Aachener Verfahrenstechnik | RWTH AACHEN UNIVERSITY

CAPD Project: Techno-Economic Analysis and Process Improvement for Dimethyl-Ether (DME) Production

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1 Background Information

Within the modern industrial engineering milieu, methanol and dimethyl ether (DME) production are crucial processes. Methanol, also known as methyl alcohol, is the most basic alcohol, with properties that include being lightweight, volatile, and combustible. Beyond its physical traits, it is a vital precursor to many commercial chemicals and is recognized for its CO2 capture and utilization.

Methanol is increasingly acknowledged as a dual-purpose fuel source, either augmenting gasoline or substituting it, paving the way to sustainable fuel alternatives.

Likewise, DME, the simplest ether, plays a significant role in the industrial chemical field. It is volatile, colorless, and flammable, serving as a precursor to commercial chemicals like dimethyl sulfate and acetic acid, and is also an aerosol propellant.

Just as methanol, DME is emerging as a potential player in the energy sector. It can be used as an additive to or replacement for diesel, indicating a pathway to lessen dependence on conventional fossil fuels. Thus, the production and applications of methanol and DME reflect industrial engineering's progress and diverse potential.

In the present work, a comprehensive industrial procedure is designed and refined, which leverages natural gas as the initial resource to generate methanol and dimethyl ether. This process optimization is achieved through the application of the ASPEN Plus software. The entire mechanism is systematically compartmentalized into three distinct stages.

The first stage involves the utilization of natural gas to synthesize synthesis gas in a process known as steam methane reforming. The subsequent stage capitalizes on this syngas to facilitate the production of methanol. Finally, the methanol generated is further processed to yield dimethyl ether. This multi-step design offers a streamlined approach to the manufacturing of these two key industrial chemical products.

2 Design objective

General design objectives

The extensive objectives of the design process include several crucial steps. Firstly, it is essential to establish reasonable production rates for syngas and methanol to ensure a steady output of 150 metric tons per day of dimethyl ether. The next step involves the construction of the process flowsheet. This step employs linear and simplified models, such as RStoic, REquil, Sep, and DSTWU for the steam reformer, methanol, and DME synthesis reactors, along with the separation units. It is of paramount importance that all boundary conditions, including product purity and production capacity, are fulfilled.

Progressing further, the process flowsheet is developed using more rigorous models such as RPlug, Flash2, and RadFrac. These models are applied to the steam reformer, methanol, and DME synthesis reactors, as well as the distillation columns. Additionally, the Langmuir-Hinshelwood-Hougen-Watson kinetics, gleaned from multiple literature sources, are integrated into the reactor models.

In terms of infrastructure, a furnace is modeled to supply the necessary heat to the plant's endothermic reactor. Concurrently, an appropriate strategy for purge stream disposal needs to be determined. If applicable, a recycle structure for the process section should be designed.

Subsequently, the size of the process units is determined, and their capital investment cost is estimated. To conclude the process, a preliminary techno-economic analysis is performed to evaluate key economic indicators. This comprehensive and methodical approach forms the backbone of our ambitious industrial procedure design.

Introduction to optimisation in ASPEN Plus using Excel

When designing any plant, numerous factors need to be considered. These range from economic to the physical aspects of the process. However, three main aspects need to be balanced: cost, purity and throughput of the system. Improving one of these factors often has a negative impact on the other two. Therefore, it is crucial to approach the design process inversely. What are the design specifications, and how can they be achieved? One effective approach to tackle this complex problem is optimization. Because optimization is a vast and intricate subject, we will only provide a brief overview.

Aspen Plus offers two primary methods for conducting optimization. Firstly, Aspen Plus offers functionality to conduct numerical optimisation directly. Additionally Aspen Plus enables the analysis of sensitivity analysis output (by hand), which can then be visualized through plots, tables, or exported to Excel. Since we often deal with complex functions, in form of Aspen Plus blocks, with multiple in- and output parameters, plotting them in a 2D or 3D graph is less feasible. Therefore, conducting optimization in Aspen Plus using the numerical optimization function or exporting the data to Excel for further analysis is more feasible. The distinction between the numerical optimization and sensitivity analysis functions in Aspen Plus lies in their execution approach. In sensitivity analysis, the target function(s) are executed on a fixed set of values. While in numerical optimization, the target function(s) are only evaluated on values that minimize them. The values for which are given by the chosen optimisation algorithm. For further information refer to the Aspen Plus documentation on the implemented optimisation algorithms. Sensitivity analysis on the other hand provides the advantage of dynamically adjusting the feasibility region and constraints after it was executed, for example in Excel, without the need for re-running the optimization process. This flexibility enables users to make adjustments without repeating the entire optimization procedure, although it does require additional overhead compared to numerical optimization. The following control diagram will give a short summary of the workflow on how optimisation was conducted for this project thesis, using Aspen Plus sensitivity analysis function and Excel, on the example of an arbitrary block.

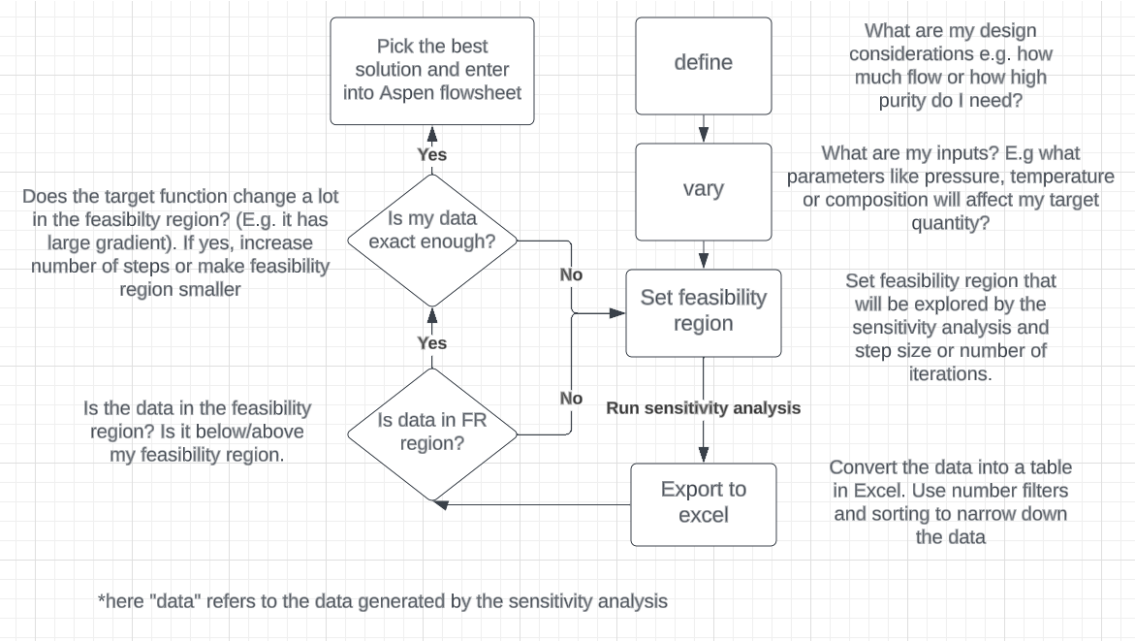

Abbildung 2.1: flowsheet for basic optimisation using Excel and Aspen Plus

3 Plant Design

3.1 Syngas Synthesis

Overview

The process initiates with the introduction of natural gas, steam, and potentially CO2, into the steam reformer to generate syngas, a blend of H2 and CO2. Given the endothermic nature of the collective reaction, it necessitates the provision of extra thermal energy to stave off temperature reductions. This vital heat supply can be provided by the combustion of natural gas with air in a furnace. Upon exiting the reformer, any unreacted water is extracted through condensation. The resulting dry syngas is then directed towards the methanol synthesis unit for further processing.

Feed streams

As mentioned, three feed streams are employed: natural gas, carbon dioxide, and water steam. Among these, water steam is subjected to high pressure (25 bar), in comparison to natural gas and carbon dioxide. Given the high-pressure requirement of the reactor input (28 bar), simply blending these three streams could result in a pressure drop, which is economically unfavorable.

To mitigate this issue, this work proposes a strategy involving the premixing of natural gas and carbon dioxide, followed by pressure augmentation. Subsequently, the high-pressure water steam is mixed in, preventing any significant pressure drop. The process of pressure augmentation is facilitated by employing multi-stage compressors, which utilize electricity as their power source. This structured approach helps maintain the

necessary process conditions while improving economic efficiency.

Reactor

In the process of syngas synthesis, a fixed bed reactor with a Ni/MgAl2O4 catalyst is deployed. This reactor facilitates three principal chemical reactions: steam methane reforming for the production of CO, the water-gas shift reaction, and steam methane reforming for the formation of CO2. These reactions occur under specific conditions, with an operating temperature of 850 degrees Celsius and a pressure of 29 bar, to ensure the successful synthesis of syngas.

Furnace

Given the endothermic nature of the overall reaction, there is a need for extra thermal energy to counteract potential decreases in temperature. This requisite heat can be provided by combusting natural gas with air within a furnace. The combustion process, carried out with surplus air to ensure a minimum oxygen content of around 3% in the dry flue gas, typically operates at a temperature ranging between 850 and 1300 degrees Celsius. The furnace exhaust possesses significant thermal energy due to its elevated temperature. Rather than squandering this resource, it is harnessed to generate high-pressure, hot water steam. Subsequently, this steam is utilized to drive a turbine designed to generate electricity, thereby enhancing the economic efficiency of the process. This approach embodies the principle of energy recovery, converting waste heat into a useful form of power.

Seperation and syngas output

Upon exiting the reactor, unreacted water is separated through a process of condensation. The resultant dry syngas is then channeled to the methanol synthesis unit. For effective methanol synthesis, the syngas components should meet specific criteria, including a stoichiometric number approximating 2.05 and a carbon oxide ratio less than 0.6. Additionally, given the high pressure of the unreacted water, another turbine is employed to harness its potential energy.

3.2 Methanol Synthesis from Synthesis Gas

Overview

Methanol synthesis has played a crucial role in the search for an alternative liquid fuel and in reusing carbon dioxide which enhances the carbon neutrality political strategies. Methanol also served as an important chemical feedstock, extractant, and solvent for the chemical industry. In this project, *synthesis gas (Syngas)*, a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), etc., is used to produce methanol. Methanol synthesis itself has established numerous fields of research. The use of biomass to produce methanol is currently under a thorough investigation. Another aspect is Power-to-X technologies which convert both carbon dioxide and hydrogen to methanol. This technology is still currently being investigated, where carbon dioxide could be retained through direct air carbon capture (DAC) or available carbon storage and hydrogen through electrolysis. The scope of this project focuses on synthesizing methanol from Syngas, improving energy integration within the process, and running a techno-economic analysis for feasibility and viability studies.

Gas Compression

The process begins with compressing the synthesis gas to around 75 bar. This is done by multi-stage compression with intermediate cooling. Syngas is compressed from **29 bar** to **75 bar**. Multi-stage compression with intermediate cooling requires only **39.7 MWh** of power, whereas compression without intermediate cooling requires **43 MWh** of power. The multi-stage compression saves around **8 %** of the power. The only setback for multi-stage compression is the amount of cooling water needed to cool off the pressurized gas from the compressors. The heat produced through cooling can also be integrated into other operation units within the flowsheet where it is required. The pressure ratio for every compressor is around *1.3* which suits best for an axial compressor. Axial compressors have been known to be more effective than radial compressors for large-volume intake.

Heat Exchanger Network

The pressurized gas is then mixed with the recycle stream and heated up to around **250 degrees Celsius**. The mixed stream is heated through a counter-current heat exchanger. The hot stream required to heat the gas before being fed into the reactor came through the heat exchanger within the reactor itself. This heat integration saves around **23 %** of the required heat. Around **77 %** of the heat required should then be provided through external hot steams. This is done heuristically through sensitivity analysis which explores feasible heat transfer within the exchanger. The cold stream from the heat exchanger before the reactor is then used to cool off the stream behind the reactor before it enters the first flash. The heated cold stream is then used to heat off the stream before entering the second flash for off-gas removal. This stream which contains pure water is then cooled off to **20 degrees Celsius** before it is then disposed to the water storage/ pond. The heat integration within the process is far from optimized. A further field of exploration includes improving the energy integration within the process through pinch analysis for a better conceptual heat integration or optimizing the integration through numerical optimization as an MINLP (mixed-integer nonlinear program) reformulation.

Reactor and Separation Units

The reaction took place within a fixed-bed catalytic reactor. It comprises two main reactions: methanol synthesis from carbon dioxide (CO_2) and hydrogen (H_2) and reverse water gas shift reaction (RWGS). The kinetic model is based on *Langmuir-Hinshelwood kinetics* which enhances the gas-solid adsorption mechanism for the catalyzed reaction. $Cu/ZnO/Al_2O_3$ is a well-known commercial catalyst for methanol synthesis. The reactor is equipped with around 1200 tubes and a height of 15m with an integrated heat exchanger within the reactor. Water is used as a cooling fluid for this reaction. 120 tons/hour of water are used to maintain the reaction. The reaction within the reactor is highly exothermic. Excess heat produced could damage the catalyst if the reactor exceeds a certain temperature. This can be prevented through the counter-current flow of cooling fluid which maintains and control the temperature within the reactor. A yield of around 30 % could be attained through the reaction with an integrated recycle stream. The reactor is followed by two flashes. The first flash serves to separate the stream to be recycled. **94 %** of the stream is being recycled back to the reactor.

The second flash separates the remaining impurities to gain better purification at the end. The distillation column does not require a purity of **99.9 %** for *dimethyl-ether (DME)* synthesis. The separation within the column should focus on reducing all the unused/inert gas to almost none. This results in a separation where the liquid phase is composed of *80 % methanol and 20 % of water*. This eases up the energy consumption within the whole process because separation processes are known to require a lot of heat either through the reboiler- or the condenser duty to reach a higher purity.

Combined Heat and Power Plant (CHP) Integration

Off-gas is removed through the purge stream, the second flash, and from the distillation column. The off-gas stream is heated to around 650 degrees Celsius before it is then flamed together within the combustion chamber/reactor with 1000 tons/hour of air intake, where the heat required is integrated through the cooling off of the cooling water. The flaming results in no trace of toxic gas such as methane (CH_4), methanol (CH_3OH), and carbon monoxide (CO) in the output stream. The combustion was modeled with an adiabatic reactor. Cooling the stream would require a huge amount of cooling fluids and thus increase the amount of utility cost at the end.

The idea is to integrate a **Rankine cycle** for **combined heat and power plant (CHP)**. Within the cycle, water will primarily be used to cool off the flamed output stream to around 85 degrees Celsius which is then disposed into the atmosphere. Through a recuperation unit, which consists of a heat exchanger, pressurized water is then heated up to 1124 degrees Celsius with a pressure of 170 bar. A turbine is then modeled to replace a generator. The hot steam from the recuperation unit is then decompressed through the turbine to produce **257 MW (925 MWh)** of power. The decompressed steam needs to be cooled off through a heat exchanger to achieve the input stream conditions. A fraction of heat is integrated into the heat exchanger in the *dimethyl-ether (DME)* process, and the excess heat would then serve to provide heat for district heating. This concept of the cogeneration process would then increase the efficiency of the Rankine cycle by utilizing the heat and decreasing the amount of cooling fluid required to cool off the stream. Thermal energy storage could also be considered to store up the excess heat, which then could be used to generate electricity and provide heating utilities when needed.

3.3 DME Synthesis from Methanol

General layout

The primary design challenge for the DME plant was to achieve a cost-effective production of very-high purity DME. Comparing the sale prices of the product DME and the reactant Methanol, which are **390 USD/Ton** and **400 USD/Ton** respectively [1],reveals a narrow margin of just **10 USD/Ton** for this part of our plant. Therefore, minimizing utility and capital costs is crucial to break even. Furthermore we need a very high purity of our final product, DME, of 99.95%. This can only be achieved by cryogenic distillation in a separation column. Additionally, as a majority of compounds in our system are toxic, it is essential to ensure that the waste water produced complies with health and safety regulations and can be safely disposed of or reused elsewhere within the plant.

Given the significant difference in boiling points among the compounds leaving the reactor, gas-liquid separation can be utilized for efficient separation. Moreover, separation of gaseous DME, along with minor trace gases, from the liquid phase, containing water and methanol, can be conducted using a flash as the initial step. Yet, the concentrations of trace gases, such as hydrogen and methane, in our system are negligible and can be disregarded for design considerations. A Sensitivity analysis has concluded that a temperature of $60\,^{\circ}$C is optimal for achieving a high DME concentration in the top stream and a low concentration in the bottom stream, while maintaining a well-distributed flow to both streams. Subsequently, column separation can be employed to obtain high purity products: DME in separation column 1 and Water in separation column 2. This approach reduces flow rates to each column and minimizes the reboiler duty required for high concentration component separation.

Design considerations for the reactor (REACTOR)

Given the excess heat produced by other processes in the plant, the primary limitation lies in cooling the reactor's outlet stream. Lowering the reactor temperature reduces reactant conversion to DME, but it also decreases the cooling and heating demand, likewise simplifying the heat integration. However, reduced conversion also poses chal-

lenges in the subsequent separation process and results in a higher reflux stream flow. A sensitivity analysis and optimization of the reactor's operating conditions, in relation to temperature and pressure, has shown the implemented parameters to be ideal for the reactor in the chosen setup.

Design considerations for separation column one (DIST1)

he objective for the second separation column is separate DME from water and methanol, that are still present in the stream after separation using the flash. The design target is to achieve a minimum DME purity of 99.95%. Since DME has a higher boiling point than some of the other gases, like hydrogen, introduced by the Methanol and Syngas production plants, it is crucial to remove them before entering the DME plant. The bottom stream, containing mostly methanol and water, is subsequently fed back in to the system. The column's operation parameters were also derived by conducting optimisation of the DME concentration and Flow.

Design considerations for separation column two (DIST2)

The objective for the second separation column is to separate Water from Methanol and DME. Since the inflow stream into the DME plant already contains a relatively high water content (around 20%), the reduction of efficiency will not be significant as long as the methanol concentration is close to that of the inflow stream, and the reflux stream is not too large. Our primary constraint, therefore, lies in the properties of the bottom purge stream. Both DME and Methanol are hazardous chemicals[2][3]. Therefore it is essential to minimize the concentration of these compounds in the purge stream to protect the environment, wildlife, and facilitate easier disposal. However it is worth to mentioning, that methanol is easily biodegraded by microorganisms. It has a half life in surface water of 1-7 days and danger to humans and wildlife only persist at concentrations higher than 10 mg/l[4]. The parameters were again derived using sensitivity analysis and optimisation with the objective of reducing the concentration of harmful compounds while assuring a small water content in the reflux stream.

Design considerations for purge and reflux stream

To prevent wastage of unreacted reactants, we introduce a reflux stream that combines with the reactor's input stream and is recycled back into the reactor. One important consideration is the magnitude of the reflux stream. A reflux stream that is too large or poorly designed, with a high input-to-reflux ratio, causes instability in the system. This is due to the side effect of the reflux stream serving as an error amplificator. Because of this minor changes in operating conditions like pressure, temperature or stream compositions can drastically affect the system, potentially leading to plant failure. Therefore, safety precautions are crucial to prevent an excessively large reflux stream. In our case, we have implemented a venting system to handle the high methanol content in the purge stream. In the event of a sudden pressure rise, this system allows us to flare off or externally store the excess reflux flow, ensuring no harm to the environment or the plant.

Design considerations for heat integration

In the DME plant, the reactor stands out as the main energy consumer, drawing 161.44 MW for heating and -129.48 MW for cooling. Compared to the second most expensive operation, separation column 2. Which only draws 51.76 MW and -49.41 MW for heating and cooling respectively. However, the reactor's high energy demand is primarily driven by its substantial flow rate, rather extreme temperatures. Achieving the necessary temperatures for the incoming and outgoing flows of the reactor, $174\,^{\circ}$C and $60\,^{\circ}$C respectively, can be achieved relatively easy by exchanging heat with other parts of the plant. Cooling of the reactor's outlet stream can be accomplished by transferring heat to the reactor's inflow. However, since the flash operates at a higher temperature than the system's inflow temperature ($44\,^{\circ}$C), the heat transfer between the incoming and outgoing flows is insufficient. To address this, a heat exchanger is used along with hot steam produced by the Rankine cycle. For heat integration of the separation columns, heat can be supplied by burning natural gas. The second columns condenser operates at $16\,^{\circ}$C, therefore it can be cooled using chilled water. However, achieving the required purity of DME, of 99.95% in column 1 requires its condenser to operate at $-25\,^{\circ}$C, necessitating cryogenic cooling.

4 Major Results

This chapter will delineate the principal outcomes of this work, divided into two core sections: stream-related results and economic results.

4.1 Stream-related results

Syngas Synthesis

The output stream from this process is syngas, with a mass flow rate of 12000 tons per day. The composition of the syngas is depicted in terms of mass fraction, as presented in the subsequent table. This syngas fulfill both stoichiometric number and carbon oxide ratio criteria.

H_2	0.114	CO	0.347	N_2	0.007
CO_2	0.452	CH_4	0.073	H_2O	0.006

Tabelle 4.1: The mass fraction of the syngas

Methanol Synthesis

The output stream generated from this stage is a mixture of methanol and water, which serves as the feed stream for the dimethyl ether (DME) synthesis phase. This stream exhibits a mass flow rate of 7739.08 tons per day. The composition of the stream, when expressed in terms of mass fraction, features a distribution of 0.805 for methanol and 0.195 for water.

Dimethyl ether(DME) Synthesis

Dimethyl ether (DME) is the ultimate product of this comprehensive process. Characterized by an exceptionally high purity level, the mass fraction of DME stands at 0.9999. The output stream exhibits a mass flow rate of 4474.03 tons per day.

4.2 Economic results

The capital expenditure required for the establishment and operation of this process amounts to **114,399,847.8 euros**. The pertinent details regarding the utilities used in this process are subsequently elaborated upon. The total utility cost per year is **85,316,384.3 euros**.

Name	Value	Unit
Total heating duty	89810024.4	cal/sec
Total cooling duty	324488355	cal/sec
Net duty (Total heating duty - Total cooling duty)	-234678330	cal/sec
Total heating cost flow	8460.37372	USD/hr
Total cooling cost flow	2361.08544	USD/hr
Net cost (Total heating cost + Total cooling cost)	10821.4592	USD/hr
Net cost flow of feeds	185247815.8	USD/year
Net cost flow of products	653621342.6	USD/year
Overall net cost flow	468373526.7	USD/year

Tabelle 4.2: Specific terms in utility

The revenue derived from the products of this process amounts to approximately 636,808,419 euros annually. When balanced against the raw material expenditure, which stands at 503,774,022 euros per annum, and factoring in the utility costs, the resulting net return is calculated to be approximately **47,718,012.7 euros** each year.

The comprehensive investment required for this operation stands at 228,799,695.6 euros, with annual depreciation accounting for approximately 5,719,992.39 euros. Given an estimated plant lifespan of 20 years, the investment ratio evaluates to 0.1836. The pay out time is **4.795 years**.

Within the entire operation, numerous pieces of equipment, such as compressors, necessitate electricity for their functionality. Alongside this, a strategic approach has

been implemented to augment the economic efficacy of the process by exploiting high-temperature exhaust for electricity generation, facilitated by the use of a turbine. This tactic is primarily designed to improve the process's financial viability and yield profitable outcomes.

The process requires a total of 106.68 MW of electricity, while generating a substantial 829.84 MW in return. This results in a surplus of 723.16 MW of electricity. Should this excess power be sold at 90% of the market price, it could potentially generate additional revenue of approximately 285,068,651 euros annually. Consequently, this substantial additional income stream dramatically reduces the payback period for the investment to just under 0.688 years, significantly enhancing the economic viability and appeal of the project.

5 Conclusion

The techno-economic analysis showed that producing dimethyl-ether (DME) from syngas is feasible and viable. The whole process integrates the **Rankine cycle** as a **combined heat and power plant (CHP)**, which uses the excess energy in the form of heat and power to be integrated into other operating units or as a source for heating and power utilities for the surrounding district. It is shown that the power generated by the turbine, which acts as a generator within the Rankine cycle, reduced the total utility cost of the whole process. A portion of the power will be used to supply compressors with the required power. The remaining power could then be used to supply district electricity. However, the process designed is far from optimized. A possible task, as an extension to this project, would be to optimize the energy integration and usage within the production. This would then lead to a **MINLP** optimization problem. The process within this project is designed through hierarchical methods. Another possibility is to redesign the whole process synthesis using superstructure optimization. This however would be computationally expensive, but an optimized flowsheet could be attained.

From the analysis, the following conclusions can be drawn and open questions as possible project extensions raised:

- Designing gasification and pyrolysis of biomass for synthesis gas production
- **Power- to - X**: methanol synthesis through green hydrogen and direct air carbon capture (DACC) or carbon storage
- Techno-economic analysis and product assessment of *methanol synthesis* in compared to products produced by *Fischer-Tropsch process*
- **Life-cycle assessment (LCA)** of dimethyl-ether (DME) production

Abbreviations and symbols

Abkürzungsverzeichnis

CHP	Combine Heat and Power Plant
DACC	Direct Air Carbon Capture
DME	Dimethyl-Ether
LCA	Life-Cycle Assessment
MINLP	Mixed- Integer Nonlinear Program
Syngas	Synthesis Gas

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