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Developing the next generation of renewable energy technologies

CONDOR

COmbined suN-Driven Oxidation and CO₂ Reduction for renewable energy storage

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= Deliverable D7.1 =
Gas treatment unit

Dissemination level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	



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Executive Summary

Within the CONDOR project, a system is designed in which sunlight, combined with CO₂, is converted in syngas, which can be further processed into valuable products, i.e., methanol and DiMethylEther (DME) in the current project. The syngas coming from the light driven reactor is a mixture of hydrogen, carbon monoxide and carbon dioxide. However, to promote the reaction towards DME, the amount of CO₂ in the syngas should be minimized and the ratio of hydrogen and carbon monoxide should be able to be tuned. In this task 7.2, the main important activity is to design and proof a gas treatment system in which the syngas produced can be used to make the DME production as good as possible. In this deliverable both membrane as adsorption-based separation methods have been assessed.

Next to the standard components present in the produced syngas, it is also expected that some larger hydrocarbons can be present as well, such as formaldehyde, formic acid and other comparable components which can damage the DME reactor and other equipment in between. Therefore, the gas treatment system is comprised of two sub systems in which firstly the larger hydrocarbons are reformed into carbon monoxide and hydrogen and in the second step, the carbon monoxide will be removed while keeping the hydrogen/carbon monoxide ratio in the right order.

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1. Introduction

The activity in which this deliverable is necessary is activity 7.2 with the following description:

The output from the PEC-cell will consist of a mixture of different gases, H₂, CO, H₂O and CO₂. For further upgrading of the reactor, water and CO₂ need to be separated as much as possible from this stream (<5% CO₂ content). A water knock-out vessel combined with a cooler will be designed to remove water, based on the specifications obtained from the heat and mass balance calculations within T7.1. The WKO vessel will be manufactured, the cooler will be acquired. Several technologies to separate CO₂ will be reviewed. It will be investigated if CO₂ can be easily separated from the stream using PSA-technology. Laboratory experiments will be done to select the proper sorbent and operational conditions. Also, the possibility to use membrane separation will be examined. The selected option will be designed according to the specifications from T7.1 and manufactured. For either option a compressor will be selected and acquired.

In general, the deliverable for this task is a demonstrator, but to validate the demonstrator and different design options, we also present the results made with this gas treatment system on simulated gas mixtures.

2. Results and discussion

In this section, the results around the different options to separate the CO₂ are discussed. Both membrane separation and pressure swing adsorption have been evaluated and tested.

2.1. Membrane separation

The objective of this test was to determine the performance of the membrane as standalone system. The results of these experiments were used to select the best operating conditions. To determine the performance of the membrane, the H₂ yield as well as the CO₂/H₂ rejection ratio should be determined for different transmembrane pressures (TMP). This variation is however limited, due to the maximum allowable pressures (lumen, shell and TMP) of the membrane module. The selected membrane is a PermSelect Silicone Membrane Module (type PDMSXA-2.1) of MedArray. The most important specifications are given in the table below in Table 1.

Table 1 Specifications of the membrane module

Gas flow rate	1 – 60 slm
Maximum shell side pressure	3 bar(g)
Maximum lumen side pressure	5 bar(g)
Maximum TMP (lumen to shell)	3 bar
Maximum TMP (shell to lumen)	1 bar

Figure 2 shows the P&ID of the test setup. The same mass flow controllers (MFC's) were used as during the VSA tests, to provide the required synthetic gas flow and composition to the membrane module. A back pressure regulator was used to control the lumen pressure and the TMP. Also the same MFC for the measurement of the product gas flow (retentate flow) was used. Since the membrane module has no cyclic operation, no buffer vessel was required to spread the production flow to the analysis equipment.

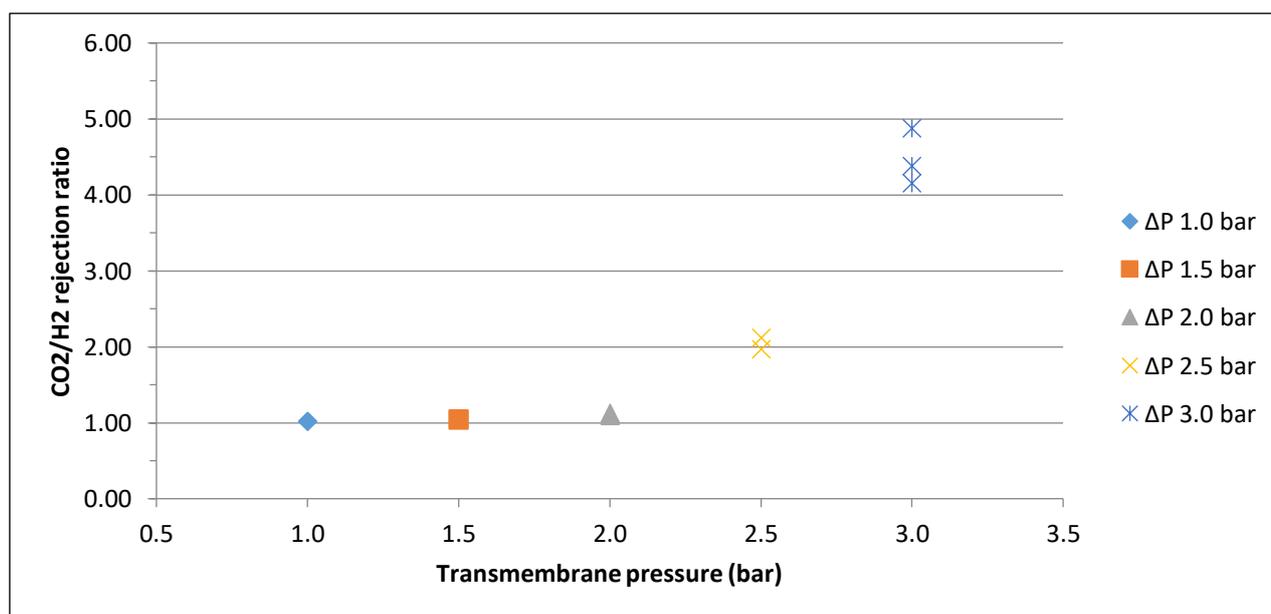


Figure 1 Membrane tests results

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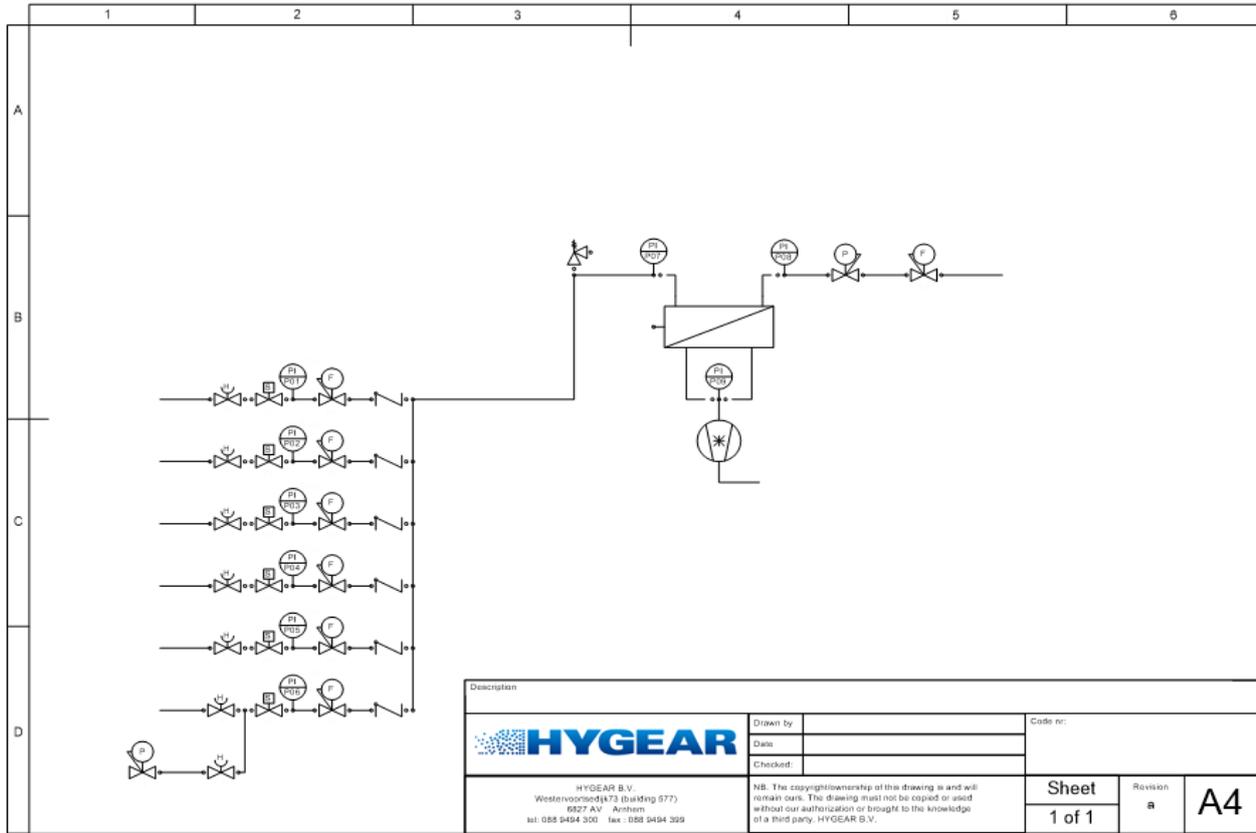


Figure 2 P&ID of membrane tests

Figure 1 shows the CO₂/H₂ rejection ratio as function of the TMP. It can be concluded that a higher TMP results into higher CO₂/H₂ rejection ratio. In addition, since the membrane has very low CO₂/H₂ rejection ratio, a TMP of at least 3.0 bar is required (which is also the maximum) for CO₂/H₂ rejection ratio of at least 4.0. This results into a CO₂ rejection of approximately 11.1% with 97.3% H₂ yield but only 89.2% combined H₂ + CO yield.



Figure 3 Picture of the membrane tests

2.2. Pressure Swing Adsorption

The basis of pressure swing adsorption relies on the difference in selectivity of adsorption on a packed adsorption bed. The bed is regenerated with the use of vacuum to ensure a full cycle of separation.

Below, the results of the experiment are given, based on different hydrogen content, it is seen that values way below 4% CO₂ can be reached (which is necessary for the DME reaction) with a yield > 90% of H₂ + CO. Furthermore, any trace components of larger hydrocarbons will be separated by this system as well, which makes this technology a suitable fit for the project. The experiments have been performed at atmospheric pressure, which brings an additional benefit to the technology as there is no compressor needed to drive the separation in this process.

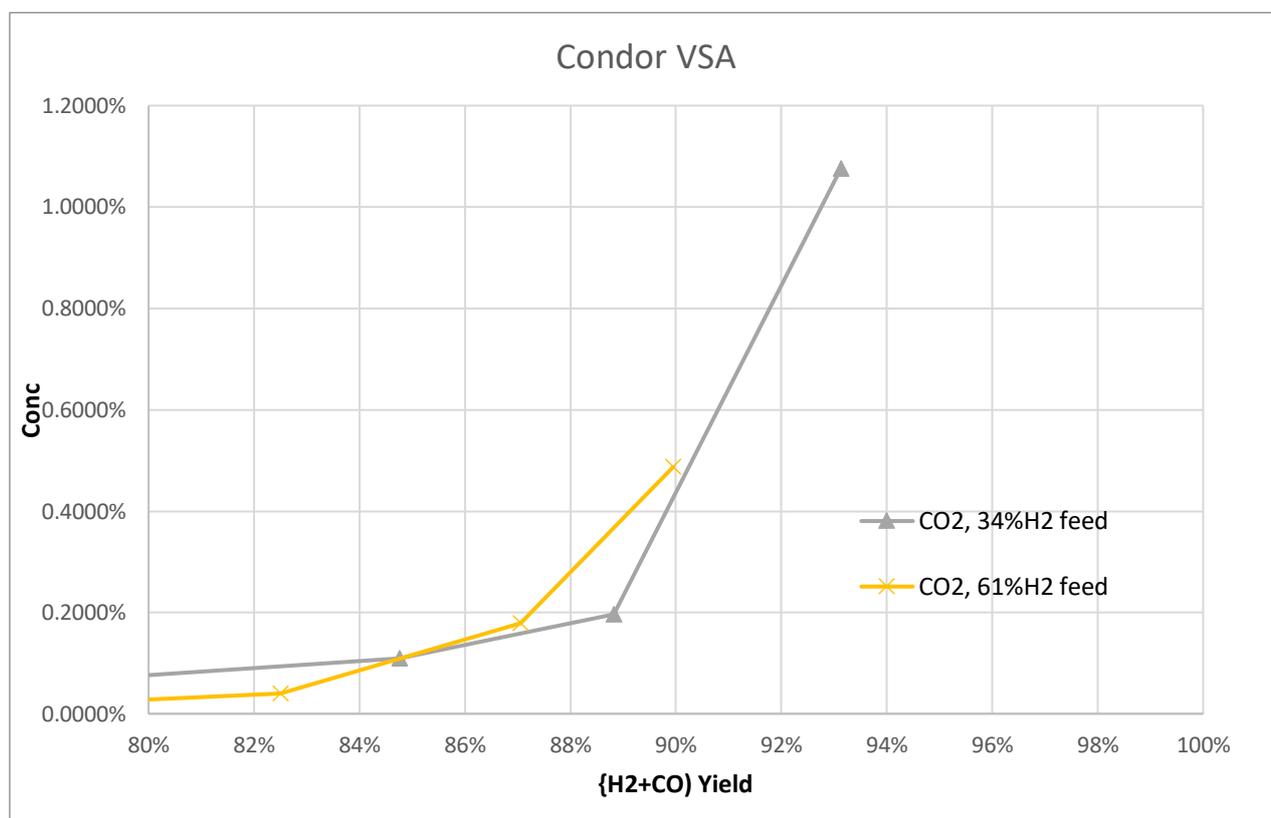


Figure 4 Results of the VSA tests

2.3. Decomposition of hydrocarbons & oxygen removal

This section handles the results of the execution of the experiments described in “HYG-CNDR-PL.001 Catalytic decomposition of PEC formed gas impurities”. This plan describes the tests on the Haldor Topsoe LK-821-2 copper catalyst.

The tests to be performed comprise of tests:

- Determine the sensibility to coke formation of this catalyst.
- The conversion and selectivity in the decomposition of organic compounds of the product gas of PEC.
- The ability of the catalyst to remove oxygen by catalysis of the reaction of hydrogen with oxygen to water.

Prior to testing the catalyst, it is reduced in a hydrogen containing atmosphere.

The cross section of the reactor is presented in Figure 5.

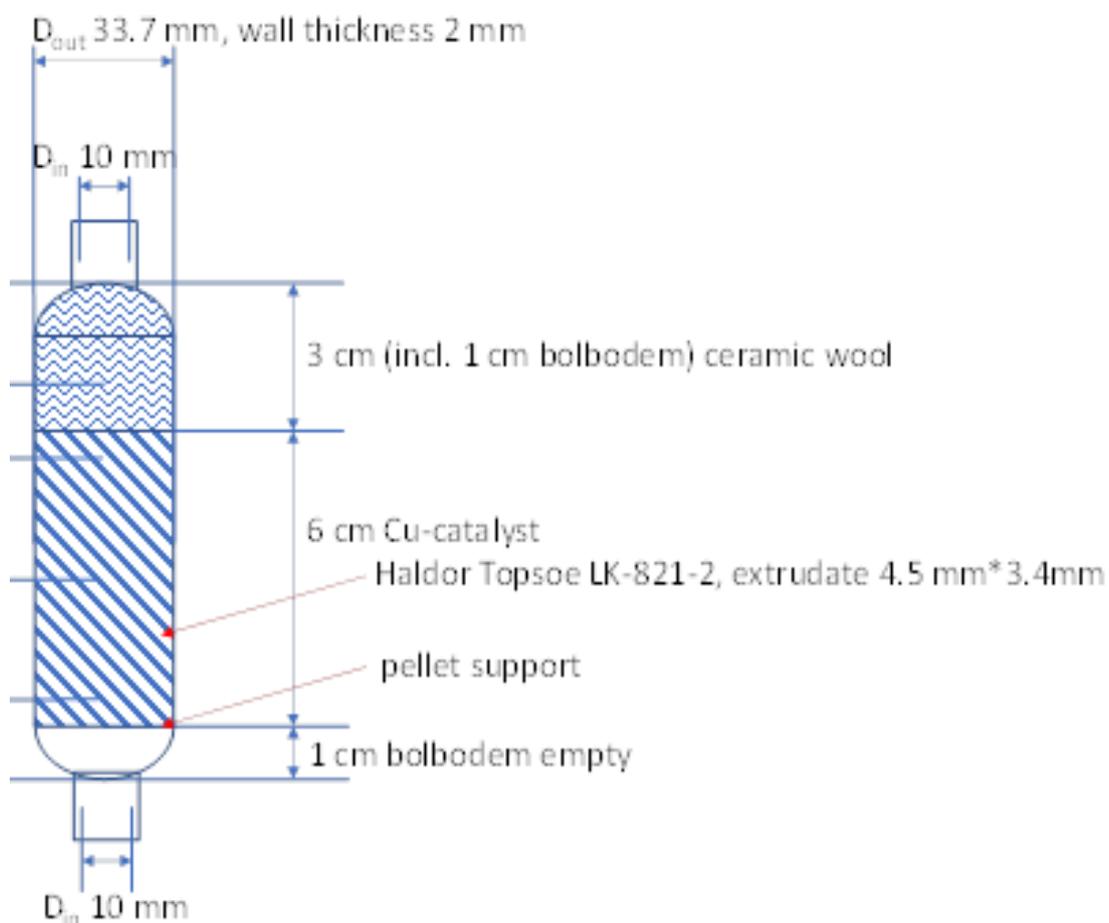


Figure 5 Schematic design of the Copper catalyst reactor

Test 1: Suppressing coke formation

Test 1 is carried out with a flow of 2 NI/min as described in the test plan. The gas composition used were as listed in Table 2.

Table 2: Gas composition Test 1

	CO	CO ₂	H ₂	CH ₄	H ₂ O
Vol% (test 1a) #	4	22	61	10	3
Vol% (test 1b) \$	22	4	61	10	3
Vol% (test 1c) &	44	9	35	10	3
Vol% (test 1d) *	9	44	35	10	3

#: CO₂ conversion in PEC cells to CO low

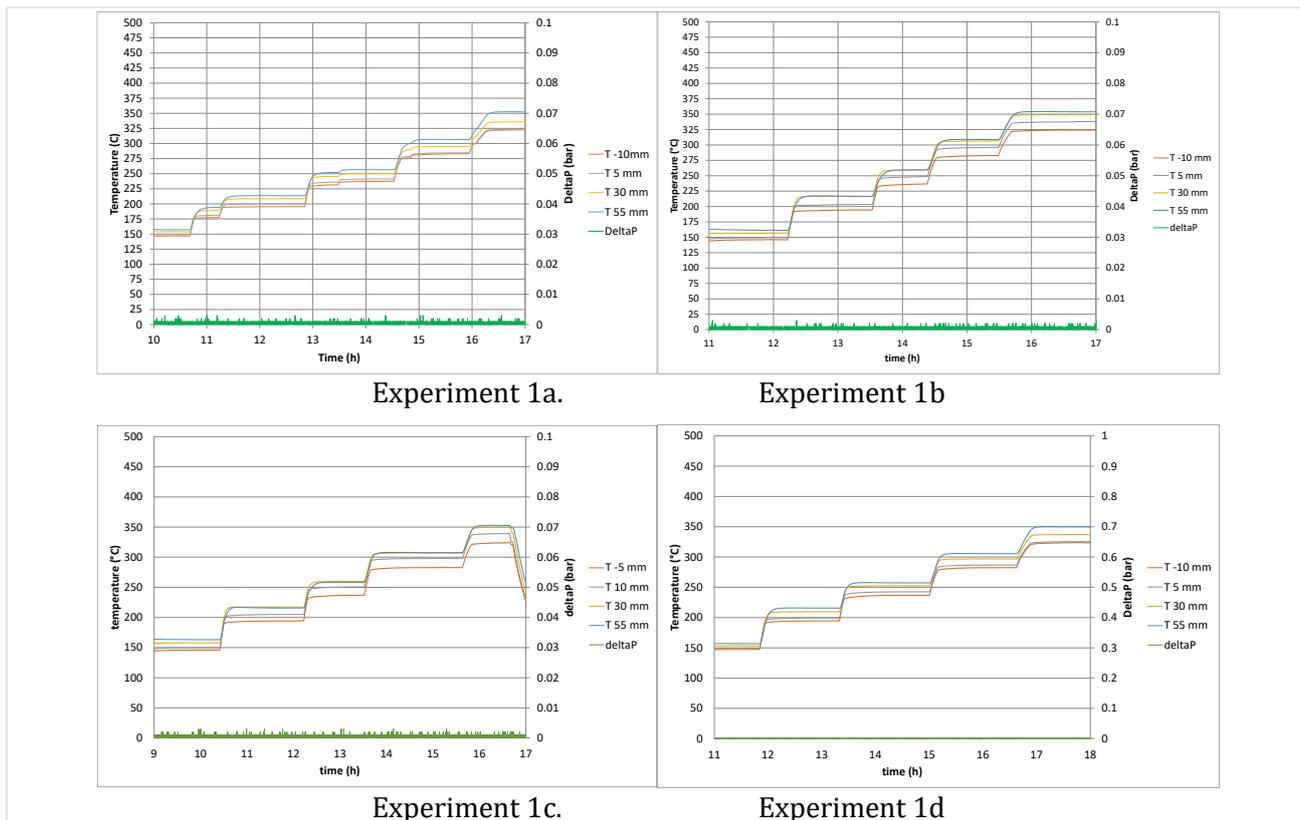
\$: CO₂ conversion in PEC cells to CO improved (target of project)

&: H₂ by-product formation suppressed, and CO₂ conversion efficiency to CO improved

*: H₂ by-product formation suppressed, but still low CO₂ conversion efficiency

The temperature was varied between 150 and 350 °C. The pressure drop (ΔP) increase (indicative of carbon formation on the catalyst) in time is monitored and logged. The results are presented in Figure 6.

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During all these experiments no pressure increase was observed. They lead to the conclusion that no or minimal coke formation had proceeded.

Test 2: Decomposition of impurities

The results of the conversion tests are gathered in table 2. All the ethene is converted to ethane above 150 °C. Also formic acid, methanol and formaldehyde are already converted at 150 °C.

Table 3. Decomposition of the impurities

	Feed	Product				
Temperature		150	200	250	300	350
H2	46.8					
CO2 %	16.3	17.2	16.4	15.3	14.1	14.1
CO %	3.4	2.9	4.2	5.7	7.2	7.2
Methane %	8.4	7.7	7.7	7.8	7.9	7.9
water	3.0					
Ethane %	0.000	0.268	0.267	0.270	0.274	0.274
Ethene %	0.288					
Formic acid	0.02					
methanol	2.00					
formaldehyde	0.02					
Nitrogen %	19.8	18.36	18.31	18.59	18.82	18.82

Test 3: De-oxidation activity

In this test the temperature is increased to around 170 °C in a flow of 2 Nl/min of hydrogen. Then 0.048 Nl/min of air is added and the hydrogen flow is reduced with the same amount, resulting in a 0.5% oxygen concentration.

Figure 7 shows the results of test 3, the de-oxidation activity. At the time of the left dotted vertical line 50 slm of air is added to the feed of the reactor. At the time of the second dotted vertical line the air flow is stopped.

No increase in oxygen concentration is measured at the outlet of the reactor. Clearly all the oxygen has reacted with the hydrogen in the gas stream. The heat of reaction caused an temperature increase of about 40 °C at the inlet of the reactor. Due to heat losses to the environment the temperature rise was less further downstream in the reactor.

The catalyst is capable of removing 0.5% of oxygen from a hydrogen stream at an average temperature of the reactor of about 180 °C.

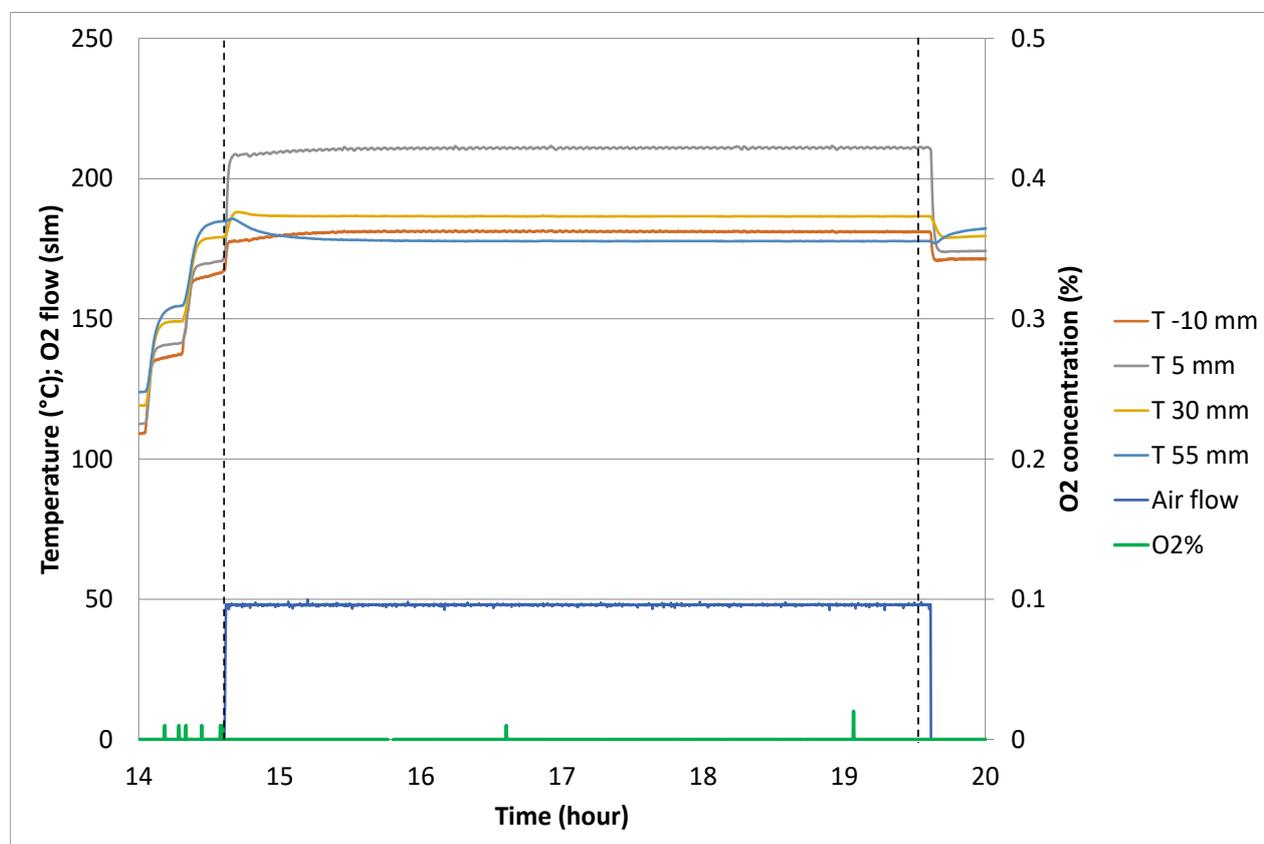


Figure 7 Temperature profile of the Copper catalyst reactor

Conclusions

The following conclusions have been drawn from the experiments 1 to 3:

- No coke formation is observed using this catalyst;
- Above a temperature of 150 °C all expected organic compounds are converted by the catalyst.
- At an inlet temperature above 180 °C all oxygen is converted with the available surplus of hydrogen to water vapor.

3. Conclusions

Gas treatment of simulated gas mixtures has been tested and validated in this exercise in which both unknown impurities in the sense of hydrocarbons and the excess of CO₂ in the syngas have been decomposed and separated, respectively. Membrane technology as well as adsorption-based technology has been evaluated to ensure the best technology possible. It turned out that adsorption-based technology does perform better than the membrane based technology and therefore will be implemented in the full CONDOR system. Furthermore, the copper catalyst has been tested and is performing as good as expected, this will ensure that larger hydrocarbons will be decomposed, oxygen will be removed and more DME can potentially be produced. The different options have been tested separately as subsystems, moreover, the membrane separation, Cu-catalyst tests and VSA technology. Finally, the Cu-catalyst and VSA technology have been assembled together for the complete CONDOR system, which is more thoroughly shown in D7.2.

4. Degree of progress

The activity can be considered 100 % complete.

5. Dissemination level

Public

Appendix I: VSA test set up

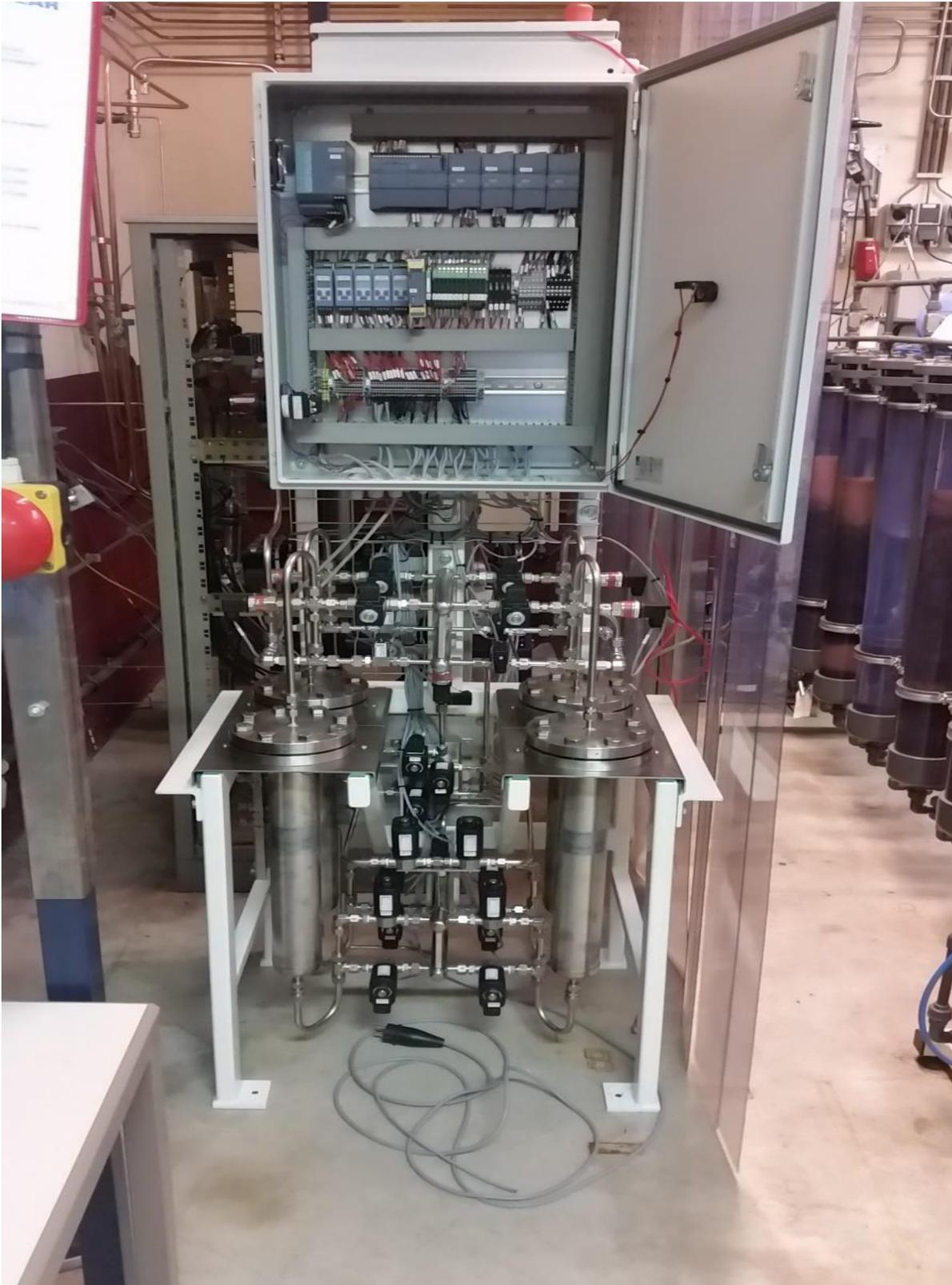


Figure 8 Set up of the VSA test

Appendix II: Cu catalyst test set up

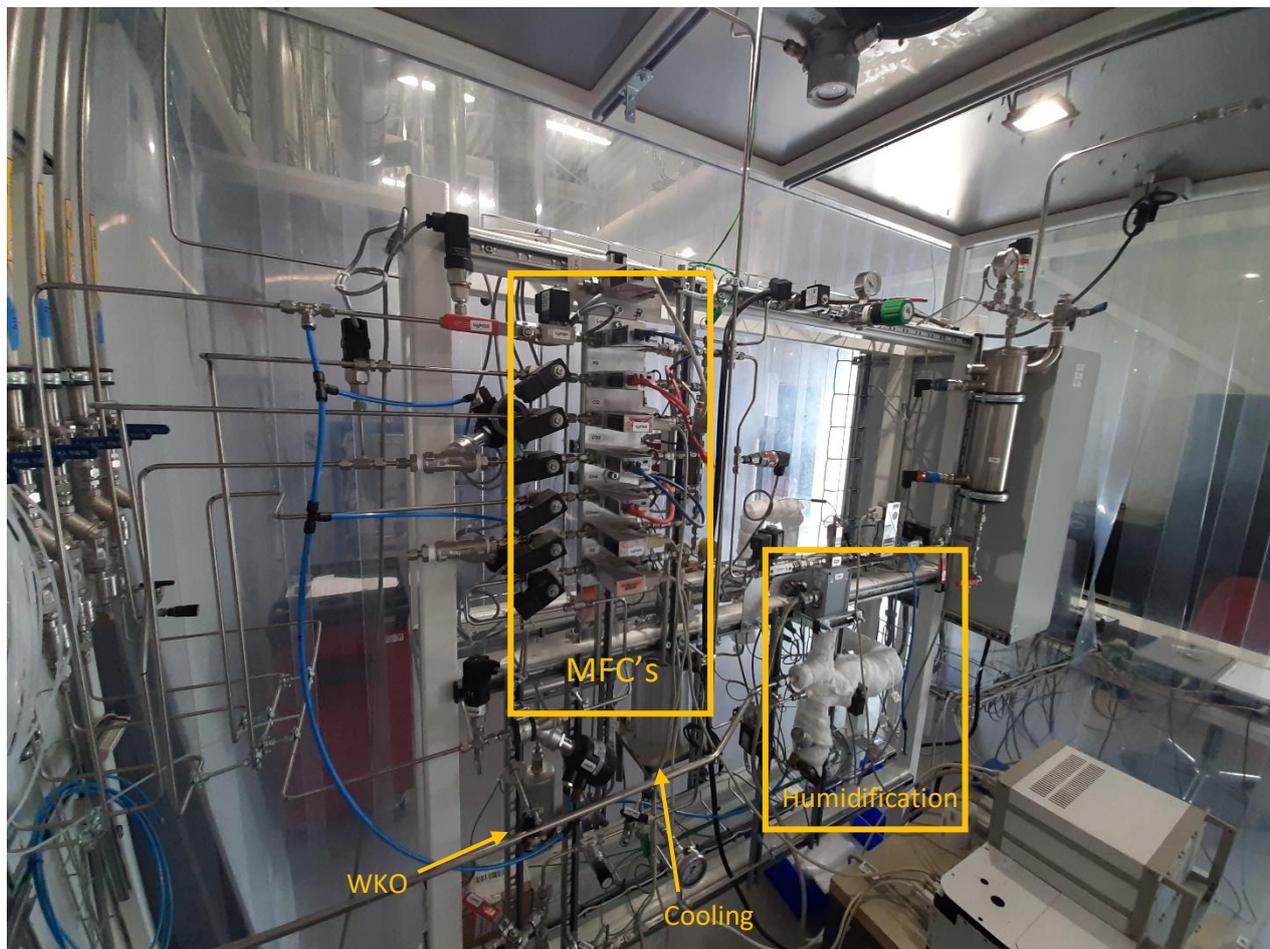


Figure 9 Set up of for the testing of the Cu catalyst



Figure 10 Set up of for the testing of the Cu catalyst