PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 **:**
C01B 3/36, C10J 3/48

A1

(11) International Publication Number: **WO 95/32148**

(43) International Publication Date: 30 November 1995 (30.11.95)

(21) International Application Number: PCT/EP95/01891

(22) International Filing Date: 16 May 1995 (16.05.95)

(30) Priority Data:
94201428.3 19 May 1994 (19.05.94) EP
(34) Countries for which the regional or international application was filed: AT et al.

(71) Applicant *(for all designated States except CA)*: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(71) Applicant *(for CA only)*: SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA).

(72) Inventors: DISSELHORST, Johannes, Hermanus, Maria; Badhuisweg 3, NL-1031 CM Amsterdam (NL). EULDERINK, Frits; Badhuisweg 3, NL-1031 CM Amsterdam (NL). OORTWIJN, Peter; Badhuisweg 3, NL-1031 CM Amsterdam (NL). SMIT, Jacobus, Antonius, Jozef; Badhuisweg 3, NL-1031 CM Amsterdam (NL). WENTINCK, Hendrik, Martinus; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: A PROCESS FOR THE MANUFACTURE OF SYNTHESIS GAS BY PARTIAL OXIDATION OF A LIQUID HYDROCARBON-CONTAINING FUEL USING A MULTI-ORIFICE (CO-ANNULAR) BURNER

(57) Abstract

A process for the manufacture of synthesis gas by reacting oxygen-containing gas (oxidizer), moderator gas and a liquid, hydrocarbon-containing fuel in a reaction zone of a substantially non-catalytic gas generator comprising the steps of simultaneously injecting the said fuel and said oxidizer into the reaction zone through a multi-orifice (co-annular) burner comprising an arrangement of n separate passages or channels coaxial with the longitudinal axis of the said burner wherein n is 3 or more. The fuel is passed through one or more of the passages advantageously at a velocity or velocities between 2 and 40 m/s, whereby at least 2 passages remain, the oxygen-containing gas is passed through one or more of the remaining passages advantageously at a velocity or velocities between 20 and 140 m/s, whereby at least 1 passage remains, the moderator is passed through one or more of the remaining passages advantageously at a velocity or velocities between 5 and 140 m/s, in such a way that any two passages through which the fuel respectively the oxygen-containing gas are passed are always separated by at least one passage through which the moderator is passed.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

A PROCESS FOR THE MANUFACTURE OF SYNTHESIS GAS BY PARTIAL OXIDATION OF A LIQUID HYDROCARBON-CONTAINING FUEL USING A MULTI-ORIFICE (CO-ANNULAR) BURNER

The invention relates to a process for the manufacture of synthesis gas by partial oxidation of a liquid hydrocarbon-containing fuel using a multi-orifice (co-annular) burner.

In particular, the invention relates to a process for partial oxidation of a liquid, hydrocarbon-containing fuel such as oil residue wherein an oxygen-containing gas which is applied as an oxidizer, and a liquid, hydrocarbon-containing fuel are supplied to a gasification zone through a multi-orifice (co-annular) burner comprising a concentric arrangement of n passages or channels coaxial with the longitudinal axis of said burner, wherein n is an integer ≥ 3, and wherein autothermically a gaseous stream containing synthesis gas is produced under appropriate conditions.

The oxygen-containing gas which is applied as an oxidizer, is usually air or (pure) oxygen or steam or a mixture thereof. Further, in order to control the temperature in the gasification zone a moderator gas (for example steam, water or carbon dioxide or a combination thereof) can be supplied to said zone.

Those skilled in the art will know the conditions of applying oxidiser and moderator.

Synthesis gas is a gas comprising carbon monoxide and hydrogen, and it is used, for example, as a fuel gas or as a feedstock for the synthesis of methanol, ammonia or hydrocarbons, which latter synthesis yields gaseous hydrocarbons and liquid hydrocarbons such as gasoline, middle distillates, lub oils and waxes.

In the specification and in the claims the term liquid, hydrocarbon-containing fuel will be used to refer to hydrocarbon-containing fuel that is a liquid, an emulsion or a pumpable slurry at gasifier feed pressure and temperature.

This includes, for example, butanes, pentanes, hexanes and on up through the entire liquid range including natural gasolines, kerosenes, gas oils, naphthas, diesel fuels, crude oils, residua, whether atmospheric or vacuum, coal tars, tar sand oils, shale oils, as well as hydrocarbons which may contain other atoms, such as oxygen; however, in such proportions as not to interfere with self-sustaining combustion. Included by definition are slurries of solid carbonaceous fuels in the aforesaid liquid hydrocarbons.

According to an established process, synthesis gas is produced by partially oxidizing in a reactor vessel a fuel such as liquid hydrocarbon, in particular heavy oil residue, at a temperature in the range of from 1000 °C to 1800 °C and at a pressure in the range of from 0.1 MPa to 6 MPa abs. with the use of an oxygen containing gas.

Synthesis gas will often be produced near or at a crude oil refinery because the produced synthesis gas can directly be applied as a feedstock for the production of middle distillates, ammonia, hydrogen, methanol or as a fuel gas, for example, for heating the furnaces of the refinery or more efficiently for the firing of gas turbines to produce electricity and heat.

In co-annular (multi-orifice) oil burners it has appeared that the burner lifetime is restricted by serious corrosion caused by flame phenomena occurring on the burner tips. By means of such phenomena the temperature of the burner-internals becomes too high and serious burner damage will occur.

It is an object of the invention to provide a process for partial oxidation of a liquid, hydrocarbon-containing fuel wherein the mixing of the oxygen-containing gas applied as oxidizer and hydrocarbon-containing fuel is achieved beyond the exit of the burner downstream and the flame is lifted from the front of the burner and wherein burner-damage by serious corrosion (high heat load) is suppressed.

The invention solves the above burner damage problem in that in the process of the invention the oxygen-containing gas applied as oxidizer and the liquid, hydrocarbon-containing fuel are supplied to the gasification zone through the respective channels of the said burner in such a manner that, in use, the oxygen-containing gas applied as oxidizer and the liquid, hydrocarbon-containing fuel are always separated by a moderator and are flowing for some time as separate streams outside the burner front.

In this manner flames occurring on the internal rims are removed and the burner-internal blades that form the internal separation wall between the passages of the burner and have a finite thickness, are remaining relatively cool and the fuel-oxidizer mixture close to the burner exit is less reactive which reduces the heat load on the internal rims.

The invention therefore provides a process for the manufacture of synthesis gas by reacting oxygen-containing gas, applied as oxidizer, hereafter called "X", moderator gas, hereafter called "M", and liquid, hydrocarbon-containing fuel, hereafter called "F" in a reaction zone of a substantially non-catalytic gas generator comprising the steps of injecting the said fuel and the said oxidizer into the reaction zone through a multi-orifice (co-annular) burner comprising an arrangement of n separate passages or channels coaxial with the longitudinal axis of the said burner wherein n is an integer ≥ 3 (3, 4, 5 ...), wherein the $(n-1)^{th}$ passage is the inner passage with respect to the n^{th} passage, measured from the longitinal axis of the said burner and wherein

F is passed through one or more of the passages whereby at least 2 passages remain,

X is passed through one or more of the remaining passages, whereby at least 1 passage remains, and

M is passed through one or more of the remaining passages in such a way that any two passages through which F resp. X are passed are separated by at least one passage through which M is passed.

Advantageously, the liquid, hydrocarbon-containing fuel is an oil residue with a viscosity between 1 and 1000 cSt and passes through one or more of the passages at a velocity or velocities between 2 and 40 m/s; the oxygen-containing gas (oxidizer) passes through one or more of the remaining passages at a velocity or velocities between 20 and 140 m/s; and the moderator gas passes through one or more of the remaining passages at a velocity or velocities between 5 and 140 m/s.

More advantageously, either oxygen-containing gas (oxidizer) or moderator gas is passed through the outermost passage.

Still more advantageously, in case of n $\geq$ 4, moderator gas is also passed through the outermost passage.

In another advantageous embodiment of the invention, with n $\geq$ 4, oxygen-containing gas oxidizer or moderator gas is also passed through the innermost passage.

In an advantageous embodiment of the invention the respective velocities are measured or calculated at the outlet of the said respective channels into the gasification zone. The velocity measurement or calculation can be carried out by those skilled in the art in any way suitable for the purpose and will therefore not be described in detail.

In another advantageous embodiment of the invention the moderator gas is steam and/or water and/or carbon dioxide. In still another advantageous embodiment of the invention the gasification process is carried out at a pressure of 0.1-12 MPa abs.

Multi-orifice burners comprising arrangements of annular concentric channels for supplying oxygen-containing gas (oxidizer), fuel and moderator to a gasification zone are known as such (vide e.g. EP-A-0,545,281 and DE-OS-2,935,754) and the mechanical structures thereof will therefore not be described in detail.

Usually such burners comprise a number of slits at the burner outlet and hollow wall members with internal cooling fluid (e.g. water) passages. The passages may or may not be converging at the burner outlet. Instead of comprising internal cooling fluid passages, the burner may be provided with a suitable ceramic or refractory lining applied onto or suspended by a means closely adjacent to the outer surface of the burner (front) wall for resisting the heat load during operation or heat-up/shut down situations of the burner. Advantageously, the exit(s) of one or more passages may be retracted or protruded.

The invention will now be described in more detail by reference to the following examples.

A number of examples are given in the Table. In this Table the following abbreviations are made:

Feed 1: A residual fuel with the following typical elemental composition:

C	83.7% by weight
H	8.6%
S	6.8%
N	0.5%
O	0.3%
ash	0.1%

The supply temperature of this feedstock is 210-290 °C, whereby the viscosity ranges from 25 to 250 cSt.

Feed 2: A mixture of liquid hydrocarbons with the following typical elemental composition:

C	85.5% by weight
H	13.2%
S	0.5%
N	0.2%
O	0.5%
ash	0.1%

The supply temperature of this feedstock is 100-180 °C, whereby the viscosity ranges from 10 to 100 cSt.

Feed 3: A mixture of heavy tar and water (emulsion) in the mass ratio of about 1:0.4, in which the tar has the following typical elemental composition:

C	84.4% by weight
H	10.5%
S	3.7%
N	0.6%
O	0.5%
ash	0.3%

The supply temperature of this feedstock is 50-100 °C, whereby the viscosity ranges from 60 to 600 cSt.

oxidiser 1 99.4% pure oxygen at a temperature of 230-250 °C,

oxidiser 2	a mixture of oxidiser 1/steam in the ratio 1:0.05
oxidiser 3	a mixture of oxidiser 1/steam in the ratio 1:0.4
Moderator gas 1	superheated steam at a temperature of 350-380 °C
Moderator gas 2	an offgas mainly consisting of CO_2 at a temperature of 200-250 °C

A number of 5 examples has been presented. The following Table indicates the distributions of the reactants for these examples. The typical synthesis gas compositions are also given. The values of n as used in the description and claims are indicated and passage 1 is the first or central passage.

TABLE WITH EXAMPLES

example number	1	2	3	4	5
value of n	7	5	4	3	3
typical synthesis gas composition					
CO_2 [% Vol, dry]	4-5	9-10	3.5-4.5	5-6	4-5
CO [% Vol, dry]	49-52	43-46	45-48	44-47	49-52
H_2 [% Vol, dry]	42-45	44-47	48-51	47-50	42-45
H_2S [% Vol, dry]	1.5-1.7	0.8-0.9	0.1-0.12	0.09-0.11	1.5-1.7
reactor pressure [MPa]	6-7	4-5	2.2-2.6	6-7	5-6
reactor temperature [deg C]	1250-1350	12[illegible]0-1300	1300-1400	1250-1350	1300-1400
passage 1					
type of reactant	oxidiser2	moderator1	oxidiser2	feed 2	oxidiser2
mass flow [kg/s]	0.8-1.2	0.4-0.6	1.8-2.7	3-4.5	3.6-5.4
velocity [m/s]	30-40	20-30	80-120	20-30	80-120
passage 2					
type of reactant	oxidiser2	feed 3	moderator1	moderator2	moderator1
mass flow [kg/s]	2-3	3.7-5.5	0.26-0.39	0.24-0.36	1.4-2.1
velocity [m/s]	80-120	6.7-10	80-120	20-30	80-120

TABLE WITH EXAMPLES (CONTINUED)

passage 3

type of reactant	moderator1	moderator1	feed2	oxidiser3	feed1
mass flow [kg/s]	0.2-0.3	0.08-0.12	1.5-2.2	4.9-7.4	3.4-5.1
velocity [m/s]	25-35	15-22	3.1-4.6	55-80	6.7-10

passage 4

type of reactant	feed1	oxidiser1	moderator1
mass flow [kg/s]	5.5-8	3.1-4.6	0.18-0.26
velocity [m/s]	8-12	90-130	27-40

passage 5

type of reactant	moderator1	moderator1
mass flow [kg/s]	0.27-0.4	0.32-0.48
velocity [m/s]	25-35	40-60

passage 6

type of reactant	oxidiser2
mass flow [kg/s]	2.7-4
velocity [m/s]	80-120

TABLE WITH EXAMPLES (CONTINUED)

passage 7	
type of reactant	moderator1
mass flow [kg/s]	1.5-2.5
velocity [m/s]	40-50

For n=6, the following data are applicable:

passage 1

type of reactant: oxidiser2

mass flow [kg/s]: 2.8-4.2

velocity [m/s] : 80-120

passages 2-6: vide data of passages 3-7 described in example number 1 (n=7)

Typical synthesis gas composition, reactor pressure and reactor temperature: vide data in question of example number 1 (n=7).

It will be appreciated by those skilled in the art that any slit width suitable for the purpose can be applied, dependent on the burner capacity.

Advantageously, the first or central passage has a diameter up to 70 mm, whereas the remaining concentric passages have slit widths in the range of 1-20 mm.

Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description. Such modifications are intended to fall within the scope of the appended claims.

CLAIMS

1. A process for the manufacture of synthesis gas by reacting oxygen containing gas, applied as oxidiser, hereafter called "X", moderator gas, hereafter called "M", and liquid, hydrocarbon-containing fuel, hereafter called "F" in a reaction zone of a substantially non-catalytic gas generator comprising the steps of injecting the said fuel and the said oxidizer into the reaction zone through a multi-orifice (co-annular) burner comprising an arrangement of n separate passages or channels coaxial with the longitudinal axis of the said burner wherein n is an integer ≥ 3 (3, 4, 5 ...), wherein the $(n-1)^{th}$ passage is the inner passage with respect to the n^{th} passage, measured from the longitudinal axis of the said burner, and wherein
F is passed through one or more of the passages, whereby at least 2 passages remain,
X is passed through one or more of the remaining passages, whereby at least 1 passage remains, and
M is passed through one or more of the remaining passages in such a way that any two passages through which F resp. X are passed are separated by at least one passage through which M is passed.

2. The process as claimed in claim 1, wherein the liquid, hydrocarbon-containing fuel has a viscosity between 1 and 1000 cSt.

3. The process as claimed in claim 1 or 2, wherein the liquid, hydrocarbon-containing fuel is passed at a velocity or velocities between 2 and 40 m/s.

4. The process as claimed in any one of claims 1-3, wherein the oxygen-containing gas (oxidiser) is passed at a velocity or velocities between 20 and 140 m/s.

5. The process as claimed in any one of claims 1-4, wherein the moderator gas is passed at a velocity or velocities between 5 and 140 m/s.

6. The process as claimed in any one of claims 1-5, wherein the

process pressure is 0.1-12 MPa abs.

7. The process as claimed in any one of claims 1-6, wherein the said fuel is oil residue.

8. The process as claimed in any one of claims 1-7, wherein the oxygen-containing gas (oxidiser) contains at least 90% pure oxygen.

9. The process as claimed in any one of claims 1-8, wherein the respective velocities are measured or calculated at the outlet of the said respective concentric channels into the gasification zone.

10. The process as claimed in any one of claims 1-9, wherein the moderator gas is steam, carbon dioxide or water or a combination thereof.

11. The process as claimed in any one of claims 1-10, wherein either X or M is passed through the outermost passage.

12. The process as claimed in any one of claims 1-11, with n is 4 or more, wherein M is passed through the outermost passage.

13. The process as claimed in any one of claims 1-11, with n is 4 or more, wherein X or M is passed through the innermost passage.

14. Synthesis gas whenever obtained from a process as claimed in any one of claims 1-13.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/01891

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/36 C10J3/48

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 6 C01B C10J

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 545 281 (HOECHST AG) 9 June 1993 cited in the application ---	1
A	EP,A,0 107 225 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) 2 May 1984 see claim 1 ---	1
A	GB,A,2 151 348 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) 17 July 1985 see page 3, line 14 - line 18 ---	1
A	EP,A,0 343 735 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 29 November 1989 see claim 1 ---	1
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] 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	Date of mailing of the international search report
12 September 1995	22.09.95

Name and mailing address of the ISA	Authorized officer
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	Clement, J-P

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/EP 95/01891

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 291 111 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) 17 November 1988 see claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/EP 95/01891

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-545281	09-06-93	DE-A-	4140063	09-06-93
		AU-B-	649599	26-05-94
		AU-A-	2992292	10-06-93
		CA-A-	2084035	06-06-93
		CN-A-	1073472	23-06-93
		JP-A-	5239473	17-09-93
		JP-B-	6070228	07-09-94
		US-A-	5273212	28-12-93
		ZA-A-	9209235	12-07-93
EP-A-107225	02-05-84	AU-B-	557682	08-01-87
		AU-B-	2022583	03-05-84
		CA-A-	1218903	10-03-87
		JP-C-	1689185	11-08-92
		JP-B-	3056365	28-08-91
		JP-A-	59089907	24-05-84
		US-A-	4523529	18-06-85
GB-A-2151348	17-07-85	CA-A-	1269842	05-06-90
		DE-A-	3444590	20-06-85
		FR-A,B	2556332	14-06-85
		JP-B-	6094361	24-11-94
		JP-A-	60141602	26-07-85
EP-A-343735	29-11-89	AU-B-	611803	20-06-91
		AU-A-	3514089	30-11-89
		GB-A-	2219003	29-11-89
		JP-A-	2043288	13-02-90
		PT-B-	90650	31-10-94
		US-A-	4888031	19-12-89
EP-A-291111	17-11-88	AU-B-	601276	06-09-90
		AU-B-	1589188	17-11-88
		CA-A-	1301458	26-05-92
		DE-A-	3869193	23-04-92
		EG-A-	18918	30-03-94
		JP-A-	63297201	05-12-88
		NO-B-	174955	02-05-94
		SU-A-	1766282	30-09-92
		ZA-A-	8803292	14-11-88