



(51) International Patent Classification:

C10G 7/00 (2006.01) C10G 45/58 (2006.01)
C10G 45/02 (2006.01) C10G 47/00 (2006.01)

(21) International Application Number:

PCT/EP2016/059503

(22) International Filing Date:

28 April 2016 (28.04.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PA 2015 70246 28 April 2015 (28.04.2015) DK

(71) Applicant: HALDOR TOPSØE A/S [DK/DK]; Haldor
Topsøes Allé 1, 2800 Kgs. Lyngby (DK).

(72) Inventors: KNUDSEN, Arne; Holsteinsgade 11, 1.th,
2100 Copenhagen Ø (DK). NIELSEN, Jan Due; c/o
Haldor Topsøe A/S, Haldor Topsøes Allé 1, 2800 Kgs.
Lyngby (DK). MENJON, Ian; Rønnegade 14, 5th, 2100
Copenhagen Ø (DK).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,

KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: HEAVY GASOLINE SEPARATION

(57) Abstract: The present relates to a plant and a process for treating raw gasoline, said process comprising the steps of (1) In a first splitter separating a raw gasoline stream into at least a first light fraction, a first durenene rich fraction and a heavy gasoline fraction, and (2) In a second splitter separating the first durenene rich fraction into a second light fraction and a second durenene rich fraction.



Title: Heavy gasoline separation

In the MTG processes, raw gasoline, light ends, LPG and water are produced from methanol. The majority of the raw gasoline is already within the gasoline range with relatively good product properties, but some fraction is too heavy or contains too much durene and therefore it needs to be treated.

10 Treatment of the raw gasoline may be achieved by a process for treating raw synthetic gasoline, said process comprising the steps of

- In a first splitter separating a raw gasoline stream into at least a first light fraction, a first durene rich fraction and a heavy gasoline fraction, and
- 15 - In a second splitter separating the first durene rich fraction into a second light fraction and a second durene rich fraction.

20 By splitting the first durene rich fraction in a second splitter it is possible to have detailed control of the composition of the second durene rich fraction. Depending on the use and further treatment of the second durene rich fraction in may be highly advantageous to have a reduced content of light gasoline in the second durene rich fraction.

25

The first light fraction may be ready for blending in the gasoline product pool.

30

The present setup with the second splitter may advantageously be applied in relation to a gasoline upgrading unit

(GUU) i.e. where the second durene rich gasoline fraction is sent to a gasoline upgrading unit in which the second durene rich fraction is upgraded to an upgraded product stream. If light gasoline is sent to the GUU it may negatively contribute to a lower product yield and a higher gas/LPG yield due to cracking/de-alkylation reactions in the GUU. Therefore the second splitter and separation of the first durene rich fraction into a second durene rich fraction and second light fraction is advantageously applied as it ensures that a good separation is achieved and an optimized stream (second durene rich fraction) is sent to the GUU.

From the GUU an upgraded product stream and a third LPG stream is withdrawn.

In the GUU the durene content may be reduced and the octane number increased in the upgraded product stream compared to the second durene rich gasoline fraction. Reduced durene content and/or increased octane number may be an advantage as durene may negatively influence cloud point and increased octane number may provide a better fuel.

In several embodiments the durene rich gasoline fraction is subject to isomerization, (mild) hydrotreatment and/or (mild) hydrocracking in the gasoline upgrading unit (GUU).

A stabilization step (such as mild hydrocracking) may also take place in the GUU. Stabilization may e.g. be carried out by stripping (e.g. with steam, N₂, LPG) and/or by distillation in the GUU.

I.e. the GUU may comprise at least one reaction step and at least one stabilization step.

The first splitter comprises a number of stages for example
5 5 - 50 stages, such as 10 - 30 stages, such as 15 - 20
stages. More stages provide a more refined separation and
fewer stages results in a more crude separation which for
example may result in more light components in the heavy
fraction and/or the need to recycle more heavy components
10 separated from the first light fraction to the first split-
ter.

Preferably, the first durene rich stream is separated from
the first splitter in the rectification zone. For example
15 the first durene rich fraction may be separated from the
first splitter in a centre zone of the splitter such as at
or near one or more middle stages. If e.g. the first split-
ter comprises 16 stages, the first durene rich stream may
be separated near the 6th - 10th stage, such as by the 8th
20 stage.

By selecting the point of separation from the first split-
ter it is possible to adjust the composition of the first
durene rich fraction.

25

If the first durene rich stream is separated from the first
splitter in order to maximize 1,2,4-trimethylbenzene and/or
durene in the second durene rich stream sent to the GUU it
may be possible to optimize its operation.

30

Also the first durene rich stream may be separated from the
first splitter in order to minimize the concentration of

xylenes since xylenes may de-alkylate in an isomerization reactor which entails a yield loss.

Thus, the present invention may advantageously be used in relation to synthetic raw gasoline as the composition of the synthetic raw gasoline may be well known whereby the specific components to be separated from the first splitter into the first durene rich stream can be selected as described above.

In some embodiments the heavy gasoline constitutes a no sulfur fuel.

The present application also relates to a plant for treating raw gasoline comprising

- A first splitter wherein raw gasoline is separated into a light fraction, a durene rich gasoline fraction and a heavy gasoline fraction
- A second splitter wherein the durene rich gasoline fraction is separated into a second light fraction and a second durene rich stream
- A GUU for upgrading the second durene rich stream into a upgraded product.

The plant may further be arranged so that the first durene rich stream is separated from the first splitter in order to maximize 1,2,4-trimethylbenzene and/or durene and/or in order to minimize the concentration of xylenes in the second durene rich stream sent to the GUU.

Thus, according to the present process and plant the second durene rich fraction is sent to the gasoline upgrading unit

(GUU), thus minimizing the LPG production and allowing a better control of the final boiling point of the final product.

5 The invention is further illustrated in the drawings

Fig. 1 illustrates the process flow and simplified plant layout.

10 Fig. 2 Illustrates Concentration curves in the first splitter.

The drawings are exemplary and are not to be construed as limiting to the invention.

15 Figure 1 illustrates the process flow and plant. The stabilized gasoline [1] is separated in a first gasoline splitter distillation column [11] into a first light fraction (IBP ~ 165°C) [5] which is ready for product blending, a first durenene rich fraction (138- 198°C) [8] and a heavy
20 gasoline fraction (195 - 260°C) [9].

The gas phase (first light fraction) leaves the overhead [2] and is condensed [12] and recovered [13]. A reflux pump [14] is typically used to return the liquid to the column
25 [4] and/or to send the first light gasoline fraction to storage and/or blending.

If light gasoline is sent to the GUU [18] it may negatively contribute to a higher gas/LPG yield due to cracking and/or
30 de-alkylation reactions, therefore a second splitter (side column) [15] ensures that a good separation is achieved. A

reboiler [17] supplies the heat input for the separation in the gasoline splitter.

5 The first durene rich fraction [6], which typically constitutes a ~25 wt% of the stabilized gasoline, is sent to a second splitter (side column) where the gas phase [7] is returned to the first splitter and a second durene rich fraction is taken from the bottom. A reboiler [16] may be used to supply the necessary heat input to drive the separation.
10

The second durene rich fraction is sent to a GUU where durene content is reduced and/or octane number (RON, MON) is increased.
15

In the GUU Durene may be isomerized to other types of tetra-methylbenzenes and/or de-alkylate to trimethyl benzenes. Tri methylbenzenes may be isomerized to other types of trimethylebenzenes and/or de-alkylate to xylenes and/or toluene and/or benzene. Gases may be produced as a consequence (C1-C4).
20

The heavy gasoline fraction may e.g. be used as a no-sulfur fuel or sent to post treatment.
25

Fig 2 illustrates where the first durene rich fraction may be taken from the first separator based on the concentrations of various components. The curves are normalised and the values on the x-axis is tray number, i.e. the present example is for a 16 tray column. Concentration curves are indicated by A, B, C. For example the first durene rich stream may advantageously be separated from the first
30

splitter at or near (e.g. +/- 1 or +/- 2) the 8th tray, as this point may result in a first durene rich fraction which is relatively low in Xylenes (A) while containing a substantial amount of the desired components (B, C) for example tetra-methlybenzenes (incl. durene) and 1,2,4-trimethylbenzene.

Claims

1. Process for treating raw gasoline, said process comprising the steps of
 - In a first splitter separating a raw gasoline stream into at least a first light fraction, a first durenene rich fraction and a heavy gasoline fraction, and
 - In a second splitter separating the first durenene rich fraction into a second light fraction and a second durenene rich fraction.
2. Process for treating raw gasoline according to claim 1 wherein the first light fraction is ready for blending.
3. Process for treating raw gasoline according to any of the preceding claims, wherein the second durenene rich gasoline fraction is sent to a gasoline upgrading unit wherein the second durenene rich fraction is upgraded to an upgraded product.
4. Process for treating raw gasoline according to any of the preceding claims, wherein the durenene content is reduced and the octane number increased in the upgraded product stream compared to the second durenene rich gasoline fraction.
5. Process for treating raw gasoline according to any of the preceding claims, wherein the second durenene rich gasoline fraction is subject to isomerization, (mild)

hydrotreatment and/or hydrocracking in the gasoline upgrading unit.

- 5 6. Process for treating raw gasoline according to any of the preceding claims, wherein the first durene rich stream is separated from the first splitter in order to maximize 1,2,4-trimethylbenzene and/or durene in the second durene rich stream sent to the GUU.
- 10 7. Process for treating raw gasoline according to any of the preceding claims, wherein the first durene rich stream is separated from the first splitter in order to minimize the concentration of xylenes in the second durene rich stream sent to the GUU.
- 15 8. Process for treating raw gasoline according to any of the preceding claims, wherein the heavy gasoline constitutes a no sulfur fuel.
- 20 9. Plant for treating raw gasoline comprising
- A first splitter wherein raw gasoline is separated into a first light fraction, a first durene rich fraction and a heavy gasoline fraction
 - A second splitter, wherein the first durene rich gasoline fraction is separated into a second light fraction
 - A GUU for upgrading the second durene rich fraction into an upgraded product.
- 25
- 30 10. A plant according to claim 9, wherein the first durene rich stream is separated from the first split-

ter in order to maximize 1,2,4-trimethylbenzene and/or
durene in the second durene rich stream sent to the
GUU.

- 5 11. A plant according to claim 9 or 10, wherein the
first durene rich stream is separated from the first
splitter in order to minimize the concentration of xy-
lenes in the second durene rich stream sent to the
GUU.

Fig. 1

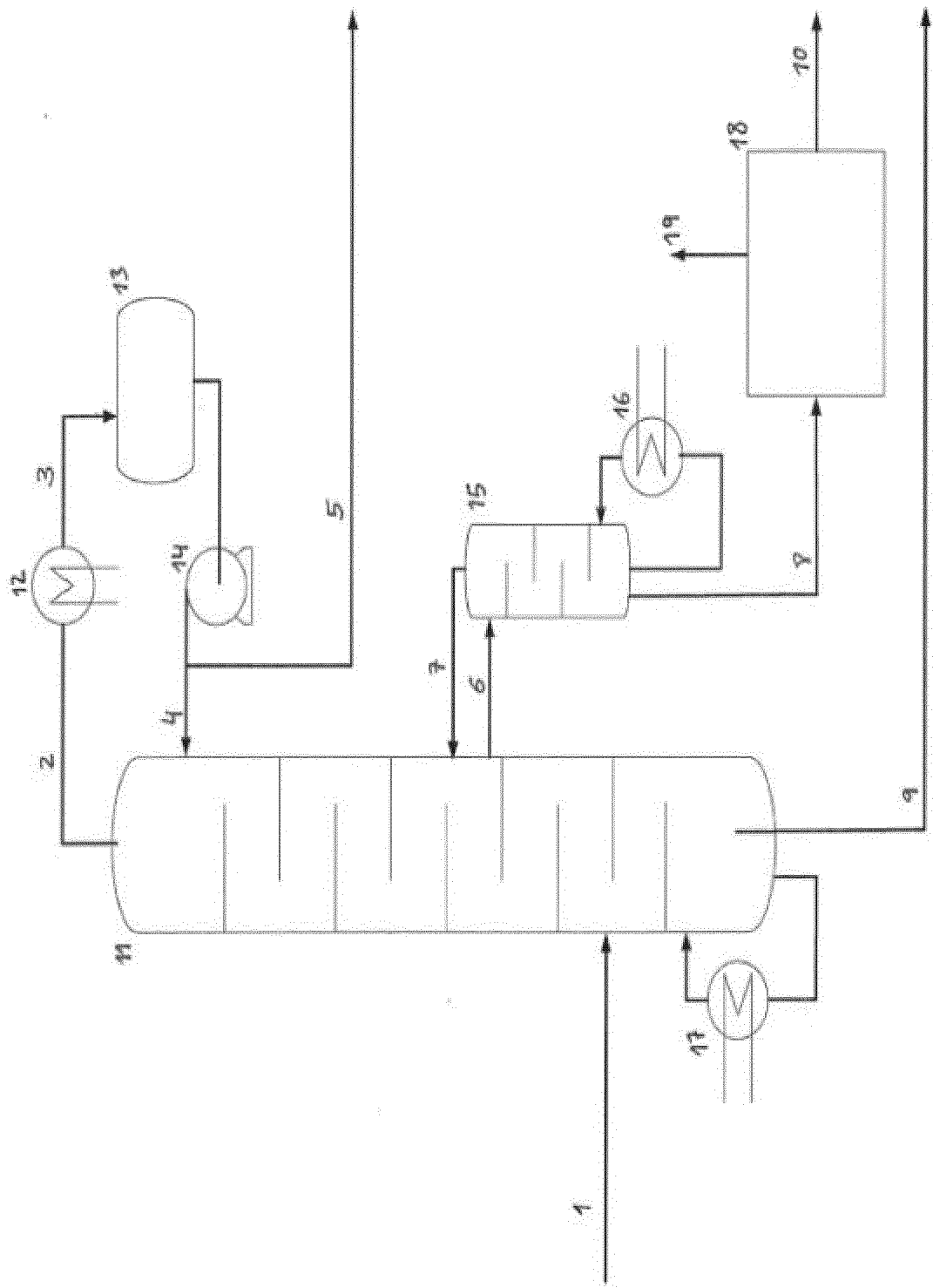
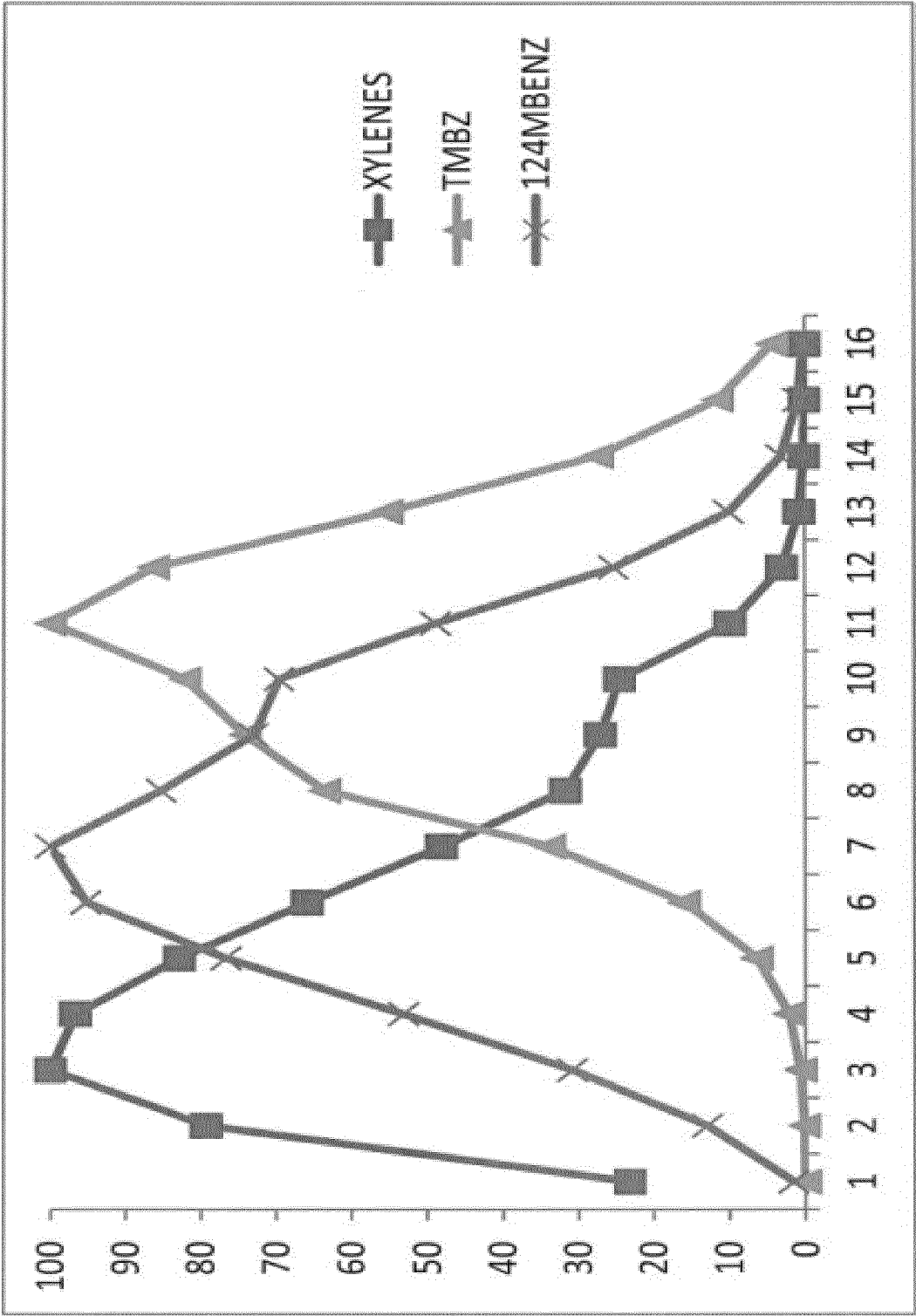


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059503

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G7/00 C10G45/02 C10G45/58 C10G47/00
ADD.

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

B. FIELDS SEARCHED

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

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/094510 A1 (HIDALGO VIVAS ANGELICA [DK] ET AL) 2 April 2015 (2015-04-02) paragraphs [0001], [0018] - [0020], [0033] -----	1-8
Y	US 4 304 951 A (GARWOOD WILLIAM E ET AL) 8 December 1981 (1981-12-08) column 2, lines 5-18 -----	1-8
X	US 2 348 815 A (FRANCIS HORTON ET AL) 16 May 1944 (1944-05-16) page 2, left-hand column, lines 9-49; figure 1 -----	9-11
Y		1-8
X	GB 1 408 758 A (SHELL INT RESEARCH) 1 October 1975 (1975-10-01) page 4, lines 63-84; figure XII -----	9-11
Y		1-8
	-/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent 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

10 June 2016

Date of mailing of the international search report

27/06/2016

Name and mailing address of the ISA/

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

Authorized officer

Pardo Torre, J

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059503

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 950 387 A (HARANDI MOHSEN N [US] ET AL) 21 August 1990 (1990-08-21)	9-11
A	figure 1 claims 1-11	1-8

X	US 2 239 965 A (HUFF LYMAN C) 29 April 1941 (1941-04-29)	9-11
A	figure 1 claims 1-3	1-8

X	US 4 747 933 A (HIBBS FREDERICK M [GB]) 31 May 1988 (1988-05-31)	9-11
A	figure 1 claims 1-16	1-8

A	CN 103 351 887 A (CHANGSHU ALLIANCE CHEMICAL CO LTD) 16 October 2013 (2013-10-16)	1-11
	figure 1 claims 1-7	

A	US 4 524 227 A (FOWLES PATRICK E [US] ET AL) 18 June 1985 (1985-06-18)	1-11
	claim 1 claims 1-9	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/059503

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015094510	A1	02-04-2015	AR 091162 A1 14-01-2015
		AU 2013269955 A1 18-12-2014	
		CA 2873955 A1 05-12-2013	
		CN 104334693 A 04-02-2015	
		EA 201492151 A1 30-09-2015	
		US 2015094510 A1 02-04-2015	
		WO 2013178375 A1 05-12-2013	
US 4304951	A	08-12-1981	AU 546183 B2 22-08-1985
		AU 7761081 A 22-07-1982	
		CA 1152923 A 30-08-1983	
		DE 3171838 D1 19-09-1985	
		EP 0057786 A2 18-08-1982	
		JP H03436 B2 08-01-1991	
		JP S57117589 A 22-07-1982	
		NZ 199000 A 31-01-1985	
		US 4304951 A 08-12-1981	
		ZA 8108036 A 27-07-1983	
US 2348815	A	16-05-1944	NONE
GB 1408758	A	01-10-1975	NONE
US 4950387	A	21-08-1990	AU 632077 B2 17-12-1992
		AU 4683989 A 20-06-1991	
		CA 2004905 A1 07-06-1991	
		EP 0432327 A1 19-06-1991	
		JP H03195798 A 27-08-1991	
		US 4950387 A 21-08-1990	
US 2239965	A	29-04-1941	NONE
US 4747933	A	31-05-1988	DE 3882222 T2 28-04-1994
		EP 0337026 A1 18-10-1989	
		ES 2043814 T3 01-01-1994	
		US 4747933 A 31-05-1988	
CN 103351887	A	16-10-2013	NONE
US 4524227	A	18-06-1985	NONE