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(54) **Title:** PROCESS AND APPARATUS FOR REMOVING ETHYLENE FROM A FLUE GAS MIXTURE

(57) **Abstract:** The invention relates to a process for removing ethylene, and possibly SO₂ and NO_x, from a flue gas mixture containing inter alia CO₂, O₂, SO₂, NO_x and ethylene, wherein in a first step SO₂ is removed from the flue gas mixture through adsorption; then, in a second step NO_x is removed through adsorption; and after this, in a third step ethylene is removed through catalytic oxidation, and to an apparatus suitable therefor.

Title: Process and apparatus for removing ethylene from a flue gas mixture.

The invention relates to a process and apparatus for removing ethylene from a flue gas mixture.

There is an increasing need to purify flue gases from engines, more particularly (bio)gas engines, to a far-reaching extent. Typically, these flue gases still contain organic compounds, such as methane and ethylene, as well as inorganic compounds, such as sulfur oxides (SO₂), nitrogen oxides (NO_x) and carbon monoxide. For the further use of flue gases, for example as a CO₂ source in greenhouses, it is desired that the flue gases contain as few pollutants as possible, in particular that they contain as few sulfur oxides, nitrogen oxides and ethylene as possible. Also for the emission of the flue gases to the atmosphere, it is desired that the content of pollutants be as low as possible.

To be able to effectively remove organic compounds and carbon monoxide, the flue gases are typically treated by passing them over an oxidation catalyst, with or without supply of extra oxygen to the flue gas. The organic compounds and the carbon monoxide in this way can be oxidized to form CO₂. A suitable catalyst has been described, for example, by Wang *et al.* (Low temperature complete combustion of methane over titania-modified alumina supported palladium, Fuel 81 (2002) 1883–1887). In that publication, the positive effect is described of titania on the activity of a palladium catalyst for the oxidation of ethylene.

Preferably, it is endeavored to combine the removal of the organic compounds and the carbon monoxide with the removal of sulfur oxides and/or nitrogen oxides. If a flue gas mixture is passed under oxidative

conditions over specific adsorbents for sulfur oxides and nitrogen oxides, also the sulfur oxides and nitrogen oxides can be effectively removed from the stream of the flue gas mixture. Such systems, in which on the one hand the carbon-containing compounds are oxidized to CO₂ and on the other hand
5 the sulfur oxides and/or nitrogen oxides are adsorbed, utilize, for example, monolithic blocks with platinum catalyst and adsorption material immobilized thereon.

As is well-known, it is desirable to supply CO₂ to horticultural greenhouses as a carbon source for the growth of the plants. This can be
10 done via gas pipes, through separate supply with tank trucks and/or storage in containers. Often, it is endeavored to use CO₂ from gas engine flue gases that are used for combined heat and power (CHP) cogeneration at the greenhouse.

To this end, it is necessary to lower the concentration of nitrogen
15 oxides, sulfur oxides and ethylene. For it is well-known that the first two gases have an adverse effect on crop growth, and that the last gas is a growth hormone for plants. Too much ethylene in (horticultural) greenhouses can lead to soft crops with fruits ripening too soon and too fast.

As expected, under oxidative conditions prevailing in the different
20 monolithic blocks, both the concentration of sulfur oxides, or nitrogen oxides, and the concentration of ethylene can be reduced. The ethylene concentration proved to be reduced from 40,000 ppb to 2,000 ppb. Through the use of an extra monolith, specifically for the oxidation of ethylene, it was found that the concentration of ethylene can be reduced to 300 ppb. While
25 this satisfies the current standards for (horticultural) greenhouses, the concentration of ethylene is still too high for future standards.

It is an object of the invention to provide a process by which the ethylene content in the CO₂ can be reduced to values in the order of magnitude of a few tens of ppb's at most.

It is in particular an object of the invention to find a procedure by which the concentration of ethylene can be reduced to less than 300 ppb, in particular to less than 10 ppb.

The invention is based on the surprising insight that through the specific choice of the order of the treatment steps in the process leads to a surprisingly good purification of the gases and yields a CO₂ gas stream that is so pure that it can be used as a CO₂ feed for greenhouses without any problems. Only with the present order is this result obtained, as appears from the examples included herein. Other orders of treatment lead only to a limited and insufficient result.

The invention accordingly relates to a process for removing ethylene, and possibly SO₂ and NO_x, from a flue gas mixture containing *inter alia* CO₂, O₂, SO₂, NO_x and ethylene, wherein in a first step SO₂ is removed from the flue gas mixture through adsorption; then, in a second step NO_x is removed through adsorption, and after this, in a third step ethylene is removed through catalytic oxidation.

The present invention further relates to an apparatus for removing ethylene from a flue gas mixture, comprising in downstream direction:

- a compartment for the removal of SO₂ from the flue gas mixture, comprising a catalytic oxidation/adsorption material for SO₂;
- a compartment for the removal of NO_x from the flue gas mixture, comprising a catalytic oxidation/adsorption material for NO_x; and
- a compartment for the removal of ethylene from the flue gas mixture, comprising an oxidation catalyst, in particular an oxidation catalyst comprising platinum or palladium or the combination of the two.

According to a preferred embodiment, for the removal of SO₂ a combination of catalytic oxidation of SO₂ into SO₃ and adsorption of SO₃ is used. The oxidation catalyst and the adsorbent are then preferably integrated in the same material, which as such, in turn, may be provided on

a monolith. Suitable catalysts are noble metals, while as adsorbent a material that forms sulfates is used. An example of a suitable combination of materials is Pt/Cu on titania.

For the removal of NO_x a comparable system is used, a preferred material being Pt/K salt, such as a carbonate, on alumina washcoat.

Ethylene is most preferably removed using a noble metal on a washcoat. Suitable noble metals are platinum, palladium or combinations thereof. As a washcoat, preferably alumina or titania is used.

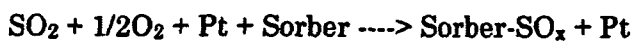
Since all process steps preferably utilize oxidation, it is desired that in the gas mixture oxidizing conditions prevail, preferably an excess of oxygen with respect to the components to be oxidized.

As soon as the materials are saturated, regeneration may be done under reducing conditions, for example through treatment with CO and/or H₂.

The invention is preferably used for the treatment of flue gases of gas engines. To be considered in this connection are, for instance, engines with powers of from 1 MWe to 22 MWe, flue gas flow rates in the range of from 5,000 kg/h to 110,000 kg/h, with temperatures of between 300 and 500°C.

In a representative example, for the removal of NO_x a Pt/KCO₃ system is used. Adsorption takes place under oxidizing conditions, the following two reaction schemes being representative of the removal and desorption.

Adsorption of SO₂ (oxidizing conditions; Pt.Cu on a titania washcoat)



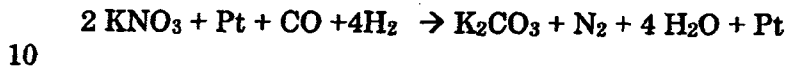
Desorption (reducing conditions)



For the removal of NO_x (NO) a comparable reaction scheme applies, where as adsorbent a Pt/ an alumina washcoat is used



Desorption (reducing conditions)



In the following examples, under comparable conditions the conversion of ethylene, SO₂ and NO_x is given with different configurations of the catalysts.

15 Flue gases of a gas engine with a temperature of 400°C were treated using a removal system with various configurations.

In the table the conversion values of NO_x and ethylene are given for different configurations. The NO_x and SO₂ removal are based on the systems as described above. Ethylene removal is done with the aid of a Pt catalyst on an alumina washcoat.

20

Average ethylene and NO_x values under practical conditions

Inlet concentration		configuration	Outlet concentration	
Ethylene (ppb)	NO _x (ppm)		Ethylene (ppb)	NO _x (ppm)
40,000	130-220	no cleaner	40,000	130-220
40,000	130-220	SO ₂ NO _x NO _x NO _x	1500 – 2000	1-3
40,000	130-220	<u>OXI</u> SO ₂ NO _x NO _x NO _x	200 – 300	1-3
40,000	130-220	SO ₂ <u>OXI</u> NO _x NO _x NO _x	200 – 300	1-3
30 40,000	130-220	SO ₂ NO _x NO _x NO _x <u>OXI</u>	< 50	1-3

This shows that the ethylene conversion before the SO₂ and before the NO_x (after the SO₂) gives the same conversion of ethylene from

approximately 40,000 ppb to approximately 200-300 ppb. This conversion satisfies the current standards for ethylene concentration to the horticultural greenhouse, but for future standards the conversion level is too low.

5 Surprisingly, the placement of the oxidation catalyst after the NO_x adsorption gives a much higher degree of conversion of ethylene (40,000 ppb to less than 50 ppb and in most cases below 10 ppb and in some cases below the detection level of 2 ppb).

10 The reasons of this surprisingly strong reduction of the ethylene content cannot be explained on the basis of the known literature and the patent literature.

Claims

1. A process for removing ethylene, and possibly SO₂ and NO_x, from a flue gas mixture containing *inter alia* CO₂, O₂, SO₂, NO_x and ethylene, wherein in a first step SO₂ is removed from the flue gas mixture through adsorption; then, in a second step NO_x is removed through adsorption; and
5 after this, in a third step ethylene is removed through catalytic oxidation, wherein in each step preferably an excess of oxygen is present.
2. A process according to claim 1, wherein the adsorption of SO₂ is done with the aid of a catalytic oxidation of SO₂ to SO₃ and adsorption of the SO₃ formed, preferably with the aid of a Pt/Cu on titania catalyst/adsorbent.
- 10 3. A process according to claim 1 or 2, wherein the adsorption of NO_x is done with the aid of a catalytic oxidation of NO_x to NO₃ and adsorption of the NO₃ formed, preferably with the aid of a Pt/alkali metal on alumina catalyst/adsorbent.
4. A process according to claims 1-3, wherein the catalytic oxidation of
15 ethylene is done with the aid of a supported noble metal catalyst, preferably a platinum on a metal oxide, such as alumina.
5. A process according to claim 4, wherein the catalytic oxidation of ethylene is done in a monolith, provided with an alumina or titania washcoat with noble metal catalyst.
- 20 6. A process according to claims 1 - 5, wherein the concentration of ethylene after the third step is lower than 300 ppb, in particular lower than 50 ppb, and more particularly lower than 10 ppb.
7. A process according to claims 1 - 6, wherein the concentration of NO_x after the third step is lower than 10 ppm, preferably lower than 5 ppm,
25 in particular lower than 2 ppm.
8. An apparatus for removing ethylene from a flue gas mixture, comprising in downstream direction

- a compartment for the removal of SO₂ from the flue gas mixture, comprising a catalytic oxidation/adsorption material for SO₂;
 - a compartment for the removal of NO_x from the flue gas mixture, comprising a catalytic oxidation/adsorption material for NO_x; and
 - 5 - a compartment for the removal of ethylene from the flue gas mixture, comprising an oxidation catalyst, in particular an oxidation catalyst comprising platinum.
9. Use of an apparatus according to claim 8 in horticultural greenhouses.
- 10 10. Use of an apparatus according to claim 8 for the purification of CO₂.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2009/050716

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/86

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)
B01D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 780 002 A (MIYADERA TATSUO [JP] ET AL) 14 July 1998 (1998-07-14) column 9, lines 14,15; claim 3	1-10
A	EP 1 226 862 A (RUHRGAS AG [DE]) 31 July 2002 (2002-07-31) the whole document	1-10
A	EP 1 090 674 A (SHIMAKAWA SEISAKUSYO CO LTD [JP]) 11 April 2001 (2001-04-11) the whole document	1-10
A	FR 2 640 889 A (TOULOUSE INST NAT POLYTECH [FR]) 29 June 1990 (1990-06-29) the whole document	1-10
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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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 11 March 2010	Date of mailing of the international search report 17/03/2010
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INTERNATIONAL SEARCH REPORT

International application No PCT/NL2009/050716

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/247196 A1 (BENESCH ROBERT [US] ET AL) 10 November 2005 (2005-11-10) the whole document -----	1-10
A	EP 0 799 633 A (LINDE AG [DE]) 8 October 1997 (1997-10-08) the whole document -----	1-10
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2009/050716

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EP 0799633	A	08-10-1997	NONE
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