Green production of dimethyl ether (DME) - indirect conversion of synthesis gas produced from biomass

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Abstract

In the transition to a fossil-free transport sector, the use of Dimethyl ether (DME) can be an environmentally friendly alternative. DME is a synthetically produced alternative to fuels like diesel or liquified petroleum gas (LPG), and has lower emissions of CO_2, NO_x and particles compared with diesel. To be a green renewable alternative, DME needs to be produced from carbon neutral resources such as biomass. DME can be produced from synthesis gas produced by gasification of biomass. The synthesis gas can be used to produce either DME directly in a single stage process with a bi-functional catalyst, or in a twostep process in which methanol is produced in the first step and converted to DME via dehydration in the second step. In this study process simulations of the DME synthesis from methanol is assessed. The paper involves assessment of process parameters and energy improvement of the DME synthesis. The study evaluates the effects of different thermodynamic models like PRSV, NRTL, WILSON and UNIQUAC in Aspen Hysys. Conversion reactor and Gibbs reactor configurations, and sensitive analysis of process parameters is studied. Heat integration is evaluated for energy resource management and cost estimation. The Gibbs reactor with the UNIQUAC model and internal heat integration resulted in an increase in DME production of 0.5% and a reduction in energy demand of 46%.

1. Introduction

The world's energy consumption is on the rise, and as greenhouse gas emissions continue to increase, a complete shift from fossil fuels to renewable energy sources has become imperative. The transport sector accounts for 15% of direct global greenhouse gas emissions (Energi og Klima 2023). The use of dimethyl ether (DME) can be an environmentally friendly alternative for the transition to a fossil-free transport sector, if DME is produced from carbon-neutral resources such as biomass. DME and diesel are fuels that can be used in the transport sector for the same purposes. DME offers some advantages over diesel, such as a higher cetane number which gives lower emissions, better cold start and lower consumption than a fuel with a lower cetane number. DME also produces lower emissions of particles, NOx, hydrocarbons, and carbon monoxide (CO) compared to diesel. However, the disadvantages of DME are lower density and viscosity which requires adaptations in the injection system (Salomonsson 2023). The volumetric energy density of DME and diesel are 21 MJ/dm^3 and 36,6 MJ/dm^3 respectively, indicating for every liter of diesel burned in an internal combustion engine there is a need of 1.74 liters of DME to achieve the same energy output.

Biomass can be used to produce energy-rich synthesis gas through a thermochemical process called gasification. The composition of the generated gas varies based on the type of biomass utilized, primarily comprising CO, H_2, CO_2, CH_4, and N_2. A pure synthesis gas predominantly comprises H_2 and CO, serving as essential building blocks for the production of biofuels or chemicals. Some examples of chemical products are ammonia, synthetic petrol and diesel, acetic acid, plastic raw materials, methanol and DME (Evans G 2012). The process of biomass gasification not only aids in waste reduction but also enables the productive utilization of materials like agricultural and forest residues.

The synthesis gas can be converted to DME in two ways; direct conversion (one-step process) or indirect conversion (two-step process), as shown in Figure 1. (U.S. Department of Energy 2023).
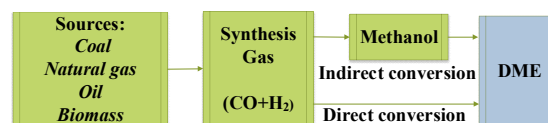

Figure 1: Dimethyl ether production diagram (Azizi Z. 2014).

The indirect conversion is a twostep process; first, methanol is made from synthesis gas in a reactor with a metallic catalyst. The methanol is dehydrated to DME in the next reactor with an acidic catalyst. In the direct conversion, DME is made in one step; the synthesis gas reacts directly to DME in a reactor with a dual catalyst system that combines the two reactions. This method has the advantage of avoiding the accumulation of methanol as an intermediate, thus increasing the yield of DME (Azizi Z. 2014). Both processes are mildly exothermic as shown in Table 1 (Guffanti S. 2021), thus it is important to control the temperature in the reactors to avoid the equilibrium reactions being reversed. (Polsen C. 2020) (Pagán-Torres Y. J. 2017). DME produced via methanol dehydration over acid catalysts such as γ-Al2O3, takes place at temperatures above 240 °C and pressures above 10 bar (Peinado C. 2020).

The reactions taking place in direct and indirect conversion is described in Table 1, where the last reaction is the main reaction taking place in the conversion of methanol to DME and water.

Table 1: Reactions and enthalpy change for the direct and indirect process (Guffanti S. 2021).

Reactions	$\Delta H°298K$ [kJ/mol]
$CO + 2H_2 \leftrightarrows CH_3OH$	-90.4
$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$	-49.4
$CO + H_2O \leftrightarrows CO_2 + H_2$	-41.1
$2CH_3OH \leftrightarrows (CH_3)_2O + H_2O$	-23.0

In this paper the focus is on the second step in the indirect conversion process which methanol is dehydrated to DME. It is assumed that methanol is available as a feed stream and that the first step, the methanol synthesis from syngas, has already been performed (Fossen M. 2022). Thus, only the reaction of methanol in a reactor to produce DME and water is simulated. Aspen Hysys simulations is used to study the process.

The objective of this research work is to assess process design, process parameter study and energy integration, as well as cost estimation of the DME synthesis.

2. Methodology

Figure 2 shows the process flow diagram for the DME synthesis simulated in Aspen Hysys (Turton R. 2018) (Larsen S. 2023).

Pure methanol (stream 1) is mixed with recycled reactant stream (stream 13) and evaporated in the heater E-201 before being fed to the reactor R-201. The reactor is set to operate at a temperature of 250 °C and 14,7 bar. The effluent from the reactor (stream 6) is cooled by the cooler E-203 before entering the first distillation column T-201 at 89°C and 10,4 bar. In this column the DME is the distillate and final product, and methanol and water are the bottom product. The methanol mixture is then cooled down in the cooler E-205, before it enters the second distillation column T-202, where the water is separated from methanol as the bottom product and is sent to wastewater treatment to remove traces of organics. Unreacted methanol in the distillate is recycled and combined with pure methanol in the mixer M-201. The purity of the DME in the first distillation column is set to 99.5%. The component recovery of methanol was set to 95% in the second distillation column. Simulated with the thermodynamic model PRSV (Peng-Robinson-Stryjek-Vera), this model is referred to as the base case.

2.1 Process parameter study

The main reaction of methanol to DME and water is an exothermic reaction. Increasing the temperature for this reaction the system will consume some of the heat by shifting the equilibrium to the left as described by the Le Chatelier's principle. This will lead to a reduction of the DME concentrations when the temperature increases. Since the main reaction has the same number of molecules on both sides of the equilibrium, the pressure has no or little effect on the composition of DME.

2.2. Thermodynamic models

Four thermodynamic models were studied in this work, all of them relevant for the synthesis of DME. These are PRSV, UNIQUAC, NRTL and Wilson. The thermodynamic models calculate physical and transport properties, as well as phase behavior for the simulated processes. These are the models recommended from Aspen Hysys for these types of polar mixtures. AspenTech (Aspen Technology, Inc 2020) describes the thermodynamic models as follow:

PRSV (Peng-Robinson-Stryjek-Vera) considers moderate deviations from ideality in gas and non-ideal liquid phases. This model is well suited for aqueous solutions containing water, methanol, or glycols.

UNIQUAC (Universal Quasi Chemical) is a model that describes the liquid structure using activity.
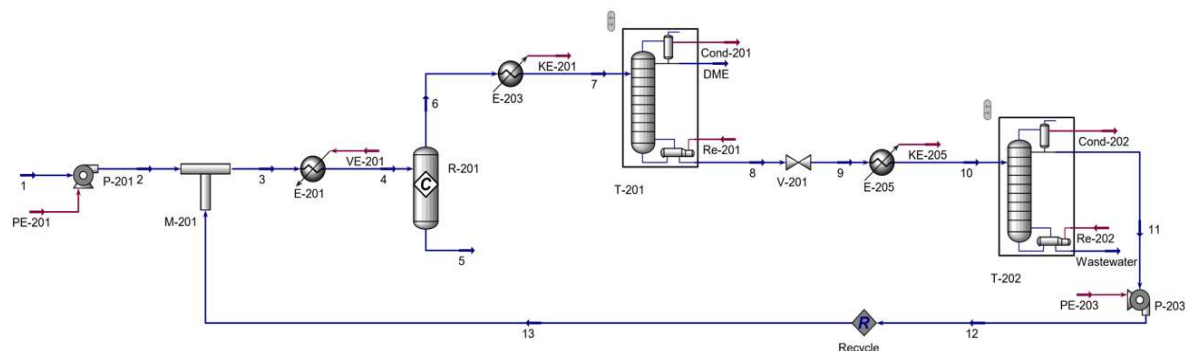
Figure 2: Process flow diagram for the base case of the synthesis of dimethyl ether (DME) in Aspen Hysys (Larsen S. 2023).
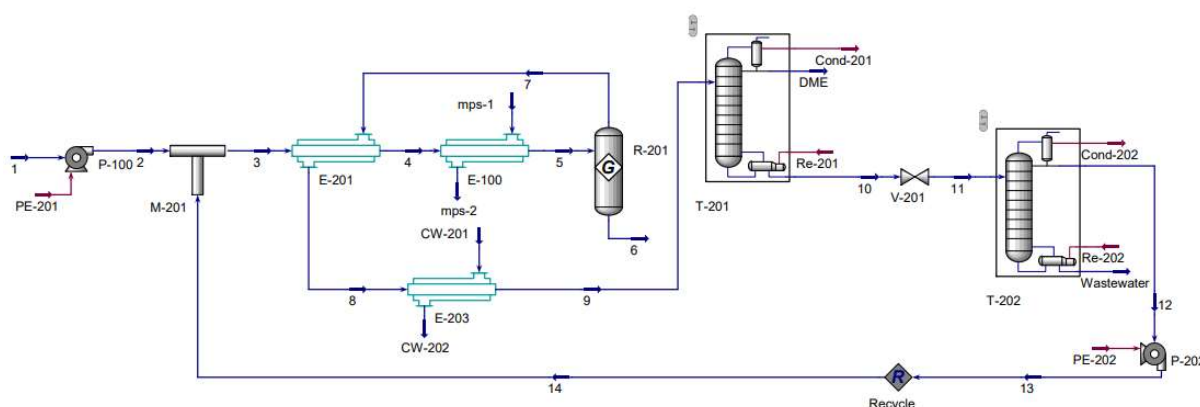

Figure 3: Process flow diagram with improved energy integration of the synthesis of dimethyl ether (DME) in Aspen Hysys (Larsen S. 2023).

These activity coefficients are factors that can account for deviations from ideality in the liquid phase at low to moderate pressures.

NRTL (Non-Random-Two-Liquid) also uses activity coefficients to represent non-ideality in the liquid phase. It can also handle electrolytes and gases with pressures above 10 bar. NRTL can calculate properties for pure components such as methanol, water and DME.

Wilson is also using activation coefficients, but with a simpler form than UNIQUAC and NRTL. It cannot be used for systems with two liquid phases.

2.2 Reactor design

Equilibrium reactions in Aspen Hysys should be performed in conversion reactors, or in Gibbs reactors. A conversion reactor is a simple type of reactor in Aspen Hysys where the conversion proportion is specified. This reactor needs a reaction kit that contains conversion reactions and operates on a stoichiometric basis. The reaction stops when the specified conversion is achieved. The advantage of this reactor is that it can integrate several different reactions in the same unit. This can be useful in extremely complex reactor designs (Hafiza Shukor P. 2023).

The reactions in a Gibbs reactor determines the effluent composition by achieving phase and chemical equilibrium. This reactor does not need to use reaction stoichiometry but calculates the product mix by minimizing the Gibbs free energy of the system. In the Gibbs reactor, we assume that neither pure substances nor the reaction mixture is ideal. An advantage of this reactor is that it can act as a separator, an equilibrium reactor, or a reactor that minimizes Gibbs free energy without specifying any reactions. The Gibbs reactor can be useful for simulating the equilibrium state or when reaction kinetics are lacking. It is also easier to converge than an equilibrium reactor with reactions when the simulation is sensitive to the input parameters (Hafiza Shukor P. 2023).

2.3 Energy integration

For energy improvement, the thermodynamic model that gave the highest DME mass production was used. However, in practical scenarios, it is crucial to validate the choice of a thermodynamic model by comparing it with experimental data. This validation process ensures that the selected model accurately represents the real-world situation.

A heat exchanger E-302, given in Figure 3, replaced the heater E-201 in Figure 2. The reaction in the reactor R-301 was exothermic, heat was generated and released. This means that the outlet flow from the reactor was hotter than the inlet flow. This heat

flow was used on the shell side of the heat exchanger E-301 in Figure 3 so the heat exchanger E-302 had a reduced energy requirement. The cooler E-203 was replaced with a heat exchanger E-303 which used cooling water to lower the temperature further before the stream enters the distillation column T-301. The second cooler E-205 was removed completely without replacement, because the temperature had been lowered by changing the operating parameters earlier, thus no need of cooling was necessary. The changes for energy improvement and operating parameters are referred to as the energy integrated case.

2.4 Cost estimation
Cost estimation was done for both investment cost (CAPEX) and operating cost (OPEX).
Calculation of investment costs was performed using Equation 1, where the CAPEX represents the investment costs. ΣC_{BM} is the sum of the purchase cost and installation cost for all appliances and equipment in the DME synthesis.

$$CAPEX = 1,18 * \Sigma C_{BM} \quad (1)$$

OPEX consists of three categories: direct production costs (DMC), fixed production costs (FMC), and general production costs (GE). To calculate the electricity cost, an average price of 0.192 USD/kWh for global businesses in 2022 was used (GlobalPetrolPrices.com 2022). For calculating the cooling water cost, a price of 0.0157 USD/m^3 in the year 2001 (Turton R. 2018) was used. To calculate the steam cost, prices from (Turton R. 2018) were used, with a medium steam pressure price of 0.00961 USD/m^3 and a high steam pressure price of 0.00954 USD/m^3. To calculate the raw material cost, a price of 1.49 USD/US gallon for methanol was used (Seaberg 2018).
The calculation of operating expenses (OPEX and COM_d) excluding depreciation was performed using Equation 2, where FCI represents the investment cost, C_{OL} denotes operating labor cost, C_{UT} signifies the cost of utilities, C_{WT} represents the cost of wastewater management, and C_{RM} represents the cost of raw materials.

$$OPEX = COM_d = 0.180*FCI + 2.73*C_{OL} + 1.23*(C_{UT} + C_{WT} + C_{RM}) \quad (2)$$

For the calculation of DME income (R), an average price (P) for DME in 2018 of 2.26 USD/US gallon was used (Seaberg 2018). This price is competitive with diesel considering the ratio between them of 1.74. The formulas and data for the cost estimation of CAPEX and OPEX are given in (Turton R. 2018). The cost was estimated for the base case, for the process parameter study, and the energy integrated process.

To calculate the net present value (NPV), a cumulative discounted cash flow was computed throughout the construction and operational phases of the DME synthesis. NPV is a measure of the project's profitability based on the present value of all incomes and expenses associated with the project. The cumulative discounted cash flow is the sum of all future cash flows (incomes - expenses) generated and accumulated, adjusted back to year zero.

3. Results

3.1 Process parameter study
In Figure 4, the production of DME was studied as a function of temperature and pressure. The mole fraction of DME in the outlet flow of the reactor as a function of temperature was studied in the temperature range 200-370°C at 14.7 bar pressure. While the mole fraction as a function of pressure were studied at 250°C in the pressure range 5-30 bar. The simulations were performed with the thermodynamic model PRSV.
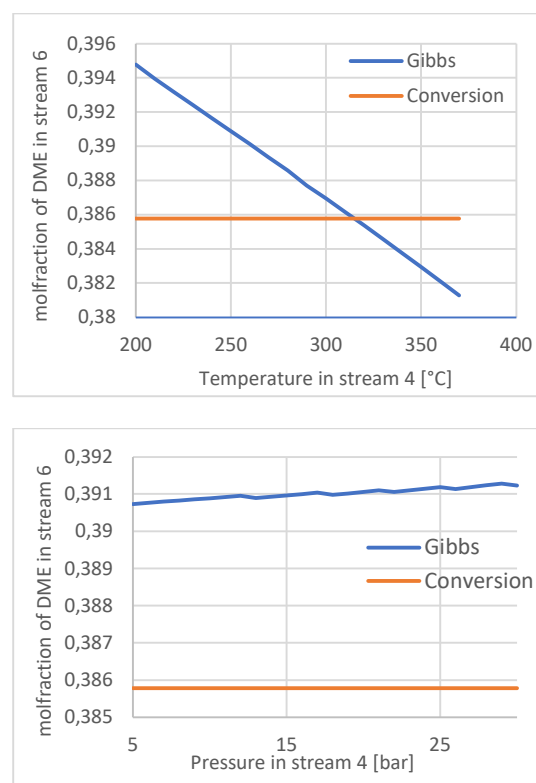

Figure 4: Mole fraction in stream 6, outlet flow of the reactor, as function of temperature and pressure, for the conversion and Gibbs reactor design.

The reaction efficiency in the conversion reactor was defined to be constant to 80%. Changing the pressure and temperature in stream 4, the inlet stream to the reactor, did not lead to a change in the DME stream mole fraction, which is reasonable as the conversion efficiency calculation was both

temperature and pressure independent. Therefore, this reactor was not assessed further.

For the Gibbs reactor, the DME mole fraction in the outlet decreases with higher temperature in the inlet. The chemical reaction is exothermic and will occur spontaneously. This results in a negative value of the Gibbs free energy and a negative enthalpy change. The reaction will be reserved to stop the temperature increase resulting in a lower DME production. An increase in pressure favors the production rate, because the first 2 reactions in Table 1 contributes to larger methanol production. However, the changes in the tested pressure range are minimal.

The Gibbs reactor at 200°C and 17 bar was tested to confirm the impact of lower temperature and increased pressure on energy improvement and increased DME production. Table 2 shows the changes in energy consumption as a result of parameter changes over the reactor system. A decrease in energy consumption of 6.6 % is observed.

A parameter evaluation was also performed over the first distillation column T-201. The temperature inlet of flow 7 was increased from 89°C to 135°C, the pressure remains as in base case at 10.4 bar.

Table 2: Simulation results for the Gibbs-reactor parameter adjustment with PRSV.

	Base case		Parameter change	
Flow	4	6	4	6
Temperature [°C]	250	363,9	200	318,3
Pressure [bar]	14.7	14.7	17	17
Mass flow DME [kg/h]	0	5 905	0	5 913
Energy consumption in the system[kW]	17 652		16 491	
Change in mass flow [%]			0.13	
Change in energy [%]			6.6	

Table 3: Simulation results for the parameter adjustment in the distillation column T201 with PRSV.

	Base case		Parameter change	
Flow	7	DME	7	DME
Temperature [°C]	89	45,78	135	45,78
Pressure [bar]	10.4	10.3	10	10.3
Mass flow DME [kg/h]	5 913	5 913	5 913	5 914
Energy consumption in the system[kW]	16 491		14 098	
Change in mass flow [%]	0		0.02	
Change in energy [%]			14.5	

Table 3 give the result of the simulation over the column. It is observed a reduction of energy of 14% in the system using an increased temperature into the

column because of reduction in cooling water. A total energy reduction of 20% are observed because of parameter adjustments.

3.2. Thermodynamic models
Based on Gibbs reactor, different thermodynamic models was simulated for comparison. Figure 5 shows an overview of the change in energy and the outlet flow of DME for the four thermodynamic models compared to the base case. The UNIQUAC model gave the lowest energy consumption before energy integration. For the mass flow an increase of 0.5% for the UNIQUAC model is observed compared to the base case.

The UNIQUAC model is well suited for gases with high pressure and a known boiling point. The UNIQUAC model was also recommended by specialist literature (Turton R. 2018). In a real process, it is essential to choose the thermodynamic model that best describes the given process. This could be done by comparing experimental data or real industry data with simulation results. For this work, process data was not available to carry out validation of the simulation model.
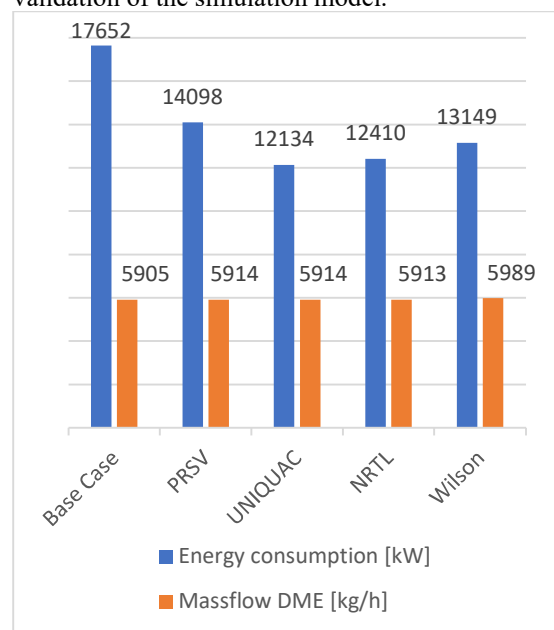

Figure 5: Comparison of energy consumption[kW] and mass flow DME [kg/h] for different thermodynamic models.

3.3 Energy integration
The UNIQUAC model has been chosen when simulating the energy integrated process. Figure 6 shows an overview and comparison between the base case, the process parameter study, and the energy integrated process. For the process parameter study the pressure and temperature are changed to 17 bar and 200°C in the reactor, and UNIQUAC is used as the thermodynamic model. For the energy integrated process two heat exchangers are inserted,

one was inserted with internal heat integration to reduce energy consumption in the heater. The second heat exchanger used external heat transfer in the form of cooling water as a replacement for two coolers. An energy reduction of 46% is observed from the base case to the energy integrated case.
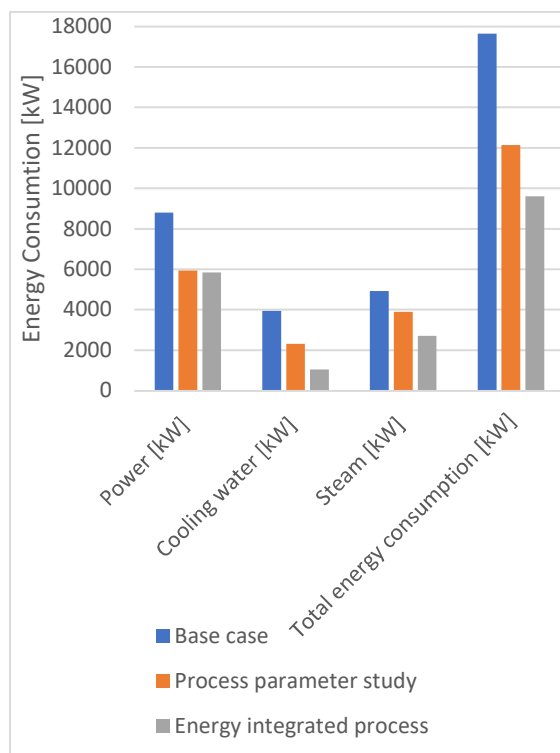

Figure 6: Comparison of energy consumption between base case, process parameter study and energy integrated process.

3.4 Cost estimation
By reducing the energy requirement, the OPEX for the energy was reduced. However, as pressure and temperature were not changed much compared to the base case, CAPEX for the equipment was approximately the same. The total OPEX was reduced with -11%, while the CAPEX was reduced with -4% compared to the base case. The project estimated the CAPEX to approximately $1.8 million, and the OPEX of approximately $58.6 million, and a revenue of approximately $54.3 million.

For the utilities, the costs of electrical energy, cooling water and steam were reduced from the base case, as shown in Table 4, by 34%, 74% and 49% respectively. This is due to lower temperature and higher pressure, which led to a lower need for energy in pumps, evaporators, and condensers altogether. It is also due to the internal heat integration that utilized the heat from the reactor to heat the inlet stream. This led to less need for steam, which also required lower pressure and thus a lower price. An increased temperature before the first distillation

column T-301, led to less need for cooling and removal of the second cooler E-205. This resulted in less need for cooling water. Total savings for utilities were 35% compared to the base case.

The pressure of the reactor was earlier set to 17 bar to examine the impact of the pressure on DME production and cost estimation. Because of small impact on DME production and cost savings, the pressure in the reactor was reduced to 10 bar. This pressure reduction reduced the cash flow with only 0.02 % or approximately 11 000 USD/year. This shows that reduction in the reactor feed pressure has insignificant impact on the cost estimation, but it is overall beneficial for safety issues.

Table 4: Overview of savings in utility cost per year and percentage for changes from the base case to the energy-integrated process.

	Change [USD/year]	Change [%]
Electrical energy	-5 000 000	-34
Cooling water	-48 000	-74
Steam	-850 000	-49
Totalt	-5 900 000	-35

During the evaluation of the net present value (NPV) reaching zero in year 25 at a discount rate of 10%, it was determined that the DME price needed to be 2.46 USD/US gallon in order to achieve the breakeven point.

4. Summary and Discussions
This paper used Aspen Hysys simulations to describe the production of green DME from indirect conversion of synthesis gas from biomass. The main aim was to evaluate process design, process parameter study and energy improvement, as well as cost estimation of the DME synthesis. The aim was to find a process with improved DME yield and energy requirement with minimal adjustments to operating parameters.

The process has been simulated and improved using various operating parameters, reactor design and thermodynamic models. The final process configuration was found to be a Gibbs reactor with the UNIQUAC model and internal heat integration. This process resulted in an increase in the DME production of 0.5% and a reduction in energy demand of 46%. The cost estimate showed that the project was not profitable with the given prices for methanol and DME of 1.49 and 2.26 USD/US gallon respectively. The price for DME had to be at least 2.46 USD/US gallon to get a positive NPV within 25 years. By setting the price at 2.50 USD/US gallon the repayment period will be approx. 6.5 years. The price of DME (Dimethyl Ether) and Methanol is indeed crucial for profitability. The choice of a discount rate of 10% also significantly impacts the

result, as operating expenses (OPEX) are much larger compared to capital expenses (CAPEX). Additionally, utility costs are also significant, and there is potential for improvement in terms of heat integration. The price of electricity, fixed at 0.19USD/kWh, will also have a considerable impact on the result.

Based on the findings, it was concluded that production of green DME from synthesis gas is technically and economically feasible.

It is also concluded that DME is an attractive fuel for the heavy transport sector and municipalities. Further research into parameter changes and energy integration is necessary to optimize the process profitability.

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