



Industria y Comercio

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Procedimiento Integrado para la producción
de derivados de olefinas.

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71. SOLICITANTE

Innovene Europe Limited

DOMICILIO

Middlesex Gran Bretaña

74. APODERADO

D.ña Maria Rodriguez D' Aleman

22. BOGOTÁ, D. C.,

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ENTRADA EN FASE NACIONAL

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2) SOLICITANTE (71)	Nombre: INNOVENE EUROPE LIMITED		IDENTIFICACIÓN C.C. ☐ NIT: ☐ C.E. ☐ OTRO ☐ Cual _____ NÚMERO _____
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***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
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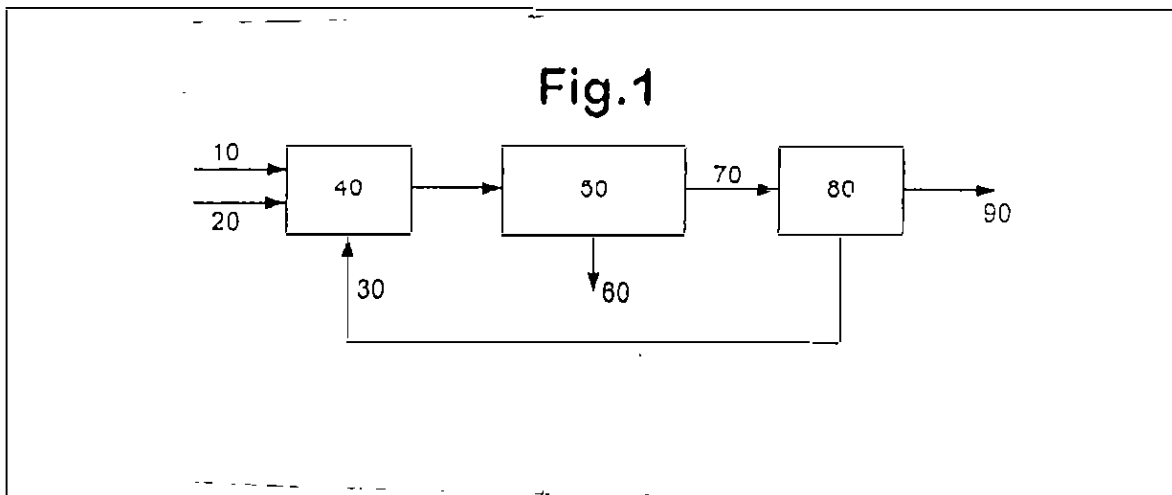
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10)

ANEXOS

- ☒ 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
- ☒ Copia de la solicitud Internacional. (Resumen, descripción, reivindicación, Dibujos).
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicación, Dibujos)
- ☒ 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
- ☐ 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.
- ☒ Otros:
 1. Solicitud PCT
 2. Notificación transmisión de la prioridad
 3. Demanda Pct Capítulo II
 4. Notificación de la recepción del examen preliminar
 5. Notificación de la transmisión del reporte de patentabilidad
 6. Información oficinas designadas
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 8. Opinión escrita de la autoridad de búsqueda
 9. Pago de tasas adicionales
 10. Notificación de cambio de nombre del solicitante

11) FIGURA CARACTERÍSTICA:



12) Solicitud concesión de la patente,

NOMBRE: DILIA RODRÍGUEZ D'ALEMAN

FIRMA:

[Handwritten signature]

C.C. 41.654.882 de Bogotá TP 20824 CSJ

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Information on patent family members

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4

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1001001	A	17-05-2000	US 6111156 A EP 1001001 A1	29-08-2000 17-05-2000
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GB 2325237	A	18-11-1998	IT MI971129 A1 CA 2235180 A1 NL 1009182 C2 NL 1009182 A1 US 6011191 A	16-11-1998 15-11-1998 19-05-1999 17-11-1998 04-01-2000
US 3987119	A	19-10-1976	BE 821397 A1 CA 1037971 A1 DE 2449563 A1 FR 2248254 A1 GB 1435069 A IT 1024701 B JP 50070307 A NL 7413046 A	17-02-1975 05-09-1978 30-04-1975 16-05-1975 12-05-1976 20-07-1978 11-06-1975 25-04-1975

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HYMERS, Ronald, Robson
BP International Limited
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Applicant

BP CHEMICALS LIMITED et al

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No. WOFor an explanation as to the reason for this republication of the international application, reference is made to INTD codes (15), (48)
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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,
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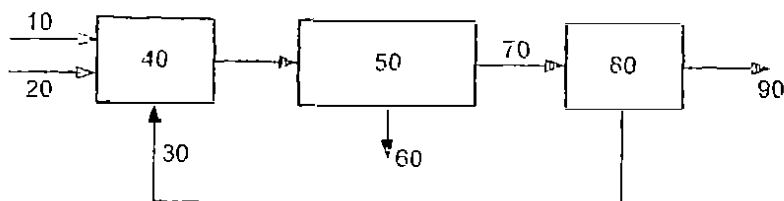
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(54) Title: INTEGRATED PROCESS FOR THE PRODUCTION OF OLEFIN DERIVATIVES



(57) Abstract: The present invention provides a process for the production of an olefin derivative, which process comprises the steps of: (a) cracking a paraffinic hydrocarbon containing feedstock to produce a first dilute olefins stream comprising both olefins and alkanes, (b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol % unreacted olefins, (c) auto-thermally cracking at least a portion of said second dilute olefins stream produced in step (b), said portion comprising alkanes and at least 5 mol % unreacted olefins.

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— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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

INTEGRATED PROCESS FOR THE PRODUCTION
OF OLEFIN DERIVATIVES

The present invention relates to a process for the production of olefin derivatives from a mixed olefin/alkane feedstream. More particularly the present invention relates to an integrated process for the production of olefin derivatives, said integrated process comprising both cracking and olefin derivative processes.

5 Numerous processes are known for the cracking of a hydrocarbon feedstock to produce olefin containing streams. For example, non-catalytic cracking processes such as steam cracking and contacting with hot non-catalytic particulate solids are described in US 3,407,789, US 3,820,955, US 4,499,055 and US 4,814,067, and catalytic cracking processes such as fluid catalytic cracking and deep catalytic cracking are described in
10 US 4,828,679, US 3,647,682, US 3,758,403, US 4,814, 067, US 4,980,053 and US 5,326,465. A further process for production of an olefin containing stream is auto-thermal cracking, as described in, for example, US 5,382,741 and US 5,625,111.

The olefins produced may themselves be used as feedstocks for olefin derivative processes. Numerous such processes are also known and include, for example, the use
15 of olefins in polymerization processes to produce polyethylene, polypropylene and other polymers.

Conventionally the olefins stream produced from the cracking process has undergone extensive and costly purification to produce high purity olefin streams, often >99% wt% olefin, for use in the olefin derivative process. One of the most costly
20 purification steps is the separation of olefins and alkanes of the same carbon number.

More recently, Purvis et al., US 5,981,818, have described a method of integrating cracking and olefin derivative processes utilizing dilute olefins, i.e. olefin streams containing significant quantities of saturated inert hydrocarbons. The olefin

derivative processes described have relatively high conversion of olefins to olefin derivatives. The off-gas from the olefin derivative process thus contains little olefin and may be recycled to the cracker.

5 Olefins, and other unsaturated hydrocarbons, in the feed to a steam cracker will cause carbonaceous fouling of the process equipment. In general, the propensity to cause fouling will depend on the nature of the unsaturated hydrocarbon and its concentration. Nevertheless, even low levels of olefins will cause fouling and reduce the run-time of the steam cracker furnace (before the cracker must be stopped and cleaned). Therefore it is desirable to reduce the concentration of unsaturated hydrocarbons, such
10 as olefins in the feed to the steam cracker, or short furnace run-times must be tolerated, with consequent financial and operational disadvantages.

Thus, the method of Purvis et al. would not apply for olefin derivative processes that are not high conversion processes, since in these processes the off-gas will still contain significant quantities of olefin and alkane.

15 Unless the amount of olefin in the off-gas stream is less than about 5mol%, such streams, if recycled to the cracker, can cause significant problems with coke formation, and significantly reduce run-times, due to the increased levels of olefin in the feed to the cracker. Although the recycle stream is diluted with "fresh" alkane-containing feed before being fed to the cracker, this "fresh" feed may also comprise alkene, and hence,
20 depending on the relative amounts of recycle stream and fresh feed mixed, the level of olefins in the mixed feed can reach levels significantly above that in the "fresh" alkane-containing feed alone. In addition, even small increases in the levels of alkene in the feed to a cracker will reduce run-times, and due to the scale of present-day commercial steam cracking processes small changes in run-time can be commercially significant.
25 Hence separation of olefin and alkane would still be required before recycle to the cracking process.

Although the off-gas stream comprising alkane and olefin may be recycled to the olefin derivative unit to improve conversion, without separation of "inert" impurities, such as the alkane, this will lead to a build-up of the "inert" impurities in the process.
30 Hence separation of alkane from olefin is still required.

Keucher et al., WO 02/06188 describe an alternative system for production of an olefin derivative from a dilute olefins stream. In this system a high quality dilute olefins stream from an olefin unit is fed to an olefin derivative unit to produce an olefin

derivative product. Unreacted olefin is separated from the vent stream in an olefins separation unit and recycled to the olefin derivative unit. A purge stream comprising ethane and lighter components is also produced and may be sent as a feed to an olefin unit. However the process of Keucher still employs significant olefin/alkane separation processes to prevent recycle of unreacted olefin from the olefin derivative unit to the olefin unit.

Hence an improved integrated process for an olefin unit and an olefin derivative unit is still required, in particular for an olefin derivative unit where the off-gas contains more than about 5mol% olefin.

10 In a first aspect the present invention provides a process for the production of an olefin derivative, which process comprises the steps of:

- (a) cracking a paraffinic hydrocarbon containing feedstock to produce a first dilute olefins stream comprising both olefins and alkanes,
- (b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol% unreacted olefins,
- (c) auto-thermally cracking at least a portion of said second dilute olefins stream produced in step (b), said portion comprising alkanes and at least 5 mol% unreacted olefins.

20 Dilute olefins streams, as used herein, refers to olefin streams comprising both olefins and alkanes, for example, both ethylene and ethane. The dilute olefins streams preferably comprise at least 1wt% alkane. Preferably, the first dilute olefins stream comprises at least 50%, and up to 99%, by weight of olefin. The first dilute olefins stream may comprise at least 75wt% olefin, such as at least 90wt% olefin. The first dilute olefins stream preferably comprises up to 50wt% alkane, such as up to 10wt%.

25 The composition of the second dilute olefins stream will generally comprise less olefin than the first dilute olefins stream due to olefin conversion to produce the first olefin derivative in step (b). In particular, the olefin content of the second olefins stream will depend on the olefin content and the olefin conversion of the portion of the first dilute olefins stream reacted in step (b).

The cracking step (a) of the present invention may be performed using any suitable cracking process, such as a non-catalytic cracking process, for example steam cracking, a catalytic cracking process, or an autothermal cracking process. The cracking

process of step (a) is preferably selected from (i) thermal cracking processes, for example of naphtha, (ii) steam cracking processes, for example of an alkane, of a mixture of alkanes or of naphtha and (iii) autothermal cracking processes, for example of an alkane, of a mixture of alkanes or of naphtha.

5 Thus, the paraffinic hydrocarbon containing feedstock fed to step (a) of the process of the present invention may suitably comprise a single alkane, such as ethane, a mixture of alkanes, such as NGL (natural gas liquids), or naphtha. The paraffinic hydrocarbon containing feedstock may additionally comprise one or more unsaturated hydrocarbons, one or more inert compounds (such as nitrogen), hydrogen and/or carbon
10 oxides (said compounds being in addition to any such compounds that may be produced and recycled where the cracking step (a) is performed using an autothermal cracking process).

Auto-thermal cracking processes are described in, for example, US 5,382,741 and US 5,625,111. In an autothermal cracking process, paraffinic hydrocarbon-
15 containing feedstock is reacted in the presence of a catalyst capable of supporting combustion beyond the normal fuel-rich limit of flammability, to produce a stream comprising olefins and alkanes.

It has now been found that auto-thermal cracking processes may be operated with higher levels of olefin in the feed than for cracking processes such as steam
20 cracking.

In the first aspect of the present invention, at least a portion of the second dilute olefins stream is auto-thermally cracked. Because the auto-thermal cracking process of step (c) may be operated with higher levels of olefin in the feed than a non-autothermal cracking process, at least a portion of the second dilute olefins stream may be passed to
25 the auto-thermal cracker without treatment to separate the olefin from the alkane. Preferably the portion of the second dilute olefins stream passed to the autothermal cracker comprises at least 50% of the alkane and at least 50% of the olefin in the second dilute olefins stream, especially at least 80% of the alkane and at least 80% of the olefin in the second dilute olefins stream. Most preferably the portion of the second dilute
30 olefins stream passed to the autothermal cracker comprises essentially all of the alkanes and of the olefins in the second dilute olefins stream. The whole of the second dilute olefins stream may be passed directly to the auto-thermal cracking step, or, alternatively, the second dilute olefins stream may be treated to remove one or more

components other than alkane and olefin therefrom, prior to the auto-thermal cracking step. Optionally, additional alkane-containing feed may be added to (the at least a portion of) the second dilute olefins stream before auto-thermal cracking. The additional feed may also comprise a low level of alkene.

5 The concentration of olefin (unreacted olefin from the second dilute olefins stream and additional olefin that may be present in any additional alkane-containing feed) in the feed to the auto-thermal cracking step may thus be greater or lower than that in the second dilute olefins stream. Typically, the concentration of olefin in the feed passed to the auto-thermal cracking step is at least 4 mol%, such as at least 5 mol%.

10 Such levels could cause significant coking in cracking processes such as steam cracking.

 In one embodiment of the first aspect of the present invention the cracking step (a) is performed using a different cracker than the auto-thermal cracking step (c). Thus, both an auto-thermal cracker and a non-auto-thermal cracker, for example a steam
15 cracker, may be used for the process of the invention. Both an auto-thermal cracker and a non-auto-thermal cracker may be present in the same location, for example, where the non-auto-thermal cracker has been debottlenecked by addition of an auto-thermal cracker. In this embodiment, the product from the auto-thermal cracking step (c), may be preferably added to the first dilute olefins stream obtained from step
20 (a), prior to reaction of said stream in step (b). The non-auto-thermal cracking process of this embodiment is preferably a thermal cracking process, for example of naphtha, or a steam cracking process, for example of an alkane, of a mixture of alkanes or of naphtha.

 Most preferably, the cracking step (a) in the first aspect of the present invention
25 is an auto-thermal cracking step, as in step (c). Hence in a preferred embodiment, the first aspect provides a process for the production of an olefin derivative, which process comprises the steps of:

(a) auto-thermally cracking a feed comprising a paraffinic hydrocarbon containing feedstock and a recycle stream to produce a first dilute olefins stream comprising both
30 olefins and alkanes,

(b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol% unreacted olefins,

(c) recycling at least a portion of said second dilute olefins stream produced in step (b) as the recycle stream in the auto-thermal cracking step of step (a), said portion comprising alkanes and at least 5 mol% unreacted olefins.

In this preferred embodiment of the first aspect of the present invention, at least a portion of the second dilute olefins stream is recycled to the auto-thermal cracking step (a). As described previously, the whole of the second dilute olefins stream may be recycled directly to the auto-thermal cracking step, or, alternatively, the second dilute olefins stream may be treated to remove one or more components other than alkane and olefin therefrom, prior to recycle to the auto-thermal cracking step. The paraffinic hydrocarbon containing feedstock may comprise a low level of alkene, for example as an impurity, typically at a level of 1 to 3mol%.

Thus, the concentration of olefin (unreacted olefin recycled from the second dilute olefins stream and additional olefin that may be present in paraffinic hydrocarbon containing feedstock) in the feed to the auto-thermal cracking step (a) may be greater or lower than that in the second dilute olefins stream. Typically, the concentration of olefin in the feed to the auto-thermal cracking step (a) is at least 4 mol%, such as at least 5 mol%.

The auto-thermal cracking process may be operated at any suitable pressure, such as, for example from 1 to 40 bar. Especially in the preferred embodiment of the first aspect of the present invention, where step (a) is an auto-thermal cracking step, the auto-thermal cracking process is preferably operated at a suitable pressure corresponding to the pressure of the first olefin derivative process i.e. to the process utilised in step (b) for reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream. For example, if the first olefin derivative process operates at relatively low pressures, such as 10 bar, it may be advantageous to operate the auto-thermal cracking process at a pressure from 5 to 15 bar, preferably 8 to 12 bar, to reduce the amount of compression required between the processes for the first dilute olefins stream and/or for the recycle stream. Similarly, if the first olefin derivative process operates at higher pressures, such as 30 bar, it may be advantageous to operate the auto-thermal cracking process at a pressure, for example, from 25 to 35 bar. Alternatively, it may be advantageous to operate the auto-thermal cracking process at relatively low pressures, such as 1 to 5 bar, even with first olefin derivative processes that operate at higher pressures than 5 bar.

The product stream from cracking process of step (a) (autothermal cracking or other) will generally comprise a mixture of olefins and alkanes. Preferably the product stream may undergo separation and purification steps, as known in the art, to remove, for example, one or more of hydrogen, methane, CO_x, acetylenic compounds and
5 dienes. At least some of the separated compounds, especially hydrogen, acetylenic compounds and/or dienes that have been separated where step (a) is an auto-thermal cracking step, may be recycled to the cracking step (a). The product stream also preferably undergoes separation to produce, for example, a C₂ stream comprising predominantly ethane and ethylene, and a C₃ stream comprising predominantly propane
10 and propylene. These streams may also be subjected to olefin purification steps to increase the olefin content. In certain embodiments of the present invention, certain components other than the olefins in the product stream may be desired in the first olefin derivative process. In particular, carbon monoxide and/or hydrogen may be retained in the product stream, and hence may be present in the first dilute olefins
15 stream, where these are reactants in the first olefin derivative process, for example, where the first olefin derivative process is a hydroformylation process or a process for the production of polyketones.

All or part of one or more of the above streams comprising olefin and alkane may subsequently be used as the first dilute olefins stream. The extent of separation and
20 purification of the product stream required to produce the dilute olefins stream will depend on the olefin derivative processes in which the dilute olefins stream is subsequently to be reacted.

However, as the present invention utilizes dilute olefins streams (comprising both olefins and alkanes), separation and purification stages will generally be less
25 extensive than conventional separation and purification, and/or may allow debottlenecking of existing cracking processes – see, for example, US 5,981,818 and WO 02/06188.

In the embodiment of the first aspect of the present invention where the cracking step (a) is performed using a different cracker than the auto-thermal cracking step (c),
30 the product stream from the auto-thermal cracking step (c) will generally comprise a mixture of olefins and alkanes. This stream may be treated as described above for the product stream from cracking of the paraffinic hydrocarbon-containing feedstock, for example, in a series of separation and purification steps, to give an olefins stream

suitable for a subsequent olefin derivative process. For example, the product stream from the auto-thermal cracking step (c) may be treated to produce a dilute olefins stream, which can subsequently be combined with the first dilute olefins stream produced in step (a) and reacted in step (b). Preferably the product stream from the auto-thermal cracking step (c) is added to the product stream from the cracking step (a), and the combined stream subjected to separation and purification as described above to give the first dilute olefins stream for step (b). This has the advantage that only one purification train is required.

The first dilute olefins stream is subsequently reacted to produce a first olefin derivative. This step may comprise reaction of the first dilute olefins stream in any suitable first olefin derivative process. The present invention has the advantage that olefin derivative processes that have relatively low olefin conversion may be employed, using dilute olefins streams, as the first olefin derivative process, and without requiring physical separation of the olefin and alkane from the off-gas (second dilute olefins stream). Hence the cost of producing high purity olefins streams as a feed or the cost of subsequent separation of the olefin and alkane can be avoided.

By low olefin conversion is meant less than 80% olefin conversion, such as 70% or lower.

In addition, certain olefin derivative processes which are conventionally operated at high conversion, such as having high conversion per pass or by recycle of unreacted olefin to produce high overall conversion, may advantageously be operated as lower conversion processes according to the process of the present invention since the unreacted components may be further utilised.

By high conversion is meant a process that produces a product stream comprising less than 5mol% olefins, preferably less than 3mol% olefins. Suitable processes typically have an olefin conversion of at least 95%. In particular, olefin derivative processes which are conventionally operated at high overall conversion by recycle of unreacted olefin often require a significant purge to prevent build-up of unreactive components in the recycle. The purges are often disposed of, for example by venting. Operating at a lower conversion (by reducing the recycle to the olefin derivative process) and recycling to an autothermal cracker according to the process of the first aspect of the present invention can reduce the requirement for a purge.

Where the dilute olefins stream comprises ethylene, suitable olefin derivative

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processes may comprise, for example, processes for the production of ethanol from ethylene and water, for the production of vinyl acetate, ethylene polymerisation processes and ethane tolerant processes for the production of ethylene oxide.

Where the dilute olefins stream comprises propylene, the olefin derivative processes may comprise, for example, processes for the production of propylene oxide, for the production of acrolein and propylene ammoxidation processes, as well as certain processes for the production of polypropylene.

The olefin derivative processes may also comprise processes utilising mixed dilute olefins streams, for example comprising ethylene and propylene. Suitable processes include, for example, ethylene/propylene co-polymerisation processes.

Other olefin derivative processes that may suitably be employed in step (b) of the present invention include processes for the production of ethyl benzene, the production of linear alpha olefins, the metathesis of ethylene with butene to give propene, hydroformylation of ethylene or propylene with CO and hydrogen, and production of polyketones from olefins and carbon monoxide, such as described in WO 93/01224.

Step (b) comprises reacting at least a portion of said first dilute olefins stream to produce a first olefin derivative stream and a second dilute olefins stream. Preferably, all of the first dilute olefins stream is reacted to produce said first olefin derivative stream and said second dilute olefins stream. However, in one embodiment of the present invention, a portion of said first dilute olefins stream may be reacted in one or more further olefin derivative processes to produce one or more further olefin derivative streams.

Step (b) may also comprise more than one olefin derivative processes operated in series. For example, the first dilute olefins stream may be reacted to produce a first olefin derivative stream and an intermediate dilute olefins stream, and at least a portion of said intermediate dilute olefins stream may be reacted to produce a further olefin derivative stream and a further dilute olefins stream. The further dilute olefins stream, and, optionally, any of the intermediate dilute olefins stream not reacted in the further olefin derivative unit, can then form the second dilute olefins stream of the invention.

In the first aspect of the present invention, at least a portion of the second dilute olefins stream is reacted in an auto-thermal cracking step, which may or may not be the same cracking step as step (a). Preferably, all of the second dilute olefins stream is

reacted in the auto-thermal cracking step. In one embodiment of the first aspect of the present invention, a portion of said second dilute olefins stream may be reacted in one or more further olefin derivative processes to produce one or more further olefin derivatives before reacting in the auto-thermal cracking step, for example, before
5 recycle to step (a) (where the cracking step in step (a) is an auto-thermal cracking step).

In a second aspect the present invention provides a process for the production of an olefin derivative, which process comprises the steps of:

- (a) cracking a paraffinic hydrocarbon containing feedstock to produce a first dilute olefins stream, comprising both olefins and alkanes,
- 10 (b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol% unreacted olefins,
- (c) reacting at least a portion of said second dilute olefins stream produced in step (b), said portion comprising alkanes and at least 5 mol% unreacted olefins, to produce a
15 second olefin derivative stream, comprising a second olefin derivative, and a recycle stream, comprising unreacted alkane and less than 5mol% olefins, and
- (d) recycling said recycle stream produced in step (c) to the cracking step of step (a).

The cracking process of step (a) of the second aspect is preferably selected from
20 (i) thermal cracking processes, for example of naphtha, (ii) steam cracking processes, for example of an alkane, of a mixture of alkanes or of naphtha and (iii) autothermal cracking processes, for example of an alkane, of a mixture of alkanes or of naphtha.

Most preferably the cracking step (a) of the second aspect comprises auto-thermally cracking the paraffinic hydrocarbon-containing feedstock.

25 Step (b) in the second aspect is preferably as described in the first aspect of the invention.

In this second aspect of the present invention, at least a portion of the second dilute olefins stream is reacted to produce (in step (c)) a second olefin derivative stream, comprising a second olefin derivative, and a recycle stream, comprising unreacted
30 alkane and less than 5mol% olefins. The second olefin derivative produced in step (c) may be the same or may be different to the first olefin derivative. For example, where the dilute olefins stream comprises ethylene and ethane, both the first and second ethylene derivatives may be polyethylene products. Alternatively, the first ethylene

derivative may, for example, be a polyethylene product and the second ethylene derivative may, for example, be an ethylbenzene product.

Preferably all of the second dilute olefins stream is reacted to produce said second olefin derivative stream, and said recycle stream. However, in one embodiment, a portion of said second dilute olefins stream may be reacted in one or more other olefin derivative processes to produce one or more further olefin derivatives.

In the second aspect, step (c) comprises reacting at least a portion of said second dilute olefins stream to produce a second olefin derivative stream and a recycle stream comprising unreacted alkane and less than 5mol% olefins. Preferably, said recycle stream comprises less than 3mol% olefins, and most preferably less than 1mol% olefins. A low concentration of olefins is preferred where the cracking step of step (a) is a steam cracker, since this will have the least detriment on cracker run-times. Hence step (c) preferably comprises reacting said at least a portion of said second dilute olefins stream in an olefin derivative process of relatively high olefin conversion, such as at least 90% conversion, preferably high olefin conversion, such as at least 95% conversion.

Where the olefin comprises ethylene, the olefin derivative process of step (c) preferably comprises a process for the production of ethylbenzene from ethylene and benzene or a process for polymerisation or co-polymerisation of ethylene, for example by the Phillips Process.

Where the olefin comprises propylene, the olefin derivative process of step (c) preferably comprises a process for the production of polypropylene from propylene.

The invention will now be exemplified by reference to Figures 1 to 5 and the Examples.

Figure 1 represents in schematic form an integrated process for the production of an ethylene derivative according to the first aspect of the present invention.

Figure 2 represents in schematic form an integrated slurry loop polyethylene process for the production of polyethylene according to the first aspect of the present invention.

Figure 3 represents in schematic form an integrated polyketone process for the production of polyketones according to the first aspect of the present invention.

Figure 4 represents in schematic form an integrated metathesis and polypropylene process for the production of polypropylene according to the first aspect of the present invention.

Figure 5 represents in schematic form an integrated polyethylene and ethyl benzene

process for the production of polyethylene and ethyl benzene according to the second aspect of the present invention.

Referring to Figure 1, an ethane feed, 10, a recycle stream, 30 comprising 40% ethylene ($C_2^=$) and 60% ethane (C_2), and an oxygen feed, 20, are fed to an ATC reactor, 40. The mixed product stream is treated, 50, to produce a by-products stream, 60, and a first dilute ethylene stream, 70, comprising approximately 30% ethane and 70% ethylene. This dilute ethylene stream is passed to an ethylene derivative process, 80, of approximately 70% ethylene conversion per pass. The ethane is inert in said process. The olefin derivative product, 90, is separated, along with any other by-products formed, to leave a second dilute ethylene stream comprising ethane and unreacted ethylene, having a composition of approximately 40% ethylene and 60% ethane (and having approximately half the volume of the first dilute ethylene stream), which is recycled to the ATC reactor.

Referring to Figure 2, ethane, 1, and oxygen, 2, and a recycle stream, 3, comprising ethane and ethylene, are fed to an ATC reactor, 4. The product stream is passed to a quench, 5, from which is separated water and higher hydrocarbons, 6, and then to an amine wash, 7, to remove carbon dioxide and further water, 8. The remaining product stream is then passed to a demethaniser, 9, to remove hydrogen, carbon monoxide and methane, 10, and to a deethaniser, 11, to separate C_3+ hydrocarbons, 12, which can be recycled to the ATC reactor, 4.

The remaining product stream is hydrogenated, 13, to remove acetylenic compounds and dienes, to form a first dilute ethylene stream, 14, comprising ethylene and ethane, which is passed to a slurry loop polyethylene process, 15, to produce a polyethylene product, 16, and a second dilute ethylene stream, 17, comprising ethane and unreacted ethylene, which is recycled to the ATC reactor, after addition of stream 12, as recycle stream 3.

Referring to Figure 3, ethane, 1, and oxygen, 2, and a recycle stream, 3, comprising ethane and ethylene, are fed to an ATC reactor, 4. The product stream is passed to a quench, 5, from which is separated water and higher hydrocarbons, 6, and then to an amine wash, 7, to remove carbon dioxide and further water, 8. The remaining product stream is then passed to a deethaniser, 11, to separate C_3+ hydrocarbons, 12, which can be recycled to the ATC reactor, 4.

The remaining product stream, 14, forms a first dilute ethylene stream

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C3

comprising ethylene, ethane, carbon monoxide and hydrogen, and is passed to a polyketones reactor, 15, where it is reacted to produce a polyketone product, 16, and a second dilute olefins stream, 17, which is recycled to the ATC reactor, 4, optionally after addition of C3+ hydrocarbons, 12, separated from the deethaniser.

5 In an alternative polyketone process (not shown), C3 hydrocarbons (propylene and propane) are not separated in the deethaniser, 11, but are fed to the polyketones reactor with the ethylene, ethane, carbon monoxide and hydrogen.

Referring to Figure 4, ethane, 1, and oxygen, 2, and a recycle stream, 3, comprising ethane and ethylene, are fed to an ATC reactor, 4. The product stream is
10 passed to a series of separation steps, including a quench, an amine wash, a demethaniser, a deethaniser and hydrogenation, as described for Figure 2.

The remaining product stream, 14, forms a first dilute ethylene stream comprising ethylene and ethane, which is passed to a metathesis reactor, 15, where it is reacted with a butene feed, 30. The product stream, 31, is passed to a separation train,
15 32, such as one or more distillation columns, to separate out unreacted butene, 33, propylene, 34 and a second dilute ethylene stream, 17, comprising unreacted ethylene and ethane, which is recycled to the ATC reactor, 4, optionally after addition of C3+ hydrocarbons, 12, separated from the deethaniser, 11. Unreacted butenes may be recycled to the metathesis reactor, 15. The propene stream, 34, is passed to a
20 polypropylene reactor, 35, to produce polypropylene, 36.

Referring to Figure 5, ethane, 1, and oxygen, 2, and a recycle stream, 3, comprising ethane, are fed to an ATC reactor, 4. The product stream is passed to a quench, 5, from which is separated water and higher hydrocarbons, 6, and then to an amine wash, 7, to remove carbon dioxide and further water, 8. The remaining product
25 stream is then passed to a demethaniser, 9, to remove hydrogen; carbon monoxide and methane, 10, and to a deethaniser, 11, to separate C3+ hydrocarbons, 12, which can be recycled to the ATC reactor, 4.

The remaining product stream, is hydrogenated, 13, to remove acetylenic compounds and dienes, and to form a first dilute ethylene stream, 14, comprising
30 ethylene and ethane, which is passed to a gas phase polyethylene process, 15, to produce a polyethylene product, 16. A second dilute ethylene stream, 17, comprising ethane and unreacted ethylene is reacted with benzene, 18, in an ethylbenzene reactor, 19, to produce ethylbenzene, 20, and a recycle stream, 21, comprising ethane, which is

recycled to the ATC reactor, 4, after addition of stream 12, as recycle stream 3. In an optional embodiment of Figure 5, a portion of the first dilute ethylene stream, 14, is passed directly to the ethylbenzene reactor, 19, as shown by the dotted line, 14a.

5 **Example 1**

 This example illustrates an integrated slurry loop polyethylene process for the production of polyethylene according to the process of Figure 2.
The slurry loop polyethylene process is operated at an ethylene conversion of 80%.
The compositions of the respective streams in the process are given in Table 1.

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TABLE 1:

Stream Number (Fig 2)	Principle components	Volume of component (kilotons per annum)
1	Ethane	750
2	Oxygen	466
3	Ethane Ethylene C3+ compounds	336 80 50
6	Water and C5+ compounds	378
8	Carbon dioxide and water	86
10	Hydrogen, carbon monoxide and methane	352
12	C3+ compounds	50
14	Ethane Ethylene	336 400
16	Polyethylene	320
17	Ethane Ethylene	336 80

 The stream comprising C3+ compounds (stream 12) comprises predominantly propene (9wt%), propylene (50wt%), butanes (9wt%), butenes (7wt%) and butadiene
15 (24wt%), with the remainder (approximately 1wt%) being C5+ hydrocarbons (including aromatics).

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Example 2

This example illustrates an an integrated polyethylene and ethyl benzene process for the production of polyethylene and ethyl benzene according to the process of Figure 5.

5 The gas phase polyethylene process is operated at an ethylene conversion of approximately 78%, and the ethyl benzene process at an ethylene conversion of approximately 100%.

The compositions of the respective streams in the process are given in Table 2.

10

TABLE 2:

Stream Number (Fig 5)	Principle components	Volume of component (kilotons per annum)
1	Ethane	759
2	Oxygen	489
3	Ethane	335
	C3+ compounds	67
6	Water	373
	C5+ compounds	69
8	Carbon dioxide	32
	Water	20
10	Hydrogen	16
	Carbon monoxide	204
	Methane	133
12	C3+ compounds	67
14	Ethane	335
	Ethylene	400
16	Polyethylene	310
17	Ethane	335
	Ethylene	90
18	Benzene	244
20	Ethylbenzene	334
21	Ethane	335

Claim

1. A process for the production of an olefin derivative, which process comprises the steps of:

(a) cracking a paraffinic hydrocarbon containing feedstock to produce a first dilute olefins stream comprising both olefins and alkanes,

5 (b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol% unreacted olefins,

10 (c) auto-thermally cracking at least a portion of said second dilute olefins stream produced in step (b), said portion comprising alkanes and at least 5 mol% unreacted olefins.

2. The process according to claim 1, wherein the first dilute olefins stream comprises at least 50wt% olefin and at least 1wt% alkane.

3. The process according to claim 1 or claim 2, wherein the cracking step (a) is
15 selected from (i) thermal cracking processes, (ii) steam cracking processes and (iii) autothermal cracking processes.

4. The process according to any one of the preceding claims, wherein the paraffinic hydrocarbon containing feedstock fed to step (a) comprises a single alkane, such as ethane, a mixture of alkanes, such as NGL (natural gas liquids), or naphtha.

20 5. The process according to any one of the preceding claims, wherein the portion of the second dilute olefins stream passed to the autothermal cracker in step (c) comprises at least 50% of the alkane and at least 50% of the olefin in the second dilute olefins stream.

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6. The process according to any one of the preceding claims, wherein the concentration of olefin (unreacted olefin from the second dilute olefins stream and additional olefin that may be present in any additional alkane-containing feed) in the feed passed to the auto-thermal cracking step is at least 4 mol%.

5 7. The process according to any one of the preceding claims, wherein the cracking step (a) is an auto-thermal cracking step, and the process for the production of an olefin derivative comprises the steps of:

(a) auto-thermally cracking a feed comprising a paraffinic hydrocarbon containing feedstock and a recycle stream to produce a first dilute olefins stream comprising both olefins and alkanes,

10 (b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol% unreacted olefins,

15 (c) recycling at least a portion of said second dilute olefins stream produced in step (b) as the recycle stream in the auto-thermal cracking step of step (a), said portion comprising alkanes and at least 5 mol% unreacted olefins.

8. A process for the production of an olefin derivative, which process comprises the steps of:

20 (a) cracking a paraffinic hydrocarbon containing feedstock to produce a first dilute olefins stream, comprising both olefins and alkanes,

(b) reacting at least a portion of said first dilute olefins stream produced in step (a) to produce a first olefin derivative stream, comprising a first olefin derivative, and a second dilute olefins stream, comprising alkanes and at least 5 mol% unreacted olefins,

25 (c) reacting at least a portion of said second dilute olefins stream produced in step (b), said portion comprising alkanes and at least 5 mol% unreacted olefins, to produce a second olefin derivative stream, comprising a second olefin derivative, and a recycle stream, comprising unreacted alkane and less than 5mol% olefins, and

30 (d) recycling said recycle stream produced in step (c) to the cracking step of step (a).

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Fig.1

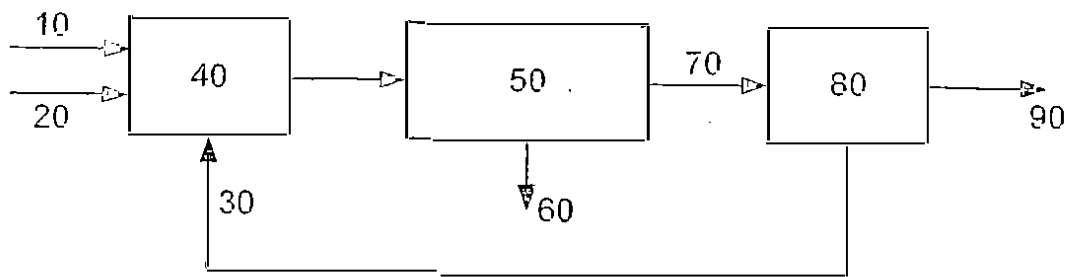


Fig.2

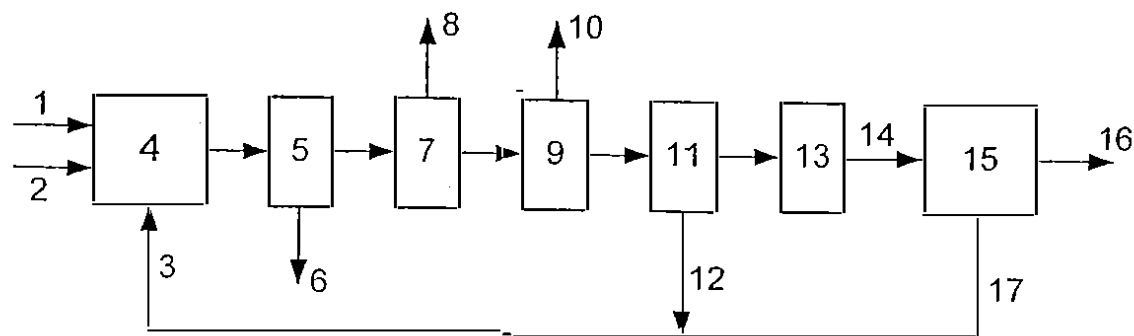


Fig.3

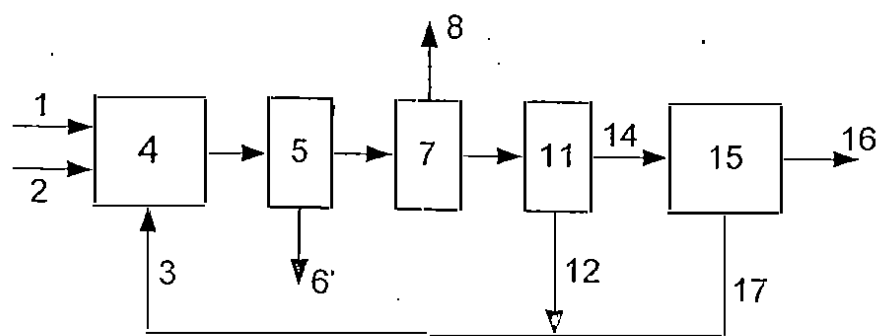


Fig.4

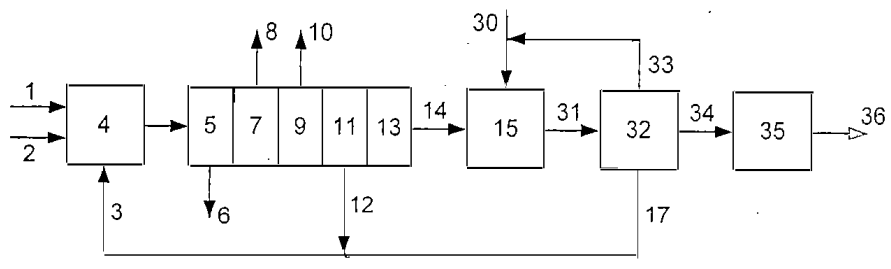
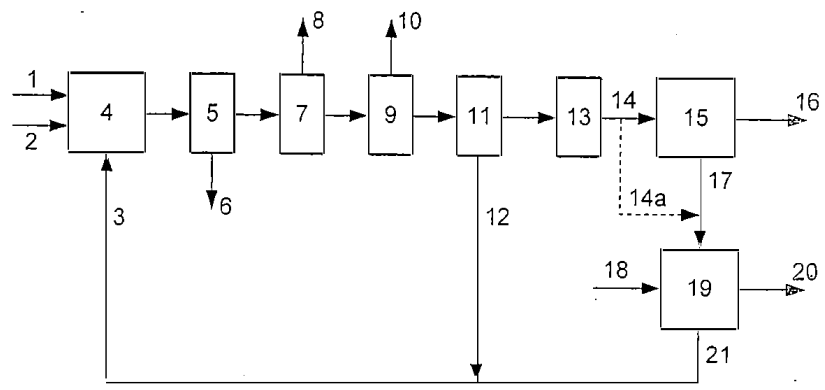


Fig.5



INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001265

18

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G11/22 C10G50/00 C10G57/00 C10G57/02

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 C10G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 001 001 A (NOVA CHEM INT SA) 17 May 2000 (2000-05-17) claims 1,12,13; figures 1B,2B page 2, paragraph 7 page 4, paragraphs 28,32 page 5, paragraph 40	1-7
X	US 5 981 818 A (PURVIS DAVID ET AL) 9 November 1999 (1999-11-09) cited in the application column 2, line 62 - column 3, line 10 column 3, line 65 - column 4, line 8 column 4, lines 23-27 column 9, lines 11-17 column 9, line 65 - column 10, line 1 column 10, lines 15-22 column 11, lines 22-25 ----- -/-	1-7

☒ 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

20 July 2004

Date of mailing of the international search report

20.08.04

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001265

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 325 237 A (SNAM PROGETTI) 18 November 1998 (1998-11-18) figure 1; example 1; tables III,IV page 9, lines 19-24 page 10, lines 17-23 page 12, lines 11-17 page 16, line 2 - page 17, line 4 -----	8
A	US 3 987 119 A (KURTZ BRUCE E ET AL) 19 October 1976 (1976-10-19) claims 1,2; figure column 1, lines 64-67 column 2, lines 7-17 column 3, lines 16-21 -----	1-7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/001265

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Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-7

process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and (iii) autothermally cracking the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins

2. claim: 8

process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream ;(iii) reacting the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins to produce a second olefin derivative stream and (iv) recycling a stream comprising unreacted alkanes and less than 5 mol-% olefins to cracking step (i)

**PROCEDIMIENTO INTEGRADO PARA LA PRODUCCION DE
DERIVADOS DE OLEFINAS**

La presente invención se refiere a un procedimiento para la producción de derivados de olefinas a partir de una corriente de alimentación mixta de olefinas/alcanos. Más particularmente, la presente invención se refiere a un procedimiento integrado para la producción de derivados de olefinas, comprendiendo dicho procedimiento integrado procesos tanto de cracking como de derivados de olefinas.

Se conocen numerosos procedimientos para el cracking de un material de alimentación de hidrocarburos para producir corrientes que contienen olefinas. Por ejemplo, en US 3.407.789, US 3.820.955, US 4.499.055 y US 4.814.067 se describen procedimientos de cracking no catalítico tales como cracking con vapor de agua y contacto con sólidos en partículas calientes no catalíticas, y en US 4.828.679, US 3.647.682, US 3.758.403, US 4.814.067, US 4.980.053 y US 5.326.465 se describen procedimientos de cracking catalítico tales como cracking catalítico fluido y cracking catalítico profundo. Otro procedimiento para la producción de una corriente que contiene olefinas es el cracking autotérmico, como se describe, por ejemplo, en US 5.382.741 y US 5.625.111.

Las olefinas producidas pueden ser utilizadas por sí mismas como materiales de alimentación para procesos de derivados de olefinas. Se conocen también numerosos procesos de ese tipo que incluyen, por ejemplo, el uso de olefinas en procesos de polimerización para producir polietileno, polipropileno y otros polímeros.

Tradicionalmente, la corriente de olefinas producida en el proceso de cracking ha sido objeto de una purificación extensiva y costosa para producir

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corrientes de olefinas de alta pureza, con frecuencia >99% en peso de olefinas, para utilizarse en el proceso de derivados de olefinas. Una de las etapas de purificación más costosas es la separación de olefinas y alcanos del mismo número de átomos de carbono.

Más recientemente, Purvis et al., US 5.981.818, han descrito un método para integrar procesos de cracking y de derivados de olefinas empleando olefinas diluidas, es decir, corrientes de olefinas que contienen cantidades importantes de hidrocarburos saturados inertes. Los procesos de derivados de olefinas descritos presentan una conversión relativamente alta de olefinas a derivados de olefinas. El gas de salida del proceso de derivados de olefinas contiene así poca olefina y debe ser reciclado al craqueador.

Las olefinas, y otros hidrocarburos insaturados, en la alimentación a un craqueador con vapor de agua causará la formación de incrustaciones carbonadas en la instalación del proceso. En general, la tendencia a causar incrustaciones dependerá de la naturaleza del hidrocarburo insaturado y de su concentración. No obstante, incluso bajos niveles de olefinas causarán tales incrustaciones y reducirán el tiempo de trabajo del horno del craqueador con vapor de agua (antes de que el craqueador deba ser detenido y limpiado). Por tanto, es conveniente reducir la concentración de hidrocarburos insaturados, tales como olefinas, en la alimentación al craqueador con vapor de agua, o deberán tolerarse cortos tiempos de trabajo del horno, con las consecuentes desventajas financieras y operativas que ello trae consigo.

De este modo, el método de Purvis et al. no sería de aplicación en procesos de derivados de olefinas que no sean procesos de alta conversión, puesto que en tales procesos el gas de salida contendrá todavía cantidades importantes de olefina y alcano.

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Salvo que la cantidad de olefina en la corriente de gas de salida sea menor de alrededor de 5 moles%, dichas corrientes, si son recicladas al craqueador, pueden causar problemas importantes con la formación de coque y reducir de manera importante los tiempos de trabajo, como consecuencia de los niveles incrementados de olefina en la alimentación al craqueador. Aunque la corriente de reciclo se diluya con una alimentación "nueva" que contiene alcano, antes de alimentarse al reactor, dicha alimentación "nueva" puede comprender también alqueno y, por tanto, dependiendo de las cantidades relativas de corriente de reciclo y alimentación nueva mezcladas, el nivel de olefinas en la alimentación mixta puede alcanzar niveles significativamente por encima del nivel presente solo en la alimentación "nueva" que contiene alcano. Además, incluso pequeños incrementos en los niveles de alqueno en la alimentación a un craqueador reducirá los tiempos de trabajo y, debido a la escala de los procesos de cracking con vapor de agua comerciales de hoy día, los pequeños cambios en el tiempo de trabajo pueden ser comercialmente importantes. En consecuencia, todavía será necesario separar la olefina y el alcano antes de efectuar el reciclo al proceso de cracking.

Aunque la corriente de gas de salida que comprende alcano y olefina puede ser reciclada a la unidad de derivado de olefina, para mejorar la conversión, sin separación de impurezas "inertes", tal como el alcano, ello conducirá a una acumulación de las impurezas "inertes" en el proceso. Por tanto, es necesario todavía efectuar la separación del alcano de la olefina.

Keucher et al., WO 02/06188, describen un sistema alternativo para la producción de un derivado de olefina a partir de una corriente diluida de olefinas. En este sistema, una corriente diluida de olefinas de alta calidad, procedente de una unidad de olefinas, se alimenta a una unidad de derivados de olefinas, para producir

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un producto derivado de olefinas. La olefina sin reaccionar se separa de la corriente de ventilación en una unidad de separación de olefinas y se recicla a la unidad de olefinas. También se produce una corriente de purga que comprende etano y componentes más ligeros, la cual puede ser enviada como alimentación a una unidad de olefinas. Sin embargo, el proceso de Keucher utiliza todavía procesos importantes de separación olefina/alcano para evitar el reciclo de olefina sin reaccionar desde la unidad de derivados de olefinas a la unidad de olefinas.

Por tanto, se requiere todavía un procedimiento integrado mejorado para una unidad de olefinas y para una unidad de derivados de olefinas, en particular para una unidad de derivados de olefinas en donde el gas de salida contiene más de alrededor de 5 moles% de olefinas.

En un primer aspecto, la presente invención proporciona un procedimiento para la producción de un derivado de olefinas, cuyo procedimiento comprende las etapas de:

- (a) craquear un material de alimentación que contiene hidrocarburos parafínicos para producir una primera corriente diluida de olefinas que comprende tanto olefinas como alcanos;
- (b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas, producida en la etapa (a), para producir una primera corriente de derivados de olefinas, que comprende un primer derivado de olefinas, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar;
- (c) craquear autotérmicamente al menos una porción de dicha segunda corriente diluida de olefinas, producida en la etapa (b), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas sin reaccionar.

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Las corrientes diluidas de olefinas, tal y como aquí se emplean, se refieren a corrientes de olefinas que comprenden tanto olefinas como alcanos, por ejemplo, tanto etileno como etano. Las corrientes diluidas de olefinas comprenden preferentemente al menos 1% en peso de alcanos. Con preferencia, la primera corriente diluida de olefinas comprende al menos 50% y hasta 99% en peso de olefina. La primera corriente diluida de olefinas puede comprender al menos 75% en peso de olefina, tal como al menos 90% en peso de olefina. La primera corriente diluida de olefinas comprende preferentemente hasta 50% en peso de alcano, tal como hasta 10% en peso.

La composición de la segunda corriente diluida de olefinas comprenderá en general menos olefina que la primera corriente diluida de olefinas, debido a la conversión de olefinas para producir el primer derivado de olefina en la etapa (b). En particular, el contenido en olefina de la segunda corriente de olefina dependerá del contenido en olefina y de la conversión de olefina de la porción de la primera corriente diluida de olefinas reaccionada en la etapa (b).

La etapa de cracking (a) de la presente invención puede ser efectuada empleando cualquier proceso de cracking adecuado, tal como un proceso de cracking no catalítico, por ejemplo cracking con vapor de agua, un proceso de cracking catalítico o un proceso de cracking autotérmico. El proceso de cracking de la etapa (a) se elige preferentemente entre (i) procesos de cracking térmico, por ejemplo de nafta, (ii) procesos de cracking con vapor de agua, por ejemplo de un alcano, de una mezcla de alcanos o de nafta y (iii) procesos de cracking autotérmico, por ejemplo de un alcano, de una mezcla de alcanos o de nafta.

De este modo, el material de alimentación que contiene hidrocarburos parafinicos, alimentado a la etapa a) del procedimiento de la presente invención,

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puede comprender adecuadamente un solo alcano, tal como etano, una mezcla de alcanos, tal como NGL (líquidos de gas natural) o nafta. El material de alimentación que contiene hidrocarburos parafínicos puede comprender además uno o más hidrocarburos insaturados, uno o más compuestos inertes (tal como nitrógeno) hidrógeno y/u óxidos de carbono (y además de dichos compuestos cualesquiera de aquellos compuestos que pueden producirse y reciclarse cuando la etapa de cracking (a) se efectúa empleando de cracking autotérmico).

Los procesos de cracking autotérmico se describen, por ejemplo, en US 5.382.741 y US 5.625.111. En un proceso de cracking autotérmico, el material de alimentación que contiene hidrocarburos parafínicos se hace reaccionar en presencia de un catalizador capaz de soportar la combustión más allá del límite de inflamabilidad normal rico en combustible, para producir una corriente que contiene olefinas y alcanos.

Se ha comprobado ahora que los procesos de cracking autotérmico pueden ser realizados con niveles de olefina en la alimentación mayores que en el caso de los procesos de cracking tal como cracking con vapor de agua.

En el primer aspecto de la presente invención, al menos una porción de la segunda corriente diluida de olefinas es sometida a cracking autotérmico. Debido a que el proceso de cracking autotérmico de la etapa (c) puede ser efectuado con niveles de olefina en la alimentación mayores que en el caso de un proceso de cracking no autotérmico, al menos una porción de la segunda corriente diluida de olefinas se puede pasar al craqueador autotérmico sin tratamiento para separar la olefina del alcano. Preferentemente, la porción de la segunda corriente diluida de olefinas, pasada al craqueador autotérmico, comprende al menos 50% del alcano y al menos 50% de la olefina en la segunda corriente diluida de olefinas, especialmente al

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menos 80% del alcano y al menos 80% de la olefina en la segunda corriente diluida de olefinas. Con suma preferencia, la porción de la segunda corriente diluida de olefinas, pasada al craqueador autotérmico, comprende esencialmente la totalidad de los alcanos y de las olefinas de la segunda corriente diluida de olefinas. La totalidad de la segunda corriente diluida de olefinas se puede pasar directamente a la etapa de cracking autotérmico o, alternativamente, la segunda corriente diluida de olefinas se puede tratar para separar de la misma uno o más componentes distintos del alcano y de la olefina, antes de la etapa de cracking autotérmico. Opcionalmente, se puede añadir más alimentación que contiene alcano a la segunda corriente diluida de olefinas (por lo menos a una porción de esta última) antes del cracking autotérmico. La alimentación adicional puede comprender también un bajo nivel de alqueno.

La concentración de olefina (olefina sin reaccionar de la segunda corriente diluida de olefinas y olefina adicional que puede estar presente en cualquier alimentación adicional que contiene alcano) en la alimentación a la etapa de cracking autotérmico, puede ser así mayor o menor que la concentración en la segunda corriente diluida de olefinas. Generalmente, la concentración de olefina en la alimentación pasada a la etapa de cracking autotérmico es de al menos 4 moles%, tal como al menos 5 moles%.

Dichos niveles podrían causar una importante coquificación en los procesos de cracking, tal como cracking con vapor de agua.

En una modalidad del primer aspecto de la presente invención, la etapa de cracking (a) se efectúa empleando un craqueador diferente al de la etapa de cracking autotérmico (c). Así, para el procedimiento de la invención se puede emplear tanto un craqueador autotérmico como un craqueador no autotérmico, por ejemplo un craqueador con vapor de agua. Tanto un craqueador autotérmico como un craqueador

no autotérmico pueden estar presentes en la misma posición, por ejemplo, cuando se ha eliminado el cuello de botella del craqueador no autotérmico por adición de un craqueador autotérmico. En esta modalidad, el producto de la etapa de cracking autotérmico (c), se puede añadir preferentemente a la primera corriente diluida de olefinas obtenida de la etapa (a), antes de la reacción de dicha corriente en la etapa (b). El proceso de cracking no autotérmico de esta modalidad es preferentemente un proceso de cracking térmico, por ejemplo de nafta, o un proceso de cracking con vapor de agua, por ejemplo de un alcano, de una mezcla de alcanos o de nafta.

Con suma preferencia, la etapa de cracking (a) en el primer aspecto de la presente invención es una etapa de cracking autotérmico, como en la etapa (c). Por tanto, en una modalidad preferida, el primer aspecto proporciona un procedimiento para la producción de un derivado de olefina, cuyo procedimiento comprende las etapas de:

- (a) craquear autotérmicamente una alimentación que comprende un material de alimentación que contiene hidrocarburos parafínicos y una corriente de reciclaje, para producir una primera corriente diluida de olefinas que comprende tanto olefinas como alcanos;
- (b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas producida en la etapa (a) para producir una primera corriente de derivado de olefina, que comprende un primer derivado de olefina, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar;
- (c) reciclar al menos una porción de dicha segunda corriente diluida de olefinas producida en la etapa (b) como la corriente de reciclaje en el cracking autotérmico de la etapa (a), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas

sin reaccionar.

En esta modalidad preferida del primer aspecto de la presente invención, al menos una porción de la segunda corriente diluida de olefinas se recicla a la etapa de cracking autotérmico (a). Como se ha descrito anteriormente, la totalidad de la segunda corriente diluida de olefinas puede ser reciclada directamente a la etapa de cracking autotérmico o, alternativamente, la segunda corriente diluida de olefinas puede ser tratada para separar de la misma uno o más componentes distintos del alcano y de la olefina, antes de efectuar el reciclo a la etapa de cracking autotérmico. El material de alimentación que contiene hidrocarburos parafínicos puede comprender un bajo nivel de alqueno, por ejemplo como una impureza, habitualmente en un nivel de 1 a 3 moles%.

De este modo, la concentración de olefina (olefina sin reaccionar reciclada a partir de la segunda corriente diluida de olefinas y olefina adicional que puede estar presente en el material de alimentación que contiene hidrocarburos parafínicos) en la alimentación a la etapa de cracking autotérmico (a), puede ser mayor o menor que la concentración en la segunda corriente diluida de olefinas. Generalmente, la concentración de olefina en la alimentación a la etapa de cracking autotérmico (a) es de al menos 4 moles%, tal como al menos 5 moles%.

El proceso de cracking autotérmico puede ser realizado a cualquier presión adecuada, tal como, por ejemplo de 1 a 40 bar. Especialmente en la modalidad preferida del primer aspecto de la presente invención, en donde la etapa (a) es una etapa de cracking autotérmico, el proceso de cracking autotérmico se efectúa preferentemente a una presión adecuada correspondiente a la presión del proceso de obtención del primer derivado de olefina, es decir, el proceso empleado en la etapa (b) para reaccionar al menos una porción de dicha primera corriente diluida de

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olefinas producida en la etapa (a) para producir corriente del primer derivado de olefina. Por ejemplo, si el proceso de obtención del primer derivado de olefina opera a presiones relativamente bajas, tal como 10 bar, puede ser conveniente efectuar el proceso de cracking autotérmico a una presión de 5 a 15 bar, preferentemente 8 a 12 bar, para reducir la cantidad de compresión requerida entre los procesos para la primera corriente diluida de olefinas y/o para la corriente de recicló. Similarmente, si el proceso de obtención del primer derivado de olefina opera a presiones más altas, tal como 30 bar, puede ser conveniente efectuar el proceso de cracking autotérmico a una presión, por ejemplo, de 25 a 35 bar. Alternativamente, puede ser conveniente efectuar el proceso de cracking autotérmico a presiones relativamente bajas, tal como de 1 a 5 bar, incluso con el proceso de obtención del primer derivado de olefina que opera a presiones mayores de 5 bar.

La corriente producto del proceso de cracking de la etapa (a) (cracking autotérmico u otro) comprenderá en general una mezcla de olefinas y alcanos. Preferentemente, la corriente producto puede someterse a etapas de separación y purificación, como es conocido en la técnica, para separar, por ejemplo, uno o más de hidrógeno, metano, CO_x, compuestos acetilénicos y dienos. Al menos algunos de los compuestos separados, especialmente hidrógeno, compuestos acetilénicos y/o dienos que han sido separados cuando la etapa (a) es una etapa de cracking autotérmico, se pueden reciclar a la etapa de cracking (a). La corriente producto también se puede someter preferentemente a separación para producir, por ejemplo, una corriente de C₂ que comprende predominantemente etano y etileno y una corriente de C₃ que comprende predominantemente propano y propileno. Estas corrientes se pueden someter también a etapas de purificación de olefinas para aumentar el contenido en olefinas. En ciertas modalidades de la presente invención,

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en el proceso de obtención del primer derivado de olefina, se pueden desear ciertos componentes distintos de las olefinas presentes en la corriente producto. En particular, en la corriente producto pueden quedar retenidos monóxido de carbono y/o hidrógeno y, por tanto, pueden estar presentes en la primera corriente diluida de olefinas, cuando aquellos son reactantes en el proceso de obtención del primer derivado de olefina, por ejemplo, cuando el proceso de obtención del primer derivado de olefina es un proceso de hidroformilación o un proceso para la producción de policetonas.

La totalidad o parte de una o más de las corrientes anteriores que comprenden olefina y alcano se puede emplear posteriormente como la primera corriente diluida de olefinas. El grado de separación y purificación de la corriente producto, requerido para producir la corriente diluida de olefinas, dependerá de los procesos de derivados de olefinas en donde la corriente diluida de olefinas ha de reaccionar posteriormente.

Sin embargo, dado que la presente invención utiliza corrientes diluidas de olefinas (que comprenden tanto olefinas como alcanos), las etapas de separación y purificación serán en general menos extensivas que las etapas convencionales de separación y purificación y/o pueden permitir eliminar el cuello de botella de los procesos de cracking ahora existentes – véase, por ejemplo, US 5.981.818 y WO 02/06188.

En la modalidad del primer aspecto de la presente invención, en donde la etapa de cracking (a) se lleva a cabo usando un craqueador diferente al de la etapa de cracking autotérmico (c), la corriente producto procedente de la etapa de cracking autotérmico (c) comprenderá en general una mezcla de olefinas y alcanos. Esta corriente puede ser tratada como se ha descrito anteriormente para la corriente producto procedente del cracking del material de alimentación que contiene

hidrocarburos parafínicos, por ejemplo, en una serie de etapas de separación y purificación, para obtener una corriente de olefinas adecuada para un posterior proceso de obtención de derivados de olefinas. Por ejemplo, la corriente producto procedente de la etapa de cracking autotérmico (c) se puede tratar para producir una corriente diluida de olefinas, la cual se puede combinar posteriormente con la primera corriente diluida de olefinas producida en la etapa (a) y hacerse reaccionar en la etapa (b). Preferentemente, la corriente producto procedente de la etapa de cracking autotérmico (c) se añade a la corriente producto procedente de la etapa de cracking (a) y la corriente combinada se somete a separación y purificación como se ha descrito anteriormente, para obtener la primera corriente diluida de olefinas para la etapa (b). Esto presenta la ventaja de que solo se requiere un tren de purificación.

La primera corriente diluida de olefinas se hace reaccionar posteriormente para producir un primer derivado de olefina. Esta etapa puede comprender la reacción de la primera corriente diluida de olefinas en cualquier proceso adecuado para la obtención de un primer derivado de olefina. La presente invención tiene la ventaja de que pueden emplearse procesos de obtención de derivados de olefinas que presentan una conversión de olefinas relativamente baja, usando corrientes diluidas de olefinas, como el proceso para la obtención del primer derivado de olefina, y sin requerir la separación física de la olefina y del alcano que se encuentran en el gas de salida (segunda corriente diluida de olefinas). Por tanto, puede evitarse el coste de producir corrientes de olefinas de alta pureza como material de alimentación o el coste de la posterior separación de la olefina y del alcano.

Por la expresión "baja conversión de olefinas" se quiere dar a entender una conversión de olefinas menor del 80%, tal como del 70% o más baja.

Además, ciertos procesos para la obtención de derivados de olefinas que

convencionalmente son realizados a una elevada conversión, tal como aquellos que tienen una alta conversión por pasada o mediante reciclo de la olefina sin reaccionar para producir una alta conversión global, pueden ser efectuados convenientemente como procesos de menor conversión de acuerdo con el procedimiento de la presente invención, puesto que los componentes sin reaccionar pueden ser utilizados adicionalmente.

Por la expresión "alta conversión" se quiere dar a entender un proceso que produce una corriente producto que comprende menos de 5 moles% de olefinas, preferentemente menos de 3 moles% de olefinas. Los procesos adecuados presentan habitualmente una conversión de olefinas de al menos 95%. En particular, los procesos para la obtención de derivados de olefinas que tradicionalmente se llevan a cabo con una alta conversión global mediante reciclo de olefinas sin reaccionar, requieren frecuentemente una purga importante para evitar la acumulación, en el reciclo, de componentes no reactivos. Las purgas suelen ser desechadas, por ejemplo, mediante ventilación. El hecho de trabajar a una conversión más baja (al reducir el reciclo al proceso de obtención del derivado de olefina) y reciclar a un craqueador autotérmico de acuerdo con el procedimiento del primer aspecto de la presente invención, puede reducir la necesidad de efectuar una purga.

Cuando la corriente diluida de olefinas comprende etileno, los procesos adecuados para la obtención de un derivado de olefina pueden comprender, por ejemplo, procesos para la producción de etanol a partir de etileno y agua, para la producción de acetato de vinilo, procesos de polimerización de etileno y procesos que toleran el etano para la producción de óxido de etileno.

Cuando la corriente diluida de olefinas comprende propileno, los procesos de obtención de derivados de olefinas pueden comprender, por ejemplo, procesos para

la producción de óxido de propileno, para la producción de acroleína y procesos de amoxidación de propileno, así como ciertos procesos para la producción de polipropileno.

Los procesos para la obtención de derivados de olefinas pueden comprender también procesos que utilizan corrientes diluidas de olefinas, mezcladas, por ejemplo, comprendiendo etileno y propileno. Procesos adecuados incluyen, por ejemplo, procesos de co-polimerización de etileno/propileno.

Otros procesos para la obtención de derivados de olefinas que pueden ser empleados adecuadamente en la etapa (b) de la presente invención, incluyen procesos para la producción de etilbenceno, para la producción de alfa-olefinas lineales, para la metátesis de etileno con butano para obtener propeno, para la hidroformilación de etileno o propileno con CO e hidrógeno, y para la producción de policetonas a partir de olefinas y monóxido de carbono, tal como se describe en WO 93/01224.

La etapa (b) comprende hacer reaccionar al menos una porción de dicha primera corriente diluida de olefinas para producir una primera corriente de derivado de olefina y una segunda corriente diluida de olefinas. Preferentemente, la totalidad de la primera corriente diluida de olefinas se hace reaccionar para producir dicha primera corriente de derivado de olefina y dicha segunda corriente diluida de olefinas. Sin embargo, en una modalidad de la presente invención, una porción de dicha primera corriente diluida de olefinas se puede hacer reaccionar en uno o más procesos adicionales de obtención de derivados de olefinas, para producir una o más corrientes adicionales de derivados de olefinas.

La etapa (b) puede comprender también más de un proceso de obtención de derivados de olefinas, realizados en serie. Por ejemplo, la primera corriente diluida

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de olefinas se puede hacer reaccionar para producir una primera corriente de derivado de olefina y una corriente intermedia diluida de olefinas, y al menos una porción de dicha corriente intermedia diluida de olefinas se puede hacer reaccionar para producir otra corriente de derivado de olefina y otra corriente diluida de olefinas. La otra corriente diluida de olefinas y, opcionalmente, cualesquiera de las corrientes intermedias diluidas de olefinas no reaccionadas en la otra unidad de obtención del derivado de olefina, pueden formar entonces la segunda corriente diluida de olefinas de la invención.

En el primer aspecto de la presente invención, al menos una porción de la segunda corriente diluida de olefinas se hace reaccionar en una etapa de cracking autotérmico, que puede ser o no la misma etapa de cracking que la etapa (a). Preferentemente, la totalidad de la segunda corriente diluida de olefinas se hace reaccionar en la etapa de cracking autotérmico. En una modalidad del primer aspecto de la presente invención, una porción de dicha segunda corriente diluida de olefinas se puede hacer reaccionar en uno o más procesos adicionales de obtención de derivados de olefinas, para producir uno o más derivados de olefinas adicionales, antes de reaccionar en la etapa de cracking autotérmico, por ejemplo, antes del reciclo a la etapa (a) (cuando la etapa de cracking en la etapa (a) es una etapa de cracking autotérmico).

En un segundo aspecto, la presente invención proporciona un procedimiento para la producción de un derivado de olefina, cuyo procedimiento comprende las etapas de:

- (a) craquear un material de alimentación que contiene hidrocarburos parafinicos para producir una primera corriente diluida de olefinas, que comprende tanto olefinas como alcanos;

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- (b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas, producida en la etapa (a), para producir una primera corriente de derivado de olefina, que comprende un primer derivado de olefina, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar;
- (c) reaccionar al menos una porción de dicha segunda corriente diluida de olefinas producida en la etapa (b), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas sin reaccionar, para producir una segunda corriente de derivado de olefina, que comprende un segundo derivado de olefina, y una corriente de reciclo que comprende alcanos sin reaccionar y menos de 5 moles% de olefinas; y
- (d) reciclar dicha corriente de reciclo producida en la etapa (c) a la etapa de cracking de la etapa (a).

El proceso de cracking de la etapa (a) del segundo aspecto se elige preferentemente entre (i) procesos de cracking térmico, por ejemplo de nafta, (ii) procesos de cracking con vapor de agua, por ejemplo de un alcano, de una mezcla de alcanos o de nafta y (iii) procesos de cracking autotérmico, por ejemplo de un alcano, de una mezcla de alcanos o de nafta.

Con suma preferencia, la etapa de cracking (a) del segundo aspecto comprende el cracking autotérmico del material de alimentación que contiene hidrocarburos parafínicos.

La etapa (b) del segundo aspecto es preferentemente como la descrita en el primer aspecto de la invención.

En este segundo aspecto de la presente invención, al menos una porción de la segunda corriente diluida de olefinas se hace reaccionar para producir (en la etapa (c)) una segunda corriente de derivado de olefina, que comprende un segundo

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derivado de olefina, y una corriente de recicló que comprende alcanos sin reaccionar y menos de 5 moles% de olefinas. El segundo derivado de olefina producido en la etapa (c) puede ser el mismo o puede ser diferente al primer derivado de olefina. Por ejemplo, cuando la corriente diluida de olefinas comprende etileno y etano, ambos derivados de etileno primero y segundo pueden ser productos de polietileno. Alternativamente, el primer derivado de etileno puede ser, por ejemplo, un producto de polietileno y el segundo derivado de etileno puede ser, por ejemplo, un producto de etilbenceno.

Preferentemente, la totalidad de la segunda corriente diluida de olefinas se hace reaccionar para producir dicha segunda corriente de derivado de olefina y dicha corriente de recicló. Sin embargo, en una modalidad, una porción de dicha segunda corriente diluida de olefinas se puede hacer reaccionar en uno o más procesos diferentes de obtención de derivados de olefinas, para producir uno o más derivados de olefinas adicionales.

En el segundo aspecto, la etapa (c) comprende hacer reaccionar al menos una porción de dicha segunda corriente diluida de olefinas para producir una segunda corriente de derivado de olefina y una corriente de recicló que comprende alcano sin reaccionar y menos de 5 moles% de olefinas. Preferentemente, dicha corriente de recicló comprende menos de 3 moles% de olefinas y más preferentemente menos de 1 mol% de olefinas. Se prefiere una baja concentración de olefinas cuando la etapa de cracking de la etapa (a) es un craqueador con vapor de agua, puesto que este irá en un menor detrimento con respecto a los tiempos de trabajo del craqueador. Por tanto, la etapa (c) comprende preferentemente hacer reaccionar dicha porción al menos de dicha segunda corriente diluida de olefinas en un proceso de obtención de derivados de olefinas con una conversión de olefinas relativamente alta, tal como una

conversión de al menos 90%, preferentemente una conversión alta de olefinas, tal como una conversión de al menos 95%.

Cuando la olefina comprende etileno, el proceso de obtención del derivado de olefina de la etapa (c) comprende preferentemente un proceso para la producción de etilbenceno a partir de etileno y benceno o un proceso para la polimerización o copolimerización de etileno, por ejemplo mediante el proceso Phillips.

Cuando la olefina comprende propileno, el proceso de obtención del derivado de olefina de la etapa (c) comprende preferentemente un proceso para la producción de polipropileno a partir de propileno.

La invención será ejemplificada ahora con referencia a las figuras 1 a 5 y a los ejemplos.

La figura 1 representa en forma esquemática un procedimiento integrado para la producción de un derivado de etileno de acuerdo con el primer aspecto de la presente invención.

La figura 2 representa en forma esquemática un procedimiento integrado de polietileno, en circuito de suspensión espesa, para la producción de polietileno de acuerdo con el primer aspecto de la presente invención.

La figura 3 representa en forma esquemática un procedimiento integrado de policetona para la producción de policetonas de acuerdo con el primer aspecto de la presente invención.

La figura 4 representa en forma esquemática un procedimiento integrado de metátesis y de polipropileno para la producción de polipropileno de acuerdo con el primer aspecto de la presente invención.

La figura 5 representa en forma esquemática un procedimiento integrado de polietileno y etilbenceno para la producción de polietileno y etilbenceno de acuerdo

con el segundo aspecto de la presente invención.

Con referencia a la figura 1, una alimentación de etano 10, una corriente de reciclo 30 que comprende 40% de etileno ($C_2^=$) y 60% de etano (C_2), y una alimentación de oxígeno 20, se alimentan a un reactor ATC 40. La corriente producto mezclada se trata, 50, para producir una corriente de subproducto 60 y una primera corriente diluida de etileno 70 que comprende aproximadamente 30% de etano y 70% de etileno. Esta corriente diluida de etileno se pasa a un proceso de obtención de un derivado de etileno 80 con una conversión de etileno del 70% aproximadamente por pasada. El etano es inerte en dicho proceso. El producto derivado de olefina 90 se separa, junto con cualesquiera otros subproductos formados, para dejar una segunda corriente diluida de etileno que comprende etano y etileno sin reaccionar, que tiene una composición de aproximadamente 40% de etileno y 60% de etano (y que tiene aproximadamente la mitad del volumen de la primera corriente diluida de etileno), la cual se recicla al reactor ATC.

Con referencia a la figura 2, al reactor ATC 4 se alimentan etano 1, oxígeno 2 y una corriente de reciclo 3 que comprende etano y etileno. La corriente producto se pasa a una etapa de enfriamiento rápido 5 en la cual se separan agua e hidrocarburos superiores 6, y luego a una etapa de lavado con amina 7 para separar dióxido de carbono y más agua 8. El resto de la corriente producto se pasa entonces a un desmetanizador 9 para separar hidrógeno, monóxido de carbono y metano 10 y a un desetanizador 11 para separar hidrocarburos C_3+ 12, que pueden ser reciclados al reactor ATC 4.

El resto de la corriente producto es hidrogenada 13, para separar compuestos acetilénicos y dienos, para formar una primera corriente diluida de etileno 14 que comprende etileno y etano, la cual se pasa a un proceso de polietileno en circuito en

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suspensión espesa 15, para producir un producto de polietileno 16 y una segunda corriente diluida de etileno 17 que comprende etano y etileno sin reaccionar, la cual se recicla al reactor ATC, después de la adición de la corriente 12, como corriente de reciclo 3.

Con referencia a la figura 3, a un reactor ATC 4 se alimentan etano 1, oxígeno 2 y una corriente de reciclo 3 que comprende etano y etileno. La corriente producto se pasa a una etapa de enfriamiento rápido 5 en donde se separan agua e hidrocarburos superiores 6, y luego a una etapa de lavado con amina 7, para separar dióxido de carbono y más agua 8. El resto de la corriente producto se pasa entonces a un desetanizador 11 para separar hidrocarburos C3+ 12, los cuales pueden ser reciclados al reactor ATC 4.

El resto de la corriente producto 14 forma una primera corriente diluida de etileno que comprende etileno, etano, monóxido de carbono e hidrógeno, y se pasa a un reactor de policetonas 15 en donde se hace reaccionar para producir un producto de policetona 16 y una segunda corriente diluida de olefinas 17 que se recicla al reactor ATC 4, opcionalmente después de la adición de hidrocarburos C3+ 12, separados del desetanizador.

En un proceso de policetonas alternativo (no mostrado), los hidrocarburos C3 (propileno y propano) no se separan en el desetanizador 11, sino que se alimentan al reactor de policetonas con el etileno, etano, monóxido de carbono e hidrógeno.

Con referencia a la figura 4, a un reactor ATC 4 se alimentan etano 1, oxígeno 2 y una corriente de reciclo 3 que comprende etano y etileno. La corriente producto se pasa a una serie de etapas de separación, incluyendo un enfriamiento rápido, un lavado con amina, un desmetanizador, un desetanizador e hidrogenación, como se ha descrito en la figura 2.

El resto de la corriente producto 14 forma una primera corriente diluida de etileno que comprende etileno y etano, la cual se pasa a un reactor de metátesis 15 en donde se hace reaccionar con una alimentación de butano 30. La corriente producto 31 se pasa a un tren de separación 32, tal como una o más columnas de destilación, para separar buteno sin reaccionar 33, propileno 34 y una segunda corriente diluida de etileno 17 que comprende etileno sin reaccionar y etano, la cual se recicla al reactor ATC 4, opcionalmente después de la adición de hidrocarburos C3+ 12 separados en el desetanizador 11. Los butenos no reaccionados pueden ser reciclados al reactor de metátesis 15. La corriente de propeno 34 se pasa a un reactor de propileno 35, para producir polipropileno 36.

Con referencia a la figura 5, a un reactor ATC 4 se alimentan etano 1, oxígeno 2 y una corriente de reciclo 3 que comprende etano. La corriente producto se pasa a un enfriamiento rápido 5 en donde se separan agua e hidrocarburos superiores 6, y luego a una etapa de lavado con amina 7, para separar dióxido de carbono y más agua 8. El resto de la corriente producto se pasa entonces a un desmetanizador 9 para separar hidrógeno, monóxido de carbono y metano 10, y a un desetanizador 11 para separar hidrocarburos C3+ 12, los cuales pueden ser reciclados al reactor ATC 4.

El resto de la corriente producto se hidrogena, 13, para separar compuestos acetilénicos y dienos, y para formar una primera corriente diluida de etileno 14 que comprende etileno y etano, la cual se pasa a un proceso de polietileno en fase gaseosa 15, para producir un producto de polietileno 16. Una segunda corriente diluida de etileno 17, que comprende etano y etileno sin reaccionar, se hace reaccionar con benceno 18, en un reactor de etilbenceno 19, para producir etilbenceno 20 y una corriente de reciclo 21 que comprende etano, la cual se recicla al reactor ATC 4, después de la adición de la corriente 12, como corriente de reciclo

3. En una modalidad opcional de la figura 5, una porción de la primera corriente diluida de etileno 14 se pasa directamente al reactor de etilbenceno 19, como se muestra por la línea de puntos 14a.

Ejemplo 1

Este ejemplo ilustra un procedimiento integrado de polietileno en circuito de suspensión espesa para la producción de polietileno según el procedimiento de la figura 2.

El procedimiento de polietileno en circuito de suspensión espesa se lleva a cabo con una conversión de etileno del 80%.

Las composiciones de las respectivas corrientes del procedimiento se ofrecen en la tabla 1.

TABLA 1:

Corriente número (Fig. 2)	Componentes principales	Volumen de componente (kilotoneladas por año)
1	Etano	750
2	Oxígeno	466
3	Etano Etileno Compuestos C3+	336 80 50
6	Agua y compuestos C5+	378
8	Dióxido de carbono y agua	86
10	Hidrógeno, monóxido de carbono y metano	352
12	Compuestos C3+	50
14	Etano Etileno	336 400
16	Polietileno	320
17	Etano Etileno	336 80

La corriente que comprende compuestos C3+ (corriente 12) comprende predominantemente propano (9% en peso), propileno (50% en peso), butanos (9% en peso), butenos (7% en peso) y butadieno (24% en peso) siendo el resto

(aproximadamente 1% en peso) hidrocarburos C5+ (incluyendo compuestos aromáticos).

Ejemplo 2

Este ejemplo ilustra un procedimiento integrado de polietileno y etilbenceno para la producción de polietileno y etilbenceno según el procedimiento de la figura 5.

El procedimiento de polietileno en fase gaseosa se lleva a cabo con una conversión de etileno de aproximadamente 78% y el procedimiento de etilbenceno con una conversión de etileno de aproximadamente 100%. Las composiciones de las respectivas corrientes del procedimiento se ofrecen en la tabla 2.

TABLA 2

Corriente número (Fig. 5)	Componentes principales	Volumen de componente (kilotoneladas por año)
1	Etano	759
2	Oxígeno	489
3	Etano Compuestos C3+	335 67
6	Agua Compuestos C5+	373 69
8	Dióxido de carbono Agua	32 20
10	Hidrógeno Monóxido de carbono Metano	16 204 133
12	Compuestos C3+	67
14	Etano Etileno	335 400
16	Polietileno	310
17	Etano Etileno	335 90
18	Benceno	244
20	Etilbenceno	334
21	Etano	335

REIVINDICACIONES

1. - Procedimiento para la producción de un derivado de olefina, caracterizado porque comprende las etapas de:

- (a) craquear un material de alimentación que contiene hidrocarburos parafinicos para producir una primera corriente diluida de olefinas que comprende tanto olefinas como alcanos;
- (b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas, producida en la etapa (a), para producir una primera corriente de derivados de olefinas, que comprende un primer derivado de olefinas, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar;
- (c) craquear autotérmicamente al menos una porción de dicha segunda corriente diluida de olefinas, producida en la etapa (b), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas sin reaccionar.

2. - Procedimiento según la reivindicación 1, caracterizado porque la primera corriente diluida de olefinas comprende al menos 50% en peso de olefina y al menos 1% en peso de alcano.

3. - Procedimiento según la reivindicación 1 o 2, caracterizado porque la etapa de cracking (a) se elige entre (i) procesos de cracking térmico, (ii) procesos de cracking con vapor de agua y (iii) procesos de cracking autotérmico.

4. - Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque el material de alimentación que contiene hidrocarburos parafinicos alimentado a la etapa (a) comprende un solo alcano, tal como etano, una mezcla de alcanos, tal como NGL (líquidos de gas natural), o nafta.

5. - Procedimiento según cualquiera de las reivindicaciones anteriores,

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caracterizado porque la porción de la segunda corriente diluida de olefinas pasada al craqueador autotérmico de la etapa (c) comprende al menos 50% del alcano y al menos 50% de la olefina en la segunda corriente diluida de olefinas.

6. - Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque la concentración de olefina (olefina sin reaccionar procedente de la segunda corriente diluida de olefinas y olefina adicional que puede estar presente en cualquier alimentación adicional que contiene alcano) en la alimentación pasada a la etapa de cracking autotérmico, es de al menos 4 moles%.

7. - Procedimiento según cualquiera de las reivindicaciones anteriores, caracterizado porque la etapa de cracking (a) es una etapa de cracking autotérmico y el proceso para la producción de un derivado de olefina comprende las etapas de:

(a) craquear autotérmicamente una alimentación que comprende un material de alimentación que contiene hidrocarburos parafinicos y una corriente de reciclado, para producir una primera corriente diluida de olefinas que comprende tanto olefinas como alcanos;

(b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas producida en la etapa (a) para producir una primera corriente de derivado de olefina, que comprende un primer derivado de olefina, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar;

(c) reciclar al menos una porción de dicha segunda corriente diluida de olefinas producida en la etapa (b) como la corriente de reciclado en el cracking autotérmico de la etapa (a), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas sin reaccionar.

8. - Procedimiento para la producción de un derivado de olefina,

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caracterizado porque comprende las etapas de:

- (a) craquear un material de alimentación que contiene hidrocarburos parafinicos para producir una primera corriente diluida de olefinas, que comprende tanto olefinas como alcanos;
- (b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas, producida en la etapa (a), para producir una primera corriente de derivado de olefina, que comprende un primer derivado de olefina, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar;
- (c) reaccionar al menos una porción de dicha segunda corriente diluida de olefinas producida en la etapa (b), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas sin reaccionar, para producir una segunda corriente de derivado de olefina, que comprende un segundo derivado de olefina, y una corriente de reciclo que comprende alcanos sin reaccionar y menos de 5 moles% de olefinas; y
- (d) reciclar dicha corriente de reciclo producida en la etapa (c) a la etapa de cracking de la etapa (a).

RESUMEN

La presente invención proporciona un procedimiento para la producción de un derivado de olefina, cuyo procedimiento comprende las etapas de: (a) craquear un material de alimentación que contiene hidrocarburos paraafínicos para producir una primera corriente diluida de olefinas que comprende tanto olefinas como alcanos, (b) reaccionar al menos una porción de dicha primera corriente diluida de olefinas, producida en la etapa (a), para producir una primera corriente de derivados de olefinas, que comprende un primer derivado de olefinas, y una segunda corriente diluida de olefinas, que comprende alcanos y al menos 5 moles% de olefinas sin reaccionar, (c) craquear autotérmicamente al menos una porción de dicha segunda corriente diluida de olefinas, producida en la etapa (b), comprendiendo dicha porción alcanos y al menos 5 moles% de olefinas sin reaccionar.

Fig.1

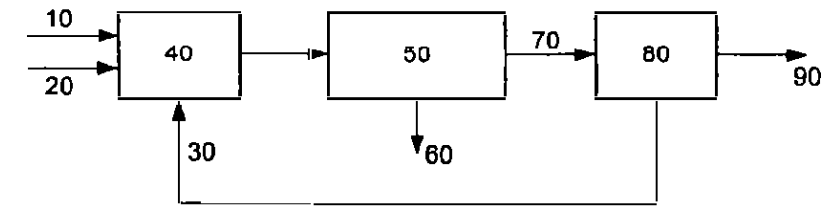


Fig.2

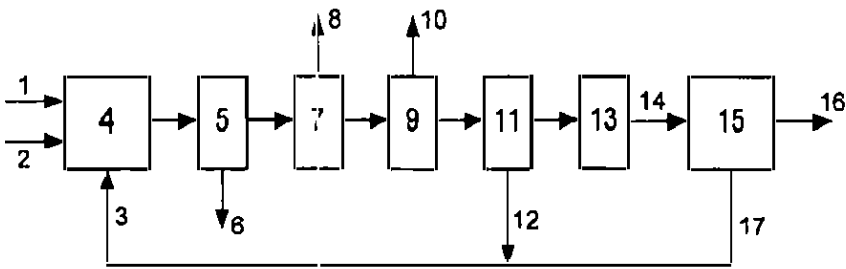


Fig.3

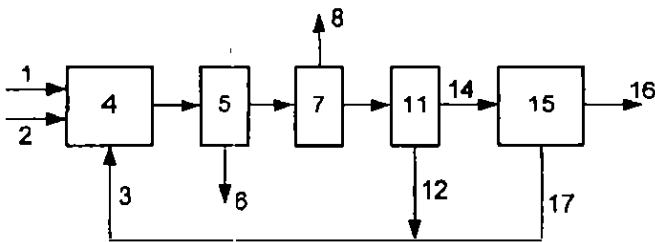


Fig.4

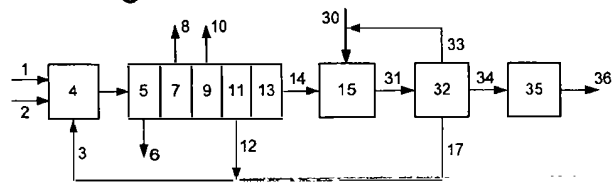
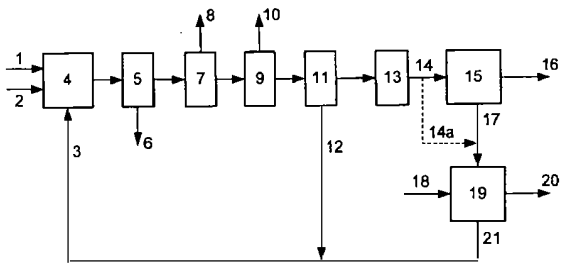


Fig.5



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) BPCL 9920

Box No. I TITLE OF INVENTION	
INTEGRATED PROCESS FOR THE PRODUCTION OF OLEFIN DERIVATIVES	
Box No. II APPLICANT	
☐ This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
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Telephone No.	
Facsimile No.	
Teleprinter No.	
Applicant's registration No. with the Office	
State (that is, country) of nationality: GB	
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This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)	
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Telephone No. 01932 763205	
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State <i>(that is, country)</i> of nationality: 		State <i>(that is, country)</i> of residence: 	
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However,

- (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.)*

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

☐ 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)(iii)).

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)

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

Number of
declarations

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

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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 are entitled to apply for and be granted a patent by virtue of the following:

BP CHEMICALS LIMITED is entitled by virtue of a contract of employment with the inventors, LITTLE, Ian Raymond, LUCY, Andrew Richard and MAUNDERS, Barry Martin.

This declaration is made for the purposes of all designations (except 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 51bis.1(a)(iv))
for the purposes of the designation of the United States of America:**

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

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

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

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

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

Prior Applications:

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

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

Name: LITTLE, Ian Raymond

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

Mailing Address: 188 Manor Road North, Thames Ditton, Surrey, KT7 OBQ, United Kingdom

Citizenship: British

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

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

Name: LUCY, Andrew Richard

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

Mailing Address: 24 Station Road, South Cave, Brough, East Yorkshire, HU15 2AA, United Kingdom

Citizenship: British

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

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

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

SA

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

Continuation of Box No. VIII

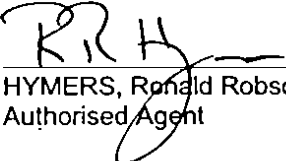
Name: MAUNDERS, Barry Martin

Residence: Woking, Surrey, United Kingdom

Mailing Address: Woodlands, 5 Paddock Way, Woodham, Woking, Surrey, GU21 5TB,
United Kingdom

Citizenship: British

Inventor's Signature:----- Date:-----

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) : 15 claims : 2 abstract : 1 drawings : 2 Sub-total number of sheets : 27 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 : 27 (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): 1. ☒ fee calculation sheet : 1 2. ☒ original separate power of attorney : 1 3. ☐ original general power of attorney : 4. ☒ copy of general power of attorney; reference number, if any: : 1 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 13ter 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 13ter : (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): Form 23/77 :	Number of items
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).  HYMERS, Ronald Robson Authorised Agent			

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: _____	

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International Application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

BPCL 9920

Applicant

BP CHEMICALS LIMITED et al

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE £55-00 [T]

2. SEARCH FEE £1078-00 [S]

International search to be carried out by

(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FILING FEE

Where items (b) and/or (c) of Box No. IX apply, enter Sub-total number of sheets }
Where items (b) and (c) of Box No. IX do not apply, enter Total number of sheets }

[i1] first 30 sheets £628-00 [i1]

[i2] x = [i2]
number of sheets fee per sheet
in excess of 30

[i3] additional component (only if sequence listing and/or tables related
thereto are filed in computer readable form under Section 801(a)(i),
or both in that form and on paper, under Section 801(a)(ii)):

400 x = [i3]
fee per sheet

Add amounts entered at i1, i2 and i3 and enter total at I £628-00 [I]

(Applicants from certain States are entitled to a reduction of 75% of the international filing fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the international filing fee.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) £22-00 [P]

5. TOTAL FEES PAYABLE £1,783-00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

MODE OF PAYMENT

- ☐ authorization to charge deposit account (see below) ☐ postal money order ☐ cash ☐ coupons
☒ cheque ☐ bank draft ☐ revenue stamps ☐ other (specify):

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT
(This mode of payment may not be available at all receiving Offices)

- ☐ Authorization to charge the total fees indicated above.
☐ (This check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.
☐ Authorization to charge the fee for priority document.

Receiving Office: RO/

Deposit Account No.:

Date:

Name:

Signature:

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
Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LN
United Kingdom

Date of mailing (day/month/year) 28 May 2004 (28.05.2004)	
Applicant's or agent's file reference BPCL 9920	IMPORTANT NOTIFICATION
International application No. PCT/GB2004/001265	International filing date (day/month/year) 24 March 2004 (24.03.2004)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 03 April 2003 (03.04.2003)
Applicant BP CHEMICALS LIMITED et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- (If applicable) An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as 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 datePriority application No.Country or regional Office
or PCT receiving OfficeDate of receipt
of priority document

03 April 2003 (03.04.2003)

0307758/3

GB

20 April 2004 (20.04.2004)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Rodrigo GARCIA CONDE
Facsimile No. (41-22) 338.89.65	Telephone No. (41-22) 338 9928

58 100

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/ EP

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 BPCL 9920
International application No. PCT/GB2004/001265	International filing date (day/month/year) 24 March 2004	(Earliest) Priority date (day/month/year) 3 April 2003
Title of invention INTEGRATED PROCESS FOR THE PRODUCTION OF OLEFIN DERIVATIVES		
Box No. II APPLICANT(S)		
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) BP CHEMICALS LIMITED Chertsey Road Sunbury-on-Thames Middlesex TW16 7BP 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
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.) LITTLE, Ian Raymond 27W650 North Lane, Naperville, Illinois 60540, United States of America formerley of : 188 Manor Road North, Thames Ditton, Surrey, KT7 OBQ, United Kingdom		
State (that is, country) of nationality: GB		State (that is, country) of residence: US
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.) LUCY, Andrew Richard 24 Station Road South Cave Brough East Yorkshire, HU15 2AA United Kingdom		
State (that is, country) of nationality: GB		State (that is, country) of residence: GB
☒ Further applicants are indicated on a continuation sheet.		

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.)

MAUNDERS, Barry Martin
Woodlands
5 Paddock Way
Woodham
Woking
Surrey, GU21 5TB
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.)

State (that is, country) of nationality:

State (that is, country) of residence:

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:

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.

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCEThe following person is ☒ agent ☐ common representativeand ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.Name and address: *(Family name followed by given name; for a legal entity, full official designation
The address must include postal code and name of country.)*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:

☒ the international application as originally filedthe description ☒ as originally filed☐ as amended under Article 34the claims ☒ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34the drawings ☒ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ 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 54bis.1(a).

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

Language for the purposes of international preliminary examination: English

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

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

Box No. VI CHECK LIST

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

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | 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 |

For International Preliminary Examining Authority use only

received	not received
----------	--------------

☐	☐
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐

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

- | | |
|--|--|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in computer readable form |
| 3. ☐ original general power of attorney | 7. ☐ tables in computer readable form related to a sequence listing |
| 4. ☐ copy of general power of attorney; reference number, if any: | 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 54bis.1(a) and item 7 or 8, below, does not apply.

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

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

For International Bureau use only

Demand received from IPEA on:

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/GB2004/001265 Applicant's or agent's file reference BPCL 9920 Applicant BP CHEMICALS LIMITED et al	For International Preliminary Examining Authority use only Date stamp of the IPEA
CALCULATION OF PRESCRIBED FEES 1. Preliminary examination fee EUR 1530-00 P 2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>) EUR 129-00 H 3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box EUR 1659-00 TOTAL	
MODE OF PAYMENT ☒ authorization to charge deposit account with the IPEA (see below) ☐ cheque ☐ postal money order ☐ bank draft ☐ cash ☐ revenue stamps ☐ coupons ☐ other (specify):	
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (<i>This mode of payment may not be available at all IPEAs</i>) ☒ Authorization to charge the total fees indicated above. ☐ (<i>This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit</i>) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above. IPEA/ <u>EP</u> Deposit Account No.: <u>28050129 BP Int Ltd</u> Date: <u>14th October 2004</u> Name: <u>Mrs A.M. Perry</u> Signature: <u>A.M. Perry</u>	

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

Ampl/A1
63
Sup
Disc

To:

HYMERS, Ronald Robson
BP INTERNATIONAL LIMITED
Patents & Agreements
Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LN
GRANDE BRETAGNE

27 OCT 2004

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

25-10-2004

Applicant's or agent's file reference
BPCL 9920

IMPORTANT NOTIFICATION

International application No.

PCT/GB2004/001265

International filing date (day/month/year)

24/03/2004

Priority date (day/month/year)

03/04/2003

Applicant

BP CHEMICALS LIMITED et al.

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

18/10/2004

2. This date of receipt is:

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

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

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

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

Name and mailing address of the IPEA/

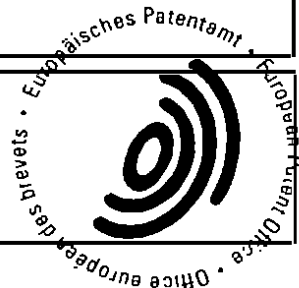


European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

HYMERS, Ronald Robson
BP INTERNATIONAL LIMITED
Patents & Agreements
Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LN
GRANDE BRETAGNE

Received in PAT

18 APR 2005

PCT

64

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing

(day/month/year)

13.04.2005

Applicant's or agent's file reference

BPCL 9920

IMPORTANT NOTIFICATION

International application No.

PCT/GB2004/001265

International filing date (day/month/year)

24.03.2004

Priority date (day/month/year)

03.04.2003

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:



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

Authorized Officer

Mazzariol, F

Tel. +49 89 2399-7911



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 BPCL 9920	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No PCT/GB2004/001265	International filing date (day/month/year) 24.03.2004	Priority date (day/month/year) 03.04.2003	
International Patent Classification (IPC) or national classification and IPC C10G11/22, C10G57/00, C10G57/02			
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 6 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 18.10.2004		Date of completion of this report 13.04.2005	
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 Harf, J Telephone No. +49 89 2399-7845 	

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

1-15 as originally filed

Claims, Numbers

1-8 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/GB2004/001265 67

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation to restrict or pay additional fees, the applicant has:
- ☒ restricted the claims.
 - ☐ paid additional fees.
 - ☐ paid additional fees under protest.
 - ☐ neither restricted nor paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
- ☐ complied with.
 - ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☐ all parts.
 - ☒ the parts relating to claims Nos. 1-7 .

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	1-7
	No: Claims	
Inventive step (IS)	Yes: Claims	1-7
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-7
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item IV

Lack of unity of invention

This Authority considers that there are 2 inventions covered by the claims indicated as follows:

I: Claims 1-7 directed to a process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and (iii) autothermally cracking the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

II: Claim 8 directed to a process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream ;(iii) reacting the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins to produce a second olefin derivative stream and (iv) recycling a stream comprising unreacted alkanes and less than 5 mol-% olefins to cracking step (i).

The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

The common concept linking together independent claims 1 and 8 is a process for producing an olefin derivative comprising (i) cracking a paraffinic feed and (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and a second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

This common concept is not considered as inventive over prior art document US-A-5981818 disclosing the cracking of an alkane feedstock followed by the polymerisation of the obtained dilute ethylene and/or propylene stream.

The requisite unity of invention (Rule 13.1 PCT) therefore no longer exists inasmuch as a technical relationship involving one or more of the same or corresponding special technical features in the sense of Rule 13.2 PCT does not exist between the subject-matter of the previously defined two groups of dependent claims.

As the applicant restricted the application to claims 1-7, no examination of the invention according to claim 8 was carried out.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement

Reference is made to the following documents:

D1: EP-A-1001001

D2: US-A-5981818

D3: GB-A-2325237

V.1 Claims 1-7

Both documents **D1** and **D2**, which could be regarded as being the closest prior art to the subject-matter of independent claim 1, disclose an integrated process for the cracking of an alkane feedstock and the subsequent polymerisation of the obtained dilute ethylene stream comprising the recycling of the unpolymerised stream to the cracker.

The subject-matter of independent claim 1 therefore differs from this known processes in that a **second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins**, which is obtained from the olefin derivation process, is **autothermally cracked**.

The subject-matter of independent **claim 1** is therefore new (Article 33(2) PCT).

The problem to be solved by the present invention may be regarded as to provide an integrated process for the production of an olefin derivative without olefin/alkane separation in the second dilute olefins stream from the olefin derivation process prior to further cracking of residual alkanes.

The solution to this problem proposed in claim 1 of the present application, i.e. the autothermal cracking of the second dilute olefins stream, appears to involve an inventive step (Article 33(3) PCT) for the following reasons:

It has been found by the applicant that autothermal cracking processes may be operated with olefin levels in the feed above 5 mol-% without significant coking contrary to steam cracking.

Annexed experimental data from an autothermal cracking process with ethylene in the ethane feed show no significant change in acetylene/benzene formation and an increase of the ethylene yield compared to feeding ethane alone.

Autothermal cracking is thus surprisingly tolerant of olefins in the feed. Hence lower conversion olefin derivative processes can be combined to autothermal cracking without separation of residual olefins from the alkane stream.

None of the available prior art documents either teaches or fairly suggests the recycling of the dilute olefins stream produced in a low conversion olefin derivation process to an autothermal cracking process without preliminary separation of olefins from alkanes to prevent coke formation.

Claims 2-7 are dependent on claim 1 and as such also appear to meet the requirements of the PCT with respect to novelty and inventive step.

From the INTERNATIONAL BUREAU

PCT

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Article 31(7) and Rule 61.3)

To:

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

U 7 DEC 2004

IMPORTANT INFORMATION

Date of mailing (day/month/year) 02 December 2004 (02.12.2004)		
Applicant's or agent's file reference BPCL 9920		
International application No. PCT/GB2004/001265	International filing date (day/month/year) 24 March 2004 (24.03.2004)	Priority date (day/month/year) 03 April 2003 (03.04.2003)
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, PL, 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

PATENT COOPERATION TREATY

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From the INTERNATIONAL SEARCHING AUTHORITY

PCT

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

To:

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

Received in PCT

23 AUG 2004

(PCT Rule 44.1)

Date of mailing
(day/month/year)

20/08/2004

Applicant's or agent's file reference

BPCL 9920

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/GB2004/001265

International filing date
(day/month/year)

24/03/2004

Applicant

BP CHEMICALS LIMITED

OFFICIAL ACTION

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

Filing of amendments and statement under Article 19:

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

When? The time limit for filing such amendments is normally 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, Facsimile 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 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

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

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

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

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

Name and mailing address of the International Searching Authority

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

Authorized officer

Véronique Baillou

NOTES TO FORM PCT/ISA/220

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

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

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

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

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

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

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

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

When?

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

Where not to file the amendments?

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

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

How?

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

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

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

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference BPCL 9920	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/GB2004/001265	International filing date (day/month/year) 24/03/2004	(Earliest) Priority Date (day/month/year) 03/04/2003
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 6 sheets.

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

1. Basis of the report

- a. ☒ With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, 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,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

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

6. With regards to the drawings,

- a. the figure of the **drawings** to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/001265**Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-7

process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and (iii) autothermally cracking the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins

2. claim: 8

process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream ;(iii) reacting the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins to produce a second olefin derivative stream and (iv) recycling a stream comprising unreacted alkanes and less than 5 mol-% olefins to cracking step (i)

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G11/22 C10G50/00 C10G57/00 C10G57/02

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 C10G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 001 001 A (NOVA CHEM INT SA) 17 May 2000 (2000-05-17) claims 1,12,13; figures 18,2B page 2, paragraph 7 page 4, paragraphs 28,32 page 5, paragraph 40	1-7
X	US 5 981 818 A (PURVIS DAVID ET AL) 9 November 1999 (1999-11-09) cited in the application column 2, line 62 - column 3, line 10 column 3, line 65 - column 4, line 8 column 4, lines 23-27 column 9, lines 11-17 column 9, line 65 - column 10, line 1 column 10, lines 15-22 column 11, lines 22-25 ----- -/-	1-7



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.

"Z" document member of the same patent family

Date of the actual completion of the international search

20 July 2004

Date of mailing of the international search report

20.08.04

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
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Harf, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No. 78
X	GB 2 325 237 A (SNAM PROGETTI) 18 November 1998 (1998-11-18) figure 1; example 1; tables III,IV page 9, lines 19-24 page 10, lines 17-23 page 12, lines 11-17 page 16, line 2 - page 17, line 4 -----	8
A	US 3 987 119 A (KURTZ BRUCE E ET AL) 19 October 1976 (1976-10-19) claims 1,2; figure column 1, lines 64-67 column 2, lines 7-17 column 3, lines 16-21 -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB2004/001265

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1001001	A	17-05-2000	US 6111156 A EP 1001001 A1	29-08-2000 17-05-2000
US 5981818	A	09-11-1999	NONE	
GB 2325237	A	18-11-1998	IT MI971129 A1 CA 2235180 A1 NL 1009182 C2 NL 1009182 A1 US 6011191 A	16-11-1998 15-11-1998 19-05-1999 17-11-1998 04-01-2000
US 3987119	A	19-10-1976	BE 821397 A1 CA 1037971 A1 DE 2449563 A1 FR 2248254 A1 GB 1435069 A IT 1024701 B JP 50070307 A NL 7413046 A	17-02-1975 05-09-1978 30-04-1975 16-05-1975 12-05-1976 20-07-1978 11-06-1975 25-04-1975

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

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To:

see form PCT/ISA/220

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

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

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

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/GB2004/001265

International filing date (day/month/year)
24.03.2004

Priority date (day/month/year)
03.04.2003

International Patent Classification (IPC) or both national classification and IPC
C10G11/22, C10G50/00, C10G57/00, C10G57/02

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 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

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

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 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.

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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2004/001265

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Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of the international application in the language in which it was filed, 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 thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2004/001265

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Box No. II Priority

1. ☒ The following document has not been furnished:

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

☐ translation of the earlier application whose priority has been claimed (Rule 43bis.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 43bis.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. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has:

☒ paid additional fees.

☐ paid additional fees under protest.

☐ not paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

☐ complied with

☒ not complied with for the following reasons:

see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

☒ all parts.

☐ the parts relating to claims Nos.

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

1. Statement

Novelty (N)	Yes: Claims	1-8
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-8
Industrial applicability (IA)	Yes: Claims	1-8
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item IV

Lack of unity of invention

This Authority considers that there are 2 inventions covered by the claims indicated as follows:

I: Claims 1-7 directed to a process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and (iii) autothermally cracking the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

II: Claim 8 directed to a process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream ;(iii) reacting the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins to produce a second olefin derivative stream and (iv) recycling a stream comprising unreacted alkanes and less than 5 mol-% olefins to cracking step (i).

The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

The common concept linking together independent claims 1 and 8 is a process for producing an olefin derivative comprising (i) cracking a paraffinic feed and (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and a second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

This common matter is already known from document US-A-5981818 disclosing the cracking of an alkane feedstock followed by the polymerisation of the obtained dilute ethylene and/or propylene stream. The requisite unity of invention (Rule 13.1 PCT) therefore no longer exists inasmuch as a technical relationship involving one or more of the same or corresponding special technical features in the sense of Rule 13.2 PCT does not exist between the subject-matter of the previously defined two groups of dependent claims.

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

D1: EP-A-1001001

D2: US-A-5981818

D3: GB-A-2325237

V.1 Inventive Step

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-8 does not involve an inventive step in the sense of Article 33(3) PCT.

V.1.1 Claims 1-7

The document **D1** (claims 1, 12 and 13; page 2, paragraph 7; page 4, paragraphs 28 and 32 and page 5, paragraph 40) is regarded as being the closest prior art to the subject-matter of independent claim 1, and discloses an integrated process for the cracking of a feed such as ethane and the subsequent polymerisation/oligomerisation of the dilute ethylene stream without passing through an ethane/ethylene splitter comprising the recycling of the unpolymersised stream to the cracker.

The subject-matter of independent claim 1 therefore differs from this known process in that a second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins, which is obtained from the olefin derivation process, is autothermally cracked.

It should be pointed out, that alleged advantages to which the applicant merely refers, without offering sufficient evidence to support the comparison with the closest prior art, cannot be taken into consideration in determining the problem underlying the invention and therefore in assessing inventive step.

The operation of autothermal cracking with a higher olefin concentration in the feed than for other cracking processes such as steam cracking is considered as such an alleged advantage of the process of the invention.

In the absence of technical evidence showing any advantage the autothermal cracking of the second dilute olefins stream offers over the recycling of this stream to the initial steam cracking step as disclosed in the closest prior art, no inventive step can thus be acknowledged for independent claim 1.

Dependent claims 2-7 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step.

Document D2 (column 9, lines 11-17; column 9, line 65 - column 10, line 1; column 10, lines 15-22 and column 11, lines 22-25) discloses the cracking of an alkane feedstock followed by the polymerisation of the obtained dilute ethylene and/or propylene stream and the recycling of the by-product stream from the olefin derivative process to the cracker. This document could also serve as a basis to assess inventive step of independent claim 1.

V.1.2 Claim 8

Document D3 (Figure 1; Example 1; Tables III and IV), which is considered to represent the closest prior art to the subject-matter of independent claim 8, discloses a process comprising (i) the dimerization with primary alcohols/ and alkyl ethers of isobutene in a first reactor; (ii) separating non-reacted isobutene and isobutane from dimers and alkyl ethers; (iii) completing the dimerisation of the non-reacted isobutene in a second reactor and (iv) separating dimers from isobutane and residual isobutene. The isobutene containing hydrocarbon stream also contains isobutane and could be obtained by FCC or steam cracking (page 9, lines 17-24). The stream obtained by separation of dimers and alkyl ethers from the first effluent contains 8.56 mol-% isobutene, thus corresponding to the second dilute olefins stream of claim 8 of the present application, and the stream obtained by separation of dimers from the second effluent contains only 0.41 mol-% residual isobutene, thus corresponding to the recycle stream of claim 8 of the present application (Table IV).

The subject-matter of independent claim 8 therefore only differs from the two-step dimerisation process of D3 in that the stream comprising alkanes and residual olefins is recycled to the initial cracking step.

The skilled person would consider recycling the mainly isobutane containing stream separated from the effluent of the second dimerisation reactor to a cracking unit in order

to maximize the olefins yield without having to exercise any inventive skills.

Consequently, the subject-matter of independent claim 8 lacks an inventive step in the sense of Article 33(3) PCT.

V.2 Further Objections

V.2.1 The term "autothermally" is vague and unclear and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of independent claim 1 unclear (cf. Article 6 PCT).

V.2.2 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in documents D1 and D3 is not mentioned in the description, nor is this document identified therein.

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(11) EP 1 001 001 A1

(12) EUROPEAN PATENT APPLICATION

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C07C 2/30

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(84) Designated Contracting States: AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE Designated Extension States: AL LT LV MK RO SI (30) Priority: 10.11.1998 US 189855 (71) Applicant: Nova Chemicals (International) S.A. 1752 Villars-sur-Glane 1 (CH) (72) Inventors: Oballa, Michael C. Cochrane, Alberta TOL 0W0 (CA)	- Purvis, David Georgetown, Ontario L7G 1X1 (CA) - Krzywicki, Andrzej Z. Calgary, Alberta T2N 3N9 (CA) - Benum, Leslie W. Red Deer, Alberta T4N 2B9 (CA) (74) Representative: Harrison, David Christopher et al MEWBURN ELLIS York House 23 Kingsway London WC2B 6HP (GB)
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(54) Process for the polymerisation of ethylene obtained by cracking

(57)

An integrated process for the cracking of a feedstock to produce ethylene and the subsequent polymerization or oligomerization of the ethylene, in the ethane/ethylene stream, without passing through an ethane splitter comprising in cooperating arrangement the steps of:

i)

feeding a feedstock to a cracker operated at a maximum allowable tube wall temperature of from 1050°C to 1600°C;

ii)

passing the resulting product through a separation step to remove hydrocarbon streams

iii)

having a carbon content of 3 and greater, subjecting the resulting stream to a treatment to convert acetylene to ethylene;

iv)

removing the methane and hydrogen from the resulting stream to produce a product having an ethylene content from 75 weight% to 95 weight%;

v)

feeding the resulting stream to a polymerization or oligomerization process and polymerizing or oligomerizing the ethylene; and

vi)

separating the unpolymerized stream from the polymer and solvent, returning it to the cracker.

EP 1 001 001 A1

Description

[0001] The present invention relates to an integrated high temperature hydrocarbon cracking and olefin polymerization or oligomerization process. More particularly the present invention relates to an integrated process for preparing polyethylene and/or alpha-olefins from hydrocarbon feedstocks by high temperature cracking the hydrocarbon feedstocks, separating the C₂ fraction from the cracked gas into a feed comprising at least 75 weight % ethylene for polymerization or oligomerization. The advantages of this invention over the conventional method of cracking hydrocarbons, producing ethylene and polymerizing/oligomerizing the ethylene include: smaller load for the furnace, smaller cracked gas compressor, smaller acetylene processing unit, the absence of an ethane/ethylene splitter, a greatly reduced recycle of ethane, lower energy requirements, lower capital investment, lower operating costs and the possibility of packaging a small integrated ethylene/polyethylene or ethylene/alpha olefins plant.

[0002] At the Tenth Ethylene Forum, May 10-12, 1995, Stone and Webster presented a paper on the concept of an integrated ethylene plant and one or more down stream chemical plants to react dilute ethylene or propylene to produce a product such as polyethylene or polypropylene and the unreacted stream of dilute ethylene or propylene would then be recycled back to the ethane cracker. The benefit from the concept was twofold:

- a reduction in the capital cost and operating cost of the ethylene unit.
- a simple and cost effective way of debottlenecking existing ethylene units especially if already coupled to solution phase polyethylene units such as NOVA's SCLAIRTECH process. However, the paper failed to disclose high temperature ethylene furnaces or reactor materials to achieve high temperatures such as ceramic tubes or ceramic reactors.

[0003] In addition to the Stone and Webster paper, U.S. patent 5,430,211 issued July 4, 1995 assigned to the Dow Chemical Company teaches the use of dilute ethylene produced using catalytic cracking to produce ethyl benzene. The patent is restricted to the use of catalytically dehydrogenated dilute ethylene.

[0004] U.S. patent 5,488,148 issued January 30, 1996 assigned to the Vista Chemical Company claims the use of dilute ethylene in making sulfonated alkyl compounds.

[0005] Chapter 17, "Steamless Pyrolysis of Ethane to Ethylene" by Y. Sony, L.T. Velenyi, A.A. Leff, W.R. Kliewer and J.E. Metcalf (in the text Novel Production Methods for Ethylene, Light Hydrocarbons and Aromatics edited by L.F. Albright et al, Marcel Dekker, Inc. N.Y. (1992)), teaches the high temperature cracking of ethane in ceramic furnace tubes, preferably silicon carbide at high temperatures.

[0006] None of the above art teaches an integrated high temperature cracking process to produce a 75 weight % ethylene feedstock integrated with a polymerization and/or oligomerization process or both together in parallel trains. Alpha olefins from oligomerization could be used directly as comonomers for polyethylene production.

[0007] The present invention provides an integrated process for the cracking of a feedstock to produce an ethylene rich stream and the subsequent polymerization or oligomerization of the ethylene stream without passing through an ethane/ethylene splitter comprising in cooperating arrangement the steps of:

- feeding a feedstock to a cracker operated at a maximum allowable tube wall temperature of from 1050°C to 1600°C;
- passing the resulting product through a separation step to remove hydrocarbon streams having a carbon content of 3 and greater;
- subjecting the resulting stream to a treatment to convert acetylene to ethylene;
- removing the methane and hydrogen from the resulting stream to produce a product having an ethylene content from 75 weight % or more;
- feeding the resulting stream to a polymerization or oligomerization process which has an inherent high ethylene conversion per pass (i.e. greater than 85%) and can operate effectively at feed ethylene concentrations as low as 75 weight %, and polymerizing or oligomerizing the ethylene; and
- separating the unpolymerized stream from the polymer and solvent, and returning it to the ethylene unit.

[0008] Figure 1 is a comparison of the mass balance in a conventional process and the process of the present invention.

[0009] Figure 2 is a comparison of the heat balance in a conventional process and the process of the present invention.

[0010] As used herein the term maximum allowable tube wall temperature refers to the maximum temperature of the external surface of an ethylene furnace tube or coil exposed to the heating section of the cracker. Although we refer to tube or coil, other physical arrangements of the reaction chamber are possible.

[0011] The feedstocks for use in the present invention are well known to those of ordinary skill in the art. For example,

feedstocks for use in accordance with the present invention include, but are not limited to, C₂₋₆ alkanes such as ethane, propane, butane, naphtha, raffinate, atmospheric gas oil, vacuum gas oil, distillate, crude oil, crude resids and mixtures thereof, etc.

[0012] The present invention employs a high temperature cracking process which produces a cracked gas containing hydrogen, methane, C₂ hydrocarbons, C₃ hydrocarbons and heavier constituents.

[0013] The steam cracking process and other cracking processes are well known to those skilled in the art. Steam cracking processes are generally carried out in radiant furnace reactors at elevated temperatures for short residence times, at low reactant partial pressures, high gas velocity, and a low pressure drop through the reaction zone. Any of the furnace designs known to those skilled in the art may be employed in the practice of the present invention.

[0014] However, the coils or tubes of the reactors should be adapted to have a high maximum allowable tube wall temperature. This refers to the outer surface of the tube or coil. In one preferred embodiment the maximum allowable tube wall temperature may range from 1050°C to 1400°C, depending on the material used and the operating severity (required conversion). For conventional HP alloys certain treatment helps to increase the tube life or reduce coking characteristics to permit a reasonable run length. For example, in the website "westaim.com" a tube or coil having an internal coating is described as Engineered Surface Coating by a company called WESTAIM. Typically, the metal beneath the coating comprises from about 23 to 35, preferably from 24 to 35 weight % of chromium. The metal may further comprise from 25 to 50, preferably from 30 to 45 weight % of nickel (Ni); from 1 to 3, preferably from 1.5 to 2.5 weight % of manganese (Mn); from 1 to 2, preferably from 1.5 to 2 weight % of silica (Si). The balance of the steel composition will be predominantly iron with other trace amounts (e.g. for elements other than carbon, typically less than 1 weight %, preferably from 0.1 to 1.0 weight %) of elements such as carbon, titanium, and tungsten, as is well known in the metallurgy arts.

[0015] Such austenitic steel tubes or coils may be used at maximum tube wall temperature from about 1050°C to 1250°C and preferably from 1050°C to 1150°C. At a temperature of 1050°C to 1250°C the conversion of the feedstock will result in about 75%-85% ethylene in the stream fed to the polymerization reaction in the absence of an ethane/ethylene splitter. At temperatures of about 1050°C to 1150°C, the conversion will result in about 75%-80% ethylene in the stream.

[0016] In a preferred embodiment of the invention, the tube or coil is ceramic. These tubes may be used at maximum allowable tube wall temperatures of about 1200°C to 1600°C. High temperature alloy tubes or coils may also be used at this temperature.

[0017] The ceramic may be silicon carbide in which case the maximum allowable tube wall temperature may be from about 1200°C to 1400°C, preferably from about 1200°C to 1350°C. At tube wall temperatures of 1200°C to 1350°C, a cracked gas stream is produced which contains ethylene in the mixed feed to the polymerization reactor which may range from about 80-97, preferably 90-97 weight %.

[0018] The hydrocarbon feed to the steam cracker is typically in vapor phase or it may comprise a mixed liquid-vapor phase. The most preferred feedstocks for steam cracking are C₂₋₄ alkanes, naphtha, and mixtures thereof.

[0019] Generally, preheated feed is introduced into a convection zone of a pyrolysis furnace to further preheat the feed to a temperature below that at which significant reaction takes place (e.g., 400°C to 640°C).

[0020] Typically small amounts of steam are added to the feed prior to introduction to the radiant reaction zone of the pyrolysis furnace to provide a weight ratio of from about 0.1 to 2 parts of steam to hydrocarbon, preferably from about 0.1 to 1 (based on the weight of the feed). The steam assists vaporization of the feed and reduces the hydrocarbon partial pressure in the reaction zone in order to improve olefin yields. The feed in process tubes or coils is then cracked at maximum tube wall temperature up to about 1400°C.

[0021] Typically operating conditions comprise an inlet temperature to the radiant heating section of the furnace ranging from about 600°C to about 650°C and an outlet temperature ranging from about 800°C to about 1000°C.

[0022] The feed velocity through the coils ranges from about 300 to about 800 feet per second, based on the total flow of steam and hydrocarbons and also coil dimensions.

[0023] The residence time of the feed in the radiant section of the cracking coil generally ranges from about 30 to about 1000 milliseconds.

[0024] The effluent product gases issuing from the radiant zone are rapidly cooled to a temperature at which the cracking reactions substantially stop. This generally ranges from about 400°C to about 600°C.

[0025] Generally, the effluent from the pyrolysis reactor is directed to a quench boiler wherein the effluent is indirectly contacted with cooling water in cooling tubes. After traversing the cooling tubes, the water is removed from the quench boiler in a line and returned to a supply tank.

[0026] The gaseous effluent from the cracking reaction then passes through an olefins purification system. Typically the gaseous effluent is water washed, compressed, caustic washed, compressed and then dried. The dried effluent is chilled and passes through a deethanizer to separate the effluent into two component streams; a light stream (e.g., hydrogen, methane, acetylene, ethane and ethylene), and a heavy stream (e.g., propane, propylene and mixed C₄⁺ hydrocarbons). Then, the light product gases are compressed, and the acetylene components are removed by absorp-

tion or hydrogenated to ethylene in an acetylene hydrogenation reactor.

[0027] The effluent stream is cooled to a very low temperature typically from about -30°C to about -60°C and fed to a demethanizer to remove methane and hydrogen from the feed stream. The final treated effluent stream typically comprises from 70-99, preferably from 90-99 weight % of ethylene.

[0028] The effluent stream obtained from the olefins purification process may be employed as the feedstock for an ethylene polymerization or oligomerization process in accordance with the present invention. The feedstock for use in the polymerization process preferably contains at least about 75 weight % ethylene, more preferably at least about 85 weight % ethylene and most preferably from about 90 to 99 weight % ethylene.

[0029] The ethylene may be polymerized or oligomerized into polyethylene or alpha olefins either by solution, slurry or gas phase methods. Generally the pressure in the polymerization reactor for a solution process may exceed about 3,000 psi (20 MPa) (e.g. about 3,000 to 10,000 psi (20 MPa to 70 MPa), preferably from 3,000 to 5,000 psi (20 MPa to 35 MPa). This moderate pressure is necessary to maintain the monomers and comonomers in solution even at the solution's high reaction temperature.

[0030] In these processes ethylene is dissolved in a liquid hydrocarbyl medium (e.g. C₅₋₁₀ alkyl and/or an aromatic hydrocarbon). The solution is contacted/mixed with a catalyst. The catalyst may be a conventional Ziegler Natta type catalyst, a metallocene type catalyst used by Exxon, a constrained geometry catalyst used by Dow or it could contain novel ligands such as phosphinimine ligands. Depending on the temperature the process may be a slurry process (polymer precipitates from solution) as are disclosed for example in patents to Phillips (typically below about 100°C) or the polymer may remain in solution (temperature from 180°C to 300°C) as described in patents to, in the name of DuPont Canada, Novacor and Nova Chemicals Ltd.

[0031] The catalyst may also be Ni, Zr, Cr or Ti based oligomerization catalyst.

[0032] In the solution polymerization process the catalyst is deactivated and remains in the polymer. The polymer and solvent are then separated and the solvent is heated to remove residual unreacted feed (e.g., ethylene and ethane). The feed is then recycled to the cracker.

[0033] In the slurry polymerization process the polymer is separated from the diluent and the diluent is then heated to remove the unreacted feed. The polymerization may be a gas phase polymerization conducted at temperatures from about 80°C to 115°C at pressures from about atmospheric to 150 psig (gauge pressure of 1 MPa).

[0034] The current state of the art of gas phase polymerization process has low conversion per pass and inherently is not suitable for dilute ethylene utilization at this time. More advancements in catalyst technology and heat transfer might in future overcome this disadvantage.

[0035] In a further aspect of the present invention the ethylene from the cracker may be feed to an oligomerization unit. Typically these units condense ethylene into higher alpha olefins such as butene, hexene and octene although higher alpha olefins, up to about C₂₀, may be produced. Generally, in these processes, ethylene is contacted with a catalyst typically comprising of an aluminum alkyl (e.g. tri methyl aluminum or tri ethyl aluminum) or an aluminum complex of the formula (R⁴)₂AlO(R⁴AlO)_mAl(R⁴)₂ wherein each R⁴ is independently selected from the group consisting of C₁₋₂₀ hydrocarbyl radicals and m is from 0 to 50, preferably R⁴ is a C₁₋₄ alkyl radical and m is from 5 to 30. The ethylene alpha olefin are at least recycled through a reaction or chain growth zone to grow the alpha olefin (e.g. increase the length by 2 carbon atoms (1 ethylene add on) as a result there is generally a statistical distribution of alpha olefins in the resulting product. The product is generally distilled to separate different alpha olefins. Generally, the process is conducted at pressures from about 2,000 to 5,000 (13 MPa to 35 MPa), preferably 2,000 to 3,500 psig (13 MPa to 25 MPa) and temperatures from about 90°C to 180°C. Such processes are well known and described for example in U. S. Patent 4,935,569 issued June 19, 1990 assigned to Ethyl Corporation.

[0036] The ethylene stream from the cracker may also be fed to an oligomerization unit which uses transition metal complexes as catalysts and may also use alkylaluminum compounds of the formula AlR_xX_{3-x} as cocatalysts wherein R is a C₁₋₈, preferably C₁₋₄ alkyl radical, X is a halogen, preferably chlorine or bromine, and x is an integer from 1 to 3. Titanium, zirconium, hafnium, chromium, nickel or molybdenum could be used as active components of the complex catalysts. These processes require milder reaction conditions - pressures from 15 to 1500 psig (gauge pressures of 0.1 to 10.5 MPa) and temperatures from 0°C to 150°C. Such processes are known and described for example in "The Nickel-Complex Catalyzed Synthesis of α-Olefins" paper by Amo Behr and Wilhelm Keim in The Arabian Journal for Science and Engineering, Vol. 10, No. 4 or in the European Patent Application 241,596 published November 21, 1987 the texts of which are herein incorporated by reference.

[0037] The present invention will be more fully described in association with the drawings. Figures 1a and 1b are the simple mass balances generated by a computer program which accurately reflect commercial operations that compare the flow of materials. The calculations are based on a plant to produce 100,000 tons/yr. of ethylene going into a polyethylene unit. In the figure the bold numbers are tons of product.

[0038] Fresh feed stream (1) is introduced into the furnace in combination with dilution steam stream (3) and ethane recycle stream (9) respectively. The mass going through the furnace is therefore stream (2) = [(1)+(3)+(9)]. After cracking in the furnace and quenching, water is recovered and dilution stream is recycled.

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[0039] The compressor which receives the cracked gases (stream 4) boosts the pressure of the stream before it goes to a deethanizer. From the deethanizer, C₃'s and heavier products are separated as stream (6) from the lighter fractions. The C₂'s and lighter materials (stream 5) enter the acetylene removal/conversion system and from there to the demethanizer. Off gases made up mainly of methane and hydrogen are removed as stream (8) while stream (7) in a conventional process goes to an ethane splitter. There ethane is separated from ethylene product (stream 10) while ethane from the stripper is recycled back to the furnace (stream 9). The figures illustrate the following improvements arising from the present invention as seen in Tables 1 to 3.

TABLE 1

Comparison Arising From Mass Balances		
Mass Flow	Invention (metric tons/yr)	Prior Art (metric tons/yr)
To Cracking Furnace	205,044	265,551
Load on Compressor	158,941	205,774
C3 + Products	11,677	11,192
Acetylene Reactor	147,265	195,551
Offgas	19,961	17,550
Load to Splitter	0	176,898
Ethane Recycle	26,800	76,901

[0040] In the process of the present invention illustrated in Figure 1b, a polyolefins or oligomerization unit serves as the separator, and the unreacted ethane is recycled back to the furnace. The advantages of this over the conventional method become obvious to anyone knowledgeable in the art, when one studies Tables 1 to 4, as follows:

- a smaller load for the furnace
- a smaller cracked gas compressor
- a smaller acetylene processing unit
- the absence of an ethane/ethylene splitter
- a greatly reduced recycle of ethane
- a small integrated ethylene/polyethylene unit
- reduced energy requirements
- lower operating costs

[0041] The capital cost for the process of this invention compared to the conventional process, for the same plant capacity, is lower.

[0042] Figures 2a and 2b show the heat balances for both the conventional and the new process. The heat loads are given in gigajoules per hour. The total energy requirements for the conventional system is 320.9 GJ/hr as opposed to 229.6 GJ/hr for the new process. Tables 2 to 4 show the Energy Requirements, Energy Consumption/Generation and Operating Cost respectively for the prior art versus the invention.

TABLE 2

Energy Requirements		
	Invention [GJ/hr.]	Prior-Art [GJ/hr.]
Furnace	159.1	198.3
Cracked Gas Compressor Driver	35.8	45.9
Dilution Steam Generation	25.3	16.2
Deethanizer Chilling train	14.0	14.0
C2 Splitter (C3 Refrigeration)	0.0	31.0
Auxiliary Firing (Steam)	21.9	15.6
TOTAL	256.1	320.9

TABLE 3

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Energy Consumption/Generation		
	Invention [GJ/metric ton of Ethylene]	Prior-Art [GJ/metric ton of Ethylene]
Energy Consumption	15.21	17.95
Energy Generation (Off-gases only)	14.85	13.52
Carbon Dioxide (off-gases only)	0.295	0.237

TABLE 4

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Operating Costs		
	Invention [\$ /Megagram]	Prior-Art [\$ /Megagram]
Ethane	232.1	226.3
Offgas	(40.7)	(37.4)
C3s	(9.4)	(14.3)
C4s	(18.4)	(13.6)
C5s	(9.5)	(8.9)
Energy	39.5	46.6
TOTAL	193.5	198.7

[0043] The conditions for the simulation are as follows:

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- Inlet pressure: around 1.97 kg/cm² A
- Internal Diameter: 0.038 M
- Coil Residence Time ≈ 120 ms
- Dilution Steam Ratio (kg steam/kg ethane) = 0.3

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[0044] The conventional runs were simulated for 65% ethane conversion in the furnace, while the new process runs were simulated for 88% ethane conversion.

Example 1:

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[0045] Table 5 shows the effect of Coil Outlet Temperature on ethylene yield based on computer simulations of an ethylene cracker.

TABLE 5

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The Effect of Coil Outlet Temperature on Ethylene Yield	
Coil Outlet Temperature (COT) [°C]	Ethylene Yield [wt.%]
875	47.97
889	52.63
901	55.83
910	58.15
919	60.14
929	61.78
932	62.30
938	63.09

TABLE 5 (continued)

The Effect of Coil Outlet Temperature on Ethylene Yield	
Coil Outlet Temperature (COT) [°C]	Ethylene Yield [wt.%]
946	64.10
950	64.39
958	65.01
967	65.36

Example 2:

[0046] Once through yields of ethylene for high conversion process which enables the close coupling with a polymerization or oligomerization unit were calculated at various conversions (temperatures) using computer programs which closely simulate actual plant operation. The results are shown in Table 6.

TABLE 6

Yields (wt%) of Components AT				
Components	65% Ethane Conversion	85% Ethane Conversion	90% Ethane Conversion	95% Ethane Conversion
Methane	2.9	7.0	7.6	7.6
Acetylene	0.7	2.7	3.9	4.6
Ethylene	52.6	65.0	65.4	66.3
Ethane	36.4	12.2	10.2	5.9
C ₃ 's & heavier	3.4	7.4	7.9	8.8
The rest are off-gases (CO, CO ₂ , H ₂)				

Example 3:

[0047] Table 7 shows the effect of conversion on Maximum Allowable Tube Metal Temperature (MATMT) for runs of various duration's of time. In the table the subscript is the run length in days and 0 is start up. The table shows that the material of construction must be carefully chosen to be able to attain the required conversion with economically adequate run length.

TABLE 7

The Effect of Conversion on Maximum Allowable Tube Metal Temperature (MATMT)				
Ethane Conversion [%]	(MATMT) ₀ [°C]	(MATMT) ₁₀ [°C]	(MATMT) ₂₀ [°C]	(MATMT) ₃₀ [°C]
56.03	986	1006	1017	1031
63.64	990	1037	1052	1071
68.54	1007	1060	1079	1103
72.35	1020	1080	1102	1129
75.87	1033	1098	1125	1155
79.09	1045	1116	1146	1180
80.19	1050	1123	1154	1189
82.00	1057	1133	1167	1204
84.62	1068	1150	1187	1227
85.51	1072	1156	1194	1235

TABLE 7 (continued)

The Effect of Conversion on Maximum Allowable Tube Metal Temperature (MATMT)				
Ethane Conversion [%]	(MATMT) ₀ [°C]	(MATMT) ₁₀ [°C]	(MATMT) ₂₀ [°C]	(MATMT) ₃₀ [°C]
87.77	1082	1171	1213	1256
89.79	1092	1186	1231	1277

Claims

1. An integrated process for the cracking of a feedstock to produce ethylene and the subsequent polymerization or oligomerization of the ethylene, in the ethane/ethylene stream, without passing through an ethane splitter comprising in cooperating arrangement the steps of:
 - i) feeding a feedstock to a cracker operated at a maximum allowable tube wall temperature of from 1050°C to 1600°C;
 - ii) passing the resulting product through a separation step to remove hydrocarbon streams having a carbon content of 3 and greater;
 - iii) subjecting the resulting stream to a treatment to convert acetylene to ethylene;
 - iv) removing the methane and hydrogen from the resulting stream to produce a product having an ethylene content from 75 weight % to 95 weight %;
 - v) feeding the resulting stream to a polymerization or oligomerization process and polymerizing or oligomerizing the ethylene;
 - and
 - vi) separating the unpolymerized stream from the polymer and solvent, returning it to the cracker.
2. The process according to claim 1, wherein the oligomerization is a solution, slurry, or gas phase operated process.
3. The process according to claim 1 or claim 2, wherein the feedstock is ethane, naphtha or gas oil.
4. The process according to any one of claims 1 to 3, wherein the residence time in the cracker is in the range 30 to 1000 milliseconds.
5. The process according to any one of the preceding claims, wherein the furnace tubes in the cracker are austenitic stainless steel and the maximum allowable tube wall temperature is in the range 1050°C to 1250°C.
6. The process according to any one of the preceding claims, wherein the furnace tubes of the reactor are made of ceramic or high temperature alloy and the maximum allowable tube wall temperature is in the range 1200°C to 1600°C.
7. The process according to claim 6, wherein the furnace tubes are made of ceramic, the ceramic being silicon carbide and the maximum allowable tube wall temperature is in the range 1200°C to 1400°C.
8. The process according to any one of the preceding claims, wherein the ethylene content in the feed to the oligomerization or polymerization process is greater than 75 weight %.
9. The process according to any one of the preceding claims, wherein the polymerization or oligomerization process is a solution process operated at a pressure in the range 3,000 psi to 5,000 psi (20 MPa to 35 MPa).
10. The process according to any one of claims 1 to 8, wherein the polymerization or oligomerization process is a slurry process.
11. The process according to any one of claims 1 to 8, wherein the oligomerization process is a gas phase process.
12. The process according to any one of the preceding claims, wherein the conversion of ethylene to polyethylene is greater than 85%.

13. The process according to claim 12, wherein the conversion of ethylene to polyethylene is greater than 85% on a once through basis.
14. The process according to any one of the preceding claims, wherein the feed from the cracking process is fed to a polymerization process.
15. The process according to any one of claims 1 to 13, wherein the feed from the cracker is fed to an oligomerization unit.
16. The process according to claim 15, wherein the catalyst in the oligomerization unit comprises an alkylaluminum compound or a transition metal complex of titanium, zirconium, hafnium, chromium, nickel or molybdenum with or without an alkylaluminum compound.
17. The process according to claim 16, wherein the alkylaluminum compound is ethyl aluminum or tri methyl aluminum.
18. The process according to claim 16, wherein the alkylaluminum compound has the formula $(R^4)_2AlO(R^4AlO)_mAl(R^4)_2$ wherein each R^4 is one of the group consisting of C_{1-20} hydrocarbyl radicals and m is in the range 0 to 50.
19. The process according to claim 18 wherein R^4 is a C_{1-4} alkyl radical and m is in the range 5 to 30.
20. The process according to claim 16, wherein the alkylaluminum compound has the formula AlR_xX_{3-x} wherein R is a linear or branched alkyl radical comprising 2 to 8 carbon atoms, X is chlorine or bromine and x is equal to 1, 2 or 3.

Figure 1a: Conventional Mass Balance [Tons/yr.]

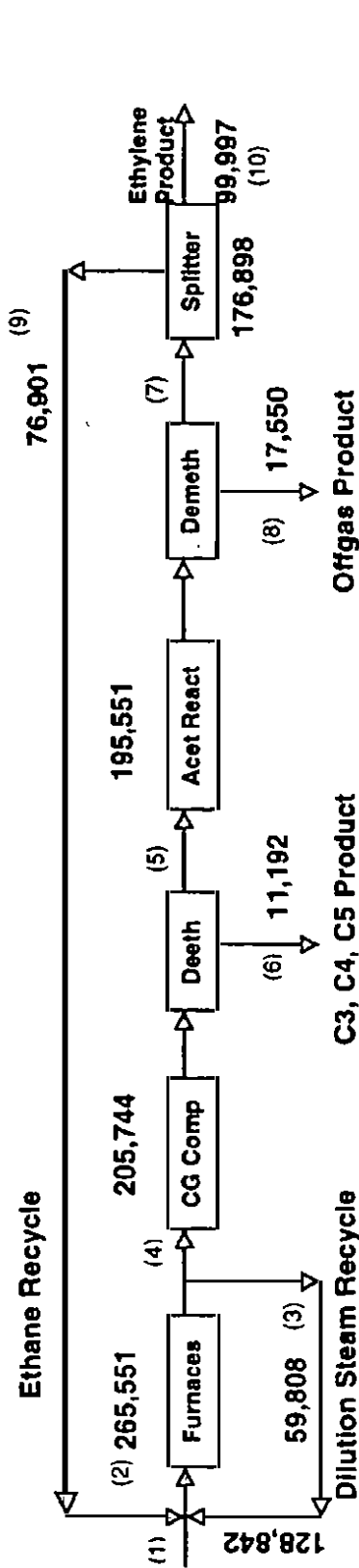
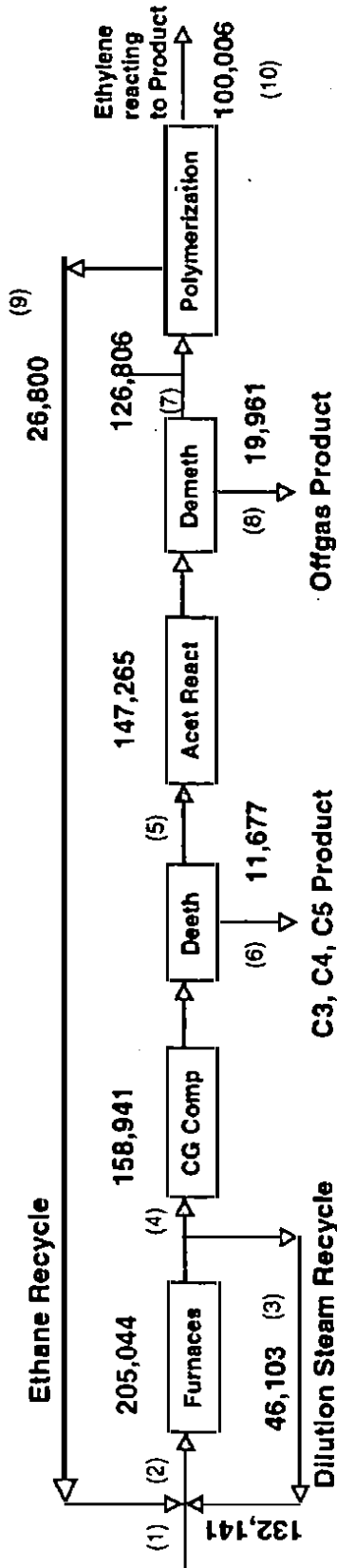


Figure 1b: New Process Mass Balance [Tons/yr.]



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Figure 2a: Conventional Heat Balance [GJ/hr.]

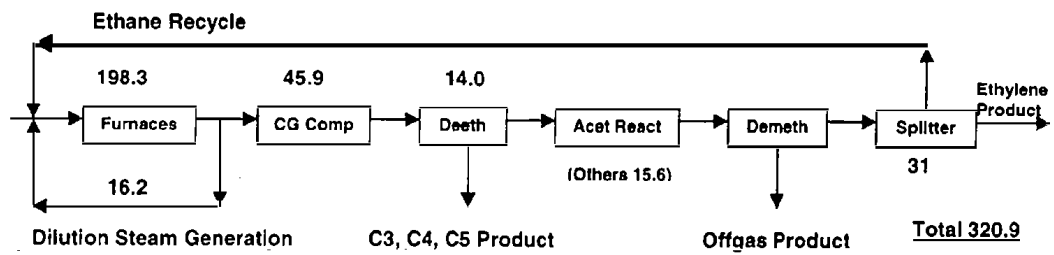
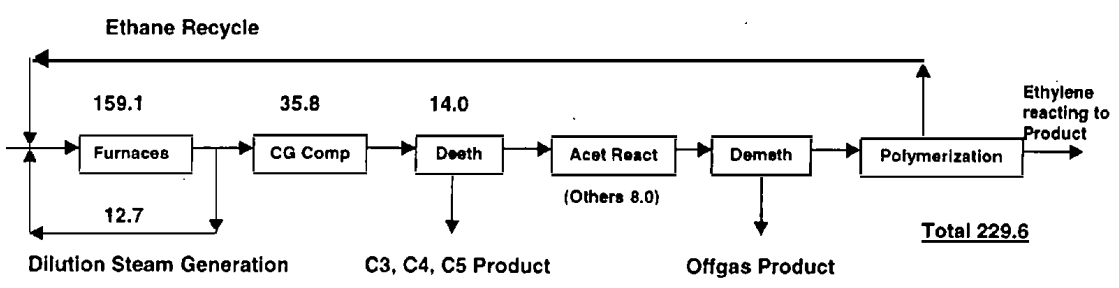


Figure 2b: New Process Heat Balance [GJ/hr.]



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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 8790

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US RE20931 E (R. F. RUTHRUFF) 29 November 1939 (1939-11-29) * claims * -----	1	C10G57/02 C07C4/04 C07C2/30
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C07C C10G C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 February 2000	Examiner Van Geyt, J
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document			

EPO FORM 1503 (03-02-EP) (P04-001)

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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

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For more details about this annex, see Official Journal of the European Patent Office, No. 12/82



US005981818A

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United States Patent [19]

Purvis et al.

[11] Patent Number: 5,981,818

[45] Date of Patent: Nov. 9, 1999

[54] INTEGRATED CRACKING AND OLEFINS
DERIVATIVE PROCESS UTILIZING DILUTE
OLEFINS

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[21] Appl. No.: 08/734,036

[22] Filed: Oct. 18, 1996

Related U.S. Application Data

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21, 1995, abandoned.

[51] Int. Cl.⁶ C07C 4/02; C08F 2/34

[52] U.S. Cl. 585/519; 585/251; 585/253;
585/271; 585/315; 585/330; 585/518; 585/648;
585/653; 568/469.9; 568/697; 568/850;
560/208; 560/210; 570/193; 526/75; 526/76;
526/901

[58] Field of Search 526/75, 76; 585/518,
585/519, 650, 651, 652, 648, 326, 251,
253, 271, 315, 330, 653; 568/469.9, 697,
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Primary Examiner—Fred Teskin

Attorney, Agent, or Firm—Hedman, Gibson & Costigan,
P.C.

[57] ABSTRACT

A novel process is provided which integrates the cracking of hydrocarbon containing feedstocks with the olefins purification and olefins derivative process utilizing dilute olefin feedstocks.

24 Claims, 9 Drawing Sheets

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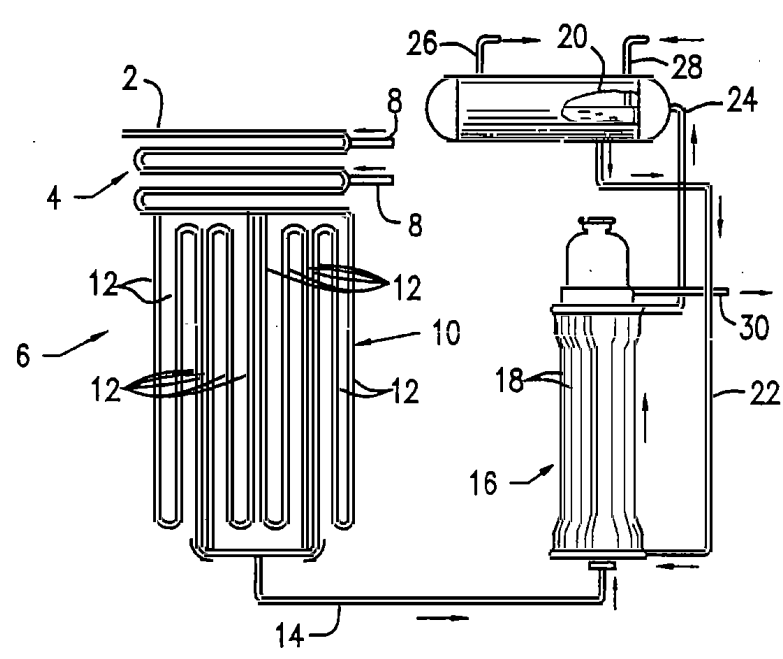


FIG. 1

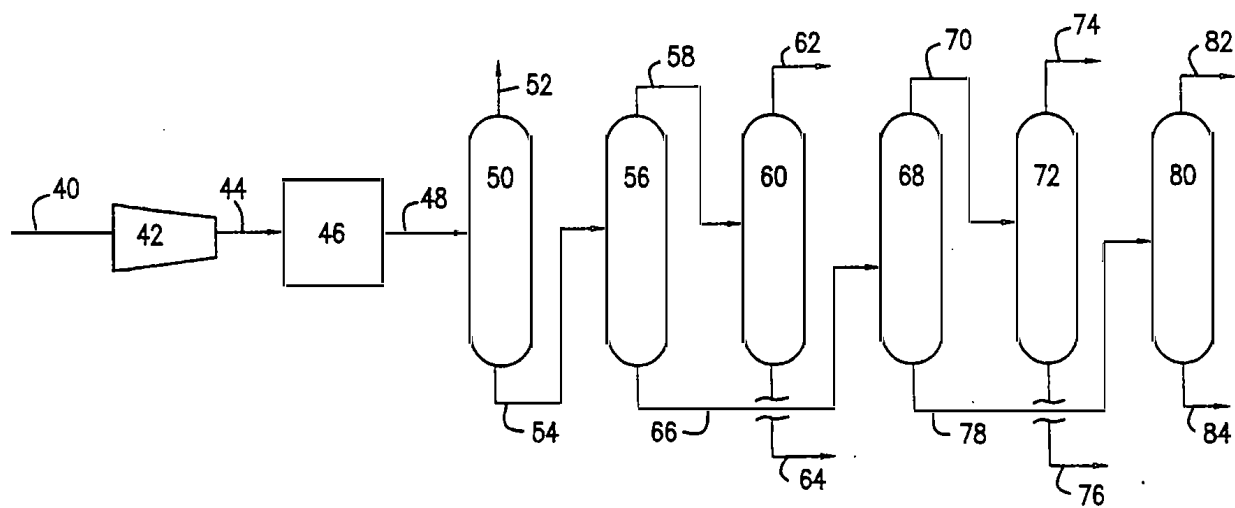


FIG. 2

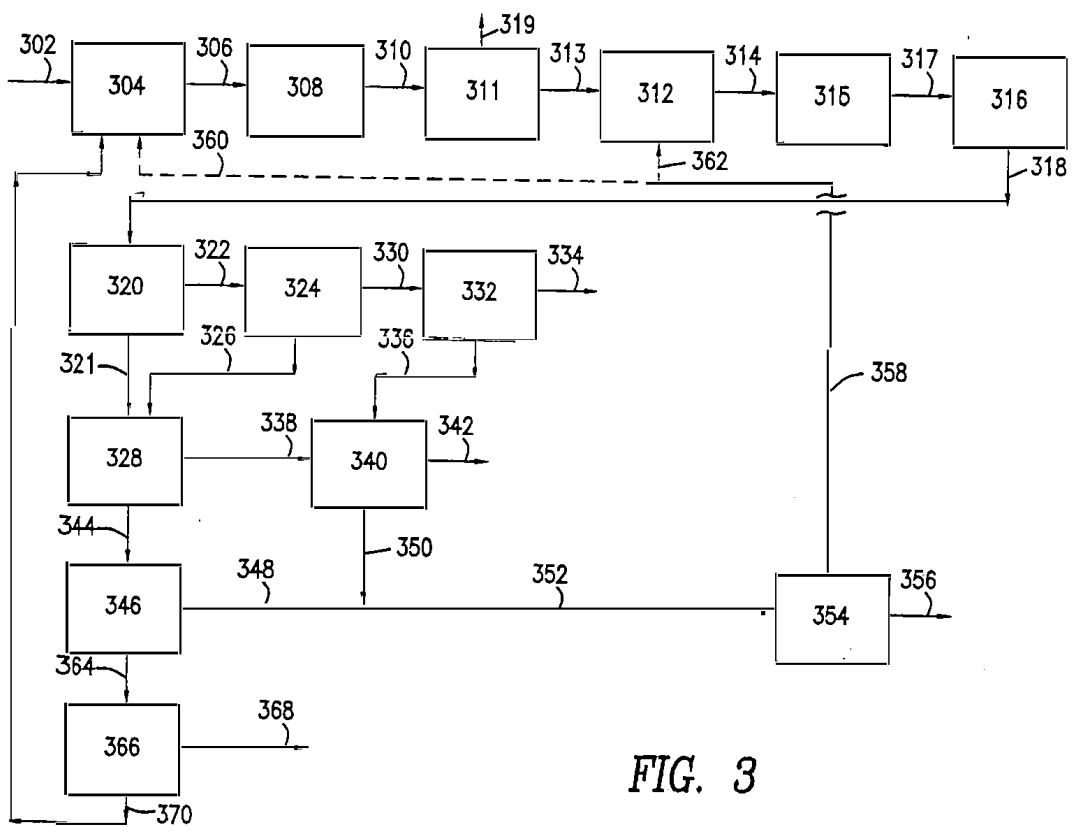


FIG. 3

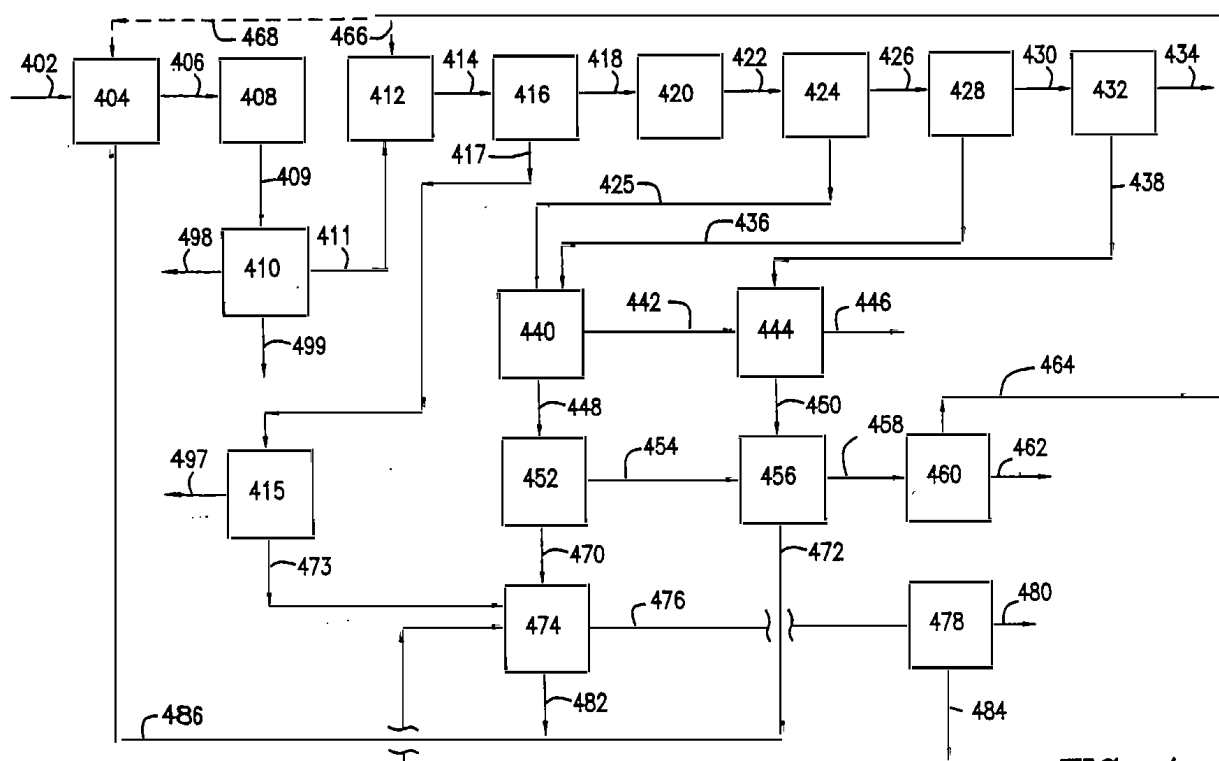


FIG. 4



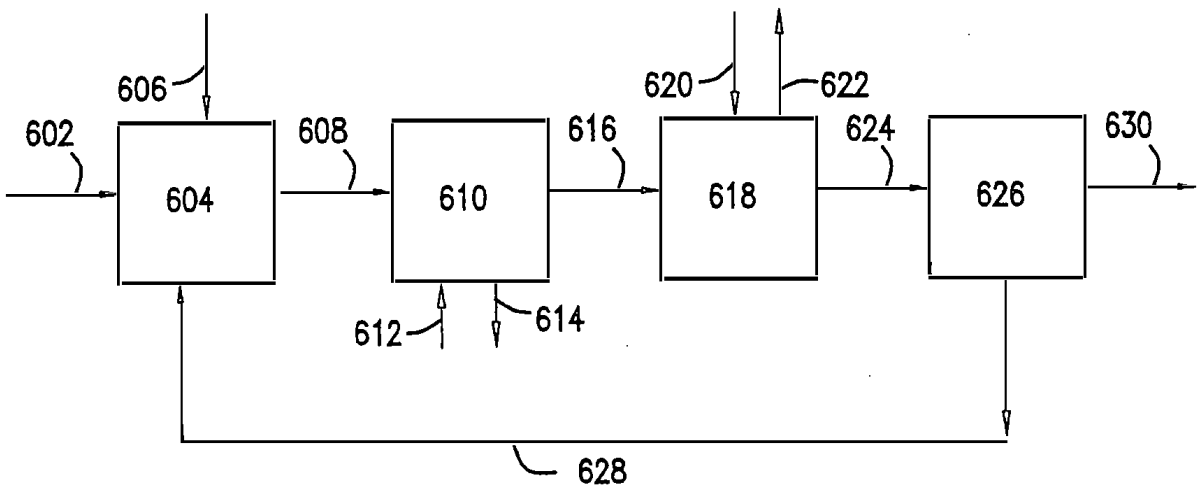


FIG. 6A

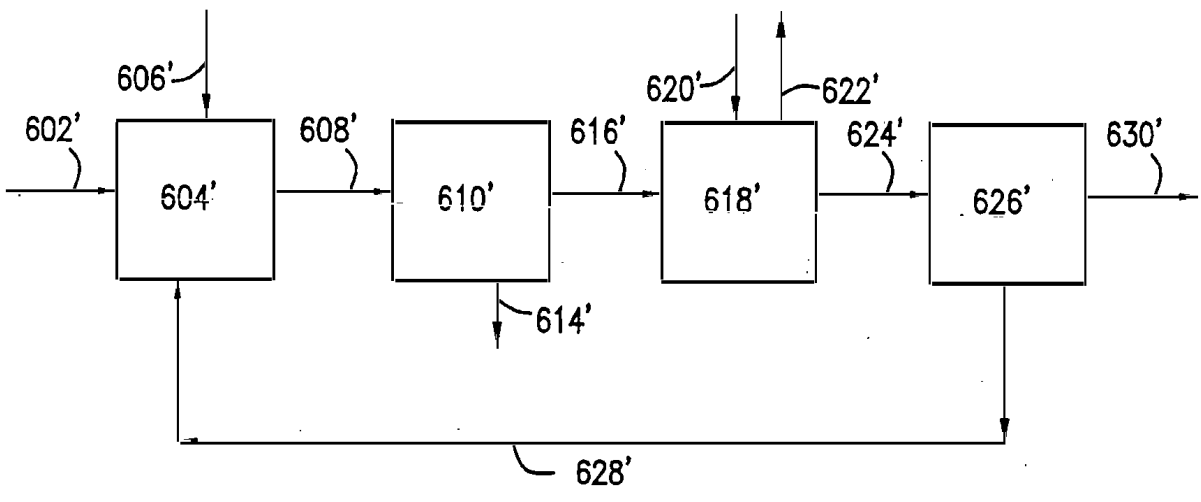


FIG. 6B

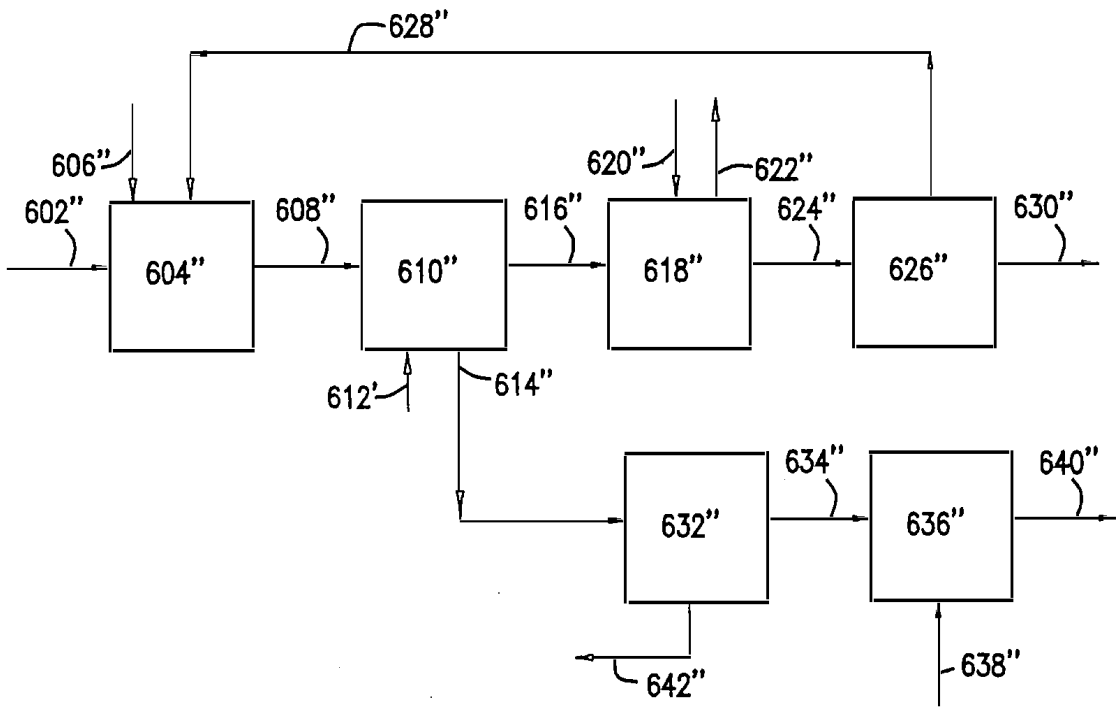


FIG. 6C

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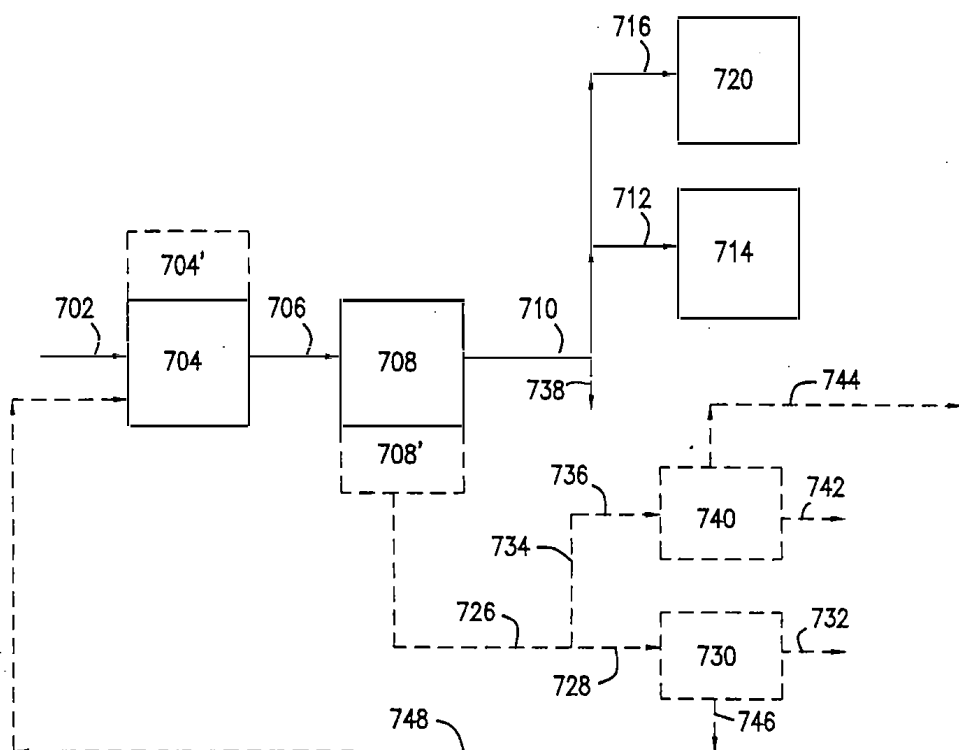


FIG. 7

INTEGRATED CRACKING AND OLEFINS DERIVATIVE PROCESS UTILIZING DILUTE OLEFINS

The present application is a continuation-in-part application of U.S. Ser. No. 08/407,920, filed Mar. 21, 1995, attorney docket 696-243, now abandoned.

FIELD OF THE INVENTION

The present invention relates to a method of integrating cracking and olefin derivative processes utilizing dilute olefins as feedstocks. More particularly the present invention relates to an integrated process for preparing olefin derivatives from hydrocarbon feedstocks by cracking the hydrocarbon feedstocks, and separating the olefins from the cracked gas into dilute olefin feeds for olefin derivative processing. Most particularly, the present invention relates to an integrated process for manufacturing ethylene and propylene derivatives from catalytic and non-catalytic cracking processes.

BACKGROUND OF THE PRESENT INVENTION

The processes of non-catalytically cracking and catalytically cracking hydrocarbon feedstocks are well known in the art. In this regard, steam cracking in a furnace and contact with hot non-catalytic particulate solids are two well known non-catalytic cracking processes, as described, for example in Hallee et al., U.S. Pat. No. 3,407,789; Woebecke, U.S. Pat. No. 3,820,955; DiNicolantonio, U.S. Pat. No. 4,499,055 and Gartside et al., U.S. Pat. No. 4,814,067. Additionally, fluid catalytic cracking and deep catalytic cracking are two well known catalytic cracking processes. See, e.g., Cormier, Jr. et al., U.S. Pat. No. 4,828,679; Rabo et al., U.S. Pat. No. 3,647,682; Rosinski et al., U.S. Pat. No. 3,758,403; Gartside et al., U.S. Pat. No. 4,814,067; Li et al., U.S. Pat. No. 4,980,053; and Yongqing et al., U.S. Pat. No. 5,326,465.

The olefins produced in these processes have long been desired as feedstocks for the petrochemical industries. Olefins such as ethylene, propylene, the butenes and the pentenes are useful in preparing a wide variety of end products, including but not limited to polyethylenes, polypropylenes, polyisobutylene and other polymers, alcohols, vinyl chloride monomer, acrylo-nitrile, methyl tertiary butyl ether and tertiary amyl methyl ether and other petrochemicals, and a variety of rubbers such as butyl rubber.

However, there has been little incentive in the industry to integrate the cracking processes which produce the olefins with the olefin derivative processes which produce the end products due to either the inability of the respective processes to handle dilute olefin feeds, the difficulty in recycling the by-products produced in the respective processes or both as well as logistical reasons.

For example, in the polymerization processes to produce polyethylene and polypropylene, historically the location and infrastructure associated with ethylene-polyolefin units has made integration a difficult logistics problem. More importantly, recycle streams from the polyolefins units have until recently contained corrosive products from the catalyst deactivation reactions and other impurities.

Additionally, the feedstocks conventionally required for the production of polyethylenes and polypropylenes have demanded that methane, ethane and propane concentrations in the ethylene and propylene feedstocks be extremely low. For example, for ethylene, the minimum concentration of

ethylene is typically about 99.9 mol % and for propylene the minimum propylene concentration for polymer grade propylene is typically about 99.0 mol %.

These ethylene and propylene feedstock specifications have required extensive and costly purification in the olefin recovery section of the cracking processes. Typically, the ethylene concentration in the C_2 stream from a cracker gas separation system ranges from about 55 to about 85 percent. The higher purity ethylene stream conventionally requires additional separation in a C_2 splitter.

Still further, advancements in polymerization catalysis, with the introduction of the "single site" metallocene catalysts, have resulted in even more stringent feedstock purity requirements due to the expanding usage of these high activity catalysts. See, e.g., Chang, U.S. Pat. No. 5,238,892; Burkhardt et al., PCT Application No. WO 9212184; and Schreck et al., U.S. Pat. No. 5,280,074.

Accordingly, the conventional wisdom in the industry is for olefin derivative producers, including, polyethylene and polypropylene producers, to purchase polymer grade ethylene and propylene from ethylene and propylene producers and then remove trace contaminants to the desired purity specifications and recover, flare or utilize the purge streams from the olefin derivative reactor within the processing plant.

Traditionally, ethylene and propylene unit operators have not accepted the recycle streams from the olefin derivative units because they typically contain undesirable light gases and inorganic acids resulting from catalyst deactivation reactions.

However, with ethylene and propylene units now being built in more remote and unsophisticated locations close to feedstock supply sources, it has now become desirable to develop a single integrated process which will produce the desired olefin derivative products as the final output of the integrated plant.

Additionally, existing refineries have long experienced problems of gas plant bottlenecking when increasing the capacity or conversion level of their various cracking units. The inability to market the relatively dilute olefins produced in the refinery to downstream purification processors has further compounded the problem. Thus, it has also become desirable to develop a means of revamping an existing refinery to debottleneck the gas plant and market the dilute olefins produced therein.

Accordingly, if such a means to integrate cracking with olefins derivative processes were to be developed it would represent a significant advancement in the state of the art including the realization of significant capital and operating cost savings for end product producers.

SUMMARY OF THE PRESENT INVENTION

To this end, the present inventors have now discovered a unique integrated process to overcome the drawbacks of the prior art and meet the commercially desirable aspects discussed above.

Accordingly, it is an object of the present invention to provide a process which will integrate olefins production with olefins derivative facilities in a "grassroots" design or revamp/expansion of an existing olefins facility.

It is another object of the present invention to provide a process which will integrate the cracking of hydrocarbons with ethylene polymerization and/or other ethylene derivative units.

It is a further object of the present invention to provide an integrated process which allows for the production of poly-

ethylene and/or other suitable ethylene derivatives from a relatively dilute ethylene feedstock.

It is a still further object of the present invention to provide a process which will integrate the cracking of hydrocarbons with propylene polymerization and/or other propylene derivative units.

It is still another object of the present invention to provide an integrated process which allows for the production of polypropylene and/or other suitable propylene derivatives from a relatively dilute propylene feedstock.

It is yet another object of the present invention to provide a process which integrates a cracking process with one or more olefin derivative processes.

It is another further object of the present invention to provide an integrated process which provides for the recycling of the olefin derivative by-product streams to the cracking unit.

It is still another further object of the present invention to integrate processes for the production of polymers, rubbers and petrochemicals from the C₄ hydrocarbons derived from the cracking process with the olefin derivative processes and cracking process.

It is yet still another further object of the present invention to integrate dilute olefin derivative processes with existing refinery offgas systems to debottleneck the refineries.

These and other objects evident to those of ordinary skill in the art are provided by the present invention discussed in detail hereinbelow.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts in flow chart form a steam cracking process useful in the practice of the present invention.

FIG. 2 depicts in flow chart form an olefins purification process useful in the practice of the present invention.

FIG. 3 depicts in flow chart form an embodiment of an integrated process for the production of polyethylene in accordance with the present invention.

FIG. 4 depicts in flow chart form an embodiment of an integrated process for the production of polyethylene and polypropylene in accordance with the present invention.

FIG. 5 depicts in flow chart form an embodiment of an integrated process for the production of olefin derivatives in accordance with the present invention.

FIGS. 6A, 6B and 6C depict in flow chart form C₄ hydrocarbon downstream processing embodiments useful in the practice of the integrated process of the present invention.

FIG. 7 depicts in flow chart form a debottlenecking embodiment of the present invention.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

As used herein throughout the present specification the term "dilute olefins" means olefins which meet the non-saturated hydrocarbon and other trace contaminant specifications of the respective olefins derivative process but still contain quantities of saturated inert hydrocarbons in excess of typical current polymer grade specifications, such as on the order of less than about 50 weight percent, preferably less than about 15 weight percent and most preferably as little as 1 weight percent.

Also as used herein throughout the present specification, the term "olefin derivative process" is meant to include any and all processes whereby olefins are converted to petro-

chemical products or intermediates in a relatively high conversion once through process, i.e., the bulk of the olefins are converted to the desired petrochemical in a single process sequence without the need for recycle or further processing steps, at high once through conversions typically on the order of at least about 50 percent, preferably at least about 75 percent and, in the ideal case, up to about 100 percent.

THE FEEDSTOCKS

The hydrocarbon feedstocks for use in the cracking processes of the present invention may vary widely and are well known to those of ordinary skill in the art. All of the known hydrocarbon feedstocks for use in the cracking processes described hereinbelow are contemplated for use in accordance with the present invention. For example, feedstocks for use in accordance with the present invention include, but are not limited to, ethane, propane, butane, naphtha, raffinate, atmospheric gas oil, vacuum gas oil, gas condensates, natural gas liquids, crude oil, crude resids, mixtures thereof, etc.

THE CRACKING PROCESSES

The process of the present invention may employ any cracking process which produces a cracked gas, such as those containing hydrogen, methane, C₂ hydrocarbons, C₃ hydrocarbons and heavier constituents. This includes both catalytic and non-catalytic cracking processes.

The steam cracking process and other non-catalytic cracking processes are well known to those of ordinary skill in the art. Steam cracking processes are generally carried out in radiant furnace reactors at elevated temperatures for short residence times while maintaining a low reactant partial pressure, relatively high mass velocity, and effecting a low pressure drop through the reaction zone. Any of the furnaces known to those skilled in the art may be employed in the practice of the present invention, e.g., Bowen et al., U.S. Pat. No. 5,151,158; Palchik et al., U.S. Pat. No. 3,274,978; Hallee et al., U.S. Pat. No. 3,407,789; Woebecke, U.S. Pat. No. 3,820,955; Alagy et al., U.S. Pat. No. 4,780,196; DiNicolantonio, U.S. Pat. No. 4,499,055; Martens, U.S. Pat. No. 4,762,958 and the like.

The hydrocarbon feed to the steam cracker can be in the liquid or vapor phase or it may comprise a mixed liquid-vapor phase. The most preferred feedstocks for steam cracking are ethane, propane, butane, naphtha, gas oils, gas condensates and mixtures thereof. The hydrocarbon feedstock is normally in the vapor phase in the reaction zone.

Referring to FIG. 1, the feed will generally be preheated in a preheat zone (not shown) from about ambient temperature, e.g., 70° F. to 80° F., to an intermediate temperature. The preheated feed in a line 2 is then introduced into a convection zone 4 of a pyrolysis furnace 6 to further preheat the feed to a temperature below which no significant reaction takes place, e.g., 1100° F. to 1300° F. During the convection zone preheating step, steam is generally added to the feed via lines 8 to essentially complete vaporization of the feed prior to the feed being introduced to the radiant reaction zone 10 of the pyrolysis furnace 6. The steam functions to facilitate vaporization and reduce the hydrocarbon partial pressure in the radiant reaction zone in order to improve desired olefin yields. The feed in process tubes or coils 12 is then cracked at very high temperatures, e.g., up to about 1650° F., in the radiant reaction zone 10 of the pyrolysis furnace 6.

Typical operating conditions comprise an inlet temperature to the radiant heating section of the furnace ranging

from about 1000° F. to about 1300° F. and an outlet temperature ranging from about 1350° F. to about 1650° F. The feed rate is such that the velocity through the radiant coils 12 ranges from about 200 ft/sec to about 800 ft/sec, based on the total flow of steam and hydrocarbon. Steam is typically employed in amounts to provide a steam to hydrocarbon feed weight ratio ranging from about 0.1 to about 2.0. The residence time of the feed in the radiant section of the cracking coil generally ranges from about 0.1 second to about 1 second, although millisecond processes are also contemplated as within the scope of the present invention.

In order to reduce the production of large amounts of undesirable by-products and in order to prevent severe coking, it is desirable to rapidly cool the effluent product gases issuing from the radiant zone from its exit temperature to a temperature at which the cracking reactions substantially stop. This can be accomplished in a suitable heat exchange apparatus or by direct quenching, wherein the product gases are cooled to a temperature below about 1200° F. to stop the cracking reaction. Further cooling is typically achieved in high level heat recovery as is known to those of ordinary skill in the art. The cooling step is preferably carried out very rapidly after the effluent leaves the radiant section of the furnace, i.e., about 1 to 30 milliseconds. See generally, e.g., Hallee et al., U.S. Pat. No. 3,407,789; Woebecke, U.S. Pat. No. 3,910,347; Woebecke et al., U.S. Pat. No. 5,427,655; Buschmann et al., U.S. Pat. No. 3,392,211; Bhojwani et al., U.S. Pat. No. 4,351,275; Woebecke, U.S. Pat. No. 3,403,722; Buschmann et al., United Kingdom Patent No. 1,095,727 and Buschmann et al., United Kingdom Patent No. 1,091,174.

As shown in FIG. 1, the cracked effluent from the pyrolysis reactor in a line 14 is directed to a quench boiler 16 wherein the effluent is indirectly contacted with boiler feed water in cooling tubes 18. The boiler feed water is supplied via a tank 20 which directs water to the bottom of the quench boiler 16 via a line 22. After traverse of the cooling tubes 18, a steam/water mixture is removed from the quench boiler 16 in a line 24 and directed back to the supply tank 20. The supply tank 20 has high pressure steam removed therefrom in a line 26 and make up boiler feed water added thereto in a line 28. The quenched product gases are removed from the quench boiler 16 via a line 30 for recovery of the dilute olefins and downstream processing into various petrochemicals.

Alternatively, instead of steam cracking other well known cracking processes may be employed to produce olefins including thermal regenerative cracking, fluidized bed cracking, fluid catalytic cracking, deep catalytic cracking, visbreaking, etc.

In thermal regenerative cracking (TRC), inert particulate solids are heated to relatively high temperatures, on the order of from about 1400° F. to about 1600° F., and introduced into a fluidized cracking zone with the hydrocarbon feed. The cracking zone may be upflow (riser), downflow or horizontal in configuration. The hydrocarbon feed is thermally cracked at temperatures ranging from about 1200° F. to about 1600° F. in the cracking zone wherein the heated particulate solids lose heat and are fouled or contaminated with the coke and tars and other heavy cracking products of the hydrocarbon feed. Thereafter, the contaminated solids are separated from the hydrocarbon product gases, stripped and regenerated for re-use in the cracking zone. Regeneration entails burning the contaminants from the particulate solids to heat the solids to a temperature necessary to crack the hydrocarbon feed. See, e.g., Gartside et al., U.S. Pat. No. 4,814,067, Boston, U.S.

Pat. No. 2,906,695; Woebecke et al., U.S. Pat. No. 4,318,800; McKinney et al., U.S. Pat. No. 4,061,562; McKinney et al., U.S. Pat. No. 4,097,363 and Gartside et al., U.S. Pat. No. 4,552,645.

In fluidized catalytic cracking (FCC), the process proceeds similar to that described for thermal regenerative cracking except that the solids are catalytic and the temperatures employed are generally lower, with cracking temperatures on the order of from about 800° F. to about 1300° F. Any of the known catalysts useful in fluidized catalytic cracking may be employed in the practice of the present invention, including but not limited to Y-type zeolites, USY, REY, RE-USY, faujasite and other synthetic and naturally occurring zeolites and mixtures thereof. See, e.g., Gartside et al., U.S. Pat. No. 4,814,067; Haddad et al., U.S. Pat. No. 4,404,095; Cartmell, U.S. Pat. No. 3,785,782; Castagnos, Jr. et al., U.S. Pat. No. 4,419,221; Cormier, Jr. et al., U.S. Pat. No. 4,828,679; Rabo et al., U.S. Pat. No. 3,647,682; Rosinski et al., U.S. Pat. No. 3,758,403; and Dean et al., U.S. Reissue Pat. No. RE 33,728.

Another cracking process contemplated for use in accordance with the present invention is deep catalytic cracking (DCC). In the DCC process a preheated hydrocarbon feedstock is cracked over heated solid acidic catalyst in a reactor at temperatures ranging from about 925° F. to about 1350° F., preferably from about 1025° F. to about 1150° F. The weight hourly space velocity of the charge may range from about 0.2 hr⁻¹ to about 20 hr⁻¹ preferably from about 1 hr⁻¹ to about 10 hr⁻¹. The catalyst-to-oil ratio may vary from about 2 to about 12, preferably from about 5 to about 10. In order to lower the partial pressure of hydrocarbon feed, steam or other gases, such as the dry gas of a catalytic cracking unit, may be added into the reactor during the conversion process.

When steam is used, a weight ratio of steam to hydrocarbon feed is preferably maintained at from about 0.01 to about 0.5:1. The total pressure of the reaction preferably ranges from about 20 psia to about 45 psia, more preferably from about 25 psia to about 35 psia.

After the reaction, the spent catalyst particles may be steam stripped to remove residual hydrocarbons absorbed on the catalyst as is known in the art. The spent catalyst particles with coke deposited thereon are then transferred to a regeneration zone as is also well known to those of ordinary skill in the art.

Regeneration is generally conducted by contacting the catalyst with an oxygen-containing gas at a temperature of from about 1175° F. to about 1350° F. Afterwards the regenerated catalyst is typically recycled to the reaction zone.

Hydrocarbon feedstocks useful in the DCC process may vary in a wide range, and typically are relatively heavy hydrocarbon feedstocks such as those selected from petroleum fractions with different boiling ranges, i.e., naphtha, gas oil, vacuum gas oil, residual oil and mixtures thereof. Crude oil may also be directly used.

Catalysts used in the deep catalytic cracking process step of the present invention are solid, acidic catalysts comprising one or more active components and a matrix material. The active components include amorphous aluminosilicates or zeolites such as pentasil shape selective molecular sieves, faujasite, rare earth cation exchanged faujasite, chemically treated and/or stabilized faujasite and mixtures thereof. The matrix material includes synthetic inorganic oxides and mineral clays. All of these catalysts are commercially available.

Exemplary of the useful catalysts are pentasil shape molecular sieves, rare earth exchanged Y sieve (REY) containing catalysts, pentasil shape molecular sieves supported on kaolinite, amorphous aluminosilicates and mixtures of any of the foregoing.

The use of these catalysts at the specified reaction conditions provides for high yields of gaseous olefins, especially propylene and butylenes. For a more detailed description of the DCC process, its catalyst and variations on the DCC process, see, Li et al., U.S. Pat. No. 4,980,053; Shu et al., U.S. Pat. No. 5,232,675; Zhicheng et al., U.S. Pat. No. 5,380,690; Yongqing et al., U.S. Pat. No. 5,326,455 and Yukang et al., U.S. Pat. No. 5,358,918.

It is further contemplated by the present invention that one or more of the above described cracking processes may be employed, either as separate cracking processes to crack different feedstocks, or in an integrated method such as described in Rubin et al., U.S. Pat. No. 5,523,502.

THE RECOVERY PROCESSES

The gaseous effluent from the cracking reaction is then directed to an olefins purification system for recovery of the dilute olefins. Typically the gaseous effluent is further cooled to remove fuel oil and the bulk of dilution steam, as known to those of ordinary skill in the art, prior to being compressed in a charge gas compressor and then chilled and passed through a series of pressurized fractionators to separate the effluent into component streams, e.g., hydrogen, methane, ethane, propane, ethylene, propylene, mixed C_4 hydrocarbon streams, and C_{5+} material. Conventional fractionation units are described in Roberts, U.S. Pat. No. 2,582,068; Rowles et al., U.S. Pat. Nos. 4,002,042, 4,270,940, 4,519,826 and 4,732,598; and Gazzi, U.S. Pat. No. 4,657,571. See also, Kaiser et al., "Hydrocarbon Processing," Nov. 1988, pp. 57-61.

Especially suitable olefins purification processes for use herein are the cryogenic separation processes described in McCue et al., U.S. Pat. Nos. 4,900,347 and 5,035,732 which employ serially connected dephlegmators upstream of serially connected demethanizers to cryogenically separate the gaseous mixtures into their component parts. Additionally, the process set forth in McCue et al., U.S. Pat. No. 5,414,170 providing for a mixed phase front end acetylene hydrogenation process is also contemplated for use in the present invention.

Thus, in a preferred embodiment, the product gases are compressed in a charge gas compressor, dried, then the acetylene components are hydrogenated in an acetylene hydrogenation reactor, and finally passed into the cryogenic chilling train.

In the preferred cryogenic chilling train the gas charge is passed through serially connected dephlegmators to separate the hydrogen and most of the methane gas from the charge. The remaining charge is then further separated into its component parts by use of serially connected towers comprising one or more of demethanizer(s), deethanizer(s), deethylenizer(s), depropanizer(s), C_2 and C_3 splitters, etc., to produce streams rich in the component parts.

In an especially preferred embodiment the olefins purification process comprises a compression system and a cryogenic separation process for recovering a plurality of component effluent streams comprising one or more of an ethane-rich stream, a propane-rich stream, a dilute ethylene stream, a dilute propylene stream, a mixed C_4 hydrocarbon-rich stream, and a gasoline-rich stream from the mixed olefin-containing effluent, wherein the cryogenic separation

process comprises (A) introducing the mixed olefin containing-effluent into a dephlegmation or separation zone operating at cryogenic temperatures; (B) dephlegmating or separating the mixed olefin-containing effluent into a primary hydrogen and methane-rich gas stream and a primary liquid condensate stream rich in C_{2+} hydrocarbon components and containing a minor amount of methane; (C) separating the primary liquid condensate stream in a moderately low cryogenic temperature primary demethanizer unit into a C_{2+} liquid bottoms stream and an intermediate methane-rich substantially C_3 free overhead vapor stream; (D) separating the intermediate methane-rich overhead vapor stream in an ultra low cryogenic temperature final demethanizer into a dilute ethylene product stream and a final demethanizer ultra-low temperature methane stream; and (E) separating the C_{2+} liquid bottoms stream from the primary demethanizer in at least one downstream fractionator into effluent streams comprising one or more of an ethane-rich stream, a propane-rich stream, a second dilute ethylene stream, a dilute propylene stream, a C_4 hydrocarbon-rich stream and a gasoline-rich stream.

The dilute ethylene and dilute propylene product streams may then be used as the dilute ethylene and dilute propylene feedstocks for the downstream integrated olefin derivative processes, as described more fully hereinbelow. The ethane-rich and propane-rich streams are typically recycled to the cracking reactor.

Alternatively, an olefins purification system as shown in FIG. 2 may be employed. The cracked gas effluent in a line 40 is first compressed in a compressor 42 to produce a compressed gas effluent in a line 44. Acid gas is removed from the stream, the acetylene is then removed via conversion and the stream dried and chilled in system 46 to produce a chilled effluent in a line 48.

The chilled effluent is directed to a demethanizer 50 wherein methane and lighter gases are separated from the heavier components. The methane is removed from the overhead in a line 52. The heavier components are removed from the bottom of the demethanizer 50 in a line 54 and directed to a deethanizer 56 for separation of the ethane and ethylene from the heavier components. Accordingly, a dilute ethylene stream comprising ethane and ethylene is removed from the top of the deethanizer 56 in a line 58. All or a portion of the dilute ethylene stream may then optionally be directed to a C_2 splitter 60, wherein the ethane and ethylene are separated into a second dilute ethylene stream in a line 62 and an ethane-rich stream in a line 64 if higher purity dilute ethylene is desired.

The bottoms from the deethanizer 56 rich in C_3 and heavier components are removed from the deethanizer 56 in a line 66 and directed to a depropanizer 68 for separation of propane and propylene from the heavier components. Accordingly, a dilute propylene stream is removed from the top of the depropanizer 68 in a line 70. All or a portion of the dilute propylene stream may then optionally be directed to a C_3 splitter 72 wherein the propane and propylene are separated into a second dilute propylene stream in a line 74 and a propane-rich stream in a line 76 if higher purity dilute propylene is desired.

The bottoms from the depropanizer 68 rich in C_4 and heavier components are removed from the depropanizer 68 in a line 78 and directed to a debutanizer 80 for separation of the C_4 hydrocarbons from the heavier components. Accordingly, a mixed C_4 hydrocarbon-rich stream is removed from the overhead of the debutanizer 80 in a line 82, and the gasoline and heavier components are removed from the bottom of the debutanizer 80 via a line 84.

The dilute ethylene, dilute propylene and mixed C₄ hydrocarbon-rich streams may then be processed into a variety of petrochemicals in accordance with the practice of the present invention. The ethane- and propane-rich streams in lines 64 and 76, respectively, are then generally recycled back to the cracking reactor.

THE OLEFIN DERIVATIVE PROCESSES

Polyethylene

The dilute ethylene stream obtained from the olefins purification process may be employed as the dilute ethylene feedstock for a polyethylene polymerization process in accordance with the present invention. The dilute ethylene feedstock for use in the polyethylene polymerization process preferably contains at least about 85 weight percent ethylene.

The ethylene is polymerized into polyethylene either by gas phase polymerization methods or by solution polymerization methods. At ethylene feedstock concentrations above about 85% but below about 95%, the solution polymerization method is employed. At concentrations of at least about 95 weight percent, either the gas phase or solution polymerization methods may be employed.

Both the gas phase and solution polymerization methods are well known to those of ordinary skill in the art and any of these known methods may be employed in the practice of the present invention. These processes are typically offered in the industry by companies including but not limited to Union Carbide Corporation, British Petroleum Company, Novacor, DSM et al. Typical operating parameters include pressures ranging from about 300 psig to about 3000 psig and temperatures ranging from about 200° F. to about 600° F. over catalysts such as those of the Ziegler-Natta (Z/N) family and the "single site" metallocene family. See, e.g., Benham et al., U.S. Pat. No. 5,364,915; Chang, U.S. Pat. No. 5,238,892; Cann et al., U.S. Pat. No. 5,102,841; Beran et al., U.S. Pat. No. 4,508,842; Geerts et al., European Patent No. 0 612 753; Wagner et al., European Patent No. 0 012 147; Karol, Frederick J., "The Polyethylene revolution," *Chemtech*, April 1983, pp. 222-28; and "New route to low-density polyethylene," *Chemical Engineering*, Dec. 3, 1979, pp. 80-85. See also, Hatch & Matar, "From Hydrocarbons to Petrochemicals," (hereinafter "HATCH & MATAR") pp. 172-176.

The practice of the present invention also provides significant unexpected advantages for the gas phase process over the current commercially practiced gas phase processes for the production of polyethylene. In the current commercially practiced gas phase processes, nitrogen is employed as the carrier gas to the gas phase polyethylene polymerization reactor. This expedient creates unwanted by-products for recycling to the cracking reactor in the olefins unit. However, with the practice of the present invention employing dilute ethylene feedstock for the gas phase polymerization, the methane or ethane (or other light saturated hydrocarbon) contained in the dilute ethylene feedstock is effective as the carrier gas thus eliminating or significantly reducing the aforementioned recycling problem.

Other Alternative Ethylene Derivative Units

Dilute ethylene can generally be employed in any derivative process which achieves high once through conversion of the ethylene. Processes, including but not limited to processes for the production of ethylene dichloride, alpha olefins, ethyl benzene, styrene and acetaldehyde are con-

templated as within the scope of the present invention. The specifics of these processes are disclosed in the literature and are well known to those of ordinary skill in the art. See, for example, HATCH & MATAR, pp. 97-98; Kurtz et al., U.S. Pat. No. 3,839,475; Severino, U.S. Pat. No. 4,172,099; Geigert et al., U.S. Pat. No. 4,426,449; Leuck et al., U.S. Pat. No. 4,554,392; HATCH & MATAR, pp. 137-138; Smith, Jr. et al., U.S. Pat. No. 5,243,115; Lee et al., U.S. Pat. No. 5,243,116; HATCH & MATAR, pp. 138-140; Hong et al., U.S. Pat. No. 4,263,212; HATCH & MATAR, pp. 99-101; Nishimura et al., U.S. Pat. No. 4,521,631; and Showa Denko, JP 51-146410.

Polypropylene

The dilute propylene stream obtained from the olefins purification process step may be employed as the dilute propylene feedstock for a polypropylene polymerization process in accordance with the present invention. The dilute propylene feedstock for polypropylene polymerization preferably contains at least about 85 weight percent propylene and most preferably at least about 95 weight percent propylene.

The propylene is polymerized into polypropylene homopolymer either by bulk phase polymerization methods or by gas phase polymerization methods. At propylene feedstock concentrations below 95%, the bulk phase polymerization method is employed. At concentrations of at least about 95 weight percent, either the bulk phase or gas phase polymerization methods may be employed.

Both the bulk phase and gas phase polypropylene polymerization methods are well known to those of ordinary skill in the art and any of these known methods may be employed in the practice of the present invention or a combination of both. These processes are offered in the industry by companies including, but not limited to, Union Carbide Corporation, Amoco Oil Company and Himont now (Montell). Typical operating parameters include pressures ranging from about 150 psig to about 1000 psig and temperatures ranging from about 200° F. to about 600° F. over catalysts such as those of the Ziegler-Natta family (Z/N) and the "single site" metallocene family. See, e.g., Schreck et al., U.S. Pat. No. 5,280,074; Ardell et al., U.S. Pat. No. 4,956,426; and Selman et al., U.S. Pat. No. 4,287,091. See also, HATCH & MATAR, pp. 176-79.

Following the polypropylene homopolymer polymerization process, the polypropylene homopolymer is typically copolymerized with ethylene, i.e., 2 to 15 weight percent ethylene, in an impact reactor. In either propylene polymerization process, the impact reactor operates in the gas phase at operating parameters of a pressure ranging from about 150 psig to about 400 psig and a temperature ranging from about 200° F. to about 400° F. over catalysts such as those of the Ziegler-Natta (Z/N) family as well as the "single site" metallocene family.

Other Alternative Propylene Derivative Units Dilute propylene can also be employed in a number of other derivative processes which achieve high once through conversion of the propylene. Potential applications would include, but not be limited to, acrylonitrile, cumene, propylene oxide, isopropanol, acrolein, allyl chloride, etc. The specifics of these processes are disclosed in the literature and are well known to those of ordinary skill in the art. See, for example, HATCH & MATAR, pp. 106-108; Shaw et al., U.S. Pat. No. 5,288,473; Suresh et al., U.S. Pat. No. 5,258,543; Paparizos et al., U.S. Pat. No. 5,235,088; HATCH & MATAR, pp. 108-112; Binns et al., U.S. Pat. No. 3,635,803; Preston et

al., U.S. Pat. No. 5,349,072; Keating et al., U.S. Pat. No. 5,274,138; HATCH & MATAR, pp. 112-115; HATCH & MATAR, pp. 115-117; Etzkorn et al., U.S. Pat. No. 5,198,578; Etzkorn et al., U.S. Pat. No. 5,183,936; Honda et al., U.S. Pat. No. 5,144,090; Caillod et al., U.S. Pat. No. 5,300,707; HATCH & MATAR, pp. 119; Dianis, U.S. Pat. No. 5,262,575; Riegel et al., U.S. Pat. No. 4,558,167; Guesinov et al., U.S. Pat. No. 4,244,892; Bach et al., U.S. Pat. No. 3,855,321; Riegel et al., United Kingdom Patent No. GB 2,039,905; HATCH & MATAR, p. 140; Smith, Jr., U.S. Pat. No. 5,262,576; Lee et al., U.S. Pat. No. 5,243,116; Johnson, U.S. Pat. No. 4,463,207; Cavani et al., U.S. Pat. No. 4,992,608; Ward, U.S. Pat. No. 4,008,290; Johnson, U.S. Pat. No. 4,524,229; Sartorio et al., U.S. Pat. No. 4,343,957; and Smith, Jr. et al., U.S. Pat. No. 5,055,627.

RECYCLING

Essential to the practice of the present invention is the expedient of recycling at least a portion of the by-product stream from the olefin derivative process to the cracking step. The recycling may be accomplished either directly or indirectly. In the embodiment of direct recycle, all or a portion of the by-product stream is directly recycled to the cracking reactor along with the fresh or recycled hydrocarbon feedstock. The direct recycle method is typically employed where there are sufficiently small amounts of contaminants such that the cracking process is not detrimentally affected.

In the embodiment of the indirect recycle, all or a portion of the by-product stream from the particular olefin derivative is first recycled to the olefins purification process step or to a separate clean up system (as known to those of ordinary skill in the art) within the integrated complex for removal of contaminants which are detrimental to the cracking process. Then, the derivative by-products as a portion of the recycle from the olefins purification process, such as in the ethane or propane-rich streams is recycled to the cracking reactor.

In either manner, direct or indirect recycle, at least a portion of the by-product stream from the olefin derivative process is recycled to the cracking reactor in order to form an integrated process and obtain the advantages over the prior art described hereinabove.

C₄ PROCESSING

Where naphtha or other liquid hydrocarbons are employed as the feedstock to the integrated process of the present invention, sufficient amounts of butylenes are produced in the cracking process and separated during the olefins purification step for conversion to C₄ containing petrochemical products and intermediates such as methyl tert butyl ether, isobutylene, butyl rubber and/or methyl methacrylate. In a preferred embodiment, especially useful in the practice of the present invention, the C₄ hydrocarbons are converted to the desired petrochemicals by a process including one or more of the steps of hydroisomerization, skeletal isomerization and, extractive distillation. These processes are discussed more fully hereinbelow.

DEBOTTLENECKING

The present invention also provides a novel means and apparatus for debottlenecking an existing cracking plant. Generally expansion of existing olefins facilities is limited by the amount of available refrigeration or fractionation capability or both. Making at least a portion of the olefins in a dilute form for use as a feedstock in an olefin derivative process would greatly increase the expansion potential of

these facilities. Coupling the incremental olefins product (in dilute form) with a process that can accept dilute olefin feedstock as described in this invention would significantly improve the expansion potential and overall profitability of the complex.

Accordingly, the present invention provides such an expansion means. The present invention contemplates the integrating the existing facility with an olefins purification system to produce dilute olefins and one or more olefins derivative processes to process the incremental dilute olefins. Because the present invention provides for the integration of one or more olefins derivative processes with the olefins facility instead of marketing the dilute olefins to downstream purification processors, the present invention provides the simple debottlenecking means long sought in the art. The present invention thereby further enables the petrochemical producer to realize significant capital and operating cost savings. This concept is especially well suited for adaptation with an Advanced Recovery System (ARS) process or revamp as described in U.S. Pat. Nos. 4,900,347; 5,035,732 and 5,414,170.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following description of preferred embodiments are intended for illustration purposes only and are not to be construed to limit the scope of the claims in any manner whatsoever.

Turning to FIG. 3, there is shown a process for the practice of the present invention to produce polyethylene from an ethane feedstock.

An ethane feedstock in a line 302 is directed to a steam cracker 304 for cracking to ethylene and other by-products. In order to prevent production of large amounts of the by-products and in order to prevent severe coking in the product line 306 from the steam cracker 304, it is desirable to cool rapidly the effluent product gases issuing from the radiant zone from an exit temperature of from about 1500° to about 1650° F. to a temperature at which the cracking reactions substantially stop. This can be accomplished by passing the cracked product to a quench boiler 308 for indirect quenching.

At ethane conversion levels between 55% and 75% in a steam cracker, a typical steam cracking yield of an ethane feedstock issuing from the quench boiler 308 in a line 310 comprises from about 1 to about 5 weight percent H₂, from about 3 to about 10 weight percent CH₄, less than about 1 weight percent C₂H₂, from about 45 to about 55 weight percent C₂H₄, from about 25 to about 45 weight percent C₂H₆, and less than about 10 weight C₃₊ material.

The quenched effluent in a line 310 is further cooled in a quench tower 311 where fuel oil and dilution steam are removed via a line 319. The effluent from the quench tower 311 is then passed to charge gas compressor 312 via a line 313 which operates to increase the pressure of the effluent to from about 350 psig to about 650 psig. Any of the known gas compressors may be employed in the practice of the present invention.

The compressed effluent in a line 314 is then sent to an acid gas removal and dehydration system 315. Acid gas is removed either by contact with a caustic or any of the amines as is known to those skilled in the art or both. Dehydration typically employs a water-absorbing molecular sieve capable of reducing the gas dew point to -200° F. or other means known to those skilled in the art. The effluent from system 315 is then directed via a line 317 to a C₂

hydrogenation reactor(s) 316 wherein the compressed effluent is contacted with a selective hydrogenation catalyst. Any hydrogenation catalyst well known to selectively hydrogenate acetylene can be employed in the hydrogenation reactor of the present invention. The Group VIII metal hydrogenation catalysts are the most commonly used and are presently preferred. The Group VIII metal hydrogenation catalysts are ordinarily associated with a support, such as alumina.

The catalysts are disclosed in the literature. See for example, La Hue et al., U.S. Pat. No. 3,679,762; Cosyns et al., U.S. Pat. No. 4,571,442; Cosyns et al., U.S. Pat. No. 4,347,392; Montgomery, U.S. Pat. No. 4,128,595; Cosyns et al., U.S. Pat. No. 5,059,732 and Liu et al., U.S. Pat. No. 4,762,956.

The hydrogenation conditions employed in the hydrogenation reactor(s) 316 according to the present invention can vary appreciably depending upon the compositional make-up of the stream being treated. Ordinarily, the temperature and pressure will be sufficient to complete the hydrogenation of substantially all of the C_2 acetylenes contained in the stream fed to the hydrogenation reactor 316. Generally, the hydrogenation process will be carried out at a temperature ranging from about 50° F. to about 400° F. and a pressure ranging from about 350 psia to about 600 psia.

Hydrogen is present in amounts at least sufficient to meet the stoichiometric requirements for converting acetylene into ethylene, and, generally, is in the range of about 1 to 100 mols of hydrogen per mol of acetylene. Reaction time can vary from about a few seconds to a few hours, and is generally in the range of from about 1 second to about 6 seconds. The process can be carried out employing the catalyst in a fixed bed(s) or other type of contacting means known to those skilled in the art.

The hydrogenated effluent in a line 318 is then further cooled against propylene refrigerant in a chilling train 320 producing a liquid stream 321 comprised primarily of C_2 and heavier material which is passed to a moderately low temperature demethanizer 328.

The vapor effluent 322 from the chilling train 320 is passed to a first serially connected dephlegmator 324 wherein the gas mixture is chilled to a temperature of from about -85° F. to about -120° F. to produce a vapor stream at least substantially free of C_{3+} hydrocarbons issuing from the top of the first dephlegmator 324 in a line 330. The vapor effluent from the first dephlegmator 324 in the line 330 comprising mostly hydrogen, methane with some C_2 hydrocarbons is then passed to a second serially connected dephlegmator 332 wherein it is chilled to a temperature ranging from about -165° F. to about -235° F. A gaseous stream issuing from the top of the second dephlegmator 332 in a line 334 comprises hydrogen with some methane. The bottoms comprising substantially methane and ethylene are removed in a line 336.

The liquid issuing from the bottom of the first dephlegmator 324 in a line 326 comprised of C_2 and heavier hydrocarbons is low in hydrogen and methane and is passed to a moderately low temperature demethanizer 328 operating at a temperature of from about -20° F. to -80° F. and a pressure of from about 350 psia to about 550 psia to produce a vapor overhead in a line 338 that is substantially C_{3+} free and a bottoms liquid in a line 344 substantially free of methane.

The substantially C_{3+} free vapor in a line 338 and the stream 336 from the bottom of the second dephlegmator 332 are directed to a low temperature demethanizer 340 operating at a temperature ranging from about -100° F. to about

-180° F. The vapor in a line 342 issuing from the top of the low temperature demethanizer 340 is substantially methane. In an especially preferred embodiment, the second demethanizer is also operated at a relatively low pressure, such as below about 175 psia and more preferably about 150 psia.

The liquid from the bottom of the moderately low temperature demethanizer 328 in a line 344 comprising from about 50 to about 65 weight percent ethylene and substantially free of methane is directed to a deethylenizer 346 operating at a pressure ranging from about 65 psia to about 400 psia. The overhead from the deethylenizer 346 in a line 348 comprising dilute ethylene is combined with the bottoms liquid substantially free of methane from the low temperature demethanizer 340 in a line 350 into a line 352 as a dilute ethylene product (at least 95.0 weight percent ethylene for a gas phase polyethylene polymerization reactor or at least about 85 weight percent for a solution phase polyethylene polymerization reactor) for feeding to an ethylene polymerization reactor 354.

As discussed above, the ethylene polymerization reactor 354 may comprise a gas phase reactor or a solution reactor. Where the concentration of the ethylene in the dilute ethylene feedstock 352 to the reactor 354 is below about 95% the solution polymerization technique is preferred in the practice of the present invention.

The product polyethylene is removed from the polymerization reactor 354 in a line 356. The purge from the reactor 354 is removed in a line 358 and is recycled either to the steam cracker via a line 360 in the case of a solution phase reaction, or preferably to the charge gas compressor 312 via a line 362 in the case of a gas phase reaction. Alternatively, return of the purge from the gas phase reactor to the cracking furnace is contemplated within the scope of the present invention with the expedient of employing a separating means (not shown), i.e., membrane technology or dephlegmation, to removed a substantial portion of the N_2 , H_2 and CH_4 contained therein.

The liquid bottoms from the deethylenization tower 346 substantially free of ethylene is removed in a line 364 and passed to a deethanizer tower 366 wherein any remaining C_2 components or if desired C_2 and C_3 components are removed in a line 370 and recycled to the steam cracker 304. The heavier components comprising C_3 and heavier compounds are removed for fuel in a line 368.

Referring now to FIG. 4, a propane, butane, naphtha, gas oil, mixture thereof, or other liquid feedstock in a line 402 is fed to a steam cracker 404 and is cracked to produce minor amounts of hydrogen, acetylene, and fuel oil, and major amounts of methane, ethylene, ethane, propylene, propane and C_4 and heavier components in a line 406. The product stream is quenched in a quench boiler 408 to substantially stop the thermal reactions as described hereinabove. The quenched products in a line 409 are then passed to an oil and water quench system 410 to further cool the gas and remove fuel oil and dilution steam via lines 498 and 499, respectively. The cooled gas then passes to the charged gas compressor 412 via a line 411 which operates to increase the pressure of the effluent to from about 180 psig to about 300 psig.

The compressed products in a line 414 are fed to acid gas removal and dehydration systems (not shown) and then to a depropanizer 416. The depropanizer 416 preferably operates at relatively high pressures ranging from about 150 psia to about 300 psia and is equipped with a reboiler (not shown). The liquid bottoms fraction containing substantially all of the C_4 and heavier components and a large portion of the C_3

components is withdrawn from the high pressure depropanizer 416 through a line 417 and fed to the low pressure depropanizer 415. The low pressure depropanizer 415 separates the C_3 hydrocarbons overhead which feed the C_3 splitter 474 via a line 473 and a C_{4+} bottoms stream 497.

The vapor overhead fraction from the high pressure depropanizer 416 in a line 418 comprising substantially the C_3 and lighter components is withdrawn and directed to an acetylene hydrogenation reactor 420. The acetylene hydrogenation reactor 420 operates as described above to hydrogenate substantially all of the acetylenes in the vapor to ethylene. Additionally some propynes and propadienes are converted to propylene.

The vapor from the hydrogenation reactor 420 in a line 422 is initially chilled in chilling train 424. The condensed effluent from the chilling train 424 is fed via a line 425 to the moderately low temperature demethanizer 440. The vapor from the chilling train 424 in a line 426 is passed to a first serially connected dephlegmator 428 wherein the gas mixture is chilled to a temperature of from about -35° F. to about -120° F. to produce a substantially C_3 free vapor issuing from the top of the first dephlegmator 428 in a line 430 comprising mostly hydrogen, methane and some C_2 hydrocarbons, which is then passed to a second serially connected dephlegmator 432 wherein it is chilled to a temperature ranging from about -165° F. to about -220° F. A gaseous stream issuing from the top of the second dephlegmator 432 in a line 434 comprises hydrogen and some methane.

The liquid issuing from the bottom of the first dephlegmator 428 in a line 436 comprising C_2 and heavier hydrocarbons and low methane and hydrogen is passed to a moderately low temperature demethanizer 440 operating at a temperature ranging from about -20° F. to about -80° F. and a pressure ranging from about 350 psia to about 550 psia to produce a vapor overhead in a line 442 at least substantially free of C_3 and heavier components and a bottoms liquid in a line 448 substantially free of methane.

The substantially free C_{3+} vapor in a line 442 and the bottoms stream 438 from the second dephlegmator 432 are fed to a low temperature demethanizer 444 operating at a temperature ranging from about -100° F. to about -180° F. The vapor in a line 446 issuing from the top of the low temperature demethanizer 444 comprises substantially methane. In an especially preferred embodiment, the second demethanizer is also operated at a relatively low pressure, such as below about 175 psia and more preferably about 150 psia.

The liquid from the bottom of the moderately low temperature demethanizer 440 in a line 448 substantially free of methane is directed to a deethanizer 452 operating at a pressure ranging from about 300 psia to about 450 psia. The overhead from the deethanizer in a line 454 containing ethylene and ethane and the bottoms liquid in a line 450 from the low temperature demethanizer 444 are fed to a C_2 splitter 456 operating at a pressure ranging from about 100 psia to about 400 psia. The overhead from the C_2 splitter 456 comprising dilute ethylene is removed via a line 458 for feeding to an ethylene polymerization reactor 460. Optionally, where the polyethylene polymerization reactor 460 is a solution phase reactor, the C_2 splitter 456 may be eliminated altogether, and the bottoms liquid in a line 450 and the deethanizer overhead in a line 454 may be directly fed to the polyethylene polymerization reactor 460.

The ethylene polymerization reactor 460 may comprise a gas phase reactor or a solution reactor. Where the concen-

tration of the ethylene in the feed to the reactor 460 is below about 95% the solution polymerization technique is preferred.

The product polyethylene is removed from the polymerization reactor 460 in a line 462. The purge from the reactor 460 is removed in a line 464 and is recycled either to the steam cracker via a line 468 in the case of a solution phase reaction, or preferably to the charge gas compressor 412 via a line 466 in the case of a gas phase reaction.

The liquid bottoms from the deethanizer 452 substantially free of C_2 hydrocarbons is removed in a line 470 and passed to a C_3 splitter 474 along with low pressure depropanizer 415 overhead via a line 473 wherein propane is removed in a line 482 and recycled to the steam cracker 404 via a line 486. The lighter fraction from the C_3 splitter 474 comprising dilute propylene, such as in an amount of at least about 85 weight percent, and more preferably about 95 weight percent, is removed via an overhead line 476 and fed to a propylene polymerization reactor 478.

The propylene polymerization reactor 478 typically comprises a polypropylene homopolymerization reactor (not shown) and an impact reactor (not shown) for copolymerizing the propylene homopolymer with minor amounts, i.e. from about 2 to about 15 weight percent ethylene, of ethylene.

Where the dilute propylene feed 476 has a propylene concentration of at least about 95 weight percent, either a bulk phase or gas phase homopolymerization reactor may be employed. The bulk phase polypropylene homopolymer reaction may employ any of the known reaction processes and preferably operates at a pressure ranging from about 400 psig to about 500 psig and a temperature ranging from about 120° F. to about 150° F. over Ziegler-Natta (Z/N) family catalysts or a single site metallocene family catalysts.

Alternatively, where the dilute propylene feed 476 has a propylene concentration of less than about 95 weight percent the gas phase homopolymerization reactor should be employed. The gas phase homopolymerization reactor may operate as is well known to those of ordinary skill in the art, typically at a pressure ranging from about 150 psig to about 400 psig, a temperature ranging from about 200° F. to about 400° F. over a Ziegler-Natta (Z/N) or a "single site" metallocene family catalyst.

The polypropylene homopolymer is then reacted with ethylene, in a concentration of from about 2 to about 15 weight percent, preferably from about 4 to about 10 weight percent, in an impact copolymerization reactor. Again this reaction is well known to those skilled in the art and any of the known operating parameters may be employed in the practice of the present invention. Typically, the impact copolymerization reactor operates at pressures ranging from about 150 psig to about 400 psig and temperatures ranging from about 200° F. to about 400° F. in the presence of a Ziegler-Natta (Z/N) or "single site" metallocene family catalyst.

The product polypropylene is removed from the polypropylene reactor 478 via a line 480. The purge from the polypropylene reactor is removed via a line 484 and is preferably recycled to the C_3 splitter 474.

The heavier components from the low pressure depropanizer 415 in a line 497 may optionally be further processed in a debutanizer (not shown) to remove the C_4 compounds for further processing into methyl tert butyl ether, polyisobutylene, butyl rubber or other petrochemicals.

In a further embodiment of the present invention, referring now to FIG. 5, a gas oil or other heavy feedstock in a

line 502 is fed to a deep catalytic cracker 504 wherein the gas oil feedstock is cracked to produce hydrogen, methane, acetylene, butylenes and other C_4 hydrocarbons, gasoline and heavier components, ethylene, ethane, propylene and propane in a line 506. The products in a line 506 are then cooled in quench system 505 where the dilution steam, heavy fuel oil and other heavy liquid fractions are removed via lines 597, 598 and 599, respectively. The remaining light gases are then passed to charge gas compressor 508 via a line 507 which operates to increase the pressure of the effluent to from about 350 psig to about 520 psig.

The compressed products in a line 510 are then fed to an acid gas removal system and dehydration system (not shown) and then to a depropanizer 512. The depropanizer 512 preferably operates at relatively high pressures ranging from 150 psia to 300 psia and is equipped with a reboiler (not shown).

The liquid bottoms fraction containing substantially all of the C_4 hydrocarbons, gasoline and heavier components is withdrawn from the high pressure depropanizer 512 through a line 514 for further processing such as through a debutanizer to remove the C_4 hydrocarbons and further rectification units to recover gasoline as is known to those skilled in the art. Portions of the heavier components may also be recycled to the deep catalytic cracker for further cracking. The vapor overhead fraction from the depropanizer 512 in a line 516 comprising substantially the C_3 and lighter components is withdrawn and directed to an acetylene hydrogenation reactor 518.

The acetylene hydrogenation reactor 518 operates as described above to hydrogenate substantially all of the acetylenes in the vapor to ethylene. Additionally propynes and propadienes are converted to propylene.

The vapor in a line 522 is then initially chilled and heavy liquids removed in drum 524. The vapor from drum 524 is then passed to a first serially connected dephlegmator 528 wherein the gas mixture is chilled to a temperature of from about -85°F . to about -120°F . to remove substantially all of the hydrogen from the gaseous mixture. The vapor issuing from the top of the first dephlegmator 528 in a line 532 comprising mostly hydrogen, methane and C_2 's is then passed to a second serially connected dephlegmator 534 wherein it is chilled to a temperature of from about -165 to about -200°F . A gaseous stream issuing from the top of the second dephlegmator 534 in a line 535 comprises hydrogen and some methane.

The liquid issuing from the bottom of the first dephlegmator 528 and from the chilling train drum 524 in lines 530 and 525, respectively, comprising C_2 and C_3 hydrocarbons and low methane and hydrogen is passed to a moderately low temperature demethanizer 538 operating at a temperature ranging from about -20°F . to about -80°F . and a pressure ranging from about 350 psia to about 550 psia to produce a vapor overhead in a line 540 at least substantially free of C_{3+} hydrocarbons and a bottoms liquid in a line 546 substantially free of methane.

The substantially C_{3+} free vapor in a line 540 and the bottoms from the second dephlegmator 534 in a line 536 are fed to a low temperature demethanizer 542 operating at a temperature ranging from about -100°F . to about -180°F . The vapor in a line 544 issuing from the top of the low temperature demethanizer 542 comprises substantially pure methane. In an especially preferred embodiment, the second demethanizer is also operated at a relatively low pressure, such as below about 175 psia and more preferably about 150 psia.

The liquid from the bottom of the moderately low temperature demethanizer 538 in a line 546 substantially free of methane is directed to a deethanizer 548 operating at a pressure ranging from about 300 psia to about 450 psia. The overhead from the deethanizer in a line 550 containing ethylene and ethane is combined with the bottoms liquid in a line 552 from the low temperature demethanizer 542 to a C_2 splitter 554 operating at a pressure ranging from about 100 psia to about 400 psia. The overhead from the C_2 splitter 554 comprises a dilute ethylene feedstock in a line 556 for feeding to an ethylene derivative reactor 558.

The ethylene derivative reactor 558 may comprise a reactor for producing any ethylene derivative petrochemical in a line 560 as described hereinabove. For example the ethylene derivative reactor may comprise a reactor for the production of polyethylene (see FIG. 4), ethylene dichloride, vinyl chloride monomer, ethyl benzene, styrene, acetaldehyde, vinyl acetate, acrylic acid and propionaldehyde. Optionally, the dilute ethylene feedstock in a line 556 may be in direct communication with one or more ethylene derivative reactors 558 in order to produce more than one ethylene derivative petrochemical product.

The purge from the ethylene derivative reactor 558 is removed in a line 562 and is recycled to a steam cracking reactor 588 via a line 585 or to the charge gas compressor 508 via a line 582 dependent upon the particular ethylene derivative reactor employed and the reaction by-products contained in the purge stream 562.

The liquid bottoms from the C_2 splitter 554 in a line 570 comprising substantially ethane is recycled to a steam cracking reactor 588 via a recycle line 580. The effluent from the steam cracking reactor can be fed to the quench system 505 via a line 590.

The liquid bottoms from the deethanizer 548 substantially free of C_2 hydrocarbons are removed in a line 564 and passed to a C_3 splitter 566 wherein propane is removed in a line 576 and recycled to the steam cracking reactor 588 via a recycle line 580. The lighter fraction from the C_3 splitter 566 comprising a dilute propylene feedstock is removed via an overhead line 568 and fed to a propylene derivative reactor 572.

The propylene derivative reactor 572 may comprise a reactor for producing a propylene derivative petrochemical in a line 574 as described hereinabove. For example the propylene derivative reactor may comprise a reactor for the production of polypropylene (see FIG. 4), acrylonitrile, propylene oxide, isopropanol, acrolein, butyraldehyde, allyl chloride, isopropyl acrylate, isopropyl acetate, allyl acetate and cumene. Optionally, the dilute propylene feedstock in a line 568 may be in direct communication with one or more propylene derivative reactors 572 in order to produce more than one propylene derivative petrochemical product.

The purge from the propylene derivative reactor 572 is removed in a line 578 and is recycled either via a line 582 to the charge gas compressor 508 or to the steam cracking reactor 588 via a line 585.

In many of the process sequences of the present invention, substantial amounts of C_4 hydrocarbons are also produced. The majority of the C_4 compounds are removed in the depropanizer along with other heavier hydrocarbons. The C_4 hydrocarbons can be recovered from the depropanizer bottoms in any conventional manner, typically from the overhead of a debutanizer tower as is well known to those skilled in the art. The C_4 hydrocarbons recovered from the debutanizer typically comprises all of the C_4 isomers, n-butane, isobutane, 1-butene, cis-2-butene, trans-2-butene, ethyl

acetylene, vinyl acetylene, 1,3-butadiene, 1,2-butadiene, and isobutylene, as well as minor amounts of C₃ and C₅ hydrocarbons.

The present invention also contemplates the further processing of the mixed C₄ compounds into petrochemical products. In an especially preferred embodiment, the mixed C₄ compounds may be further processed by steps including hydrogenation, extractive distillation and skeletal isomerization in combination with a methyl tert butyl ether synthesis step, a polyisobutylene polymerization step, or a butyl rubber producing step. See generally, Rubin et al., U.S. Pat. No. 5,382,707.

Referring to FIG. 6A, in this manner the mixture of C₄ compounds from the overhead of a debutanizer (not shown) in a line 602 is first fed to a hydroisomerization unit 604. Alternatively, the hydroisomerization unit can comprise any butadiene hydrogenation unit known to those of ordinary skill in the art which converts butadiene to butenes, such as a selective hydrogenation unit. Preferred is a hydroisomerization unit which in addition to converting butadiene to butenes also isomerizes at least a portion of the butene-1 component to the butene-2 components. The hydroisomerization unit 604 is fed with hydrogen by a line 606. The C₄ compounds in line 602 are typically a mixture of all of the C₄ isomers (acetylenes, dienes, olefins and paraffins), and small quantities of C₃ and C₅ hydrocarbons.

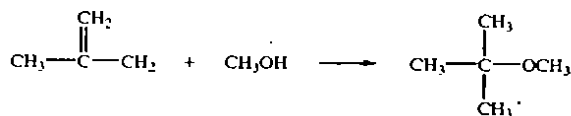
In the hydroisomerization unit 604, most of the acetylenes and dienes are catalytically converted to butenes and most of the 1-butene is catalytically converted to the 2-butenes, i.e., cis-2-butene and trans-2-butene, in the presence of hydrogen.

Hydroisomerization is a process which is well known to those of ordinary skill in the art and any particular hydroisomerization process may be employed. Typically, the hydroisomerization step is carried out in the presence of a catalyst comprising at least one hydrogenating metal and a moderately acidic carrier. A preferred catalyst can comprise a Group VIII metal, such as platinum, palladium and/or nickel, on a microporous crystalline silicate, such as a mordenite with a surface area of from 100 to 800 m²/g.

Suitable hydroisomerization conditions may include a temperature ranging from about 100° F. to about 750° F., a pressure ranging from about 1 bar to about 100 bar and a space velocity ranging from about 0.5 to about 20 kg hydrocarbon feed/kg catalyst hour. Preferred conditions are a mixed phase process at a temperature ranging from about 100° F. to about 1400° F., a pressure ranging from about 145 psia to about 580 psia and a space velocity ranging from about 1 to about 15 lb feed/lb catalyst hour. See, e.g., Grandvallet et al., U.S. Pat. No. 5,023,389.

The effluent stream 608 from the hydroisomerization unit 604 substantially comprising isobutylene, cis-2-butene, trans-2-butene, isobutane, n-butane, unconverted 1-butene and C₃ and C₅ components is then directed to an MTBE synthesis unit 610.

The synthesis of methyl tertiary butyl ether (MTBE) from isobutylene and methanol, supplied via a line 612, is a process which is well known to those of ordinary skill in the art and any particular synthesis process may be employed in the practice of the present invention. The general reaction scheme is set forth below.



Typically, the synthesis step is carried out at mild temperatures, in the liquid phase, in the presence of a sulfonated polystyrene resin. See, Hatch and Matar, "From Hydrocarbons to Petrochemicals," Gulf Publishing Co., 1981, pp. 128-29.

The reaction usually employs an acid type ion exchange resin, such as a high molecular weight carbonaceous material containing sulfonate groups —SO₃H. Sulfonated resins of various types are available such as the sulfonated coals, phenol formaldehyde resins reacted with sulfuric acid, sulfonated resinous polymers of cumarone-indene with cyclopentadiene, strongly acidic cationic exchange resins such as sulfonated divinylbenzene polystyrene copolymers, and others, under various commercial names. The catalyst can be employed in a particulate solid form with sizes ranging from about 10 to about 50 U.S. sieve employing from about 0.5 to about 50 percent dry weight of catalyst relative to liquid content of the reactor. A fixed bed of particulate solid ion exchange resin catalyst, e.g., such as Amberlyst 15 from Rohm & Haas Co., or Dowex M31 or M32 from Dow Chemical Co., may be employed. The same catalyst may also be employed in tubular reactors or supported in bags or other devices which permit catalytic distillation to be practiced.

The reaction of the isobutylene with methanol can be carried out under any suitable reaction conditions. The mole ratio of methanol to isobutylene generally is in the range of from about 0.05 to about 10, preferably from about 0.1 to about 5, and still more usually about 1 to 1, at a temperature in the range of from about 100° F. to about 250° F., employing a pressure sufficient to maintain the reactants substantially in the liquid state, typically in the range of from about 80 psig to about 400 psig. The liquid hourly space velocity, volume of feed per volume of catalyst per hour, is preferably from about 0.5 to about 10.

More specific processes of MTBE synthesis are described in Childs, U.S. Pat. No. 4,440,963, Wentzheimer et al., U.S. Pat. No. 4,198,530, Masilamani et al., U.S. Pat. No. 4,792,639, Smith, Jr. et al., U.S. Pat. No. 4,950,803, Lee, U.S. Pat. No. 3,946,450 and Leum et al., U.S. Pat. No. 2,480,940.

The resultant product MTBE, along with the C₃ and heavier components, are withdrawn from the MTBE unit through a line 614 by fractionation, as is well known to those skilled in the art.

The remaining components of the MTBE synthesis feed, the cis-2-butene, trans-2-butene, isobutane, n-butane, unconverted 1-butene and C₃ components are then directed through a line 616 to a paraffin/olefin separation unit. The paraffin/olefin separation can be carried out by a wide variety of separation processes known to those skilled in the art, including, but not limited to, extractive distillation and/or molecular sieve separation. Particularly suitable for use in the practice of the present invention is an extractive distillation unit 618 to remove paraffins and C₃ components.

Extractive distillation is a well known process, and has been employed in the past to separate butadiene from C₄ feedstreams, as well as other separations such as separating MTBE from cyclopentane. See, e.g., Berg, U.S. Pat. No. 4,661,209. Extractive distillation generally refers to processes where a higher boiling selective solvent is added to the separation feed mixture to alter the relative volatilities of

the components in the feed mixture. See, generally, Perry and Chilton, "Chemical Engineers' Handbook," McGraw Hill, 5th ed., 1973, pp. 13-43 to 13-48.

A wide variety of solvents may be employed in the extractive distillation step of the present invention, including, but not limited to, tetra-hydrofuran, diethyl ketone, diethyl carbonate, methyl ethyl ketone, pentanedione, cyclopentanone, acetone, butyronitrile, acetyl piperidine, acetophenone, pyridine, diethyl oxalate, propionitrile, dimethyl acetamide, n-methyl pyrrolidone, acetonyl acetone, tetrahydrofurfuryl alcohol, dimethyl sulfolane, dimethyl cyanamide, methyl carbitol, dimethyl formamide, methyl cellosolve, furfural, acetonitrile, ethylene chlorhydrin, gamma-butyrolactone, methanol, beta-chloropropionitrile, pyrrolidone, propylene carbonate, nitromethane, ethylene diamine and mixtures of any of the foregoing. Especially preferred is acetonitrile. Further, these solvents may also be employed with a water diluent.

The solvent, in a line 620, is introduced near the top of the extractive distillation column or tower (not shown), usually a few plates from the top, and flows downward until it reaches the stillpot or reboiler. Its presence on each plate of the distillation column alters the relative volatility of the close boiling compounds to make the separation on each plate greater than would be possible without the solvent and thus requires either fewer plates to effect the same degree of separation, makes possible a greater degree of separation with the same number of plates, or makes possible separations which could not be achieved with conventional distillation.

The lighter compounds, C₃ and lighter boiling hydrocarbons, as well as the C₄ paraffins, isobutane and n-butane, are thereby removed from the top of the extractive distillation unit through a line 622. The bottoms from the extractive distillation are directed to a stripper (not shown) wherein the cis-2-butene, trans-2-butene and unconverted 1-butene are recovered from the overhead of the stripper, withdrawn through a line 624 and fed to the skeletal isomerization unit 626.

Skeletal isomerization is a process by which the normal butenes, cis-2-butene, trans-2-butene and 1-butene, are converted to isobutylene. Skeletal isomerization of olefins is known to be conducted by contacting unbranched olefins with acidic catalysts at pressures near atmospheric and temperatures ranging from about 600° F. to about 1100° F. The isomerization of olefins is well known to be limited by the thermodynamic equilibrium of reacting species. Useful catalysts and processes are described in the patent literature, inter alia, Smith, Jr., U.S. Pat. No. 4,482,775, Sun, U.S. Pat. No. 4,778,943, Schwerdtel et al., U.S. Pat. No. 4,548,913, Del Rossi et al., U.S. Pat. No. 5,107,047 and Chih-Cheng, et al., EP 0 508 008.

Accordingly, in the skeletal isomerization reactor 626 a portion of the normal butenes are converted to isobutylene with a small amount of light and heavy hydrocarbon by-products (gasoline) and the effluent from the skeletal isomerization unit is recycled in a line 628 to the hydroisomerization reactor 604 wherein the butene-1 component can be further isomerized to butene-2 components. Alternatively, the skeletal isomerization effluent 628 can be directly recycled to the MTBE synthesis unit for conversion of the isobutylene to MTBE product. The heavy hydrocarbon by-products (gasoline) from the skeletal isomerization unit are withdrawn through a line 630.

When a relatively minor quantity of heavy hydrocarbon (gasoline) by-product is produced in the skeletal isomerization unit the heavy hydrocarbon takeoff stream 630 can be

omitted and the heavy hydrocarbon can be recycled with the rest of the effluent from the skeletal isomerization unit in a stream 628 to the hydroisomerization or MTBE synthesis unit where it can be purged or removed from the process with the methyl tertiary butyl ether product stream 614.

Alternatively, the C₄ processing step of FIG. 6A can be operated to produce polyisobutylene, butyl rubber or methyl methacrylate or any other petrochemicals employing isobutylene as a reactant. These are exemplified in FIGS. 6B and 6C wherein like reference numerals with a ' or a " thereafter employed to represent similar process steps as discussed hereinabove with regard to FIG. 6A.

In the case of polyisobutylene, referring to FIG. 6B, a polymerization reactor 610' is employed in place of the methyl tert butyl reactor 610. The polymerization reaction process may be any known to those of ordinary skill in the art to effect polymerization of isobutylene to polyisobutylene, such as the Finna process. Typical operating parameters are temperatures of from about 35° F. to about 100° F. and a pressure ranging from about 10 psig to about 150 psig. See, e.g., Eaton, U.S. Pat. No. 5,068,490; Chen et al., U.S. Pat. No. 4,558,170; McCaulay, U.S. Pat. No. 4,288,649; and Johnson et al., United Kingdom Patent No. GB 1,378,330.

Referring to FIG. 6C in the case of butyl rubber, the hydroisomerized C₄ stream in a line 608" is fed to a methyl tert butyl ether reactor 610" which is fed with methanol via a line 612". Optionally, a solvent extractor for selectively removing isobutylene may be employed as separator unit 610". The product methyl tert butyl ether in a line 614" is then fed to a decomposition reactor 632" wherein the methyl tertiary butyl ether is decomposed into methanol and isobutylene. The methanol is removed in a line 642" and may be recycled to the methyl tertiary butyl ether reactor via a line 612".

The isobutylene in a line 634" is then fed to butyl rubber reactor 636" wherein it is contacted with isoprene via a line 638". Butyl rubber is produced by the cationic copolymerization of isobutylene in amounts ranging from about 95 to about 99, preferably about 97.5 weight percent and isoprene in amounts ranging from about 5 to about 1, preferably about 2.5 weight percent. The polymerization is typically carried out at low temperatures, on the order of from about -30° F. to about -100° F. in the presence of a Lewis acid catalyst such as AlCl₃ and a very small amount of water as a cocatalyst. See generally, Hatch and Matar, "From Hydrocarbons to Petrochemicals," 1981, pp. 212-213. The butyl rubber product is then removed in a product line 640".

Alternatively, the isobutylene in line 634" may be reacted to produce methyl methacrylate or other petrochemicals employing reactor 636". In the case of methyl methacrylate, the isobutylene may be catalytically oxidized over a complex molybdenum oxide catalyst at temperatures ranging from about 660° F. to about 850° F. and from about 15 psig to about 25 psig to produce methacrolein. The methacrolein is then oxidized over a molybdenum catalyst at temperatures of from about 480° F. to about 670° F. and from about 15 psig to about 25 psig to produce methacrylic acid.

The methacrylic acid is then esterified with methanol to produce methyl methacrylate at conditions well known to those skilled in the art. See, Kida et al., U.S. Pat. No. 4,343,959. See also, Hatch and Matar, "From Hydrocarbons to Petrochemicals", 1981, pp. 127-130; and Shimizu et al., "Methyl methacrylate from isobutylene via vapor-phase catalytic oxidation," Energy Proj., 8(3), 1988, pp. 169-172.

In another embodiment the present invention also provides for the debottlenecking of an existing olefins facility.

Olefins units are frequently limited in capacity either by the availability of refrigeration or limitations in the ethylene and/or propylene fractionation equipment or both. This invention, coupled with the expansion techniques of the Advanced Recovery System (ARS) (U.S. Pat. Nos. 4,900, 347; 5,035,732 and 5,414,170) can significantly increase the economic expandability of existing olefins facilities.

In FIG. 7, the solid lines could represent a process sequence for the production of gas phase polyethylene and high pressure low density polyethylene with polymer grade ethylene. The process represented by the solid lines of FIG. 7 does not exist in the prior art in one facility and is not integrated. The cracking, purification and polymerization processes conventionally take place in separate facilities. The flow chart is merely provided to simplify the explanation of the means of debottlenecking provided by the present invention.

The dotted lines represent an example of a means for debottlenecking such a process sequence in accordance with the present invention.

In the typical process sequence, an ethane feedstock in a line 702 is steam cracked in a cracking furnace 704 to produce ethylene and other hydrocarbon byproducts. The effluent from the cracking furnace 704 in a line 706 is then fed to a purification system 708 wherein the effluent is subjected to various rectification steps to produce a polymer grade ethylene product at about 99.9% purity in a line 710.

The highly pure ethylene in a line 710 is then fed to a facility for polymerization to polyethylene by solution or gas phase polymerization in a reactor 714 and high pressure low density polyethylene in a reactor 720 via lines 712 and 716 respectively, as is well known to those skilled in the art.

This process sequence can be conveniently revamped to provide a debottlenecked integrated process by adding additional furnace capacity 704' and by modifying the purification system 708 to produce one ethylene product at the current purity and one as a dilute stream in a line 726. The dilute ethylene feedstock can then be employed in a variety of ethylene derivative processes such as feeding dilute ethylene in a line 728 to a solution phase polyethylene reactor 730 to produce polyethylene in a line 732, and feeding a dilute ethylene feedstock via a line 734 to a reactor 740 to produce ethyl benzene or other ethylene derivative in a line 742.

Still further, a portion of the highly pure ethylene in a line 710 may optionally be directed to the polyethylene polymerization reactor 730, ethylene derivative reactor 740 or both via a line 738. The purges from the downstream derivative reactors 730 and 740 in lines 746 and 744, respectively, can then be recycled to the cracking reactor 704 via a line 748 to provide the integrated process of the present invention.

Many variations of the present invention will suggest themselves to those skilled in the art in light of the above-detailed description. All such obvious modifications are within the full intended scope of the appended claims.

All of the above-reference patents, patent applications and publications are hereby incorporated by reference in their entirety.

We claim:

1. An integrated process for the production of an olefin derivative product from a hydrocarbon feedstock in a grass-roots plant or expansion of an existing facility comprising the steps of:

- (a) cracking a hydrocarbon feedstock to produce a cracked product comprising a cracked gas comprising ethylene, or propylene or both and optionally one or

more of ethane, acetylenes, methane, hydrogen, propane, and C_4 and heavier components;

- (b) recovering a dilute ethylene stream, a dilute propylene stream or both from said cracked gas;

- (c) processing either

- (i) said dilute ethylene stream to produce at least one ethylene derivative product and byproduct, or
- (ii) said dilute propylene stream to produce at least one propylene derivative product and byproduct, or
- (iii) both; and

- (d) recycling the by-product streams from said processing step (c) to the cracking step (a).

2. A process as defined in claim 1 wherein said hydrocarbon feedstock is selected from the group consisting of ethane, propane, butane, naphtha, gas condensates, raffinate, atmospheric gas oil, vacuum gas oil, natural gas liquids, distillate, crude oil, crude resid and mixtures of any of the foregoing.

3. A process as defined in claim 1 wherein said cracking step comprises a steam cracking process comprising the steps of:

- (i) preheating the feedstock to a temperature of from about 1000° F. to about 1300° F. in a convection zone of a thermal cracking furnace;

- (ii) mixing steam with said hydrocarbon feedstock in said convection zone to produce a vapor feedstock/steam mixture;

- (iii) thermally cracking said feedstock by passing the feedstock/steam mixture through at least one process coil in a radiant zone of said thermal cracking furnace, whereby said feedstock/steam mixture is heated to an outlet temperature of from about 1350° F. to about 1650° F. and cracked in said radiant zone to produce a cracked product gas stream comprising one or more of ethylene, ethane, acetylenes, methane, hydrogen, propane, propylene and C_4 and heavier components.

4. A process as defined in claim 3 which further comprises quenching the cracked product stream from said steam cracking step to produce a quenched product stream.

5. A process as defined in claim 1 wherein said cracking step comprises a non-catalytic thermal regenerative cracking process comprising the steps of:

- (a) contacting said feedstock with hot non-catalytic particulate solids;

- (b) thermally cracking said hydrocarbon feedstock at a temperature ranging from about 1200° F. to about 1600° F. with heat provided by said hot non-catalytic particulate solids to produce a cracked product gas comprising one or more of ethylene, ethane, acetylenes, methane, hydrogen, propane, propylene and C_4 and heavier components and coked solid particulates;

- (c) separating said cracked product gas from said coked solid particulates;

- (d) regenerating said coked particulate solids by burning off the coke therefrom and thereby heating the particulate solids; and

- (e) recycling said heated regenerated particulate solids to the contacting step (a).

6. A process as defined in claim 1 wherein said cracking step comprises a fluid catalytic cracking process comprising the steps of:

- (a) contacting said feedstock with catalytic particles;

- (b) catalytically cracking said hydrocarbon feedstock at a temperature ranging from about 800° F. to about 1300° F. with heat provided by said hot catalytic particles to

produce a cracked product gas comprising one or more of ethylene, ethane, acetylenes, methane, hydrogen, propane, propylene and C_4 and heavier components and coked catalytic particles;

- (c) separating said cracked product gas from said coked catalytic particles;
- (d) regenerating said coked catalytic particles by burning off the coke therefrom and thereby heating the catalytic particles; and
- (e) recycling said heated regenerated catalytic particles to the contacting step (a).

7. A process as defined in claim 1 wherein said cracking step comprises a deep catalytic cracking process comprising the steps of:

- (a) contacting a hydrocarbon feedstock with a solid acidic catalyst selected from the group consisting of pentasil shape selective molecular sieves, ultrastable hydrogen Y sieves and a mixture of ultrastable hydrogen Y sieves and pentasil shape selective molecular sieves in a fluidized or moving bed or dense phase transfer line reactor;
- (b) cracking said hydrocarbon feedstock in the presence of steam at a temperature ranging from about 925° F. to about 1350° F. and a pressure ranging from about 20 psia to about 45 psia at a weight hourly space velocity ranging from about 0.2 to about 20 hr^{-1} , a catalyst-to-oil ratio of from about 2 to about 12 and a steam-to-feedstock ratio of from about 0.01 to about 0.5:1 by weight to produce a cracked gas and coked catalytic particles;
- (c) separating said cracked product gas from said coked catalytic particles;
- (d) regenerating said coked catalytic particles by burning off the coke therefrom and thereby heating the catalytic particles; and
- (e) recycling said heated catalytic particles to the contacting step (a).

8. A process as defined in claim 1 wherein said cracked gas comprises a mixed olefin stream and said recovery step (b) comprises:

- (I) compressing said mixed olefin stream to a pressure of from about 350 psig to about 650 psig to produce a compressed mixed olefin stream;
- (II) removing acid gas from said compressed mixed olefin stream with a caustic or amine acid gas removal system;
- (III) drying said acid gas removed mixed olefin stream over water-absorbing molecular sieve to a dew point of about -200° F. to produce a dried mixed olefin stream;
- (IV) selectively hydrogenating the acetylenes in said dried mixed olefin stream to produce a hydrogenated mixed olefin stream;
- (V) dephlegmating said dried mixed olefin stream to produce a first vapor stream substantially free of C_{3+} hydrocarbons and a first liquid stream rich in C_{2+} hydrocarbons;
- (VI) further dephlegmating said first vapor stream to produce a second vapor stream comprising hydrogen and methane, and a second liquid stream rich in methane and ethylene;
- (VII) separating said first liquid stream in a moderately low temperature demethanizer to produce a third vapor stream substantially free of C_{3+} hydrocarbons and a third liquid stream rich in C_{2+} hydrocarbons;

(VIII) passing said second liquid stream and said third vapor stream to a low temperature demethanizer to produce a fourth vapor stream comprising substantially methane and a fourth liquid stream comprising dilute ethylene;

(IX) separating said third liquid stream in a deethylenization tower to produce an overhead stream comprising dilute ethylene and a fifth liquid stream substantially free of ethylene;

(X) recovering said fourth liquid stream and said deethylenization overhead stream as said dilute ethylene stream;

(XI) separating said fifth liquid stream in a deethanizer tower to produce a sixth liquid stream comprising C_3 and heavier components and a fifth gaseous stream rich in ethane; and

(XII) recycling said fifth gaseous stream to said cracking step.

9. A process as defined in claim 1 wherein said cracked gas comprises a mixed olefin stream and said recovery step (b) comprises the steps of:

- (i) compressing said mixed olefin stream to a pressure of from about 350 psig to about 520 psig to produce a compressed mixed olefin stream;
- (ii) removing acid gas from said compressed mixed olefin stream with a caustic or amine acid gas removal system;
- (iii) drying said acid gas removed mixed olefin stream over water-absorbing molecular sieve to a dew point of about -200° F. to produce a dried mixed olefin stream;
- (iv) selectively hydrogenating the acetylenes in said dried mixed olefin stream to produce a hydrogenated mixed olefin stream;
- (v) separating said hydrogenated mixed olefin-containing effluent in a demethanizer to produce a demethanizer overhead vapor effluent rich in methane and lighter gases and a demethanizer bottoms effluent rich in ethylene and heavier components;
- (vi) separating the demethanizer bottoms in a deethanizer to produce a deethanizer overhead vapor effluent rich in ethane and ethylene and a deethanizer bottoms effluent rich in C_{3+} hydrocarbons;
- (vii) separating the deethanizer overhead vapor effluent in a C_2 splitter to produce a C_2 splitter overhead effluent comprising dilute ethylene and a C_2 splitter bottoms effluent rich in ethane;
- (viii) separating the deethanizer bottoms effluent in a depropanizer to produce a depropanizer overhead vapor effluent rich in propane and propylene and a depropanizer bottoms effluent rich in C_{4+} hydrocarbons;
- (ix) separating said depropanizer overhead vapor effluent in a C_3 splitter to produce a C_3 splitter overhead effluent comprising dilute propylene and a C_3 splitter bottoms effluent rich in propane; and optionally;
- (x) further separating said depropanizer bottoms effluent in at least one downstream fractionator into effluent streams comprising one or more of a C_4 hydrocarbon-rich stream and a gasoline-rich stream.

10. A process as defined in claim 1 wherein said cracked gas comprises a mixed olefin stream and said recovery step (b) comprises the steps of:

- (i) compressing said mixed olefin stream to a pressure of from about 350 psig to about 520 psig to produce a compressed mixed olefin stream;

- (ii) removing acid gas from said compressed mixed olefin stream with a caustic or amine acid gas removal system;
 - (iii) drying said acid gas removed mixed olefin stream over water-absorbing molecular sieve to a dew point of about -200° F. to produce a dried mixed olefin stream;
 - (iv) separating said dried mixed olefin stream in a demethanizer to produce a demethanizer overhead vapor effluent rich in methane and lighter gases and a demethanizer bottoms effluent rich in ethylene and heavier components;
 - (v) separating the demethanizer bottoms in a deethanizer to produce a deethanizer overhead vapor effluent rich in ethane and ethylene and a deethanizer effluent bottoms rich in C_{3+} hydrocarbons;
 - (vi) selectively hydrogenating the acetylenes in said deethanizer overhead vapor to produce a hydrogenated deethanizer overhead vapor;
 - (vii) separating the hydrogenated deethanizer overhead vapor effluent in a C_2 splitter to produce a C_2 splitter overhead effluent comprising dilute ethylene and a C_2 splitter bottoms effluent rich in ethane;
 - (viii) separating the deethanizer bottoms effluent in a depropanizer to produce a depropanizer overhead vapor effluent rich in propane and propylene and a depropanizer bottoms effluent rich in C_{4+} hydrocarbons;
 - (ix) separating said depropanizer overhead vapor effluent in a C_3 splitter to produce a C_3 splitter overhead effluent comprising dilute propylene and a C_3 splitter bottoms effluent rich in propane; and optionally;
 - (x) further separating said depropanizer bottoms effluent in at least one downstream fractionator into effluent streams comprising one or more of a C_4 hydrocarbon-rich stream and a gasoline-rich stream.
11. A process for the expansion of an existing process having a cracking capacity wherein said existing process produces polymer grade ethylene, polymer grade propylene or both, said expansion comprising modifying said existing process to a process as defined in claim 1 whereby the overall capacity of said existing process is increased.
12. A process as defined in claim 11 wherein said existing process comprises:
- (i) cracking a hydrocarbon feedstock in a cracking reactor having a cracking capacity to produce a cracked product;
 - (ii) compressing said cracked product to produce a compressed gas stream;
 - (iii) removing acid gas from said compressed gas stream to produce an acid gas removed stream;
 - (iv) drying said acid gas removed stream to produce a dried gas stream;
 - (v) selectively hydrogenating the acetylenes in said dried gas stream to produce a hydrogenated gas stream;
 - (vi) separating said hydrogenated gas stream in a demethanizer to produce a demethanizer overhead vapor effluent rich in methane and lighter gases and a demethanizer bottoms effluent rich in ethylene and heavier components;
 - (vii) separating said demethanizer bottoms in a deethanizer to produce a deethanizer overhead vapor effluent rich in ethane and ethylene and a deethanizer bottoms rich in C_{3+} hydrocarbons;
 - (viii) separating said deethanizer overhead effluent in a C_2 splitter to produce a C_2 splitter overhead effluent com-

- prising polymer grade ethylene and a C_2 splitter bottoms effluent rich in ethane; and optionally
 - (ix) separating the deethanizer bottoms effluent in a depropanizer to produce a depropanizer overhead effluent rich in propane and propylene and a depropanizer bottoms effluent rich in C_{4+} hydrocarbons; and optionally
 - (x) separating said depropanizer overhead vapor effluent in a C_3 splitter to produce a C_3 splitter overhead effluent comprising polymer grade propylene and a C_3 splitter bottoms rich in propane;
- wherein said expansion comprises:
- (I) increasing the capacity of said cracking step (i);
 - (II) modifying said step (vi) to comprise the following steps:
 - (a) dephlegmating or separating at least a portion of said hydrogenated gas to produce a primary methane-rich gas stream, a primary ethylene-rich liquid stream and a primary liquid condensate stream rich in C_{2+} hydrocarbon components;
 - (b) separating said primary liquid condensate stream in a moderately low cryogenic temperature primary demethanizer into a C_{2+} liquid bottoms stream and an intermediate methane-rich overhead vapor stream;
 - (c) separating the intermediate methane-rich overhead vapor stream and the primary ethylene rich liquid stream in an ultra low cryogenic temperature final demethanizer into a second dilute ethylene product stream and a final demethanizer methane vapor stream;
 - (d) separating said C_{2+} liquid bottoms stream in at least one downstream fractionator into effluent streams comprising one or more of a dilute ethylene stream, a dilute propylene stream, an ethane-rich stream, a propane-rich stream, a C_4 hydrocarbon rich stream and a gasoline rich stream;
 - (III) processing either or both the dilute ethylene stream and dilute propylene stream to produce at least one ethylene derivative product and/or at least one propylene derivative product and by-products thereof; and
 - (IV) recycling said by-products to said cracking step.
13. A process as defined in claim 1 wherein said processing step (c) comprises converting said dilute ethylene stream to polyethylene by a process comprising the steps of:
- (1) polymerizing said ethylene to produce polyethylene and polymerization reaction by-products wherein said polymerization is carried out either
 - (i) by a gas phase polymerization reaction wherein said dilute ethylene stream comprises at least about 95 weight percent ethylene, or
 - (ii) by a solution phase polymerization wherein said dilute ethylene stream comprises at least about 85 weight percent ethylene; and
 - (2) recovering said polyethylene product;
- and wherein said recycling step (d) comprises recycling said polymerization by-products to said cracking step (a).
14. A process as defined in claim 13 wherein the polymerization by-products from said gas phase polymerization reaction are recycled to said recovery step (b) and at least a portion of said polymerization by-products are recycled from said recovery step (b) to said cracking step (a).
15. A process as defined in claim 1 wherein said processing step (c) comprises the steps of:
- (i) utilizing said dilute ethylene stream in any high once through conversion process amenable to the use of

dilute ethylene to produce the derived derivative product plus byproducts,

(ii) recovering said derived derivative product;

(iii) recycling at least a portion of said byproducts to said cracking step (a).

16. A process as defined in claim 15 wherein said high once through conversion process is selected from the group consisting of polyethylene polymerization, ethylene dichloride production, alpha olefins production, ethyl benzene production, styrene production, acetaldehyde production, and combinations of one or more of the foregoing.

17. A process as defined in claim 1 wherein said processing step (c) comprises the steps of:

(i) polymerizing said dilute propylene stream to produce polypropylene and polypropylene polymerization by-products wherein said propylene polymerization is carried out either

(1) by a bulk phase polymerization reaction wherein said propylene-containing stream comprises at least about 85 weight percent propylene, or

(2) by a gas phase polymerization reaction wherein said propylene-containing stream comprises at least about 95 weight percent propylene;

(ii) recovering said polypropylene; and

(iii) recycling at least a portion of propylene polymerization by-products to said cracking step (a).

18. A process as defined in claim 1 wherein said processing step (c) comprises the steps of:

(i) utilizing said dilute propylene stream in any high once-through conversion process amenable to the use of dilute propylene to produce the desired derivative product and by-products;

(ii) recovering said derivative product; and

(iii) recycling said by-products to said cracking step (a).

19. A process as defined in claim 18 wherein said high once through conversion process is selected from the group consisting of polypropylene polymerization, acrylonitrile production, cumene production, propylene oxide production, isopropanol production, acrolein production, allyl chloride production, and combinations of one or more of the foregoing.

20. An integrated process for the production of polyethylene and polypropylene comprising the steps of:

(a) cracking a hydrocarbon feedstock in a cracking reactor to produce a cracked product comprising ethylene, ethane, methane, hydrogen, propylene, propane, other C_3 components, C_4 components and heavier compounds;

(b) separating ethylene from said cracked product to produce a dilute ethylene stream comprising at least about 85 weight percent ethylene and separating propylene from said cracked product to produce a dilute propylene stream comprising at least about 85 weight percent propylene;

(c) polymerizing ethylene in said ethylene-containing stream to produce polyethylene and polyethylene polymerization by-products wherein said ethylene polymerization is carried out either

(i) by a gas phase polymerization reaction wherein said dilute ethylene stream comprises at least about 95 weight percent ethylene, or

(ii) by a solution phase polymerization reaction wherein said dilute ethylene stream comprises at least about 85 weight percent ethylene;

(d) recovering said polyethylene product;

(e) polymerizing propylene in said propylene-containing stream to produce polypropylene and polypropylene polymerization by-products wherein said propylene polymerization is carried out either

(i) by a bulk phase polymerization reaction wherein said propylene-containing stream comprises at least about 85 weight percent propylene, or

(ii) by a gas phase polymerization reaction wherein said propylene-containing stream comprises at least about 95 weight percent propylene;

(f) recovering said polypropylene; and

(g) recycling said ethylene polymerization by-products to said cracking step (a) in the case of a gas phase ethylene polymerization reaction or recycling said polymerization by-products to said ethylene separation step (b) in the case of a solution phase ethylene polymerization reaction.

21. A process as defined in claim 20 wherein said ethylene polymerization reaction is a solution phase polymerization reaction, said ethylene and propylene separation step (b) comprises:

(I) compressing said cracked product stream to a pressure of from about 350 psig to about 520 psig to produce a compressed product stream;

(II) removing acid gas from said compressed product stream with a caustic or amine system to produce an acid gas removed product stream;

(III) drying said acid gas removed product stream over water-absorbing molecular sieve to a dew point of about -200° F. to produce a dried product stream;

(IV) removing C_4 and heavier components from said dried product stream in a depropanizer tower to produce a depropanized product stream and a C_4 and heavier stream;

(V) selectively hydrogenating the acetylenes in said dried product stream to produce a hydrogenated product stream;

(VI) dephlegmating said dried product stream to produce a first vapor stream substantially free of C_{3+} hydrocarbons and a first liquid stream rich in C_{2+} hydrocarbons;

(VII) further dephlegmating said first vapor stream to produce a second vapor stream comprising hydrogen and methane and a second liquid stream rich in methane and ethylene;

(VIII) separating said first liquid stream in a moderately low temperature demethanizer to produce a third vapor stream substantially free of C_{3+} hydrocarbons and a third liquid stream rich in C_{2+} hydrocarbons;

(IX) separating said second liquid stream and said third vapor stream in a low temperature demethanizer to produce a fourth vapor stream comprising substantially methane and a fourth liquid stream comprising dilute ethylene;

(X) separating said third liquid stream in a deethylenization tower to produce an overhead stream comprising dilute ethylene and a fifth liquid stream substantially free of ethylene;

(XI) recovering said fourth liquid stream and said overhead stream as said dilute ethylene stream;

(XII) separating said fifth liquid stream to produce a fifth vapor stream comprising recycle ethane and a sixth liquid stream rich in C_3 hydrocarbons;

(XIII) separating said sixth liquid stream to produce a dilute propylene overhead stream and a bottoms propane stream; and

(XIV) recycling said bottoms propane stream to said steam cracking step.

22. A process as defined in claim 20 wherein said by-products from polypropylene polymerization step are recycled to said separation step (XII).

23. A process as defined in claim 1 wherein said C₄ and heavier stream comprising one or more of ethyl acetylene, vinyl acetylene, 1,3-butadiene, 1,2-butadiene, isobutylene, cis-2-butene, trans-2-butene, 1-butene, isobutane, and n-butane is recovered from said cracked product stream and processed in a C₄ processing system comprising:

(A) catalytically hydrogenating ethyl acetylene, vinyl acetylene, 1,3-butadiene and 1,2-butadiene to butenes and catalytically converting 1-butene to 2-butenes in the presence of a catalyst comprising at least one hydrogenating metal and a moderately acidic carrier at a temperature ranging from about 40° C. to about 400° C. and a pressure ranging from about 1 to about 100 bars in a hydroisomerization zone to produce a hydrogenated stream comprising isobutylene, 1-butene, 2-butenes and C₄ paraffins;

(B) reacting isobutylene in the hydrogenated stream either

(1) with methanol in a methyl tertiary butyl ether synthesis zone in the presence of an acid type ion exchange resin catalyst at a temperature ranging from about 60° F. to about 300° F. and a pressure ranging from about 80 to 400 psig to produce a methyl tertiary butyl ether-rich product effluent and a by-product effluent comprising C₄ paraffins and C₄ olefins; or

(2) polymerizing said isobutylene in a polymerization zone to produce a polyisobutylene-rich product effluent and a by-product effluent comprising C₄ paraffins and C₄ olefins;

(C) separating the C₄ paraffins from the C₄ olefins in said by-product effluent in a paraffin/olefin separation zone to produce a C₄ paraffin-rich effluent and a C₄ olefin-rich effluent comprising 1-butene and 2-butenes;

(D) catalytically converting 2-butenes in said C₄ olefin rich effluent to isobutylene in a skeletal isomerization zone in the presence of an acidic catalyst at a pressure of about atmospheric and a temperature ranging from about 600° F. to about 1100° F. to produce a skeletal isomerized effluent;

(E) recycling said skeletal isomerized effluent to step (A) or step (B); and

(F) where methyl tertiary butyl ether is produced in step (B) either

(1) recovering said methyl tertiary butyl ether as product; or

(2) producing methyl methacrylate from the methyl tertiary butyl ether by a process comprising:

(i) decomposing said methyl tertiary butyl ether into a methanol-containing stream and an isobutylene-containing stream;

(ii) catalytically oxidizing the isobutylene over a complex molybdenum oxide catalyst at temperatures ranging from about 350 to about 450° C. and from about 15 to about 25 psig to produce methacrolein;

(iii) oxidizing the methacrolein over a molybdenum catalyst at temperatures of from about 250 to about 350° C. and from about 15 to about 25 psig to produce methacrylic acid;

(iv) esterifying the methacrylic acid with methanol to produce methyl methacrylate; or

(3) producing butyl rubber from the methyl tertiary butyl ether by a process comprising:

(i) decomposing said methyl tertiary butyl ether into a methanol-containing stream and an isobutylene-containing stream;

(ii) cationically copolymerizing the isobutylene in said isobutylene-containing stream with isoprene at temperatures ranging from about -30 to about -100° F. in the presence of a Lewis acid catalyst and a small amount of water as a cocatalyst; and

(iii) recovering butyl rubber product; or

(G) where polyisobutylene is produced in step (B)(2), recovering said polyisobutylene product.

24. An integrated process for the processing a mixed C₄ hydrocarbon feedstock comprising ethyl acetylene, vinyl acetylene, 1,3-butadiene, 1,2-butadiene, isobutylene, cis-2-butene, trans-2-butene, 1-butene, isobutane and n-butane, said process comprising the following process steps conducted in sequence:

(A) catalytically hydrogenating ethyl acetylene, vinyl acetylene, 1,3-butadiene and 1,2-butadiene to butenes and catalytically converting 1-butene to 2-butenes in the presence of a catalyst comprising at least one hydrogenating metal and a moderately acidic carrier at a temperature ranging from about 40° C. to about 400° C. and a pressure ranging from about 1 to about 100 bars in a hydroisomerization zone to produce a hydrogenated stream comprising isobutylene, 1-butene, 2-butenes and C₄ paraffins;

(B) reacting isobutylene in the hydrogenated stream either

(1) with methanol in a methyl tertiary butyl ether synthesis zone in the presence of an acid type ion exchange resin catalyst at a temperature ranging from about 60° F. to about 300° F. and a pressure ranging from about 80 to 400 psig to produce a methyl tertiary butyl ether-rich product effluent and a by-product effluent comprising C₄ paraffins and C₄ olefins; or

(2) polymerizing said isobutylene in a polymerization zone to produce a polyisobutylene-rich product effluent and a by-product effluent comprising C₄ paraffins and C₄ olefins;

(C) separating the C₄ paraffins from the C₄ olefins in said by-product effluent in a paraffin/olefin separation zone to produce a C₄ paraffin-rich effluent and a C₄ olefin-rich effluent comprising 1-butene and 2-butenes;

(D) catalytically converting 2-butenes in said C₄ olefin rich effluent to isobutylene in a skeletal isomerization zone in the presence of an acidic catalyst at a pressure of about atmospheric and a temperature ranging from about 600° F. to about 1100° F. to produce a skeletal isomerized effluent;

(E) recycling said skeletal isomerized effluent to step (A) or step (B); and

(F) where methyl tertiary butyl ether is produced in step (B) either

(1) producing methyl methacrylate from the methyl tertiary butyl ether by a process comprising:

(i) decomposing said methyl tertiary butyl ether into a methanol-containing stream and an isobutylene-containing stream;

(ii) catalytically oxidizing the isobutylene over a complex molybdenum oxide catalyst at temperatures ranging from about 350 to about 450° C. and from about 15 to about 25 psig to produce methacrolein;

- (iii) oxidizing the methacrolein over a molybdenum catalyst at temperatures of from about 250 to about 350° C. and from about 15 to about 25 psig to produce methacrylic acid,
- (iv) esterifying the methacrylic acid with methanol to produce methyl methacrylate, or
- (2) producing butyl rubber from the methyl tertiary butyl ether by a process comprising:
 - (i) decomposing said methyl tertiary butyl ether into a methanol-containing stream and an isobutylene- 10 containing stream,

- (ii) cationically copolymerizing the isobutylene in said isobutylene-containing stream with isoprene at temperatures ranging from about -30 to about -100° F. in the presence of a Lewis acid catalyst and a small amount of water as a cocatalyst, and
- (iii) recovering butyl rubber product; or
- (G) where polyisobutylene is produced in step (B)(2), recovering said polyisobutylene product.

* * * * *

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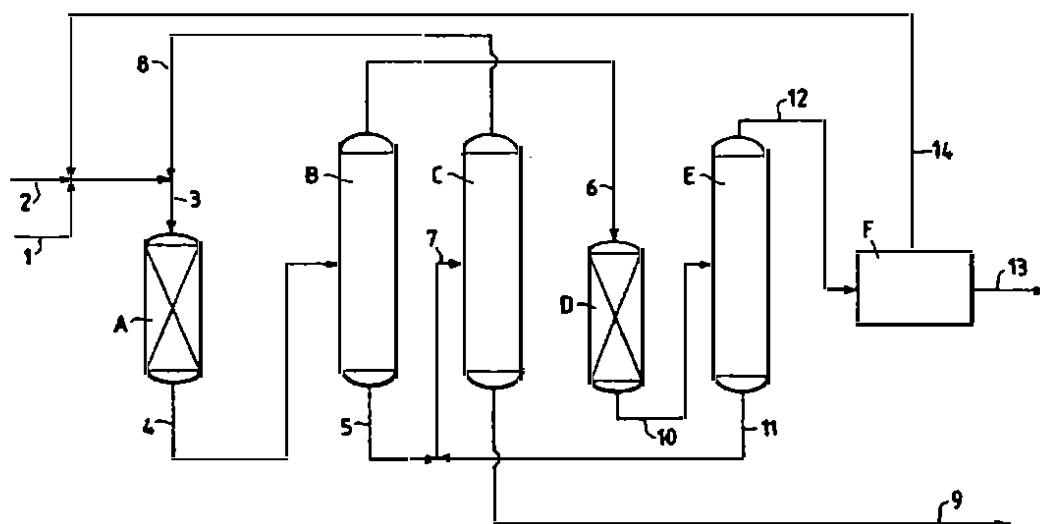
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(54) Abstract Title

Production of high octane hydrocarbons by the selective dimerization of isobutene

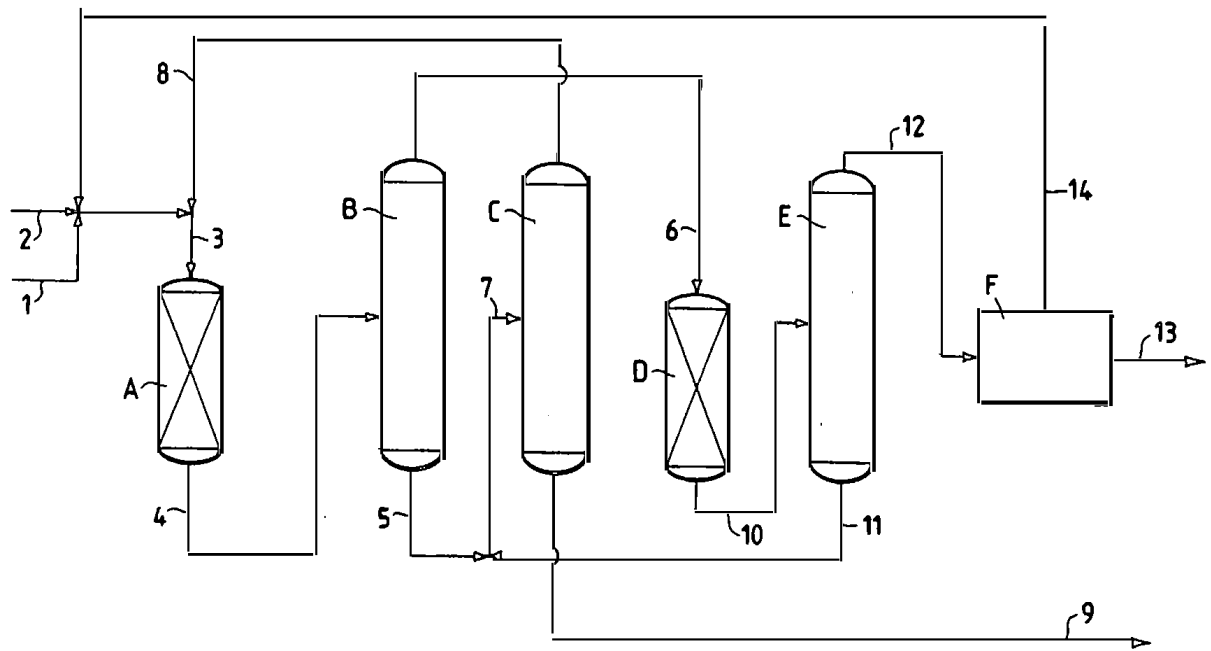
(57) High octane hydrocarbons are produced by reacting hydrocarbon cuts containing isobutene with an acid catalyst in the presence of an alkyl ether, preferably MTBE, and a primary alcohol, preferably methanol, such that the molar ratio of primary alcohol + alkyl ether/isobutene is more than 0.1 and the molar ratio of primary alcohol/isobutene is less than 0.2. The starting mixture is introduced to a first reactor (A) and bottoms products are sent to a separator (B) from which the head is sent to a second reactor (D). Combined bottoms product from separators (B) and (E) are sent to a third separator (C) to yield bottoms products (9) comprising mainly dimerized isobutene. Alkyl ethers from the head of third separator (C) are recycled (8). Alcohol may optionally be removed by an absorption unit (F) and recycled (14).

FIG. 1



At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

FIG. 1



PROCESS FOR THE PRODUCTION OF HYDROCARBONS WITH A HIGH
OCTANE NUMBER BY THE SELECTIVE DIMERIZATION OF ISOBUTE-
NE.

The present invention relates to a process for the
5 production of hydrocarbons with a high octane number,
obtained by the selective dimerization reaction of
isobutene contained in hydrocarbon cuts and to a lesser
extent of possible linear butenes, in the presence of
moderate quantities of primary alcohols and alkyl
10 ethers, which favour the production of higher selecti-
vities on the part of the catalyst. The mixture ob-
tained can then be hydrogenated with the conventional
methods to obtain a product with a further improvement
in the octane characteristics.

15 For reasons of an environmental nature the compo-
sition of fuels is being reformulated; the "Clean Air
Act Amendments" (CAAA) in the United States are provid-
ing general regulations which will probably also be
adopted with a few variations by other countries in the

near future.

In short the general tendency is towards the production of fuels which burn better and have fewer evaporative emissions. The main measures for reaching this objective are the following (for more specific details see for example: G.H. Unzelman, Fuel Reformulation, 31(2), (1993), 41 and D. Sanfilippo, F. Ancillotti, M. Marchionna, Chim. & Ind., 76, (1994), 32 and references contained therein):

- 10 - oxygenated compounds will have an ever increasing role as fuel components;
- the content of aromatic compounds will be greatly reduced, especially in benzene;
- there will be a reduction in the volatility of fuels
- 15 to minimize evaporative losses;
- the content of light olefins, photochemically reactive and precursors responsible for the formation of atmospheric ozone, will be reduced;
- both the sulfur content and final boiling point of
- 20 fuels will also be reduced.

All these measures therefore lead to the necessity of planning new processes which can positively contribute to fulfilling the above demands.

As well as oxygenated compounds to which the CAAA have assigned a fundamental role in future reformulated

25

fuels both for raising the octane number and supplying oxygen, purely hydrocarbon products are also proving to be particularly attractive.

Among these the alkylate is particularly distinctive as it has a high octane number, a low volatility and is practically without olefins and aromatics. The alkylation process in liquid phase is a reaction between isoparaffinic hydrocarbons, such as for example, isobutane, and olefins, for example propylene, butenes, pentenes and relative mixtures, in the presence of an acid catalyst for the production of C₇-C₉ hydrocarbons with a high octane number to be used in fuels (see for example: A. Corma, A. Martinez, Catal. Rev.- Sci. Eng., 35, (1993), 483 and references contained therein).

The main problem of the alkylation process is due to the fact that with the increase in environmental regulations both traditional processes (with hydrofluoric acid and sulfuric acid) are having considerable difficulties which makes their future uncertain; the process with hydrofluoric acid owing to the toxicity of this acid, especially in populated areas, and that with sulfuric acid owing to the large production of acid mud and also to the highly corrosive power of the catalyst.

Alternative processes with solid acid catalysts

are in the process of being developed but their commercial applicability is still to be proved.

On the other hand a hydrocarbon product of this type is in ever-increasing demand owing to its octane characteristics (high Research Octane Number (RON) and Motor Octane Number (MON) and those relating to its boiling point (poor volatility but low final point) which place it in the category of compositions which are extremely interesting for obtaining fuels that are more compatible with present-day environmental demands.

In addition, hydrocarbon products with a high octane number such as those generated by the alkylation reaction also have a low sensitivity (difference between RON and MON) and it is known that ethers such as MTBE, ETBE, TAME, etc. favourably react to the reduced sensitivity of the fuel, increasing their already high octane number even more.

This means that there are many advantages in combining a saturated hydrocarbon product with a high octane number (such as alkylate) with ethers such as MTBE. In addition the joint presence of considerable quantities of the two products also allows the content of undesired components such as aromatics, olefins and sulfur to be considerably decreased, by dilution.

In refining, an alternative process for obtaining

products with similar characteristics to alkylate can be offered by the hydrogenation of the so-called "polymer" fuel.

The oligomerization process (often erroneously
5 called, in the field of refining, polymerization) was widely used in the years 1930-1940 to convert low-boiling C_3 - C_4 olefins into fuels. The process leads to the production of a fuel with a high octane number (RON about 97) but with a high sensitivity owing to the
10 purely olefinic nature of the product (for more specific details on the process see: J.H. Gary, G.E. Handwerk, "Petroleum Refining: Technology and Economics", 3rd Ed., M. Dekker, New York, (1994), 250).

Typical olefins which are oligomerized are mainly
15 propylene, which gives slightly higher dimers or oligomers depending on the process used, and isobutene which mainly gives dimers but always accompanied by large quantities of higher oligomers.

With particular respect to the oligomerization of
20 isobutene it is known that this reaction can be carried out in batch, in semicontinuous or in continuous, in both gas-solid phase and liquid phase, generally at temperatures of between 50 and 300°C and at atmospheric pressure or at such pressures as to maintain the
25 reagents in liquid phase, if deemed suitable.

Typical catalysts for the industrial oligomerization of isobutene are represented by phosphoric acid, generally supported on a solid (for example kieselguhr), or acid resins with cation exchange. The latter
5 allow blander conditions of both temperature and pressure to be used than with supported phosphoric acid (100°C and 1-2 Mpa vs 200-220°C and 3-10 MPa).

Other catalysts have also been claimed in literature, both liquid acids such as H_2SO_4 or sulfonic acid
10 derivatives, and solids such as for example silico-aluminas, mixed oxides, zeolites, fluorinated or chlorinated aluminas, etc.; on the other hand none of these catalysts has as yet enabled the setting up of an industrial process as in the case of supported phosphoric acid (F. Asinger, "Mono-olefins: Chemistry and
15 Technology", Pergamon Press, Oxford, pages 435-456) and in that of cationic resins (G. Scharfe, Hydrocarbon Proc., April 1973, 171).

From the product point of view, the main problem
20 of this process lies in the fact that in the oligomerization phase heavy oligomers such as trimers (selectivity of 15-30%) and tetramers (selectivity of 1-2%) of isobutene are produced in excessive percentages. Tetramers are completely outside the fuel fraction as
25 they are too high-boiling and therefore represent a

distinct loss in fuel yield; with respect to trimers
(or their hydrogenated derivatives) it is desirable to
strongly reduce their concentration as their boiling
point (170-180°C) is on the limit of future specifica-
5 tions on the final point of reformulated fuels.

On the other hand the problem of minimizing the
formation of higher oligomers to dimers with percentag-
es of less than 10% is a problem which is typical of
the oligomerization of isobutene, as is also specified
10 in literature (C.T. O'Connor, M.Kojima, K.W. Schumann,
Appl. Catal., 16 (1985), 193).

This level of heavy compounds is analogous to that
of an alkylate and is still tolerated in the fuel pool.

From what has been said above, it is evident that
15 there is a wide interest in obtaining a new dimeriza-
tion process of isobutene which allows the synthesis of
a higher quality product, by reaching greater selecti-
vities.

It has now been surprisingly found that by carry-
20 ing out the selective dimerization reaction of isobute-
ne in the presence of moderate quantities of primary
alcohols and alkyl ethers, the production of a fraction
of oligomers is selectively obtained, particularly rich
in dimers (>90%) and practically without tetramers and
25 higher oligomers (<0.05%), containing small quantities

of dimer ethers.

The reaction product is then preferably hydrogenated to give a completely saturated end-product with a high octane number and low sensitivity. The hydrogenation can be carried out with the conventional methods as described for example in F. Asinger, "Mono-olefins: Chemistry and Technology", Pergamon Press, Oxford, page 455.

As an example, table I indicates the octane numbers and relative boiling points of some of the products obtained with the process of the present invention.

TABLE I

Product	RON	MON	b.p. (°C)
di-isobutenes	100	89	100-105
iso-octane	100	100	99
tri-isobutenes	100	89	175-185
hydrogenated			
tri-isobutenes	101	102	170-180

The process of the present invention for the production of hydrocarbons with a high octane number starting from hydrocarbon cuts containing isobutene, by selective dimerization with acid catalysts is charac-

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terized in that the reaction is carried out in the presence of primary alcohols in such a quantity as to have in the feeding a molar ratio primary alcohols + alkyl ethers/isobutene of more than 0.1, preferably
5 between 0.1 and 0.7, and a ratio primary alcohol/isobutene of less than 0.2, preferably between 0.005 and 0.1.

It should also be pointed out that in the case of C₄ hydrocarbon streams also comprising linear olefins it
10 has been observed that at least a part of the latter can be converted by reaction with isobutene into a hydrocarbon product without threaten their octane number. It is also preferable to carry out an enriching treatment, by means of pre-isomerization, of the
15 internal linear olefins, which would benefit the total octane number of the mixture.

The process claimed herein can be applied to cuts containing isobutane, isobutene, n-butane and n-butenes.

20 Although a wide variety of sources is available for supplying these streams, the most common ones concern those deriving from dehydrogenation processes of iso-paraffins, from FCC units and streams coming from steam cracking.

25 When the streams from steam-cracking contain

diolefins in addition to the desired mono-olefins, it is necessary to eliminate them by the typical removal treatment (for example extractions or selective hydrogenations).

5 As well as the hydrocarbon components, the stream comprises as specified above, primary alcohol (in great molar defect with respect to the iso-olefin) and alkyl ether.

10 The primary alcohol used can be selected from primary alcohols containing from 1 to 6 carbon atoms: methanol and/or ethanol are preferred.

15 The alkyl ether used can be selected from those containing from 5 to 10 carbon atoms: MTBE (methyl-ter-butyl ether), ETBE (ethyl-ter-butyl ether), MSBE (methyl-sec-butyl ether), ESBE (ethyl-sec-butyl ether) or mixtures of these are preferred.

20 The isobutene together with the hydrocarbon stream in which it is contained is sent with the primary alcohol and alkyl ether, in strong stoichiometric defect, into contact with the acid catalyst where the dimerization takes place. The primary alcohol is almost completely converted under the reaction conditions to dimer ether.

25 The presence of a constant level of primary alcohol in the reactors is fundamental for obtaining

the desired high selectivities as it enables the use of a catalytic species with the correct activity.

The fact of operating with the correct catalytic activity makes the reaction much more controllable also
5 from a thermal point of view with a consequent improvement in the quality of the product.

The quantity of alkyl ether sent to the reactors is such that, depending on the operating conditions, it can be either further produced or partially decomposed:
10 in the latter case, as the decomposition process is of endothermal ether, a part of the heat developed in the dimerization reaction can be absorbed, thus further improving the temperature control in the reactor. In addition, the alcohol liberated by the decomposition of
15 the ether, as well as interacting with the catalyst, can react with the dimers and butenes present in the reactor.

The optimum level of the sum of primary alcohol and alkyl ether which must be present in the reaction
20 environment to obtain selectivities to dimers close to or higher than 90% by weight, depends on the composition of the hydrocarbon charge.

When the charge consists of C_4 hydrocarbon cuts containing isobutene in a quantity of between 10 and
25 30% by weight and n-butenes in a quantity of between 25

and 50% by weight, it is advisable, to obtain better results, to operate with a molar ratio primary alcohol + alkyl ether/isobutene of between 0.2 and 0.6.

When the charge consists of C₄ hydrocarbon cuts
5 containing isobutene in a quantity of between 30 and 60% by weight, n-butenes in a quantity of more than 30% by weight and C₄ paraffins in a quantity of less than 15% by weight, it is advisable, to obtain better results, to operate with a molar ratio primary alcohol
10 + alkyl ether/isobutene of between 0.1 and 0.6.

When the charge consists of C₄ hydrocarbon cuts containing isobutene in a quantity of between 28 and 60% by weight, C₄ paraffins in a quantity of more than 30% by weight and n-butenes in a quantity of less than
15 10% by weight, it is advisable, to obtain better results, to operate with a molar ratio primary alcohol + alkyl ether/isobutene of between 0.3 and 0.6.

When the charge consists of C₄ hydrocarbon cuts containing isobutene in a percentage of more than 80%
20 by weight, it is advisable to obtain better results, to operate with a molar ratio primary alcohol + alkyl ether/isobutene of between 0.5 and 0.7.

Table II indicates the average compositions of typical C₄ hydrocarbon fractions coming from different
25 sources (FCC, Steam Cracking, dehydrogenation of

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isobutane, streams of isobutene with a high concentration).

TABLE II

Typical percentage compositions of C₄ streams

5	=====
	Steam cracking FCC Dehydrogen. Conc.isobutene
	Isobutene 30-46 10-25 45-55 >90
	n-butenes 35-60 25-50 <10
	C ₄ satur. 4-8 30-60 45-55 <10
10	=====

For charges different from those generally available in industrial practice, it can be observed that the addition of considerable quantities of linear olefins with respect to the charge compositions cited above, causes a slight increase in the selectivity to dimers and therefore a limited reduction in the lower limit of the molar ratio primary alcohol + alkyl ether/isobutene previously indicated. On the contrary, an increase in the content of saturated hydrocarbons causes a slight deterioration in the selectivity and therefore the value of the lower limit of the ratio is slightly increased.

A wide variety of acid catalysts can be used for this process, among these, for example, mineral acids such as sulfuric acid, BF₃, supported phosphoric acid,

suitably modified zeolites, heteropolyacids and sulfonated polymeric resins, for example Amberlyst 15 and Amberlyst 35, etc, can be mentioned. Among these catalysts the use of macrolattice sulfonated resins, 5 generally copolymers of styrene and benzene, is preferred; the characteristics of these resins are amply described in literature (see for example A. Mitschker, R.Wagner, P.M. Lange, "Heterogeneous Catalytic and Fine Chemicals", M. Guisnet ed., Elsevier, Amsterdam (1988), 10 61).

A wide range of operating conditions can be used for producing hydrocarbons with a high octane number in the desired selectivities by the process of the present invention. It is possible to operate in vapor phase or 15 in liquid-vapor phase but the operation conditions in liquid phase are preferred.

The process of the present invention can operate under both batch and continuous conditions, considering however that the latter are much more advantageous in 20 industrial practice. The reactor configuration selected can be optionally selected from fixed bed, tubular fixed bed, adiabatic, stirred and finally column reactor which also allows the separation of the products (a description on the general use of this technology 25 is provided for example in : J.L. De Garmo, V.N.

Paruledar, V. Pinjala, Chem. Eng. Progr., March 1992, 43).

The range of process conditions, operating in liquid phase, comprises a wide variety of operating conditions which are described hereunder.

The pressure is preferably superatmospheric to maintain the reagents in liquid phase, generally below 5 MPa, more preferably between 0.2-2.5 MPa. The reaction temperature is preferably between 30 and 120°C.

10 The feeding space velocities of the alcohol-hydrocarbon stream should preferably be less than 30 h⁻¹, more preferably between 1 and 15 h⁻¹.

The isobutene is mainly converted in the reaction zone, however also part of the n-olefins can be converted to useful product; for the most part, there are no limits in the concentration of iso-olefin in the hydrocarbon fraction even if it is preferable to have concentrations of between 2 and 60%; there are no limits in the ratio between isobutene and linear

15

20 olefins. It should be observed that in the case of streams coming from the dehydrogenation of isobutane there are no significant concentrations of linear butenes in the charge.

The process of the present invention can be carried out in particular by means of the following

25

basic steps:

- 5 a) feeding to a dimerization reactor the hydrocarbon cut containing isobutene together with a stream consisting of primary alcohols and a stream containing alkyl ethers;
- 10 b) sending the product leaving the dimerization reactor to a fractionation column from whose head a stream is obtained containing non-reacted isobutene and small quantities of ethers and alcohols and from the bottom of which a stream containing dimers and alkyl ethers is removed;
- c) sending the stream containing non-reacted isobutene to a second reactor to complete the conversion of isobutene;
- 15 d) sending the product leaving the second reactor to a second fractionation column from whose head a stream is obtained containing C_4 hydrocarbons and primary alcohols and from whose bottom a stream containing C_4 hydrocarbons, dimers and alkyl ethers is removed;
- 20 e) sending to a third fractionation column the bottom streams removed from the two fractionation columns obtaining the desired hydrocarbon product at the bottom and a stream containing alkyl ethers at the head, which is recycled to the first reactor;
- 25

f) sending the stream leaving the head of the second fractionation column to a separation unit of the primary alcohols which are subsequently recycled to the first reactor.

5 A recommended process scheme is shown in the enclosed FIG.1 to provide a clearer illustration of the present invention.

The stream (1) containing isobutene, joined to the feeding of primary alcohol (2) (methanol), is sent to
10 a first reactor (A) in which the C₄ iso-olefin is selectively converted to dimers.

The effluent (4) from the reactor (A) is sent to a separation column (B) where a stream (6) is removed at the head, essentially containing non-converted
15 olefins, alkyl ether (MTBE) and alcohol (methanol) in such quantities as to satisfy the molar ratios specified above, whereas at the bottom a stream (5) is removed essentially containing dimers, oligomers, ethers of dimers and alkyl ether (MTBE).

20 This stream (5) is sent to a separation column (C) where a stream is removed at the head, essentially containing alkyl ether (MTBE) recycled to the reactor (A), whereas at the bottom the synthesis product is obtained essentially consisting of dimers and small
25 quantities of oligomers and ethers of dimers.

The stream (6) is fed to a second reactor (D) in which the isobutene present is selectively converted to dimers. The effluent (10) from the reactor (D) is separated in a column (E) from which a bottom stream 5 (11) is removed, essentially containing alkyl ether (MTBE) and dimers, which is sent, together with the stream (5), to the column (C).

Optionally, the stream (12) at the head can be treated to remove the alcohol (methanol) contained 10 therein in a unit (F) which can consist for example of an absorption system of the primary alcohol on molecular sieves or an extraction of the alcohol itself with water. In both cases the alcohol recovered can be sent (14) to the reaction, whereas the hydrocarbon stream 15 (13) can be used in subsequent operations.

An example is now provided for a better illustration of the invention without limiting its scope in any way.

Example 1

20 With reference to the diagram in the figure, a hydrocarbon stream containing 50% by weight of isobutene, of the type obtained by the dehydrogenation of isobutane, is converted in the presence of suitable quantities of methanol and MTBE into a hydrocarbon 25 product with a high octane number containing about 90%

by weight of di-isobutenes, the rest consisting of trimers of isobutenes and ethers of di-isobutenes.

Tables III and IV show with reference to the enclosed figure, the quantities of the various streams
5 of the plant indicated in kg/h, % weight, Kmole/h and % mol.

The reactors (A) and (D) operate at a temperature at the outlet of 70°C and 75°C respectively and both at an operating pressure of 2 MPa.

10 The molar ratio methanol+MTBE/isobutene is 0.375 in reactor (A) and 0.154 in reactor (B).

The corresponding molar ratios methanol/isobutene are 0.008 in reactor (A) and 0.017 in reactor (B).

The catalyst used is a commercial macroporous
15 sulfonated resin of the type Amberlyst 35 produced by Rohm & Haas, Co.

TABLE III

kgm	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Isobutene	1000.0	0.0	1008.5	98.2	0.0	98.2	6.5	8.5	0.0	12.5	8.5	4.0	4.0	0.0
Isobutane	1000.0	0.0	1070.4	1070.4	0.0	1070.4	70.4	70.4	0.0	1070.4	70.4	1000.0	1000.0	0.0
C0	0.0	0.0	12.9	829.8	0.0	0.0	809.3	12.9	898.4	79.5	79.5	0.0	0.0	0.0
C12	0.0	0.0	0.0	83.5	0.0	0.0	91.6	0.0	91.6	8.1	8.1	0.0	0.0	0.0
Methanol	0.0	2.3	4.6	1.0	0.0	1.0	0.0	0.0	0.0	2.3	0.0	2.3	0.0	2.3
MTBE	0.0	0.0	581.9	586.1	564.9	21.2	581.9	581.9	0.0	16.9	16.9	0.0	0.0	0.0
C9 Ethane	0.0	0.0	0.0	9.3	9.3	0.0	10.2	0.0	10.2	0.9	0.9	0.0	0.0	0.0
	2000.0	2.3	2678.3	2678.3	1487.6	1190.7	1672.0	673.7	998.3	1190.7	184.4	1006.3	1004.0	2.3

% weight	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Isobutene	50.00	0.00	37.65	3.67	0.00	8.24	0.51	1.26	0.00	1.05	4.61	0.40	0.40	0.00
Isobutane	50.00	0.00	39.97	39.97	0.00	89.90	4.21	10.46	0.00	89.90	38.19	99.38	99.60	0.00
C0	0.00	0.00	0.48	30.08	55.78	0.00	54.39	1.92	89.79	6.68	43.11	0.00	0.00	0.00
C12	0.00	0.00	0.00	3.12	5.61	0.00	5.46	0.00	9.18	0.68	4.41	0.00	0.00	0.00
Methanol	0.00	100.00	0.17	0.04	0.00	0.08	0.00	0.00	0.00	0.19	0.01	0.23	0.00	100.00
MTBE	0.00	0.00	21.72	21.68	37.98	1.78	34.80	66.36	0.00	1.42	9.18	0.00	0.00	0.00
C9 Ethane	0.00	0.00	0.00	0.35	0.63	0.00	0.61	0.00	1.03	0.08	0.40	0.00	0.00	0.00
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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TABLE IV

Material	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Isobutene	17.825	0.000	17.977	1.750	0.000	1.750	0.152	0.151	0.000	0.223	0.152	0.071	0.071	0.000
Isobutane	17.206	0.000	18.418	18.418	0.000	18.418	1.212	1.212	0.000	18.418	1.212	17.206	17.206	0.000
C8	0.000	0.000	0.115	7.396	7.396	0.000	8.105	0.115	7.909	0.709	0.709	0.000	0.000	0.000
C12	0.000	0.000	0.000	0.498	0.498	0.000	0.544	0.000	0.544	0.048	0.048	0.000	0.000	0.000
Methanol	0.000	0.071	0.143	0.030	0.000	0.030	0.000	0.000	0.000	0.072	0.000	0.071	0.000	0.071
MTBE	0.000	0.000	6.601	6.649	6.409	0.240	6.601	6.601	0.000	0.192	0.192	0.000	0.000	0.000
C3 Ethane	0.000	0.000	0.000	0.065	0.065	0.000	0.071	0.000	0.071	0.006	0.006	0.000	0.000	0.000
	35.03	0.07	43.25	34.80	14.37	20.44	16.60	8.08	8.61	19.67	2.32	17.35	17.28	0.07

Material	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Isobutene	50.88	0.00	41.56	5.03	0.00	8.56	0.91	1.87	0.00	1.13	6.53	0.41	0.41	0.00
Isobutane	49.12	0.00	42.58	52.92	0.00	90.12	7.26	15.00	0.00	93.64	52.26	99.18	99.59	0.00
C8	0.00	0.00	0.27	21.25	51.48	0.00	48.57	1.43	92.84	3.60	30.55	0.00	0.00	0.00
C12	0.00	0.00	0.00	1.43	3.45	0.00	3.26	0.00	6.33	0.25	2.08	0.00	0.00	0.00
Methanol	0.00	100.00	0.33	0.09	0.00	0.15	0.00	0.00	0.00	0.37	0.02	0.41	0.00	100.00
MTBE	0.00	0.00	15.26	19.10	44.61	1.17	39.56	81.70	0.00	0.98	6.28	0.00	0.00	0.00
C3 Ethane	0.00	0.00	0.00	0.19	0.45	0.00	0.43	0.00	0.83	0.03	0.27	0.00	0.00	0.00
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

LP

CLAIMS

- 1) A process for the production of hydrocarbons with a high octane number starting from hydrocarbon cuts containing isobutene, by selective dimerization with acid catalysts characterized in that the
5 dimerization reaction is carried out in the presence of primary alcohols and alkyl ethers in such a quantity as to have in the feeding a molar ratio primary alcohols + alkyl ethers/isobutene of
10 more than 0.1 and a molar ratio primary alcohols/isobutene of less than 0.2.
- 2) The process according to claim 1, operating, at a reaction temperature of between 30 and 120°C, at a pressure of less than 5 MPa and feeding space
15 velocities of less than 30 h⁻¹.
- 3) The process according to claim 1 wherein the molar ratio in the feeding of primary alcohols + alkyl ethers/isobutene is between 0.1 and 0.7.
- 4) The process according to claim 1 wherein the molar
20 ratio in the feeding of primary alcohols/isobutene is between 0.05 and 0.1.
- 5) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in a quantity of between 10 and 30% by
25 weight and n-butenes in a quantity of between 25

and 50% by weight and the molar ratio primary alcohols + alkyl ethers/isobutene is between 0.2 and 0.6.

- 5 6) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in a quantity of between 30 and 60% by weight and n-butenes in a quantity of more than 30% by weight and C₄ paraffins in a quantity of less than 15% by weight and the molar ratio
- 10 primary alcohols + alkyl ethers/isobutene is between 0.1 and 0.6.
- 15 7) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in a quantity of between 30 and 60% by weight and C₄ paraffins in a quantity of more than 30% by weight and n-butenes in a quantity of less than 10% by weight and the molar ratio primary alcohols + alkyl ethers/isobutene is between 0.3 and 0.6.
- 20 8) The process according to claim 1 wherein the charge consists of hydrocarbon cuts containing isobutene in quantities of more than 80% by weight and the molar ratio primary alcohols + alkyl ethers/isobutene is between 0.5 and 0.7.
- 25 9) The process according to claim 1 wherein the space

velocities in the feeding are between 1 and 15 h⁻¹.

- 10) The process according to claim 1 wherein the primary alcohol has from 1 to 6 carbon atoms.
- 11) The process according to claim 10 wherein the
5 primary alcohol is selected from methanol and/or ethanol.
- 12) The process according to claim 1 wherein the alkyl ether has from 5 to 10 carbon atoms.
- 13) The process according to claim 12 wherein the
10 alkyl ether is selected from MTBE, ETBE, MSBE, ESBE or mixtures of these.
- 14) The process according to at least one of the previous claims comprising the following basic steps:
 - 15 a) feeding to a dimerization reactor the hydrocarbon cut containing isobutene together with a stream consisting of primary alcohols and a stream containing alkyl ethers;
 - b) sending the product leaving the dimerization
20 reactor to a fractionation column from whose head a stream is obtained containing non-reacted isobutene and small quantities of ethers and alcohols and from the bottom of which a stream containing dimers and alkyl
25 ethers is removed;

- c) sending the stream containing the non-reacted isobutene to a second reactor to complete the conversion of isobutene;
- 5 d) sending the product leaving the second reactor to a second fractionation column from whose head a stream is obtained containing C_4 hydrocarbons and primary alcohols and from whose bottom a stream containing C_4 hydrocarbons, dimers and alkyl ethers is removed;
- 10 e) sending to a third fractionation column the bottom streams removed from the two fractionation columns obtaining the desired hydrocarbon product at the bottom and a stream containing alkyl ethers at the head, which is recycled to the first reactor;
- 15 f) sending the stream leaving the head of the second fractionation column to a separation unit of the primary alcohols which are subsequently recycled to the first reactor.



Application No: GB 9810558.8
Claims searched: 1-14

Examiner: Dr J Houlihan
Date of search: 21 July 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.P): C5E (ECA, ECC, ECD, ECF, ECK), C5G (GAD)
Int CI (Ed.6): C07C 2/14, C10G 50/00, C10L 1/02
Other: ONLINE: WPI, CLAIMS, JAPIO, TULSA

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0048893 A1 (EC ERDÖLCHEMIE GMBH) page 1 lines 1-5; Beispiel 2; & WPI Abstract Acc. No. 82-28939E/198215	1-13
X	US 4540839 (KEYWORTH D A & McFARLAND C G) column 2 lines 55-67; column 3 lines 15-17; Example 3; Claims 2 & 5	1-13

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

[54] **PRODUCTION OF VINYL CHLORIDE FROM ETHANE**

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[52] U.S. Cl. **260/656 R; 260/659 A; 260/683.3**

[51] Int. Cl.² **C07C 21/02**

[58] Field of Search **260/656 R, 654 A, 683.3**

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Primary Examiner—James O. Thomas, Jr.

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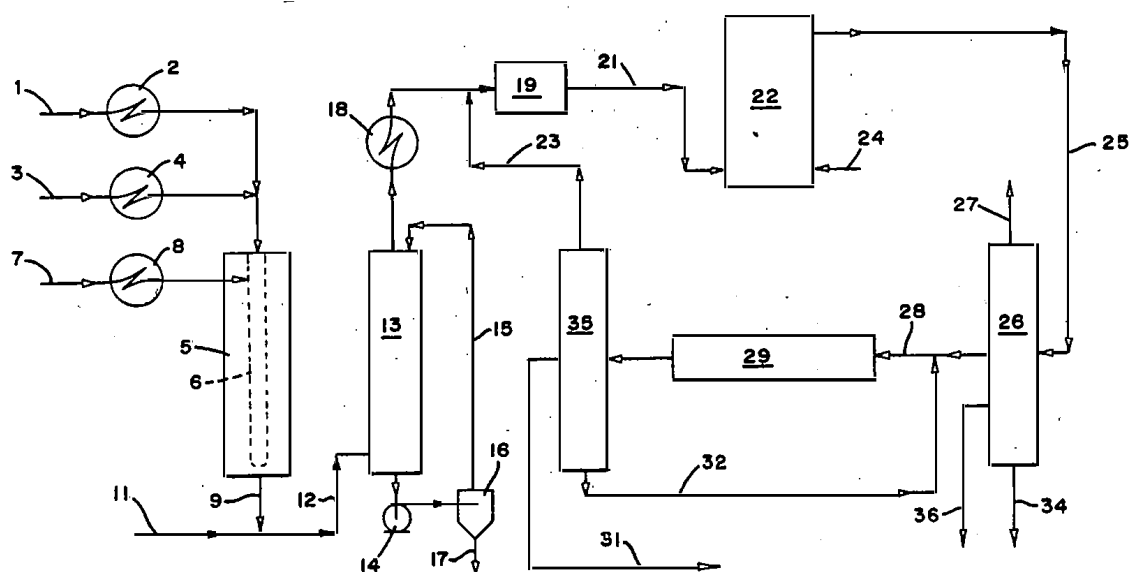
Attorney, Agent, or Firm—Gerard P. Rooney; Gerhard H. Fuchs; Jack B. Murray, Jr.

[57] **ABSTRACT**

A process is disclosed for the production of ethylene dichloride from ethane. Ethane is introduced into an autothermic (self-sustaining) cracking zone together with controlled proportions of chlorine and oxygen. The autothermic cracking zone is maintained at a temperature above about 700° C. but below 1000° C. for a sufficient time to convert from about 20 to 95 percent of the ethane having about 96 to 74 percent ethylene yield, respectively, based on the converted ethane. The reaction mixture, containing predominantly ethylene and hydrogen chloride, is quenched with a volatile liquid. The quenched mixture is passed, together with oxygen, into a catalytically activated oxyhydrochlorination zone to convert the ethylene, hydrogen chloride and oxygen to ethylene dichloride. If vinyl chloride is desired as a product, part or all of the produced ethylene dichloride is passed to a second cracking zone for conversion to vinyl chloride product and hydrogen chloride. The hydrogen chloride produced is recycled to the oxyhydrochlorination zone. Ethylene dichloride, vinyl chloride or mixtures of ethylene dichloride and vinyl chloride can be recovered as product, with substantially complete utilization of the hydrogen chloride produced.

5 Claims, 1 Drawing Figure

VINYL CHLORIDE PRODUCTION FROM ETHANE



PRODUCTION OF VINYL CHLORIDE FROM
ETHANE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The technology for producing ethylene dichloride and vinyl chloride has undergone major changes in the past decade. Until the mid-1960's vinyl chloride was generally manufactured by the hydrochlorination of acetylene. Acetylene, however, is substantially more costly than ethylene; hence, strong motivation existed to develop a process based entirely on ethylene. Such a process was successfully developed in the past, having as its key step, the oxyhydrochlorination of ethylene to ethylene dichloride. As a result, the acetylene-based process has, in recent years, been almost completely replaced by the more economical ethylene-based process.

2. Description of the Prior Art

While ethane is even less expensive than ethylene and consequently considerable effort has been expended in the past to develop an ethane-based ethylene dichloride process, these efforts, however, did not culminate in a commercially adaptable process.

SUMMARY OF THE INVENTION

It has been found that when ethane is subjected to autothermic cracking in the presence of specified amounts of chlorine and oxygen, and under specified conditions of time and temperature, high conversions of ethane ranging from 20 to 98 percent with concomitant production of ethylene in yields based on the converted ethane ranging from 100 to 70 percent can be obtained without the need for catalytic agents. The term "oxygen" herein means oxygen gas or an oxygen-containing gas such as air. Cracking which does not require the continuous input of large quantities of heat is referred to herein as "autothermic" cracking. Autothermic cracking minimizes heat input requirements, capital investment requirements, recycling, and by-product and carbon formation. This autothermic cracking operation comprises a step in a process for economic production of ethylene dichloride in high yield. The cracking step can be controlled so that only hydrogen chloride actually required in the production of ethylene dichloride is formed. The raw materials are ethane, chlorine and oxygen. The oxygen can, if desired, be entirely supplied by air.

The autothermic cracking process of our invention for use in the production of ethylene from ethane is as follows: Ethane, chlorine and oxygen are introduced, preferably after preheating, as reactants into an autothermic reaction zone in controlled proportions, with a molar ratio of chlorine:ethane of from about 0.2 to 1.2:1 and a molar ratio of oxygen:ethane of from about 0.005 to 0.5:1, preferably between about 0.1:1 and 0.4:1. The reactants are maintained in the reaction zone under autothermic cracking conditions including a temperature ranging from above about 700° C. to below 1000° C., preferably between about 850° C. to 950° C., for a time period of from about 0.1 to 10 seconds, preferably between about 0.25 and 2.5 seconds. Products of this autothermic reaction comprise a major amount of ethylene and hydrogen chloride and a minor amount of water, methane, carbon monoxide, hydrogen and acetylene. Thereafter this reaction product stream is cooled, preferably by quenching with a

volatile liquid such as water and preferably to a reaction product temperature below about 600° C. Then the quenched autothermic reaction products may be further reacted to obtain, as desired final product, ethylene dichloride, vinyl chloride, or a mixture of ethylene dichloride and vinyl chloride.

Where ethylene dichloride is desired as final product, the quenched autothermic reaction product containing ethylene and hydrogen chloride is passed together with oxygen to a catalytically activated oxyhydrochlorination zone under oxychlorination conditions sufficient to convert the ethylene, hydrogen chloride and oxygen to ethylene dichloride. Thereafter the ethylene dichloride is recovered as product. When ethylene dichloride is the desired product, the preferable molar ratio of chlorine:ethane in the autothermic cracking reaction zone is maintained between about 0.9:1 and 1.2:1.

Where vinyl chloride is desired as final product, all of the ethylene dichloride produced in the oxyhydrochlorination zone is passed to an externally heated cracking zone so as to convert ethylene dichloride to vinyl chloride and hydrogen chloride. The vinyl chloride is recovered as product. Thereafter the hydrogen chloride formed in the externally heated cracking zone is recycled to the oxyhydrochlorination zone. Preferably the ethylene dichloride which is not converted to vinyl chloride in the externally heated cracking zone is recycled to the externally heated cracking zone. When vinyl chloride is the desired product, the preferable molar ratio of chlorine:ethane in the autothermic cracking reaction zone is maintained between about 0.4:1 and 0.6:1.

Where both vinyl chloride and ethylene dichloride are desired as final products, a portion of the ethylene dichloride produced in the oxyhydrochlorination zone is removed therefrom and recovered as a product. The remaining amount of the ethylene dichloride produced in the oxyhydrochlorination zone is passed to an externally heated cracking zone under conditions sufficient to convert ethylene dichloride to vinyl chloride and hydrogen chloride. The vinyl chloride is recovered as product. The hydrogen chloride formed in the externally heated cracking zone is recycled to the oxyhydrochlorination zone. Preferably, chlorine introduced into the autothermic reaction zone is increased beyond that required for vinyl chloride as product by the chlorine equivalent to the portion of the ethylene dichloride which is removed as product. When both vinyl chloride and ethylene dichloride are the desired products, the preferable molar ratio of chlorine:ethane in the autothermic cracking reaction zone is maintained between about 0.6:1 and 0.9:1.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying diagram illustrates the manner in which ethane may be converted in good yield in a single pass to ethylene in accordance with a preferred embodiment of our invention. The ethylene may be used in the production of ethylene dichloride, mixtures of vinyl chloride and ethylene dichloride, or vinyl chloride. The autothermic cracking of ethane in the presence of controlled amounts of chlorine and oxygen, and within the preferred temperature range of our process, produces ethylene in high yield, as well as hydrogen chloride. Both the ethylene and the hydrogen chloride are consumed in the production of ethylene dichloride. The flow diagram also illustrates one way in which the ethylene and hydrogen chloride produced in

the autothermic cracking step can be utilized in the economic production of vinyl chloride as the final product.

With reference to the drawing, chlorine in line 1 is preheated in heat exchanger 2, and mixed with oxygen entering at line 3, which is preheated in heat exchanger 4. The molar ratio of chlorine to ethane is from 0.2 to 1.2:1, and the molar ratio of oxygen to ethane is from 0.005 to 0.5:1. The hot gaseous mixture is introduced into reaction chamber 6 of gas-gas reactor 5. Ethane gas in line 7 is preheated in heat exchanger 8, and enters reactor chamber 6 simultaneously with the stream of chlorine and oxygen. Autothermic cracking takes place at a temperature from about 700° C. to below 1000° C. for a retention time from about 0.1 to 10 seconds. Autothermic cracking can be controlled by varying the composition of the feed, the degree of preheating, the reaction temperature and the retention time to obtain conversion of between about 20 and 98 percent of the ethane, with yields of ethylene, based on the converted ethane, of from about 100 to 70%. The hot reaction product comprising predominantly ethylene and hydrogen chloride leaves the reactor at line 9 and is cooled, preferably quenched by a volatile liquid which is substantially unreactive toward the reaction products and which enters at line 11. The quenched mixture, which also contains by-products and carbon, passes through line 12 to scrubber 13 through which quench liquid circulates via line 15, by means of pump 14. A solids separator is shown at 16 for collection and removal of particulate carbon at line 17.

Ethylene, hydrogen chloride and by-products including acetylene are reheated at heat exchanger 18 to at least about 150° C. to 200° C. and passed through a catalytically activated hydrogenator 19 containing a conventional hydrogenation catalyst such as palladium or activated alumina, which converts the acetylene present to ethylene.

Ethylene and hydrogen chloride leaving the hydrogenator 19 pass through line 21 to the oxyhydrochlorinator 22. This may be a conventional fixed or fluid bed oxyhydrochlorinator having a conventional catalyst such as copper chloride on an alumina base. The oxyhydrochlorinator operates within a temperature range of about 200° C. to 250° C. Additional hydrogen chloride from the subsequent cracking of ethylene dichloride is also received through line 23. Oxygen (or air) enters oxyhydrochlorinator 22 through line 24. The ethylene dichloride produced, together with by-products, passes through line 25 to recovery system 26. Non-condensibles are separated via line 27, among them being unreacted ethane. If substantially pure oxygen gas is used, rather than air, this ethane which is generally contaminated with carbon monoxide, hydrogen and methane may, after removal of carbon monoxide and purging of methane, be recycled through line 7 and heat exchanger 8 to the autothermic cracking reactor 5. The concentration of the contaminating methane is held to a low value, preferably by employing a continuous purge, while the carbon monoxide is removed by conventional means, such as by scrubbing with acidic cuprous chloride solution. Water is removed from the recovery system 26 at line 34.

If vinyl chloride is to be a final product, the separated ethylene dichloride leaves recovery system 26 through line 28, and is thermally cracked by passage through tubular furnace 29 at a temperature such that products exit at about 500° C. to 600° C. producing vinyl chlor-

ide. The vinyl chloride is withdrawn from recovery system 35 for further purification or storage via line 31. If, on the other hand, ethylene dichloride is to be the product, or if it is to be recovered together with vinyl chloride, it is withdrawn through line 36. When part or all of the ethylene dichloride leaving recovery system 26 is to be thermally cracked to produce vinyl chloride and hydrogen chloride at thermal cracking unit 29, the hydrogen chloride is recovered in recovery system 35 and passed through line 23 to join the ethylene and hydrogen chloride stream enroute to the oxyhydrochlorinator 22 via line 21. Unconverted ethylene dichloride is recycled from recovery system 35 to the tubular cracking furnace 29 through line 32.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The ethane-based ethylene dichloride process of the present invention involves two main reactions: the autothermic cracking of ethane; and the oxyhydrochlorination of ethylene. If vinyl chloride is desired as product, it is produced by thermal cracking of ethylene dichloride. The combination of these three reactions constitutes an overall process for vinyl chloride production.

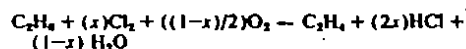
1. Autothermic Cracking of Ethane to Ethylene

The key reaction step is the autothermic cracking of ethane.

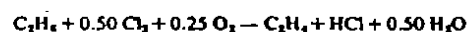
Maximization of the ethylene yield is largely a matter of proper reactant ratios, temperature and residence time.

All the reactants may be preheated before passage into the autothermic cracking zone but it is preferable to avoid temperatures above 600° C. for ethane so as to prevent thermal cracking and to avoid temperatures above 400° C. for chlorine so as to protect the processing equipment. At elevated temperatures chlorine becomes highly corrosive.

The degree of preheating of reactants and the proportions of reactants used in the autothermic reaction zone will affect reaction temperature, reaction efficiency and product purity. Increasing the oxygen input will raise the temperature; but as the ratio of oxygen to ethane is increased, the quantity of by-products, particularly carbon monoxide and methane, is also increased with a corresponding decrease in ethylene yield. Also, small amounts of free hydrogen are formed during the autothermic reaction. Such free hydrogen formation makes it possible to use less than the "theoretical" oxygen-to-ethane molar ratio, thus reducing the formation of carbon monoxide. However, free hydrogen also tends to reduce the heat of reaction of the autothermic cracking step and thus to increase the temperature to which the reactants must be pre-heated. In general, the theoretical oxygen-to-ethane (O_2/C_2H_6) molar ratio can be defined as $(1-x)/2$ where $x = Cl_2/C_2H_4$, i.e.



Hence, a "theoretical" oxygen/ethane molar ratio of 0.25 applies if the chlorine/ethane molar ratio is 0.50:



The actual temperatures chosen for preheating the chlorine, as well as the air and ethane, should be those

found best to achieve a temperature ranging from above about 700° C. to below 1000° C., preferably between about 850° C. and 950° C., in the autothermic cracking unit.

The heat exchangers for preheating feed gases to the autothermic reactor can be included in a single unit, comprising for example, coils or tube bundles in a single encompassing heater. Also, if desired, such coils or tube bundles can be included in an encompassing "hot box" or "heated zone" which includes the autothermic reaction zone of a multiplicity of tubular reactors arranged for parallel operation.

The reactants are maintained in the reaction zone for at least about 0.1 second, preferably between about 0.25 to 2.5 seconds, or for a time sufficient to convert concomitantly from about 20 to 98 percent of the ethane to 100 to 70 percent of the ethylene, respectively, based on the converted ethane. The autothermic cracking products stream comprises mainly ethylene and hydrogen chloride, with smaller amounts of water, methane, carbon monoxide, hydrogen and acetylene.

The conversion and yields obtained are much better at temperatures ranging from above about 700° C. to below 1000° C. and retention times of from about 0.1 to 10 seconds than when the autothermic cracking step is carried out at temperatures in excess of 1000° C. with retention times of less than 0.1 second. The percent conversion of ethane and the percent ethylene yield, based on the ethane converted, bear approximately an inverse relationship as shown in the tabulation below. The results shown were determined at a chlorine:ethane ratio of about 0.5:1 and an oxygen:ethane ratio of about 0.1:1.

Conversion	Yield
20%	96%
40%	95%
60%	93%
80%	87%
90%	80%
95%	74%

By lowering the reactor temperature or decreasing residence time, the conversion is decreased and the yield increased. At an ethane conversion of about 70%, the ethylene yield is about 90% and the ethylene yield per pass (conversion times yield) is 63%. Increasing conversion decreases yield so that at a conversion of 95%, the yield of ethylene is about 74% and the yield per pass is 70%. The ethylene yield per pass generally reaches a maximum at an ethane conversion of about 90%. This means that in a process using air as the source of oxygen, in which it is not practical to recycle the unreacted ethane because of dilution with nitrogen, it would be desirable to run with a conversion which maximizes the yield per pass. On the other hand, with a process using oxygen gas, in which unreacted ethane can be recycled, it would be preferable to run at a much lower conversion in order to take advantage of the higher ethylene yield. Hence, the operation may be carried out either in a single pass where the oxygen is supplied by air and where a lower yield, offset by a savings in equipment and operational costs, is acceptable; or as a multipass operation where pure oxygen is used and where a high yield is the primary consideration.

The molar ratio of chlorine:ethane ranges preferably between from about 0.4 to 0.6:1 for the recovery of vinyl chloride as product in the overall process. The theoretical chlorine/ethane molar ratio for the production of vinyl chloride in the overall process is 0.5:1. Where vinyl chloride is to be the desired product, chlorine/ethane ratios higher than 0.6 can be used. However, more hydrogen chloride will be produced in the autothermic cracking step than is required for subsequent oxyhydrochlorination of ethylene when the chlorine/ethane ratio is greater than 0.6. To avoid an excess of hydrogen chloride in the overall production of vinyl chloride, it is preferable to keep the molar ratio of chlorine:ethane below about 0.6:1. Ratios below 0.4:1 may be used if desired and high yields may be obtained, but the need for recycling ethane increases as the ratio of chlorine:ethane is lowered.

Where ethylene dichloride is to be recovered as a second product in addition to vinyl chloride, the molar ratio of chlorine:ethane is increased to preferably between about 0.6 to 0.9:1. The upper limit of the chlorine/ethane ratio is a function of the amount of ethylene dichloride, as opposed to vinyl chloride monomer, that is to be recovered. The amount of ethylene dichloride withdrawn as product from the system is preferably substantially equivalent in chlorine content to the chlorine used in excess of 0.5:1 molar ratio of chlorine:ethane.

Where ethylene dichloride is to be recovered as product, the molar ratio of chlorine:ethane should range from about 0.9 to 1.2:1, more preferably at 1.0:1.

It is to be understood that any of these combinations of recovered products can be achieved where the chlorine molar ratio based on ethane ranges from 0.2 to 1.2:1. But low chlorine/ethane ratios require considerable recycling of ethane whereas relatively high chlorine/ethane ratios lead to an unwanted excess of hydrogen chloride. It is a feature of the process of the present invention, that vinyl chloride, vinyl chloride together with ethylene dichloride in any desired proportion, or ethylene dichloride, can be recovered without an excess of unwanted hydrogen chloride as by-product. Where vinyl chloride is the desired product to be recovered, the molar ratio of chlorine:ethane is most desirably about 0.5:1. Where ethylene dichloride is the desired product, the molar ratio of chlorine:ethane is most desirably 1.0:1. Where the desired products are vinyl chloride and ethylene dichloride, the molar ratio of chlorine to ethane is preferably selected with respect to the relative quantities of each product to be recovered, so that no appreciable excess of unwanted hydrogen chloride is produced.

The amount of chlorine which can be reacted in the process of our invention depends on the overall hydrogen chloride (HCl) balance. A half mol of chlorine will form one mol of HCl. A second mol of HCl is formed by the thermal cracking of ethylene dichloride, giving the required two mols of HCl for the oxyhydrochlorination. Hydrogen which cannot be removed from the ethane by reaction with chlorine must be removed by reaction with oxygen. In actuality, somewhat less than the theoretical amount of oxygen can be used, as a certain amount of hydrogen is also removed as molecular hydrogen by thermal dehydrogenation. If the chlorine-to-ethane ratio is increased, the oxygen-to-ethane ratio may be decreased.

The factors involved in maintaining the temperature of the autothermic reaction zone from about 700° C. to

below 1000° C., or preferably between about 850° C. to 950° C., include the amount of oxygen introduced with the chlorine, the degree of preheating of the feed gases, the retention time, the possible application of external heat, and the degree of thermal insulation. Although either air or substantially pure oxygen gas can be used in both the autothermic cracking unit and in the oxyhydrochlorinator to follow, the use of substantially pure oxygen will permit the use of smaller preheaters and an appreciable reduction in the size of the scrubbing system required. The use of substantially pure oxygen gas also provides considerable yield improvement, particularly because ethane can be recovered and recycled. The feed rate into the reactor is correlated with reactor dimensions to preferably give a residence time in the autothermic reaction zone of between about 0.25 to 2.5 seconds.

The mol. ratio of the oxygen:ethane in the autothermic reaction zone feed is in the range of about 0.005 to 0.5:1, preferably about 0.1 to 0.4:1. The lower ratios improve the ethylene yield by reducing carbon monoxide methane formation, but also decrease the heat of reaction. The use of these lower ratios requires that the reactants be preheated to a higher temperature. The residence time in the reactors themselves is so short that little heat can be transferred there. Hence we depend on the heat of reaction to raise the reactants to the desired reaction temperature. If the oxygen-to-ethane ratio is adjusted downward to give a near zero heat of reaction, then the reactant preheat temperatures are preferably such that the desired reactor temperature is attained before introduction of the reactants into the reactor. In general, this is not very practical, so that the oxygen-to-ethane ratio is preferably kept high enough to give a significant temperature rise due to heat of reaction. This temperature rise is increased by using oxygen rather than air, so that required preheat temperatures are then reduced.

We have obtained high conversions of ethane to ethylene where the reaction zone includes any conventional gas-gas reactor which will not tend to enhance either reactor plugging or substantial product yield loss when ethane, oxygen and chlorine are the reactants therein. An example of such a reactor is disclosed in U.S. patent application Ser. No. 167,733, filed July 30, 1971 by Bruce E. Kurtz and entitled "Isothermal Chlorination of Methane, Ethane and Other Compounds in a Porous Tube Reactor".

The autothermic cracking reaction products are next quenched with a volatile liquid which cools the reaction products and which can be added to the reaction products as they leave the reaction zone, or injected directly into the reaction zone at a point to permit the desired retention time at the desired autothermic reaction temperatures before quenching. Suitable quench liquids include carbon tetrachloride, chlorinated biphenyls or water. Water is preferred because it is especially effective in suppressing carbon formation.

The volatile quenching liquid is introduced into the reaction product gases in an amount to, by vaporization, cool the gases to a temperature below about 600° C., preferably below about 500° C. The point of introduction of the quench is a major factor in establishing the residence time of the reactants in the reaction zone. Good results have been obtained by introducing the quench directly into the reactor at a point opposite that at which the preheated reactants are introduced. Quenching per se has little effect on conversions or

yields, but is important in suppressing carbon formation and preventing reactor plugging.

The quenched gases preferably pass next to a scrubber, the design of which is not critical. Its purpose is to remove particulate carbon from the product of the autothermic reactor. It may consist of a spray tower with a small amount of the quenching liquid, preferably water, circulated by a pump to form a spray. The scrubber generally operates at between about 100° C. and 200° C., so that the exit is vapor phase. A solids separator is placed in the line to trap the carbon for removal. A liquid cyclone represents one type of solids separator.

The autothermic reaction zone product gases are preferably reheated by a heat exchanger to at least about 150° C. to 200° C. This exchanger may if desired be included in a "hot box" or cabinet furnace with other heat exchangers. Preferably the gases next pass to a conventional catalytic hydrogenator to convert any acetylene present to ethylene.

2. Oxyhydrochlorination of Ethylene to Produce Ethylene Dichloride

The reaction product gases containing predominantly ethylene and hydrogen chloride are next passed into a catalytically activated oxyhydrochlorination zone together with at least about the stoichiometric amount of oxygen. The oxygen may, if desired, be supplied by air, and may be used in an excess of up to 100 percent or more. The oxyhydrochlorination generally proceeds at a temperature between about 200° C. to 250° C. The hydrogen chloride (HCl) obtained from the autothermic cracking zone is insufficient for this oxyhydrochlorination step if the preferred molar ratio of 0.4 to 0.6:1 of chlorine to ethane has been used, or if the ratio of chlorine to ethane is less than 1.0:1. An additional stream of HCl, however, from the subsequent cracking of ethylene dichloride in an externally heated cracking zone for the production of vinyl chloride may also be directed to the oxyhydrochlorination zone.

Substantially pure ethylene dichloride may be separated and recovered as product. Where it is desired to recover only ethylene dichloride, no subsequent reaction step is required. Although the molar ratio of chlorine:ethane may be taken between 0.2:1 and 1.2:1, it is preferred that the molar ratio of chlorine:ethane be held between 0.9:1 and 1.2:1. The most preferred molar ratio of chlorine/ethane in the production of ethylene dichloride as desired final product is the theoretical molar ratio of 1.0:1 because undue recycling and production of an excess of hydrogen chloride is avoided.

The product of the oxyhydrochlorinator preferably passes to a conventional recovery system having distillation or stripping columns. Water and non-condensibles are separated. The latter may contain ethane, methane, carbon monoxide, and oxygen. If substantially pure oxygen gas rather than air has been used in the process, the ethane obtained at this point, after removal of any carbon monoxide and purging of methane, may be returned as recycle to the autothermic cracking reactor.

3. Cracking of Ethylene Dichloride to Vinyl Chloride Monomer

The ethylene dichloride produced by oxyhydrochlorination may be passed to an externally heated

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cracking zone comprising a continuously heated tubular furnace maintained at a temperature such that the products exit at about 500° C. to 600° C. On cracking of ethylene dichloride to vinyl chloride, hydrogen chloride and ethylene dichloride are also recovered. The ethylene dichloride which is unreacted is recycled to the entrance to the externally heated cracking zone. The hydrogen chloride is directed to the oxyhydrochlorination zone to supply the amount of hydrogen chloride which is required for the oxyhydrochlorination. The vinyl chloride is recovered as product.

If it is desired to simultaneously produce ethylene dichloride with the vinyl chloride, an excess of chlorine ranging from about 0.6 to 0.9 mol per mol of ethane may be used, with the continuous withdrawal of an amount of ethylene dichloride from the oxyhydrochlorination step sufficient to maintain a balance between the HCl produced and that consumed. No catalyst need be employed and the temperature is maintained by external heating so that the cracked gases containing vinyl chloride exit at between about 500° C. and 600° C. These gases leaving the externally heated cracking zone may enter a recovery system which may consist of a series of distillation or stripping columns.

The hydrogen chloride formed in cracking the ethylene dichloride, as previously explained, may be passed to the oxyhydrochlorinator. If the system is run in proper balance, the hydrogen chloride entering the oxyhydrochlorinator from the autothermic cracking unit and that from the externally heated ethylene dichloride cracking zone, equal that needed in the oxyhydrochlorination of the ethylene. Unreacted ethylene dichloride bottoms from the recovery system are recycled to the ethylene dichloride cracking zone, and the separated vinyl chloride is removed as product.

EXAMPLES 1 - 6

In the case of Examples 1-3, ethane was introduced into the top of the reaction zone at the rate of 12.5 grams per minute (g/m). In Example 4, the rate was 6.2 grams of ethane per minute; in Example 5, 12.5 g/m and in Example 6, 25.0 g/m. The ethane and oxygen were preheated to about 500° C. and the chlorine to about 400° C. before entering the reactor zone.

The progress of the autothermic cracking step and control of the operation was obtained by taking periodic samples for analysis. A thermocouple extended into the reaction zone for temperature determination.

The operating conditions, yields and by-products are given in Table I.

feed ratio. In Example 3, about 1.14 mols of HCl were obtained because the chlorine used was in excess of 0.5 mols. Only 1.0 mol of HCl is required for the balanced production of vinyl chloride. Examples 4, 5 and 6 illustrate the minor effect of decreasing residence time.

The average yield of vinyl chloride based on ethane is 90 percent and based on chlorine is 95 percent when using oxygen. When air is used rather than substantially pure oxygen gas in the autothermic cracking step and the oxyhydrochlorination operation, the yield of vinyl chloride drops to about 70 percent. This is primarily because the ethane recovered is diluted with nitrogen and cannot readily be recycled.

EXAMPLE 7

In this run the chlorine and oxygen entered the autothermic reactor from the bottom, and the ethane also entered at the bottom at a rate of 12.5 grams per minute. The reaction gases exited through a side arm at the top of the cylindrical reactor. In this Example, quench liquid was vaporized in the quenching operation, and the reaction gases, together with the vaporized quench liquid, exited the reactor at a temperature of 500° C.

The operating conditions, yields and by-products obtained in Example 7 are also included in Table I for comparison. A lower reaction temperature (850° C.) was used, compensated for by a longer residence time.

EXAMPLE 8

The preheated ethane entered the reactor at a rate of 25 grams per minute. The reactor had a side opening for exit gases and a top-center quench liquid inlet, as with Example 7. The results of this run are also tabulated in Table I for comparison.

As in the case of Example 7, the autothermic reaction, as a result of lower oxygen input, ran at lower temperature compensated for by a longer residence time. The overall yield was slightly below that of Example 7. Here also, somewhat more acetylene and methane were produced.

EXAMPLE 9

Ethane preheated to 500° C. was passed into the reactor at a rate of 12.5 grams per minute. A mixture of preheated oxygen at 600° C. and preheated chlorine at 400° C. was also passed therein simultaneously with the ethane. The molar ratio of the chlorine:ethane was 0.57:1.0 and the molar ratio of oxygen:ethane was 0.22:1.0. The reaction temperature was 950° C. The results of the autothermic cracking reaction are tabulated in Table I.

TABLE I

Example	Reactor Temp. ° C.	Ethane Feed g/m	Residence Time Seconds	EXAMPLES 1 - 9 INCLUSIVE					C ₂ H ₄ Yield/pass %	Mol By-Products Per 100 mols C ₂ H ₄			
				Cl ₂ /C ₂ H ₆ Mol ratio	O ₂ /C ₂ H ₆ Mol ratio	C ₂ H ₆ Conv. Percent	C ₂ H ₄ Yield %	C ₂ H ₄ Yield/pass %		CH ₄	CO	CO ₂	C ₂ H ₂
1	900	12.5	0.29	0.19	0.09	76.6	87.2	66.8	14.0	14.8	0.3	0	
2	900	12.5	0.26	0.38	0.09	85.1	87.4	74.4	12.6	15.2	0.4	0	
3	900	12.5	0.24	0.57	0.09	91.7	86.9	79.7	11.2	10.4	0.4	0	
4	900	6.2	0.43	0.38	0.19	92.7	75.7	70.2	23.6	32.1	0.9	0	
5	900	12.5	0.21	0.38	0.19	93.9	80.4	75.5	17.2	27.0	0.8	0	
6	900	25.0	0.11	0.38	0.19	88.4	81.2	71.8	16.2	27.3	0.6	0	
7	850	12.5	1.12	0.50	0.08	94.5	80.9	76.4	22.8	18.2	3.3	1.5	
8	850	25.0	1.68	0.50	0.08	89.9	80.9	72.7	24.4	17.2	1.2	2.2	
9	950	12.5	0.18	0.57	0.22	89.3	87.6	78.2	39.7	11.1	1.3	2.6	

In the above runs air was used rather than substantially pure oxygen gas. Examples 1, 2 and 3 illustrate the favorable effect of increasing the chlorine to ethane

blulated in Table I.

In the production of vinyl chloride from this reaction mixture, the reaction products, predominantly ethylene

(1 mol) and hydrogen chloride (1.14 mols), react in the presence of a slight excess of oxygen and an additional 0.86 mol of hydrogen chloride in a catalytic oxyhydrochlorinator to produce a mol of ethylene dichloride.

Ethylene dichloride amounting to 0.14 mol is withdrawn as a first product, and the remaining 0.86 mol subjected to thermal cracking in a tubular furnace heated to a degree such that the reactants exit at between about 500° C. and 600° C. Unreacted ethylene dichloride is recovered and recycled to the furnace.

When vinyl chloride is recovered as a second product, the 0.86 mol of hydrogen chloride obtained from the vinyl chloride production step, together with the 1.14 mols of hydrogen chloride obtained from the autothermic cracking step, comprise the two mols of HCl required in the oxyhydrochlorination of 1.0 mol of ethylene. Thus, by using an excess of chlorine in the autothermic reactor and bleeding ethylene dichloride from the system in an amount corresponding to the excess of chlorine used, both ethylene dichloride and vinyl chloride can be manufactured without the production of unwanted hydrogen chloride.

Since changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. The process for making vinyl chloride from ethane comprising the steps of:

- a. reacting a gaseous stream containing ethane, chlorine and oxygen in mol ratio of chlorine to ethane of from about 0.4:1 to 0.6:1, and oxygen to ethane in mol ratio of from about 0.1:1 to 0.4:1, under non-catalytic, autothermic conditions at a temperature within the range of from about 700° C to below 100° C for a time period of from about 0.1 to

10 seconds to obtain a gas stream comprising ethylene and hydrogen chloride;

- b. passing said gas stream comprising ethylene and hydrogen chloride together with the hydrogen chloride obtained in step c, below, and with oxygen in at least about stoichiometric amount through a catalytically activated oxyhydrochlorination zone under oxyhydrochlorination condition to convert the ethylene to ethylene dichloride, and recovering the ethylene dichloride; and

- c. thermally cracking the ethylene dichloride to obtain vinyl chloride and hydrogen chloride, recovering the vinyl chloride, and recycling the hydrogen chloride to step (b), above.

2. The process for making ethylene from ethane which comprises reacting a gaseous stream containing ethane, chlorine and oxygen in mol ratio of chlorine to ethane of from about 0.2:1 to 1.2:1, and mol ratio of oxygen to ethane of from about 0.005:1 to 0.5:1, under non-catalytic, autothermic conditions at temperature within the range of from about 700° to below 1000° C. for a time period of from about 0.1 to 10 seconds to obtain a gas stream comprising ethylene, hydrogen chloride and water.

3. The process of claim 2 wherein reaction is conducted at temperature within the range of from about 850° to 950° C. for a time period of from about 0.25 to 10 seconds.

4. The process of claim 2 wherein the mol ratio of chlorine to ethane is from about 0.4:1 to 0.6:1 and the mol ratio of oxygen to ethane is from about 0.1:1 to 0.4:1.

5. The process of claim 4 wherein reaction is conducted at temperature within the range of from about 850° to 950° C. for a time period of from about 0.25 to 10 seconds.

* * * * *



Dr A King

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31 January 2005

PAT/AK/JCD/024/9920

BY FACSIMILE: 00 49 89 2399 4465

Dear Sirs,

International Application No. PCT/GB2004/001265
Applicant: BP Chemicals Limited
Our ref: 9920

In response to the written opinion of the international searching authority dated 20th August 2004, Applicant submits a written reply.

Inventive Step of Claim 1

Claim 1 of the process of the present invention relates to an integrated process for the production of an olefin derivative said integrated process comprising cracking a paraffinic hydrocarbon containing feedstock to produce a first dilute olefins stream, reacting at least a portion of said first dilute olefins stream to produce a first olefin derivative stream, and a second dilute olefins stream comprising at least 5 mol% unreacted olefins, and auto-thermally cracking at least a portion of said second dilute olefins stream.

In particular, the invention takes advantage of the fact that it has been found that autothermal cracking processes are tolerant of olefins in the feed thereto without causing coking. This allows integrated processes as claimed to be operated with autothermal cracking of the second dilute olefins stream comprising unreacted olefins therein even though the olefins are at relatively high levels.

Cont'd.....

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Sunbury on Thames Middlesex TW16 7BP

Thus, treatment steps to reduce the olefin content are not required. Olefin derivative processes of relatively low conversion per pass may be operated using a dilute olefins stream, even though the product stream may comprise large amounts of unreacted olefins which are subsequently recycled (see p.8, lines 11-16 as filed).

In contrast, it is desirable to minimise the amount of olefins in the feed to a steam cracking process because the olefins will have a tendency to increase coke formation, leading to shorter cracker run times. (Olefins produced thermally crack further to produce diolefins, alkynes, aromatics and cycloolefins, and, ultimately, to produce coke)

In response to the Examiner's comments, Applicant submits, as Appendix 1, experimental data from an autothermal cracking process with olefins in the feed thereto.

These results show no significant changes in acetylene or benzene. Since these are precursors to coke formation, these results indicate no increased propensity for coke formation.

As the issue of coking in steam cracking processes due to the presence of olefins is well-known to the person skilled in the art, the fact that autothermal cracking processes are tolerant of olefins in the feed thereto without causing coking is surprising.

In addition, although ethylene is fed to the autothermal cracking process the yield of ethylene is increased compared to feeding of ethane alone.

With respect to the cited art, there is no mention in either D1 or D2 of autothermal cracking. In addition, there is no mention in either D1 or D2 of the levels of olefins in the respective recycles, and thus, no teaching away from the generally held knowledge that the levels of olefins to a steam cracker should be minimised to reduce coking.

In fact, the general teaching of the cited art is to reduce or remove any olefins in the recycle stream to the cracking step, consistent with the fact that it is desirable to minimise the levels of olefins fed to a steam cracker. Thus, in D1, the general teaching is to use a polymerisation process or oligomerisation process as an ethane/ethylene separator. The processes have a high conversion per pass (see p.1, lines 46-47), and the Example only cites the recycle stream as "Ethane Recycle".

Similarly, in D2, the suitable processes for production of an olefin derivative are generally described as "high conversion once through processes" (for example, col. 9, lines 63-65, col. 10, lines 56-59). Further, D2 explicitly allows for the subsequent treatment of the recycle stream to remove contaminants that would be detrimental to the cracking process (col. 11, lines 18-34).

Thus, there is no motivation in either D1 or D2 to recycle a second dilute olefins stream comprising unreacted olefins at relatively high levels to an autothermal cracking process as in claim 1.

Not least for this reason, claim 1, and its dependent claims, has inventive step over D1 and D2, either alone or in combination.

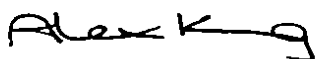
Further Objections

Applicant submits that "autothermally" is not vague or unclear and would be understood by the person skilled in the art.

Thus, Applicant submits the claims do meet the requirements of Article 6 PCT.

Finally, Applicant prefers not to add references to D1 and D3 at this stage, but will do so if required in the respective national offices.

Yours faithfully



Alex King



Mike T. Barlow
Authorised Representative No. 67

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Appendix 1

Experimental

Ethane or ethane and ethylene as detailed in Table 1 were passed with hydrogen and oxygen (H₂:O₂ ratio of 1:1 by volume) to an autothermal cracking reactor where autothermal cracking occurred in the presence of a 60mm bed of a catalyst comprising 3wt% platinum on alumina.

Table 1

Run	Pressure	Feed composition			Conv.	Yields					
	(barg)	C2H6	C2H4	O:C	C2H6	C2H4	CO	CO2	CH4	C2H2	C6H6
1	10	100.0	0	0.554	64.82	37.47	15.18	2.09	7.13	0.25	0.5
2	10	96.0	4	0.602	68.6	41.49	20.62	2.68	9.17	0.31	0.98
3	10	92.5	7.5	0.578	65.54	41.83	20.89	2.68	8.92	0.36	0.67
4	10	90.0	10	0.566	62.02	41.48	20.62	2.91	8.62	0.26	0.82
5	10	100.0	0	0.641	77.72	41.29	21.18	2.35	9.96	0.59	2.73
6	10	96.0	4	0.631	75.36	42.69	23.37	3.06	10.71	0.6	2.16
7	10	92.5	7.5	0.623	74.6	44.9	24.74	3.18	11.04	0.66	2.08
8	10	90.0	10	0.62	75.11	45.91	25.55	3.21	11.33	0.73	2.56
9	20	100.0	0	0.518	64.24	33.92	14.26	2.46	9.07	0.16	2.7
10	20	95.0	5	0.535	67.21	37.43	16.92	2.76	10.49	0.32	3.44
11	20	92.5	7.5	0.525	65.36	37.95	17.48	2.57	10.35	0.27	3.01
12	20	90.0	10	0.511	63.11	38.97	18.32	2.54	10.49	0.31	2.94

(Yields are in g/100g feed
O:C ratio is by weight
Ethane and ethylene feed composition is by weight %)

PATENT COOPERATION TREATY

AK/SES
131

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

HYMERS, Ronald Robson
BP INTERNATIONAL LIMITED
Patents & Agreements
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GRANDE BRETAGNE

Received in PAT

16 MAR 2005

PCT

INVITATION TO RESTRICT OR
TO PAY ADDITIONAL FEES

(PCT-Article 34(3)(a) and Rule 68.2)

OFFICIAL ACTION

Date of mailing
(day/month/year)

14.03.2005

Applicant's or agent's file reference
BPCL 9920

REPLY OR
PAYMENT DUE

within 1 month(s)
from the above date of mailing

International application No.
PCT/GB2004/001265

International filing date
(day/month/year)

24.03.2004

Applicant
BP CHEMICALS LIMITED et al.

1. This International Preliminary Examining Authority
 - (i) considers that **the international application does not comply with the requirements of unity of invention** (Rule 13.1, 13.2 and 13.3) for the reasons indicated in the Annex.
 - (ii) therefore considers that there are **2 inventions** claimed in the international application as indicated in the Annex.
 - (iii) recalls that claims relating to inventions in respect of which no international search report has been established need not be the subject of international preliminary examination (Rule 66.1 (e)).
2. Consequently the applicant is hereby **invited**, within the time limit indicated above, **to restrict the claims** as suggested under item 3, below, **or to pay** the amount indicated below:

EUR 1530,00

1

EUR 1530,00

Fee per additional invention

x

number of additional inventions

=

total amount of additional fees

The applicant is informed that, according to Rule 68.3 (c), **the payment of any additional fee may be made under protest**, i.e. a reasoned statement to the effect that the international application complies with the requirement of unity of invention or that the amount of the required additional fee is excessive.

3. **If the applicant opts to restrict the claims**, this Authority suggests the restriction possibilities indicated in the Annex, which in its opinion would be in compliance with the requirement of unity of invention.
4. **In the absence of any response** from the applicant, this Authority will establish the international preliminary examination report on those parts of the international application indicated in the Annex which, in the opinion of this Authority appear to relate to the main invention.

Name and mailing address of the international
preliminary examining authority:



European Patent Office
D-80298 Munich
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Authorized Officer

Harf, J

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**INVITATION TO RESTRICT
OR TO PAY ADDITIONAL FEES**

International application No. PCT/GB2004/001265

This Authority considers that there are 2 inventions covered by the claims indicated as follows:

I: Claims 1-7 directed to a process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and (iii) autothermally cracking the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

II: Claim 8 directed to a process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream ;(iii) reacting the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins to produce a second olefin derivative stream and (iv) recycling a stream comprising unreacted alkanes and less than 5 mol-% olefins to cracking step (I).

The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

The common concept linking together independent claims 1 and 8 is a process for producing an olefin derivative comprising (i) cracking a paraffinic feed and (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and a second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

This common concept is not considered as inventive over prior art document US-A-5981818 disclosing the cracking of an alkane feedstock followed by the polymerisation of the obtained dilute ethylene and/or propylene stream.

The requisite unity of invention (Rule 13.1 PCT) therefore no longer exists inasmuch as a technical relationship involving one or more of the same or corresponding special technical features in the sense of Rule 13.2 PCT does not exist between the subject-matter of the previously defined two inventions.

PATENT COOPERATION TREATY

OFFICIAL ACTION 133

PCT

From the INTERNATIONAL SEARCHING AUTHORITY

To:

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

INVITATION TO PAY ADDITIONAL FEES

(PCT Article 17(3)(a) and Rule 40.1)

Date of mailing
(day/month/year)

09/06/2004

Applicant's or agent's file reference

BPCL 9920

PAYMENT DUE

within ~~30~~ **30** days/days
from the above date of mailing

International application No.

PCT/GB2004/001265

International filing date
(day/month/year)

24/03/2004

Applicant

BP CHEMICALS LIMITED

1. This International Searching Authority

- (i) considers that there are 2 (number of) inventions claimed in the international application covered by the claims indicated ~~XXXX~~ on the extra sheet:

and it considers that the international application does not comply with the requirements of unity of invention (Rules 13.1, 13.2 and 13.3) for the reasons indicated ~~XXXX~~ on the extra sheet:

- (ii) ☒ has carried out a partial international search (see Annex) ☐ will establish the international search report on those parts of the international application which relate to the invention first mentioned in claims Nos.:

1 - 7

- (iii) will establish the international search report on the other parts of the international application only if, and to the extent to which, additional fees are paid

2. The applicant is hereby invited, within the time limit indicated above, to pay the amount indicated below:

EUR 1.550,00 x 1 = EUR 1.550,00
Fee per additional invention number of additional inventions total amount of additional fees

Or, _____ x _____ = _____

The applicant is informed that, according to Rule 40.2(c), the payment of any additional fee may be made under protest, i.e., a reasoned statement to the effect that the international application complies with the requirement of unity of invention or that the amount of the required additional fee is excessive.

3. ☐ Claim(s) Nos. _____ have been found to be unsearchable under Article 17(2)(b) because of defects under Article 17(2)(a) and therefore have not been included with any invention.

Name and mailing address of the International Searching Authority



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Authorized officer

Véronique Baillou

EINSCHREIBEN

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-7

process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and (iii) autothermally cracking the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins

2. Claim : 8

process for producing an olefin derivative comprising (i) cracking a paraffinic feed; (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream ;(iii) reacting the obtained second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins to produce a second olefin derivative stream and (iv) recycling a stream comprising unreacted alkanes and less than 5 mol-% olefins to cracking step (i)

The common concept linking together independent claims 1 and 8 is a process for producing an olefin derivative comprising (i) cracking a paraffinic feed and (ii) reacting the obtained first dilute olefins stream to produce a first olefin derivative stream and a second dilute olefins stream comprising alkanes and at least 5 mol-% unreacted olefins.

This common matter is already known from document US-A-5981818 disclosing the cracking of an alkane feedstock followed by the polymerisation of the obtained dilute ethylene and/or propylene stream. The requisite unity of invention (Rule 13.1 PCT) therefore no longer exists inasmuch as a technical relationship involving one or more of the same or corresponding special technical features in the sense of Rule 13.2 PCT does not exist between the subject-matter of the previously defined two groups of dependent claims.

Patent Family Annex
Information on patent family members

International Application No
PCT/GB2004/001265

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1001001	A	17-05-2000	US 6111156 A EP 1001001 A1	29-08-2000 17-05-2000
US 5981818	A	09-11-1999	NONE	
US 3987119	A	19-10-1976	BE 821397 A1 CA 1037971 A1 DE 2449563 A1 FR 2248254 A1 GB 1435069 A IT 1024701 B JP 50070307 A NL 7413046 A	17-02-1975 05-09-1978 30-04-1975 16-05-1975 12-05-1976 20-07-1978 11-06-1975 25-04-1975

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

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

Date of mailing (day/month/year)

26 August 2005 (26.08.2005)

Applicant's or agent's file reference

BPCL 9920

IMPORTANT NOTIFICATION

International application No.

PCT/GB2004/001265

International filing date (day/month/year)

24 March 2004 (24.03.2004)

1. The following indications appeared on record concerning:

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

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.

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

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

Name and Address

O & D TRADING 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:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☒ the elected Offices concerned
☐ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.89.65

Authorized officer

Diana NISSEN (Fax 338 8270)

Telephone No. (41-22) 338 8054

PATENT COOPERATION TREATY

137

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) 29 August 2005 (29.08.2005)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference BPCL 9920	
International application No. PCT/GB2004/001265	International filing date (day/month/year) 24 March 2004 (24.03.2004)

1. The following indications appeared on record concerning:

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

Name and Address O & D TRADING 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.	

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

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

Name and Address INNOVENE EUROPE 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:
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:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☒ the elected Offices concerned
☐ the International Preliminary Examining Authority ☐ 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

Expediente No			No de Folio
Item		No de unidades	✓
1	CD		
2	DVD		
3	REVISTA		
4	LIBRO		
5	PERIODICO		
6	DISQUETES		
7	SOBRE DE MANILA X	2	1
8	SOBRE BLANCO TAMAÑO CARTA		
9	SOBRE BLANCO TAMAÑO OFICIO		
10	OTROS:		

Observaciones: Osk Final

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION <i>PCT</i> MODELO DE UTILIDAD	()	()
- Indicación de que se solicita la concesión de una patente.	()	(X)
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	(X)
- Descripción de la invención.	()	(X)
- Dibujos de ser estos pertinentes.	()	(X)
- Comprobante de Pago de las tasas establecidas.	()	()
COMPLETA () INCOMPLETA	()	()
DISEÑO INDUSTRIAL ()		
- Indicación de que se solicita el registro de Diseño Industrial	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()	()
- Representación gráfica o fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño.	()	()
- Comprobante de pago de las tasas establecidas	()	()
COMPLETA () INCOMPLETA	()	()
ESQUEMA DE TRAZADO ()		
- Indicación de que solicita el registro de un Esquema de trazado.	()	()
- Datos de identificación del solicitante o de la persona que presenta La solicitud.	()	()
Representación gráfica del esquema de trazado	()	()
Comprobante de pago de las tasas establecidas.	()	()
COMPLETA () INCOMPLETA	()	()

Firma Responsable:

Fecha:



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REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
RODRIGUEZ D'ALEMAN DILIA MARIA

600

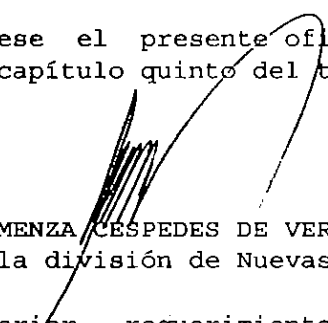
REFERENCIA	Radicación No.	5 98883
	Solicitud internacional	GB2004/001265
	Fecha inicio fase nacional	03/11/2005
	Trámite	11
	Evento	379
	Actuación	430
	Oficio No.	10685

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 CÉSPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de fecha 17 de nov 2005
adpa11