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(71) Applicant: **SAUDI ARABIAN OIL COMPANY**
[SA/SA]; Post Office Box 5000, Dhahran, 31311 (SA).

(71) Applicant (for AG only): **ARAMCO SERVICES COMPANY** [US/US]; 9009 West Loop Road, Houston, Texas 77210-4535 (US).

(72) Inventors: **CHOI, Ki-Hyouk**; c/o Saudia Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA).
ALABDULHADI, Abdullah T.; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA).
ALABDULLAH, Mohammad A.; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA).

(74) Agent: **MOLLOY, Matthew A.** et al.; Dinsmore & Shohl LLP, One South Main Street, Fifth Third Center - Suite 1300, Dayton, Ohio 45402 (US).

(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, DJ, DK, DM, DO,

(54) Title: SUPERCRITICAL REACTOR SYSTEMS AND PROCESSES FOR PETROLEUM UPGRADING

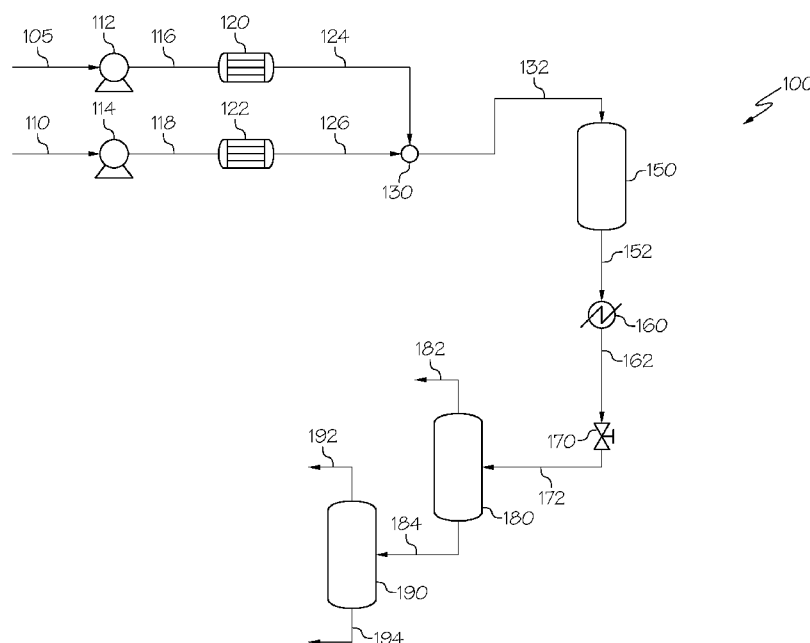


FIG. 1

(57) Abstract: Supercritical upgrading reactors and reactor systems for upgrading a petroleum-based compositions comprising one or more catalyst layers and, in some embodiments, one or more purging fluid inlets, where one or more catalyst layers at least partially sift and convert heavy hydrocarbon fractions to light hydrocarbon fractions to produce an upgraded supercritical reactor product. In some embodiments, upgrading reactor systems comprise one or more supercritical upgrading reactors and one or more supercritical standby reactors alternating functions such that a supercritical upgrading reactor is converted to a supercritical standby reactor and the supercritical standby reactor is converted to a supercritical upgrading reactor, where the supercritical upgrading reactor upgrades a combined feed stream while a supercritical standby reactor delivers a cleaning fluid into the supercritical standby reactor.

DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, 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.

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Declarations under Rule 4.17:

- *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))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/066367

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J3/00 C10G31/08 C10G75/00
 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)

B01J 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.
X	WO 2008/055152 A1 (CHEVRON USA INC [US]; HE ZUNQING [US]; LI LIN [US]; LI LIXIONG [US]; Z) 8 May 2008 (2008-05-08) page 8, lines 28-34 page 10, lines 26-27 page 11, lines 10-14, 25-28 claim 1 figure 1	1-25, 28-38
X	GB 1 298 904 A (CHEVRON RES [US]) 6 December 1972 (1972-12-06)	39-67
A	claims 1, 2, 3, 6 page 3, lines 11-54	1-5,7-25
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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

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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

Ruiz Martínez, C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/066367

Box No. 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 No. 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 fees, this Authority did not invite payment of additional fees.
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 and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/066367

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA 2 938 409 A1 (BAKER HUGHES INC [US]) 13 August 2015 (2015-08-13) paragraph [0002] claim 1 figure 1 -----	1-5, 7-25, 39-41, 43-47, 50-67
X	US 2006/260927 A1 (ABAZAJIAN ARMEN [US]) 23 November 2006 (2006-11-23)	26,27
A	paragraph [0030] -----	28-38
X	US 6 306 287 B1 (BILLON ALAIN [FR] ET AL) 23 October 2001 (2001-10-23)	26,27
A	figure 1 claim 1 -----	28-38
X	US 2009/139902 A1 (KRESSMANN STEPHANE CYRILLE [SA] ET AL) 4 June 2009 (2009-06-04)	26,27
A	paragraph [0060] -----	28-38
A	WO 2013/033301 A2 (EXXONMOBIL RES & ENG CO) 7 March 2013 (2013-03-07) paragraphs [0095], [0096]; claim 1 -----	1-5, 7-25, 39-41, 43-47, 50-67

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/066367

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		WO 2013033301 A2	07-03-2013

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 1-5, 13-23, 28-41, 50-53, 60-67(completely); 7-12, 24, 25, 43-47, 54-59(partially)

Process for upgrading a petroleum-based composition comprising: combining a supercritical water stream with a pressurized, heated petroleum-based composition in a mixing device to create a combined feed stream, introducing the combined feed stream into an upgrading reactor system comprising one or more downflow supercritical upgrading reactors operating at a temperature greater than a critical temperature of water and a pressure greater than a critical pressure of water, where the downflow supercritical upgrading reactor comprise at least one catalyst layer, where the at least one catalyst layer is a heterogeneous porous metal containing catalyst having a void volume ratio, and where the downflow supercritical upgrading reactor includes at one or more purging fluid inlet disposed on one or more side locations of the downflow supercritical upgrading reactor proximate the catalyst layer; passing the combined feed stream through the catalyst layer, where light hydrocarbons in the combined feed stream at least partially flow through the catalyst layer while heavy hydrocarbons in the combined feed stream are at least partially sifted in the voids of the catalyst layer, or both; at least partially converting the blocked heavy hydrocarbons to light hydrocarbons in the catalyst layer in the presence of the supercritical water; injecting purging fluid through the purging inlets to contact the first catalyst layer, the second catalyst layer, or both to reduce plugging; and passing upgraded product comprising light hydrocarbons and the converted light hydrocarbons out of the downflow supercritical upgrading reactor.
Reactor used in the aforementioned process of upgrading a petroleum-based composition.

2. claims: 6, 42, 48, 49(completely); 7-12, 24, 25, 43-47, 54-59(partially)

- Process for upgrading a petroleum-based composition comprising: combining a supercritical water stream with a pressurized, heated petroleum-based composition in a mixing device to create a combined feed stream, introducing the combined feed stream into an upgrading reactor system comprising at least one supercritical upgrading reactor operating at a temperature greater than a critical temperature of water and a pressure greater than a critical pressure of water, where the supercritical upgrading reactor comprises a first catalyst layer and a second catalyst layer, the second catalyst layer disposed vertically below the first catalyst layer in the supercritical upgrading reactor where the first catalyst layer is a heterogeneous

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

porous metal containing catalyst having a first void volume ratio and the second catalyst layer is a heterogeneous porous metal containing catalyst having a second void volume ratio, and where the second void volume ratio is lesser than the first void volume ratio, passing the combined feed stream through the first catalyst layer and the second catalyst layer, where light hydrocarbons in the combined feed stream at least partially flow through the first catalyst layer and the second catalyst layer while heavy hydrocarbons in the combined feed stream are at least partially sifted in voids of the first catalyst layer, voids of the second catalyst layer, or both; at least partially converting the sifted heavy hydrocarbons to light hydrocarbons in the first catalyst layer or the second catalyst layer in the presence of the supercritical water; passing upgraded product comprising light hydrocarbons and the converted light hydrocarbons out of the supercritical upgrading reactor.

- Reactor used in the aforementioned process of upgrading a petroleum-based composition.

3. claims: 26, 27

Supercritical upgrading reactor system comprising: one or more supercritical upgrading reactors and one or more supercritical upgrading standby reactors; and one or more controllers coupled to at least one of the one or more supercritical upgrading reactors and at least one of the one or more supercritical standby reactors, in which the controller allows the supercritical upgrading reactor and the supercritical standby reactor to alternate functions, such that the supercritical standby reactor is converted to a supercritical upgrading reactor that upgrades a combined feed stream and the supercritical upgrading reactor is converted to a supercritical standby reactor that performs a cleaning operation by the delivery of a cleaning fluid.
