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(54) Title: PROCESS FOR THE OXIDATION OF A HYDROCARBONACEOUS FEEDSTOCK

(57) Abstract: A process for the oxidation of a hydrocarbonaceous feedstock with an oxygen-containing gas, wherein the hydrocarbonaceous feedstock is mixed with the oxygen-containing gas prior to oxidation in an oxidation zone and wherein an oxidant is added to the hydrocarbonaceous feedstock before the feedstock is mixed with the oxygen-containing gas in an amount in the range of from 0.005 to 10% (mole/mole) of oxidant based on the feedstock.

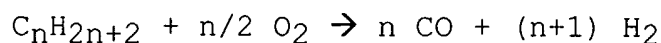


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PROCESS FOR THE OXIDATION OF A HYDROCARBONACEOUS  
FEEDSTOCK

The present invention relates to a process for the oxidation of a hydrocarbonaceous feedstock, in particular a process for the catalytic partial oxidation of a hydrocarbonaceous feedstock.

5 Partial oxidation of a hydrocarbonaceous feedstock, in particular hydrocarbons, in the presence of a catalyst is an attractive route for the preparation of mixtures of carbon monoxide and hydrogen, normally referred to as synthesis gas. The partial oxidation of hydrocarbons is  
10 an exothermic reaction represented by the equation:



There is literature in abundance on the catalysts and the process conditions for the catalytic partial oxidation of gaseous hydrocarbons, in particular methane. Reference is  
15 made, for instance, to EP-A-303 438, US-A-5,149,464, EP-B-576 096, and EP-A-629 578.

Since the catalytic partial oxidation reaction proceeds at very short contact times (in the order of tens of milliseconds), it is important that the reactants  
20 are well-mixed when brought into contact with the catalyst. Otherwise, the reaction will proceed at an undesirable stoichiometry and the desired product selectivity will not be obtained.

The mixture of the reactants of the catalytic partial oxidation process, i.e. a hydrocarbonaceous feedstock and  
25 an oxygen-containing gas, is highly reactive and explosive, especially at the mixing conditions which are typically applied, i.e. at elevated temperature and

pressure and in amounts giving an oxygen-to-carbon ratio in the range of from 0.3 to 0.8.

5 In a catalytic partial oxidation process, the yield of carbon monoxide and hydrogen, i.e. conversion times selectivity, increases with increasing temperature of the mixture of hydrocarbonaceous feedstock and oxygen-  
10 containing gas that is fed to the catalyst. Thus, there is an incentive to increase the temperature of the mixture, but the temperature of the mixture is bound to a maximum set by the risks of ignition, such as auto  
15 ignition and particle induced ignition, and explosion. Moreover, for commercial applications, it is often desired to perform the mixing at elevated pressure, i.e. at pressures well above atmospheric pressure.

20 It has now been found that the risk for explosion and/or ignition, especially particle induced ignition, in a mixture of a hydrocarbonaceous feedstock and an oxygen-containing gas can be reduced, and therefore the temperature and pressure of the mixture can be increased,  
25 by adding a relatively small amount of oxidant to the hydrocarbonaceous feedstock before it is mixed with the oxygen-containing gas.

30 This finding may be advantageously applied in the above-mentioned catalytic partial oxidation process. It will be appreciated that the present finding may also be applied in other oxidation processes wherein a mixture of hydrocarbonaceous feedstock and oxygen-containing gas may be formed prior to the actual oxidation. Non-limiting  
35 examples of such oxidation processes are non-catalytic partial oxidation, combustion, e.g. in a gas turbine, and the oxidation step in autothermal reforming.

Accordingly, the present invention relates to a process for the oxidation of a hydrocarbonaceous feedstock with an oxygen-containing gas, wherein the  
hydrocarbonaceous feedstock is mixed with the oxygen-

containing gas prior to oxidation in an oxidation zone and wherein an oxidant is added to the hydrocarbonaceous feedstock before the feedstock is mixed with the oxygen-containing gas in an amount in the range of from 0.005 to 10% (mole/mole) of oxidant based on the feedstock.

The addition of oxidant is especially advantageous in oxidation processes wherein the hydrocarbonaceous feedstock and the oxygen-containing gas are mixed at elevated temperature and/or at elevated pressure.

Reference herein to elevated temperature and pressure is to temperatures well above room temperature and pressures well above atmospheric pressure. In the process of the present invention, the mixture of hydrocarbonaceous feedstock and oxygen-containing gas preferably has a temperature in the range of from 100 to 800 °C, more preferably of from 150 to 600 °C, even more preferably of from 200 to 400 °C. The pressure at which the feedstock and the oxygen-containing gas are mixed is preferably in the range of from 2 to 100 bar (absolute), more preferably of from 5 to 80 bar (absolute), even more preferably of from 10 to 50 bar (absolute).

The oxidant to be added is preferably oxygen or water, more preferably oxygen. Oxygen may be added as substantially pure oxygen or as a diluted oxygen stream, such as air or oxygen-enriched air. If the oxidant is water, it is preferred to add the water as steam. Alternatively, atomised liquid water may be added to a preheated stream of the hydrocarbonaceous feedstock.

In the process of the invention, the oxidant is added to the hydrocarbonaceous feedstock before the feedstock is mixed with the oxygen-containing gas, i.e. upstream of the zone where the feedstock and the oxygen-containing gas are mixed. The oxidant may for example be injected into the conduit supplying the feedstock to the mixing zone. It is advantageous to add the oxidant well before

the mixing zone such that the oxidant is well-mixed through the hydrocarbonaceous feedstock when the feedstock is mixed with the oxygen-containing gas. Preferably, the residence time of the oxidant in the stream of hydrocarbonaceous feedstock before it is entering the mixing zone is at least 0.5 second, more preferably at least 1 second.

Typically in catalytic partial oxidation processes, the feedstock and the oxygen-containing gas are preheated before mixing them. In the process of the invention the oxidant may be added to the feedstock before the feedstock is preheated or to the preheated feedstock.

Especially in the case that the oxidant added is oxygen, the amount of oxidant added to the feedstock must be below the flammability limit of the thus-obtained feedstock-oxidant mixture, i.e. the amount may not be so high that ignition or explosion of the feedstock-oxidant mixture occurs at the prevailing process conditions. Preferably, the oxidant is added in an amount in the range of from 0.01 to 5% (mole/mole) based on the feedstock, more preferably of from 0.02 to 2% (mole/mole), even more preferably of from 0.05 to 1% (mole/mole), in particular of from 0.05 to 0.5% (mole/mole).

Suitable hydrocarbonaceous feedstocks comprise hydrocarbons, oxygenates or mixtures thereof. Oxygenates are defined as molecules containing apart from carbon and hydrogen atoms at least 1 oxygen atom which is linked to either one or two carbon atoms or to a carbon atom and a hydrogen atom. Examples of suitable oxygenates are methanol, ethanol, dimethyl ether and the like.

Preferred hydrocarbonaceous feedstocks comprise methane, natural gas, associated gas or other sources of "light hydrocarbons". In this respect, the term "light hydrocarbon" is a reference to hydrocarbons having 1 to

5 carbon atoms. Preferably the feedstock comprises methane in an amount of at least 50% by volume, more preferably at least 70% by volume, even more preferably at least 80% by volume.

5       The oxygen-containing gas that is mixed with the hydrocarbonaceous feedstock prior to oxidation may be oxygen, air, or oxygen-enriched air, preferably oxygen.

10       The oxidation process of the present invention is preferably a combustion process or a partial oxidation process, more preferably a catalytic partial oxidation process.

15       In the catalytic partial oxidation process according to the invention, a mixture of hydrocarbonaceous feedstock and oxygen-containing gas is contacted with a catalyst to obtain synthesis gas by means of an exothermic reaction. Suitable catalysts are known in the art.

20       In a catalytic partial oxidation process, the hydrocarbonaceous feedstock and the oxygen-containing gas are preferably present in the mixture in such amounts as to give an oxygen-to-carbon ratio in the range of from 0.3 to 0.8, more preferably, in the range of from 0.45 to 0.75. References herein to the oxygen-to-carbon ratio refer to the ratio of oxygen in the form of molecules (O<sub>2</sub>) to carbon atoms present in the hydrocarbon feedstock. Oxygen-to-carbon ratios in the region of the stoichiometric ratio of 0.5, i.e. ratios in the range of from 0.45 to 0.65, are especially preferred. If oxygenate feedstocks are used, e.g. methanol, oxygen-to-carbon ratios below 0.3 can suitably be used.

30       The mixture of hydrocarbonaceous feedstock and oxygen-containing gas may optionally comprise steam. If steam is present, the steam-to-carbon ratio is preferably in the range of from above 0.0 to 3.0, more preferably

from 0.0 to 2.0. Optionally, the mixture may comprise carbon dioxide.

5 The hydrocarbonaceous feedstock and the oxygen-containing gas are preferably preheated, resulting in a preheated mixture of hydrocarbonaceous feedstock and oxygen-containing gas. It is an advantage of the catalytic partial oxidation process according to the present invention that the mixture may be heated to a relatively high temperature without the occurrence of  
10 ignition or explosion upstream of the catalyst. Preferably, the temperature of the mixture is in the range of from 100 to 800 °C. Due to the exothermic character of the catalytic partial oxidation reaction, the temperature of the gas leaving the catalyst is  
15 typically in the range of from 750 to 1400 °C, preferably of from 850 to 1350 °C.

The mixture may be contacted with the catalyst at any suitable gas hourly space velocity (expressed as normal litres of gas per kilogram of catalyst at STP  
20 conditions). Preferably, the gas hourly space velocity is in the range of from 20,000 to 100,000,000 Nl/kg/h, more preferably of from 50,000 to 50,000,000 Nl/kg/h, even more preferably of from 100,000 to 30,000,000 Nl/kg/h.

25 The invention will now be illustrated by means of the following examples.

EXAMPLE 1 (according to the invention)

Into a stream of 390 kg/h of natural gas, 0.1% (mole/mole) of pure oxygen was injected. After oxygen injection, the natural gas stream was preheated  
30 and fed to a mixing zone at a pressure of 30 bar (absolute). Simultaneously, a separate stream of 310 kg/h of pure oxygen having a temperature of 100 °C was fed to the mixing zone.

35 The preheating temperature of the natural gas stream was varied. Up to a preheating temperature of 360 °C,

resulting in a temperature of the mixture in the mixing zone of 300 °C, no ignition was observed.

EXAMPLE 2 (comparative)

5       The same experiment as in Example 1 was carried out, without addition of oxygen to the natural gas stream. Ignition was observed at a temperature of the mixture in the mixing zone of 278 °C.



C L A I M S

1. A process for the oxidation of a hydrocarbonaceous feedstock with an oxygen-containing gas, wherein the hydrocarbonaceous feedstock is mixed with the oxygen-containing gas prior to oxidation in an oxidation zone  
5 and wherein an oxidant is added to the hydrocarbonaceous feedstock before the feedstock is mixed with the oxygen-containing gas in an amount in the range of from 0.005 to 10% (mole/mole) of oxidant based on the feedstock.
2. A process according to claim 1, wherein the mixture  
10 of hydrocarbonaceous feedstock and oxygen-containing gas has an elevated temperature, preferably a temperature in the range of from 100 to 800 °C, more preferably of from 150 to 600 °C, even more preferably of from 200 to 400 °C.
3. A process according to claim 1 or 2, wherein the  
15 hydrocarbonaceous feedstock is mixed with the oxygen-containing gas at an elevated pressure, preferably at a pressure in the range of from 2 to 100 bar (absolute), more preferably of from 5 to 80 bar (absolute), even more  
20 preferably of from 10 to 50 bar (absolute).
4. A process according to any of the preceding claims, wherein the oxidant is oxygen or water, preferably oxygen.
5. A process according to any of the preceding claims,  
25 wherein an amount of oxidant in the range of from 0.01 to 5% (mole/mole) is added, preferably of from 0.02 to 2% (mole/mole), more preferably of from 0.05 to 1% (mole/mole), even more preferably of from 0.05 to 0.5% (mole/mole).
6. A process according to any of the preceding claims,  
30 wherein the hydrocarbonaceous feedstock comprises

methane, natural gas, associated gas or a source of light hydrocarbons, preferably natural gas or methane.

7. A process according to any of the preceding claims, wherein the oxygen-containing gas is oxygen.

5 8. A process according to any of the preceding claims, which is a process for the partial oxidation of the hydrocarbonaceous feedstock, preferably for the catalytic partial oxidation of the hydrocarbonaceous feedstock.

## INTERNATIONAL SEARCH REPORT

Inte Application No

PCT/EP 01/04852

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C01B3/36 C01B3/38

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 7 C01B B01J F23D F23C F23L

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)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 673 877 A (EXXON RESEARCH ENGINEERING CO) 27 September 1995 (1995-09-27) the whole document	1-8
A	--- DATABASE WPI Section Ch, Week 197412 Derwent Publications Ltd., London, GB; Class E36, AN 1974-22205V XP002133587 & JP 49 008633 B (AJINOMOTO KK), 27 February 1974 (1974-02-27) abstract	1
A	--- US 3 138 438 A (L. PÉRAS) 23 June 1964 (1964-06-23) claim 1 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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\*G\* document member of the same patent family

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## INTERNATIONAL SEARCH REPORT

Int Application No  
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## 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 0 842 894 A (TOPSOE HALDOR AS) 20 May 1998 (1998-05-20) the whole document ---	1
A	US 4 089 639 A (REED ROBERT D ET AL) 16 May 1978 (1978-05-16) claim 1 ---	1
A	EP 0 629 578 A (SHELL INT RESEARCH) 21 December 1994 (1994-12-21) cited in the application example 1 ---	1-3,6-8
A	WO 01 18451 A (WENTINCK HENDRIK MARTINUS ;SHELL INT RESEARCH (NL)) 15 March 2001 (2001-03-15) claims ---	1
E	EP 1 095 903 A (SHELL INT RESEARCH) 2 May 2001 (2001-05-02) the whole document -----	1-8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/04852

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0673877	A	27-09-1995	AU 682751 B2	16-10-1997
			AU 1504695 A	05-10-1995
			CA 2143962 A1	26-09-1995
			DE 69501225 D1	29-01-1998
			DE 69501225 T2	09-07-1998
			EP 0673877 A1	27-09-1995
			NO 951103 A	26-09-1995
			ZA 9501926 A	09-01-1996
-----				
JP 49008633	B	27-02-1974	NONE	
-----				
US 3138438	A	23-06-1964	NONE	
-----				
EP 0842894	A	20-05-1998	AT 199366 T	15-03-2001
			CN 1185416 A	24-06-1998
			DE 69704147 D1	05-04-2001
			DE 69704147 T2	16-08-2001
			EP 0842894 A1	20-05-1998
			ES 2157512 T3	16-08-2001
			JP 10245201 A	14-09-1998
-----				
US 4089639	A	16-05-1978	CA 1054041 A1	08-05-1979
			DE 2552882 A1	12-08-1976
			FR 2292932 A1	25-06-1976
			GB 1529808 A	25-10-1978
			IT 1052380 B	20-06-1981
			JP 51077933 A	06-07-1976
			NL 7513222 A	31-05-1976
-----				
EP 0629578	A	21-12-1994	EP 0629578 A1	21-12-1994
			AT 195922 T	15-09-2000
			AU 672901 B2	17-10-1996
			AU 6478694 A	22-12-1994
			BR 9402445 A	24-01-1995
			CA 2126036 A1	19-12-1994
			CN 1101891 A ,B	26-04-1995
			DE 69425692 D1	05-10-2000
			DE 69425692 T2	19-04-2001
			ES 2152965 T3	16-02-2001
			JP 7010503 A	13-01-1995
			NO 942284 A	19-12-1994
			NZ 260621 A	26-03-1996
			RU 2123471 C1	20-12-1998
			ZA 9404286 A	10-02-1995
-----				
WO 0118451	A	15-03-2001	AU 7001400 A	10-04-2001
			WO 0118451 A1	15-03-2001
-----				
EP 1095903	A	02-05-2001	EP 1095903 A1	02-05-2001