WORLD INTELLECT

INTERNATIONAL APPLICATION PUBLISHED

(51) International Patent Classification 6:

C01B 3/36

9603345A1 WO

(43) International Publication Date:

8 February 1996 (08.02.96)

(21) International Application Number:

PCT/EP95/02877

(22) International Filing Date:

18 July 1995 (18.07.95)

(30) Priority Data:

94202150.2 22 July 1994 (22.07.94) 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

(72) Inventors: DISSELHORST, Johannes, Hermanus, Maria; Badhuisweg 3, NL-1031 CM Amsterdam (NL). EULDERINK, Frits; 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, UG, 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 GASEOUS 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, applied as oxidiser and gaseous hydrocarboncontaining fuel in a reaction zone of a non-catalytic gas generator comprising the steps of injecting the said fuel and the said oxidiser into the reaction zone through a multi-orifice (co-annular) burner comprising arrangement of n separate passages or channels coaxial with the longitudinal axis of said burner, wherein n is an integer ≥ 2 (2, 3, 4, 5...) wherein the (n-1)th passage is the inner passage with respect to the nth passage, measured from the longitudinal axis of the said burner, and wherein geseous hydrocarbon-containing fuel and, optionally, a moderator is passed through one or more of the passages, but at least through the nth (outer) passage whereby at least one passage remains; oxidiser and, optionally, a moderator, is passed through one or more of the remaining passages, but at least through the (n-1)th passage. In any two adjacent passages in which oxidiser is passed through the one passage, and gaseous hydrocarbon-containing fuel is passed through the other passage, the said oxidiser has a higher velocity than said hydrocarbon-containing fuel.

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
ΑU	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	SD	Sudan
CG	Congo		of Korea	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		-		

- 1 -

A PROCESS FOR THE MANUFACTURE OF SYNTHESIS GAS
BY PARTIAL OXIDATION OF A GASEOUS 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 gaseous hydrocarbon-containing fuel using a multi-orifice (co-annular) burner.

5

10

15

20

25

In particular, the invention relates to a process for partial oxidation of a gaseous hydrocarbon-containing fuel wherein an oxygen-containing gas, which is applied as an oxidiser, and a gaseous 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 ≥ 2 , and wherein autothermically a gaseous stream containing synthesis gas is produced under appropriate conditions.

The oxygen-containing gas, which is applied as an oxidiser, is usually air or (pure) oxygen or steam or a mixture thereof. 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 clean medium-calorific value 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 gaseous hydrocarbon-containing fuel will be used to refer to hydrocarbon-containing fuel that is gaseous at gasifier feed pressure and temperature.

- 2 -

According to an established process, synthesis gas is produced by partially oxidising in a reactor vessel a gaseous fuel such as gaseous hydrocarbon, in particular petroleum gas or natural gas, 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.

5

10

15

20

25

30

35

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) gas burners it has appeared that the burner lifetime is restricted by phenomena of pre-ignition or flame-flashback. Because of such phenomena the temperature of the burner-internals becomes too high and serious burner damage will occur. Further, there are problems with corrosion of the gas burner tips.

It is an object of the invention to provide a process for partial oxidation of a gaseous hydrocarbon-containing fuel wherein a good and rapid mixing or contacting of oxygen-containing gas (oxidiser), fuel and, optionally, moderator gas in the gasification zone is achieved beyond the exit of the burner and wherein burner-damage by corrosion, pre-ignition or flame-flash-back is suppressed.

The invention solves the above burner damage problem in that in the process of the invention the oxygen-containing gas applied as oxidiser and the gaseous hydrocarbon-containing fuel are supplied to the gasification zone through specific passages at specific velocities.

The invention therefore provides a process for the manufacture of synthesis gas by reacting oxygen-containing gas, applied as oxidiser, and gaseous hydrocarbon-containing fuel in a reaction zone of a substantially non-catalytic gas generator comprising the steps of injecting the said fuel and the said oxidiser 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 said burner, wherein n is an integer ≥ 2 (2, 3, 4, 5 ...), wherein the (n-1)th passage is the inner passage with respect to the nth passage, measured from the longitudinal axis of the said burner, and wherein the said gaseous hydrocarbon-containing fuel (optionally with a moderator gas) is passed through one or more of the passages, but at least through the nth passage, whereby at least one passage remains; the said oxidiser (optionally with a moderator gas) is passed through one or more of the remaining passages, but at least through the (n-1)th passage, and in such a manner that in any two adjacent passages in which oxidiser is passed through the one passage, and gaseous hydrocarbon-containing fuel is passed through the other passage, the said oxidiser has a higher velocity than said hydrocarbon-containing fuel.

5

10

15

20

25

30

35

In this manner the oxygen-containing gas (oxidiser) entrains the gaseous hydrocarbon-containing fuel after which the partial oxidation takes place in the gasification zone, and the burner-internal blades that form the internal separation wall between the oxygen-containing gas (oxidiser) and the hydrocarbon-containing gas and which have a finite thickness, are cooled by the oxygen-containing gas (oxidiser) and the hydrocarbon-containing gas (in particular by convective cooling) to lower the flame temperature just behind the tips.

Behind the tip of the blade there is unavoidably at least a recirculation area in which both gaseous fuel and oxygen-containing gas, applied as oxidiser, are present.

If the hydrocarbon-containing gas would have the highest velocity, there will be oxygen-rich conditions at the burner-internal-tip by means of "entrainment" which will lead to high flame temperatures, high tip temperatures and serious loss of burner material.

If the oxygen-containing gas, applied as oxidiser, has the highest velocity, in the recirculation area there will be mainly oxygen-depleted conditions, which will lead to lower flame temperature. Thus, serious burner damage will not occur, which leads

- 4 -

to a long burner-lifetime.

5

10

15

20

25

30

35

Advantageously, for $n \ge 3$, at least part (e.g. 20%) of the gaseous hydrocarbon-containing fuel is passed through the said n^{th} passage and the remainder of the gaseous hydrocarbon-containing fuel is passed through one or more of the remaining passages. The velocity of the oxygen-containing gas, applied as oxidiser, is advantageously 20-150 m/s.

The velocity of the gaseous hydrocarbon-containing fuel is advantageously 0.2-0.8 times the velocity of the oxygen-containing gas, applied as oxidiser, in any two adjacent passages in which oxidiser is passed through the one passage, and gaseous hydrocarbon-containing fuel is passed through the other 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 and the oxidiser contains at least 90% pure O_2 . 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 (oxidiser), fuel and moderator gas 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

- 5 -

resisting the heat load during operation or heat-up/shut down situations of the burner.

No fuel passage is reserved for a fuel other than gaseous hydrocarbon-containing fuel.

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: Natural Gas with the following typical composition

10 CH₄ : 94.4% by volume

5

15

25

30

 $C_{2}H_{6}$: 3.0% $C_{3}H_{8}$: 0.5% $C_{4}H_{10}$: 0.2%

C5H12+: 0.2%

CO₂ : 0.2%

N₂ : 1.5%

The supply temperature to the burner of this feedstock is 150-250 $^{\circ}\text{C}.$

Feed 2:Natural Gas with the following typical composition

20 CH₄ : 81.8% by volume

с₂н₆ : 2.7%

C₃H₈ : 0.4%

 $C_4H_{10}: 0.18$

C5H12+: 0.1%

CO₂ : 0.9%

N₂ : 14.0%

 ${\rm CO_2}$ is supplied as a moderator gas to the said natural gas in such a manner that the mass ratio of moderator gas ${\rm CO_2}$ to Natural Gas is 0.6-0.8. The supply temperature to the burner of this feedstock is 280-320 °C.

oxidiser 1: 99.5% pure O_2 with a temperature of 230-250 °C. oxidiser 2: a mixture of a gas with 99.5% pure O_2 with 20-30% (by mass) of moderator gas. This mixture has a temperature of 250-270 °C and the moderator gas is steam at a temperature of 280-300 °C.

- 6 -

A number of 9 examples has been presented. The following Table indicates the distributions of the respective fuels and oxidisers 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.

5

- 7 Table With Examples

1	2	3
-		
7	6	6
		ĺ
2-3	6-7	2-3
34-35	39-40	34-35
52-63	47-48	62-63
1-5	2-3	5-7
300-1400	1250-1350	1300-1400
eed 1	oxidiser 1	oxidiser 1
-1.5	1.2-1.8	1-1.5
0-45	80-120	50-75
xidiser 1	feed 2	feed 1
.6-4	0.4-0.6	1.1-1.6
0-120	30-45	25-35
eed 1	feed 2	oxidiser 1
.1-3.1	2.1-3.1	2-3
0-45	80-120	50-75
xidiser 1	feed 2	feed 1
.7-4	0.6-0.9	1.8-2.7
0-120	30-45	25-35
eed 1	oxidiser 1	oxidiser 1
.1-3.1	1.2-1.8	2-3
0-45	80-120	50-75
xidiser 1	feed 2	feed 1
-4.5	0.76-1.1	1-1.5
0-120	30-45	20-30
eed 1		
-1.5		
0-45		
	34-35 32-63 -5 300-1400 eed 1 -1.5 0-45 xidiser 1 .6-4 0-120 eed 1 .1-3.1 0-45 xidiser 1 .7-4 0-120 eed 1 .1-3.1 0-45 xidiser 1 .7-4 0-120 eed 1 .1-3.1 0-45 xidiser 1 .7-4 0-120 eed 1 .1-3.1	39-40 39-40 47-48 -5 2-3 300-1400 1250-1350 eed 1 -1.5 0-45 80-120 xidiser 1 feed 2 .6-4 0.4-0.6 0-120 30-45 eed 1 feed 2 .1-3.1 0-45 80-120 xidiser 1 feed 2 .7-4 0.6-0.9 0-120 30-45 eed 1 0.1-3.1 1.2-1.8 0-45 80-120 xidiser 1 feed 2 .7-4 0.6-0.9 0-120 30-45 eed 1 0.1-3.1 1.2-1.8 0-45 80-120 xidiser 1 1.2-1.8

- 8 Table With Examples (Continued)

~	,	
4	5	6
5	4	3
9-10	4-5	4-5
36-37	32-33	32-33
47-48	62-63	62-63
2-3	1-1.5	2-3
1200-1300	1300-1400	1300-1400
feed 2	feed 1	feed 1
1-1.5	2-3	0.7-1.1
40-60	80-120	45-80
oxidiser 2	feed 1	oxidiser 1
1.6-2.4	0.6-0.9	1.7-2.6
95-140	30-45	100-150
feed 2	oxidiser 2	feed 1
2-3	6.2-9.3	0.9-1.3
40-60	80-120	35-40
oxidiser 2	feed 1	moderator gas
1.6-2.4	1.3-2	0.6-0.9
70-100	25-35	55-80
feed 2		-
1-1.5		
30-45		
	9-10 36-37 47-48 2-3 1200-1300 feed 2 1-1.5 40-60 oxidiser 2 1.6-2.4 95-140 feed 2 2-3 40-60 oxidiser 2 1.6-2.4 70-100 feed 2 1-1.5	9-10

- 9 Table With Examples (Continued)

7	8	9
3	3	2
4-5	2-3	4-5
32-33	34-35	32-33
62-63	62-63	62-63
2-3	4-5	7-10
1300-1400	1300-1400	1300-1400
oxidiser 2	feed 1	oxidiser 2
2.5-3.5	2-3	6-8
40-60	40-70	45-60
oxidiser 2	oxidiser 1	feed 1
1.7-2.6	4-6	4-5.6
100-150	80-120	25-35
feed 1	feed 1	
2.5-3.7	1.3-2	
30-45	30-45	
	3 4-5 32-33 62-63 2-3 1300-1400 oxidiser 2 2.5-3.5 40-60 oxidiser 2 1.7-2.6 100-150 feed 1 2.5-3.7	3 3 4-5 2-3 32-33 34-35 62-63 62-63 2-3 4-5 1300-1400 1300-1400 oxidiser 2 feed 1 2.5-3.5 2-3 40-60 40-70 oxidiser 2 oxidiser 1 1.7-2.6 4-6 100-150 80-120 feed 1 feed 1 2.5-3.7 1.3-2

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.

5

10

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.

- 10 -

CLAIMS

1. A process for the manufacture of synthesis gas by reacting oxygen-containing gas, applied as oxidizer, and gaseous hydrocarboncontaining fuel in a reaction zone of a substantially non-catalytic gas generator comprising the steps of injecting the said fuel and the said oxidiser 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 said burner, wherein n is an integer > 2 (2, 3, 4, 5 ...), wherein the (n-1)th passage is the inner passage with respect to the nth passage. measured from the longitudinal axis of the said burner, and wherein the said gaseous hydrocarbon-containing fuel (optionally with a moderator gas) is passed through one or more of the passages, but at least through the nth passage, whereby at least one passage remains, the said oxidiser (optionally with a moderator gas) is passed through one or more of the remaining passages, but at least through the (n-1)th passage, and in such a manner that in any two adjacent passages in which oxidiser is passed through the one passage, and gaseous hydrocarbon-containing fuel is passed through the other passage, the said oxidiser has a higher velocity than said hydrocarbon-containing fuel.

5

10

15

20

25

30

- 2. The process as claimed in claim 1, wherein the velocity of the gaseous hydrocarbon-containing fuel is 0.2-0.8 times the velocity of the oxygen-containing gas (oxidiser) in any two adjacent passages in which oxidiser is passed through the one passage, and gaseous hydrocarbon-containing fuel is passed through the other passage.
- 3. The process as claimed in claim 1 or 2, wherein, for $n \ge 3$, at least part (e.g. 20%) of the gaseous hydrocarbon-containing fuel is passed through the said n^{th} passage and the remainder of the gaseous hydrocarbon-containing fuel is passed through one or more of the remaining passages.

- 11 -

- 4. The process as claimed in any one of claims 1-3, wherein the velocity of the oxidiser is 20-150 m/s.
- 5. The process as claimed in any one of claims 1-4, wherein the process pressure is 0.1-12 MPa abs.
- 5 6. The process as claimed in any one of claims 1-5, wherein the fuel is natural gas.
 - 7. The process as claimed in any one of claims 1-6, wherein the oxidiser contains at least 90% pure oxygen.
- 8. The process as claimed in any one of claims 1-7, wherein the respective velocities are measured or calculated at the outlet of the said respective concentric passages or channels into the gasification zone.

15

20

- 9. The process as claimed in any one of claims 1-8, wherein the moderator gas is steam, carbon dioxide or water or a combination thereof.
- 10. The process as claimed in any one of claims 1-9, wherein moderator gas is passed through an (n+1)th passage.
- 11. The process as claimed in any one of claims 1-10, wherein no fuel passage is reserved for a fuel other than gaseous hydrocarbon-containing fuel.
- 12. Synthesis gas whenever obtained from a process as claimed in any one of claims 1-11.

INTERNATIONAL SEARCH REPORT

Int ional Application No PCT/EP 95/02877

	•		
A. CLASSI IPC 6	ification of subject matter C01B3/36		
According to	o International Patent Classification (IPC) or to both national cla	ssification and IPC	
	SEARCHED		
Minimum d IPC 6	ocumentation searched (classification system followed by classification ${\tt C01B}$	cation symbols)	
Documentat	non searched other than minimum documentation to the extent th	at such documents are included in the fields s	earched
Electronic d	ata base consulted during the international search (name of data	hase and, where practical, search terms used)	
C. DOCUM	IENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the	e relevant passages	Relevant to claim No.
A	EP,A,O 343 735 (SHELL INTERNATION RESEARCH MAATSCHAPPIJ B.V.) 29 1989 see page 3, line 16 - line 25	DNALE November	1
A	EP,A,O 098 043 (TEXACO DEVELOPM CORPORATION) 11 January 1984 see claim 12	ENT	1
A	US,A,3 945 942 (MARION ET AL) 2 1976 see claims 1-4 	3 March	1
Furt	her documents are listed in the continuation of box C.	X Patent family members are listed	in annex.
* Special ca *A* documents of the consider of the cuments of the c	tegories of cited documents: ient defining the general state of the art which is not lered to be of particular relevance document but published on or after the international date ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another in or other special reason (as specified) ient referring to an oral disclosure, use, exhibition or	"T' later document published after the int or priority date and not in conflict we cited to understand the principle or timvention "X' document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the de "Y' document of particular relevance; the cannot be considered to involve an indocument is combined with one or in ments, such combination being obvious in the art. "&' document member of the same patent	ernational filing date th the application but heory underlying the claimed invention t be considered to ocument is taken alone claimed invention hventive step when the hore other such docu- bus to a person skilled
	actual completion of the international search 1 November 1995	Date of mailing of the international se	•
Name and	mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,	Authonzed officer Clement, J-P	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No
PCT/EP 95/02877

Patent document cited in search report	Publication date	Patent family member(s)		Publication date	
EP-A-343735		AU-B- AU-B- GB-A- JP-A- PT-B- US-A-	611803 3514089 2219003 2043288 90650 4888031	20-06-91 30-11-89 29-11-89 13-02-90 31-10-94 19-12-89	
EP-A-98043	11-01-84	US-A- AU-B- AU-B- CA-A- JP-A- US-A-	4443228 558256 1573883 1190046 59022991 4491456	17-04-84 22-01-87 05-01-84 09-07-85 06-02-84 01-01-85	
US-A-3945942	23-03-76	AT-B- BE-A- CA-A- DE-A- FR-A- GB-A- LU-A- NL-A- SE-B- US-A-	348974 778544 947973 2204601 2155185 1335521 64685 7200927 384843 3758037	12-03-79 26-07-72 28-05-74 12-04-73 18-05-73 31-10-73 23-08-72 06-04-73 24-05-76 11-09-73	