(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
04 January 2018 (04.01.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/002838 A1

(51) International Patent Classification:
C07C 1/04 (2006.01) *C07C 27/00* (2006.01)

(21) International Application Number:
PCT/IB2017/053865

(22) International Filing Date:
28 June 2017 (28.06.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201621022322 29 June 2016 (29.06.2016) IN

(71) Applicant: **RELIANCE INDUSTRIES LIMITED** [IN/IN]; 3rd Floor Makers Chamber-IV, 222, Nariman Point, Mumbai, Maharashtra 400021 (IN).

(72) Inventors: **BHATT, Ujjval Bhadrashankar**; B - 607 Mahavir Vaibhav Chs, Plot 13, sector 11, Kopar khairane Navi Mumbai, Maharashtra 400709 (IN). **KALANTRI, Pravin Badrinarayan**; 402 Charleville, A-Road, Churchgate Mumbai, Maharashtra 400020 (IN). **KELKAR, Jayant Vishnu**; 602-B Govind Complex, Sector 14 Vashi Navi Mumbai, Maharashtra 400703 (IN). **DINGANKAR, Shridhar Bhalchandra**; 1303 Siddhachal Ph. V, Off. Pokhran Road no. 2 Thane, Maharashtra 400610 (IN).

(74) Agent: **DEWAN, Mohan**; R. K. Dewan & Co. Podar Chambers, S. A. Brelvi Road, Fort, Mumbai, Maharashtra 400001 (IN).

(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, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, 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.

(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,

(54) Title: AN IMPROVED PROCESS FOR PRODUCING OLEFINS FROM SYNGAS

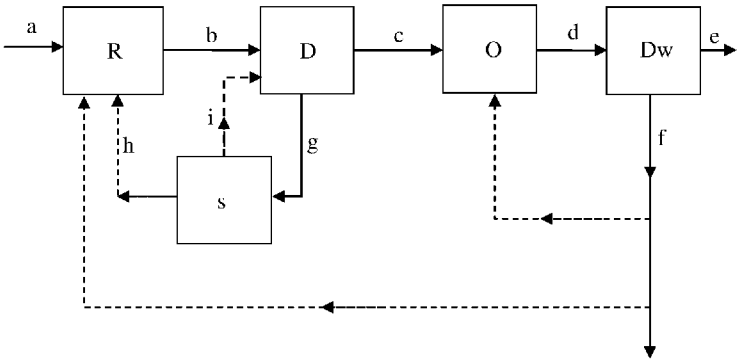


Figure 2

(57) Abstract: The present disclosure relates to an improved process for producing olefins from syngas. Raw material is treated to produce syngas comprising H_2, CO and CO_2. The ratio of H_2 and CO in the syngas is 1:1. The syngas is contacted with at least one first catalyst to produce an intermediate stream comprising dimethyl ether (DME), and unconverted CO_2, H_2 and CO. The unconverted H_2 and CO is recycled to a first catalyst section and a portion of the separated CO_2 is recycled for producing the syngas. The remaining intermediate stream is contacted with at least one second catalyst to produce a second stream comprising olefins, H_2O, methane, ethane, and propane. H_2O, methane, ethane, and propane are separated to obtain the olefins. The separated methane, ethane, and propane are further recycled for producing the syngas. The CAPEX and OPEX of the improved process are reduced.

WO 2018/002838 A1

[Continued on next page]

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))*
— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

AN IMPROVED PROCESS FOR PRODUCING OLEFINS FROM SYNGAS

FIELD

The present disclosure relates to an improved process for producing olefins from syngas.

BACKGROUND

Syngas is generally a mixture of hydrogen (H_2), carbon monoxide (CO). However, due to process inefficiency, carbon dioxide (CO_2) is also produced along with syngas. Syngas can be used in a variety of applications such as production of methanol, production of dimethyl ether (DME), production of olefins, production of ammonia, production of urea, heating, generation of steam and generation of power. Syngas can be produced by utilizing methane or natural gas, liquid fuels or solid fuels such as coal, petcoke, biomass, solid wastes, and the like.

The following reactions or processes illustrate the production of syngas:

i. steam reforming:
$CH_4 + H_2O = CO + 3H_2$;

ii. partial oxidation:
$2CH_4 + O_2 = 2CO + 4H_2$;

iii. coal gasification:
$3C + O_2 + H_2O = 3CO + H_2$;

iv. dry reforming:
$CH_4 + CO_2 = 2CO + 2H_2$; and

v. water-gas shift reaction:
$CO + H_2O \rightleftharpoons H_2 + CO_2$

The ratio of H_2 and CO in syngas varies depending upon the raw materials used and the process or reaction conditions used for producing syngas.

Figure 1 depicts a flow-path, illustrating a conventional process for producing olefins from syngas. Syngas (1) is first converted into methanol (3), and then methanol is converted into olefins. For the production of methanol, syngas (1) comprising 2:1 ratio of H_2 and CO is used. Syngas (1) is introduced into a water-gas shift reactor/section (50), wherein the

proportion of H_2 can be increased. Since the amount of CO_2 (2) produced during the production of syngas (1) is significant, in order to meet the requirement of 2:1 ratio of H_2 and CO, there is a need to separate CO_2 (2) from the syngas (1). Therefore, the syngas (1) from the water-gas shift reactor/section (50) is introduced into a separator (100). After the separation of CO_2 (2), the syngas (1), which is deficient of CO_2, is introduced into a reactor (200) for producing methanol (3). The reaction for producing methanol (3) is depicted herein below:

$$2H_2 + CO = CH_3OH \text{ (methanol)}$$

Methanol (3) is then introduced into a reactor (300), wherein methanol (3) is dehydrogenated to produce a stream (4) comprising olefins (5), unconverted DME (6) and H_2O (7) in the reactor (300). The stream (4) is further introduced into a separator (400) for separating unconverted DME (6) and H_2O (7) from stream (4) to obtain olefins (5). The separated H_2O (7) and the unconverted DME (6) can be further utilized for producing syngas (1) and olefins (5) respectively.

Moreover, the amount of CO_2 produced during this process is significant because:

- CO_2 is present in syngas; and
- syngas with low H_2 and high CO needs to be converted to syngas comprising 2:1 ratio of H_2 and CO. This can be done by water-gas shift, wherein CO is reacted with water to generate H_2, and CO_2 as a by-product.

A separate process equipment is required for separating carbon dioxide from syngas. Also, the amount of energy required to separate carbon dioxide from syngas is more due to the presence of a significant amount CO_2 in syngas. This increases the capital expenditure (CAPEX) and operational expenditure (OPEX) of the conventional process for producing olefins.

Moreover, syngas comprising 2:1 ratio of H_2 and CO results in the conversion of syngas to methanol at a particular temperature (in the range of 300°C to 400°C) and pressure (in the range of 60 bar to 90 bar) conditions, thereby requiring a reactor for producing methanol. Also, different process equipment like heaters and compressors are required for achieving the specific temperature and pressure conditions in the reactor. This results in further increase in the capital expenditure (CAPEX) and operational expenditure (OPEX) of the conventional process for producing olefins.

Therefore, there is a need for a process for producing olefins with reduced generation and possible utilization of CO_2. Further, there is a need for a process for producing olefins with reduced CAPEX and OPEX of the process, which minimizes the multiple reactors operating at different temperature and pressure conditions.

OBJECTS

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows.

An object of the present disclosure is to provide a process with reduced generation of CO_2.

Yet another object of the present disclosure is to provide a process which can inherently consume less energy along with elimination of equipment/process conditions for the intermediate process.

Yet another object of the present disclosure is to separate CO_2 post the DME production to minimize the energy need for separation.

Still another object of the present disclosure is to efficiently utilize separated streams like CO_2, methane, ethane, and propane to produce syngas.

Another object of the present disclosure is to provide a process for producing olefins with reduced CAPEX and OPEX of the process.

Other objects and advantages of the present disclosure will be more apparent from the following description, which is not intended to limit the scope of the present disclosure.

SUMMARY

The present disclosure envisages a process for producing olefins from syngas comprising H_2, CO and CO_2. Typically, the ratio of H_2 and CO of the syngas (first stream), is 1:1. The syngas is contacted with at least one first catalyst, at a pre-determined temperature and at a pre-determined pressure, to produce an intermediate stream comprising dimethyl ether (DME) and unconverted CO_2, H_2 and CO. The unconverted H_2 and CO is recycled to a first catalyst section, and a portion of the separated CO_2 is recycled for producing the syngas. The remaining intermediate stream is further contacted with a second catalyst, at a pre-determined temperature and at a pre-determined pressure, to produce a second stream comprising olefins,

H_2O, methane, ethane, and propane. H_2O, methane, ethane, and propane are separated from the second stream to obtain olefins. The separated CO_2, H_2O, methane, ethane, and propane are further recycled for producing the syngas.

The olefins can be at least one of ethylene and propylene.

The process of the present disclosure reduces the generation of CO_2.

The process of the present disclosure also reduces the CAPEX and the OPEX of the entire process.

BRIEF DESCRIPTION OF ACCOMPANYING DRAWING

A process for producing olefins from a gaseous mixture will now be described with the help of the accompanying drawing, in which:

Figure 1 depicts a flow-path, illustrating a conventional process for producing olefins; and

Figure 2 depicts a flow-path for producing olefins in accordance with the present disclosure.

Table 1 provides a list the elements of the process of the present disclosure and their respective reference letters:

Table 1

Elements	**Reference letters**
Raw material	(a)
Gasifier/reformer	(R)
First stream (Syngas)	(b)
DME (dimethyl ether) reactor	(D)

Intermediate stream	(c)
Separator	(s)
Separated portion	(g)
Separated CO_2	(h)
Separated H_2 and CO	(i)
Reactor	(O)
Second stream	(d)
Fractionation column or divided wall column	(Dw)
Olefins	(e)
Separated stream	(f)

DETAILED DESCRIPTION

2:1 ratio of H_2 and CO in syngas leads to generation of an excess amount of CO_2, and an excess use of H_2O. Moreover, for economic viability of the methanol production process, CO_2 should be minimum or nil in the feed. Therefore, it is necessary to completely separate or remove CO_2. Separation of CO_2 requires bigger separation units, which consume a significant amount of energy, and H_2O passes through all the equipment due to which the size of the equipment increases, thereby increasing the CAPEX and OPEX of the entire process.

The present disclosure, therefore, provides an improved process for producing olefins with reduced generation of CO_2 and with reduced CAPEX and OPEX of the entire process.

The process for producing olefins is illustrated with reference to **Figure 2**. Raw material (a) is treated in a gasifier/reformer (R), typically at a temperature in the range of 300°C to 1000°C and at a pressure in the range of 1 kg/cm^2 to 80 kg/cm^2, to produce a first stream (b), i.e., syngas comprising H_2, CO and CO_2, wherein the ratio of H_2 and CO in the syngas is 1:1.

The raw material (a) can be at least one of coal, petcoke, biomass, natural gas or liquid fuels.

In the process of the present disclosure, the amount of CO_2 produced during the production of syngas is significantly less. Additionally, the one-step dimethyl ether (DME) process of the present disclosure can handle a significant amount of CO_2 in the feed, as compared to the conventional methanol process. Therefore, separation of CO_2 from syngas (b) in a separate process equipment is obviated at this stage.

The first stream, i.e., syngas, (b) is directly introduced into a DME reactor (D), wherein syngas (b) is contacted with a first catalyst in the DME reactor (D), typically at a temperature in the range of 100°C to 400°C and at a pressure in the range of 1 kg/cm^2 to 60 kg/cm^2, to produce an intermediate stream (c) comprising dimethyl ether (DME) and unconverted CO_2, H_2 and CO. CO_2, and the unconverted H_2 and CO can be separated from the intermediate stream (c) with less energy requirement as CO_2 concentration is relatively higher. Due to the reduced criticality of the process equipment used for separating CO_2, a simpler separation process equipment can be used. The separated portion (g) is introduced into a separator (s) for separating CO_2 (h), H_2 and CO (i). The separated CO_2 (h) can be recycled for producing syngas, and the separated H_2 and CO (i) can be recycled to the DME reactor (D).

The first catalyst includes, but is not limited to, copper oxide, chromium oxide, zinc oxide and aluminium oxide.

One-step DME process requires H_2: CO ratio of 1:1, which leads to smaller water-gas shift reaction and lower water consumption and CO_2 generation. As the portion of CO_2 in the syngas is lower, the one-step DME process can handle syngas without removing CO_2.

The intermediate stream (c) is introduced into a reactor (O) and contacted with a second catalyst in the reactor (O), typically at a temperature in the range of 200°C to 600°C and at a pressure in the range of 0.5 kg/cm^2 to 10 kg/cm^2, to produce a second stream (d) comprising olefins, H_2O, unreacted DME, methane, ethane, and propane.

The second catalyst includes, but is not limited to, molecular sieve catalysts.

In accordance with one embodiment of the present disclosure, the second catalyst is at least one selected from the group consisting of salts, aluminophosphate (ALPO) molecular sieves, and silicoaluminophosphate (SAPO) molecular sieves, as well as substituted forms thereof.

In accordance with another embodiment of the present disclosure, the second catalyst is ZSM-5.

The second stream (d) is introduced into a fractionation column or a divided wall column (Dw) for separating H_2O, unreacted DME, methane, ethane, and propane from the second stream (d) to obtain olefins (e) and a separated stream (f).

The separated CO_2, H_2O, methane, ethane, and propane can be recycled into the reformer for producing syngas by at least one of dry reforming, bi-reforming, or tri-reforming, wherein syngas with higher H_2 and CO is produced as compared to gasification.

Dry reforming of natural gas is depicted herein below:

$$CH_4 + CO_2 = 2CO + 2H_2$$

Moreover, the amount of raw materials required for producing syngas (b) is reduced, since the separated methane, ethane and propane are utilized for producing syngas, which is significantly rich in H_2. Also, the separated unreacted DME can be recycled into the DME reactor (D) for producing the intermediate stream (c).

In accordance with one embodiment of the present disclosure, a portion of the separated CO_2 is recycled into the reformer and a remaining portion of the separated CO_2 is vented out to the atmosphere.

Moreover, the amount of H_2O generated in the reactor (O) can be approximately 50% less as compared to that generated conventionally during the production of olefins from syngas comprising 2:1 ratio of H_2 and CO.

In accordance with one embodiment of the present disclosure, the second stream (d) can be introduced into a de-methanation column (not shown in **Figure 2**) for separating methane contained therein.

As described herein above, syngas (b) comprising 1:1 ratio of H_2 and CO is utilized for producing olefins (e). Due to 1:1 ratio of H_2 and CO:

- the amount of raw materials required for producing syngas (b) is reduced, because the separated CO_2, methane, ethane and propane are utilized for producing syngas which is significantly rich in H_2;
- the amount of CO_2 produced during the production of syngas (b) and water-gas shift reaction is significantly less, and one step DME process can accommodate CO_2 in the feed, which leads to smaller and less severe CO_2 separating process equipment post DME;
- the intermediate step of methanol production, of conventional processes, is obviated, thereby eliminating the use of a reactor for producing methanol;
- efficient separation of the streams by the use of a divided wall column leads to an even more reduction in energy need for separation and saving in the CAPEX of the entire process; and
- the amount of water being circulated from gasification to olefins is significantly reduced, which leads to reduced volume of many intermediate sections.

Due to the above mentioned factors, the CAPEX is significantly reduced and the OPEX is reduced upto 30%, as compared to that of the conventional process.

TECHNICAL ADVANCES AND ECONOMICAL SIGNIFICANCE

The present disclosure described herein above has several technical advantages including, but not limited to, the realization of an improved process that:

- reduces generation of CO_2 during the process for producing olefins;
- utilizes CO_2 in olefins production;
- reduces energy needs for separating products;
- reduces energy needs for separating CO_2;
- reduces circulation of H_2O in the process with lower water-gas shift reaction; and
- reduces CAPEX and OPEX for producing olefins.

The disclosure has been described with reference to the accompanying embodiments which do not limit the scope and ambit of the disclosure. The description provided is purely by way of example and illustration.

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the following description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein.

The foregoing description of the specific embodiments so fully revealed the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

CLAIMS:

1. An improved process for producing olefins from syngas, said improved process comprising the following steps:
   a) treating raw material, at a temperature in the range of 300°C to 1000°C and at a pressure in the range of 1 kg/cm^2 to 80 kg/cm^2, to produce a first stream, containing syngas comprising H_2, CO and CO_2, wherein the ratio of H_2 and CO in said syngas is 1:1, wherein said raw material is at least one selected from the group consisting of coal, petcoke, biomass, natural gas and liquid fuels;
   b) contacting said syngas with at least one first catalyst, at a temperature in the range of 100°C to 400°C and at a pressure in the range of 1 kg/cm^2 to 60 kg/cm^2, to produce an intermediate stream comprising dimethyl ether (DME), unconverted CO_2, H_2, and CO, wherein said at least one first catalyst is selected from the group consisting of chromium oxide, zinc oxide and aluminium oxide;
   c) separating a portion of CO_2, H_2, and CO from said intermediate stream and recycling the separated portion of CO_2 to step (a) for producing said syngas and recycling the separated portion of H_2, and CO to step (b) for producing said DME;
   d) contacting said intermediate stream with at least one second catalyst, at a temperature in the range of 200°C to 600°C and at a pressure in the range of 0.5 kg/cm^2 to 10 kg/cm^2, to produce a second stream comprising olefins, H_2O, methane, ethane, and propane, wherein said at least one second catalyst is ZSM-5;
   e) separating H_2O, methane, ethane and propane from said second stream to obtain said olefins; and
   f) recycling the separated CO_2, methane, ethane and propane to reforming for producing said syngas.

2. The improved process as claimed in claim 1, wherein said olefins is at least one of ethylene and propylene.

3. The improved process as claimed in claim 1, wherein the separated CO_2 is recycled to the step a), for producing said syngas by reforming at least one of:
    - natural gas; and
    - one of the separated methane, ethane, and propane, with CO_2.

5

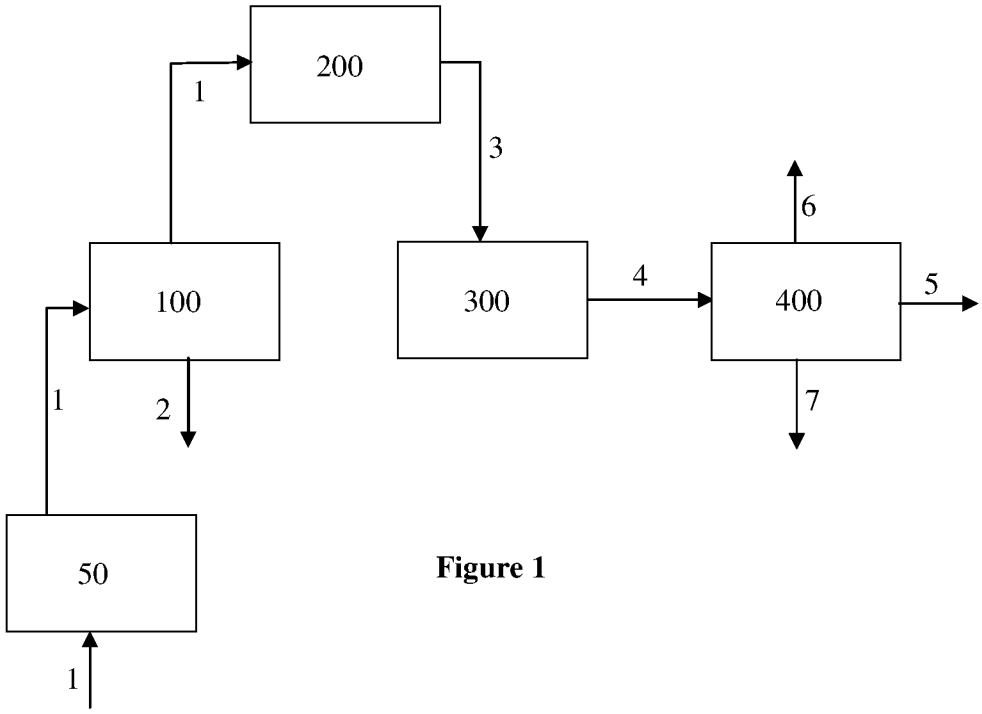


Figure 1

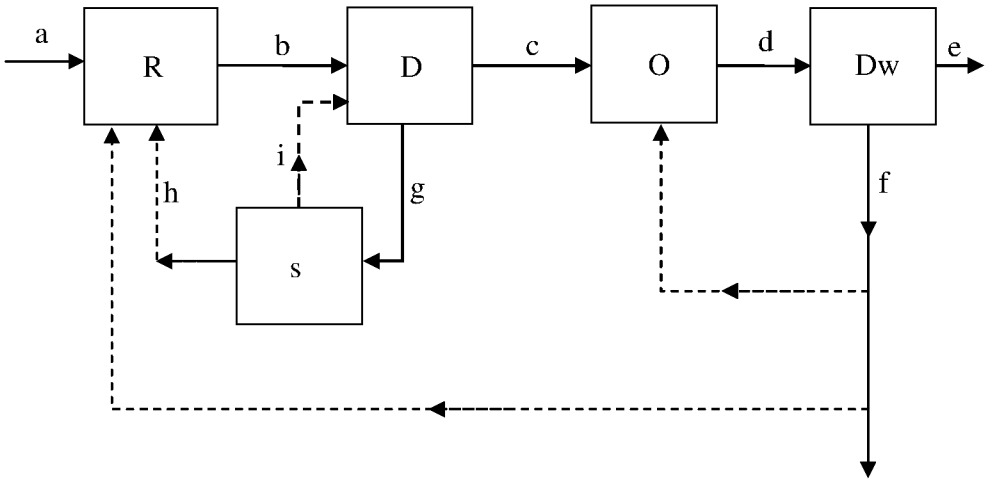


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/053865

A. CLASSIFICATION OF SUBJECT MATTER
C07C1/04,C07C27/00 Version=2017.01

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)

C07C

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)

Patseer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US2013197288(A1) BASF SE[DE] 01-08-2013(01 August 2013) Paragraphs [0011]-[0017], [0022] [0027], Example 5 and Claim 59	1-3
X	WO2008101403(A1) CHINA PETROLEUM & CHEMICAL[CN] 28-08-2008(28 August 2008) ParagraphS [0011]-[0017], [0022] [0027], Example 5	1-3
X	WO2009130292(A2) SHELL INT RESEARCH[NL] 29-09-2009(29 September 2009) Whole document	1-3

☐ 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	Date of mailing of the international search report
21-09-2017	21-09-2017

Name and mailing address of the ISA/	Authorized officer
Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075	Ramesh Vanaparthi
Facsimile No.	Telephone No. +91-1125300200

International application No.
PCT/IB2017/053865

Citation	Pub.Date	Family	Pub.Date
US 2013197288 A1	01-08-2013	AE NONE	
WO WO2008101403 A1	28-08-2008	AU 2008217457 A1	28-08-2008
		CN 101239868 A	13-08-2008
		US 2010016648 A1	21-01-2010
WO 2009130292 A2	29-09-2009	AU 2009239950 A1	29-10-2009
		CN 102046566 A	04-05-2011
		US 2011112347 A1	12-05-2011