



SP4 Public Summary Report

Based on the Del. 4.3.6.: Progress report on reactor modelling and component development

Based on the Del. 4.3.7.: Final report on the development of membrane assisted reactor.

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This report should be cited as:

Colin et al. Public summary report of ENCAP deliverable D4.3.6 "Progress report on reactor modelling and component development" and Asbroek et al. Public summary report of ENCAP deliverable D4.3.7 "Final report on the development of membrane assisted reactor" [online]. Available from Internet:

www.encapco2.org

The aim of ENCAP's SP4 is to provide entirely new combustion technology – with no contact between fuel and combustion air – featuring the inherent separation of CO₂ and avoidance of nitrogen oxide formation. This report presents the final results of the study regarding the use of novel reactors (rotating reactor and membrane reactor) for Chemical Looping Combustion (CLC) using a gas turbine power cycle, focusing on natural gas as the primary fuel.

In a search of concepts for innovative reactors allowing CO₂ capture in gas turbine, IFP has identified the rotating monolith based CLC as a promising concept. To define the design rules and to select the materials to be specified a precise simulation of the CLC in a monolith was required. Based on the model used to simulate rotating reactor performances, reactors are designed and sized to match the process requirements. Finally, rotating reactor technology cost was estimated.

Moreover, TNO has developed the membrane assisted CLC reactor concepts. The pilot set-up has been constructed at TNO facilities in Apeldoorn, Netherlands, where the membrane assisted internals for the pilot were also produced. In this report is described the development and the first results of the tests performed with this device.

1) IFP ACTIVITIES

In standard combustion, the CO₂ produced by oxidation of fuel is mixed with excess oxygen, nitrogen and steam. But CO₂ capture requires its separation from other gases. To ease the CO₂ recovery, IFP has selected the Chemical Looping Combustion using materials that store oxygen by forming metal oxides (oxidation) and that release the oxygen in presence of the fuel. The oxidation phase releases heat, enabling air heating to power gas turbines. In standard gas turbine, natural gas is burned with air in large excess to provide pressurized hot gas to the turbine. It is proposed to replace the traditional combustion chamber with a CLC chamber to enable CO₂ capture after steam condensation but without gas separation units. To fit this requirement, IFP selected the rotating reactor that allows a continuous production of hot air in one side and of CO₂ in the other side. The oxido-reduction reactions take place in a monolith coated with appropriate material.

Experimental work

The experiments were conducted in a lab scale test bench consisting of a gas preparation section, following by a reaction section and a gas analysis section (Fig. 1). These experiments allowed testing 300 NI/h of methane or natural gas diluted with steam (dilution up to 50%). The feed preparation section was equipped with gas bottles containing pure nitrogen, oxygen/nitrogen mix and methane.

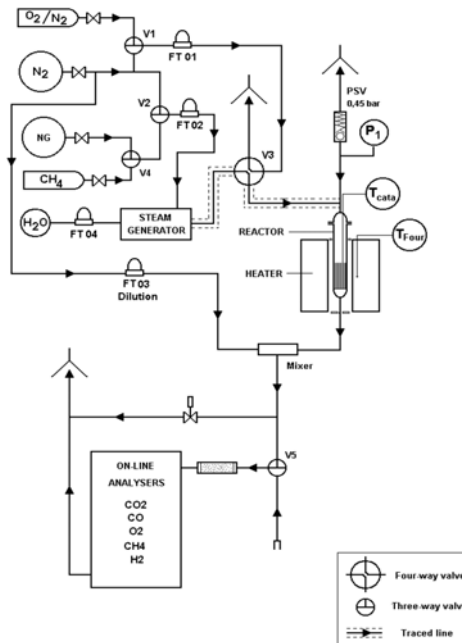


Figure 1: Experimental set-up

In addition, the unit was connected to the natural gas network. Prepared gas mixture enters a quartz reactor containing coated monoliths. This quartz reactor was contained in an electric furnace keeping the monoliths in an appropriate temperature before the beginning of tests. The gas was heated in the coil section before reaching the reactive section. This reaction was achieved in four parallel piled monoliths (Fig. 2).

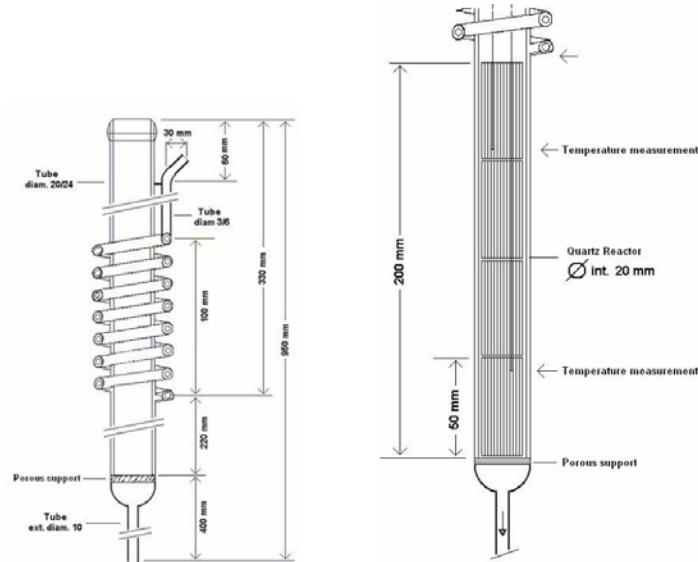


Figure 2: Reactor arrangement

The monolith internal temperature and its evolution can be monitored during the reaction on account of the two thermocouples inserted through the stacked monoliths. The reactor effluent was then cooled by the air and diluted 10 times by the nitrogen while this diluted affluent flowed to the analyzer section. This analyzer section recorded the online composition of CH_4 , CO , CO_2 , O_2 and H_2 volume fraction during the operation.

Experimental data treatment

Figure 3 presents data where the production flow was diluted with 2700 NI/h of nitrogen in order to lower the measured gas concentrations to match analyzer requirements. The analyzers were located as close as possible to the monolith exit. There was a time shift between the times of a gas molecule exits the monolith and the time was detected in the analyzers. Furthermore, some analyzers were queued and the delay for the next one was added to the delay for the previous one.

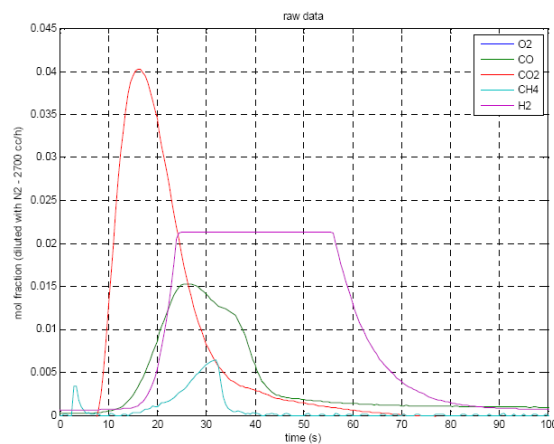


Figure 3: Experiment #1 with -90% CH₄, 10% H₂O-, 90 μm washcoat width

In addition, the analyzers induced a convolution on the true gas concentrations that exit the monolith. It was possible to estimate the true concentration by deconvolution of the measured ones. To estimate the transfer functions for the deconvolution, was recorded the analyzer responses after injecting a squared shape concentration for every gas into the analyzers. The result was presented on Figure 4.

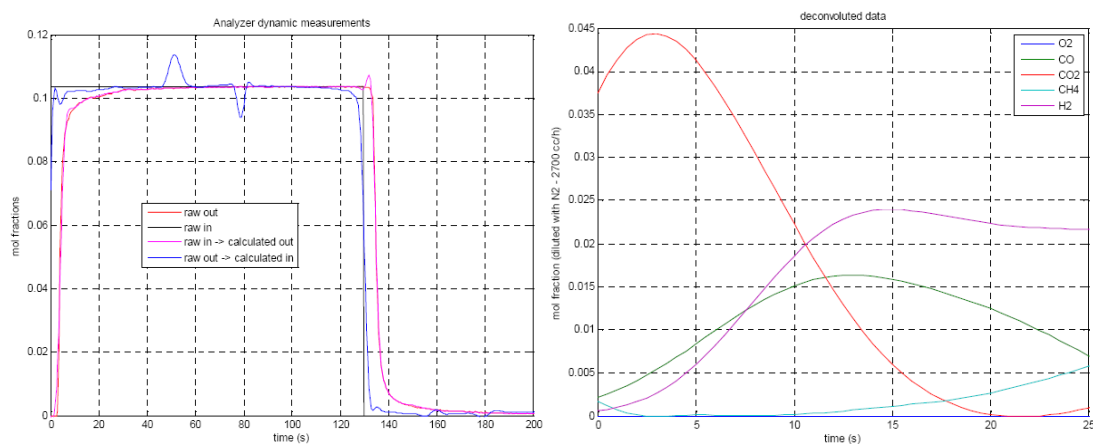


Figure 4: a) CH₄ analyzer responses: comparison between actual CH₄ pulse and simulated CH₄ pulse from measured CH₄ analyser response
b) Deconvoluted data from experiment #1

The black "Raw in" is the input signal. Red "Raw out" is the recorded signal. Pink "Raw in -> calculated out" is the convolution of the black curve with the transfer

function. Blue "Raw out -> calculated in" is the calculated injection with deconvolution of the actual (red) analyzer response. We can see that the transfer functions give rise to a pretty good matching between the black and blue curves on Figure 4.

On figure 4b it can be noted that:

- CH₄ presents a very small pulse of unburned gas at t = 0
- In the first seconds, CH₄ is oxidized into CO₂ then into CO
- Hydrogen is continuously increasing starting at t = 0
- After 10 s, CH₄ begins to breakthrough
- Hydrogen measurement limitation at 2% occurs later than 10 s. By that time CH₄ has already breakthrough. Hence t > 10 s is of no interest for the process and the measurement limitation appears not to be a fatal drawback for the experiment
- CO₂ is decreasing rapidly and no more exhibits long tail (as in Figure 3). The little increase at t = 25 s is not actual and corresponds to a ripple.

Lab numerical simulator

The objective was to simulate the lab results, to gain knowledge for the rotating reactor simulation and performance evaluation. The simulator presented was designed and developed to analyze the lab experiments in order to identify the chemical reactions that take place in the monolith. Because the monolith was a bundle of identical channels, it has been assumed that channels are identical and behave the same way. Hence, the simulator just modelled one channel. As presented in the figure 5 below, a channel is parallelepiped in shape with an internal coating than can be more or less cylindrical. To avoid time consuming 3D transient simulations was assumed a cylindrical channel and was modelled it in a 2D transient axial symmetry.

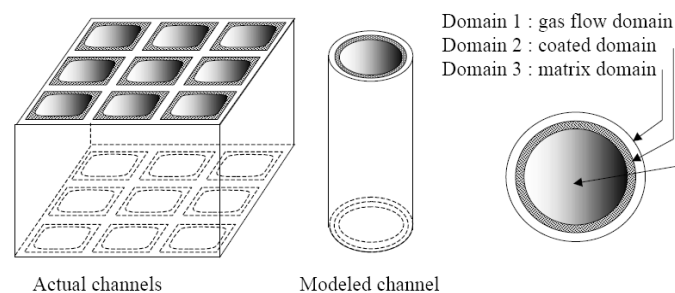


Figure 5: 2D axial symmetry assumption for the channels

The gas flow was located in the centre of the channel where the flow was laminar. It was assumed that seven different gas components composed the gas phase (O₂, N₂, H₂O, CO, CO₂ and CH₄). The mass and energy fluxes that go from the gas phase to the solid phase are simulated. The reactions took place in the washcoat. By construction, the washcoat contained Ni and NiO. To simplify, it was lumped all of these adsorbed components into one single CH₄⁻ form. In addition, it is also assumed that CH₄ coking occurred in the washcoat leading to carbon content C_k and releasing H₂.

Lab simulations results

Figure 6 presents the best fit obtained with the simulator for experiment # 1. To get this best fit, was selected the chemical reactions that are relevant for the process and was estimated the parameters that enter the chemical equations. The Figure 6 presents also the gas composition calculated at the exit of the monolith, together with the experimental values (dotted lines). The simulated gas composition have been numerically "diluted" with 2700 NI/h nitrogen as it has been experimentally done to match analyzer measurement range. This is the reason why the mol fractions are below 5%.

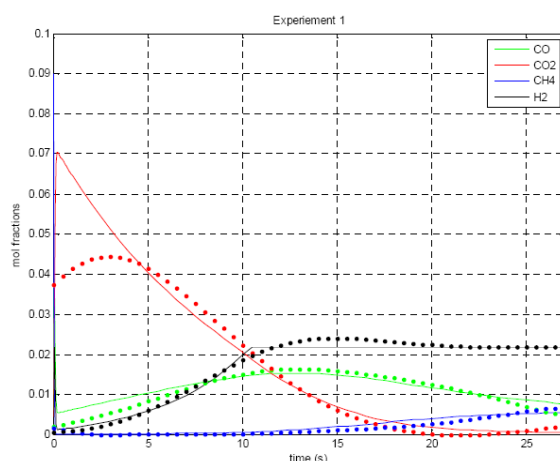


Figure 6: Comparison of measured and simulated compositions for experiment #1

On Figure 6, it can be observed a rather good matching between the simulation and the raw data. The same was done for the other two experiments for which did not matched the experimental results but just simulate them correctly using the matching of experiment #1. According to the results, it can be concluded that the simulator was good enough to be used for rotating reactor performance estimations.

Rotating reactor concept

The reactor consists in a rotating monolith whose channels are parallel to the revolution axis. Special gas distribution and collection devices send and collect the gases in the channels depending on the angular position (Fig. 7a). These equipments prevent any mixing between air and methane. Figure 7b shows an example of the distribution sectors.

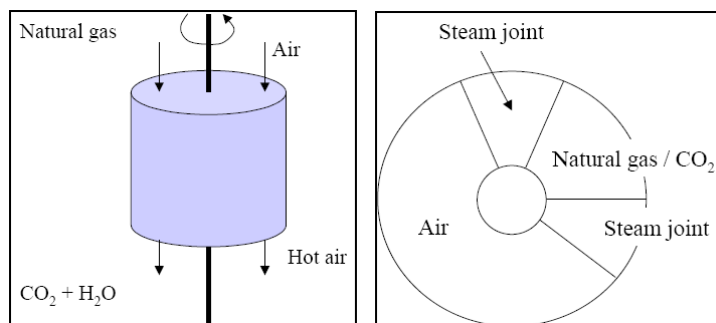


Figure 7: a) Rotating reactor, b) Example of gas distribution with angular positions

Rotating reactor simulation and evaluation

To take both air and hydrocarbon injections plus safety aspects into account, a typical sequence for the cycling chemical looping should involve four injection phases:

- Steam injection: lasts typically 0.5 s
- Air injection: lasts typically 5 s
- Steam injection: lasts typically 0.5 s
- Natural gas (CH₄) injection: lasts typically 2 s

While injections change, the product gases were directed towards two different exits:

- The CO₂ storage unit
- The turbine

Of course injection and production phases are not simultaneous but production phases are determined according to the outlet gas composition.

Simulator improvements and limitations: The simulator developed for the lab has been used for rotating reactor simulation. To achieve these simulations, improvements and limitations have been introduced in the simulator:

- The monolith channel in the rotating reactor was much longer than for the lab experiment
- Unlike lab experiments, the injections were switched every few seconds
- Limitations were introduced in the simulator to avoid coke formation and CH₄ absorption which is linked to the use of nickel in the experimental work conducted. It is known that other oxygen carriers could be used which do not have the same drawbacks

Conclusions about the simulation: IFP has built a 2D axi-symmetry and transient simulator that has been used to simulate experiments lab results. To achieve the matching between lab results and simulations, a chemical kinetics scheme has been derived that involves 12 oxido-reductions reactions, apart from the 2 side reactions leading to CH₄ adsorption and coking that were not considered. According to this assumption IFP could estimate rotating reactor performances that seem to be very promising.

Reactor economic evaluation

IFP delivered a design for monolith based CLC system for a 360 MW gas turbine. In this concept, the traditional high temperature combustion chamber was replaced by either a single reheat system using 2 chemical looping reactors heating up air to 1000°C at decreasing pressure level or a double reheat system using 3 chemical looping reactors heating up air to 1000°C at decreasing pressure levels. Double reheat system allows the global efficiency to reach 52% instead of 51% in the single reheat process. This was proven in a dedicated process study where other partners such as NTNU were involved too.

Table 1: Cost evaluation

		Single Reheat		Double Reheat		
		Reactor 1	Reactor 2	Reactor 1	Reactor 2	Reactor 3
Reactor cost	K€	3132	3497	2868	2690	3699
Total Cost*	K€	6630		9257		

* *CO₂ separation and compression, and turbine costs are not included*

II) TNO ACTIVITIES

TNO is developing the membrane assisted Chemical Looping Combustion (CLC) reactor concepts. These concepts use membranes to form a physical barrier between the active metal containing particles and the oxidizing and reducing gas streams. This barrier is macro porous ($0.2 \mu\text{m}$) allowing for gas streams to diffuse while the solid particles stay fixed. The technique is described in another ENCAP's report. The membrane assisted reactor is intended to replace the combustion chamber of a gas turbine according to the process scheme defined by the other teams of this SP. In this concept, the traditional high temperature combustion chamber is replaced by a double reheat system using three chemical looping reactors heating up air to $1000 \text{ }^\circ\text{C}$ at decreasing pressure levels. Using this double reheat system, a process efficiency of 52% can be achieved, which is in the upper range of the actual state of the art turbine technology ($1300 \text{ }^\circ\text{C}$ inlet temperature, no CO_2 capture) and is higher than most post combustion CO_2 recovery processes.

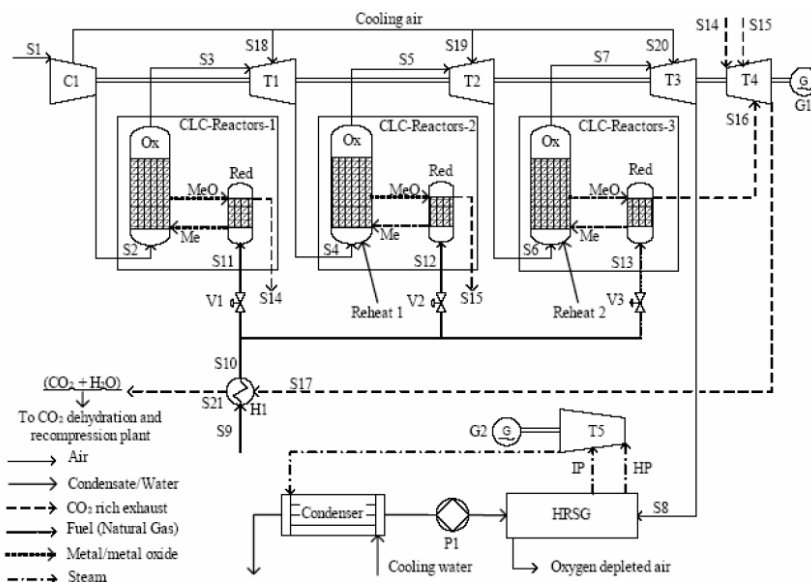


Figure 8: 360 MW turbine process with double reheat

The basic process design of the plant

The basic building blocks of the process were membrane assisted CLC reactor modules. These reactor modules composed of thousands of ceramic membrane fibres. In the most likely configuration the fibres are filled with the CLC particles and the air is flowing through the space between the fibres. The membrane reactor module will include some non-filled both ends open ceramic fibres in order to facilitate sufficient mass flow of gas, prevent large pressure drop and allowing sufficient heat transfer. A modular approach is chosen in which standardized membrane assisted reactors are used to build the required size of power plant, in this case at a length of 1 meter and a diameter of 1 meter. These dimensions represent the maximum currently feasible production methods of ceramic membrane tubes and module building techniques.

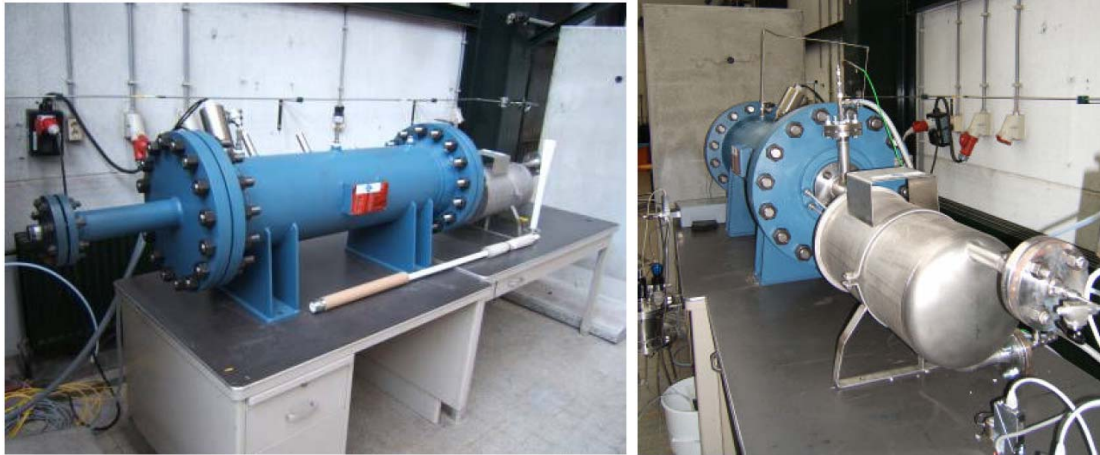


Figure 9: The membrane assisted chemical looping reactor at TNO (Specification: up to 35 bar and 1300 °C)

The process design employed the concept of separating the pressure component from the high temperature component resulting in a double enveloped pressure housing design. Double enveloped metal tubes will be employed housing a standard membrane assisted CLC reactor modules. In order to turn membrane assisted reactors into a continuous combustion process is used fixed reactors and simulated a constant combustion process by changing gas type in each reactor according to a preset cycle using valves. Applying this scheme results in each reaction zone going through a cycle of air, then steam, natural gas, steam and then it start again with air.

Furthermore, a control of the oxidizing process is needed to ensure stable operation of the process (no under or over heating). The driving force for oxidizing is controlled by adjusting the oxygen content in the air feed to the reactor. An adjustment to the oxygen content of the feed stream is possible by recirculation part of the in nitrogen rich spent air stream over the compressor.

Critical item for process control will be the hot air valve directing 1000 °C hot air to the turbine. This valve has to be made of expensive materials and the amount of these costly valves is limited one per reactor, risking some leakage. However, this leakage can be reduced by operating the reduction cycle with a little overpressure and ensuring that the inlets are good tight by double valve sealing.

The bench scale setup has been designed to be able to test the concept as realistic as possible. The reactor was built as a double envelope design for testing membrane assisted CLC internals up to 35 bar and 1300 °C. In addition to the main reactor the setup also consists of a gas cooler and pressure control equipment. The single reactor can alternately be oxidized and reduced. The setup was able to run with air, nitrogen, methane, steam and natural gas, while the first experiments have been performed with methane. Analysing and flow control equipment has been installed just as an automatic control system programmed. The setup can monitor all gas flows, regulate pressure and temperature and analyse the produced flue gas on CH₄, CO₂, CO, NO_x and H₂, while H₂O and N₂ were not monitored. Because of the risks involved using natural gas at 30 bar and 1000 °C, the device was operated with a remote control.

Results

Several experiments were conducted at various temperatures and pressures, increasing both slightly to the boundary of the device's current specifications, being 1000 °C and 30bar. Experiments were performed at 1200°C, after receiving a dedicated thermocouple recently. The temperature (Y-axis 1) was measured at various positions within the bed as is displayed in figure below. The first experiment started at the moment the flow (Y-axis 2; purple line) was increased from 120 to 400 l/hr. At this point oxygen was flowing into the reactor. This had an effect on the temperature. Temperature 1 (blue line), measured closed to the inlet, decreases slightly, before increasing. This was due to cooling of increased gas flow before the reaction starts up and warms it up again. After the temperature peak at the first thermocouple an increase of the temperature at the second thermocouple (pink line) was observed. Because this thermocouple was positioned deeper in the bed, the oxygen front needs more time to reach it, the peak temperature occurs later. Finally the oxygen front reached the third thermocouple (yellow line) and created the third temperature peak. As can be observed the peaks get wider as they are measured by thermocouples that lie deeper in the reactor bed. When the gas flow was lowered, the temperature of the first thermocouple increased due to less cooling effects caused by cold gas in flow. At the same time the thermocouple that measured the temperature in the end of the reactor (yellow line) indicated a decreasing temperature, because less hot gas flows through the reactor and so less heat was transported towards the end of the reactor. Therefore the cooling effect of the cooling applied to cool down the gasket was getting a slight influence on the temperature of the bed. Initial problems with coke formation were solved by the addition of steam to the methane.

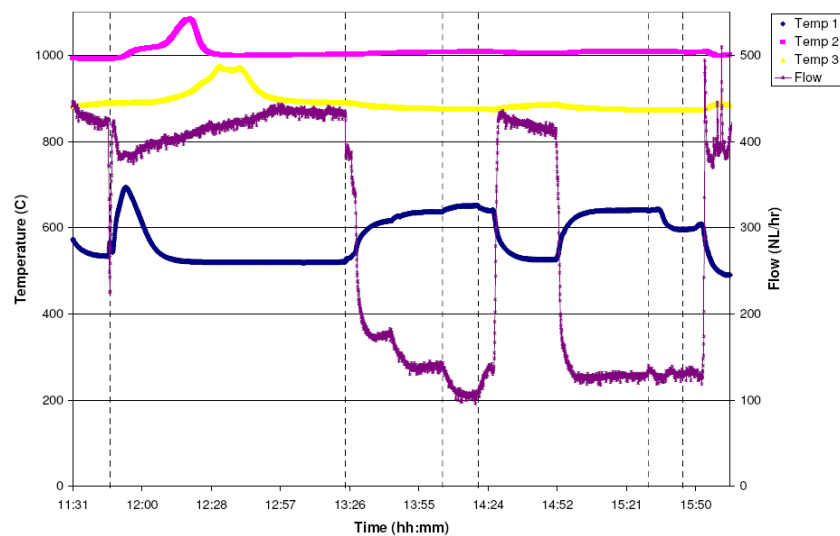


Figure 10: Results of an experiment at 30 bar and 1000 °C using 21% oxygen for oxidising and 30% methane for reduction

Advantages

The advantages of membrane assisted chemical looping, which enhances the performance of turbines, concern the lower losses at the exhaust because of a lower heat capacity of the exhaust gasses, due to the absence of water and therefore less energy is lost. The performance of the system can be enhanced by a higher reactivity because of increased turbine efficiency and the possibility to perform more cycles per time unit. Furthermore, the advantage of using membrane chemical looping combustion regards the immobilization of the particles, which results in no attrition

and less stress on the particles. This means that probably it allows us to raise temperature beyond the limitations regarding fluidized bed reactors (thereby increasing the yield of the turbine cycle) and no separation of fines is needed at the exit of the CLC before entering the turbine.

A further advantage is that higher pressure can be applied as the design contains no moving parts except for a valve, switching between the oxidation and reduction step. Also an increased reactivity will result in an increased yield of the gas cycles. If more surface is created to increase reactivity by decreasing the particle size, the pressure drop increases as well. Up to a certain level this will result in an increased performance or beyond a certain pressure drop this will become a handicap and the overall performance become less efficient. Pressure drop problems can be solved by the addition of membrane contractors that allows for an increased surface contact area without the implication of an extra pressure drop.