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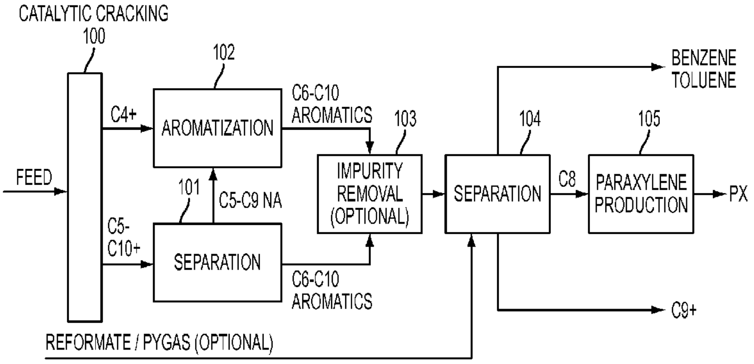

FIG. 1

(57) Abstract: Methods and processes for producing paraxylene from catalytic cracking hydrocarbons, particularly C_4 and C_{5+} streams, are disclosed. Each of the processing steps may be tailored to the overall objective of high paraxylene yield from a relative inexpensive feedstock.

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PROCESSES AND SYSTEMS FOR OBTAINING AROMATICS FROM CATALYTIC CRACKING HYDROCARBONS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This Application claims the benefit under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application Ser. No. 61/711,934 filed October 10, 2012, which is incorporated herein by reference in its entirety as if fully set forth herein.

BACKGROUND OF THE INVENTION

[0002] Xylene isomers, orthoxylene (OX), metaxylene (MX), and paraxylene (PX), and ethylbenzene (EB) are C_8 aromatics from reforming process or other petrochemical processes. The purified individual xylene products are used on a large scale as industrial solvents and intermediates for many products. The most important isomer, PX, is used for the production of terephthalic acid (TPA) and dimethyl terephthalate (DMT), which are used for the production of fibers, films and polyethylene terephthalate (PET) bottles. In these applications high purity (>99.7%) PX is required. Demand for high purity PX has increased greatly over the past years to meet rapidly growing markets.

[0003] Traditional feedstock for aromatics and paraxylene production is catalytic reforming (reformate) or pyrolysis (pygas). Catalytic cracking, or fluid catalytic cracking (FCC), including various variations such as DCC, High-Severity FCC (HS-FCC), Residue FCC (RFCC), is another well-known process that produces fuels, light olefins, and a similar C_6 to C_{10+} aromatics rich stream, known as catalytic naphtha, cat naphtha, or FCC gasoline.

[0004] Until recently, refiners did not consider recovering aromatics from FCC gasoline, because the extraction technology would not function with olefinic or sulfur impurities in the feed. There is a known technology which is designed specifically to make this operation by extraction, which permits the direct recovery of aromatics, while rejecting the olefin-rich fraction as raffinate. The sulfur species are also extracted into the aromatic fraction, which are removed in the downstream impurity removing step in the absence of olefins.

[0005] There is a known technology, namely Aromatization, to take olefinic hydrocarbon streams, as well as paraffinic or other type hydrocarbon streams, and produces

BTX (benzene, toluene, and xylenes). This process technology will take any olefinic components in the C_4-C_8 range as feed to produce the aromatics. Byproducts are light paraffins and LPG off gases.

[0006] It is known to produce xylenes by methylation of toluene and/or benzene, for instance methylation of toluene over catalyst using methanol. The feedstock can be toluene, benzene, or a mixture of toluene and benzene, or a pygas feedstock, or a reformate feedstock, and the methylation product has higher paraxylene content than the paraxylene content of the feedstock.

[0007] There are other xylene formation technologies known to the industry which use benzene, toluene, C_9-C_{10} aromatics, or a combination of them as feedstock. Examples of these are benzene/C_9-C_{10} transalkylation, toluene/C_9-C_{10} transalkylation, benzene/toluene/C_9-C_{10} transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP).

[0008] To date, the art does not disclose a practical process for production of paraxylene from light catalytic cracking hydrocarbons and catalytic naphtha. In addition, the above processes have not been integrated into a single system that creates significant advantages, including higher xylene yields and lower energy consumption over operation of these processes separately.

[0009] In present invention, an improved process is disclosed which uses light and heavy hydrocarbons as feedstock particularly the light and heavy hydrocarbons from catalytic cracking unit, including, in embodiments, the combination of various streams and processes which provides significant advantages over prior systems.

SUMMARY OF THE INVENTION

[00010] In various embodiments, systems and processes for producing paraxylene from catalytic cracking hydrocarbons are disclosed. The methods comprise: 1) a separation section to separate C_5 and C_{10+} from the C_{5+} catalytic naphtha, which also includes one extraction zone to separate C_6-C_9 non-aromatics from C_6-C_9 aromatics; 2) an aromatization section to form aromatics from C_4-C_9 non-aromatics (or a subset) that contains significant amount of olefins; 3) providing an optional impurity removal section to clean the aromatics before they are sent to the downstream processes; 4) a second separation section to

separate C_6-C_7, C_8, C_{9+} streams, and to separate non-aromatics in the C_6-C_7 or C_6-C_8 stream to yield high purity aromatics, as final product or as feedstock for downstream paraxylene production section or xylene formation processes; 5) a xylene production section which includes paraxylene separation zone and xylene isomerization zone. The paraxylene separation zone can use crystallization method or adsorption method or a combination of these to produce high-purity paraxylene. The xylene isomerization zone can use EB-dealkylation type of catalyst or EB-isomerization type of catalyst to convert EB either to benzene or xylene; 6) optionally inclusion of a xylene formation section, which include one or more of the following processes: benzene methylation, toluene methylation, benzene/toluene methylation, benzene/C_9-C_{10} transalkylation, toluene/C_9-C_{10} transalkylation, benzene/toluene/C_9-C_{10} transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP).

BRIEF DESCRIPTION OF THE DRAWINGS

[00011] For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions to be taken in conjunction with the accompanying drawings describing specific embodiments of the disclosure, wherein:

[00012] FIG. 1 shows an illustrative paraxylene production system from catalytic cracking C_4-C_{10+} stream with option to include reformate and pygas feedstock in accordance with an embodiment of the invention; and

[00013] FIG. 2 shows an illustrative paraxylene production system from catalytic cracking C_4-C_{10+} stream with option to include reformate and pygas feedstock and additional xylene formation systems for additional paraxylene production in accordance with an embodiment of the invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[00014] In the following description, certain details are set forth such as specific feedstock, quantities, temperature, etc. so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be obvious to those skilled in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such

details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[00015] Fluid catalytic cracking is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products. There are different variations of the technology for different purposes, and there is a trend to increase the cracking severity to increase propylene yield from the system. High-severity FCC is intended to increase olefin yields, driven by the fast growing global demand for propylene. The propylene yields can be increased from 3-5% in conventional FCC to 15-28% when these units are operated at high severity. In high-severity FCC operation, the aromatic content in the cracked naphtha product is 50-70%, which is suitable for aromatics recovery, but, it contains significant amounts of thiophenic sulfur impurities and is highly olefinic. For example, Sinopec/Shaw's Deep Catalytic Cracking (DCC) uses heavy hydrocarbon feedstocks, such as VGO, VR or VGO blended with DAO to produce light olefins (ethylene, propylene and butylenes), LPG, gasoline, and middle distillates etc.

[00016] Aromatics cannot be directly recovered at high purity by conventional distillation, because of the close-boiling components and azeotropes which form with the aromatics. Therefore, the aromatics are typically recovered by extraction with a selective solvent. This can be accomplished either by liquid-liquid extraction, or by extractive distillation. Extractive distillation offers better plant economics and flexibility, and is generally preferred for BTX purification.

[00017] Until recently, refiners did not consider recovering aromatics from FCC gasoline, because the extraction technology would not function with olefinic or sulfur impurities in the feed. The new technology is designed specifically to make this operation by extraction, which permits the direct recovery of aromatics, while rejecting the olefin-rich fraction as raffinate. The sulfur species are also extracted into the aromatic fraction, which are removed by hydrotreatment in the absence of olefins. Thus, there is very little hydrogen consumption and no octane loss. The hydrogenation unit is much smaller than conventional, and can be a simple HDS design or other means. The raffinate from the extraction unit can be sweetened in a conventional caustic unit, or used directly in the gasoline. However, the raffinate stream contains significant amount of olefins and is an ideal feedstock for aromatization process to produce aromatics.

[00018] The aromatization process takes olefinic hydrocarbon streams and produces BTX, with an aromatic yield approximating the concentration of olefins in the feed. This process technology will take any olefinic components in the C_4-C_9 range as feed to produce the aromatics. Byproducts are light paraffins and LPG off gases. The unit can take the FCC C_4 and C_5 cuts along with the C_6-C_9 raffinate from catalytic cracking naphtha extraction unit mentioned above as feed to add another aromatics increment.

[00019] In the process illustrated in FIG. 1, the catalytic cracking naphtha (C_{5+} stream) is first sent to a Separation Section 101, where C_5 and C_{10+} streams are separated from the rest by distillation. The C_6-C_9 stream is then sent to extraction zone to separate non-aromatics from aromatics. The extraction zone can use extractive distillation method or liquid-liquid extraction method. The C_4 stream from catalytic cracking unit and C6-C9 non-aromatics from Separation Section 101, along with other olefin rich feedstock (optional) are sent to the Aromatization Section 102 to produce aromatics. The Aromatization Section can contain one reactor or multiple reactors, and they can be fixed bed reactors or continuous regeneration (CCR) type reactor systems.

[00020] The aromatics from the Separation Section 101 and Aromatization Section 102 are sent to an Impurity Removal Section 103, which can be optional depending on the impurities presented in the combined aromatics feed to the section. The Impurity Removal Section 103 can include one or more of the following processes to remove different impurities: hydrogenation, adsorption, absorption, solvent extraction, etc.

[00021] The cleaned-up C_{6+} stream from 103 is fed to a second Separation Section 104 to separate benzene, toluene, xylenes, C_{9+}. Optionally, traditional C_{6+} feedstock can also be processed in this section, such as reformate and hydrotreated pygas. Usually C_6-C_7 streams are first separated by distillation and then fed to an aromatics extraction zone to separate non-aromatics from C_6 and C_7 aromatics. The separation of C_6-C_7 non-aromatics from aromatics can be done using an extractive distillation method, liquid-liquid extraction method, or other methods known to the industry. C_6-C_7 aromatics from the extraction zone can be further separated to obtain individual benzene and toluene product. C_8 and C_{9+} are also separated from the C_{6+} feed stream by distillation. Sometimes the C_6-C_8 stream is separated and fed to the aromatics extraction zone to purify C_6-C_8 aromatics. The C_{9+} stream can be used elsewhere and C_{8+} stream is sent to Paraxylene Production Section 105.

[00022] Production Section 105 includes two main zones: a paraxylene recovery zone and a xylene isomerization zone. The function of Paraxylene Production Section is to purify the paraxylene, and to convert non-paraxylene C8 aromatics to paraxylene. Two major methods can be used for paraxylene recovery: crystallization and adsorption. A third method is a combination of these two. Xylene isomerization zone can use EB-isomerization type of catalyst, or EB-dealkylation type of catalyst.

[00023] In the method illustrated in FIG. 2, it is similar to the method illustrated in Figure 1 except for the addition of Xylene Formation Section 106. The second Separation Section 104 can be optional and in this section C_9-C_{10+} stream is also separated from C9+ stream in the distillation zone, which can be used as feedstock for the Xylene Formation Section 106. The extraction zone in the second Separation Section 104 can be optional, as the C_6-C_7 stream is consumed in the downstream Xylene Formation Section and does not required high purity. The addition of the Xylene Formation Section allows utilization of the available benzene rings to form xylenes; the resulted xylenes are then recovered in the Paraxylene Production Section. One or more of the following technologies or processes (but not limited to) can be included in the Xylene Formation Section: benzene methylation, toluene methylation, benzene/toluene methylation, benzene/C_9-C_{10} transalkylation, toluene/C_9-C_{10} transalkylation, benzene/toluene/C_9-C_{10} transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP).

[00024] To save the number of pieces of equipment and investment cost, some of the equipment in one section can be shared with other sections. For example, the benzene and toluene columns in the distillation zone of the second Separation Section 104 can be shared with the transalkylation process in the Xylene Formation Section 106.

[00025] From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the disclosure to various usages and conditions. The embodiments described hereinabove are meant to be illustrative only and should not be taken as limiting of the scope of the disclosure, which is defined in the following claims.

CLAIMS

What is claimed is:

1. A process for producing paraxylene from light and heavy hydrocarbons, particularly C_4 stream and C_{5+} naphtha stream from catalytic cracking unit, said process comprising:

a) separating C_5 and C_{10+} from the C_{5+} catalytic naphtha and separating C_6-C_9 non-aromatics from C_6-C_9 aromatics;

b) forming aromatics from C_4-C_9 non-aromatics or a subset thereof, wherein the C_4-C_9 non-aromatics or the subset contains olefins;

c) removing impurities from the aromatics before they are sent to the downstream processes;

d) separating non-aromatics in the C_6-C_7 stream or C_6-C_8 stream to yield high purity aromatics, and to separate C_8 and C_{9+} streams; and

e) producing a high-purity paraxylene product.

2. The process of claim 1, wherein step a) includes a distillation step and an extraction step.

3. The process of claim 2, wherein said extraction step is carried out by using extractive distillation method or liquid-liquid extraction method.

4. The process of claim 1, wherein step b) is carried out in a single reactor or multiple reactors that are fixed bed reactors or continuous regeneration (CCR) type reactor systems.

5. The process of claim 1, wherein said C_4-C_9 non-aromatics or the subset in step b) contains 15-85 wt% olefins.

6. The process of claim 1, wherein the removing of impurities in step c) is carried out using hydrogenation, adsorption, absorption, or solvent extraction, or a combination thereof.

7 The process of claim 1, wherein the removing of impurities in step c) is optional.

8. The process of claim 1, wherein step d) includes a distillation step and an extraction step.

9. The process of claim 8, wherein said extraction step is carried out by using extractive distillation method, liquid-liquid extraction method, or other methods known to the industry.

10. The process of claim 1, wherein the production of paraxylene includes paraxylene recovery and xylene isomerization.

11. The process of claim 10, wherein paraxylene recovery is carried out by using a crystallization method or adsorption method or a combination thereof.

12. The process of claim 10, wherein xylene isomerization uses EB-isomerization type of catalyst or EB-dealkylation type of catalyst.

13. A process for producing paraxylene from light and heavy hydrocarbons, particularly C4 stream and C_{5+} naphtha stream from catalytic cracking unit, said process comprising:

a) separating C_5 and C_{10+} from the C_{5+} catalytic naphtha and separating C_6-C_9 non-aromatics from C_6-C_9 aromatics;

b) forming aromatics from C_4-C_9 non-aromatics or a subset thereof, wherein the C_4-C_9 non-aromatics or the subset contains olefins;

c) removing impurities to clean the aromatics before they are sent to the downstream processes;

d) producing a high-purity paraxylene product; and

e) producing xylenes from C_6, C_7, C_9-C_{10} aromatics.

14. The process of claim 13, wherein step a) includes a distillation step and an extraction step.

15. The process of claim 14, wherein said extraction step is carried out by using extractive distillation method or liquid-liquid extraction method.

16. The process of claim 13, wherein step b) is carried out in a single reactor or multiple reactors that are fixed bed reactors or continuous regeneration (CCR) type reactor systems.

17. The process of claim 13, wherein said C_4-C_9 non-aromatics or the subset in step b) contains 15-85 wt% olefins.

18. The process of claim 13, wherein the removing of impurities in step c) is carried out using hydrogenation, adsorption, absorption, or solvent extraction, or a combination thereof.

19. The process of claim 13, wherein the removing of impurities in step c) is optional.

20. The process of claim 13, wherein an optional second separation step is provided

downstream of step c) to separate C_6-C_7, C_8, C_9-C_{10}, and C_{11+} streams.

21. The process of claim 20, wherein the second separation step includes a distillation step and an extraction step.

22. The process of claim 21, wherein said extraction step is to separate non-aromatics in the C_6-C_7 stream or C_6-C_8 steam to yield high-purity aromatics.

23. The process of claim 21, wherein said extraction step is carried out by using extractive distillation method, liquid-liquid extraction method, or other methods known to the industry.

24. The process of claim 13, wherein the production of paraxylene includes paraxylene recovery and xylene isomerization.

25. The process of claim 24, wherein paraxylene recovery is carried out by using a crystallization method or adsorption method or a combination thereof.

26. The process of claim 24, wherein xylene isomerization uses EB-isomerization type of catalyst or EB-dealkylation type of catalyst.

27. The process of claim 13, wherein the production of xylenes uses benzene methylation, toluene methylation, benzene/toluene methylation, benzene/C_9-C_{10} transalkylation, toluene/C_9-C_{10} transalkylation, benzene/toluene/C_9-C_{10} transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP) or a combination thereof.

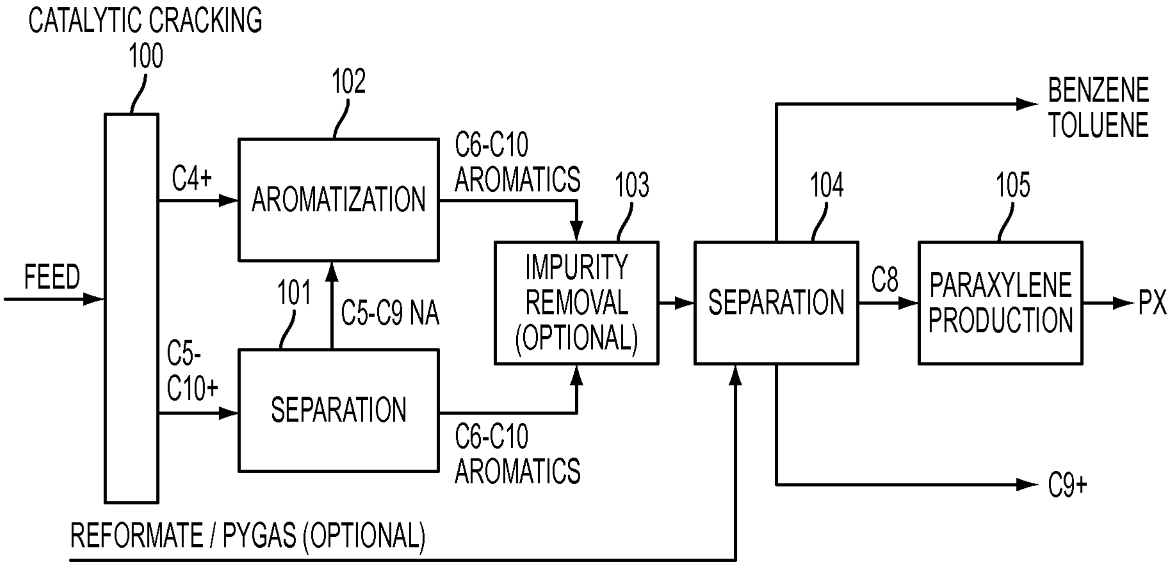
CATALYTIC CRACKING
100
102
AROMATIZATION
C4+
C6-C10 AROMATICS
103
FEED
101
C5-C9 NA
IMPURITY REMOVAL (OPTIONAL)
C5-C10+
SEPARATION
C6-C10 AROMATICS
104
SEPARATION
BENZENE TOLUENE
C8
105
PARAXYLENE PRODUCTION
PX
C9+
REFORMATE / PYGAS (OPTIONAL)

FIG. 1

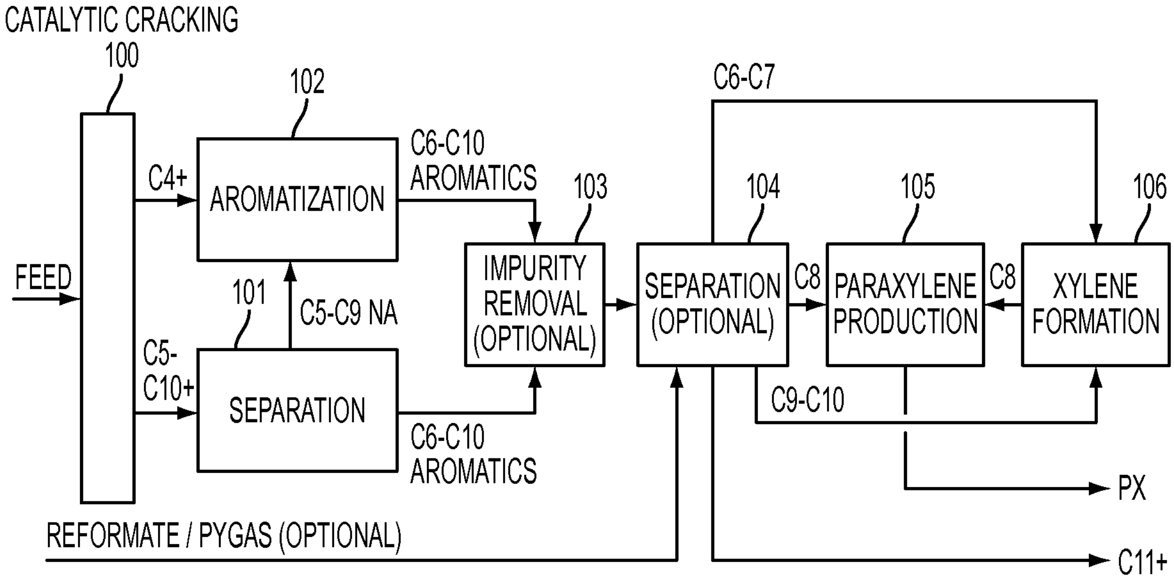
CATALYTIC CRACKING
100
102
AROMATIZATION
C4+
C6-C10 AROMATICS
103
FEED
101
C5-C9 NA
IMPURITY REMOVAL (OPTIONAL)
C5-C10+
SEPARATION
C6-C10 AROMATICS
C6-C7
104
SEPARATION (OPTIONAL)
C8
105
PARAXYLENE PRODUCTION
C8
106
XYLENE FORMATION
C9-C10
PX
C11+
REFORMATE / PYGAS (OPTIONAL)

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/31146

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C10G 35/00 (2013.01)
USPC - 585/450
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)
USPC - 585/450

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - all classes; NPL (key word limited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase; Google Scholar
Search terms: Paraxylene, naphtha, stabilizing, heavy, fraction, distillation, extractive, distillation, olefinic, feed, JIN, Weihua, DING, Zhongyi, CRETOIU, Mircea, GENTRY, Joseph, LOCKHART, Mark, SHYAMKUMAR, Calambur, WANG, Pinti

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,004,452 A (Ash et al.) 21 December 1999 (21.12.1999); col 5, ln 55-57; col 7, ln 20-24; col 8, ln 13-15;	1-27
Y	US 5,609,751 A (Wall) 11 March 1997 (11.03.1997); col 7, ln 35-37	1-27
Y	US 2011/0319688 A1 (Ou) 29 December 2011 (29.12.2011); para [0039], [0045], [0054]	12 and 26

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"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 01 May 2013 (01.05.2013)	Date of mailing of the international search report 23 MAY 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774