Project Title:

Truly Carbon Neutral electricity enhanced Synthesis of Liquefied Natural Gas (LNG) from biomass

Project Acronym:

CarbonNeutralLNG

PUBLIC

Work Package 2

Deliverable D2.1

"D21 Design and Performance dual function ADDmeth reactor"

Responsible for Deliverable:

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)

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Content

Abstract

The CarbonNeutralLNG project is funded by Horizon Europe and aims at a cost-competitive and carbon effective exploitation of carbon sources from biomass in order to replace fossil diesel fuels with renewable 'electricity enhanced GreenLNG' on a global scale. Low-carbon transportation will increasingly depend on liquid energy carriers like Liquefied Natural Gas from biomass (GreenLNG). Low-cost renewable energy (electricity and biomass) and reduced process complexity will be the main drivers for reduced marginal costs and increased carbon efficiency of the GreenLNG synthesis.

In this report, the design process of the additively manufactured catalytic methanation reactor is described. An additional experimental campaign was conducted on top of the described work in WP2 in order to collect data and to obtain experience with the reactor concept. The new reactor design is based on the findings from the experimental campaign.

1. Development of the new reactor Design

1.1 The Existing ADDmeth1 Reactor Layout

The development of the new methanation reactor in WP2 is based on an existing reactor concept that was developed at FAU's institute for Energy Process Engineering previously. The Design process and the reactor layout are described in detail by Hauser et al. [1]. The first additively manufactured methanation reactor (ADDmeth1) itself was based on the structured reactor (Figure 1) developed by Neubert et al. before at the same institute [2].

The concept of the structured reactor was based on heat pipes that efficiently cool the catalyst in order to maintain favorable operating parameters. The structured reactor consisted of multiple tubular reaction channels with a diameter of 8 mm each. A maximum radius of 4 mm was found out to be ideal for efficiently removing heat of the methanation reaction by Neubert [3]. If the radius is exceeded, the thermal resistance of the catalyst bed prevents efficient heat removal and therefore uncontrollable hotspots may form, which could damage the catalyst due to exceeding its operational temperature, which leads to catalyst deactivation by sintering.

During experimental campaigns run on the structured reactor, the efficient heat removal using heat pipes was proven to be a promising way to increase methane quality in a once-through process. However, the heat removal was actually too efficient near the outlet, where the methanation reaction produces less heat. The heat pipes therefore cooled the reaction more than desired, leading to kinetic limitations near the outlet of the reaction channel.

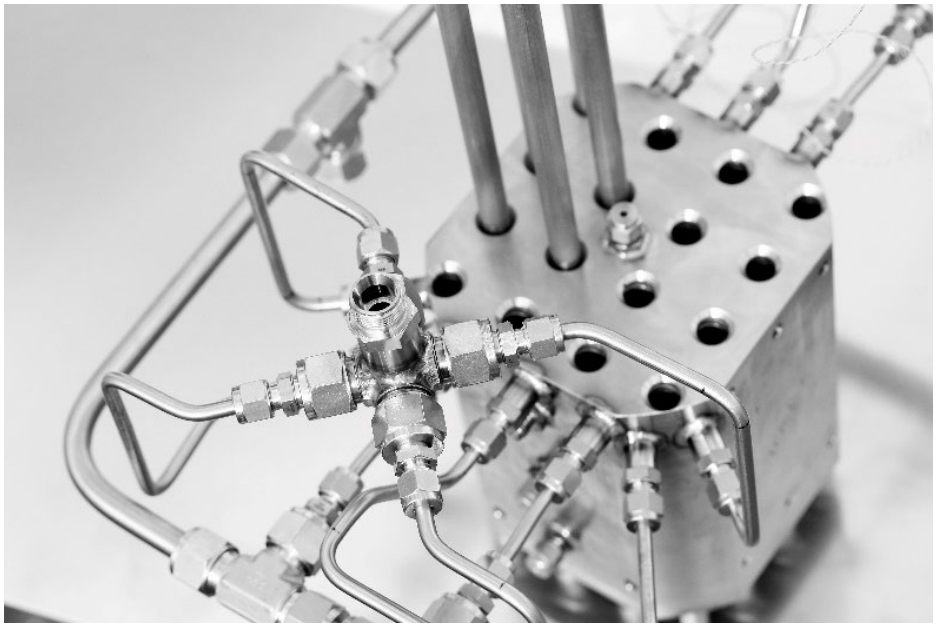

Figure 1: Structured Methanation reactor developed at FAU [3]

The development of the ADDmeth1 reactor addressed this issue by making use of the advantages of the additive manufacturing process. Due to the flexibility in designs and geometries, that the additive manufacturing process makes available, the reaction channel was modelled after the needs of the chemical reaction, instead of being constrained by the conventional manufacturing process. The kinetic limitation

near the outlet was therefore addressed by conically widening the reaction channel near the outlet (the upper part of the reaction channel). This increased the thermal resistance between the catalyst bed and the heat pipes, which led to improved kinetics near the outlet. Additionally, the widening increased local residence times by reducing the gas velocity. This further improves the quality of the product gas. [1]

Figure 2: Cross-sectional front view of the conical reaction channel of the ADDmeth1 reactor

The ADDmeth1 reactor is easily scalable due to its triangle based geometric shape, that allows to easily upscale the reactor by connecting multiple reactor cells in parallel, which still maintains the optimized geometry of each reaction channel. The 5 kW ADDmeth1 reactor was therefore previously upscaled to the 20 kW ADDmeth2 reactor, by connecting four cells in parallel.

Older experiments on the ADDmeth1 reactor showed, that shortly after the inlet, the reactor has a hotspot, which has good conditions for the reforming of tars. We are therefore adapting the reactor to optimize the temperature profile for the in-situ co-reforming of tars during the methanation reaction (Figure 3).

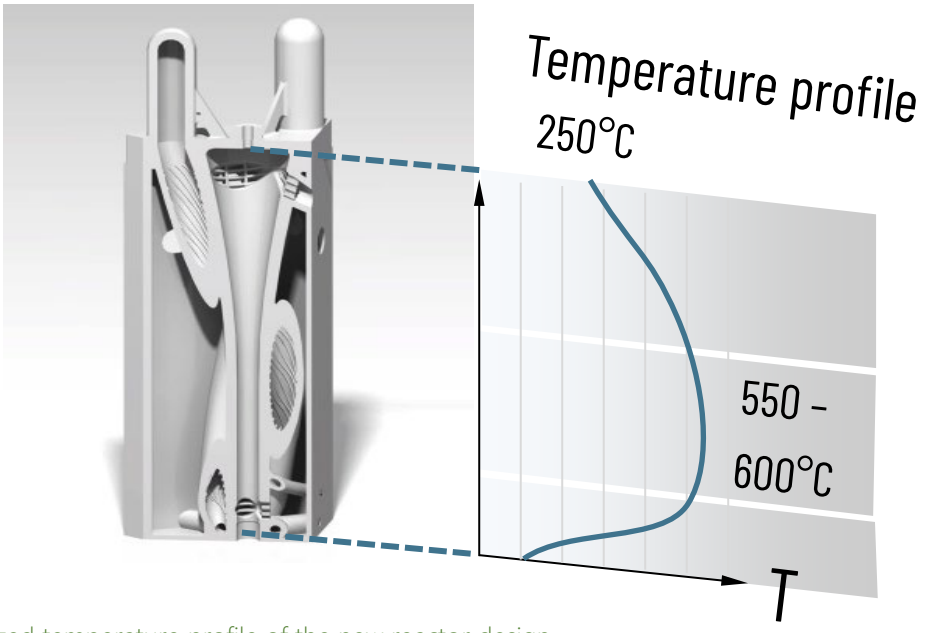

Figure 3: Idealized temperature profile of the new reactor design

1.1 Dedicated Experimental Campaign for the new Reactor Design

During the summer of 2023, a new experimental campaign was run on the existing ADDmeth1 reactor design. The experimental campaign was conducted on top of the described works in WP2, in order to generate an even better foundation of data and experience for the new design process.

1.1.1. Goal and Methodology of the Experimental Campaign

The goal of the new experimental campaign was to obtain data for the CFD simulations, in order to verify and improve the quality of the simulations. Additionally, another important objective was to gain experiences in the handling of the reactor and how to make improvements to the reactor performance.

It was intended to vary all of the key variables that are available in the reactor control, with the goal of understanding the reactor's behavior and finding possible ways to improve the reactor performance in upcoming designs. The reference case was chosen to be easily repeatable, while also producing surplus hydrogen as intended in the reactor setup for tar co-reforming developed in WP2. The experimental matrix, where each variable has been varied independently from all the other variables in the reference experiment is shown in Table 1 below.

Table 1: Experimental Matrix of the Campaign Conducted during the Summer of 2023

Test run	Pressure (bar)	Volume flow Educt Gas (Nl/min)	Educt Gas Composition	Electrical Heating Temperature (°C)	Heatpipe Air Cooling Power	Heatpipe Fluid
00_reference	8	6	CO2/H2, σ_{H2}=1,25	340	Adapted to maintain $p_{Heatpipe}$ < 90 bar	Water
01_pressure	6 - 10	6	CO2/H2, σ_{H2}=1,25	340	Adapted to maintain $p_{Heatpipe}$ < 90 bar	Water
02_power/GHSV	8	4 - 11	CO2/H2, σ_{H2}=1,25	340	Adapted to maintain $p_{Heatpipe}$ < 90 bar	Water
03_composition	8	6	CO2/H2; σ_{H2} = 0,75 – 2 SER Composition	340	Adapted to maintain $p_{Heatpipe}$ < 90 bar	Water
04_heating	8	6	CO2/H2, σ_{H2}=1,25	0 – 400	Adapted to maintain $p_{Heatpipe}$ < 90 bar	Water
05_cooling	8	6	CO2/H2, σ_{H2}=1,25	340	0 – 8 Nm^3/h Air Cooling	Water
06_heatpipe_fluid	8	6	CO2/H2, σ_{H2}=1,25	340	Adapted to maintain $p_{Heatpipe}$ < 90 bar	Water (Variation of fill levels) Dowtherm A
07_heat_loss	No Gas Flow	No Gas Flow	No Gas Flow	200 – 400	No Cooling	No Cooling
08_heatpipe_heat	No Gas Flow	No Gas Flow	No Gas Flow	340	0 – 8 Nm^3/h Air Cooling	Water (Variation of fill levels) Dowtherm A

1.1.2. Results from the Experimental Campaign

The experimental campaign gave valuable insights into the operation of the reactor. Several key results have been obtained and will be explained in further detail.

One of the key findings corresponds to the variation of the educt gas flow rate. Under our specific conditions with a high hydrogen content (σ_{H2}=1,25), which corresponds to the assumed operation in the real process, while still maintaining easy reproducibility, the desired reactor power of 5 kW could not be reached (Figure 3). The most stable operating points proved to be between 4 to 6 Nl/min of educt gas flow rate, which using the σ_{H2}=1.25 composition corresponds to 600 to 900 W of educt gas power. The 5 kW are therefore not reached using our assumptions, which means that some major structural changes to the reactor topology are necessary in order to achieve the desired power rating. Furthermore, regarding the shape of the temperature profiles for each operating point it is clear, that the required hotspot for the co-reforming of tars as sketched out in Figure 3 is only reached for lower educt gas powers. For operating points exceeding 1 kW, the gas velocity increases above feasible levels and the local residence is shortened. The reaction rate is therefore limited by mass transfer due to the high GHSV. The temperatures for the operating points with higher flow rates show a steep increase in temperature after the widening, resulting in the hotspot being moved into the widened zone. Controlling the temperature in this area proved difficult and the maximum operating temperature of the catalyst was exceeded frequently, which could not be stopped by increased cooling.

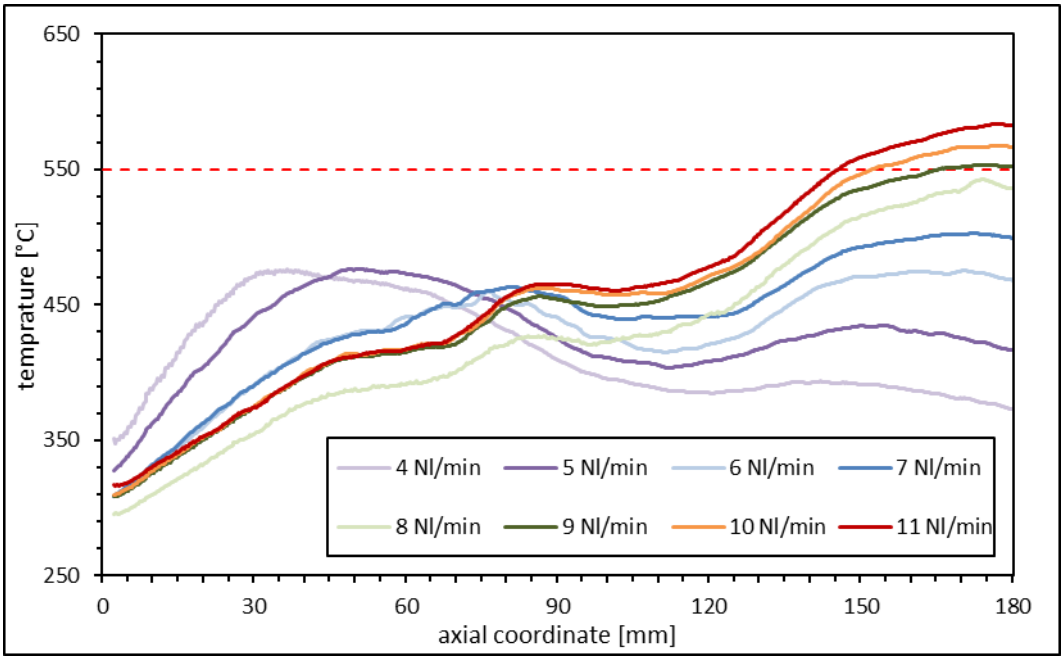

Figure 4: Temperature profile for the variation of the Educt flow rate, corresponding to the reactor power and GHSV – All other parameters kept at reference conditions (Table 1)

This experiment shows, that the ADDmeth1 reaction channel geometry delivers the desired results in lower power settings, however it must be considered that the operating point used in our case is not the same as the reactor was designed for. A reactor that is better suited to handle the typical operating conditions in the CarbonNeutralLNG process, with feed gas from the sorption-enhanced e-gasifier developed in WP1 requires some adaptations to achieve longer residence times in the lower section.

Another significant result of the experimental campaign is the variation of the cooling air at the heat pipe condenser section (Figure 5). Since the operating point is set at only 900 W of educt gas power in order to achieve the required operation, cooling air was used to cool the heat pipe condenser section. In

operating points with higher power throughput, water is intended to be used as a cooling medium in order to efficiently remove heat while also producing steam to be used in the process.

The graph clearly shows that the heat removal can be controlled by modulating the cooling air flow. The heat could even be almost totally removed in the lower section, preventing the reaction from properly igniting (8 Nm^3/h in Figure 5). While this demonstrates, that the widening of the reaction channel has the envisioned effect, for the operating points corresponding to the use case in the CarbonNeutralLNG process, the heat pipes are oversized significantly.

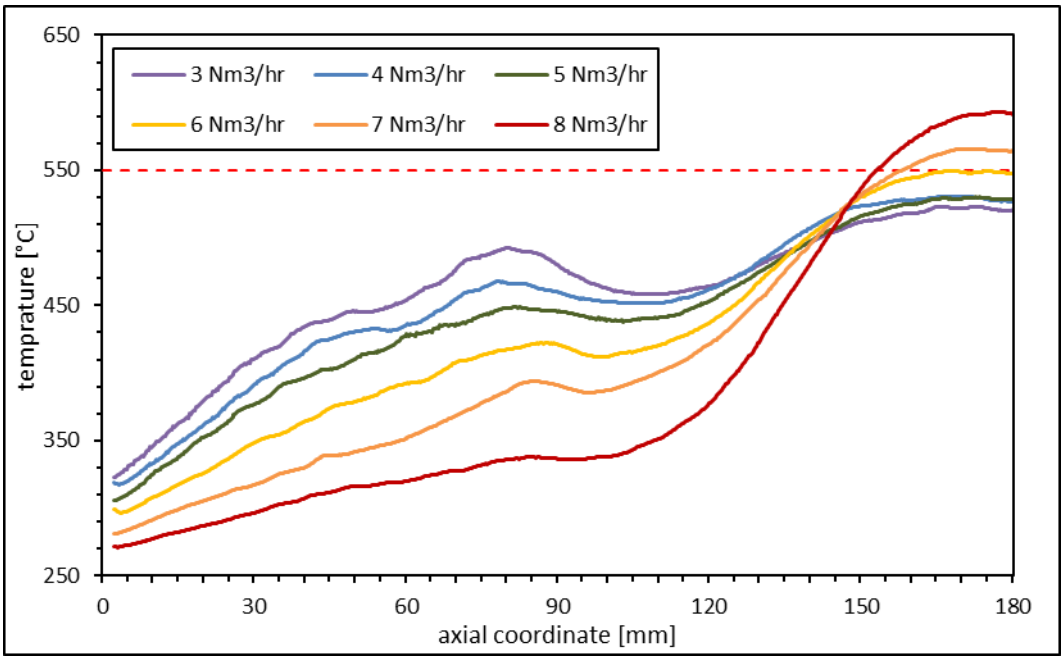

Figure 5: Temperature profile for the variation of the heat pipe cooling air flow – All other parameters kept at reference conditions (Table 1)

This can further be proven by the results of the variation of filling levels of the heat pipe. The heat pipes were initially filled with water to a level of 30 mm above the inlet. Changing the filling levels and also the heat pipe medium showed a significant influence on the temperature profile of the reactor. A lower fill rate with water led to a so called burn out of the heat pipe, an operating condition where the radial heat flow density exceeds the critical heat flow density. This results in the liquid film of the water being transported back on the walls completely evaporating. The heat pipe is effectively shortened up to the upper point of the burn out section. This allowed to obtain an almost ideal temperature profile for the other parameters being kept at reference conditions. From this experiment, it can be concluded that if the heat pipe removes less heat in the lower section, the operating conditions are favorable for the CarbonNeutralLNG process.

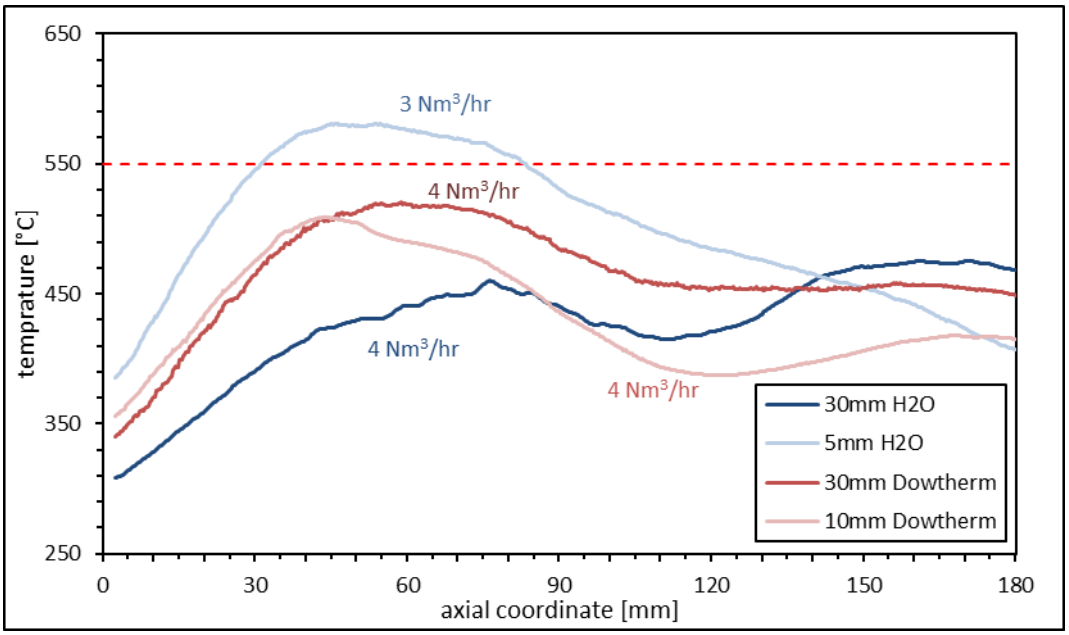

Figure 6: Temperature profile for the variation of different fill levels and heat pipe media at otherwise reference conditions

1.1.3. Discussion of the Results of the Experimental Campaign and their Significance for WP2

The results of the experimental campaign show three key findings. The first one is that a future reactor design needs to allow for longer residence times in the lower section, in order to achieve a higher power density in the reactor. The second key finding, is that the heat pipe should be sized smaller for those specific process intentions. The last key finding is that the reactor performance can be influenced and controlled by adjusting the heat pipe filling level, changing heat pipe media and modulating the heat pipe cooling. The largest distance between the catalyst and the heat pipe cooled wall should not exceed 4 mm in order to efficiently cool the catalyst bed, which could be validated for ADDmeth1.

1.2 Newly Developed ADDmeth3 Design

The new ADDmeth3 design has several key changes made to the geometry of ADDmeth1, in order to optimize the reactor for the in-situ co-reforming of tars.

1.2.1. Increase of Local Residence Times

Increasing the local residence times in the lower section is crucial for the formation of a hotspot, in which tar co-reforming can take place. However, the temperature should still be controllable, making the criterion of a maximum radius of 4 mm catalyst bed a necessity. This problem can be solved by moving the heat pipes from the outside of the reaction channel into the center, where the reaction channel is concentrically surrounding the heat pipe. By moving the heat pipe, the reaction channel effectively transforms its cross section from a circle to an annulus, which by still maintaining a radius of 4 mm has a significantly larger area. This is due to the quadratic relation of the area and the radius. The cross-sectional area of the reaction channel and therefore the local residence time can be increased while still maintaining the 4 mm criterion.

1.2.2. Different Reactor Concepts

The aforementioned change in the reactor topology makes two different design strategies possible. The first one is simply based on a singular heat pipe in the middle and a concentrical reaction channel, that is conically widened in its upper part (Figure 7).

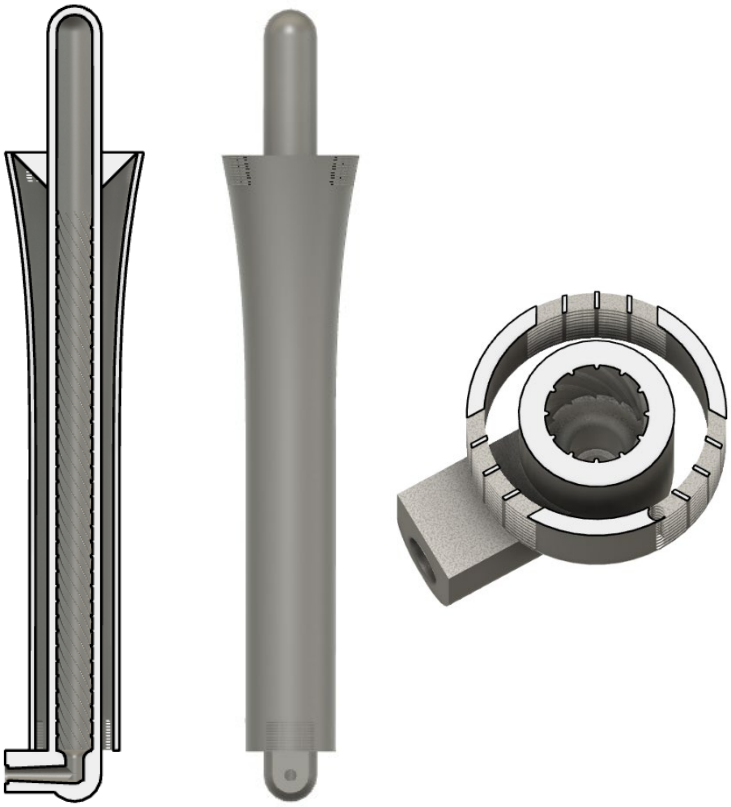

Figure 7: ADDmeth3.1 reactor design with a single heat pipe in the middle and a concentrically placed reaction channel

The second option is modelled after another existing reactor design at FAU's Institute of Energy Process Engineering, where a fix bed reactor has heat pipes inserted into the catalyst bed to maintain the 4 mm criterion. In order to optimize the space occupied by the reactor, three heat pipes are used as the center of overlapping circles forming a cloverleaf shaped reaction channel, which is conically widened in the upper part, with the heat pipes being left in the center of each circle (Figure 8). This shape ideally uses the triangular shape of the ADDmeth reactor cells.

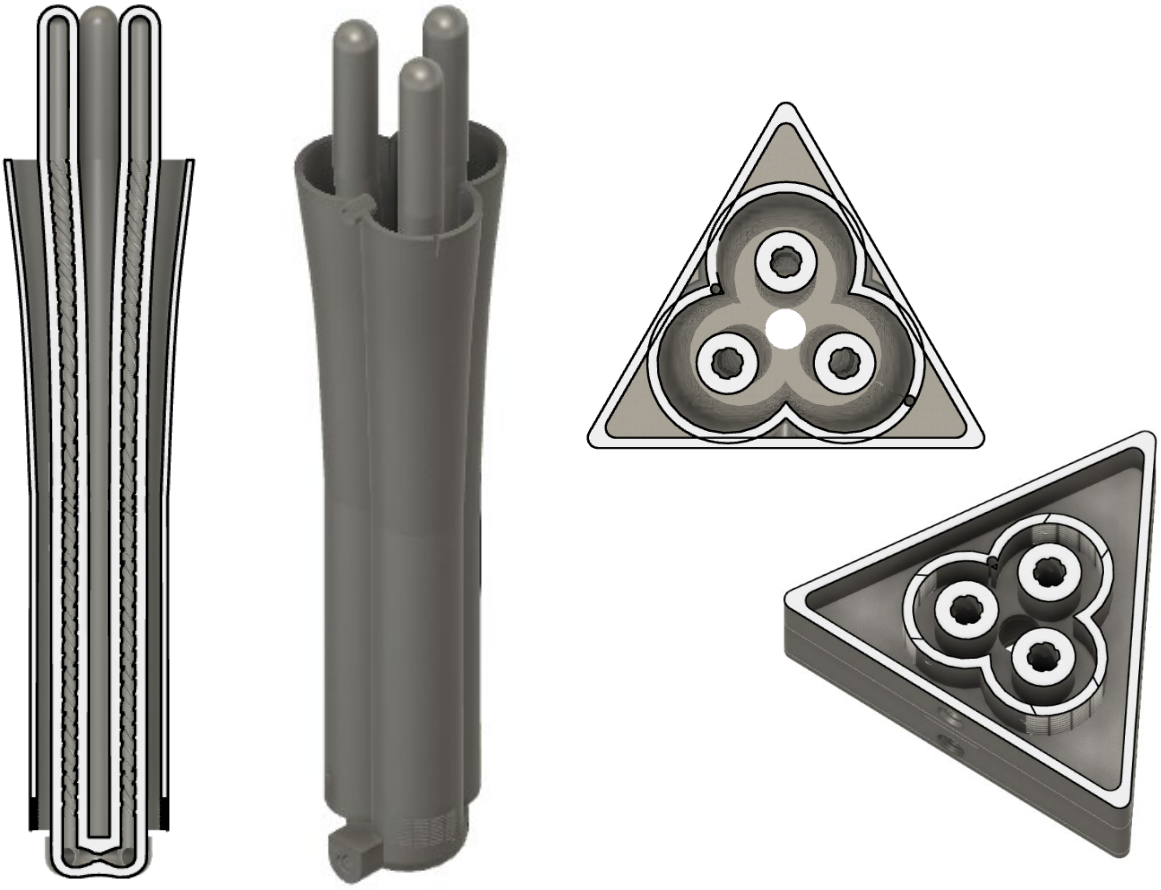

Figure 8: ADDmeth3.2 reactor design with three heat pipes in the center of circles forming a cloverleaf shape

In both of the designs, the lower section was also stretched by 20 mm each, in order to further improve residence times in the unwidened section.

For the new designs, the catalyst volume was compared with the ones of ADDmeth1, in order to validate the improvements that are envisioned by the geometric change (Figure 9). The catalyst volume corresponds to the achievable power of the reactor. Compared to ADDmeth1, the simple ADDmeth3.1 design shows an increase in catalyst volume by a factor of 2.9. In the ADDmeth3.2 design, which is optimized to fill the triangle shape as best as possible, an increase by a factor of 5.2 is achieved when compared to ADDmeth1. This shows, that both designs are feasible.

Figure 9: Comparison of the catalyst volume in the ADDmeth1, ADDmeth3.1 and ADDmeth3.2 designs

Another comparison was made to show the increase of cross-sectional area in the lower part of the reaction channel, showing that in the case of ADDmeth3.1, the area corresponding to local residence times in the lower section is increased by a factor of 5.5 when compared to ADDmeth1. In the case of ADDmeth3.2, the increase is even larger, amounting to a factor of 11.7 when compared to ADDmeth1 (Figure 10).

Figure 10: Comparison of the lower cross-sectional area in the ADDmeth1, ADDmeth3.1 and ADDmeth3.2 designs

These metrics of the new designs show a significant improvement of the points that need to be adapted as proposed in section 1.2.1.

Since we arrived at two different design concepts, both versions will be printed and tested in experimental campaigns as written in the project proposal. The upscale will then make use of the design that proves to be more suitable under the real testing conditions. For the validation using a CFD model of the reactor, even the scale up would use only one reaction channel for the calculations. Therefore, postponing the scale up to a later stage poses no significant alterations of the proposed project plan.

1.3 Validation of the New ADDmeth3 Design

Since the new reactor setup poses significant changes to the inner geometry of the reactor, some key properties had to be calculated to make sure, that the new reactor design is feasible and operates safely.

1.3.1. Heat pipe limits

The heat pipes were resized significantly for the new purpose of the reactor design. This makes the calculation of the heat pipe limits a necessity. Both reactor designs are sized to deliver up to 5 kW of educt gas power. The methanation reaction produces up to 1 kW of heat at 5 kW educt gas power and a stoichiometric CO-Methanation. For a stoichiometric CO_2-Methanation, 850 W are produced under ideal circumstances. The heat pipes are sized to remove more than 1 kW of heat, to ensure safe operation.

One of the heat pipe limits of significance to the design is the entrainment limit, which is a measure of the maximal heat that the heat pipe can transfer, without the vapor velocity forcing droplets out of the condensate film. The entrainment limit was calculated using a specifically generated tool at FAU's Institute of Energy Process Engineering. The tool uses material properties of the heat pipe material, fluid properties of the heat pipe fluid and the operational parameters at the specified design point like temperature, pressure, etc. The cylindrical shape and the spiral grooves from our heat pipe design are used as additional geometric input of the the calculations. The entrainment limit was found to be 1.9 kW for ADDmeth3.1 and 1.4 kW for ADDmeth3.2 at the specific design points, where ADDmeth3.1 uses a single spirally grooved heat pipe with an inner diameter of 12 mm and a wall thickness of 3 mm. ADDmeth3.2 uses three spirally grooved heat pipes with an inner diameter of 6 mm and a wall thickness of 3 mm. both heat pipes are manufactured from stainless steel 1.4404 (316L) in the additive manufacturing process.

The other significant heat pipe limit is the boiling limit, which was calculated using the critical heat flux density calculations from the VDI Heat Atlas [4]. The boiling limit is a measure for the critical heat flux density, at which the condensate film is completely evaporated, resulting in a burn out of the heat pipe under the specific operating conditions. The resulting boiling limit is 1.3 kW in the case of ADDmeth3.1 and 1.9 kW in the case of ADDmeth3.2.

Both limits have been calculated for the maximum possible heat removal under ideal circumstances without heat loss and are therefore maintained at a secure level. However, the heat pipes are also not oversized which would result in too much heat being removed as was exhibited in the experimental campaign that was detailed in section 1.1.2.

1.3.2. Structural stability

The new design has also been subject to a finite element analysis using the Autodesk Fusion Simulation Environment (Figure 11). A simplified version of the inner geometry was used as a representation of the reactor setup. The simulation focused on reaching acceptable safety factors within the design while neglecting the use of the support structure, based on the diamond lattice unit cell. A simulation of the support structure would require an infeasible computational effort, therefor the design process relies on a sufficient stability even without the support structure. Sufficient safety factors were reached in the design of ADDmeth3.1 without the support structure. In the case of ADDmeth3.2, this was achieved by adding macro support structures in the form of perforated plates.

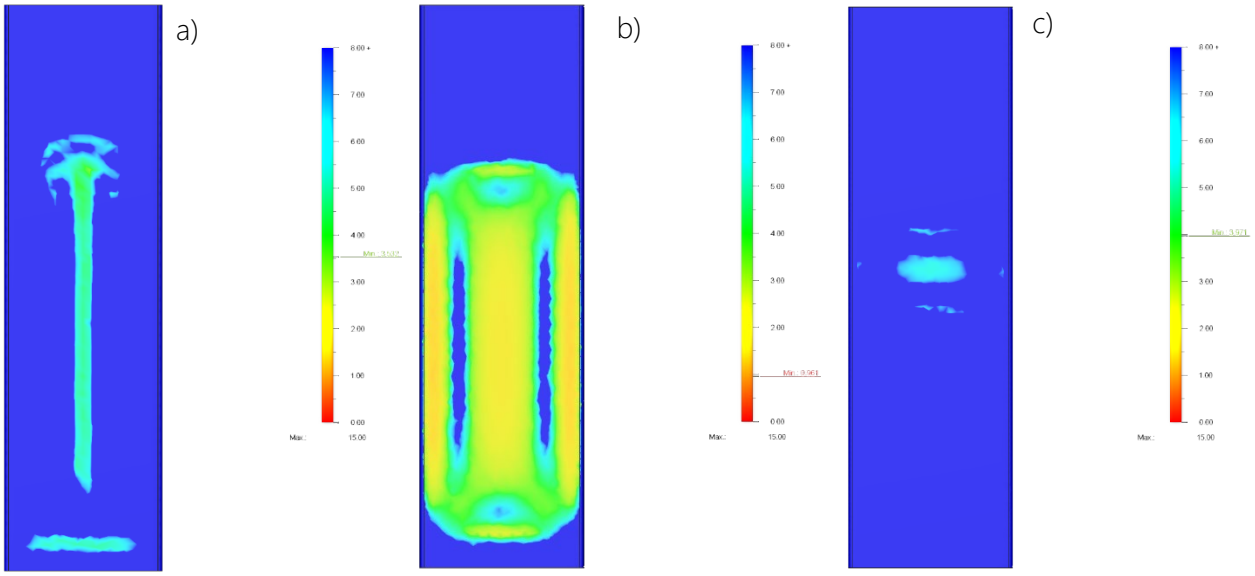

Figure 11: Finite element analysis of a) ADDmeth3.1 with sufficient support b) ADDmeth3.2 without sufficient support c) ADDmeth3.2with added macro support structures to reach a desired safety factor

However, the lattice support structure greatly increases the structural stability of the reactor (Figure 11). The design can therefore be assumed to be structurally sound under the assumed operating conditions with a sufficient safety factor.

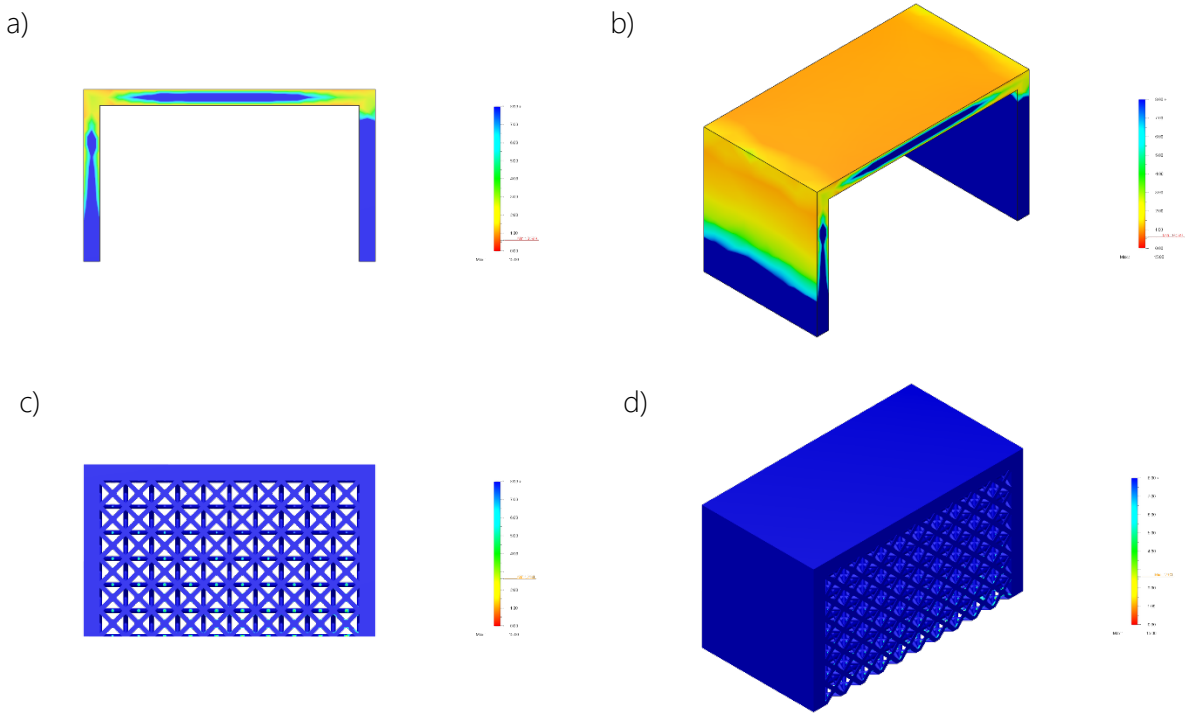

Figure 12: Finite Element Analysis using Autodesk Fusion Simulation Environment: Minimum safety factor a) without lattice support, front view b) without lattice support: safety factor 0.58 c) with lattice support, front view d) with lattice support: safety factor: 2.61

1.4 Tar Reforming Catalyst Screening

The progress made on the catalyst screening (Task 2.2) is described in the following sections.

1.4.1. Current Progress

For the catalyst screening, an existing test rig had to be modified and a new gas mixing station had to be built, which can introduce tars into the educt gas mixture.

The old existing gas mixing station did not reach the needed safety standards for the requirements of the tar screening. It was therefore dismantled and some of its parts were reused where it was possible.

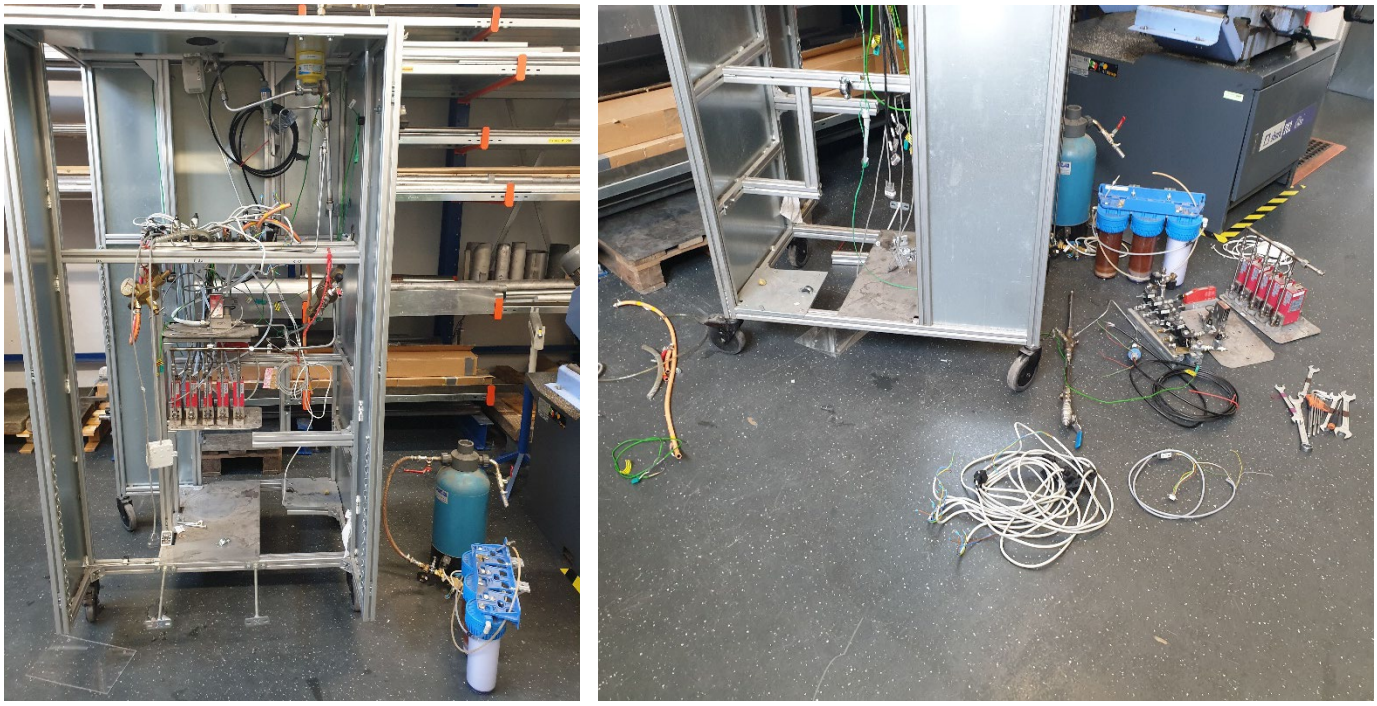

Figure 13: Dismantling of the old gas mixing station

The new gas mixing station design is based on an existing gas mixing station at FAU's Institute of Energy Process Engineering.

The new setup is shown in Figure 14. The upper part features the circuit box with all the electronics, the PLC system and safety relevant mechanics. The lower part features the tar saturators, which are devices constructed to saturate a nitrogen stream with a specific amount of tar components. The middle part is the actual gas mixing station with several mass flow controllers to control the educt gas composition and flow rates. A gas preheating loop was incorporated to prevent the tar components from condensing.

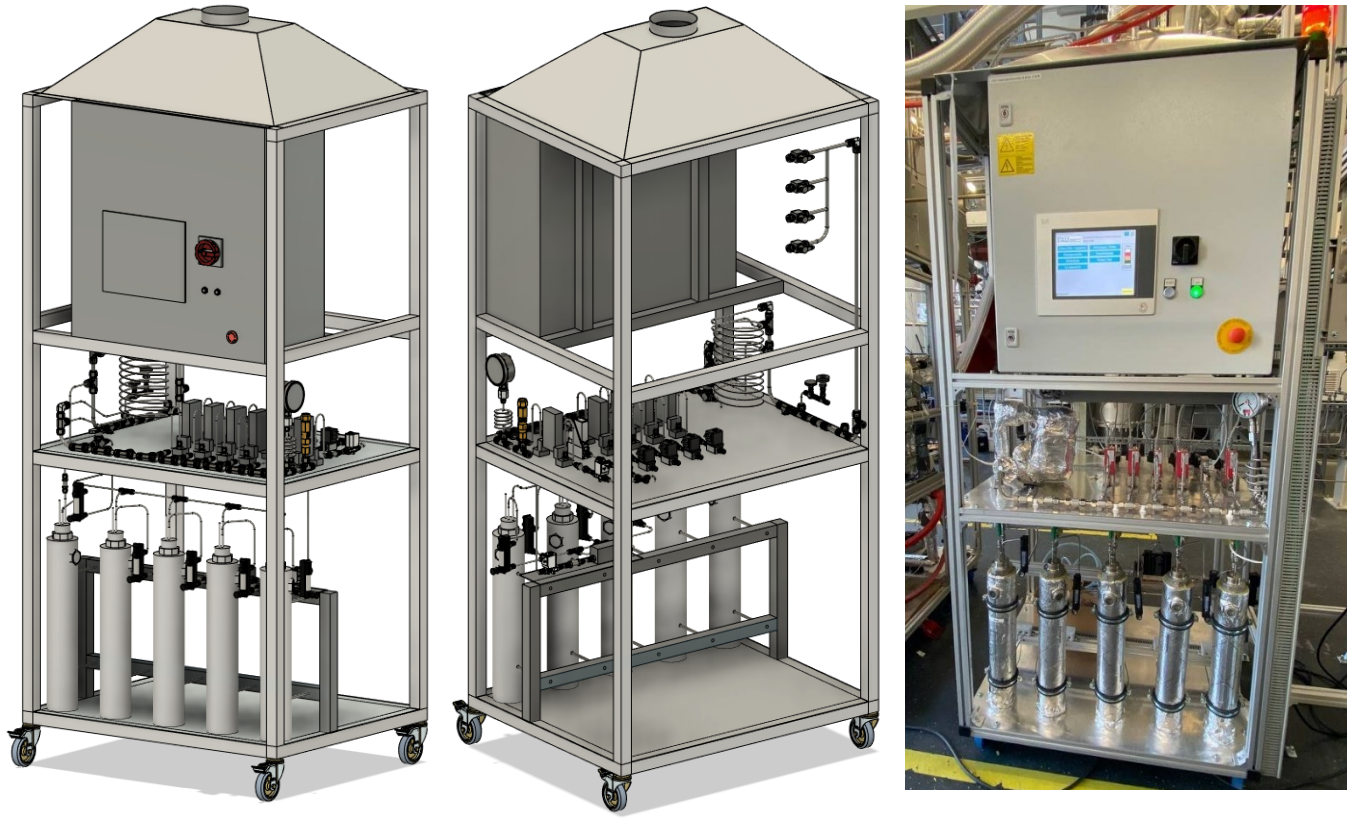

Figure 14: CAD model of the new gas mixing station and actual picture of the gas mixing station

The tar saturators (Figure 15) consist of multiple tubes, that are filled with each tar species. Nitrogen is bubbled through the column of the liquid tars, until a certain saturation has been reached. The amount of tar dosed into the educt gas mixture can be varied by controlling the temperature and the nitrogen flow rate through the tar saturators.

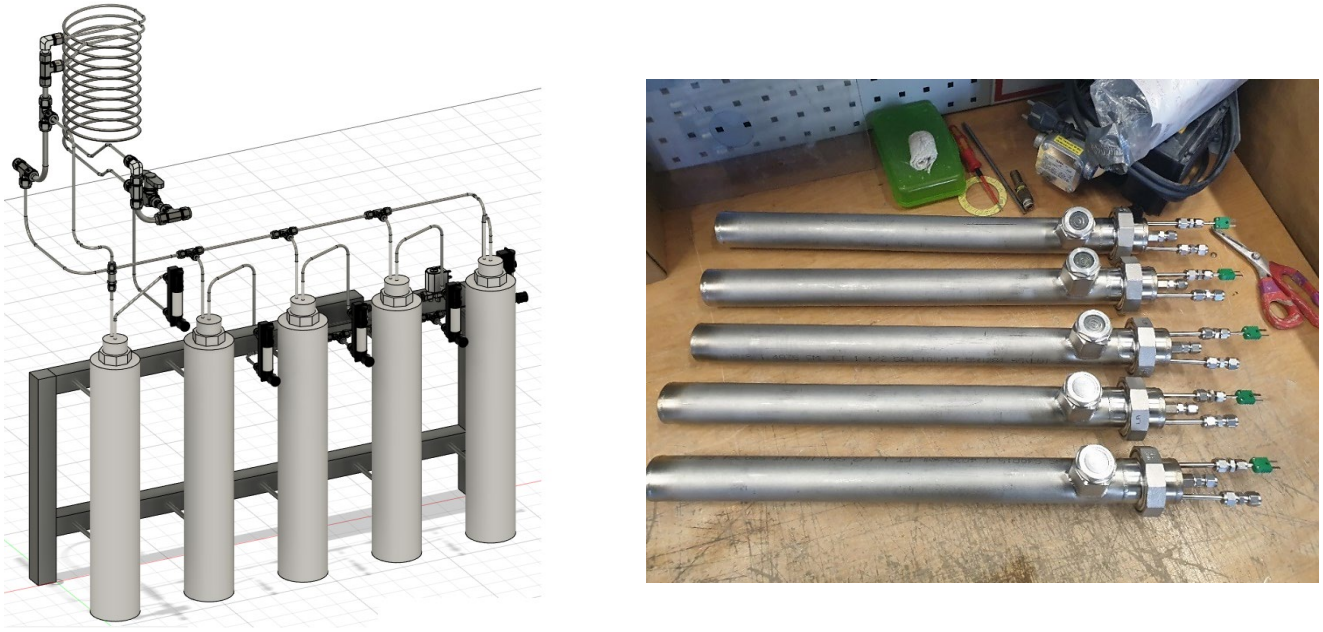

Figure 15: CAD model and actual picture of the tar saturators

An exemplary calibration graph is shown in Figure 16, where the principle of tar saturation can be taken from. A calibration factor is derived from multiple such experiments, in order to control the amount of tars present in the educt gas.

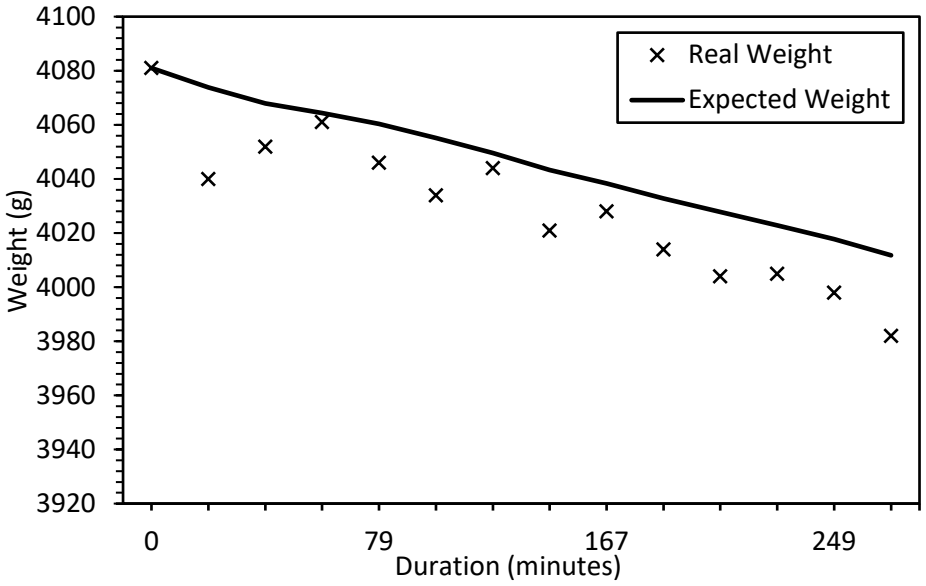

Figure 16: Calibration graph for a tar saturator at 25°C and 10 l/min air flow rate using deionized water as fluid

The new gas mixing station follows the usual safety principles and passed an internal review. However, due to the elaborate process of designing, commissioning and calibrating the gas mixing station, the work was not conducted at the same time scale as in the proposal, where the erection of a new gas mixing station was not planned. The need became apparent during early adaptations of the old gas mixing stations, when safety issues were determined. Furthermore, the commissioning process was delayed due to issues in the delivery process. A safety valve and some key components of the PLC system were subject to significant delays in the supply chain of the manufacturer. Some of the PLC components only arrived as late as November 2023. However, since then the gas mixing station was successfully commissioned, passed internal safety reviews and is under operation.

1.4.2. Status of the Experimental Campaign

The experimental campaign is currently still in progress, first experiments have already been conducted but the full results will be available and reviewed later in the year 2024. The complete results will be added to Deliverable D2.3 – Experimental data dual function ADDmeth reactor operation. However, preliminary results will be used for the other WP2 tasks.

1.4.3. Future Results

The full experimental campaign is currently focused on five different commercially available catalysts listed in Table 2. Please note that the used catalysts should be treated as SENSITIVE:

Table 2: Catalysts used in the tar co-reforming catalyst screening

Active Material	Composition	Carrier	Particle Size	Internal Name	Comment
Nickel	~55% NiO	Al_2O_3	4.5 mm	EVT08	Standard Ni
Nickel	>50% NiO	-	1.5 mm	EVT11	Standard Ni
Nickel	14% NiO	$CaAl_{12}O_{19}$	19 x 16 mm	EVT10	Reduces carbon formation
Ruthenium	2% Ru	Al_2O_3	2 – 4 mm	EVT12	Standard Ru

Platinum, Palladium, Rhodium	Pt, Pd, Rh (exact composition unknown)	-	1.8 – 2 mm	EVT09	Pt and Pd both show good performance for hydration of tars at low T

The particle size of all catalysts was reduced to between 1 – 4 mm by crushing the catalyst pellets and obtaining sieve fractions (Figure 17). A filler material was used for the inlet.

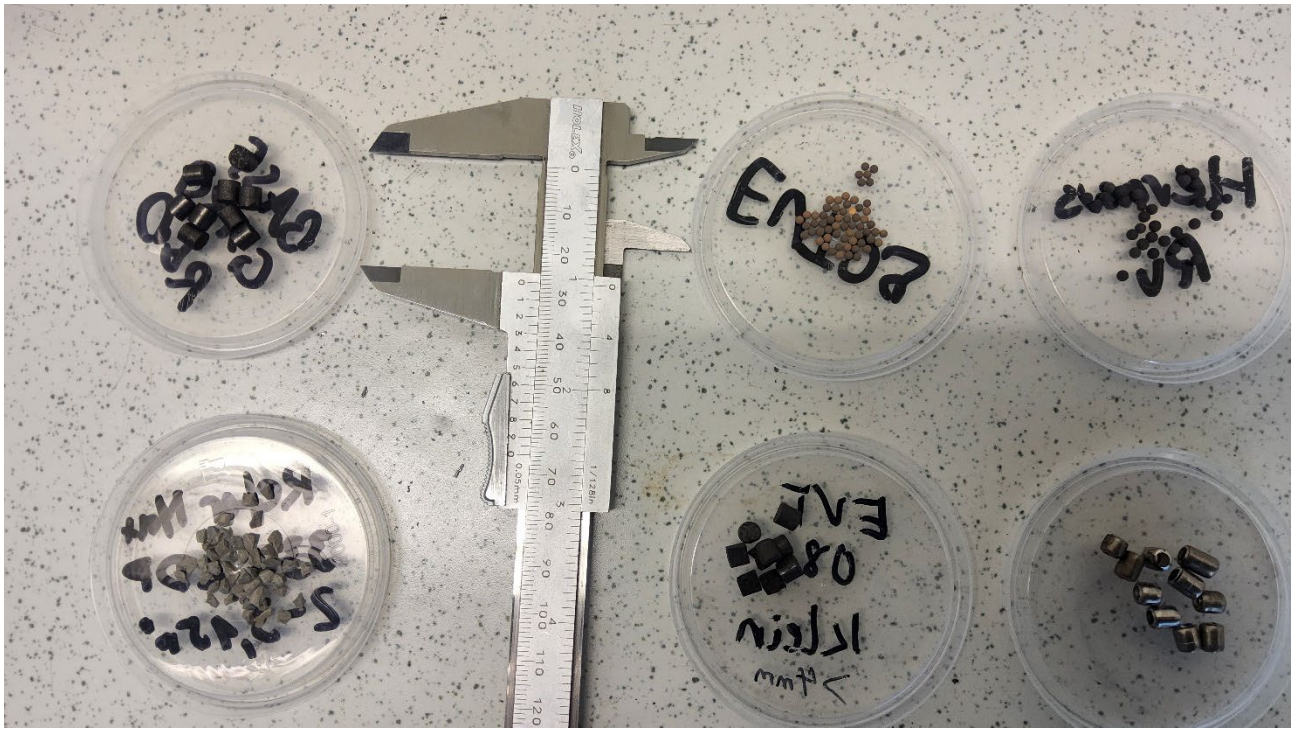

Figure 17: Catalysts used for the catalyst screening in Task 2.2

The following parameters will be varied in the catalyst screening: The gas composition will vary, using different dry educt gas compositions, ranging from stoichiometric CO_2-methanation to a typical gas composition with tars dosed as expected from the SER gasifier from WP1. The steam to carbon ratio (S/C-ratio) will be varied, as this is one of the main factors to limit carbon formation that is expected when using a tar-heavy syngas. The temperature at which the reactors are electrically heated is also varied. All the parameters are varied for each catalyst. Later during the experimental campaign, short hydrocarbons, namely ethane, ethylene and acetylene will be added to the gas mixture, as they are known to increase carbon formation. Finally, organic sulfur components will be added to the mixture. These are known catalyst poisons. We will compare how the different catalysts cope with the poisons.

Currently, the experiments with CO_2-methanation have already been completed, so a benchmark has been obtained for the catalyst activity (Figure 18).

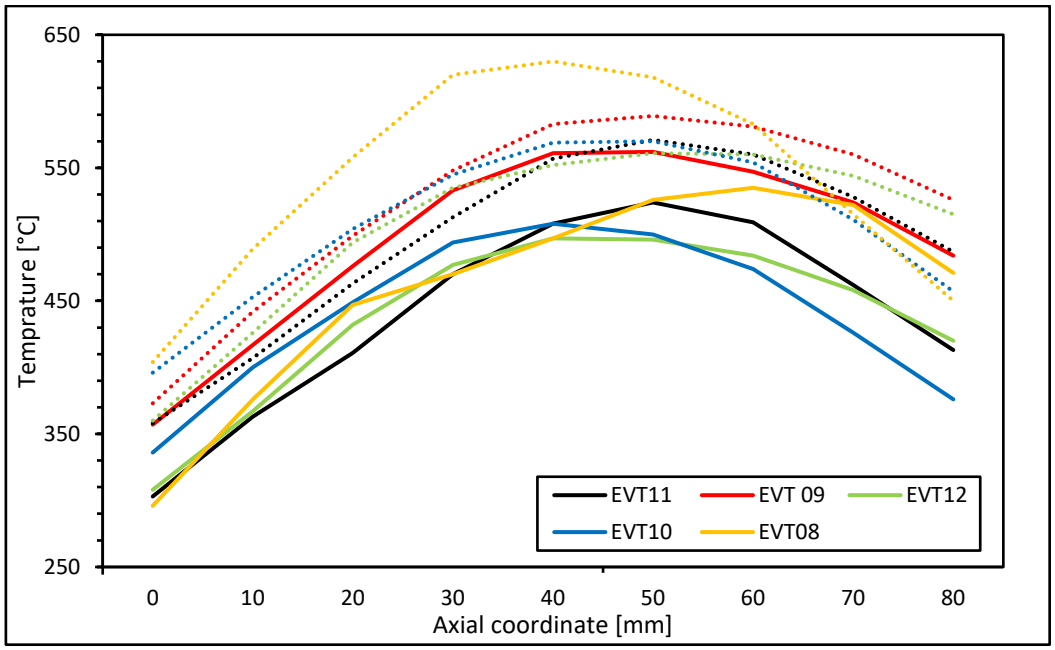

Figure 18: Temperature profile of the different catalysts for CO2 methanation at 400°C (solid) and 500°C (dashed) of external heating

The methane content of the product gas is another important criterion for the catalyst activity (Figure 12).

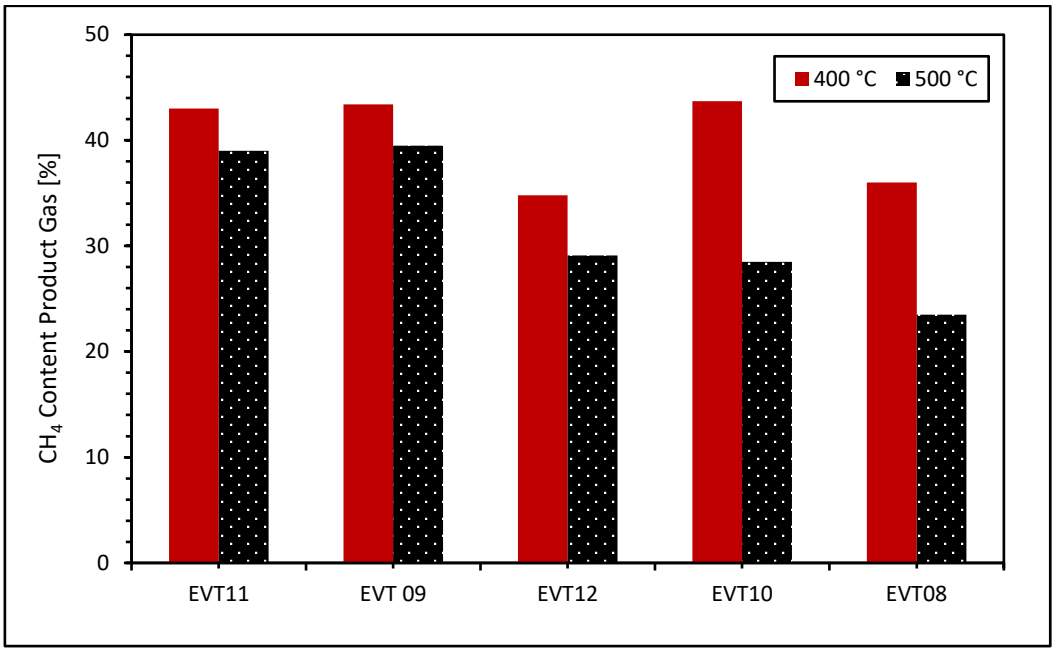

Figure 19: CH_4 content in the product gas of the different catalysts for CO2 methanation at 400°C (solid) and 500°C (dashed) of external heating

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