1/2 1/3

Clarke, Modet & C°

COLOMBIA

SUPERINDUSTRIA Y COMERCIO
Radicacion : 03000677 00000003 Folios: 2
Fecha (Hora): 2004-09-24 17:25:02
Tramite 011 PCT-PATENT 279 PAGS. NACI 538 PETICION
Dependencia 2020 DIVISION DE NUEVAS CREACIONES

SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E.S.D

REF EXPEDIENTE No. : **03000677**
SOLICITANTE : **BP CHEMICAL LIMITED**
SLICITUD FECHA : ENERO 8, 2003
PATENTE : PROCEDIMIENTO PARA LA PRODUCCIÓN DE OLEFINAS

ASUNTO: SOLICITUD ESTUDIO DE FONDO

DILIA RODRÍGUEZ D´ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial No.539 de fecha Abril 30, 2004 se proceda con el estudio de Fondo.

Para tal fin me permito anexar la tasa correspondiente No. 04.75231.

Agradezco continuar con el presente trámite.

Señor Jefe,

DILIA RODRÍGUEZ D´ALEMAN
T.P.No. 20824 del CSJ

P-477
MR

113

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Radicacion : 03000677 00000003 Folios: 2
Fecha (AMD): 2004-09-24 17:25:03
Tramite : 511 PCT-PATENT 579 FASE NACI 538 PETICION
Dependencia: 2060 DIVISION DE NUEVAS CREACIONES

NIT : 900174089-2

RECIBO OFICIAL DE CAJA : 04 - 75,231
FECHA : SEPTIEMBRE 22 DE 2004

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. COLOMB	CONSIGNACION	BANCO POPULAR	030-00110-6	31534172	21/09/2004	7,593,000.00

C O N C E P T O

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	95 EXAMEN DE PATENTABILIDAD DE INVEN	353,000.00
		TOTAL : $	353,000.00

SON: TRESCIENTOS CINCUENTA Y TRES MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No._____

P. 471

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. **03-677**

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCI N PCT** FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **539**, DE FECHA **30** DE **ABRIL** DE **2004**, EL TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL **02** DE **AGOSTO** DE **2004**.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI ____ _____ NO ___X_____

116

115

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

p.472

2020
Bogotá, D. C., 4 de Agosto de 2006

Doctora
DILIA RODRÍGUEZ D' ALEMÁN
Representante **BP CHEMICALS LIMITED**

ASUNTO	Radicación No.	**03-00677**
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	8834
	Folios	015

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) **Documentos estudiados:**

a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 5 a 39 de la solicitud en estudio.

b) Para el presente estudio se tendrán en cuenta los dibujos comprendidos en los folios 46 a 52 de la solicitud en estudio.

c) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 33 reivindicaciones en los folios 40 a 44 de la solicitud en estudio.

d) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 8 de enero de 2003, y en el momento de la radicación se presentó como solicitud PCT fase nacional, y **SI** se reclamo prioridad de la primera solicitud presentada en Gran Bretaña GB/2000/0017173.6.

2) **Objeto de la invención**

a) Las reivindicaciones 1 a 33 de la solicitud en estudio se refieren a un procedimiento para la producción de una olefina, caracterizado porque comprende pasar una mezcla de un hidrocarburo y un gas conteniendo oxígeno a través de una zona catalítica que es capaz de soportar la combustión más allá del límite de inflamabilidad rico en combustible, para producir dicha olefina, comprendiendo dicha zona catalítica al menos un primer lecho catalítico y un segundo lecho catalítico, en donde el segundo lecho catalítico está situado aguas abajo del primer lecho catalítico y es de una composición diferente a la del primer lecho catalítico y comprende al menos un metal seleccionado del grupo consistente en Mo, W y Grupos IB, IIB, IIIB, IVB, VB, VIIB y VIII de la Tabla Periódica.

b) El anterior "procedimiento" busca una mejor forma de obtener olefinas.

c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 07 C 11/02

3) **Claridad de la Solicitud**

a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

> *"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"*

La descripción no es clara toda vez que se evidencia que quién tradujo la solicitud al español no era un conocedor de la materia, y el documento en español tampoco fue revisado por un técnico. La solicitud está llena de traducciones no técnicas que lleva a que se pierda el sentido del documento. Por ejemplo, "cracking" sí tiene una palabra equivalente en español y es "craqueo". Es lógica la expresión "más allá del límite de inflamabilidad rico en combustible". Técnicamente no dice nada. Es en efecto una mala traducción. De la misma forma sucede con múltiples frases y palabras del documento. La solicitud debe ser revisada por alguien que entienda del arte

b) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

> *"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."*

El capítulo reivindicatorio no es claro toda vez que:

I) El objeto de la solicitud se encuentra mal identificado. El solicitante encabeza las reivindicaciones como "procedimiento", pero lo que considera como materia patentable no es un procedimiento. En efecto, de acuerdo a lo visto en este capítulo por su redacción y en la descripción, lo que sería el objeto de la protección es un sistema catalizador de varios lechos con características específicas para cada lecho. Tal como está redactada cada reivindicación se entiende que dichos sistemas catalíticos **se usan** para producir olefinas partiendo de hidrocarburos y gases conteniendo oxígeno. Por tanto, no hay "procedimientos" como objetos de patente, sino un equipo de catálisis.

ii) La reivindicación 28 habla de un hidrocarbilo cuando antes nunca se había mencionado. Aclarar.

iii) Todos los comentarios hechos en el punto 3)a) son válidos aquí también.

iv) No se aceptan términos ambiguos tales como "sustancialmente". No permiten delimitar el alcance de la solicitud.

v) No es claro a lo que se refiere el solicitante con 'la velocidad espacial horaria del gas'. Puede tratarse de una mala traducción.

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) **Determinación del Estado de la Técnica**

Cuando el solicitante haya corregido el capítulo reivindicatorio y lo haya orientado de forma tal que sea claro lo que quiere le sea protegido, en ese momento esta oficina podrá elaborar una determinación correcta del estado de la técnica y una evaluación correcta de los requisitos de patentabilidad.

Sin embargo, se hará un examen previo basado en la documentación anexada por el Tratado PCT fase internacional

El artículo 16 de la Decisión 486 de la Comisión establece:

> *"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."*
>
> *"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."*

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones **C 07 C 5/48** y las más cercanas a ellas, se encontró que antes del 12 de julio de 2000 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con procesos y sistemas para la producción de olefinas.

De acuerdo con o establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	WO 00/14036	Process for the production of olefins	2000.03.16

5) **Evaluación de los requisitos de patentabilidad**

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

> *"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".*

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación de la novedad y el del Nivel Inventivo

El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

> *"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."*
>
> *"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."*

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

> *"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".*

El documento WO 00/14036 relaciona procesos para la producción de olefinas, donde se utilizan sistemas de catalizadores con configuraciones equivalentes a las esbozadas por la presente solicitud. Podría decirse que D1 anticipa la presente solicitud.

120

119

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO 00-14036	1 - 33	Novedad
			Nivel Inventivo

6) **Notificación**

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

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

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

11 AGO. 2006

Concepto Técnico Nº	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
1231	202003	

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [7] : C07C 5/48, C10G 11/20 | A1

(11) International Publication Number: WO 00/14036

(43) International Publication Date: 16 March 2000 (16.03.00)

(21) International Application Number: PCT/GB99/02965

(22) International Filing Date: 7 September 1999 (07.09.99)

(30) Priority Data:
9819603.3 8 September 1998 (08.09.98) 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*): GRIFFITHS, David, Charles [GB/GB]; 75 Common Road, Claygate, Esher, Surrey KT10 0HU (GB). GRESLER, Carl [DE/GB]; 12 Sullivans Reach, Walton-on-Thames, Surrey KT12 2QB (GB). REID, Ian, Allan, Beattie [GB/GB]; 13 Crowthorne Close, Southfields, London SW18 5RX (GB).

(74) Agent: SMITH, Julian, Philip, Howard; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, 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, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, 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), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR THE PRODUCTION OF OLEFINS

(57) Abstract

This invention relates to a process for the production of olefins from a hydrocarbon, said process comprising the steps of: a) providing a first feed stream comprising a gaseous fuel and an oxygen-containing gas, b) contacting said first feed stream with a first catalyst under conditions so as to produce a product stream and unreacted oxygen, c) providing a second feed stream comprising a hydrocarbon feedstock, and d) contacting said second feed stream, said product stream of step b) and said unreacted oxygen of step b) with a second catalyst which is capable of supporting oxidation, thereby consuming at least a part of the unreacted oxygen to produce an olefin product.

PROCESS FOR THE PRODUCTION OF OLEFINS

The present invention relates to a process for the production of olefins. Olefins such as ethylene and propylene may be produced by the catalytic dehydrogenation or cracking of a hydrocarbon feed. In this application the term "cracking" will be used to embrace both these chemical reactions. In an auto-thermal cracking process, a hydrocarbon feed is mixed with an oxygen-containing gas and contacted with a catalyst capable of supporting combustion beyond the fuel rich limit of flammability. The hydrocarbon feed is partially combusted and the heat produced is used to drive the cracking reaction.

An example of an auto-thermal cracking process is described in EP 0 332 289. The document describes the use of a paraffinic feed of, for example, ethane, propane and/or butane which is mixed with oxygen, and cracked to produce an olefinic mixture. The cracking reaction is endothermic and is carried out at elevated temperatures above 800°C.

The energy required for the cracking reaction is provided by combustion of a part of the feed. The feed may also be preheated but the temperature is limited due to the risk of autoignition. It is desirable to maximise the amount of feed available for cracking by reducing the amount of feed required for combustion.

It is among the objects of the present invention to find an additional or alternative source of heat to drive the cracking step of the auto-thermal cracking process.

This is achieved by providing an auto-thermal process comprising a preliminary heat-generating step. In this step, a gaseous fuel such as a hydrocarbon reacts with oxygen in an exothermic reaction in the presence of a catalyst. The

reaction conditions are controlled to ensure that not all of the oxygen is consumed during this process. The thermal energy produced by the reaction heats the unreacted oxygen, thereby providing an additional source of heat to drive the cracking of the hydrocarbon feedstock.

According to the present invention, there is provided a process for the production of olefins from a hydrocarbon, said process comprising the steps of:

a) providing a first feed stream comprising a gaseous fuel and an oxygen-containing gas,

b) contacting said first feed stream with a first catalyst under conditions so as to produce a product stream and unreacted oxygen,

c) providing a second feed stream comprising a hydrocarbon feedstock, and

d) contacting said second feed stream, said product stream of step b) and said unreacted oxygen of step b) with a second catalyst which is capable of supporting oxidation, thereby consuming at least a part of the unreacted oxygen to produce an olefin product.

According to a preferred embodiment of the present invention, there is provided a process for the production of olefins from a hydrocarbon, said process comprising the steps of:

a) providing a first feed stream comprising a gaseous hydrocarbon and an oxygen-containing gas,

b) contacting said first feed stream with a first catalyst under conditions so as to produce a product stream and unreacted oxygen,

c) providing a second feed stream comprising a hydrocarbon feedstock, and

d) contacting said second feed stream, said product stream of step b) and said unreacted oxygen of step b) with a second catalyst which is capable of supporting oxidation, thereby consuming at least a part of the unreacted oxygen to produce an olefin product.

The process of the present invention provides a means of minimising the amount of hydrocarbon feedstock consumed to generate the heat required to drive the cracking of the hydrocarbon feedstock. By reducing the amount of hydrocarbon consumed in this manner, a larger proportion of the hydrocarbon feedstock is available for conversion into olefinic products. This may result in higher olefin yields and enhanced selectivities

towards the olefin product. The throughput through the reactor is also enhanced.

The process of the present invention also provides a means of maintaining the second catalyst at an elevated temperature. In doing so, non-volatile hydrocarbons are prevented from condensing on the catalyst and reducing the catalyst's activity. This allows a higher through put through the reactor. On heavy residue-containing feeds the process of the present invention provides the additional advantage of increasing the time on oil processing between catalyst decokes.

The gaseous fuel of the first feed stream is any gaseous fuel which is capable of reacting with oxygen in an exothermic reaction. Suitable examples include hydrocarbons, such as methane, ethane, propane and butane; with methane being preferred. Other suitable fuels include hydrogen, carbon monoxide, alcohols (eg methanol, ethanol), oxygenates and/or ammonia. Waste fuel streams may also be employed.

The oxygen-containing gas may comprise air, oxygen and/or an air/oxygen mixture. The oxygen-containing gas may be mixed with an inert gas such as nitrogen, helium or argon. Additional feed components such as hydrogen, carbon monoxide, carbon dioxide and steam may also be included.

The first feed stream is preferably fuel-rich with a fuel to oxygen ratio above the stoichiometric ratio required for complete combustion. For example, the fuel to oxygen ratio in the feed may be 1.5 to 4 times, preferably 3 times, the stoichiometric ratio required for complete combustion to carbon dioxide to water.

The gaseous fuel and oxygen-containing gas are contacted with a first catalyst under reaction conditions which are controlled to ensure that some of the oxygen in the first feed stream remains unreacted during step b). The thermal energy produced in step b) heats the unreacted oxygen, thereby providing part of the heat necessary for cracking the hydrocarbon feedstock in step d).

The reaction between the gaseous fuel and oxygen-containing gas may be a combustion reaction. Accordingly, gaseous fuel (eg hydrocarbon) in the first feed stream may react with oxygen to produce a product stream comprising oxides (eg carbon oxides) and water. In such an embodiment, a combustion catalyst is employed as the first catalyst. Suitable combustion catalysts include Group VIII metals such as platinum and/or palladium. The catalyst may comprise 0.1 to 5 wt% and, preferably, 0.25 to 3 wt%, of metal. It will be understood that the metal loadings of the catalyst may be selected to

ensure that not all the oxygen in the first feed stream is consumed in step b).

In an alternative embodiment, the gaseous fuel of the first feed stream reacts with the oxygen-containing gas to produce synthesis gas. In this embodiment, a first feed stream comprising hydrocarbon (eg methane) is employed, which reacts with oxygen to produce carbon monoxide and hydrogen. These gaseous products may react endothermically, for example with oxygen, thereby providing a further source of heat to drive the cracking reaction in step d). In this embodiment, the catalyst employed is one which is capable of supporting a synthesis gas production reaction is employed. Suitable catalysts comprise rhodium, platinum, palladium, nickel or mixtures thereof. Preferably, a rhodium catalyst is used. The catalyst may comprise 0.1 to 5 wt% and, preferably, 0.25 to 3 wt%, of metal. As with combustion catalysts, the metal loadings of the catalyst may be varied to ensure that not all the oxygen in the first feed stream is consumed in step b).

In a further embodiment, a gaseous fuel is reacted with an oxygen-containing gas in a combustion reaction, and another gaseous fuel (which may or may not be the same as the first gaseous fuel) is reacted with an oxygen-containing gas to produce synthesis gas. Both these reactions are exothermic, and may provide part of the heat for driving the subsequent cracking reaction in step d). In at least one of these reactions, however, not all of the oxygen-containing gas employed is consumed. At least part of this unreacted oxygen is consumed in step d) to produce the olefin product of the present invention.The first catalysts of present invention may be supported. Suitable catalyst supports include a range of ceramic and metal supports, with alumina supports being preferred. The support may be in the form of spheres or other granular shapes, and may be present as a thin layer or wash coat on another substrate. Preferably, the substrate is a continuous multi-channel ceramic structure such as a foam or a regular channelled monolith. In a preferred embodiment, a gamma alumina coated alpha alumina. Alternatively, zirconia or a gamma alumina coated lithium aluminium silicate foam support may be employed. The nature of the catalyst support may be varied to ensure that not all the oxygen in the first feed stream is consumed in step b).

The first feed stream may be contacted with the first catalyst at a temperature of between 600 and 1200°C, preferably between 700 and 1100° C, and most preferably between 950 and 1050°C.

The first feed stream may be contacted with the first catalyst at any suitable

pressure, e.g. atmospheric or elevated pressure. If elevated pressures are employed, any pressure above 1 bara may be used. Suitable elevated pressures range from 1.1 to 50 bara, for example, 5 to 50 bara, although pressures of 1.1 to 8 bara, for example, 1.8 bara are preferred. It will be understood that the precise pressures employed will vary depending on the specific reaction conditions and gaseous feeds employed.

The process of the present invention may be carried out in a reactor comprising at least two reaction zones, which are in fluid communication with one another. Where a two-reaction-zone reactor is employed, the first reaction zone is provided with the first catalyst, whilst the second reaction zone is provided with the second catalyst. Accordingly, when the first feed stream is introduced into the first reaction zone under suitable reaction conditions, the reaction of step b) takes place. The unreacted oxygen produced in step b) is then introduced into the second reaction zone, where it comes into contact with the second catalyst and the second feed stream as described in step d).

In one embodiment, the present invention is carried out in a reactor having a main chamber, and a side chamber. The side chamber may define the first reaction zone, and the main reaction chamber the second reaction zone, or vice-versa. In an alternative embodiment, the first and second reaction zones are defined by nested, generally concentric tubular housings. Preferably, the outer housing extends beyond the end of the inner housing, such that fluid entering the outer housing from the inner housing mixes with the second feed stream before coming into contact with the second catalyst. Advantageously, mixing means may be provided between the first and second reaction zones. Suitable mixing means include a grid, a perforated plate, and/or a baffle plate.

The rate at which the first feed stream may be introduced into the first reaction zone may be measured in terms of gas hourly space velocity (h^{-1}). This is defined as:

GHSV = volume of total feed /(time x volume of catalyst bed)

Suitably, the first feed stream is introduced at a gas hourly space velocity of greater than 10,000 h^{-1}, preferably above 100,000 h^{-1} and most preferably, greater than 300,000 h^{-1}. It will be understood that the optimum gas hourly space time velocity will depend upon the pressure and nature of the feed composition. In general, high superficial linear velocities are preferred to ensure that not all of the oxygen in the first feed stream is consumed.

In step d) of the present invention, the unreacted oxygen and product stream of

step b) are contacted with a second catalyst together with the second feed stream. In the ensuing reaction, at least a part of the unreacted oxygen is consumed, and an olefinic product is produced. Preferably, substantially all of the unreacted oxygen is consumed.

As mentioned above, this reaction may occur in a second reaction zone of a reactor. In such an embodiment, the unreacted oxygen and product stream of step c) are introduced into the second reaction zone at a velocity of greater than 1 m/s, preferably greater than 3 m/s calculated under feed conditions. These velocities are sufficiently high to prevent flashback into the first reaction zone. The product stream from step b) may be pre-mixed with the second feed stream and the resulting reactant mixture may be contacted with the second catalyst. Suitable mixing means include a baffle plate, a grid or a perforated plate. Alternatively, the unreacted oxygen and product stream of step c) may be contacted with the second catalyst together with the second feed stream, in the absence of a pre-mixing step.

The second feed stream may comprise any suitable hydrocarbon. For example, gaseous hydrocarbons, heavy hydrocarbons or mixtures thereof may be employed. Suitable gaseous hydrocarbons include ethane, propane, butane and mixtures thereof. Suitable heavy hydrocarbons include naptha, gas oil, vacuum gas oil, refinery residues, atmospheric residues, vacuum residues, and crude and fuel oils. Additional feed components such as hydrogen, nitrogen, carbon monoxide, carbon dioxide and steam may also be included in the second feed stream. Hydrogen and/or carbon monoxide may react with the unreacted oxygen present to produce additional heat for driving the cracking process.

Heavy hydrocarbon feed may be contacted with the second catalyst in a liquid or vaporised state. Where the hydrocarbon is contacted as a liquid, the hydrocarbon may be introduced to the second catalyst as a spray of droplets so that partial vaporisation and homogeneous mixing may result. In an embodiment of the invention, liquid hydrocarbon is introduced to the second catalyst using a nozzle.

In the second feed stream, a gaseous hydrocarbon may be alternated with a heavy hydrocarbon, as the hydrocarbon feed stock. Conventionally, this is done to limit exposure of the catalyst to heavier, less volatile hydrocarbons, which may condense on the catalyst and reduce its activity. With the present invention, the second catalyst is maintained at an elevated temperature by virtue of step b). Thus, the present invention allows the catalyst

to be contacted with heavy hydrocarbons for longer periods of time, allowing a higher throughput through the reactor. The efficiency of the heavy hydrocarbon cracking process is thus increased. The second feed stream is introduced 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 time velocity will depend upon the pressure and nature of the feed composition.

The hydrocarbon feed in the second feed stream may be cracked into olefins such as ethene, propene, butene and pentene or a mixtures thereof.

The second catalyst is a catalyst which is suitable for catalysing an auto-thermal cracking process. The catalytic metal is typically platinum. In one embodiment of the present invention, a second metal such as copper, tin, and/or palladium is added to the platinum. Preferably, platinum and/or palladium containing catalyst is used. The catalyst may comprise 0.1 to 5 wt%, preferably 0.25 to 1 wt% of metal.

The second catalyst is preferably supported. Suitable catalyst supports include a wide range of ceramic and metal supports, with alumina supports being preferred. The support may be in the form of spheres or other granular shapes, and may be present as a thin layer or wash coat on another substrate. Preferably, the substrate is a continuous multi-channel ceramic structure such as a foam or a regular channelled monolith. In a preferred embodiment, a gamma alumina coated alpha alumina support is employed. However, a gamma alumina coated lithium aluminium silicate (LAS) foam support or a zirconia ceramic foam may also be employed. In an alternative embodiment, the second catalyst is a metal oxide compound having a perovskite structure.

Advantageously, heat may also be supplied by pre-heating the hydrocarbon in the second feed stream. In the present invention, oxygen and the crackable hydrocarbons may be introduced separately into the cracking or second reaction zone. Accordingly, the temperature of the pre-heated stream need not be limited by auto-ignition considerations, and the hydrocarbon feedstock in the second feedstream may be heated to a temperature of 200°C to 600°C, and preferably to 500° to 600°C.

The cracking reaction may be suitably carried out at a temperature of between 600 and 1200°C , preferably between 850 and 1050 °C and most preferably, between 900 and 1000 °C. It will be understood that the optimum temperature will depend upon the feed mixture and operating pressure.

The cracking reaction may be carried out at atmospheric or elevated pressure. Suitable elevated pressures range from 1.1 to 50 bara, for example, 5 to 50 bara, although pressures of 1.1 to 8 bara, for example, 1.8 bara are preferred. It will be understood that the precise pressures employed will vary depending on the specific reaction conditions and gaseous feeds employed.

Where the cracking reaction is carried out at elevated pressure, the reaction products may be quenched as they emerge from the reaction chamber to avoid further reactions taking place. The reaction product may be quenched within 50 milliseconds from formation. It will be understood, however, that the time required between product formation and the act of quenching will depend upon reaction conditions such as pressure and temperature.

The products may be quenched using rapid heat exchangers of the type familiar in steam cracking technology. Additionally or alternatively, a direct quench may be employed. Suitable quenching fluids include water and hydrocarbons such as ethane or naphtha.

The process of the present invention may be carried out in a fluid bed, fixed bed or spouted bed reactor. Fixed bed reactors are preferred.

Any coke produced in the process of the present invention may be removed by mechanical means, or using one of the decoking methods described in EP 0 709 446, incorporated herein by reference.

These and other aspects of the present invention will now be described with reference to the following Examples.

Example 1

In this Example, a metal reactor comprising i) a first reaction zone in the form of a side reaction chamber (inner diameter 18mm), and ii) a second reaction zone in the form of a main reaction chamber (inner diameter 35 mm) was employed. The side reaction chamber was connected to the main reaction chamber via an inlet.

Methane, oxygen, hydrogen co-feed and nitrogen were introduced into the side reaction chamber at feed rates of about 8.2 g/min, 13.6 g/min, 0.4 g/min and 1.1 g/min, respectively. Ethane and nitrogen co-feed were introduced into the main reaction chamber at rates of about 22.5 to 24.48 g/min, and 1.1 to 1.3 g/min, respectively. The

ethane was pre-heated between 200° and 500°C.

A side catalyst in the form of a 0.5 wt% Pt/0.1 wt% Pd-loaded LAS (lithium alumina silicate) monolith (15 mm diameter x 30 mm length, 10 ppi) was positioned in the side reaction chamber adjacent the inlet connecting the side and main chambers. The side feed stream was contacted with the side catalyst to produce a product stream and unreacted oxygen. The properties of the first catalyst, e.g. catalyst length, metal loading, porosity, were selected to ensure that sufficient unreacted oxygen was present in the stream entering the main reaction chamber to support an auto-thermal cracking reaction.

A main catalyst in the form of a catalyst support, lithium alumina silicate (LAS) foam loaded with 1.0/0.2 wt% Pt/Pd (28 mm diameter x 15 mm length, 30 ppi) was located in the main reaction chamber. The main catalyst was positioned below the side reaction chamber/main reaction chamber interface to allow sufficient mixing between the product stream from the side reaction chamber and the main feed stream. The resulting mixture is contacted with the main catalyst thereby consuming substantially all of the unreacted oxygen to produce an olefinic product comprising ethene.

Both reaction chambers contained quartz inserts to minimise heat losses. The reactors were operated at close to atmospheric pressure.

Feed rates, molar ratios, reaction conditions and experimental results are shown in Table 1a. Ethene selectivity is defined as ratio of mass ethene over mass ethane utilised. Product Composition (wt% C) is defined as ratio of weight of carbon in product over total weight of carbon in feed.

Table 1a

Total Flow nl/min	Ethane Preheat (°C)	Main Feed [illegible] nl/min	Ethane feed second stream nl/min	C_2H_6/O_2	CH_4/O_2	H_2/O_2	N_2/O_2	O/C Mass Ratio	Product Temperature (°C)	Ethane Conversion (wt%)	Methane Conversion (wt.%)	Ethene Selectivity (%)
43.43	226	26.03	16.3	1.96	1.5	0.41	0.2	0.57	[illegible]	72	-1.33	63
44.55	297	26.96	18.71	2.07	1.2	0.41	0.3	0.58	945	80.9	-4.35	67
43.10	339	26.03	16.58	1.92	1.5	0.41	0.3	0.55	904	68.1	-3.39	67
43.62	434	26.03	16.6	1.96	1.5	0.41	0.3	0.57	886	71.2	-3.01	65
44.45	440	26.76	17.83	1.85	1.2	0.41	0.3	0.54	897	71.3	-1.5	67

Product Composition wt%C

C_2H_4	C_2H_6	C_2H_2	CH_4	CO	CO_2	$C_3/C_4/C_5$	C_6H_6
30.50	37.26	0.37	23.75	11.01	1.48	3.31	0.87
31.38	32.74	0	23.31	8.5	1.37	3.14	0.85
33.5	37.65	0.3	24.36	9.83	1.13	3.03	0.11
34.59	40.33	0.61	28.64	11.86	1.84	3.9	0.64
31.38	30.87	0.4	24.35	10.36	0.96	3.1	0.86

<u>Comparative Example</u>

In this comparative example, a metal reactor having a single reaction chamber was employed. The chamber was loaded with a 0.1wt%Pd/0.2wt% Pt on LAS catalyst which was identical to the main Pd/Pt catalyst of Example 1. Ethane, oxygen and nitrogen co-feed were introduced into the reaction chamber at the feed rates listed in Table 1b below. The reactants were preheated to a temperature of 150°C.

The pre-heated reactants were reacted in the presence of the Pd/Pt catalyst to produce an olefinic product comprising ethene. Table 1b compares the selectivities and ethane/oxygen mass ratios achieved in Example 1 with those achieved in the Comparative Example.

Table 1b shows the advantages in terms of selectivity and ethane/oxygen mass ratio in comparison to experiments carried out with a metal reactor comprising only a main reaction chamber.

Table 1b

	[illegible]				[illegible]		
	1	2	3	4	1	2	3
Preheat (°C)	210	350	400	440	130	130	130
Feed flow rates (g/min)							
Methane	0.16	0.16	0.16	0.16	0	0	0
Hydrogen	0.30	0.33	0.30	0.33	0	0	0
Ethane	22.5	24.40	22.5	20.61	21.86	15.21	15.21
Oxygen	13.63	13.63	13.63	13.63	13.0	12.0	8.39
Nitrogen	2.44	2.44	2.44	2.44	4.13	2.89	3.04
Ethane Conversion (%)	70	68.1	72.8	71.5	77.8	75.3	71.8
Ethene Selectivity (%)	63.0	67	65	67	50.6	60.5	55.8
Ethane / Oxygen	0.77	0.83	0.83	0.83	0.83	0.81	0.78

Example 2

This Example was carried out using the reactor and main catalyst of Example 1. However, instead of a Pt/Pd side catalyst, a 30 ppi, approximately 2 wt% Rh catalyst (15 mm diameter x 15 mm length) was employed.

Reaction conditions and experimental results are tabulated in Table 2.

Table 2

Total Flow (nl/min)	Ethane Preheat (°C)	C_2H_6/O_2	H_2/O_2	N_2/O_2	CH_4/O_2	O2:C Mass Ratio	Product Temperature (°C)	Ethane Conversion (wt%)	Ethene Selectivity[1] (%)	C_2H_4	C_2H_2	CH_4	Yield CO	(with C) CO_2	C_3/C_4	C_6H_6	[illegible]
33.40	352	2.0	0	0.37	1.78	0.46	[illegible]	41.1	78.1	30.10	0.8	24.94	3.30	1.72	1.78	0	30.1
34.46	352	1.98	0.39	0.26	1.78	0.47	[illegible]	47.5	80.0	25.31	0.8	24.07	10.19	1.54	1.65	0	22
30.97	301	2.21	0.04	0.11	1.59	0.46	[illegible]	30.5	71.9	34.31	0.9	23.01	0.83	1.41	1.57	0.04	7.3
33.02	304	1.88	0	0.19	1.58	0.54	[illegible]	50.7	68.5	28.97	0.8	25.53	13.51	1.58	1.41	0	7

Example 3

In this Example, a main stream comprising a heavy hydrocarbon oil was employed. As can be seen in Table 3, hydrocarbon feedstocks such as Forties Vacuum Residue, Arabian Light Vacuum Residue and Arabian Light Atmospheric Residue were employed. The Example was carried out using a reactor which was formed of a metal tube flanged at both ends and fitted with a quartz liner to minimise heat loss. The reactor comprises a first reaction zone in the form of a side reaction chamber (inner diameter 18 mm) This is connected at right angles to a second reaction zone in the form of a main reaction chamber (inner diameter 35 mm) via an inlet.

The side reaction chamber was provided with a catalyst (15 mm OD * depth of 30 mm, 10 ppi) which was supported on LAS foam. The foam support was loaded with 1.5 wt% Pt and 0.3 wt% Pd when Forties VR was employed in the main catalyst feed stream. In contrast, when Arabian Light Vacuum Residue and Arabian Light Atmospheric Residue were employed in the main feed stream, metal loadings of 0.25 wt% Pt and 0.05 wt% Pd were employed, respectively.

The main reaction chamber was provided with a catalyst bed (28 mm OD * 30 mm depth, 10 ppi LAS foam) comprising1.0 wt% Pt and 0.2 wt% Pd on LAS foam.

Methane, oxygen and hydrogen co-feed were introduced into the side reaction chamber at a rate of 8 g/min, 12.7 g/min and 0.5 g/min, respectively. These gases were contacted with the side catalyst to produce a product stream and unreacted oxygen. The properties of the first catalyst, e.g. catalyst length, metal loading, porosity, were selected to ensure that sufficient unreacted oxygen was present in the stream entering the main reaction chamber to support an auto-thermal cracking reaction.

Hydrocarbon oil was fed into the main reaction chamber using a gas assist hydraulic nozzle (0.6 mm / 30 or 60 degree). Nitrogen (current gas) was fed at 1.5 nl/min into the nozzle through a 1/16th inch tube immediately above a swirl chamber to produce an oil/gas mixture. The flow rate for the oil and nitrogen are approximately 33.0 g/min and1.5 g/min, respectively.

The main catalyst was positioned approximately 50 mm from the nozzle and a conical spray of the gas/oil mixture is sprayed onto the catalyst at a conical angle of 30 or

60 degrees.

The distance between the side chamber inlet and the nozzle was approximately 50 mm. The length of the main reaction chamber exit pipe to the collection vessel was equivalent to a residence time between 100 to 150 ms dependent on temperature.

Feed rates, molar ratios, reaction conditions and experimental results for different feedstocks are shown in Table 3.

Table 3

Feedstock	Total Gas Flow (nl/min)	CH_4/O_2	N_2/O_2	O_2/C Mass Ratio	Main Catalyst Temperature (°C)	Feedstock Conversion (wt%)	C_2H_4	C_3H_6	CH_4	CO	CO_2	C_2H_2	C_4H_6	Coke	Liquid
Forties VR	20.3	1.59	0.33	0.38	335	58.4	8.45	0.86	20.68	6.51	1.85	1.11	1.57	3.3	36.5
Forties VR	20.0	1.29	0.33	0.36	350	61.8	11.3	0.53	21.10	3.53	2.91	1.10	1.64	4.36	33.4
Arabian Light VR	24.3	1.39	0.33	0.35	700	34.8	9.65	1.04	14.74	7.88	1.79	1.13	0.35	7.39	40.6
Arabian Light AR	20.3	1.40	0.33	0.36	690	47.5	10.47	1.30	14.69	8.65	1.34	1.13	0.80	2.98	43.9

Claims

1. A process for the production of olefins from a hydrocarbon, said process comprising the steps of:

a) providing a first feed stream comprising a gaseous fuel and an oxygen-containing gas,

b) contacting said first feed stream with a first catalyst under conditions so as to produce a product stream and unreacted oxygen,

c) providing a second feed stream comprising a hydrocarbon feedstock, and

d) contacting said second feed stream, said product stream of step b) and said unreacted oxygen of step b) with a second catalyst which is capable of supporting oxidation, thereby consuming at least a part of the unreacted oxygen to produce an olefin product.

2. A process as claimed in claim 1, wherein the gaseous fuel is selected from the group consisting of a hydrocarbon, hydrogen, carbon monoxide, an alcohol, an oxygenate and/or ammonia.

3. A process as claimed in claim 2, wherein the gaseous fuel is methane, ethane, propane and/or butane.

4. A process as claimed in claim 3, wherein the reaction between the gaseous fuel and oxygen-containing gas is a synthesis gas producing reaction.

5. A process as claimed in any of claims 1 to 3, wherein the reaction between the gaseous fuel and oxygen-containing gas is a combustion reaction.

6. A process as claimed in any preceding claim, wherein the first catalyst comprises rhodium, platinum, palladium, nickel or a mixture thereof.

7. A process as claimed in any preceding claim wherein the gaseous fuel to oxygen ratio in the first feed stream is 1.5 to 4 times the stoichiometric ratio required for complete combustion to carbon dioxide to water.

8. A process as claimed in any preceding claim, which is carried out in a reactor comprising at least two reaction zones which are in fluid communication with one another.

9. A process as claimed in claim 8, wherein the first reaction zone is provided with the first catalyst, and the second reaction zone is provided with the second catalyst.

10. A process as claimed in claim 9, wherein the reactor comprises a main chamber and a side chamber, and wherein one of said chambers defines the first reaction zone, and the other of said chambers defines the second reaction zone.

11. A process as claimed in claim 9, wherein the first and second reaction zones are defined by at least two nested tubular housings.

12. A process as claimed in claim 11, wherein the outer of said housings extends beyond the end of the inner of said housings, such that fluid entering said outer housing from said inner housing mixes with the second feed stream before coming into contact with the second catalyst.

13. A process as claimed in any preceding claim wherein the hydrocarbon feedstock of the second feed stream comprises a gaseous hydrocarbon, a heavy hydrocarbon or a mixture thereof.

14. A process as claimed in claim 13, wherein the hydrocarbon feedstock is ethane, propane, butane and mixtures thereof.

15. A process as claimed in claim 13, wherein the hydrocarbon feedstock is naphtha, gas oil, vacuum gas oil, refinery residues, atmospheric residues, vacuum residues, and/or crude and fuel oils.

16. A process as claimed in any preceding claim wherein at least one of hydrogen, nitrogen, carbon monoxide, carbon dioxide and steam may also be included in the first or second feed stream as an additional feed component.

17. A process as claimed in any preceding claim wherein the second catalyst comprises copper, tin, platinum and/or palladium.