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# On the development of novel reactor concepts for chemical looping combustion

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## Abstract

The paper describes the development of a novel reactor concept for natural gas fueled chemical looping combustion (CLC). The reactor is best described as a rotating bed reactor in which a doughnut shaped fixed bed containing an oxygen carrier material is rotated between different sectors where air and methane are fed. The gases are fed radially outwards through the fixed bed. Between the air and methane sectors are sectors where an inert gas is fed to avoid uncontrolled mixing of air and methane. The rationale for the choice of reactor is discussed and a CuO/Al<sub>2</sub>O<sub>3</sub> based oxygen carrier has been selected for the initial reactor evaluation. A major challenge with the proposed reactor setup is to avoid mixing between the air and methane side caused by the unavoidable insufficient sealing between the moving parts. Initial testing show that mixing is only partly avoided, and a degree of separation corresponding to around 80% is observed at ambient temperature for the first reactor prototype. Further work will be to improve the design in order to reduce gas mixing further and to demonstrate real CLC operation utilizing the reactor.

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*Keywords:* carbon dioxide separation, chemical looping combustion, rotating reactor, CuO based oxygen carrier, enthalpy.

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## 1. Introduction

Chemical looping combustion (CLC) is one way to generate energy from natural gas with inherent carbon dioxide capture. In this concept a solid oxide material is used to oxidize natural gas to water and carbon dioxide, while the (partly) reduced oxide is re-oxidized by air in a separate gas stream.<sup>1</sup> By splitting the oxidation and reduction reactions in this manner, the effluent gas from the reactor in which the oxidation of natural gas takes place

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will be a “pure”  $\text{CO}_2/\text{H}_2\text{O}$  stream as if pure oxygen was used as oxidant. Thermodynamic cycle analyses indicate that the CLC concept can give more than 55% energy efficiency.<sup>2</sup>

In the present paper we will present the development of a new reactor setup for natural gas combustion using the CLC methodology. First, we will discuss the different reactor alternatives for the implementation of natural gas based CLC, then our choice of reactor concept and the components involved will be discussed.

## 2. Choice of reactor set-up for CLC

Basically, there are three ways to implement continuous natural gas fired CLC: Either one can keep the oxygen carrier material static in a fixed bed and switch the feed to this reactor between different gas compositions, an approach we here denote “*move feed*”. A second alternative is to move the oxygen carrier material between different reactors that are fed by the different gas compositions. Such an approach will here be termed “*move material*”. The third approach we consider in this context is to move a fixed reactor between different gas streams. Such a concept we here denote “*move reactor*”. Below the advantages and disadvantages for these three different concepts are discussed, and our choice of reactor system for the present study has been described.

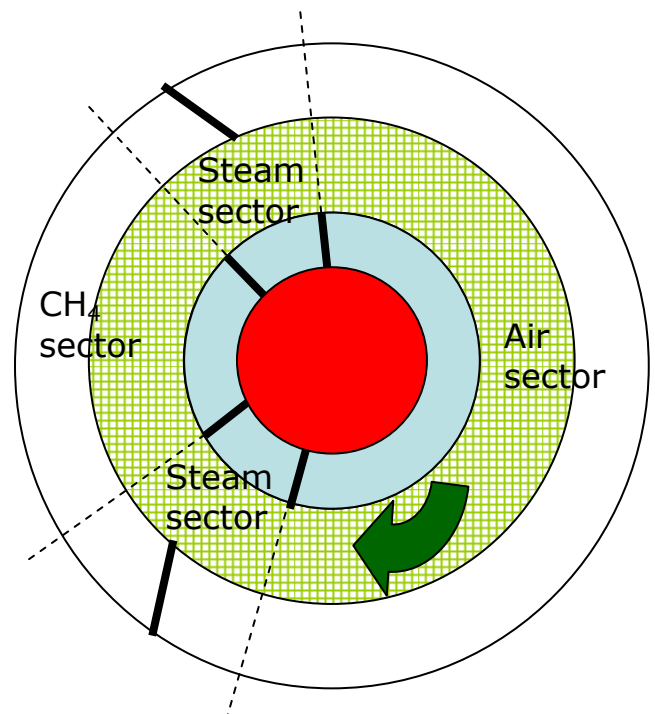
### 2.1. Move feed:

Such a concept has previously been suggested for sorbent enhanced reforming reactions by Air Products. Typically, a number of fixed bed reactors are linked together in a serial way where each reactor goes through the same number of steps in order to have a close to continuous operation. For natural gas fired CLC at least the following steps should be necessary: 1) Full oxidation of natural gas by the oxygen carrier material, 2) flushing, typically by the use of steam, 3) re-oxidation of the oxygen carrier with air, and 4) flushing. The setup will need a sophisticated valving system that should allow different feeds and also different outlets for the effluent gases. In addition, for a full scale power plant using this technology, valve size might be a problem. Initial non-continuous demonstration of CLC was typically carried out in a single fixed bed reactor switching feed.<sup>3</sup>

Operating such a setup in a way so the turbines experience a close to constant feed might be possible, but probably hard to achieve. A general problem for fixed bed setups is the low tolerance for particle volume changes during operation, which will necessarily lead to particle crushing and thus formation of fines over time. However, fines might be removed by post-reactor cyclones.

### 2.2. Move material:

This is the reactor concept most commonly visualized for CLC process, and several pilot and demonstration units of this kind have been constructed during the last 5 years.<sup>4</sup> In most cases this is a circulating fluidized bed (CFB) setup having one riser reactor and one bubbling bed reactor that are connected via so called loop-seals that avoid mixing of the feed gases on the natural gas and air side, respectively. One important advantage is that CFB technology is mature, and has been used for decades for other processes such as for example fluidized catalytic cracking (FCC). The oxygen carrier particles are circulated by fluidization, which mean that particle volume changes during the process should not be



**Figure 1:** Schematic drawing of the rotating reactor having radial gas flow. The gases are fed in the different light blue inner sectors. The light green part denotes the rotating oxygen carrier bed. The thick solid lines are separation walls.

important, however, attrition problems have to be addressed.

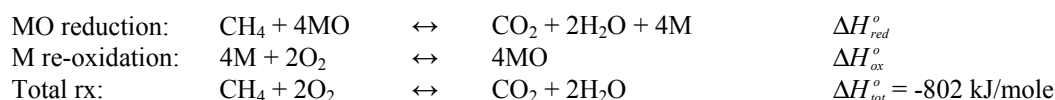
### 2.3. Move reactor

The “move reactor” concept we consider in the present study is a rotating bed reactor where a doughnut shaped fixed bed is rotated between the natural gas stream and the air stream. Between the two reacting gas streams one should preferably have streams of an inert gas (for example steam) to avoid mixing of the two reacting gases. We imagine that such a reactor could be very compact and easy to operate as compared to the “move feed” concept described above. A similar spinning wheel setup has previously been suggested by Shimomura for the high temperature separation of CO<sub>2</sub> from gas mixtures.<sup>5</sup> Fines formation through potential particle volume changes under cycling condition might also for this concept be a problem as the fixed bed setups in general.

The reactor chosen for the present study (see Figure 1) is best described as a rotating bed reactor where the oxygen carrier material is rotated between different gas streams flowing radially outwards through the metal oxide bed. A radially directed gas flow will give the best gas flow performance since volume expansion due to the increase in moles of gas and gas temperature due to reaction exothermicity best will be compensated by the radial reactor volume increase. However, the main challenge with such a reactor concept is to avoid gas mixing between the fuel and air gas streams. This will be discussed in more details in section 4 below.

### 3. Choice of oxygen carrier

In natural gas fired CLC the combustion reaction is split up in the following part-reactions:



MO denotes the oxidized metal oxide and M the reduced metal oxide. In the CLC process the total reaction enthalpy noted will be divided into the two part-reactions. How the enthalpy splits between the two reactions is strongly dependent on the nature of the metal oxide used. In Table 1 below, the enthalpies for the two half-reactions have been given for a selection of different metal oxides.

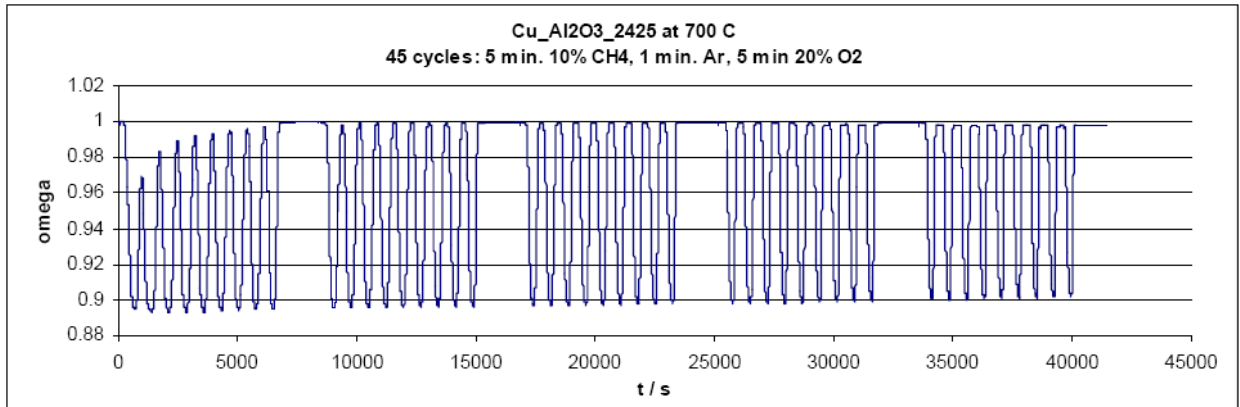
**Table 1:** Enthalpies of metal oxide (MO) reduction by methane reaction and for the reduced metal oxide (M) re-oxidation by O<sub>2</sub> reaction for different metal oxides. The enthalpies noted are relative to the reactions given above.

MO/M pair	$\Delta H_{red}^{\circ}$ (kJ/mole)	$\Delta H_{ox}^{\circ}$ (kJ/mole)
Fe <sub>3</sub> O <sub>4</sub> /FeO	386	-1192
NiO/Ni	132	-934
CoO/Co	-8	-794
CuO/Cu	-206	-596
LaCoO <sub>3</sub> /LaCoO <sub>2.5</sub>	-280	-522
La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>3</sub> / La <sub>0.6</sub> Sr <sub>0.4</sub> Fe <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>3-δ</sub>	-320	-482

In our initial setup, in order to avoid unwanted effects of large temperature gradients inside the oxygen carrier bed, we want to use a metal oxide having as close to equal enthalpies for both half-reactions. In addition to high oxygen capacity, which always is advantageous, we want to use an oxide that have high reactivity at relatively low temperatures since our first tests preferably are carried out below 800°C. Since the perovskites noted at the lower end of Table 1 have low capacities, our choice is a CuO based carrier which have been reported to have fast kinetics already at around 700°C.<sup>6</sup>

Specially formulated oxygen carriers giving low pressure drop over the bed have been developed. Low pressure drop is needed to minimize internal gas mixing. Wet impregnation of Cu(NO<sub>3</sub>)<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used to prepare oxygen carrier having > 10wt% oxygen capacity. The figure below show the cyclic red-ox capacity and stability of

the CuO based oxygen carrier having the shape of approximately 2 mm spheres. The spheres show stable performance after an initial activation period during the first five cycles.



**Figure 2:** TG trace of CuO/Al<sub>2</sub>O<sub>3</sub> material under red-ox cycling in 10% CH<sub>4</sub> and 20% O<sub>2</sub> at 700°C.

## 4. Results and discussion

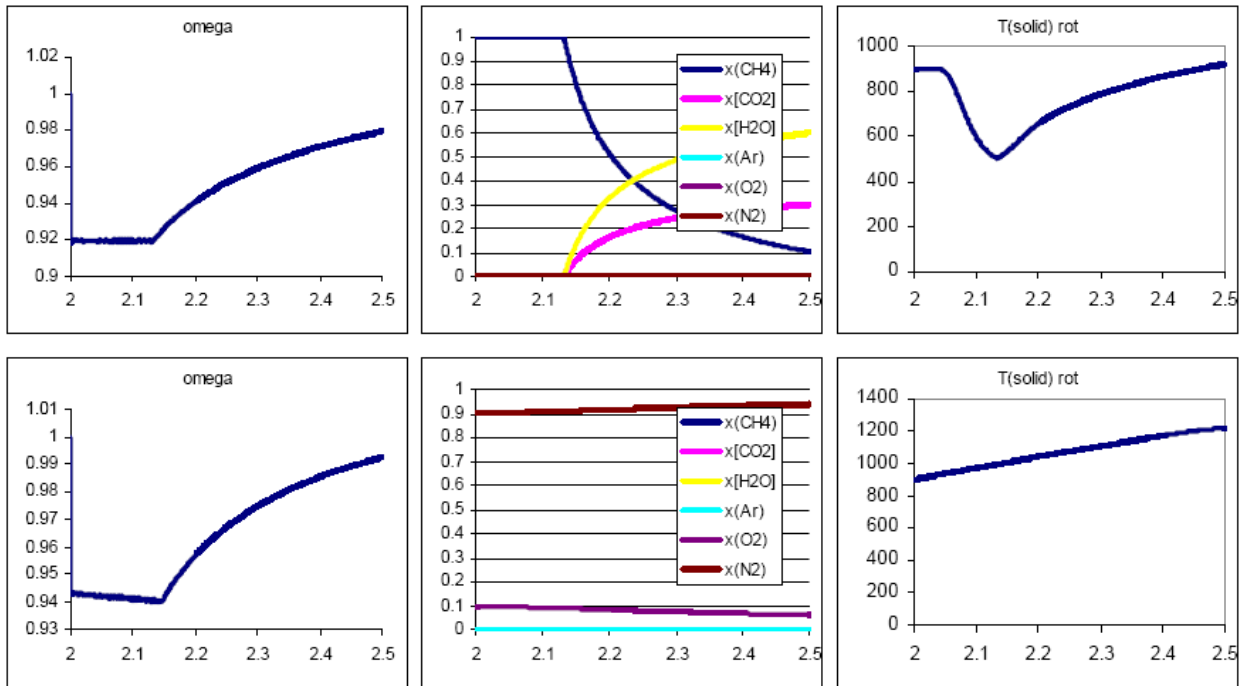
In the following we will shortly discuss two topics; firstly a simulation of the rotating reactor during operation where the main aim was to get information about the effect of the oxygen carrier material on the reactor performance. Secondly, we will discuss the results obtained when operating the reactor at ambient temperature with special emphasis on the internal mixing of gases.

### 4.1. Reactor simulation

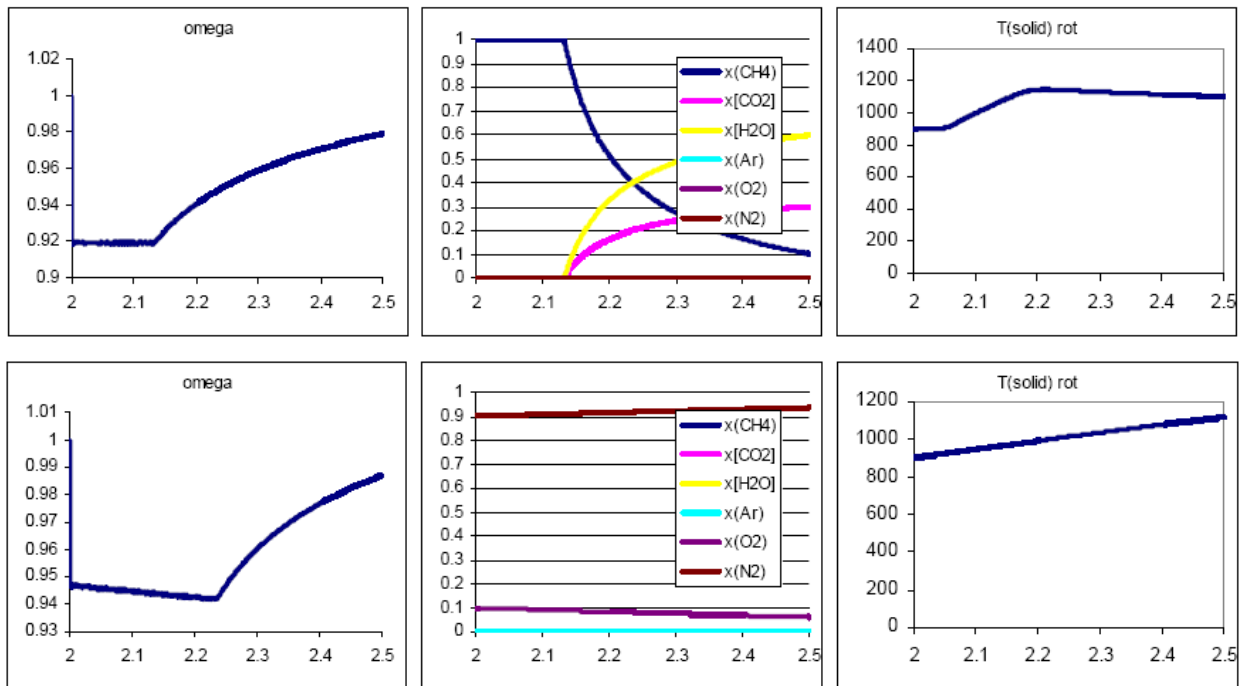
The main purpose with the simulation was to obtain information about the operation stability during prolonged CLC operation using oxygen carriers having different split of  $\Delta H_{tot}^o$  into  $\Delta H_{red}^o$  and  $\Delta H_{ox}^o$ . Typical kinetic parameters for oxygen carriers were used.<sup>7</sup> A linear model, where one can follow the gas composition and temperature profile through a radial bed segment was implemented in Microsoft Excel. Simulation of the bed rotation was done by rotating the segment through the different feed sectors. The methane feed sector of methane was chosen to 60°, the air sector to 240°, and the two steam sectors to 30° each.

In the following we discuss two examples using two different oxygen carriers. The first example is using NiO/NiAl<sub>2</sub>O<sub>4</sub> having endothermic  $\Delta H_{red}^o$  and strongly exothermic  $\Delta H_{ox}^o$ . Figure 3 shows two different bed profiles: The upper three curves show the degree of oxidation, the gas composition, and the bed temperature in the middle of the methane sector. With the parameters used, the inner part of the oxygen carrier bed ( $r < 2.13$ ) is fully reduced (corresponds to  $\omega = 0.92$ ) while the outer part of the bed ( $r > 2.13$ ) still contain reactive oxygen. This is reflected in the gas composition diagram where no reaction takes place before the gas reach the part of the bed still having reactive oxygen left. The temperature profile throughout the bed shows a minimum which is a consequence of the endothermic nature of the NiO reduction with methane. The three lower diagrams in Figure 3 show the same profiles during re-oxidation by air. In this case diluted air (only 10% O<sub>2</sub>) with a high space velocity is used causing a low oxygen conversion in order to keep the outlet temperature below 1200°C. With the parameters chosen, steady operation is achieved with close to 100% conversion of methane, and full re-oxidation is achieved on the air side. For NiO both gas expansion due to temperature increase (air side) and molar gas expansion (methane side) can be used for energy production.

The second example is with a CuO/Al<sub>2</sub>O<sub>3</sub> carrier with a much more equal split of  $\Delta H_{tot}^o$ ; both  $\Delta H_{red}^o$  and  $\Delta H_{ox}^o$  being exothermic. Simulations with this material are shown in Figure 4. In the methane sector (top three diagrams) the situation is similar to NiO for the degree of reduction and gas composition diagrams, but the temperature of the bed increases due to the exothermal nature of CuO reduction by methane. Using this material the bed will have a



**Figure 3:** Simulation of trajectories through the NiO bed of 1) degree of oxidation ( $\omega$ ), 2) gas composition (middle), and 3) gas/solid temperature (right). The top three curves are in the middle of the methane sector, while the three bottom curves are in the air sector.



**Figure 4:** Simulation of trajectories through the CuO bed of 1) degree of oxidation ( $\omega$ ), 2) gas composition (middle), and 3) gas/solid temperature (right). The top three curves are in the middle of the methane sector, while the three bottom curves are in the air sector.

more uniform temperature during operation. This might be advantageous to avoid attrition of oxygen carrier material. We also believe that a uniform temperature is wanted to avoid stress in reactor construction which ultimately could lead to leakages.

#### 4.2. initial reactor tests

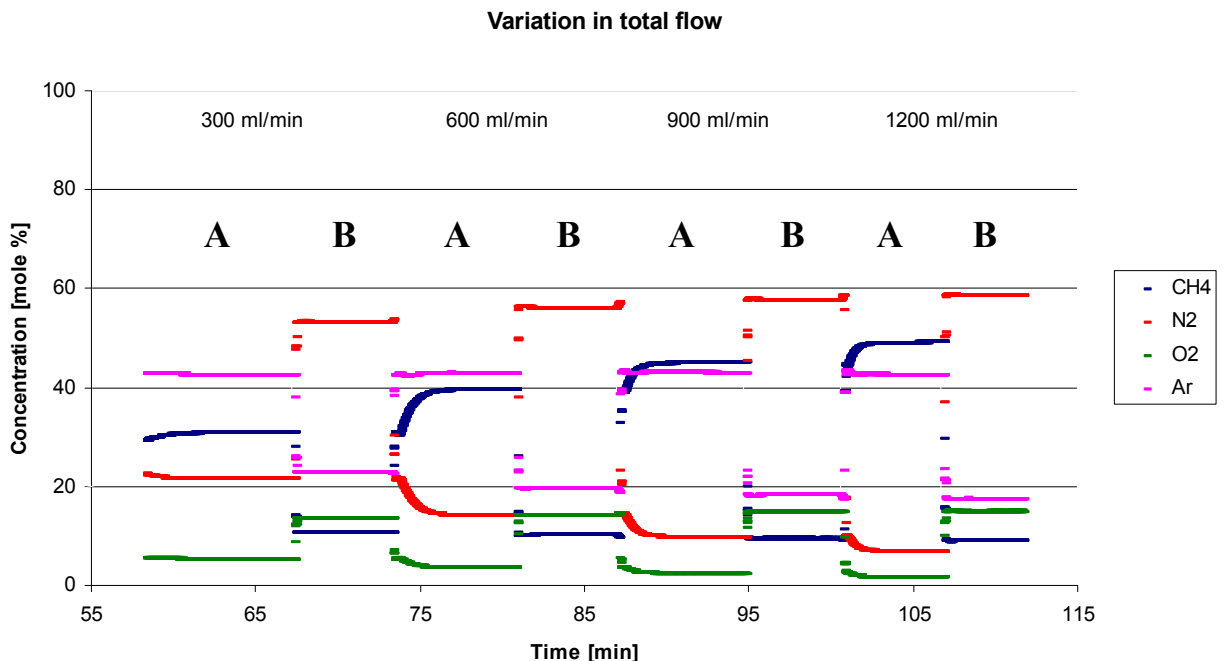
A lab-scale rotating reactor has, based on knowledge of oxygen carrier capacity and kinetics been designed and constructed. Still the setup undergoes initial testing and modifications are carried out continuously. A more detailed description of the setup will therefore be published later when real chemical looping combustion has been demonstrated.

In the prototype lab-scale reactor, the oxygen carrier bed has an outer radius of 6.0 cm, a radial thickness of 1.0 cm and an axial height of 4.0 cm. The gases are fed through porous metal membranes to assure an even and directional gas feed. The separation walls between the air and methane exit chambers have initially been positioned in the middle of the steam sectors as indicated in Figure 1.

As noted previously, the major challenge with a rotating reactor system is to avoid internal mixing of gases between the methane side and the air side during operation. Since parts are moving relative to each other no fixed sealings are possible, so our approach is to make physical hindrance that maximize the diffusion distance between the air and methane side. In addition, the steam sectors can be regarded as “gas walls” between the two sides.

Pressure differences between the air and methane sides also strongly influence the amount of internal mixing. In our setup we have the possibility to fine-tune the effluent gas flow from each side by the use of needle valves and mass flow meters mounted on the exit lines. Figure 5 show the exit gas compositions on the methane side (A) and the air side (B) when feeding methane, air and argon (as “steam”) into their respective sectors. The flow rate of each gas ( $F_i$ ) is proportional to the feed sector, i.e.  $F_{\text{methane}}:F_{\text{argon}}:F_{\text{air}}:F_{\text{argon}} = 60:30:240:30$ . Total flows are given in the figure. By regulating the exit gas flows to the predicted values assuming that the argon split evenly between the two sides, we obtained the gas compositions shown in Figure 5 using different total gas flows.

At low gas flows internal mixing is significant, actually, at total flow of 300 ml/min, around 50% of the methane ends up at the air exit. The mixing is reduced at higher gas velocities; at a total flow of 1200 ml/min only 1/3 of the methane ends up at the air exit. As a consequence of the large difference in the sizes of the air and methane sectors,



**Figure 5:** Results from MS analyses of effluent gas from CH<sub>4</sub> side (A) and air side (B) of the rotating reactor.

only around 11% of the O<sub>2</sub> and N<sub>2</sub> end up on the methane exit side at total flow of 300 ml/min. When feeding 1200 ml/min, the concentration of these gases on the methane exit side is only around 3.4% each. In summary, in our best experiments having high gas velocities, the effluent gas on the methane exit side contains around 50% methane. Assuming similar separation conditions during CLC operation, this can be translated into 50% CO<sub>2</sub> capture. The concentration of CO<sub>2</sub> in the effluent gas stream after removal of steam will be around 85%.

It should be stressed that these are the very first experiments using the reactor setup. There are several ways to reduce the degree of internal gas mixing. The first will be to improve the quality of the separation walls dividing the exit chambers. The results from these improved versions of the reactor will be reported in future papers.

## 5. Conclusions

A novel rotating reactor concept for natural gas fueled CLC have been designed and a prototype has been constructed. In the reactor, the oxygen carrier material is rotated between methane and air gas streams with steam gas streams between the two reactive gases. Since large temperature gradients inside the rotating reactor is unwanted, a CuO based oxygen carrier having similar enthalpies for the reduction by methane and re-oxidation by air has been chosen. Initial testing shows that internal gas mixing is unavoidable, however, indirectly derived separation factors corresponding to 50% CO<sub>2</sub> capture and 85% CO<sub>2</sub> purity are obtained. The potential for further improvement of the construction and running conditions are large and will be followed up in the future.

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