Aspen Hysys simulation of the methanol synthesis based on gas from biomass gasification

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Abstract

From the gasification of biomass, the produced gas mainly consists of CO, H_2, CO_2, and CH_4. After gas cleaning and conditioning, the syngas obtained can be used to produce methanol, dimethyl ether, polymers, biofuels, etc. Methanol is one of the important industrial chemicals that can be used directly as a fuel or can be blended into conventional fuels. Methanol produced from renewable biomass sources can limit greenhouse gas emissions. Based on data on gas composition from experiments and simulations of the fluidized bed gasification reactor at the University of South-Eastern Norway, the methanol process is simulated with Aspen Hysys. It is desirable to assess how different process parameters affect the yield of methanol production. A Gibbs reactor was modeled with three gas-phase exothermic reactions. The product from the reactor is depressurized to separate gas from the liquid. The liquid enters the distillation column to give CH_3OH in the distillate and the water as the bottom product. The yield of methanol is evaluated with regard to pressure, temperature, and H_2/CO ratio. The theoretical H_2/CO ratio for the methanol synthesis should be approximately between 1,5-2. However, different gas compositions were obtained from different types of fluidizing agents in the gasification reactor, and a low ratio of H_2/CO gives a low yield of methanol. Fluidized bed gasification with steam as gasifying agent is preferable to increase the H_2/CO ratio and give a higher methanol yield.

Keywords: Methanol, Aspen Hysys, Gasification, Biomass

1. Introduction

According to the report, Methanol Market - Growth, Trends, and Forecast (2021-2026), the market share for methanol in 2020 was 83.8 million tons, and it is predicted that from 2021 to 2026 the market would experience an average annual growth of around 5% (Research and Markets, 2018). All large-scale methanol plants currently use steam-reformed natural gas and pure oxygen as raw materials in the process. Research to improve current production methods to reduce the climate footprint is constantly evaluated. At the same time, new studies are constantly being evaluated on whether methanol can be produced from other sources, such as using synthesis gas from biomass gasification, to produce green methanol.

Gasification of biomass is a thermochemical conversion process where the chemical bonds are broken due to high temperature and partial oxidation with air or steam as the oxidizing agent. The product gas from the gasification reactor consists of CH_4, CO, CO_2, and H_2, as well as other light gases such as ethane (C_2H_6) and propane (C_3H_8) in addition to various condensable gases. The gas will also contain some nitrogen (N_2). The proportion of N_2 will vary based on the type of fluidizing agent used. When using air, the nitrogen content will be relatively high, while when using pure oxygen or steam, the proportion will be significantly lower. The product gas will also have proportions of sulfuric compounds, chlorine, heavy metals, and other trace elements from the biomass (Bandara, 2021).

The composition of feed gas used in methanol synthesis has changed in recent years. Earlier, only H_2 /CO was used, as the producers were convinced that the process was re-hydrogenation of CO and therefore removed all CO_2 from the gas with absorption. However, Waugh (Waugh, 2012) found that after running parallel experiments with H_2/CO_2/CO and H_2/CO, it was discovered that H_2/CO_2/CO produced methanol faster than H_2/CO. Tests were performed with a Cu/ZnO/Al_2O_3 catalyst, and it turns out that the highest production was achieved with a composition of CO/CO_2/H_2 in the ratio of 10:10:80 at a temperature of 290°C (Waugh, 2012).

In an exothermic reaction, energy is released, which results in an increase in the temperature. According to Le Chatelier's principle, the equilibrium will shift towards the reactants as energy is consumed from the reaction mixture. If the pressure in the mixture is increased, the equilibrium of the mixture will be shifted towards the product as there will be fewer molecules in the mixture (Moulijn J. A., 2013). Methanol synthesis from syngas is a low-temperature, high-pressure exothermic reaction (Yang L., 2016). The reactions and the reaction enthalpies are given in Tab. 1. Methanol is usually produced with high selectivity, although minor amounts of side products are found. The synthesis is usually conducted at 200–300 °C and 35–100 bar (Klerk, 2020). Common by-products of methanol formation are methane, methyl-formate, higher alcohols, and acetone.

Table 1: Reactions and reaction enthalpies for the methanol synthesis (Moulijn J. A., 2013)

Reactions	Reaction enthalpy (kJ/mol)
$CO + 2\ H_2 \rightleftharpoons CH_3OH$	-90.64
$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	-49.67
$CO + H_2O \rightleftharpoons CO_2 + H_2$	-41

The University of South-Eastern Norway has a pilot plant bubbling fluidized bed (BFB) gasification reactor. Fig. 1 is a sketch of the reactor. The BFB reactor with optional equipment consists of a silo tank for biomass (1), a hopper for filling bed material (2), the gasification reactor (3), feed screws for biomass, cold and hot (4 and 5), gas heater for the fluidizing agent (6), and a compressor for the fluidizing agent (7). At the bottom of the reactor, there is an outlet for solid material (8). In several places of the reactor, it is mounted connection points for pressure and temperature readings (9). The gasification reactor is operated within the temperature range of 700-1100°C, with atmospheric pressure. The temperature is achieved by the heated fluidizing agent, heat generated in exothermic reactions, and electric heating cables mounted around the reactor (Timsina, 2022). Experiments were performed using wood chips of an irregular shape and with lengths ranging from 1 to 15 mm. with air as a fluidizing agent (Timsina R., 2020). The experiment was performed at 1100 K. Computational Particle Fluid Dynamics (CPFD) modeling is applied to simulate the bubbling fluidized bed gasifier reactor aiming at finding consistency between the experimental results and the simulation results. After validating the CPFD hydrodynamic model, related to the experimental results, the model has been used to investigate the effects of temperature on the steam gasification process (Samani N.A., 2022). Based on the experimental data from the gasification pilot plant and the computational particle fluid dynamic simulations, the focus of this study is to determine the yield of methanol production based on the gas composition from the gasification of wood chips. The gas from the gasifier must be purified, cooled, and compressed before entering the methanol reactor for optimal conversion.

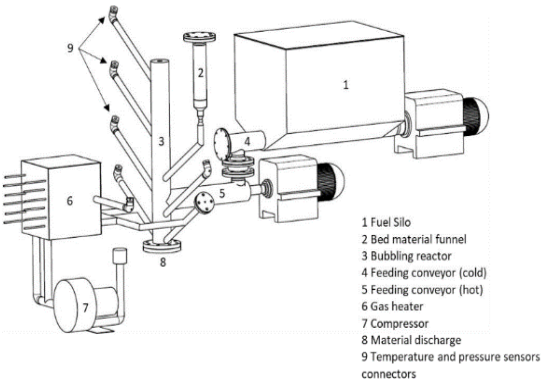

Figure 1: A schematic sketch of the bubbling fluidized bed gasifier at the University of South-Eastern Norway (Timsina, 2022)

2. Methodology

Simulations have been performed on the methanol synthesis using Aspen Hysys. The flowsheet is presented in Fig. 2. The feed consists of purified product gas from the gasification of wood chips with either air or steam as the fluidizing agent. It is also possible to supply the feed with a supplemental stream that goes inside the MIX-100 to give the possibility to adjust the feed gas ratio. Stream 1 is compressed in the K-100 and sent to the MIX-101 where stream 2 is mixed with 7_RCY which is a recycle stream. After the compression, the gas is heated or cooled before the gas enters the GBR-100, a Gibbs reactor. The gases are converted to methanol, and the reactions taking place are shown in Tab. 1. Stream 5 is cooled down in the cooler E-101, before entering V-100, a gas-liquid separator. The TEE-100 split the stream 7_gas in 7_Purge, while the stream to be recycled goes to 7_RCY and back into the MIX-101 together with the feed gas. The stream 7_Liquid is depressurized and enters the distillation column T-100 where methanol and water are separated. The remaining gases go out in the stream 8_Gas.

The Gibbs Reactor of Aspen HYSYS can work solely as a separator, a reactor that minimizes the Gibbs free energy without an attached reaction set or as a reactor using equilibrium reactions. When a reaction set is attached, the stoichiometry involved in the reactions is used in the Gibbs Reactor

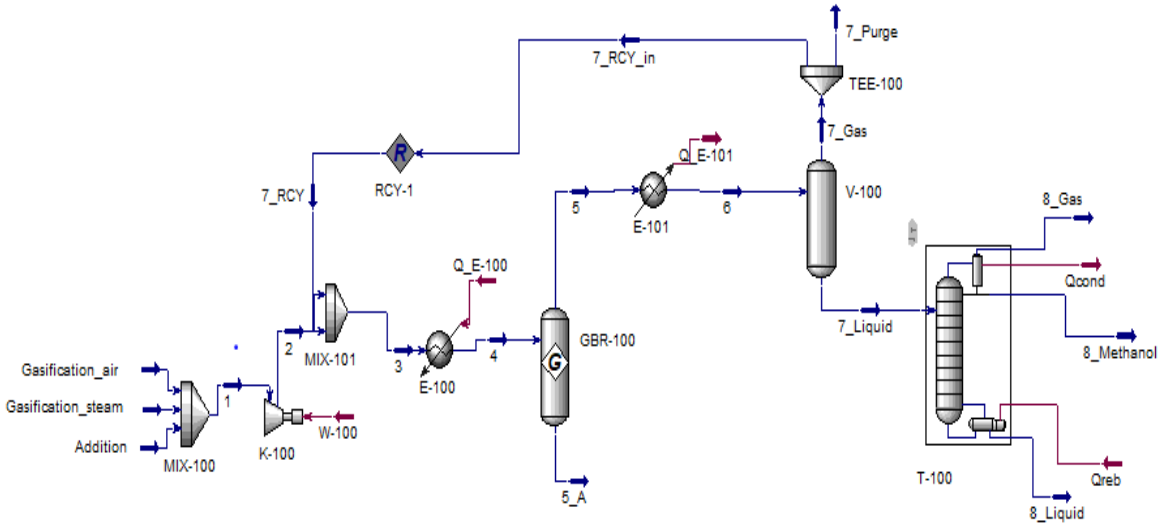

Figure 2: Process flowsheet for the Aspen Hysys Simulation (M Fossen, 2022)

calculations (Haydary, 2018). In this study, the reaction set is defined based on the stoichiometric reactions given in Tab. 1.

Most industrial methanol synthesis plants produce methanol with a purity of between 95-99.9% by weight (Equinor, 2022), (Timsina R., 2020). The requirements set for the distillation column in the simulations are 99% by weight.
Other requirements are set to obtain the lowest possible amount of methanol in the bottom product and the gas flow is the overhead in the distillate. The distillation column has been simulated with 10 stages, at a pressure of 1 bar.
Since the methanol synthesis is enhanced by low temperatures and high pressures, 200°C and 100 bar are chosen for this study. The feed is set to 200 kmole/h. The composition of the feed gas for methanol synthesis is taken from experiments and simulations done at the University of South-Eastern Norway, and the ideal ratio suggested by Waugh (Waugh, 2012) is used for comparison. The gas composition data are presented in Tab. 2. For the simulation, the gases N_2, H_2O, and CH_4 are not included. A recirculation rate of 1100 kmol/h is used in the simulation.

3. Results

The gas mixtures compositions defined in Tab. 2, are used in the simulation in Aspen Hysys. All cases have been simulated with and without recirculation. The single-pass conversion of the components is defined as (Felder R, 1986):

$$\text{Single} - \text{Pass Conversion} = \frac{\text{reactant in to reactor} - \text{reactant out from reactor}}{\text{reactant into reactor}} \quad (1)$$

Table 2: Gas composition in mol% from bubbling fluidized bed gasification of wood chips. a. composition of produced gas, b.recalculated without N_2, H_2O and CH_4

	Ideal ratio	Experimental data from gasification with air (Timsina, 2022)		CPFD Simulation data for gasification with steam (Samani N.A., 2022)	
		a.	b.	a.	b.
CO	10	22.59	42.55	49.47	54.29
CO_2	10	20.46	38.54	9.36	10.27
H_2	80	10.04	18.91	32.3	35.44
CH_4		7.5	-	8.66	-
H_2O		0	-	2.01	-
N_2		38,4	-	0	-

The result of single conversion calculations shows - that hydrogen is the limiting reactant in gas mixtures from the gasification system. In the case of the ideal ratio, CO is the limiting reactant.
The overall conversion of the process is given in Tab. 3 and defined as (Felder R, 1986):

$$\text{Overall Conversion} = \frac{\text{reactant in to process} - \text{reactant out from process}}{\text{reactant in to process}} \quad (2)$$

For all cases, the overall conversion is high, where losses are in the purge stream 7_Purge, and the stream 8_gas, overhead gas from the distillation column.

Table 3: Overall gas conversion

	Limiting component	without recycling	with recycling
Ideal ratio	CO	98.8 %	99.9%
Gasification with air	H_2	88.3%	95.9%
Gasification with steam	H_2	93.6%	98.9%

Fig. 3 shows the methanol fraction in stream 5, after the reactor, as a function of temperature. The

methanol formation is higher at low temperatures; however, a low temperature will also reduce the kinetic energy, and an elevated temperature is needed to obtain the activation energy that leads to reactions between molecules. Therefore, in this study 200°C is used in the further simulations. The formation of methanol for the gas mixture from ideal ratio and gasification with steam is approximately the same at 200°C and higher temperatures, however, at lower temperatures, a high ratio of H_2/CO gives a higher formation of methanol. Fig. 4 shows the methanol fraction in stream 5, as a function of pressure.

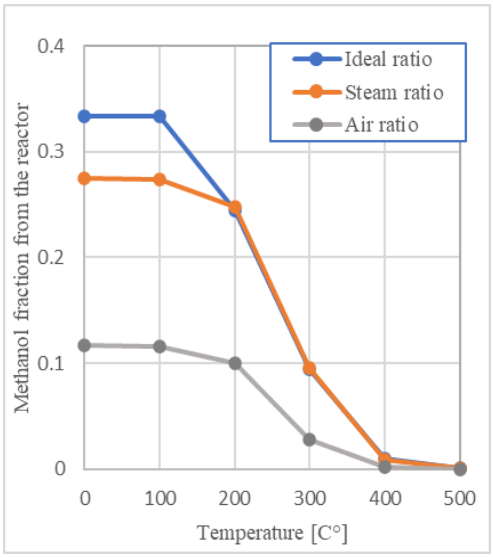

Figure 3: Mole fraction methanol from the reactor vs. temperature at 100 bar

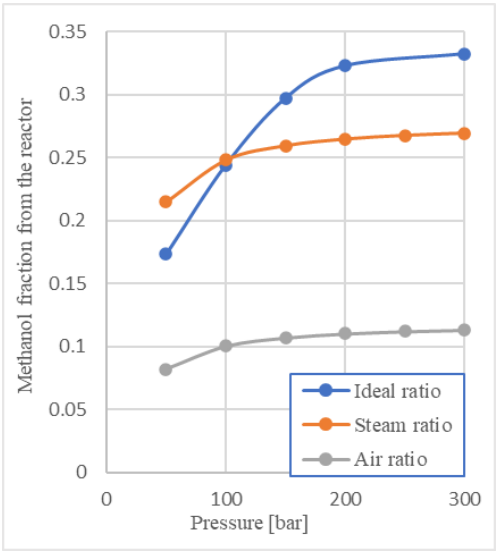

Figure 4: Mole fraction methanol from reactor vs. pressure at 200°C.

The methanol mole fraction increases with increasing pressure. However, an increase in pressure would also be considered related to the increased cost of equipment, and energy in the compressor and cooling/heating systems. A pressure of 100 bar is used in this study. At this pressure the formation of methanol for the gas mixture from ideal ratio and gasification with steam is approximately the same, however, at higher pressures, a higher ratio of H_2/CO gives a higher formation of methanol. At lower pressure, the methanol formation is lower for the ideal ratio mixture, indicating a shift in the reaction equilibriums.
The methanol yield is defined as (Felder R, 1986):

$$\textbf{Yield} = \frac{\textbf{moles of desired products}}{\textbf{mols of reactant fed}} \quad (3)$$

The results are given in Tab. 4. A higher molar yield is obtained with a higher H_2/CO ratio in the gas mixture. However, the yield is approximately the same for the ideal ratio mixture and the mixture from the gasification with steam. Recirculation in the system will also enhance a higher methanol yield.

Table 4: Methanol yield

	without recycling	with recycling
Ideal ratio	15.9%	19.2%
Gasification with air	7.6 %	8.3%
Gasification with steam	16.1%	17.1%

Table 5 gives the mass flow rates of methanol produced in the different cases simulated.

Table 5: Methanol from distillation column in kg/h

	without recycling	**with recycling**
Ideal ratio	1016.8	1230.8
Gasification with air	488.5	532.4
Gasification with steam	1030.7	1097.5

15-35% of the reactor product, on a mole basis, is sent to the distillation column when recycling is not installed. The rest is unreacted gases that can be sent out of the system or recycled. Fig. 5 shows that the molar flow of methanol is increasing when the unreacted gas is sent to recirculation. However, the increase is limited to a recycling molar flow of around 300 kmol/h. The methanol yield will be approximately the same above this recycle flow.
Fig. 6 illustrates how the mole fraction of methanol changes when extra hydrogen is added to the system. A hydrogen feed of 150 kmole/ h gives a methanol mole fraction of 0.82, for the gas mixture from the steam gasification. Also, the gas mixture from air gasification gives the highest mole fraction with an H_2 feed at 150 kmol/h. The methanol yields for these two feed mixtures are approximately 28% and

22% respectively. The H_2/CO ratio in the feed is after adding H_2 at 2,0 and 2,2 respectively.

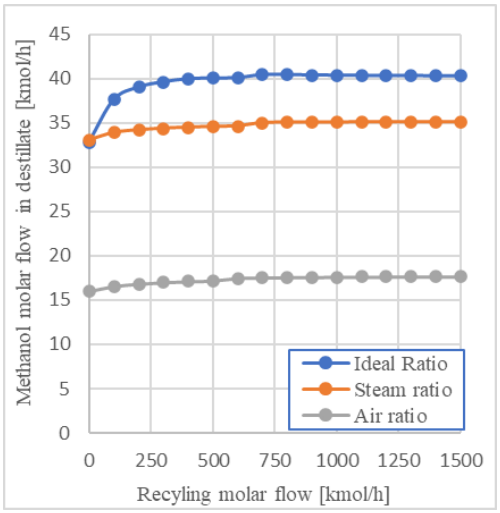

Figure 5: The molar flow of methanol in distillate vs. recycled flow.

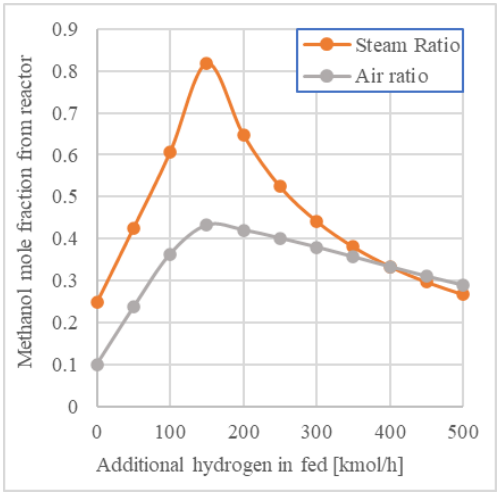

Figure 6: Mole fraction methanol from reactor vs. additional hydrogen fed to the system

4. Summary and Discussions

In this study, Aspen Hysys has been used to evaluate the conversion of gas mixtures to methanol. Gibbs rectors are based on the calculation of minimization of Gibbs free energy for the reactions and the results are based on reaction equilibrium. In a practical situation, the residence time for the reaction is short and equilibrium is not likely to occur. The results given in this study are thus an optimistic approach, and the methanol yield will be lower than estimated. Performing the simulation with a continuous stirred tank reactor (CSTR), which needs the reaction kinetics, would have given a better insight into both reaction speed, residence time, and how pressure and temperature affect the reaction. In CSTR catalytic reactions can also be studied. The results from the Gibbs reactor nevertheless give a good indication of the process parameters, and the energy needs of the process.

The methanol synthesis is enhanced by low temperature and high pressure. In this study, different gas mixtures have been evaluated regarding temperature, pressure, and H_2/CO ratio.

From the simulation of the mole fraction of methanol, the gas mixture from gasification with air as a fluidizing agent has the lowest H_2/ CO and H_2/CO_2 ratios of 0.44 and 0.49 respectively, giving the lowest methanol mole fraction from the reactor, and the lowest methanol yield. The H_2/CO ratio for the gas mixture from gasification with steam as a fluidizing agent has the H_2/CO and H_2/CO_2 ratios of 0.65 and 3.45 respectively. The H_2/CO and H_2/CO_2 ratios for the ideal mixture are both 8. The methanol mole fraction becomes the same for these two mixtures at 200°C and higher temperatures. The impact of the H_2/CO and H_2/CO_2 ratios is not significant when reaching these temperatures. For the pressure, low H_2/ CO and H_2/CO_2 ratios give low methanol mole fraction out of the reactor, however increasing the gas ratios an increase in the methanol formation and yield is observed. An interesting observation is that the gas mixtures from steam gasification give a better mole fraction at pressures lower than 100 bar compared to the ideal ratio. Indicating that there is an optimal gas ratio between the two mixtures. At higher pressures high H_2/ CO ratio is preferable. The methanol yields are given in Tab. 4 results from the simulation at 200°C and 100 bar, and the approximately same result for the gas mixtures from steam gasification and the ideal ratio is directly related to the analysis above. In this study a recycle of 1100 kmole/h is used in the simulation. The methanol yield reported in the results will be approximately the same with a recirculation stream above 300 kmole/h. The disadvantages of having too large recirculation streams are the increased energy requirements for cooling and heating the gas flows. Also, high dilution of stream 5 gives low methanol concentrations in the reactor product, which will be challenging to the gas-liquid separation in the two-phase separator and to the distillation columns, increasing the cost of the system.

The addition of extra hydrogen increases the methanol yield of the system. The simulation shows that an optimal addition of 150 kmole/h hydrogen gives the best result. Hydrogen cost versus the extra income for the methanol produced must be evaluated before hydrogen is chosen as feed to the system. The calculations with H_2 addition show that an H_2/CO ratio of approximately 2 is preferable.

Fluidized bed gasification with steam as gasifying agent is preferable compared to air gasification to increase the H_2/CO ratio to achieve a higher methanol yield in the methanol synthesis.

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