

Chemical-Looping with Oxygen Uncoupling for capture of carbon dioxide February 2, 2005 (Translation of Swedish patent application)

Applicants and inventors
Anders Lyngfelt and Tobias Mattisson

1 Chemical-Looping with Oxygen Uncoupling (CLOU)

The patent application addresses a method of combustion, Chemical-Looping with Oxygen Uncoupling, with capture of carbon dioxide. Chemical-Looping with Oxygen Uncoupling means that the combustion involves three steps in two reactors, one air reactor where a metal oxide captures oxygen from the combustion air (step 1), and a fuel reactor where the metal oxide decomposes and releases oxygen (step 2) and where this oxygen reacts with a fuel (step 3). The method is suitable to capture carbon dioxide during combustion, for example in order to reduce effects on climate.

2 Background

Developing carbon dioxide separation processes with low cost could be of great importance for reducing carbon dioxide emissions from combustion.

Geological storage of carbon dioxide on a large scale has been demonstrated in the North Sea¹ by 1 million tonnes/year since 1996, as well as in Canada. Such storage is relatively inexpensive. There are several techniques for separating carbon dioxide from combustion. Most of these require costly and energy-consuming gas separation.² A common estimate of the cost of separating carbon dioxide with these methods is around 500 SEK/tonne of carbon dioxide, or an estimated increase in the cost of producing electricity by 50 to 100%.

An alternative carbon capture process for combustion currently being studied in several parts of the world is chemical-looping combustion. There is a large number of publications related to this process, and here are some examples.^{3,4,5,6,7} A characteristic of chemical-looping combustion is that carbon dioxide can be separated without any actual gas separation step, potentially reducing the cost of carbon capture. The process of the patent application, Chemical-Looping with Oxygen Uncoupling, has some basic similarities to chemical-looping combustion and therefore chemical-looping combustion, and its limitations will be described below. The main limitation of chemical-looping combustion is that the process is difficult to

¹Torp, G, and Gale, J, Demonstrating storage of CO₂ in geological reservoirs: the Sleipner and SACS projects, Proceedings of the 6th International Conference on Greenhouse Gas Control Technologies, Kyoto, October 1-4, 2002, Pergamon 2003, pp. 311-316.

² Lyngfelt, A. and Leckner, B. "Technologies for CO₂ separation." Minisymposium on Carbon Dioxide Capture and Storage, Chalmers University of Technology and Göteborg University, Göteborg, October 22, 1999, pp. 25-35. (available on <http://www.entek.chalmers.se/~anly/symp/sympCO2.html>)

³ Lyngfelt A, Leckner B, and Mattisson T. 2001. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. *Chemical Engineering Science* Vol. 56: 3101-3113.

⁴ Jin H, Okamoto T, and Ishida M. 1999. Development of a Novel Chemical-Looping Combustion: Synthesis of a Solid Looping Material of NiO/NiAl₂O₄. *Industrial and Engineering Chemistry Research* Vol. 38: 126-132.

⁵ Copeland, R.J, Alptekin, G., Cesario, M., and Gershanovich, Y., A Novel CO₂ Separation System, First National Conference on Carbon Sequestration, May 14-17, 2001, U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA, USA.

⁶ Song, K., Seo, Y., Yoon, H., and Cho, S., 2003. Characteristics of the NiO/Hexaaluminate for Chemical Looping Combustion, *Korean Journal of Chemical Engineering* Vol. 20, No. 3: 471-475.

⁷ Lyngfelt, A., Kronberger, B., Adanez, J., Morin, J.-X., and Hurst, P., The GRACE project. Development of oxygen carrier particles for chemical-looping combustion. Design and operation of a 10 kW chemical-looping combustor. *7th International Conference on Greenhouse Gas Control Technologies*, Vancouver, Canada, 5th-9th September 2004.

apply to solid fuels. The process for which the patent application relates, Chemical-Looping with Oxygen Uncoupling, is, however, very well suited for use with solid fuels.

3 Chemical-looping combustion

Chemical-looping combustion, is a process for CO₂ capture that utilizes the transfer of oxygen between air and a gaseous fuel by means of a metal oxide. The gaseous fuel reacts with the metal oxide to CO₂ and steam in one reactor, and is regenerated by combustion air in another reactor, as illustrated by the reactions below.



Netreaction (reaction 1 + 2):

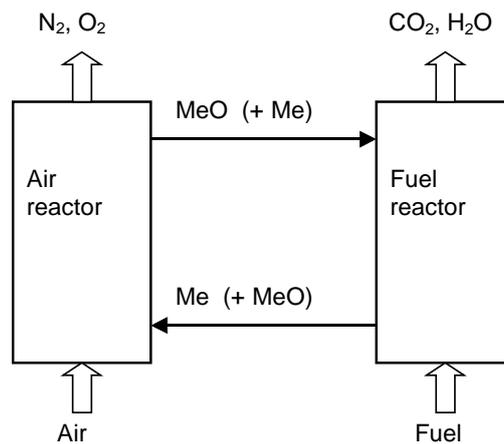
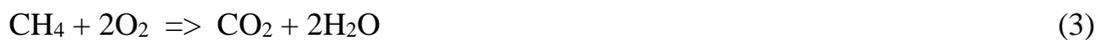
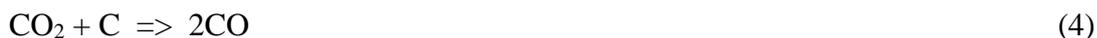


Figure 1: Chemical-looping combustion. MeO/Me denote recirculated oxygen carrier solid material.

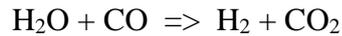
Chemical-looping combustion can also be applied to directly to solid fuels, although this involves a solid-solid reaction (solid fuel particles – metal oxide). The transfer of oxygen in this solid-solid reaction can be accomplished by gases like CO₂, H₂O or SO₂, as illustrated by the reactions below, where the solid fuel for simplicity is assumed to consist only of carbon (C). :



The net reaction in fuel reactor is then:



Similarly steam can also transfer oxygen:



Again the net reaction in the fuel reactor is:



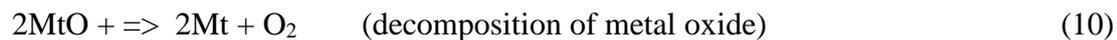
4 Problem

A possible problem in the adaption of chemical-looping combustion to solid fuels could be that reactions (4) and (7) are known to be slow, which in combination with a high circulation flow of particles would mean that the solids inventory in the fuel reactor would be high.

5 Solution to the problem, Chemical-Looping with Oxygen Uncoupling, CLOU

In the method proposed, "Chemical-Looping with Oxygen Uncoupling", the oxidation of the solid fuel proceeds through two steps. Firstly the oxygen carrier is decomposed and releases gaseous oxygen. Secondly the fuel, which can be a solid fuel, reacts with this oxygen. This demands another type of oxygen carrier than those normally used in chemical-looping combustion. The oxygen carriers needed in CLOU must have the ability to both react with oxygen and decompose through oxygen release at suitable temperatures.

These oxygen carriers are below denoted by $\text{MtO} - \text{Mt}$, where MtO is a metal oxide and Mt is the reduced metal oxide. Below the fuel, which could be a solid fuel, is represented by carbon (C). The two steps in the fuel reactor are then:



If the fuel also contains hydrogen there will also be a formation of steam, reaction (11b)



The third step is the regeneration of the metal oxide:



The net reaction is then (reaction 10 + 11 + 12):



Here is seen that reactions (10) and (12) cancel each other and the net reaction (13) is identical to reaction (11). If the fuel also includes hydrogen the net reaction will become identical to reaction (11b). Thus the metal oxide particles are used to transfer the oxygen to the fuel reactor, where the actual combustion takes place.

Figure 2 shows the layout of the process. The important different compared to chemical-looping combustion, Fig. 1, is that a metal oxide is used that spontaneously decomposes in the fuel reactor. Thus, the fuel does not need to react with the metal oxide, and instead it burns as in normal combustion, through reaction with the oxygen released. This creates large possibilities for the use of solid fuels that cannot react directly with the metal oxide.

The solution means that the solid fuel does not need to be converted through the slow gasification reactions (4) and (7), but instead the fuel may react directly with the oxygen (a fast reaction, known as combustion).

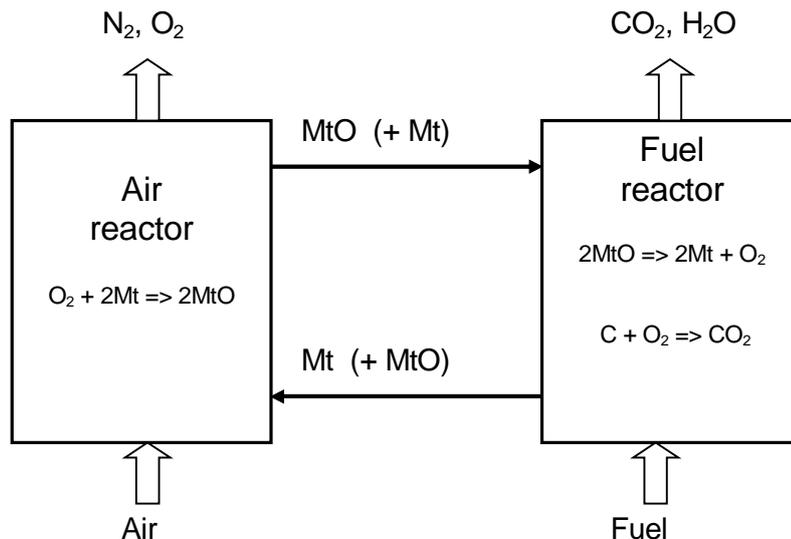


Fig. 2. Principal layout of Chemical-Looping with Oxygen Uncoupling. The oxygen carrier is denoted by MtO – Mt, where MtO is a metal oxide and Mt is a metal or a metal oxide with lower oxygen content compared to MtO. The fuel is here carbon (C). A carrier gas, e.g. recirculated CO₂ or steam, is most likely needed for the case of solid fuel. Most likely the reactors are fluidized beds.

5.1 Metal oxides that can be used in the process

As mentioned above the process needs oxygen carriers that have both the ability to release and capture oxygen at suitable temperatures. Three such carriers have been identified: CuO/Cu₂O, Mn₂O₃/Mn₃O₄, and Co₃O₄/CoO. CuO decomposes spontaneously in air at temperatures above 1030 C, Mn₂O₃ at temperatures above 820 C and Co₃O₄ at temperatures above 890 C. There may also be other metal oxides that could be used in this process.

Table 1 shows the equilibrium pressure of O₂ versus temperature for these oxide pairs.

As can be seen in Table 1, Mn₃O₄, should react with air under formation of Mn₂O₃, and be able lower the oxygen concentration to 5% if the temperature is 750 C or below. (5% corresponds to an excess air of 25%⁸, which is a rather normal level in combustors.) When these particles are transferred to the fuel reactor they will decompose and release gaseous O₂, and at this temperature this reaction could give an maximum oxygen partial pressure of appr.

⁸ Note that the calculation of excess air for this process is somewhat different from conventional combustion, because the gas is more concentrated as the combustion products, CO₂ and H₂O, leave the process in a separate stream.

5%. Because of the reactions taking place in the fuel reactor together are exothermal, it is possible to have at temperature increase that produces a significantly higher partial pressure of O₂, which can be seen in Table 1. Thus, for instance a temperature increase of 50 C, to 800 C, would give an maximum oxygen partial pressure of appr. 14%. The heat balances below shows that a temperature of this order may well be realistic.

Tabell 1. Equilibrium partial pressure over oxygen carriers.

T, C	P _{O2} over CuO/Cu ₂ O	P _{O2} over Mn ₂ O ₃ /Mn ₃ O ₄	P _{O2} over Co ₃ O ₄ /CoO
700		0.017	
725		0.030	
750		0.051	0.000635
775		0.086	
800	0.0012	0.139	0.005826
825	0.0024	0.222	
850	0.0046	0.345	0.043192
875	0.0084	0.526	
900	0.015	0.787	0.265291
925	0.026	1.157	
950	0.045		
975	0.076		
1000	0.124		
1025	0.199		
1050	0.313		

Similarly, Cu₂O should react with air under formation of CuO, and be able lower the oxygen concentration at most to slightly below 5% if the temperature is 950 C or below, see Table 1. (5% corresponds to an excess air of 25%⁹, which is a rather normal level in combustors.) When these particles are transferred to the fuel reactor they will decompose and release gaseous O₂, and at this temperature this reaction could give an maximum oxygen partial pressure of somewhat above 4%. Because of the reactions taking place in the fuel reactor together are exothermal, it is possible to have at temperature increase that produces a significantly higher partial pressure of O₂, which can be seen in Table 1. Thus, for instance a temperature increase of 50 C, to 1000 C, would give an maximum oxygen partial pressure of appr. 12%. The heat balances below shows that a temperature of this order may well be realistic.

It is also possible to use the temperature increase in the fuel reactor to choose a lower temperature in the air reactor. With for instance 925 C in the air reactor it is possible to reduce the oxygen concentration at most to 2.6%, and with 975 C in the fuel reactor would a maximum concentration of O₂ of 7.6% be possible to achieve.

Similarly, CoO should react with air under formation of Co₃O₄, and be able lower the oxygen concentration at most to slightly below 5% if the temperature is 850 C or below, see Table 1. (5% corresponds to an excess air of 25%, which is a rather normal level in combustors.) When these particles are transferred to the fuel reactor they will decompose and release gaseous O₂, and at this temperature this reaction could give an maximum oxygen partial

⁹ Note that the calculation of excess air for this process is somewhat different from conventional combustion, because the gas is more concentrated as the combustion products, CO₂ and H₂O, leave the process in a separate stream.

pressure of somewhat above 4%. For cobalt oxide the reactions in the fuel reactor are slightly endothermic. Thus, no temperature increase is possible in the fuel reactor

5.2 Heat balances

5.2.1 Heat balance for manganese oxide

To simplify, we assume that the solid fuel is represented by carbon (C), and overall reaction in the fuel reactor, reaction (10) plus (11), is then for manganese oxide:



Table 2 shows heat capacities for reactants and products.

Tabell 2. Heat capacity for reactants and products.

	c_p J/K,mol (at 1200 K)
Mn ₂ O ₃	144,719
Mn ₃ O ₄	203,563
CO ₂	56,342
CuO	86,123
Cu ₂ O	56,978
CO ₂	49,7 (medelvärde 0-1000 C)

If we assume 20% conversion of the fuel we obtain the molar balance shown in Table 3.

Table 3. Molar balance for reaction (14) assuming 20% conversion of the oxide

	Reactants, mol	Products, mol
Mn ₂ O ₃	30	24 (unreacted reactant)
C	1	
Mn ₃ O ₄		4
CO ₂		1

From the molar balance it is possible to derive the heat capacity, c_p , for the products:

$$c_{p, \text{products}} = 4343.8 \text{ J/K}$$

and the reaction enthalpy for reaction (14) should then give the following temperature increase for the products¹⁰:

$$\Delta T = -\Delta H / c_{p, \text{products}} = 47 \text{ K}$$

which would give a temperature of approximately 800, if the particles entering are 750 C.

Furthermore, we assume that we may need a gas stream to fluidize the fuel reactor in the form of recycled CO₂, that the recycle flow is 0.5 mol per mol of CO₂ produced and that this flow is not preheated and needs to be heated from 100 C to 900 C. The temperature increase would then be a few degrees lower, i.e. 42 C. It is also possible to use steam as fluidization

¹⁰ The reaction enthalpy is here taken at 950 C, but it is reasonably independent on temperature, so the error because of this is small.

gas. Steam has a somewhat lower heat capacity, compared to carbon dioxide, but that would only affect the temperature increase marginally.

Comment to the heat balance / molar balance. It is not at all excluded that a much higher could be feasible. Tests with CuO suggest that a more or less full conversion of the oxide could be feasible. The temperature increase would correspond to the conversion, and for an almost complete conversion be above 200 C. On the other hand it is not unlikely that the active oxide is mixed with an inert support material, which would increase the heat capacity of the oxide, as taken per mol of active oxide.

If high conversion is possible it may not necessarily be used. Particle circulation may be increased so that the change in conversion is decreased, thus reducing the temperature difference between the two reactors. If high conversion is possible it means that a significant freedom to choose suitable temperatures of operation for the reactors.

5.2.2 Heat balance CuO

Again, we assume that the solid fuel is represented by carbon (C), and overall reaction in the fuel reactor, reaction (10) plus (11), is then for copper oxide:



Table 4 shows heat capacities for reactants and products.

Table 4. Heat capacities for reactants and products.

	cp J/K,mol (at 1200 K)
CuO	86,123
Cu ₂ O	56,978
CO ₂	56,342

If we assume 20% conversion of the fuel we obtain the molar balance shown in Table 5.

Table 5. Molar balance for reaction (15) assuming 20% conversion of the oxide

	Reactants, mol	Products, mol
CuO	20	16 (not reacted)
C	1	
Cu ₂ O		2
CO ₂		1

From the molar balance it is possible to derive the heat capacity, c_p , for the products:

$$c_{p, \text{products}} = 1548.3 \text{ J/K}$$

and the reaction enthalpy for reaction (15) should then give the following temperature increase for the products:

$$\Delta T = -\Delta H / c_{p, \text{products}} = 86 \text{ K}$$

which would give a temperature of approximately 975, if the particles entering are 890 C.

Furthermore, we assume that we may need a gas stream to fluidize the fuel reactor in the form of recycled CO₂, that the recycle flow is 0.5 mol per mol CO₂ produced, and that this flow is not preheated and needs to be heated from 100 C to 900 C. The temperature increase would then be a somewhat lower, i.e. 73 C.

Comment to the heat balance / molar balance. Just as in the case of Mn₂O₃/Mn₃O₄, it is not at all excluded that a much higher conversion could be feasible, which would give a correspondingly larger temperature increase.

5.2.3 Heat balance for Co₃O₄

Again, we assume that the solid fuel is represented by carbon (C), and overall reaction in the fuel reactor, reaction (10) plus (11), is then for cobalt oxide:



Table 6 shows heat capacities for reactants and products.

Table 6. Heat capacities for reactants and products.

	cp J/K,mol (at 1200 K)
Co ₃ O ₄	236,733
CoO	57,922
CO ₂	56,342

If we assume 20% conversion of the fuel we obtain the molar balance shown in Table 7.

Table 7. Molar balance for reaction (16) assuming 20% conversion of the oxide

	Reactants, mol	Products, mol
Co ₃ O ₄	10	8 (not reacted)
C	1	
CoO		6
CO ₂		1

From the molar balance and the c_p values in Table 6, it is possible to derive the heat capacity, c_p, for the products:

$$c_{p, \text{products}} = 2297.7 \text{ J/K}$$

and the reaction enthalpy for reaction (16) should then give the following temperature change for the products:

$$\Delta T = -\Delta H / c_{p, \text{products}} = -2 \text{ K}$$

Furthermore, we assume that we may need a gas stream to fluidize the fuel reactor in the form of recycled CO₂, that the recycle flow is 0.5 mol per mol CO₂ produced, and that this flow is not preheated and needs to be heated from 100 C to 900 C. This would give a temperature decrease of totally 10 C.

Comment to the heat balance / molar balance. The reaction with the fuel is slightly endothermal and the temperature change will be small.

5.2 Test results for CuO

Figure 3 shows a test where O₂ is released from copper oxide at appr. 947 C. At the time 5320 s, the air is shifted from air to nitrogen. The figure shows that the copper oxide spontaneously decomposes at this temperature giving 2.6% of oxygen in the exiting gas. The level is very constant and is most likely limited due to thermodynamics. (This means that if there was a consumption of the oxygen by char particles, the oxygen would be released more rapidly.) At the time 5620 s gaseous fuel, methane, is added. The methane reacts directly with the copper oxide producing CO₂, but it also gives a temperature increase promoting the spontaneous release of O₂. The peak in O₂ concentration is 13% at a temperature of 973 C. This oxygen concentration is above what is expected according to the thermodynamics, Table 1. However, it should be pointed out that the bed is in an oven with a temperature of appr. 950 C, and the thermocouple is slightly above the bed and does not measure the bed temperature directly. With an exothermal reaction it is possible that the bed may reach a higher temperature than what is shown by the thermocouple.

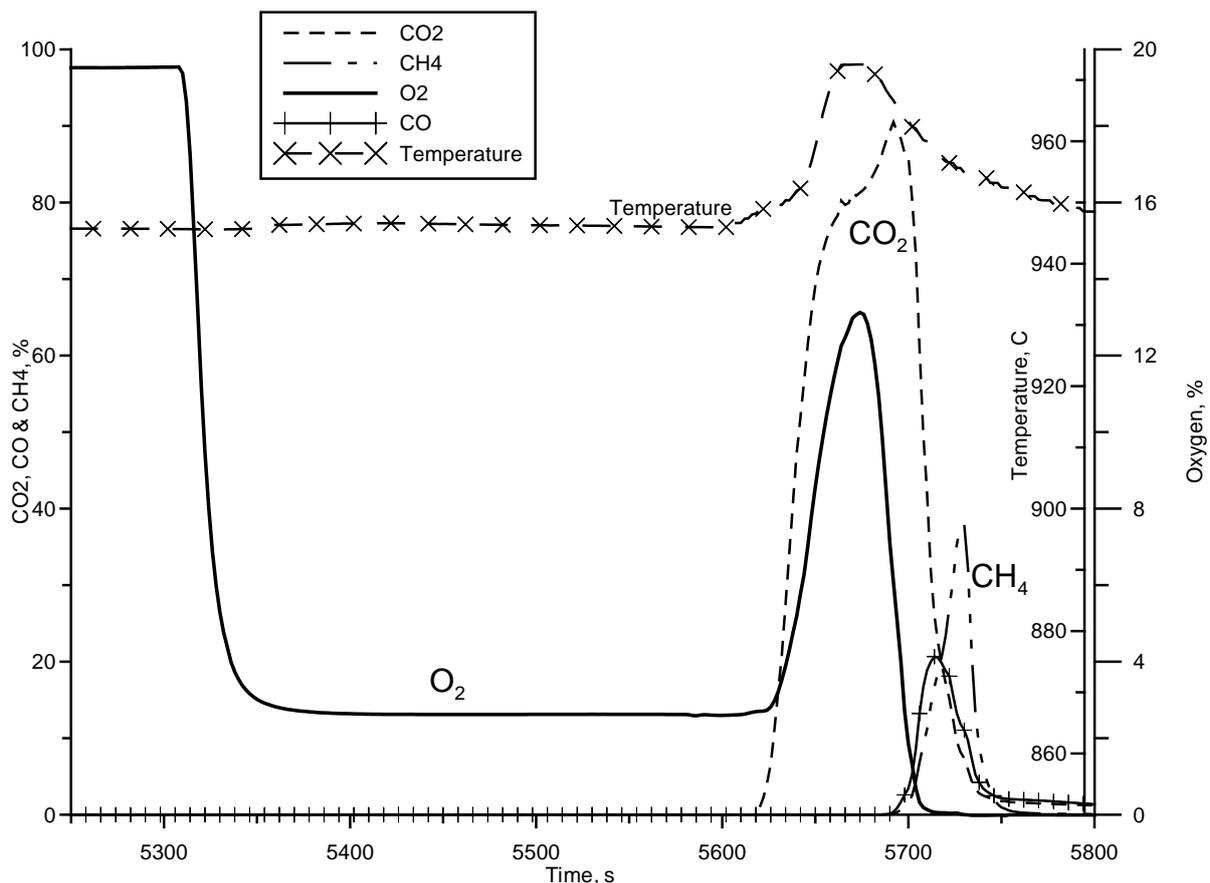


Figure 3. Decomposition of oxide with oxygen release. After the oxidation period the nitrogen addition is started at appr. 5320 s, and methane addition is started at 5620 s.

In Fig. 4 is shown that the metal oxide at this temperature, 950 C, is able to capture oxygen from air and regenerate the CuO. The small CO₂/CO peaks at 6050 s, are caused by the formation of small amounts of char on the particles during the last phase of the reduction

period when the methane concentration is high. When the oxidation period starts this char burns.

In the first part of the period all available oxygen is consumed, which can be explained by the fact that the methane in the previous reduction cycle reduced the copper oxide all the way to Cu, and it can be assumed that this Cu is first oxidized to Cu_2O . The oxidation becomes gradually slower and the oxygen concentration rises to the inlet concentration. The latter part of the oxidation phase then shows the oxidation of Cu_2O to CuO .

The reduction/oxidation cycle shown in Figure 3 and 4, was repeated another four times and the five cycles are shown in Figure 5. The cycles are very similar, although there is some variation in the oxygen concentration peak that appears when fuel is added. These peaks varies between 4 and 13%, which is likely caused by differences in the temperature increase.

It can be noted that the oxygen concentration during the inert period is very constant, with the lowest values between 2.6 and 2.7%.

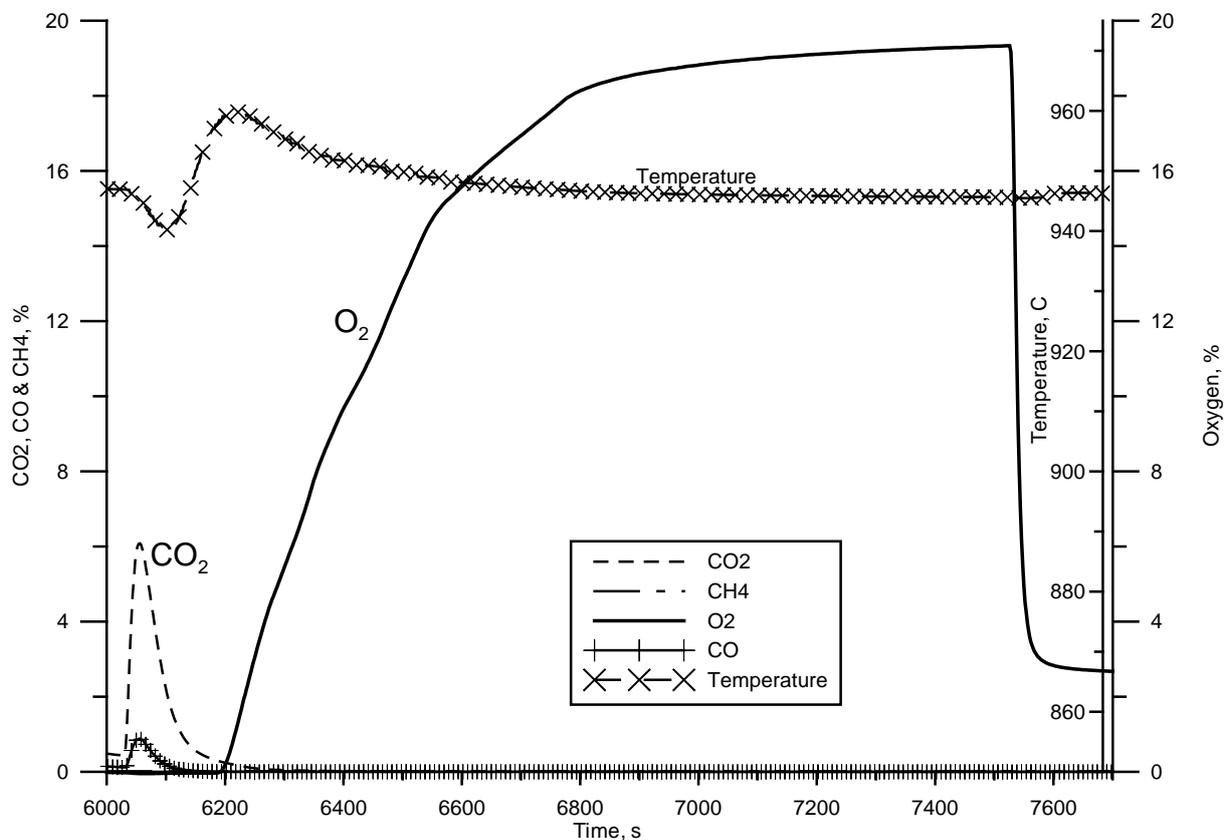


Figure 4. Oxidation period following the reduction period shown in Fig. 3.

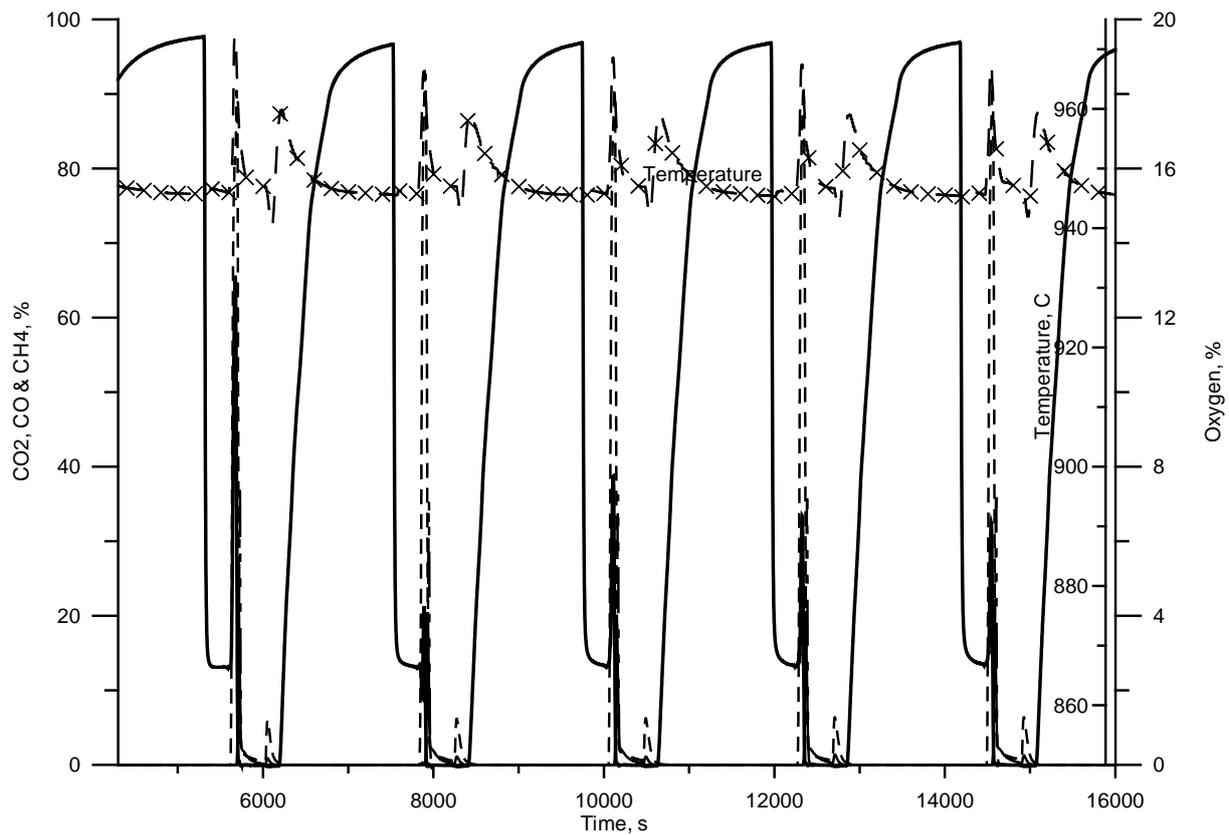


Figure 5. Five cycles of reduction and oxidation.

6 Fuels

The process can be applied to gaseous, solid and liquid fuels, but the major advantages for the process is for solid fuels.

7 Configuration of process

For the process interconnected fluidized beds can be used, see Fig. 6.

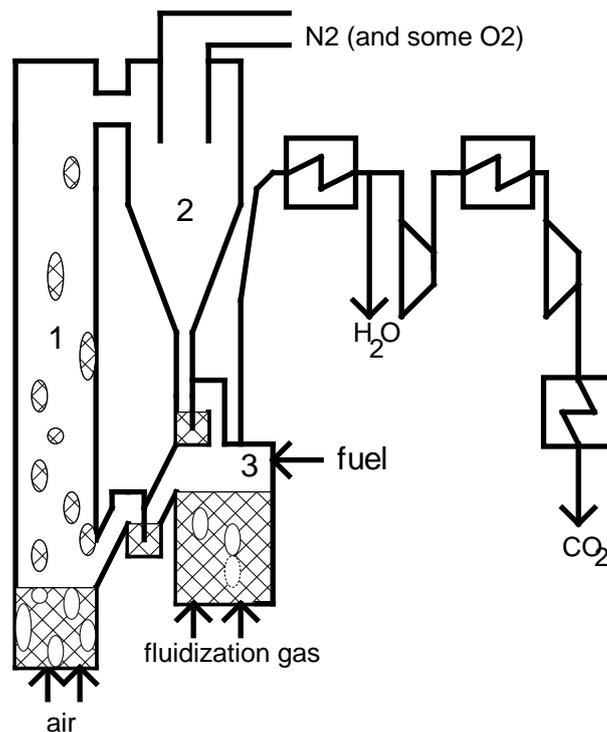


Figure 6. Simplified view of configuration of reactor system. . 1 air reactor, 2 particle separation, 3 fuel reactor.

8 Conclusions

The patent application addresses a method of combustion, Chemical-Looping with Oxygen Uncoupling, with capture of carbon dioxide. Chemical-Looping with Oxygen Uncoupling means that the combustion involves three steps in two reactors, one air reactor where a metal oxide captures oxygen from the combustion air (step 1), and a fuel reactor where the metal oxide decomposes and releases oxygen (step 2) and where this oxygen reacts with a fuel (step 3) The method is suitable to capture carbon dioxide during combustion, for example in order to reduce effects on climate.

Thermodynamic data for some different oxides shows that these should work in an indirect combustion process where they capture oxygen in an air reactor and then spontaneously decompose under oxygen release in a fuel reactor. In the fuel reactor the oxygen released then reacts with a fuel. The reaction with the fuel lowers the oxygen concentration and may thus enhance the decomposition of the metal oxide particles. In some cases the overall reaction in the fuel reactor is exothermal, as in the examples above with copper oxide and manganese oxide, which may give a temperature increase in the fuel reactor. This temperature increase is beneficial for the for the process as it further promotes the decomposition in the fuel reactor, or, as an alternative, allows for a lower temperature in the air reactor. The latter would then make a more complete conversion of the air possible, i.e. yield a lower oxygen concentration.

Tests with copper oxide shows that this may both capture and release oxygen as can be expected from the thermodynamic calculations.

The process gives a possibility to burn solid and other fuels in such a way that the combustion products carbon dioxide and steam are obtained in a separate flow. Steam is easy to separate from the carbon dioxide just by lowering the temperature below the point point of

condensation, and thus more or less pure carbon dioxide can be obtained from the combustion method proposed.

If the capture is made with the purpose of avoiding emissions of this greenhouse gas, it is for instance possible to store the gas geologically.

Summary

The patent application addresses a method of combustion, Chemical-Looping with Oxygen Uncoupling, with capture of carbon dioxide. Chemical-Looping with Oxygen Uncoupling means that the combustion involves three steps in two reactors, one air reactor where a metal oxide captures oxygen from the combustion air (step 1), and a fuel reactor where the metal oxide decomposes and releases oxygen (step 2) and where this oxygen reacts with a fuel (step 3) Metal oxides with suitable thermodynamic properties have been identified, and tests with one of these indicate that the process should be possible. Fluidized beds may be used as reactors. The method is suitable to capture carbon dioxide during combustion, for example in order to reduce effects on climate, and may potentially give substantially reduced costs for carbon dioxide capture. The method may be especially suitable for solid fuels.

Patent claims

1. Three step procedure for combustion characterized by a solid material containing metal oxide being oxidized by an oxygen-containing gas in a reactor, is transferred to another reactor where the solid material with metal oxide releases oxygen which is used to oxidize a fuel.
2. A method as claimed in Claim 1, wherein the fuel partially reacts directly with the metal oxide.
3. A method as claimed in Claim 1 or Claim 2, wherein the solid material containing metal oxide is in the form of particles and the reactors used are fluidized beds.
4. A method as claimed in Claim 1, Claim 2 or Claim 3, wherein at least 30% of the fuel reacts with the oxygen released.
5. A method as claimed in Claim 1, Claim 2 or Claim 3, wherein at least 50% of the fuel reacts with the oxygen released.
6. A method as claimed in Claim 1, Claim 2 or Claim 3, wherein at least 70% of the fuel reacts with the oxygen released.
7. A method as claimed in any preceding claim, wherein at least 80% of the fuel react is a solid fuel.
8. A method as claimed in any of the preceding claims 1 to 6, wherein at least 60% of the fuel react is a solid fuel.
9. A method as claimed in any preceding claim, wherein a temperature increase occurs during the release of oxygen and including the oxidation of fuel as a consequence of these reactions together are exothermal.
10. A method as claimed in any of the preceding claims 1 to 9, wherein a copper oxide is used for the transfer of oxygen.
11. A method as claimed in any of the preceding claims 1 to 9, wherein a manganese oxide is used for the transfer of oxygen.
12. A method as claimed in any of the preceding claims 1 to 9, wherein a cobalt oxide is used for the transfer of oxygen.