperatura mayor de 800° C, por ejemplo mayor de 900° C, y a una presión normalmente de 10-50 barg, más preferentemente de 20-40 barg y convenientemente de 25-35 barg, por ejemplo 30 barg.

Con preferencia, los productos se enfrían rápidamente en una zona de enfriamiento de los mismos. Esto asegura un alto rendimiento olefínico debido a que la etapa de enfriamiento de los productos decelera la velocidad de reacción en la corriente gaseosa de producto evitando así que tengan lugar otras reacciones.

Convenientemente, la corriente gaseosa de producto se enfría inyectando un condensado en la corriente gaseosa de producto, preferentemente en múltiples puntos, de manera que la vaporización del condensado enfríe a la corriente gaseosa de producto.

El condensado puede ser un gas o un líquido. Cuando el condensado es un gas, preferentemente es un gas inerte. Con preferencia, el condensado es un líquido, por ejemplo, agua.

La inyección del condensado a elevada presión y elevada temperatura asegura que una proporción grande del condensado se vaporice de forma instantánea a la presión del reactor y, por tanto, proporciona una caída de temperatura muy rápida en la corriente gaseosa de producto. En consecuencia, el condensado, tal como agua, se inyecta normalmente a una presión mayor que la presión de la corriente gaseosa de producto, tal como 100 barg y normalmente se inyecta a una temperatura de 100-400° C, con preferencia de 200-350° C, por ejemplo 300° C.

Preferentemente, la temperatura de la corriente gaseosa de producto se reduce a 800° C, preferentemente a 600° C, en el plazo de 60 mS, preferentemente 40 mS y convenientemente 20 mS después de salir de la zona de reacción.

La presente invención será ilustrada ahora con ayuda de figuras, en donde:

La figura 1 representa un aparato según la primera modalidad de la presente invención.

La figura 2a representa esquemáticamente una sección de una configuración

entremezclada de primeros y segundos tubos de inyección para un aparato según la segunda modalidad de la presente invención.

La figura 2b representa esquemáticamente una vista lateral de un aparato según la segunda modalidad de la presente invención.

En la figura 1, un gas que contiene oxígeno se pasa por vía de una primera entrada (1) al interior de una primera cámara (2) y luego al interior de una pluralidad de tubos de inyección (3). Un hidrocarburo parafínico gaseoso se pasa por vía de una segunda entrada (4) al interior de una segunda cámara (5) y luego al interior de la pluralidad de conductos (6). El gas que contiene oxígeno se inyecta por vía de los tubos de inyección (3) al interior de los conductos (6) en donde el hidrocarburo parafínico gaseoso se mezcla con el gas que contiene oxígeno.

La mezcla gaseosa se pasa entonces a la zona de resistencia (7) en donde se toma el impulso de la mezcla gaseosa de manera que pase de un modo uniforme a la zona de reacción (8) que comprende un catalizador capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible. Los reactantes gaseosos se convierten en la zona de reacción (8) para proporcionar una corriente de producto que comprende olefinas.

Antes de pasar la mezcla gaseosa a la zona de resistencia (7), se emplea una primera zona de enfriamiento (9) que contacta con el extremo aguas abajo de la pluralidad de conductos, para reducir la temperatura de la mezcla gaseosa.

Finalmente, la corriente de producto que comprende olefinas se pasa a una zona de enfriamiento del producto (10) para reducir la temperatura de la corriente de producto antes de su recuperación.

En la figura 2a, una serie de primeros tubos de inyección (23), mostrados por círculos blancos, están dispuestos según una configuración triangular. Las salidas de

los primeros tubos de inyección están dispersas entre las salidas de una pluralidad de segundos tubos de inyección (26), los cuales están dispuestos según una configuración rectangular. En la configuración completa (la figura solo muestra una sección) existen aproximadamente dos veces más de segundos tubos de inyección que de primeros tubos de inyección en esta configuración.

En la figura 2b, un gas que contiene oxígeno se pasa al interior de una primera cámara (22) y luego al interior de la pluralidad de primeros tubos de inyección (23). Un hidrocarburo parafínico gaseoso se pasa al interior de una segunda cámara (25) y luego al interior de la pluralidad de segundos tubos de inyección (26). El gas que contiene oxígeno y el hidrocarburo parafínico gaseoso salen de los respectivos tubos de inyección y se mezclan rápidamente.

La mezcla gaseosa se pasa entonces a la zona de resistencia (27) en donde la velocidad de la mezcla gaseosa es uniformizada (se toma el impulso de la mezcla gaseosa) de manera que pase de un modo uniforme a una zona de reacción (28) que comprende un catalizador capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible. Los reactantes gaseosos se convierten en la zona de reacción (28) para proporcionar una corriente de producto que comprende olefinas.

Por último, la corriente de producto que comprende olefinas se pasa a una zona de enfriamiento del producto (no mostrada) para reducir la temperatura de la corriente de producto antes de su recuperación.

REIVINDICACIONES

1.- Aparato para hacer reaccionar un primer reactante gaseoso con un segundo reactante gaseoso para formar un producto gaseoso,

caracterizado porque comprende al menos un primer medio de suministro para el primer reactante gaseoso, al menos un segundo medio de suministro para el segundo reactante gaseoso, una zona de resistencia y una zona de reacción, que preferentemente comprende un catalizador,

porque el primer medio de suministro comprende una pluralidad de primeras salidas para el suministro del primer reactante gaseoso y el segundo medio de suministro comprende una pluralidad de segundas salidas para el suministro del segundo reactante gaseoso,

porque la zona de resistencia es porosa, está situada aguas abajo de los primero y segundo medios de suministro con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con los primero y segundo medios de suministro,

porque la zona de reacción está situada aguas abajo de la zona de resistencia con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con la zona de resistencia, y

porque el primer medio de suministro y el segundo medio de suministro están dispuestos de manera que el primer gas y el segundo gas se ponen en contacto de una forma esencialmente paralela y se mezclan antes de entrar en contacto con la zona de resistencia.

2.- Aparato según la reivindicación 1, caracterizado porque comprende al menos 100, preferentemente al menos 500, más preferentemente al menos 1.000, de primeras y segundas salidas por metro cuadrado de sección transversal de la zona de

reacción.

3.- Aparato según la reivindicación 1 o 2, caracterizado porque el primer medio de suministro comprende al menos una primera entrada para suministrar un primer reactante gaseoso a por lo menos un primer colector y una pluralidad de tubos de inyección que salen de dicho primer colector para suministrar el primer reactante gaseoso, y el segundo medio de suministro comprende al menos una segunda entrada para suministrar un segundo reactante gaseoso a por lo menos un segundo colector y una pluralidad de conductos que salen de dicho segundo colector para suministrar el segundo reactante gaseoso,

porque el segundo colector está situado aguas abajo del primer colector con respecto al flujo del primer reactante gaseoso,

porque la zona de resistencia es porosa, está situada aguas abajo del segundo colector con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con los conductos que salen del segundo colector,

porque la zona de reacción está situada aguas abajo de la zona de resistencia con respecto al flujo de los primero y segundo reactantes gaseosos y está en comunicación fluídica con la zona de resistencia, y

porque cada conducto comprende un extremo aguas arriba que sale del segundo colector y un extremo aguas abajo en comunicación fluídica con la zona de resistencia y en donde los tubos de inyección que salen del primer colector están dispuestos de manera que los mismos se extienden a través del segundo colector y se proyectan axialmente al interior del extremo aguas arriba de los conductos.

4.- Aparato según la reivindicación 3, caracterizado porque comprende también una primera zona de enfriamiento que contacta con el extremo aguas abajo de la pluralidad de conductos que salen del segundo colector, dispuesta de manera

que se enfríe el extremo aguas abajo de la pluralidad de conductos.

5.- Aparato según la reivindicación 3 o 4, caracterizado porque el primer colector es una primera cámara y el segundo colector es una segunda cámara y porque los tubos de inyección que salen de la primera cámara forman una pluralidad de pasadizos alargados que se extienden a través de la segunda cámara y van a parar al extremo aguas arriba de la pluralidad de conductos que salen del segundo colector.

6.- Aparato según cualquiera de las reivindicaciones 3 a 5, caracterizado porque los tubos de inyección finalizan en una tobera que proporciona una restricción en la abertura, y que preferentemente tiene un diámetro interno del orden de 0,5 a 3 mm, tal como entre 1 y 2 mm.

7.- Aparato según cualquiera de las reivindicaciones 3 a 6, caracterizado porque están previstos restrictores del flujo entre la superficie exterior de los tubos de inyección y la superficie interior de los conductos, en una posición en o cerca de donde los tubos de inyección entran en los conductos en el extremo aguas arriba de los conductos.

8.- Aparato según la reivindicación 1 o 2, caracterizado porque el primer medio de suministro comprende al menos una primera entrada para suministrar un primer reactante gaseoso a por lo menos un primer colector y una pluralidad de primeros tubos de inyección que salen de dicho primer colector para suministrar el primer reactante gaseoso, y el segundo medio de suministro comprende al menos una segunda entrada para suministrar un segundo reactante gaseoso a por lo menos un segundo colector y una pluralidad de segundos tubos de inyección que salen de dichos segundo colector para suministrar el segundo reactante gaseoso,

porque cada tubo de inyección tiene una salida en el extremo distante del colector y que tiene una abertura en sección transversal de 1 mm^2 o menos y

porque las salidas de los primeros y segundos tubos de inyección están situadas de manera conjunta en una configuración entremezclada.

9.- Aparato según la reivindicación 8, caracterizado porque existen en total al menos 10.000 de los primeros y segundos tubos de inyección por metro cuadrado.

10.- Aparato según la reivindicación 8 o 9, caracterizado porque las salidas de los tubos de inyección están situadas todas ellas según una configuración esencialmente plana.

11.- Aparato según cualquiera de las reivindicaciones 8 a 10, caracterizado porque cada tubo de inyección tiene una salida en el extremo distante del colector y que tiene una abertura en sección transversal de 0,5 mm^2 o menos, más preferentemente de 0,2 mm^2 o menos, tal como de 0,1 mm^2 o menos.

12.- Aparato según cualquiera de las reivindicaciones 8 a 11, caracterizado porque los tubos de inyección están formados como pasadizos en un bloque aglomerado por difusión.

13.- Aparato según cualquiera de las reivindicaciones anteriores, caracterizado porque comprende una zona de enfriamiento del producto aguas abajo de la zona de reacción, de manera que los productos gaseosos pueden ser enfriados tras salir de la zona de reacción.

14.- Aparato según cualquiera de las reivindicaciones anteriores, caracterizado porque la zona de resistencia tiene un coeficiente de gradiente de presión inercial en promedio de 1.000-5.000/m, con preferencia de 2.000-4.000/m, tal como de 2.500-3.500/m.

15.- Procedimiento para la producción de una mono-olefina utilizando el aparato según la reivindicación 1 o 2, caracterizado porque comprende:

pasar un gas que contiene oxígeno al interior de un primer medio de

suministro y pasar un hidrocarburo parafínico gaseoso al interior de un segundo medio de suministro, de manera que el hidrocarburo parafínico gaseoso se pone en contacto de una forma esencialmente paralela y se mezcla con el gas que contiene oxígeno,

pasar la mezcla gaseosa a una zona de reacción por vía de una zona de resistencia porosa y

quemar parcialmente la mezcla gaseosa en la zona de reacción, preferentemente en presencia de un catalizador capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir la mono-olefina.

16.- Procedimiento para la producción de una mono-olefina utilizando el aparato según cualquiera de las reivindicaciones 3 a 7, caracterizado porque comprende:

pasar un gas que contiene oxígeno al interior de un primer colector e inyectar el gas que contiene oxígeno por vía de una pluralidad de tubos de inyección al interior de una pluralidad de conductos,

pasar un hidrocarburo parafínico gaseoso por vía de un segundo colector al interior de la pluralidad de conductos, en donde el hidrocarburo parafínico gaseoso se pone en contacto de una forma esencialmente paralela y se mezcla con el gas que contiene oxígeno,

pasar la mezcla gaseosa a una zona de reacción por vía de una zona de resistencia porosa y

quemar parcialmente la mezcla gaseosa en la zona de reacción, preferentemente en presencia de un catalizador que es capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir la mono-olefina.

17.- Procedimiento para la producción de una mono-olefina utilizando el aparato según cualquiera de las reivindicaciones 8 a 12, caracterizado porque comprende:

pasar un gas que contiene oxígeno desde al menos una primera entrada por vía de al menos un primer colector a una pluralidad de primeros tubos de inyección y pasar un hidrocarburo parafínico gaseoso desde al menos una segunda entrada por vía de al menos un segundo colector a una pluralidad de segundos tubos de inyección, en donde cada tubo de inyección tiene una salida en el extremo distante del colector y que tiene una abertura en sección transversal de 1 mm^2 o menos, y en donde las salidas de los primeros y segundos tubos de inyección están situadas de manera conjunta según una configuración entremezclada,

pasar la mezcla gaseosa a una zona de reacción por vía de una zona de resistencia porosa y

quemar parcialmente la mezcla gaseosa en la zona de reacción, preferentemente en presencia de un catalizador que es capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir la mono-olefina.

18.- Procedimiento según cualquiera de las reivindicaciones 15 a 17, caracterizado porque el hidrocarburo parafínico gaseoso es etano, propano o butano, opcionalmente en mezcla con otros hidrocarburos y opcionalmente con otros materiales, tal como metano, nitrógeno, monóxido de carbono, dióxido de carbono, vapor de agua o hidrógeno.

19.- Procedimiento según cualquiera de las reivindicaciones 15 a 18, caracterizado porque la relación del hidrocarburo parafínico gaseoso a la mezcla gaseosa que contiene oxígeno es de 5 a 20 veces la relación estequiométrica de

hidrocarburo a gas que contiene oxígeno para la combustión completa a dióxido de carbono y agua, preferentemente de 5 a 10 veces la relación estequiométrica de hidrocarburo a gas que contiene oxígeno.

20.- Procedimiento según cualquiera de las reivindicaciones 15 a 19, caracterizado porque la presión en las primeras y segundas entradas es preferentemente de 10-50 barg, más preferentemente de 20-40 barg y convenientemente de 25-35 barg.

21.- Procedimiento según cualquiera de las reivindicaciones 15 a 20, caracterizado porque la corriente gaseosa de producto de la zona de reacción se enfría rápidamente en una zona de enfriamiento del producto, preferentemente inyectando un condensado en la corriente gaseosa de producto en múltiples puntos, de manera que la vaporización del condensado enfríe a la corriente gaseosa de producto.

RESUMEN

La presente invención proporciona un diseño de reactor que permite realizar un procedimiento de cracking auto-térmico a cualquier presión adecuada, en donde los reactantes gaseosos se precalientan por separado antes de su mezcla y luego se ofrecen a la zona de reacción de una manera uniformemente distribuida. En particular, la presente invención se refiere a un aparato para hacer reaccionar un primer reactante gaseoso con un segundo reactante gaseoso para formar un producto gaseoso, en donde el aparato comprende al menos un primer medio de suministro para el primer reactante gaseoso, al menos un segundo medio de suministro para el segundo reactante gaseoso, una zona de resistencia y una zona de reacción, que preferentemente comprende un catalizador, en donde el primer medio de suministro comprende una pluralidad de primeras salidas para el suministro del primer reactante gaseoso y el segundo medio de suministro comprende una pluralidad de segundas salidas para el suministro del segundo reactante gaseoso, la zona de resistencia es porosa, la zona de reacción está situada aguas abajo de la zona de resistencia con respecto al flujo de los primero y segundo reactantes gaseosos y en donde el primer medio de suministro y el segundo medio de suministro están dispuestos de manera que el primer gas y el segundo gas se ponen en contacto de una forma esencialmente paralela y se mezclan antes de entrar en contacto con la zona de resistencia. La presente invención proporciona también un procedimiento para la producción de una mono-olefina utilizando dicho aparato.

REIVINDICACIONES (Modificadas)

1.- Procedimiento para la producción de una mono-olefina por reacción de un gas que contiene oxígeno con un hidrocarburo parafínico gaseoso para formar dicha mono-olefina, cuyo procedimiento utiliza un aparato que comprende un primer medio de suministro que comprende una pluralidad de primeras salidas para el suministro del gas que contiene oxígeno, y un segundo medio de suministro que comprende una pluralidad de segundas salidas para el suministro del hidrocarburo parafínico gaseoso, una zona de resistencia y una zona de reacción,

en donde la zona de resistencia es porosa, está situada aguas abajo de los primero y segundo medios de suministro con respecto al flujo del gas que contiene oxígeno y del hidrocarburo parafínico gaseoso y está en comunicación fluídica con los primero y segundo medios de suministro, la zona de reacción está situada aguas abajo de la zona de resistencia con respecto al flujo del gas que contiene oxígeno y del hidrocarburo parafínico gaseoso y está en comunicación fluídica con la zona de resistencia, y en donde el primer medio de suministro y el segundo medio de suministro están dispuestos de manera que el primer gas y el segundo gas se ponen en contacto de una forma esencialmente paralela y se mezclan antes de entrar en contacto con la zona de resistencia,

caracterizándose el procedimiento porque comprende:

pasar el gas que contiene oxígeno al interior de dicho primer medio de suministro y pasar el hidrocarburo parafínico gaseoso al interior de dicho segundo medio de suministro, de manera que el hidrocarburo parafínico gaseoso se pone en contacto de una forma esencialmente paralela y se mezcla con el gas que contiene oxígeno,

pasar la mezcla gaseosa a la zona de reacción por vía de la zona de resistencia

porosa y

quemar parcialmente la mezcla gaseosa en la zona de reacción en presencia de un catalizador capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir la mono-olefina.

2.- Procedimiento según la reivindicación 1, caracterizado porque el aparato comprende al menos 100, preferentemente al menos 500, con suma preferencia al menos 1.000, primeras y segundas salidas por metro cuadrado de la sección transversal de la zona de reacción.

3.- Procedimiento según la reivindicación 1 o 2, caracterizado porque el aparato comprende una zona de enfriamiento de producto aguas abajo de la zona de reacción, en donde la corriente gaseosa producto se enfría rápidamente en la zona de enfriamiento de producto mediante inyección de un condensado en la corriente gaseosa producto en múltiples puntos, de manera que la vaporización del condensado enfría la corriente gaseosa producto.

4.- Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque la temperatura de la corriente gaseosa producto se reduce a menos de 800° C en el plazo de 60 ms después de salir de la zona de reacción.

5.- Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque la zona de resistencia tiene un coeficiente de gradiente de presión inercial media comprendido entre 100-500/m, con preferencia entre 2.000-4.000/m, tal como entre 2.500-3.500/m.

6.- Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque el hidrocarburo parafínico gaseoso es etano, propano o butano, opcionalmente en mezcla con otros hidrocarburos y opcionalmente con otros materiales, por ejemplo metano, nitrógeno, monóxido de carbono, dióxido de

carbono, vapor de agua o hidrógeno.

7.- Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque la relación del hidrocarburo parafínico gaseoso a la mezcla de gas que contiene oxígeno es de 5 a 20 veces la relación estequiométrica de hidrocarburo a gas que contiene oxígeno para la combustión completa a dióxido de carbono y agua, preferentemente de 5 a 10 veces la relación estequiométrica de hidrocarburo a gas que contiene oxígeno.

8.- Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque la presión en las primeras y segundas salidas es con preferencia de 10-50 barg, con suma preferencia de 20-40 barg y convenientemente de 25-35 barg.

9.- Procedimiento según cualquiera de las reivindicaciones anteriores, en donde el primer medio de suministro comprende al menos una primera entrada para suministrar el gas que contiene oxígeno a por lo menos un primer colector y una pluralidad de tubos de inyección que salen desde dicho primer colector para el suministro del gas que contiene oxígeno, y el segundo medio de suministro comprende al menos una segunda entrada para suministrar el hidrocarburo parafínico gaseoso a por lo menos un segundo colector y una pluralidad de conductos que salen de dicho segundo colector para el suministro del hidrocarburo parafínico gaseoso,

en donde el segundo colector está situado aguas abajo del primer colector con respecto al flujo del gas que contiene oxígeno y

la zona de resistencia está situada aguas abajo del segundo colector con respecto al flujo del gas que contiene oxígeno y del hidrocarburo parafínico gaseoso y se encuentra en comunicación fluídica con los conductos que salen del segundo colector y

en donde cada conducto comprende un extremo aguas arriba que sale del segundo colector y un extremo aguas abajo en comunicación fluídica con la zona de resistencia y en donde los tubos de inyección que salen del primer colector están dispuestos de manera que los mismos se extienden a través del segundo colector y se proyectan axialmente al interior del extremo aguas arriba de los conductos, caracterizándose el procedimiento porque comprende:

pasar el gas que contiene oxígeno al interior del primer colector e inyectar el gas que contiene oxígeno, por vía de la pluralidad de tubos de inyección, al interior de la pluralidad de conductos, y

pasar el hidrocarburo parafínico gaseoso, por vía del segundo colector, al interior de la pluralidad de conductos en donde el hidrocarburo parafínico gaseoso se pone en contacto de una forma esencialmente paralela y se mezcla con el gas que contiene oxígeno.

10.- Procedimiento según la reivindicación 9, caracterizado porque el aparato comprende también una primera zona de enfriamiento que entra en contacto con el extremo aguas abajo de la pluralidad de conductos que salen del segundo colector y dispuesta de manera que se enfrían los extremos aguas abajo de la pluralidad de conducto.

11.- Procedimiento según la reivindicación 9 o 10, caracterizado porque el primer colector es una primera cámara y el segundo colector es una segunda cámara y los tubos de inyección que salen de la primera cámara forman una pluralidad de pasadizos alargados que se extienden a través de la segunda cámara al interior del extremos aguas arriba de la pluralidad de conductos que salen del segundo colector.

12.- Procedimiento según cualquiera de las reivindicaciones 9 o 11, caracterizado porque los tubos de inyección finalizan en una tobera que proporciona

una restricción en la abertura y que preferentemente tiene un diámetro interno entre 0,5 y 3 mm, tal como entre 1,0 y 2,0 mm.

13.- Procedimiento según cualquiera de las reivindicaciones 9 o 12, caracterizado porque están previstos restrictores del flujo entre la superficie exterior de los tubos de inyección y la superficie interior de los conductos, en una posición en o cerca de donde los tubos de inyección entran en los conductos en el extremo aguas arriba de los conductos.

14.- Procedimiento según cualquiera de las reivindicaciones 1 o 8, en donde el primer medio de suministro comprende al menos una primera entrada para suministrar el gas que contiene oxígeno a por lo menos un primer colector y una pluralidad de primeros tubos de inyección que salen de dicho primer colector para el suministro del gas que contiene oxígeno, y el segundo medio de suministro comprende al menos una segunda entrada para el suministro del hidrocarburo parafínico gaseoso a por lo menos un segundo colector y una pluralidad de segundos tubos de inyección que salen de dicho segundo colector para el suministro del hidrocarburo parafínico gaseoso,

en donde cada tubo de inyección tiene una salida en el extremo distante del colector y que tiene una abertura en sección transversal de 1 mm^2 o menos y

en donde las salidas de los primeros y segundos tubos de inyección están situadas de forma conjunta en una configuración entremezclada,

caracterizándose el procedimiento porque comprende:

pasar el gas que contiene oxígeno desde al menos una primera entrada por vía de al menos un primer colector a la pluralidad de primeros tubos de inyección y pasar el hidrocarburo parafínico gaseoso desde al menos una segunda entrada, por vía de al menos un segundo colector, a la pluralidad de segundos tubos de inyección, de

manera que el hidrocarburo parafínico gaseoso se pone en contacto de un modo esencialmente paralelo con el gas que contiene oxígeno y se mezcla con este último.

15.- Procedimiento según la reivindicación 14, caracterizado porque existen al menos 100.000 de primeros y segundos tubos de inyección en total por metro cuadrado.

16.- Procedimiento según la reivindicación 15, caracterizado porque existen al menos 1.000.000 de primeros y segundos tubos de inyección en total por metro cuadrado.

17.- Procedimiento según cualquiera de las reivindicaciones 14 a 16, caracterizado porque las salidas de los tubos de inyección están situadas todas ellas en una configuración esencialmente plana.

18.- Procedimiento según cualquiera de las reivindicaciones 14 a 17, caracterizado porque cada tubo de inyección tiene una salida en el extremo distante respecto del colector que tiene una abertura en sección transversal de 0,5 mm^2 o menos, más preferentemente de 0,2 mm^2 o menos, tal como 0,1 mm^2 o menos.

19.- Procedimiento según cualquiera de las reivindicaciones 14 a 18, caracterizado porque los tubos de inyección están formados como pasadizos en un bloque aglomerado por difusión.

20.- Aparato adecuado para hacer reaccionar un primer reactante gaseoso con un segundo reactante gaseoso para formar un producto gaseoso, siendo el aparato como el definido en cualquiera de las reivindicaciones 9 a 13.

21.- Aparato adecuado para hacer reaccionar un primer reactante gaseoso con un segundo reactante gaseoso para formar un producto gaseoso, siendo el aparato como el definido en cualquiera de las reivindicaciones 14 a 19.

Fig.1

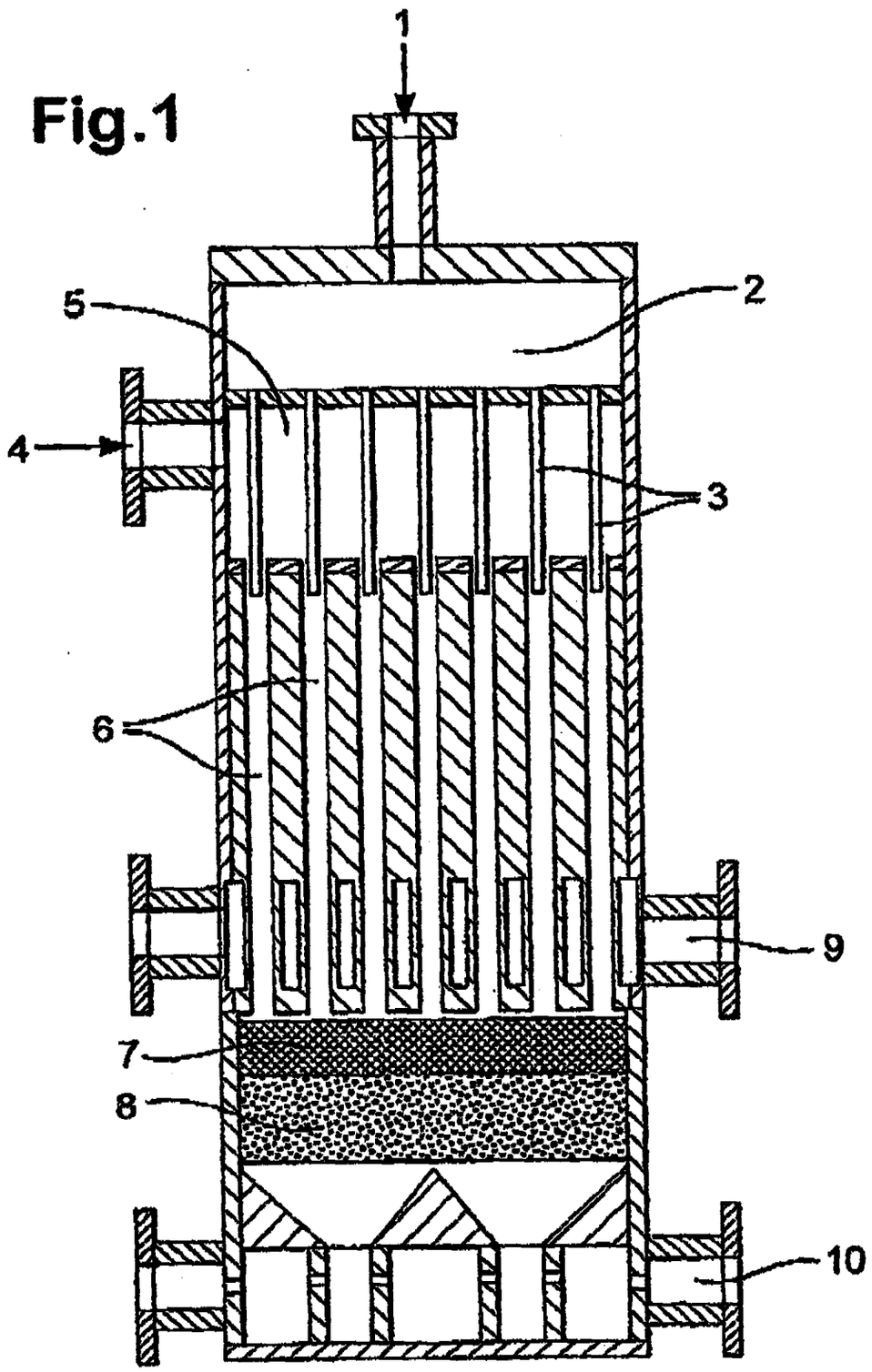


Fig.2a

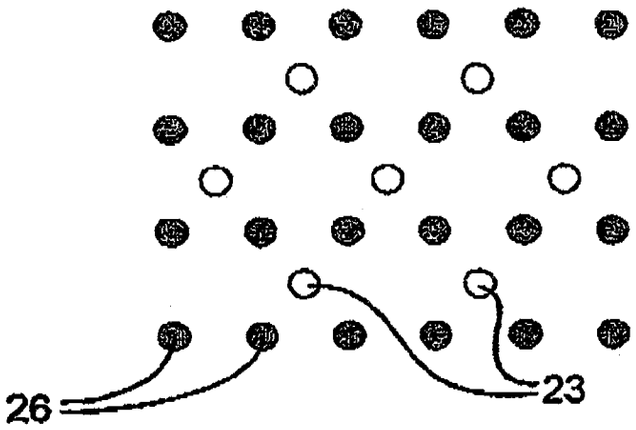
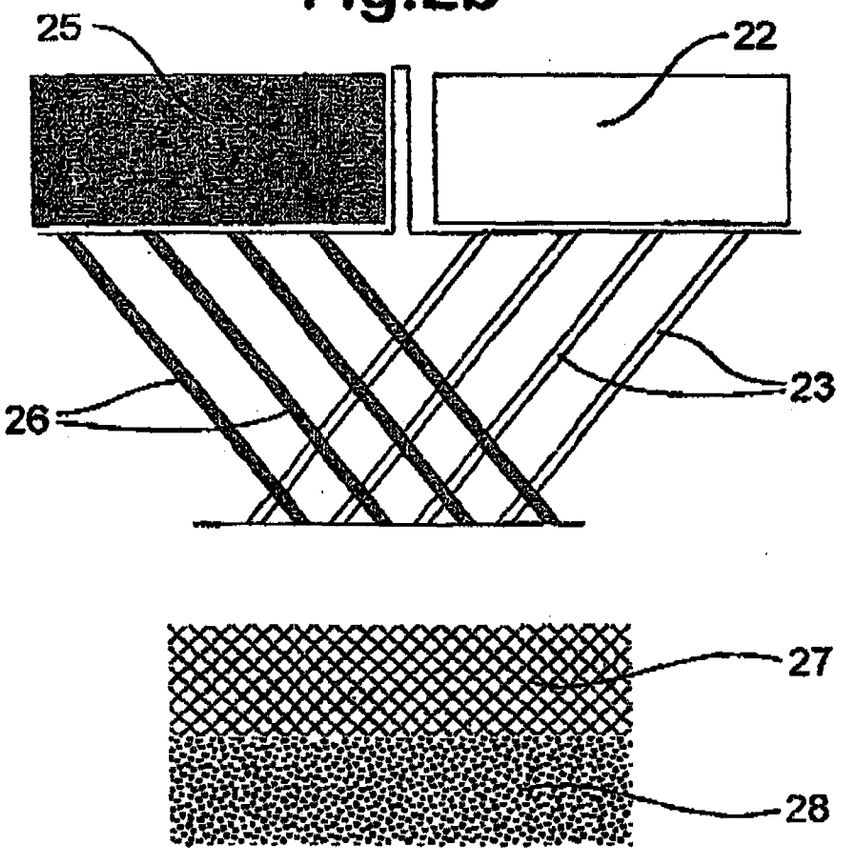


Fig.2b



PATENT COOPERATION TREATY

SES/AHT 62

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

HYMERS, Ronald, Robson
BP International Limited
Patents & Agreements
Chertsey Road
Middlesex TW16 7LN
GRANDE BRETAGNE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	10.02.2005
Applicant's or agent's file reference 9983	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB2004/000488	06.02.2004	18.02.2003

Applicant
BP CHEMICALS LIMITED et al.

1. 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.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. 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.

4. **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:	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Parriche, S Tel. +49 89 2399-7890

Form PCT/IPEA/416 (January 2004)

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 9983	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/GB2004/000488	International filing date *(day/month/year)* 06.02.2004	Priority date *(day/month/year)* 18.02.2003
International Patent Classification (IPC) or national classification and IPC C07C5/48		
Applicant BP CHEMICALS LIMITED et al.		

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 4 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 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 computer readable 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 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 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	Date of completion of this report
24.08.2004	10.02.2005
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 Kleidernigg, O Telephone No. +49 89 2399-2143

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/GB2004/000488

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, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

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	
1-17	as originally filed
Claims, Numbers	
1-21	as originally filed
Drawings, Sheets	
1/2-2/2	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)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/GB2004/000488

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	1-21
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-21
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (SEPARATE SHEET)

International application No.
PCT/GB2004/000488

Section V

The present application is directed to an apparatus for reacting a first gaseous reactant with a second gaseous reactant to form a gaseous product; wherein the apparatus comprises supply means for the first and the second gaseous reactant and both supply means comprise a plurality of outlets; a porous resistance zone and a reaction zone. Further the supply means are arranged in a manner that the first and the second gas are contacted in essentially parallel manner (claims 1-14). The second embodiment is directed to a process for the production of monoolefins using the apparatus as claimed (claims 15-21).

WO 01/83405 (D1) represents the closest prior art and differs from the matter of the present application insofar, that the features of "both supply means comprise a plurality of outlets" and "porous resistance zone" is not disclosed.

The technical problem maybe regarded as the provision of an improved auto thermal cracking reactor.

The solution is given in claim 1 and concerns the plurality of outlets of the supply means as well as the fact that the resistance zone is porous. This reactor design leads to a reduced time scale between forming the mixture of the two gaseous reactants and contacting the mixture with the catalyst. This was problematic with former reactor designs due to flammability constrains. However, the solution proposed by the present application is not deducible for the skilled person in the art from the presently available prior art.

Consequently the subject matter of claims 1-21 fulfills the criteria of Article 33(2) and (3) PCT.

Section VII

The closest prior art of D1 should be mentioned in the description.

Claims:

1. A process for the production of a mono-olefin by reacting an oxygen containing gas with a gaseous paraffinic hydrocarbon to form said mono-olefin, which process utilizes an apparatus which comprises a first supply means which comprises a plurality of first outlets for delivery of the oxygen containing gas, and a second supply means which comprises a plurality of second outlets for delivery of the gaseous paraffinic hydrocarbon, a resistance zone and a reaction zone,

wherein the resistance zone is porous, is positioned downstream of the first and second supply means with respect to the flow of the oxygen containing gas and the gaseous paraffinic hydrocarbon and is in fluid communication with the first and second supply means, the reaction zone is positioned downstream of the resistance zone with respect to the flow of the oxygen containing gas and the gaseous paraffinic hydrocarbon and is fluid communication with the resistance zone, and wherein the first supply means and the second supply means are arranged such that the first gas and the second gas are contacted in an essentially parallel manner and mixed prior to contacting the resistance zone,

which process comprises:

passing oxygen containing gas into said first supply means and passing gaseous paraffinic hydrocarbon into said second supply means, such that the gaseous paraffinic hydrocarbon is contacted in an essentially parallel manner and mixed with the oxygen-containing gas,

passing the gaseous mixture to the reaction zone via the porous resistance zone and

partially combusting the gaseous mixture in the reaction zone in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability, to produce the mono-olefin.

2. The process according to claim 1, wherein the apparatus comprises at least 100, preferably at least 500, most preferably at least 1000, first and second outlets per metre squared of the transverse cross section of the reaction zone.

3. The process according to claim 1 or claim 2 wherein the apparatus comprises a product cooling zone downstream of the reaction zone, wherein the gaseous product stream is rapidly cooled in the product cooling zone by injecting a condensate into the gaseous product stream at multiple points such that the vaporisation of the condensate cools the gaseous product stream.

4. The process according to any one of the preceding claims wherein the temperature of the gaseous product stream is reduced to less than 800°C within 60ms from exiting the reaction zone.

5. The process according to any one of the preceding claims, wherein the resistance zone has an average inertial pressure gradient coefficient of between 1000-5000/m, preferably between 2000-4000/m, such as between 2500-3500/m.

6. The process as claimed in any one of the preceding claims, wherein the gaseous paraffinic hydrocarbon is ethane, propane or butane, optionally in admixture with other hydrocarbons and optionally with other materials, for example methane, nitrogen, carbon monoxide, carbon dioxide, steam or hydrogen.

7. A process as claimed in any one of the preceding claims, wherein the ratio of the gaseous paraffinic hydrocarbon to the oxygen-containing gas mixture is from 5 to 20 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas for complete combustion to carbon dioxide and water, preferably from 5 to 10 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas.

8. A process as claimed in any one of the preceding claims, wherein the pressure at the first and second inlets is preferably between 10-50barg, most preferably between 20-40barg, and advantageously between 25-35barg.

9. The process according to any one of the preceding claims, wherein the first supply means comprises at least one first inlet for supplying the oxygen containing gas to at least one first manifold and a plurality of injection tubes exiting said first manifold for delivery of the oxygen containing gas, and the second supply means comprises at least one second inlet for supplying the gaseous paraffinic hydrocarbon

to at least one second manifold and a plurality of conduits exiting said second manifold for delivery of the gaseous paraffinic hydrocarbon,

wherein the second manifold is positioned downstream of the first manifold with respect to the flow of the oxygen containing gas, and

the resistance zone is positioned downstream of the second manifold with respect to the flow of the oxygen containing gas and the gaseous paraffinic hydrocarbon and is in fluid communication with the conduits exiting the second manifold,

and wherein each conduit comprises an upstream end exiting the second manifold and a downstream end in fluid communication with the resistance zone and wherein the injection tubes exiting the first manifold are arranged such that they extend through the second manifold and project axially into the upstream end of the conduits,

which process comprises

passing the oxygen containing gas into the first manifold and injecting the oxygen-containing gas via the plurality of injection tubes into the plurality of conduits,

and passing the gaseous paraffinic hydrocarbon via the second manifold into the plurality of conduits wherein the gaseous paraffinic hydrocarbon is contacted in an essentially parallel manner and mixed with the oxygen-containing gas.

10. The process according to claim 9, which the apparatus also comprises a first cooling zone contacting the downstream end of the plurality of conduits exiting the second manifold arranged such that the downstream ends of the plurality of conduits are cooled.

11. The process according to claim 9 or claim 10, wherein the first manifold is a first chamber and the second manifold is a second chamber and the injection tubes exiting the first chamber form a plurality of elongated passageways extending through the second chamber into the upstream end of the plurality of conduits exiting the second manifold.

12. The process according to any one of claims 9 to 11, wherein the injection tubes end in a nozzle which provides a restriction at the opening, and which preferably has an internal diameter in the range between 0.5 to 3.0mm, such as between 1.0 to 2.0mm.

13. The process according to any one of claims 9 to 12, wherein flow restrictors are provided between the outer surface of the injection tubes and the inner surface of the conduits, at a location at or close to where the injection tubes enter the conduits at the upstream end of the conduits.

14. A process according to any one of claims 1 to 8, wherein the first supply means comprises at least one first inlet for supplying the oxygen containing gas to at least one first manifold and a plurality of first injection tubes exiting said first manifold for delivery of the oxygen containing gas, and the second supply means comprising at least one second inlet for supplying the gaseous paraffinic hydrocarbon to at least one second manifold and a plurality of second injection tubes exiting said second manifold for delivery of the gaseous paraffinic hydrocarbon,

wherein each injection tube has an exit at the end remote from the manifold and which has a cross-sectional opening of $1mm^2$ or less, and

wherein the exits from the first and second injection tubes are co-located in an intermixed configuration,

which process comprises:

passing the oxygen containing gas from the least one first inlet via the least one first manifold to the plurality of first injection tubes and passing the gaseous paraffinic hydrocarbon from the least one second inlet via the least one second manifold to the plurality of second injection tubes such that the gaseous paraffinic hydrocarbon is contacted in an essentially parallel manner and mixed with the oxygen-containing gas.

15. The process according to claim 14, wherein there are at least 100000 first and second injection tubes in total per square metre.

16. The process according to claim 15, wherein there are at least 1000000 first and second injection tubes in total per square metre.

17. The process according to any one of claims 14 to 16, wherein the exits from the injection tubes are all located in an essentially planar configuration.

18. The process according to any one of claims 14 to 17, wherein each injection tube has an exit at the end remote from the manifold which has a cross-sectional opening of $0.5mm^2$ or less, more preferably 0.2 mm^2 or less, such as $0.1mm^2$ or less.

19. The process according to any one of claims 14 to 18, wherein the injection tubes are formed as passageways in a diffusion bonded block.

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)* 9983

Box No. I TITLE OF INVENTION

AUTO THERMAL CRACKING REACTOR

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.)*

BP CHEMICALS LIMITED
Britannic House
1 Finsbury Circus
London EC2M 7BA
United Kingdom

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.)*

COLMAN, Derek Alan
21 Knoll Road
Fleet
Hampshire, GU51 4PR
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: 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

☒ 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.)*

HYMERS, Ronald Robson
BP International Limited
Patents & Agreements
Chertsey Road, Sunbury on Thames
Middlesex, TW16 7LN
United Kingdom

Telephone No.
01932 763205

Facsimile No.
01932 762388

Teleprinter No.

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.

73

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

If none of the following sub-boxes is used, this sheet should not be included in the request.

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.)*

MATTHEWMAN, Michael John Alexander
25 Old Pasture Road
Frimley
Surrey, GU16 8SA
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: 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

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.)*

REID, Ian Allan Beattie
12 Crowthorne Close
Southfields
London, SW18 5RX
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: 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

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.)*

WILLIAMS, Vaughan Clifford
88 Shaftesbury Crescent
Laleham, Staines
Middlesex, TW18 1QW
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: 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

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.)*

WOODFIN, William Terence
Chalk Cottage, Chapel Street
North Waltham
Hampshire, RG25 2BZ
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: 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

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

74

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

☐ 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 be used to exclude (irrevocably) the designations concerned in order to avoid the ceasing of the effect, under the national law, of an earlier national application from which priority is claimed. See the Notes to Box No. V as to the consequences of such national law provisions in these and certain other 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) 18/02/2003	0303723.1	GB		
item (2) 22/12/2003	0329710.8	GB		
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) :	2
☐	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 Chemicals Limited is entitled to apply for and be granted a patent by virtue of the following :

BP Chemicals Limited is entitled as employer of the inventors Derek Alan COLMAN, Michael John Alexander MATTHEWMAN, Ian Allan Beattie REID, Vaughan Clifford WILLIAMS and William Terence WOODFIN

This declaration is made for the purposes of all designations (except the designation of the United States of America)

☐ 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 51*bis*.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 26*ter*).

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: Derek Alan COLMAN

Residence: Hampshire, United Kingdom
(city and either US state, if applicable, or country)

Mailing Address: 21 Knoll Road, Fleet, Hampshire, GU51 4PR, United Kingdom

.....

Citizenship: British

Inventor's Signature: ..... Date: .....
(if not contained in the request, or if declaration is corrected or added under Rule 26*ter* after the filing of the international application. The signature must be that of the inventor, not that of the agent)

(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26*ter* after the filing of the international application)

Name: Michael John Alexander MATTHEWMAN

Residence: Surrey, United Kingdom
(city and either US state, if applicable, or country)

Mailing Address: 25 Old Pasture Road, Frimley, Surrey, GU16 8SA, United Kingdom

.....

Citizenship: British

Inventor's Signature: ..... Date: .....
(if not contained in the request, or if declaration is corrected or added under Rule 26*ter* after the filing of the international application. The signature must be that of the inventor, not that of the agent)

(of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26*ter* after the filing of the international application)

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

Continuation of Box No. VIII (i) to (v) DECLARATION

If the space is insufficient in any of Boxes Nos. VIII (i) to (v) to furnish all the information, including in the case where more than two inventors are to be named in Box No. VIII (iv), in such case, write "Continuation of Box No. VIII ..." (indicate the item number of the Box) and furnish the information in the same manner as required for the purposes of the Box in which the space was insufficient. If additional space is needed in respect of two or more declarations, a separate continuation box must be used for each such declaration. If this Box is not used, this sheet should not be included in the request.

Name : Ian Allan Beattie REID

Residence : London, United Kingdom

Mailing Address : 12 Crowthorne Close, Southfields, London, SW18 5RX, United Kingdom

Citizenship : British

Signature_____ Date :

Name : Vaughan Clifford WILLIAMS

Residence : Middlesex, United Kingdom

Mailing Address : 88 Shaftesbury Crescent, Laleham, Staines, Middlesex, TW18 1QW, United Kingdom

Citizenship : British

Signature_____ Date :

Name : William Terence WOODFIN

Residence : Hampshire, United Kingdom

Mailing Address : Chalk Cottage, Chapel Street, North Waltham, Hampshire, RG25 2BZ, United Kingdom

Citizenship : British

Signature_____ Date :

78

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application **contains:**

(a) **in paper form,** the following number of sheets:

request (including declaration sheets)	:	7
description (excluding sequence listing and/or tables related thereto)	:	17
claims	:	5
abstract	:	1
drawings	:	2
Sub-total number of sheets	:	32
sequence listing	:	
tables related thereto	:	
(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (c) below)		
Total number of sheets	:	32

(b) ☐ **only in computer readable form** (Section 801(a)(i))
- (i) ☐ sequence listing
- (ii) ☐ tables related thereto

(c) ☐ **also in computer readable form** (Section 801(a)(ii))
- (i) ☐ sequence listing
- (ii) ☐ tables related thereto

Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the
- ☐ sequence listing: .....
- ☐ tables related thereto: .....

(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)

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
1. ☒ fee calculation sheet	:	1
2. ☒ original separate power of attorney	:	1
3. ☒ original general power of attorney	:	1
4. ☐ copy of general power of attorney; reference number, if any:	:	
5. ☐ statement explaining lack of signature	:	
6. ☐ priority document(s) identified in Box No. VI as item(s):	:	
7. ☐ translation of international application into *(language)*:	:	
8. ☐ separate indications concerning deposited microorganism or other biological material	:	
9. ☐ sequence listing in computer readable form *(indicate type and number of carriers)*		
(i) ☐ copy submitted for the purposes of international search under Rule 13*ter* only (and not as part of the international application)	:	
(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 13*ter*	:	
(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column	:	
10. ☐ tables in computer readable form related to sequence listing *(indicate type and number of carriers)*		
(i) ☐ copy submitted for the purposes of international search under Section 802(b-*quater*) only (and not as part of the international application)	:	
(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*)	:	
(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column	:	
11. ☒ other *(specify)*: 2377	:	2

Figure of the drawings which should accompany the abstract: 1

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).

PREECE, Michael
Additional Authorised Agent

M. Pree

For receiving Office use only

1. Date of actual receipt of the purported international application:
2. Drawings: ☐ received: ☐ not received:
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:

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

HYMERS, Ronald, Robson
BP International Limited
Patents & Agreements
Chertsey Road
Sunbury on Thames
Middlesex TW16 7LN
United Kingdom

8 APR 2004

Date of mailing (day/month/year) 31 March 2004 (31.03.2004)	
Applicant's or agent's file reference 9983	IMPORTANT NOTIFICATION
International application No. PCT/GB2004/000488	International filing date (day/month/year) 06 February 2004 (06.02.2004)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 18 February 2003 (18.02.2003)
Applicant BP CHEMICALS LIMITED et al	

1. 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).

2. (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.

3. (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 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
18 Febr 2003 (18.02.2003)	0303723.1	GB	05 Marc 2004 (05.03.2004)
22 Dece 2003 (22.12.2003)	0329710.8	GB	22 Marc 2004 (22.03.2004)

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

Facsimile No. (41-22) 338.89.65

Authorized officer
Farid ABBOU

Telephone No. (41-22) 338 8169

81

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 9983
International application No. PCT/GB04/00488	International filing date *(day/month/year)* 06/02/2004	(Earliest) Priority date *(day/month/year)* 18/02/2003
Title of invention Auto thermal cracking reactor		

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.)*	Telephone No.
BP CHEMICALS LIMITED Chertsey Road, Sunbury on Thames, Middlesex, TW16 7BP, United Kingdom (formerly of Britannic House, 1 Finsbury Circus, London, EC2M 7BA, United Kingdom)	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

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.)*
COLMAN, Derek Alan
21 Knoll Road
Fleet
Hampshire GU51 4PR
United Kingdom

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.)*
MATTHEWMAN, Michael John Alexander
25 Old Pasture Road
Frimley
Surrey GU16 8SA
United Kingdom

State *(that is, country)* of nationality: GB	State *(that is, country)* of residence: GB

☒ Further applicants are indicated on a continuation sheet.

International application No.
PCT/GB04/00488

Continuation of Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet should not be included in the demand.

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.)*

REID, Ian Allan Beattie
12 Crowthorne Close
Southfields
London SW18 5RX
United Kingdom

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
GB	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.)*

WILLIAMS, Vaughan Clifford
88 Shaftesbury Crescent
Laleham
Staines
Middlesex TW18 1QW
United Kingdom

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
GB	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.)*

WOODFIN, William Terence
Chalk Cottage
Chapel Street
North Waltham
Hampshire RG25 2BZ
United Kingdom

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
GB	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.)*

State *(that is, country)* of nationality:	State *(that is, country)* of residence:

☐ Further applicants are indicated on another continuation sheet.

International application No.
PCT/GB04/00488

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

The following person is [X] agent [ ] common representative

and [X] 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.)*

HYMERS, Ronald Robson
BP International Limited
Patents & Agreements
Chertsey Road, Sunbury on Thames,
Middlesex, TW16 7LN, United Kingdom

Telephone No.
01932 763205

Facsimile No.
01932 762388

Teleprinter No.

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:**

[X] the international application as originally filed

the description [X] as originally filed
[ ] as amended under Article 34

the claims [X] as originally filed
[ ] as amended under Article 19 (together with any accompanying statement)
[ ] as amended under Article 34

the drawings [X] as originally filed
[ ] as amended under Article 34

2. [ ] The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. [ ] The applicant wishes the start of the international preliminary examination **to be postponed** 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 54*bis*.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

[X] 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.

International application No.
PCT/GB04/00488

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:			For International Preliminary Examining Authority use only: received	not received
1. translation of international application	:	sheets	☐	☐
2. amendments under Article 34	:	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	:	sheets	☐	☐
6. other *(specify)*	:	sheets	☐	☐

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

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

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).

HYMERS, Ronald Robson
Authorised Agent

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 54*bis*.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 54*bis*.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 54*bis*.1(a), the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/GB04/00488	For International Preliminary Examining Authority use only
Applicant's or agent's file reference 9983	Date stamp of the IPEA
Applicant: BP Chemicals Limited, et al	

CALCULATION OF PRESCRIBED FEES

1. Preliminary examination fee	1530.00 P	
2. Handling fee *(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.)*	129.00 H	
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	1659.00 TOTAL	

MODE OF PAYMENT

- [x] 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)

IPEA/ EP

- [ ] 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.

Deposit Account No.: 28050129

Date: 23rd August 2004

Name: Christine Gravenell

Signature: CGravenell

PATENT COOPERATION TREATY

86

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

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

From the INTERNATIONAL BUREAU

To:

HYMERS, Ronald, Robson
BP International Limited
Patents & Agreements
Chertsey Road
Sunbury on Thames
Middlesex TW16 7LN
United Kingdom

Date of mailing (day/month/year)
11 November 2004 (11.11.2004)

Applicant's or agent's file reference
9983

IMPORTANT NOTIFICATION

International application No.
PCT/GB2004/000488

International filing date (day/month/year)
06 February 2004 (06.02.2004)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address
BP CHEMICALS LIMITED
Britannic House
1 Finsbury Circus
London EC2M 7BA
United Kingdom

State of Nationality: GB
State of Residence: GB
Telephone No.:
Facsimile No.:
Teleprinter No.:

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

[ ] the person [ ] the name [X] the address [ ] the nationality [ ] the residence

Name and Address
BP CHEMICALS LIMITED
Chertsey Road
Sunbury on Thames
Middlesex TW16 7BP
United Kingdom

State of Nationality: GB
State of Residence: GB
Telephone No.:
Facsimile No.:
Teleprinter No.:

3. Further observations, if necessary:

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

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No. (41-22) 338.89.65

Authorized officer
Peggy Steunenberg
Telephone No. (41-22) 338 9482

PATENT COOPERATION TREATY

87

PCT

From the INTERNATIONAL BUREAU

To:

HYMERS, Ronald, Robson
O & D Trading Limited
Patents and Agreements
Compass Point
79-87 Kingston Road
Staines, Middlesex TW18 1DT
United Kingdom

NOTIFICATION OF THE RECORDING OF A CHANGE

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

Date of mailing (day/month/year) 08 July 2005 (08.07.2005)	
Applicant's or agent's file reference 9983	IMPORTANT NOTIFICATION
International application No. PCT/GB2004/000488	International filing date (day/month/year) 06 February 2004 (06.02.2004)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
BP CHEMICALS LIMITED Chertsey Road Sunbury on Thames Middlesex TW16 7BP United Kingdom	GB	GB
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

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

[X] the person [ ] the name [ ] the address [ ] the nationality [ ] the residence

Name and Address	State of Nationality	State of Residence
O & D TRADING LIMITED Chertsey Road Sunbury on Thames Middlesex TW16 7BP United Kingdom	GB	GB
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:
Assignment.

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

[X] the receiving Office
[ ] the International Searching Authority
[ ] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Diana NISSEN (Fax 338 8270)
Facsimile No. (41-22) 338.89.65	Telephone No. (41-22) 338 8054

88

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

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

To:

HYMERS, Ronald, Robson
Innovene Europe Limited
European Patents Group
Compass Point
79-87 Kingston Road
Staines, Middlesex TW18 1DT
United Kingdom

Date of mailing (day/month/year)	
08 July 2005 (08.07.2005)	
Applicant's or agent's file reference	**IMPORTANT NOTIFICATION**
9983	
International application No.	**International filing date (day/month/year)**
PCT/GB2004/000488	06 February 2004 (06.02.2004)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
O & D TRADING LIMITED Chertsey Road Sunbury on Thames Middlesex TW16 7BP United Kingdom	GB	GB
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

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

[ ] the person [X] the name [ ] the address [ ] the nationality [ ] the residence

Name and Address	State of Nationality	State of Residence
INNOVENE EUROPE LIMITED Chertsey Road Sunbury on Thames Middlesex TW16 7BP United Kingdom	GB	GB
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:
All future correspondence should be sent to the address as indicated in the addressee box above.

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

[X] the receiving Office
[ ] the International Searching Authority
[ ] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Diana NISSEN (Fax 338 8270)
Facsimile No. (41-22) 338.89.65	Telephone No. (41-22) 338 8054

PATENT COOPERATION TREATY

PCT/GB2004/000488

From the INTERNATIONAL BUREAU

89

PCT

INFORMATION CONCERNING ELECTED OFFICES NOTIFIED OF THEIR ELECTION

(PCT Article 31(7) and Rule 61.3)

To:

HYMERS, Ronald, Robson
BP International Limited
Patents & Agreements
Chertsey Road
Sunbury on Thames
Middlesex TW16 7LN
ROYAUME-UNI

- 1 NOV 2004

Date of mailing *(day/month/year)*	
28 October 2004 (28.10.2004)	
Applicant's or agent's file reference	**IMPORTANT INFORMATION**
9983	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB2004/000488	06 February 2004 (06.02.2004)	18 February 2003 (18.02.2003)

Applicant

BP CHEMICALS LIMITED et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

   EP: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR
   National: BG, CA, CN, CZ, DE, JP, KP, KR, MN, NO, PL, RO, RU, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

   AP: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW
   EA: AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
   OA: BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
   National: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BR, BW, BY, BZ, CH, CO, CR, CU, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MW, MX, MZ, NA, NI, NZ, OM, PG, PH, PT, SC, SD, SE, SG, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW

3. Since the election(s) was (were) made before the expiration of 19 months from the priority date, the applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary report on patentability (Chapter II of the Patent Cooperation Treaty) (Article 36(3)(b) and Rule 74.1).

Some Offices have fixed time limits expiring later than the above-mentioned time limit. 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, the *PCT Newsletter* and the WIPO Internet site, updated regularly.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Nora Lindner
Facsimile No.+41 22 740 14 35	Facsimile No.+41 22 338 89 65

Form PCT/IB/332 (January 2004)

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
BP INTERNATIONAL LIMITED
Patents & Agreements
Attn. Hymers, Ronald Robson
Chertsey Road, Sunbury-on-Thames
Middlesex, TW16 7LN
UNITED KINGDOM

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

(PCT Rule 44.1)

Applicant's or agent's file reference 9983	Date of mailing *(day/month/year)* 24/05/2004
International application No. PCT/GB2004/000488	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
Applicant BP CHEMICALS LIMITED	International filing date *(day/month/year)* 06/02/2004

OFFICIAL ACTION

1. [x] 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 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

   Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Fascimile No.: (41-22) 740.14.35

   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 90*bis*.1 and 90*bis*.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 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Dominique Hundt

NOTES TO FORM PCT/ISA/220

91

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, 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.

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 (Administrative Instructions, 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.

92

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped),whether

(i) the claim is unchanged;

(ii) the claim is cancelled;

(iii) the claim is new;

(iv) the claim replaces one or more claims as filed;

(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."

2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."

3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."

4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international appplication is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

PCT

93

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
9983		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/GB2004/000488	06/02/2004	18/02/2003
Applicant		
BP CHEMICALS 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.

[X] 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, unless otherwise indicated under this item.
      [ ] The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 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 II).

3. [ ] **Unity of invention is lacking** (see Box III).

4. With regard to the **title**,
   [X] 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**,
   [X] 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 regards to the **drawings**,
   a. the figure of the **drawings** to be published with the abstract is Figure No. _____
      [ ] 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. [X] none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/000488

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C5/48 C07C11/02 B01J19/26

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)
IPC 7 C07C 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, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/83405 A (COLMAN DEREK ALAN ;HESKETH TREVOR JOHN (GB); WOODFIN WILLIAM TEREN) 8 November 2001 (2001-11-08) page 6, line 6 - page 7, line 21; page 11, line 33 - page 13, line 12; page 16, lines 28-31; figure 1; table 1	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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	Date of mailing of the international search report
11 May 2004	24/05/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kleidernigg, O

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB2004/000488

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0183405 A	08-11-2001	AU 9519001 A	12-11-2001
		BR 0110586 A	01-04-2003
		CA 2407831 A1	08-11-2001
		CN 1440373 T	03-09-2003
		EP 1278711 A1	29-01-2003
		WO 0183405 A1	08-11-2001
		JP 2003531876 T	28-10-2003
		NO 20025218 A	31-10-2002
		ZA 200208620 A	03-06-2003

PATENT COOPERATION TREATY

96

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43*bis*.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.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/GB2004/000488	06.02.2004	18.02.2003

International Patent Classification (IPC) or both national classification and IPC
C07C5/48, C07C11/02, B01J19/26

Applicant
BP CHEMICALS 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 43*bis*.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"). However, this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(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 three 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

Authorized Officer

Kleidernigg, O

Telephone No. +49 89 2399-2143

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/GB2004/000488

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 field, unless otherwise indicated under this item.

   ☐ This opinion has been established on the basis of a translation from the original language into the following language , which is the language of a translation furnished for the purposes of international search (under Rules 12.3 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:

   ☐ in written format

   ☐ in computer readable form

   c. time of filing/furnishing:

   ☐ contained in the international application as filed.

   ☐ filed together with the international application in computer readable 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 the 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/GB2004/000488

Box No. II Priority

1. ☒ The following document has not been furnished:

   ☒ copy of the earlier application whose priority has been claimed (Rule 43*bis*.1 and 66.7(a)).

   ☐ translation of the earlier application whose priority has been claimed (Rule 43*bis*.1 and 66.7(b)).

   Consequently it has not been possible to consider the validity of the priority claim. This opinion has nevertheless been established on the assumption that the relevant date is the claimed priority date.

2. ☐ This opinion has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid (Rules 43*bis*.1 and 64.1). Thus for the purposes of this opinion, the international filing date indicated above is considered to be the relevant date.

3. Additional observations, if necessary:

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

1. Statement

Novelty (N)	Yes:	Claims	1-21
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-21
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Section V

The present application is directed to an apparatus for reacting a first gaseous reactant with a second gaseous reactant to form a gaseous product, wherein the apparatus comprises supply means for the first and the second gaseous reactant and both supply means comprise a plurality of outlets; a porous resistance zone and a reaction zone. Further the supply means are arranged in a manner that the first and the second gas are contacted in essentially parallel manner (claims 1-14). The second embodiment is directed to a process for the production of monoolefins using the apparatus as claimed (claims 15-21).

WO 01/83405 (D1) represents the closest prior art and differs from the matter of the present application insofar, that the features of "both supply means comprise a plurality of outlets" and "porous resistance zone" is not disclosed.

The technical problem maybe regarded as the provision of an improved auto thermal cracking reactor.

The solution is given in claim 1 and concerns the plurality of outlets of the supply means as well as the fact that the resistance zone is porous. This reactor design leads to a reduced time scale between forming the mixture of the two gaseous reactants and contacting the mixture with the catalyst. This was problematic with former reactor designs due to flammability constrains. However, the solution proposed by the present application is not deducible for the skilled person in the art from the presently available prior art.

Consequently the subject matter of claims 1-21 fulfills the criteria of Article 33(2) and (3) PCT.

Section VII

The closest prior art of D1 should be mentioned in the description.

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 November 2001 (08.11.2001)

PCT

(10) International Publication Number
WO 01/83405 A1

(51) International Patent Classification[7]: C07B 41/00, C07C 5/48, C07D 303/04, C07C 69/15, C07D 307/89, C07C 253/26, C01B 3/36, C07D 307/33

(21) International Application Number: PCT/GB01/01898

(22) International Filing Date: 30 April 2001 (30.04.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0010693.0 3 May 2000 (03.05.2000) GB

(71) Applicant *(for all designated States except US)*: **BP CHEMICALS LIMITED** [GB/GB]; Britanic House, 1 Finsbury Circus, London EC2M 7BA (GB).

(72) Inventors; and

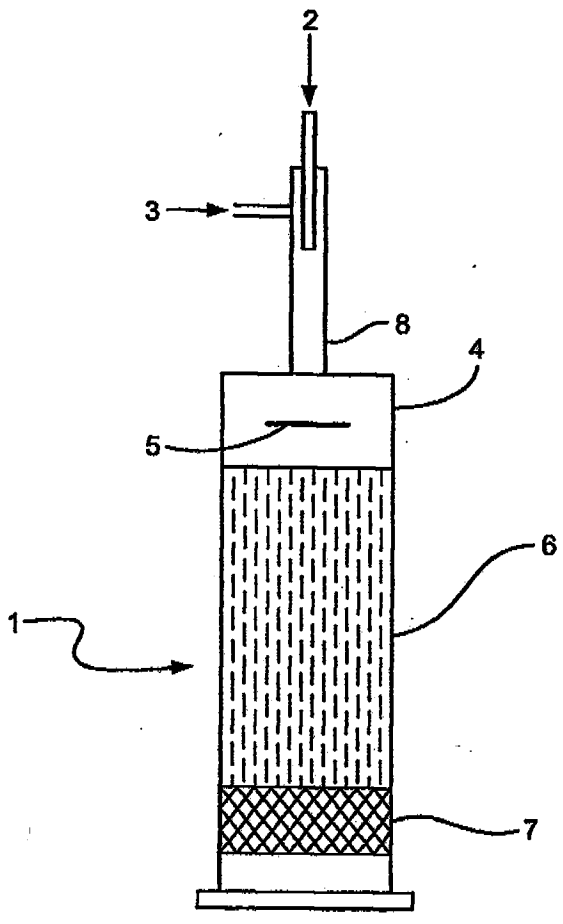
(75) Inventors/Applicants *(for US only)*: **COLMAN, Derek, Alan** [GB/GB]; 21 Knoll Road, Fleet, Hampshire GU13 8PR (GB). **HESKETH, Trevor, John** [GB/GB]; 2 Sarum Green, Waybridge, Surrey KT13 9RX (GB). **REID, Ian, Allan, Beattie** [GB/GB]; 12 Crowthorne Close, Southfields, London SW18 5RX (GB). **WOODFIN, William, Terence** [GB/GB]; Chalk Cottage, Chapel Street, North Waltham, Hampshire RG25 9NF (GB).

(74) Agent: **BROOKE, Caron**; BP International Limited, Patents & Agreements, Chertsey Road, Sunbury on Thames, Middlesex TW16 7LN (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,

[Continued on next page]

(54) Title: PROCESS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS



(57) Abstract: A process for the oxidation of a hydrocarbon, said process comprising partially oxidising in a reaction zone, a mixture comprising a hydrocarbon and an oxygen-containing gas in the presence of a catalyst whic his capable of supporting oxidation of the hydrocarbon, wherein prior to said partial oxidation, said mixture comprising the hydrocarbon and the oxygen-containing gas is passed through a heat exchanger. Preferably the heat exchanger is a compact heat exchanger. Prior to passage through the heat exchanger a mixture of hydrocarbon and oxygen-containing gas may be passed through a baffle zone which comprises a housing containing at least one baffle plate. In a preferred embodiment, the invention relates to a process for the production of an olefin such as ethylene by the catalytic oxidative dehydrogenation of a hydrocarbon or mixture of hydrocarbons.

WO 01/83405 A1

NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designationsAE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG)*

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*

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.

PROCESS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS

The present invention relates, in general, to the catalytic oxidation of hydrocarbons and, in particular, to the catalytic oxidative dehydrogenation of hydrocarbons to produce olefins.

Processes for the catalytic oxidation of hydrocarbons are well known, for example, the oxidation of methane to produce syngas; the oxidation of ethylene to produce ethylene oxide; the oxidation of ethylene and acetic acid to produce vinyl acetate; the production of maleic anhydride from the oxidation of butene, butane or benzene; the production of phthalic anhydride by the oxidation of naphthalene or o-xylene; the ammoxidation of propane to acrylonitrile.

The catalytic oxidative dehydrogenation of hydrocarbons is a known process for the production of olefins. An example of such a process is described in EP-A- 0 332 289. In this process, a hydrocarbon and an oxygen-containing gas are contacted with a catalyst, which is capable of supporting combustion beyond the fuel rich limit of flammability. The hydrocarbon is partially combusted, and the heat produced is used to drive the dehydrogenation of the hydrocarbon feed into olefins. Optionally, a hydrogen co-feed is also burned, and the heat produced by this combustion reaction is used to drive the dehydrogenation of the hydrocarbon.

Generally, in a catalytic oxidative dehydrogenation process, the reactants (hydrocarbon and an oxygen-containing gas) are passed over the catalyst directly to produce olefin product. Typically, the hydrocarbon is a saturated hydrocarbon such as a C_2- C_{10} saturated hydrocarbon, such as ethane or a mixture of saturated hydrocarbons such as a mixture of C_2-C_{10} hydrocarbons, naphtha or gas oil. The hydrocarbon may be gaseous or liquid at ambient temperature and pressure but is typically gaseous.

It is desirable in processes for the catalytic oxidation of hydrocarbons to have effective mixing of the reactants and/or uniform velocity profile of the reactant mixture prior to contact with the catalyst. However, although the reactants (hydrocarbon and oxygen-containing gas) may be pre-mixed prior to being introduced into the reactor, the velocity profile of the reactant mixture is often still non-uniform. Such a non-uniform velocity profile can lead to an unstable reaction. For example, high velocity gas mixtures over only part of the catalyst can lead to a decrease in selectivity. Where the oxidation reaction is one which is carried out close to its flammable limit, such as in the catalytic oxidative dehydrogenation of hydrocarbons, low velocity gas mixtures over only part of the catalyst can result in flash-backs.

Moreover, the heat generated by the oxidation reaction is generally not distributed evenly, reducing the efficiency of the oxidation process and resulting in potential loss of product.

We have now found that the above disadvantages may be alleviated by passing the reactants (hydrocarbon and an oxygen-containing gas) through a heat exchanger prior to contacting the reactants with the catalyst.

Accordingly, the present invention provides a process for the oxidation of a hydrocarbon said process comprising:

partially oxidising in a reaction zone, a mixture comprising a hydrocarbon and an oxygen-containing gas in the presence of a catalyst which is capable of supporting oxidation of the hydrocarbon, wherein prior to said partial oxidation, said mixture comprising the hydrocarbon and the oxygen-containing gas is passed through a heat exchanger.

The heat exchanger employed in the present process provides a pressure drop, which acts to even the velocity profile of the reactant mixture. This ensures that the reactants subsequently flow uniformly over the catalyst, improving the efficiency of the oxidation reaction.

Suitable heat exchangers include, but are not limited to, shell and tube or plate fin heat exchangers. The velocity profile of the reactant mixture will generally be dependent on the distance between adjacent gas outlets of the heat exchanger. Thus, an improved reactant mixture velocity profile may be achieved by minimising the distance between adjacent gas outlets. Suitably, the adjacent gas outlets may be several

millimetres apart, for example in the range 1 to 10 mm, preferably, 1 to 5 mm, especially 2 to 5 mm.

In a preferred embodiment of the present invention the heat exchanger is a compact heat exchanger. Compact heat exchangers generally comprise a plurality of channels, which ensure that fluid (gas or liquid) entering the channels develops fully into a substantially uniform velocity profile within a relatively short distance of exiting the channel outlets. Preferably, the fluid develops fully into a substantially uniform velocity profile within a distance of less than 100 mm from exiting the channel outlets. More preferably, a substantially uniform velocity profile may be achieved within a distance of less than 60 mm, even more preferably, less than 40 mm, and most preferably, less than 25 mm and especially less than 15 mm from exiting the channel outlets.

The compact heat exchanger may be made by diffusion bonding a plurality of metal plates together to form a stack. Grooves may be etched or otherwise formed into the surface of each plate, such that the resulting structure defines a plurality of channels. Preferably, the channels of the compact heat exchanger are parallel to one another. The channels may be of any suitable shape such as linear or z-shaped. The cross-section of each channel may be any suitable shape. Preferably, each channel is of the same shape. Preferably, each channel is semi-circular. Where the channels are semi-circular, the radius of each channel may measure 0.1 to 2.5 mm, preferably 0.25 to 1.5 mm, and most preferably, 0.5 to 1 mm.

The compact heat exchanger may be any suitable shape in cross section, for example, circular, rectangular or square. Preferably, the compact heat exchanger is square in cross section. Where a compact heat exchanger of square cross section is employed, each side of the square may be in the range 100 to 3000 mm, preferably, in the range 400 and 2000 mm, more preferably, in the range 1200 and 1800 mm. Similarly, where a circular compact heat exchanger is employed, the diameter of the exchanger may be in the range 100 to 3000 mm, preferably, in the range 400 and 2000 mm, more preferably, in the range 1200 and 1800 mm.

The reactant mixture may be preheated and, preferably, is preheated, prior to entry into the reaction zone. Generally, the reactant mixture is preheated to temperatures below the autoignition temperature of the reactant mixture. Typically, in the catalytic oxidative dehydrogenation of hydrocarbons, preheat temperatures of up to 200° C but

below the autoignition temperature of the reactants are employed. Preferably, the heat exchanger preheats the reactant mixture to a temperature of up to 30°C below the autoignition temperature of the mixture.

Advantageously, the use of the heat exchanger may allow the reactant mixture to be heated to high preheat temperatures such as temperatures at or above the autoignition temperature of the reactant mixture. The benefits of using preheat temperatures above the autoignition temperature of the reactant mixture will vary depending on the particular catalytic oxidation process employed. Where the process is the catalytic oxidative dehydrogenation of hydrocarbon to produce olefin, the use of high pre-heat temperatures is beneficial in that less oxygen reactant is required which leads to economic savings. In addition, in the catalytic oxidative dehydrogenation of hydrocarbon to produce olefin, the use of high preheat temperatures can result in improved selectivity to olefin product. It should be understood that the autoignition temperature of a reactant mixture is dependent on pressure as well as the feed composition: it is not an absolute value. Typically, in the catalytic oxidative dehydrogenation of hydrocarbon to produce olefin, where the hydrocarbon feed is ethane at a pressure of 2 atmospheres, a preheat temperature of up to 450° C may be used.

It should be understood that the residence time of the reactant mixture in the heat exchanger will be dependent upon a number of factors such as the length of the heat exchanger tubes and the velocity of the reactant mixture through the heat exchanger. However, where the reactant mixture is heated to above its autoignition temperature premature reaction of the reactants may occur. To avoid such premature reaction the heat exchanger should preferably provide a residence time of the reactant mixture which is less than the ignition delay time for the temperature of the reactant mixture. Typically, the residence time may be in the range 10 to 1000 milliseconds, preferably 10 to 100 milliseconds.

In use, the heat exchanger employed in the present invention may be heated by any suitable means. Suitably, the heat exchanger may be indirectly heated by the heat generated by the partial combustion of the reactants. It may also be possible to supplement the heat generated by the partial oxidation reaction by heating the heat exchanger by external means. For example, the whole or part of the heat exchanger may be heated electrically. Alternatively or additionally, a hot fluid, such as steam, may

be passed through the heat exchanger. In certain circumstances, for example to prevent flashback into the heat exchanger, it may be desirable to cool the whole or part of the heat exchanger. This may be achieved by passing a cooling fluid such as cooling water through the exchanger.

Although the hydrocarbon and oxygen-containing gas may be pre-mixed prior to being introduced into a reaction zone, the extent of mixing of the gaseous reactants is often still uneven. Such uneven mixing of the reactants can lead to an unstable reaction.

Advantageously, improved mixing and/or improved velocity profile of the reactants may be achieved by passing the reactant mixture through a baffle zone prior to entry into the heat exchanger.

Thus, in another aspect of the invention, the hydrocarbon and oxygen-containing gas are mixed in at least one baffle zone, prior to being passed through the heat exchanger. The baffle zone is defined by a housing, which contains at least one baffle plate. By baffle plate is meant any device which serves to correct the flow of reactants thereby improving mixing and/or velocity profile of the reactants.

The housing may be any suitable shape in cross-section, for example, square, rectangular or circular. A housing having a square cross section is preferred. Most preferably, the housing defines a cubic baffle zone. To minimise the volume of the reactant mixture in the housing, it is preferable to minimise the volume of the baffle zone housing.

The housing may be of any suitable material such as metal.

Suitably, the baffle plate may be solid (non-perforated). Preferably, the baffle plate is of circular cross section. The baffle plate may be of any suitable material such as metal.

Preferably, the baffle plate is disposed substantially at a right angle to the direction of flow of the reactant mixture entering the baffle zone. Such orientation of the plate promotes mixing of the reactants. It has been found that where the angle of the plate deviates slightly from the perpendicular, for example, by a few degrees, the extent of mixing is inferior to that obtained when the plate is perpendicular to the flow of reactants.

Preferably, the baffle plate is located substantially midway along the length of the housing such that the distance from the outlet of the mixing device to the plate is

approximately equal to the distance from the plate to the inlets of the heat exchanger channels.

Suitably, where the baffle plate is circular and the housing is of square cross section, the ratio of the length of the housing to the diameter of the baffle plate is in the range 4 : 1 to 1: 1, such as 2:1.

The hydrocarbon and oxygen-containing gas reactants are pre-mixed prior to introduction into the baffle zone. Pre-mixing of the reactants may be carried out by any suitable means. Suitable mixing means include devices which are capable of causing substantial mixing of the reactants prior to entry into the baffle zone such as one or more injectors, for example, gas injectors. Preferred mixing devices are those which provide for mixing of at least 80% of the reactants prior to entry into the baffle zone.

Suitably, the hydrocarbon is entrained in the oxygen-containing gas prior to entry into the baffle zone. Preferably, the oxygen-containing gas is injected into the baffle zone by one or more gas injectors. Suitably, the gas injector may be located within a tube or other housing such that the oxygen-containing gas stream can be entrained with a hydrocarbon stream entering the tube or housing. The injector may have a flared section around the injector nozzle so as to provide a constriction in the tube. The hydrocarbon is fed over the flared section at lower velocity than the velocity of the oxygen-containing gas. The difference in velocities, and the shear between the oxygen containing gas and hydrocarbon streams causes the hydrocarbon to become entrained in the oxygen-containing gas. Preferably, the velocity ratio of the oxygen-containing gas to hydrocarbon is 20 : 1 to 2 :1, more preferably, 3 : 1 to 8 :1. The relative velocities of the reactants and the distance they have to travel before reaching the baffle zone should be carefully calculated and monitored, to ensure that the reactants are sufficiently dispersed as they leave the exit port of the injector and enter the baffle zone.

The reactant mixture entering the baffle zone impinges the baffle plate and is deflected by the baffle plate thereby reducing the momentum of the mixture. This reduction in momentum provides a more uniform velocity and pressure profile of the mixture prior to entry into the heat exchanger. The reduction in momentum is enhanced when the baffle plate is positioned in-line with the outlet of the mixing device (such as the exit port of an injector nozzle), that is, the outlet of the mixing device is disposed substantially perpendicular to the baffle plate.

Preferably, the dimensions of the baffle plate are such that substantially all of the reactants impinge on the baffle plate. The ratio of the diameter of a circular baffle plate to the diameter of the outlet of the mixing device is preferably, 1 – 5 : 1, more preferably, 1 – 3 : 1, and most preferably, 2 : 1.

A plurality of baffle zones may be employed in the process of the present invention. Each baffle zone housing may be fed with a single mixing device or a plurality of mixing devices, preferably a plurality of mixing devices. Preferably, where a plurality of mixing devices feeds a single baffle zone housing the ratio of baffle plates to mixing devices is 1:1. However, a baffle zone housing fed by a plurality of mixing devices may house a single baffle plate.

Preferably, to ensure that the flow rates of reactants through the mixing devices are uniform, the outlet of each mixing device has substantially the same diameter.

Alternatively, the baffle zone may comprise a housing without a baffle plate. In this instance, the hydrocarbon/oxygen-containing gas mixture may be fed substantially tangentially into the housing using one or more mixing devices.

Optionally, the hydrocarbon and/or oxygen-containing gas may be preheated before being introduced into the baffle zone. The temperature to which the reactants may be preheated, however, is limited by the autoignition temperature of the feed.

Once the reactant mixture has passed through the baffle zone and the heat exchanger, it is contacted with a catalyst which is capable of supporting oxidation of the hydrocarbon.

The catalyst which is used in the oxidation reaction of the present invention will depend on the specific oxidation process to be employed. For example, where the oxidation process is the oxidation of methane to produce syngas suitable catalysts include platinum/rhodium or nickel based catalysts. Suitable catalysts for the oxidation of ethylene to produce ethylene oxide include silver based catalysts. In the oxidation of ethylene and acetic acid to produce vinyl acetate suitable catalysts include palladium based catalysts such as palladium/gold catalysts. Suitable catalysts for the production of maleic anhydride from the oxidation of butene, butane or benzene include vanadium and/or molybdenum based catalysts. Typically, in the production of phthalic anhydride by the oxidation of naphthalene or o-xylene vanadium based catalysts are employed. Suitable catalysts in the ammoxidation of propane to acrylonitrile include bismuth based

catalysts. These and other suitable catalysts for the afore-mentioned and other hydrocarbon oxidation reactions are known in the art.

Preferably, the oxidation reaction is carried out in a fixed bed reactor.

Any suitable hydrocarbon may be employed, for example, C_1 to C_6 hydrocarbons, such as, C_1 to C_6 alkanes, or C_2 to C_6 olefins. The C_1 to C_6 hydrocarbon may be linear, branched or cyclic. Aromatic hydrocarbons such as benzene and naphthalene may also be employed.

Any suitable oxygen-containing gas may be employed, for example molecular oxygen or air.

Suitably, the oxidation reaction of the present invention is any hydrocarbon oxidation reaction which may be carried out in a fixed bed reactor. Suitably, the oxidation reaction reaction may be the oxidation of ethylene to ethylene oxide, the oxidation of ethylene and acetic acid to vinyl acetate, the oxidation of napthalene to phthalic anhydride, the oxidation of ortho-xylene to phthalic anhydride, the ammoxidation of propane to acrylonitrile, the oxidation of gaseous paraffinic hydrocarbons, such as methane, to syngas, the oxidation of C_4 hydrocarbon, such as butane and/or butene to maleic anhydride and the oxidation of benzene to maleic anhydride.

The oxidation reaction conditions such as temperature and pressure will depend on the specific oxidation reaction employed. Suitable reaction conditions are known in the art.

In a preferred embodiment of the present invention there is provided a process for the catalytic oxidative dehydrogenation of hydrocarbons to produce olefins such as ethylene.

Accordingly, the present invention provides a process for the production of an olefin said process comprising:

partially combusting in a reaction zone, a mixture of a hydrocarbon and an oxygen-containing gas in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability to produce the olefin, wherein prior to said partial combustion, said mixture of the hydrocarbon and the oxygen-containing gas is passed through a heat exchanger.

The process comprises contacting a hydrocarbon or a mixture of hydrocarbons and an oxygen-containing gas with a catalyst under catalytic oxidative dehydrogenation reaction conditions to produce the olefin.

The hydrocarbon may be any hydrocarbon which can be converted to an olefin, preferably a mono-olefin, under the catalytic oxidative dehydrogenation reaction conditions employed.

The process of the present invention may be used to convert both liquid and gaseous hydrocarbons into olefins. Suitable liquid hydrocarbons include naphtha and gas oils. Preferably, however, gaseous hydrocarbons such as ethane, propane, butane and mixtures thereof are employed.

Any suitable oxygen-containing gas may be employed, for example molecular oxygen, air or molecular oxygen diluted with an unreactive gas such as nitrogen, argon, carbon dioxide or helium.

Any molar ratio of hydrocarbon to oxygen is suitable provided the desired olefin is produced in the process of the present invention. The preferred stoichiometric ratio of hydrocarbon to oxygen is 5 to 16, preferably, 5 to 13.5 times, preferably, 6 to 10 times the stoichiometric ratio of hydrocarbon to oxygen required for complete combustion of the hydrocarbon to carbon dioxide and water.

The hydrocarbon is passed over the catalyst at a gas hourly space velocity of greater than 10,000 h^{-1}, preferably above 20,000 h^{-1} and most preferably, greater than 100,000 h^{-1}. It will be understood, however, that the optimum gas hourly space velocity will depend upon the pressure and nature of the feed composition.

Advantageously, the hydrocarbon may be pre-heated. The temperature to which the hydrocarbon, oxygen-containing gas and (optionally) hydrogen mixture may be preheated, however, is limited by the autoignition temperature of the feed.

Preferably, hydrogen is co-fed with the hydrocarbon and molecular oxygen-containing gas into the reaction zone. The molar ratio of hydrogen to oxygen can vary over any operable range provided that the desired olefin product is produced. Suitably, the molar ratio of hydrogen to oxygen is in the range 0.2 to 4, preferably, in the range 0.5 to 3.

In the presence of the catalyst, hydrogen combusts preferentially relative to the hydrocarbon, thereby increasing the olefin selectivity of the overall process.

In addition, the feed may comprise a diluent such as nitrogen, carbon monoxide and steam.

The partial combustion reaction may be suitably carried out at a catalyst exit temperature of between 600°C and 1200°C, preferably between 850°C and 1050°C and most preferably, between 900°C and 1000°C.

The catalytic oxidative dehydrogenation process may be carried out at atmospheric or superatmospheric pressure. Suitably, the pressure may be within the range 0 to 2 bara, preferably, 1.5 to 2 bara, for example, 1.6 to 1.8 bara, especially 1.65 bara. Pressures of, for example, 2 to 50 bara, may also be suitable.

The catalyst employed in the catalytic oxidative dehydrogenation process is one which is capable of supporting combustion beyond the fuel rich limit of flammability. Suitable catalysts may comprise one or more Group VIII transition metals. The Group VIII transition metals include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. Preferably, the Group VIII transition metal is rhodium and more particularly, platinum and palladium.

Preferably, the Group VIII transition metal is employed in combination with a catalyst promoter. The promoter may be a Group IIIA (aluminium, gallium, indium and thallium), IVA (for example, germanium, tin and lead) and/or VA (for example, arsenic and antimony) metal. Alternatively, the promoter may be a transition metal which is different to the Group VIII transition metal.

Preferred Group IIIA metals include gallium and indium. Preferred Group IVA metals include germanium, tin and lead. Preferred Group VA metals include antimony. Preferred transition metals include those from Groups IB, IIB, VIB, VIIB and VIIIB of the Periodic Table. Examples of suitable transition metals include chromium, molybdenum, tungsten, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, platinum, copper, silver, gold, zinc, cadmium and mercury. Preferred transition metal promoters are molybdenum, rhodium, ruthenium, iridium, platinum, copper and zinc.

Suitably, the catalyst may be Pt/Ga, Pt/In, Pt/Sn, Pt/Ge, Pt/Cu, Pd/Sn, Pd/Ge, Pd/Cu, Pd/Sn, Pd/Ge and Rh/Sn. Of these Pt/Cu and Pt/Sn are preferred.

In another embodiment of the present invention, the catalyst comprises platinum and palladium, and a further metal selected from Group IIIA, Group IVA or the transition metal series of the Periodic Table. Suitably, the catalyst may be Pt/Pd/Cu.

For the avoidance of doubt, the Group VIII transition metal and promoter may be present in any form, for example, as the metal or in the form of a metal compound, such as a metal oxide.

Suitable catalytic oxidative dehydrogenation catalysts are described in more detail in EP-A- 0 332 289, WO 97/26987, GB 9930598.9 and GB 9930597.1, the contents of which are herein disclosed by reference.

The catalyst employed in the present invention may be unsupported, for example, the catalyst may be in the form of a metal gauze.

Preferably, the catalyst is supported on any suitable support. Suitably, the support is a metal or ceramic support, preferably a ceramic support. Suitable ceramic supports include lithium aluminium silicate (LAS), alumina (α-Al_2O_3), yttria stabilised zirconia, alumina titanate, niascon, and calcium zirconyl phosphate. The support may be wash-coated, for example, with γ- Al_2O_3.

The catalyst may be employed in the form of tiles, preferably, with chamfered edges. Such tiles may be placed adjacent to one another to form a catalyst bed of a desired size. It may be desirable to seal the area between the bed and the reactor walls to avoid unreacted reactants from flowing through the gap between the bed and the reactor. Preferably, an intumescent sealant such as vermiculite base is employed. Alternatively, the sealant may comprise compressed silica-fibre mats.

Where possible, the heat produced by the partial combustion of the hydrocarbon and oxygen-containing gas hydrogen is recycled, for example, to heat the reactants in the heat exchanger.

Where the cracking reaction is carried out at superatmospheric pressure, the reaction products may be quenched, for example, with water, as they emerge from the reaction chamber to avoid further reactions taking place. Quenching may not be necessary for reactions carried out at relatively low pressure, for example, pressures less than 5 bara.

Any coke produced in the process of the present invention may be removed by mechanical means, or by decoking. Suitable decoking methods are described in EP 0-A-709 446.

The invention will now be illustrated by way of example only and with reference to Figure 1 and to the following examples.

Figure 1 represents in schematic form, apparatus suitable for use in the process of

the present invention.

The apparatus (1) is provided with means for supplying an oxygen-containing gas (2) and a means for supplying a hydrocarbon and optionally hydrogen (3). Depending on the scale of the process there may be a single means or several means for the supply of reactants. The means for supplying an oxygen-containing gas (2) and a means for supplying a hydrocarbon and optionally hydrogen (3) are welded to the baffle zone housing (4).

The apparatus (1) also comprises a baffle zone housing (4) which is provided with a baffle plate (5). The baffle zone housing (4) is cubic and made of stainless steel. The baffle plate (5) is solid (non-perforated) and made of monel. The ratio of the length of the baffle zone housing to the diameter of the baffle plate is 2:1. The baffle plate (5) is disposed substantially perpendicular to the outlet(s) of the reactant supply means and approximately midway along the length of the baffle zone housing (4). The ratio of the diameter of the baffle plate to the diameter of the exit port of the nozzle of the injector (8) is 2:1. Depending on the scale of the process, the baffle zone may comprise either a single baffle zone or several baffle zones. Each baffle zone may comprise a single or several baffle plates.

The baffle zone housing (4) is bolted to a heat exchanger (6).

The apparatus (1) further comprises a compact heat exchanger (6) of square cross-section and having substantially z-shaped channels of semi-circular cross-section and 1mm in radius. The heat exchanger (6) is bolted to the reactor (7). Suitable compact heat exchangers are manufactured by Heatric Limited.

The apparatus (1) also comprises a reactor (7). The cross-sectional shape of the reactor is square, so as to substantially match the cross-sectional shape of the heat exchanger (6). To minimise heat losses, the reactor is insulated both internally and externally.

In use, the reactor (7) is provided with at least one catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability. Suitably, the catalyst is a supported catalyst. The catalyst is placed below an alumina heat shield (not shown). An oxygen-containing gas is fed to the apparatus (1) from a supply (2) suitably via a gas injector (8). A gaseous hydrocarbon feedstock suitably comprising ethane and optionally hydrogen is fed to the apparatus (1) from supply (3) suitably via a gas injector (8). The ratio of the velocity of the oxygen containing gas to the velocity of the

hydrocarbon feed is 5:1. The oxygen-containing gas, hydrocarbon and optionally hydrogen mix in the injector (8) to form a reactant mixture prior to exiting the outlet of the injector (8) into baffle zone (4). On entering baffle zone (4) the reactant mixture impinges the baffle plate (5) and is deflected into the channels of the compact heat exchanger (6). The compact heat exchanger (6) is heated by steam. On passage through the channels of the compact heat exchanger (6) the reactant mixture is preheated to the required temperature. On exiting the channels of the compact heat exchanger (6) the reactant mixture passes into reactor (7) whereupon it contacts the catalyst. In the reactor (7) at least a portion of the hydrocarbon feed combusts to produce water and carbon oxides. The hydrogen co-feed, if present, combusts to produce water. Both of these combustion reactions are exothermic and the heat thereby produced is used to drive the dehydrogenation of hydrocarbon to olefin product.

General Ethane Catalytic Oxidative Dehydrogenation Reaction Method

Typically, a platinum-copper catalyst comprising nominal loadings of 3 wt% platinum and 1 wt% copper was supported on 99.5% alumina foam (of porosity 45 pores per inch) (Vesuvius Hi-Tech Ceramics Inc) to provide a catalyst bed sized to match the cross sectional area of heat exchanger, 60 mm in depth and a volume of 1008 cm^3. The supported catalyst was then loaded into a fixed bed reactor. An alumina heat shield was positioned above the catalyst. The catalyst was heated under nitrogen to 200° C. A flow of nitrogen was maintained immediately below the catalyst to ensure a non-flammable atmosphere until reaction was established on the catalyst.

Flows of ethane, hydrogen and oxygen were then introduced into an apparatus as described for Figure 1. The flows of ethane, hydrogen and oxygen were gradually increased over a 1 hour period to provide a gas velocity at the upstream catalyst face of 4.35 m/s at the feed temperature with the following feed mass ratios to oxygen: ethane : oxygen 1.84 and hydrogen : oxygen 0.12 . During this period the catalyst exit temperature rose steadily and then stabilized at 850° C.

After the 1 hour equilibration period the nitrogen flow was reduced to 0 kg/h over a 2 hour period. The ethane, hydrogen and oxygen flows were adjusted to achieve target flows.

The reactant mixture was heated to the required pre-heat temperature by the compact heat exchanger.

The catalytic oxidative dehydrogenation reaction was carried out at a pressure of 1.8 bara.

The product composition was analysed by gas chromatography. The feed and product flow rates were determined by coriolis type flow meters.

From analysis of the feed and product flow rates and compositions the ethane conversion and selectivity to ethylene was calculated.

The velocity profile and the degree of mixing of the reactants may be determined by techniques such as computational fluid dynamic modelling (CFD modelling) and physical flow models. Alternatively and/or additionally, thermocouples may be located below the catalyst to confirm uniform reaction across the catalyst. Uniform reaction will be obtained when the velocity profile and the extent of mixing of the reactant mixture fed to the catalyst is uniform.

Example 1

In this Example, ethane, oxygen and hydrogen were utilised as feed in the general reaction method above. The reactant mixture was pre-heated to a temperature below the autoignition temperature of the mixture. The results are shown in Table 1 below.

Example 2

The data in this Example was obtained by thermochemical analysis of the data in Example 1. The preheat temperature of the reactant mixture was set at a temperature above its autoignition temperature. The results are shown in Table 1 below.

Table 1

	Example 1	Example 2
Preheat Temperature °C	195	450
Ethane : Oxygen ratio	2.43	3.08
Hydrogen : Oxygen ratio	0.12	0.12
Feed velocity at catalyst face at preheat temperature m/s	5.47	7.43
Ethane conversion %	69.14	68.71
Ethylene selectivity (g/100g C2 converted)	72.29	73.74
Carbon monoxide selectivity (g/100g C2 converted)	15.28	12.13
Carbon dioxide selectivity (g/100g C2 converted)	2.01	1.59
Methane selectivity (g/100g C2 converted)	8.57	8.74
Acetylene selectivity (g/100g C2 converted)	0.59	0.60
C3 selectivity (g/100g C2 converted)	2.16	2.19
C4 selectivity (g/100g C2 converted)	2.0	2.1
C5+ selectivity (g/100g C2 converted)	0.38	0.38

It is expected and believed that in the absence of the heat exchanger and/or baffle zone, the conversion of ethane and/or selectivity to ethylene would be inferior to the results obtained above.

Example 2 demonstrates that the use of a preheat temperature above the autoignition temperature of the reactant mixture results in improved selectivity to olefin product and

a reduction in oxygen usage compared to the use of a preheat temperature below the autoignition temperature of the reactant mixture (Example 1).

Example 3

Using the apparatus as described in Figure 1, the distribution of oxygen in an oxygen/ethane gas mixture (ratio of oxygen to ethane, 1 : 2.4) fed into the baffle zone (4) by the injector (8), passing through the baffle zone (4) and into the compact heat exchanger (6) was analysed by 3D CFD modelling using Fluent™ software. In this Example the baffle plate (5) was disposed perpendicularly i.e at 90 degrees to the oxygen/ethane gas flow.

The CFD modelling results demonstrated that the oxygen and ethane partially mix in the injector (8) prior to entry into the baffle zone (4). After deflection by the baffle plate (5) the oxygen and ethane gases appear to be substantially mixed (approximately 99% mixed)

No further mixing of the gases was observed after exit from the baffle zone (4).

Example 4

Example 3 was repeated except that the baffle plate (5) was placed at an angle to the oxygen/hydrocarbon gas flow of 2.6 degrees.

The CFD modelling results show that the mixing of the oxygen and ethane gases after deflection by the baffle plate (5) was not as good (approximately 96% mixed) as that obtained in Example 4 (where baffle plate was perpendicular to the gas flow).

Examples 3 and 4 clearly demonstrate that the mixing of oxygen and ethane is not complete at the baffle plate. Thus, in the absence of a baffle zone there would be a range of ethane/oxygen gas mixtures contacting the catalyst resulting in a less efficient auto-thermal cracking process.

The CFD modelling also demonstrated that in both Examples 3 and 4 the momentum of the injected reactant mixture was reduced by the baffle plate (5) resulting, in each case, in an improved, that is a more uniform velocity profile of the reactant mixture prior to entry into the heat exchanger (6).

Claims

1. A process for the oxidation of a hydrocarbon said process comprising:

partially oxidising in a reaction zone, a mixture comprising a hydrocarbon and an oxygen-containing gas in the presence of a catalyst which is capable of supporting oxidation of the hydrocarbon, wherein prior to said partial oxidation, said mixture comprising the hydrocarbon and the oxygen-containing gas is passed through a heat exchanger.

2. A process for the production of an olefin, said process comprising:

partially combusting in a reaction zone a mixture of a hydrocarbon and an oxygen-containing gas in the presence of a catalyst which is capable of supporting combustion beyond the fuel rich limit of flammability to produce the olefin, wherein prior to said partial combustion, said mixture of the hydrocarbon and the oxygen-containing gas is passed through a heat exchanger.

3. A process according to claim 1 or claim 2 wherein the heat exchanger has gas outlets and the distance between adjacent gas outlets is in the range 1 to 10 mm

4. A process according to any one of claims 1 to 3 wherein the heat exchanger provides a residence time in the range 10 to 1000 milliseconds

5. A process according to any one of the preceding claims wherein the heat exchanger is a compact heat exchanger.

6. A process according to claim 5 wherein the fluid exiting the channel outlets of the compact heat exchanger develops into a substantially uniform velocity profile within a distance of less than 100 mm from the channel outlets.

7. A process according to claim 6 wherein a substantially uniform velocity profile is achieved within a distance of less than 25 mm from the channel outlets.

8. A process according to any one of claims 5 to 7 wherein the compact heat exchanger has a square cross section.

9. A process according to claim 8 wherein each side of the square is in the range 100 to 3000 mm.

10. A process according to any one of claims 1 to 9 wherein the heat exchanger preheats the mixture of the hydrocarbon and oxygen-containing gas to a temperature of up to the autoignition temperature of the mixture.

11. A process according to any one of claims 1 to 9 wherein the heat exchanger preheats the mixture of the hydrocarbon and oxygen-containing gas to a temperature at or above the autoignition temperature of the mixture.

12. A process according to any one of claims 1 to 11 wherein the hydrocarbon and oxygen-containing gas are mixed in at least one baffle zone prior to being passed through the heat exchanger.

13. A process according to claim 12 wherein the baffle zone comprises a housing and at least one baffle plate is contained within the housing.

14. A process according to claim 13 wherein the baffle plate is of circular cross section.

15. A process according to claim 13 or claim 14 wherein the baffle plate is disposed substantially perpendicularly to the direction of flow of the hydrocarbon and oxygen-containing gas mixture.

16. A process according to any one of claims 13 to 15 wherein the baffle plate is located substantially midway along the length of the housing.

17. A process according to any one of claims 13 to 16 wherein the housing defines a cubic baffle zone.

18. A process according to claim 17 wherein the baffle plate is of circular cross section and the ratio of the length of the housing to the diameter of the baffle plate is in the range 4 : 1 to 1 : 1.

19. A process according to any one of claims 12 to 18 wherein the hydrocarbon and oxygen-containing gas mixture is pre-mixed in at least one mixing device prior to entry into the baffle zone.

20. A process according to claim 19 wherein the baffle zone comprises a circular baffle plate and the ratio of the diameter of the baffle plate to the diameter of the outlet of the mixing device is 1-5 : 1.

21. A process according to claim 19 or claim 20 wherein a plurality of mixing devices feed a single baffle zone housing which comprises a plurality of baffle plates.

22. A process according to claim 21 wherein the ratio of baffle plates to mixing devices is 1:1

23. A process according to claim 12 wherein the baffle zone comprises a housing into which the hydrocarbon/oxygen-containing gas mixture is fed substantially tangentially using one or more mixing devices.

24. A process according to any one of claims 2 to 23 wherein the catalyst comprises one or more Group VIII transition metals.

25. A process according to any one of claims 2 to 24 wherein the stoichiometric ratio of hydrocarbon to oxygen is 5 to 16.

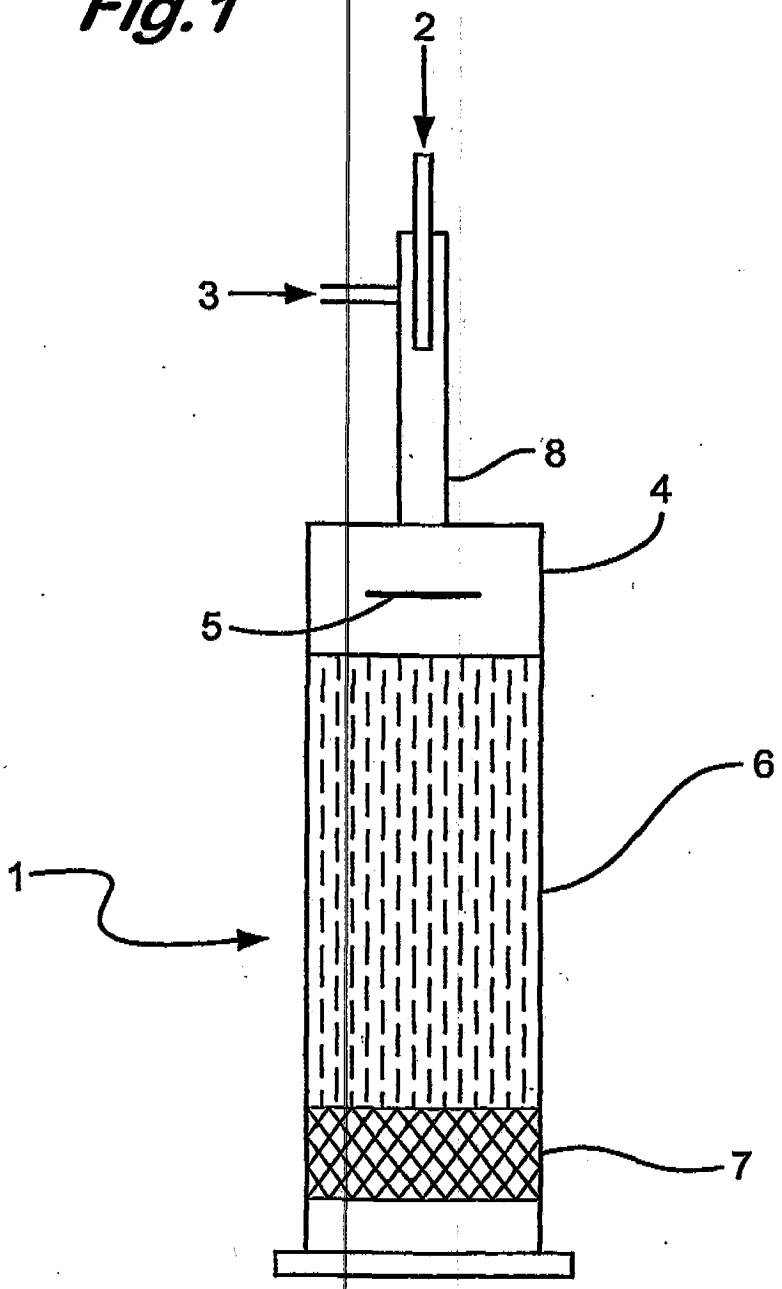
26. A process according to any one of claims 2 to 25 wherein the partial combustion is carried out in the presence of hydrogen.

27. A process according to any one of claims 2 to 26 wherein the partial combustion is carried out at a catalyst exit temperature in the range 600°C to 1200° C

28. A process according to any one of claims 2 to 27 wherein the partial combustion is carried out at a pressure in the range 0 to 2 bara.

29. A process according to any one of claims 1 to 23 wherein the oxidation reaction is selected from the group consisting of the oxidation of ethylene to ethylene oxide, the oxidation of ethylene and acetic acid to vinyl acetate, the oxidation of napthalene to phthalic anhydride, the oxidation of ortho-xylene to phthalic anhydride, the ammoxidation of propane to acrylonitrile, the oxidation of gaseous paraffinic hydrocarbons to syngas, the oxidation of C_4 hydrocarbon to maleic anhydride and the oxidation of benzene to maleic anhydride.

Fig. 1



INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/GB 01/01898

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07B41/00 C07C5/48 C07D303/04 C07C69/15 C07D307/89
C07C253/26 C01B3/36 C07D307/33

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)
IPC 7 C07C C07B C07D C01B

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	WO 94 04632 A (BP CHEMICALS) 3 March 1994 (1994-03-03) claims; figures	1-29
A	WO 82 02548 A (SWEENEY, M) 5 August 1982 (1982-08-05) claims	1-29

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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	Date of mailing of the international search report
23 July 2001	31/07/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Geyt, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

'ormation on patent family members

Inte[illegible]onal Application No
PCT/GB 01/01898

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9404632 A	03-03-1994	AT 148914 T	15-02-1997
		AU 4727193 A	15-03-1994
		BG 99508 A	31-01-1996
		BR 9306931 A	12-01-1999
		CN 1090566 A	10-08-1994
		CZ 9500373 A	18-10-1995
		DE 69308145 D	27-03-1997
		DE 69308145 T	28-05-1997
		EP 0656044 A	07-06-1995
		HR 931121 A	31-12-1994
		HU 71164 A,B	28-11-1995
		PL 307559 A	29-05-1995
		RU 2115692 C	20-07-1998
		SI 9300441 A	31-03-1994
		SK 23195 A	11-07-1995
		US 5625111 A	29-04-1997
		ZA 9306019 A	17-02-1995
WO 8202548 A	05-08-1982	AU 8200982 A	16-08-1982
		BR 8205841 A	11-01-1983
		EP 0070304 A	26-01-1983
		ES 509059 D	01-07-1983
		ES 8307691 A	01-11-1983
		IT 1190673 B	24-02-1988
		JP 58500128 T	20-01-1983
		NO 823138 A	16-09-1982
		US 4760210 A	26-07-1988

HB
113

ZACION DEL

RADICADOR

[redacted]

( )

( )
( )

( )
( )

( )

( )

( )
( )
( )

( )

112

Firma Responsable:

Fecha:

SUPERINDUSTRIA Y COMERCIO
Radicacion : 05078164 00000000 Folios: 112
Fecha (AMD): 2005-08-08 16:20:50
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

REPUBLICA DE COLOMBIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
RODRÍGUEZ D´ALEMAN DILIA MARÍA

REFERENCIA	Radicación No.	5 78164
	Solicitud internacional	
	Fecha inicio fase nacional	
	Trámite	11
	Evento	379
	Actuación	430
	Oficio No.	8470

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.

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.

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

El anterior requerimiento fue notificado por fijación en lista de fecha 16 SET. 2005
adpa11