SOMMER

Solar-Based Membrane Reactor for Syngas Production

D3.3 Definition of Downstream Process Parameters

WP3 – System Analysis: Economics, Energetic, Environmental - Task 3.2: Pre-design of downstream process

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Disclaimer

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About the Project

SOMMER aims to develop and demonstrate an innovative carbon-neutral process for syngas production by directly integrating solar energy into a catalytic membrane reactor, facilitating the decomposition of H_2O and CO_2 (e.g., captured from carbon-emitting industries or through direct air capture). This approach enables SOMMER to overcome reliance on fossil-based energy for syngas production, utilizing CO_2 instead of natural gas as a feedstock. Syngas, a critical intermediate for the chemical industry, prompts SOMMER to encompass the entire value chain - from CO_2 provision in a cement plant to syngas formation and further processing into valuable products like DME or methanol. The core of SOMMER's technology is the optimized energy integration of a novel thermochemical conversion process of CO_2 and H_2O in a single step. This process is supported by highly selective catalysts, an oxygen transport membrane, and a concentrated solar-thermal plant fulfilling the thermal energy demand. The key outcomes of SOMMER involve the experimental demonstration and evaluation of the innovative solar-powered membrane technology. Additionally, it focuses on developing high-performance, cost-effective membranes as pivotal components, elevating the technology to new heights. SOMMER's strategy involves advancing membrane manufacturing through slip-casting, a more mature approach, and additive manufacturing to optimize the effective membrane surface area in the reactor. The concept anticipates future advantages, allowing prolonged and flexible operation by seamlessly switching between two operational cases: I) Purely solar approach at 1500 °C and II) a biogas-supported approach at 900 °C. Furthermore, SOMMER aims to identify the technological, ecological, and economical potential for flexible and highly efficient solar syngas production, contributing to the formulation of a detailed roadmap and providing a foundation for pre-commercialization through subsequent R&D development activities.

DLR	Deutsches Zentrum Für Luft - und Raumfahrt e.V.	DE	
FZJ	Forschungszentrum Jülich GmbH	DE	
IREC	Fundacio Institut De Recerca De L'Energia De Catalunya	ES	
HTE	HTE GmbH The High Throughput Experimentation Company	DE	
CSIC	Agencia Estatal Consejo Superior De Investigaciones Científicas	ES	
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Document Summary

Based on the syngas composition obtainable from the membrane reactor unit the layout of the downstream process producing methanol or dimethyl ether was performed. To streamline the workflow a set of boundary conditions was defined as basis for the downstream process. These boundary conditions include syngas composition for the main constituents (CO, CO_2 and H_2), as well as inert gases and side components which can act as catalyst poisons. The possibility of preconditioning after the syngas obtained from the solar reformer prior to downstream conversion into methanol or dimethyl and ether is part of the evaluation. Within the work package it was decided to focus on syngas compositions suitable for methanol production. The reasons for this focus were bifold: a) Methanol is a traded commodity chemical with an international large volume market and established logistics, b) from the current perspective DME can be produced from methanol at competitive cost in a single step operation from methanol via dehydration. The definition of the downstream process parameters has happened in close collaboration with task 3.1 to focus the operational parameters of the upstream unit as a fit to purpose of the downstream process. All data obtained will be used in task 3.3 regarding process assessment and techno economic analysis.

Changes with Respect to the DoA

To simplify the discussion and focus the work package and the simulation work for the work package of the membrane reformer, a limitation was made on methanol production as downstream process. DME can be produced from methanol in a single step operation through dehydration or alternatively under similar operational parameters directly from syngas.

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1. General Considerations for Design of the Downstream Process

Based on the syngas composition obtainable from the membrane reactor unit the layout of the downstream process producing methanol or dimethyl ether was performed. To streamline the workflow a set of boundary conditions was defined as basis for the downstream process. These boundary conditions include syngas composition for the main constituents (CO, CO_2 and H_2) as described in chapter 2, as well as inert components and side components which can act as catalyst poisons as described in chapter 3. The possibility of preconditioning after the syngas obtained from the solar reformer prior to downstream conversion into methanol or dimethyl and ether is part of the evaluation. Within the work package it was decided to focus on syngas compositions suitable for methanol production. The reasons for this focus were bifold: a) Methanol is a traded commodity chemical with an international large volume market and established logistics, b) from the current perspective DME can be produced from methanol at competitive cost in a single step operation from methanol via dehydration. The definition of the downstream process parameters has happened in close collaboration with task 3.1 to focus the operational parameters of the upstream unit as a fit to purpose of the downstream process. All data obtained will be used in task 3.3 regarding process assessment and techno economic analysis.

The overall design process was conducted in the following order:

i) Definition of parameters defining the optimum syngas composition corridor for Downstream
ii) Considerations for acceptable Contents of Inert Gases and Impurities for Downstream
iii) Transfer of information to DLR for assessment of Solar Reformer product properties

Based on the output of iii) and WP 3.1 a second loop will be initiated to gather the information for the TEA analysis based on an improved retrofitted design:

iv) Definition of alternative parameters defining the optimum syngas composition corridor for Downstream based on Solar Reformer Output
v) Considerations for acceptable Contents of Inert Gases and Impurities for Downstream based on Solar Reformer Output
vi) Transfer of information to DLR for assessment of Solar Reformer product properties, further finetuning of Solar Reformer Output
vii) Gathering of balances for heat and material including integration in the cement plant for TEA

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2. Considerations for the Optimum Syngas Composition Corridor

With an annual global consumption of around 5.3 × 10^6 t, methanol is one of the most important basic chemicals in the chemical industry [1]. The large-scale production of methanol production from syngas today mainly takes place through the low-pressure process developed by ICI in the 1960s. In this process, synthesis gas (H_2, CO and CO_2) is today primarily produced from natural gas subsequently reacted over $Cu/ZnO/Al_2O_3$ catalysts. Because temperature, partial pressures and subsequently composition of the reaction mixture within the methanol reactor unit vary in terms of residence time and location, typically the process conditions at the reactor inlet are defined as base parameters for the methanol process. The low-pressure methanol process works as recycle process with synthesis cycle Pressures of 50 to 100 barg at temperatures in the range of 493 - 503K at the reactor inlet [2]. Two reactions starting from the two existing carbon oxides, CO (Equation 2.1) and CO_2 (Equation 2.2) can lead to the formation of methanol, both in an exothermic reaction.

Equation 2.1:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{300\,K} = -90{,}77\,kJ\,mol^{-1}$$

Equation 2.2:

$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{300\,K} = -49{,}16\,kJ\,mol^{-1}$$

In addition to the two methanol formation reactions, it occurs in the presence of water the water gas shift reaction or its reversal according to Equation 2.3:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H_{300\,K} = 41{,}21\,kJ\,mol^{-1}$$

Modern systems basically consist of three process parts. The first unit is usually the syngas production unit. In conventional units, natural gas is converted to syngas, then compressed and purified, this compressed synthesis gas is converted into methanol in the high-pressure part of the plant and the product methanol is condensed out and methanol is then purified by distillation in the cleaning section.

Syngas compositions are usually defined through their stoichiometry number S (Equation 2.4):

$$S = \frac{p_{H_2} - p_{CO_2}}{p_{CO} + p_{CO_2}}$$

Where p_{H2}, p_{CO} and p_{CO2} are the respective partial pressures of the gases. The ratio of the relevant components, given in partial pressures, allows for a simple evaluation of the synthesis gas in relation

[1] M. Bertau u. a. Methanol: The Basic Chemical and Energy Feedstock of the Future. Editor M. Bertau, Springer, 2014

[2] E. Fiedler u. a. „Methanol“. In: Ullmanns Encyclopedia of Industrial Chemistry 23 (2012), pp. 25–48

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to optimal methanol synthesis stoichiometry. A stoichiometry number of 2 is optimal for methanol synthesis, whereas a deviation to smaller numbers than 2 is related to a lack of hydrogen and an excess of 2 is interpreted as an excess of hydrogen [3]. Depending on the reactor type and the prevailing temperatures and pressures, the thermodynamic equilibrium can only be equilibrium, only a maximum of 50% of the gas mixture entering the reactor can be gas mixture can be converted to methanol. In practice, however, the conversion must be limited even more to control the high heat enthalpy of methanol formation. This prevents local overheating of the catalyst. This means that after the methanol separation, considerable quantities of cycle gas (containing unreacted H_2, CO and CO_2) must be recycled and recompressed. Due to the large production volumes, even minimal improvements in the activity and stability of the catalysts lead to major cost savings and productivity benefits. An additional aspect of importance is the sensitivity of the methanol catalyst regarding the carbon dioxide partial pressure. Although variants of the methanol catalysts based on Cu/Zn/Al are reported that can tolerate high carbon dioxide partial pressures, typically these catalyst types show an optimum performance at a stoichiometry number close to 2 and an absolute carbon dioxide content of 3 to 8 vol%. Operation in this compositional corridor allows maximum space-time-yields and therefore ensures therefore minimization of CAPEX and OPEX (particularly equipment size and recompression cost come to play here as major factors).

Together with the team of WP 3 it was in the following decided to focus on I) methanol as key target product for the downstream process, II) a scenario where CAPEX and OPEX of the downstream process could be minimized. Therefore, the following boundary conditions were given to the WP 3.1 as parameter set to be optimized the production of a syngas with a stoichiometry number of 1.9 to 2.2. It was anticipated that the solar reformer would produce such as syngas mixture at close to atmospheric pressure and that the syngas would have to be compressed up to a pressure level of 50 to 100 barg. Common consensus of the team is that based on the outcome of the modelling work of WP 3.1 adaptations to the downstream input parameters should be made according to the simulation results and be analyzed via a sensitivity analysis, these include particularly the carbon dioxide content in the syngas mixture, as well as the content of inert gases.

3. Considerations for acceptable Contents of Inert Gases and Impurities for the Optimum Syngas Composition Corridor

Two additional types of gaseous constituents may have a major impact on the CAPEX and OPEX of the downstream process: inert gases and impurities that are known catalyst poisons. Whereas inert gases do not have a direct impact on the catalyst as such, they act as diluent and therefore limit the productivity of the methanol unit. Typical inert gases that may appear as diluents in the SOMMER process scenario are nitrogen and methane. From a general process perspective, a certain amount of diluents may even be desirable to improve flexibility of the recycle process, beyond the acceptable minimum though compromises with regard to the achievable space-time-yield must be accepted. In the framework of the project SOMMER the acceptable concentration of inert gasses (nitrogen,

[3] E. Fiedler u. a. „Methanol“. In: Ullmanns Encyclopedia of Industrial Chemistry 23 (2012), pp. 25–48

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methane are assumed to be the inert gasses occurring in the process) are set to a value lower than 10 vol% as the sum of inert gases. Based on the outcome of the simulations of Task 3.1 adaptations may be made.

In difference to the inert gas content certain components may have harmful impact on the methanol catalyst and act as catalyst poisons limiting the performance of the material and its lifetime. For traditional methanol processes many of these poisons occur as trace components in the carbon containing feedstock and a range of technical solutions are available with which these compounds can be taken care of. Most of the compounds are adsorbed on adsorber beds containing selective adsorption materials. Typically, syngas produced from coal and lignite contains most contaminants along with the highest level of contaminations [4], similar levels and contaminants are seen in steel mill off-gases, although here particularly the amounts of interest are higher [5]. Major contaminants that need abatement are sulfur containing components, heavy metals like mercury, halogens like chorine. Nitrogen containing components like NO or ammonia are typically not considered catalyst poisons but are problematic, as they may be converted to methylamines in the process and become then an undesired and not easily separable component in the product methanol. Oxygen is also an undesired component in the syngas, levels should be as low as possible, preferential catalytic oxidation technologies are available.

It is expected that some of the mentioned compounds (sulfur containing compounds, nitrogen containing compounds, heavy metals and halogens) can also have major impact on the material used as membrane in the solar reformer. As the final material for the solar reformer has not yet been fixed, the limits of tolerance are only taken with regard to the tolerance of the downstream process.

Table 3.1 summarizes the target amount of impurities in the syngas considered tolerable for the downstream process

Table 1: target impurity levels for syngas

Impurity	Accetable Level	Catalyst Poison Y/N	Other Impact
N_2/CH_4	< 10 vol%	N	Diluent
Sulfur containing Impurities	< 0.5 ppmV	Y	-
Halogens particularly Chlorine	< 1 ppbV	Y	Corrosive Reagent
NO and NH_3	< 1 ppmV	N	Trace product ends in Methanol
Metals and metal Carbonyls	< 1 ppbV	Y	Potentially corrosive

[4]https://doi.org/10.1016/C2009-0-20067-5
[5]https://doi.org/10.1002/cite.201800026

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Oxygen	< 1ppmV	N	Easily abated

4 Conclusion

The given document summarizes the demands of the downstream process of the project SOMMER. Based on the above-described limits simulation work for the solar membrane reactor was carried out to elucidate whether operation resulting in a suitable syngas product is feasible. Based on the results of WP 3.1 a complete analysis of the process chain will be subsequently done to uncover the best mode of operation of the process chain.

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