

Modelling of Methanol Synthesis: Improving Hydrogen Utilisation

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Hydrogen is a key component in the methanol (MeOH) synthesis process. It affects both the environmental and economic performance, since renewable hydrogen (usually produced by electrolysis) is the most expensive component of the process. The addition of renewable hydrogen improves the carbon balance of the process but necessitates the planning of a suitable strategy to account for the stochastic nature of renewable energy and the respective costs. For this reason, the focus of this work is the efficient hydrogen utilization in contrast to most of the past literature works that mainly focus on the conversion of the carbonaceous feedstock. Several operating parameters such as the extent of recycling, operating temperature and pressure, stoichiometric number, inlet temperature and total mass flow per tube affect the methanol yield, carbon conversion and hydrogen consumption of the process. The scope of this work is to provide insight on the effect of those parameters on the efficient hydrogen utilisation using a methanol synthesis modelling tool. The findings of this study showed that hydrogen utilisation could be considerably improved if operating at certain conditions. Lower stoichiometric numbers and mass flows per tube, inlet and cooling temperatures up to 510 K and higher operating pressures could reduce the required hydrogen per produced methanol unit. Especially the employment of recycling, could lead to substantial reduction of the associated hydrogen requirements. In particular, recycling 50 % of the residual off-gases could lead to 10 % less fresh hydrogen requirements and 90 % recycling results to 40 % less hydrogen for the production of the same amount of methanol.

1. Introduction

Methanol (CH₃OH) is an important feedstock for the chemical industry and a potential fuel component/additive due to its favourable properties and combustion characteristics. More than 60 % of the produced methanol is used as an intermediate to produce chemicals such as formaldehyde, acetic acid and olefins. Methanol has an already established and growing market with 98 Mt of methanol being produced in 2019, which in 2027 is estimated to reach 135 Mt. Most of the current methanol production is derived from fossil resources such as coal (especially in China) and natural gas (IRENA and Methanol Institute, 2021). To convert coal or natural gas to methanol, the main steps include the conversion of the feedstock to syngas by gasification or reforming. After removing the contained impurities, hydrogen is added in the optimal stoichiometry to produce methanol. To avoid, however, the related carbon emissions during the synthesis, the carbon feedstock as well as the added hydrogen, should be derived by renewable or waste sources (Riaz et al., 2013).

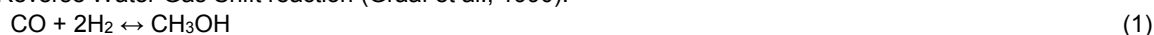
An option to produce renewable or low-carbon methanol is the usage of captured CO₂ or carbonaceous, industrial off-gases, such as steelworks off-gases (Bampaou et al., 2021) with the addition of renewable hydrogen by electrolysis (Zaccara et al., 2020). The production process is similar to the fossil-based process and leads to the production of similar quality methanol. The renewable path emissions are significantly lower than the fossil-based (Zang et al., 2021), but the current costs of renewable methanol production, far surpass the fossil-based production routes (IRENA and Methanol Institute, 2021). Those costs are mainly associated to hydrogen production and are linked to the electricity prices (operational cost) and the electrolyser capital costs. Special attention should be paid on the usage of electricity generated by renewable sources to also avoid the

related carbon emissions. It is estimated that almost 80 % of the total production costs are attributed to the operational and capital expenses of hydrogen production (Atsonios et al., 2016).

The methanol synthesis process results in close to the thermodynamic equilibrium conversion; any additional hydrogen is not consumed throughout the process and remains unexploited in the reactor off-gases. For this reason, methanol synthesis is usually conducted in a loop, where the unreacted off-gases are recycled to the synthesis reactor (Lovik, 2001). Most of the past literature works mainly focus on the conversion of the carbonaceous feedstock; but since hydrogen is the most expensive component in this scheme, an efficient utilisation strategy of the added hydrogen could prove crucial for the economic viability of the process. The scope of this work is to provide an overview of the operating parameters that could lead to the efficient utilisation of the added hydrogen. The crucial investigated operating parameters are the operating pressure, hydrogen stoichiometry (stoichiometric number), cooling and inlet temperature, mass flow per tube and recycling ratio. A methanol synthesis model was developed that incorporates the unit operations comprising the synthesis loop and investigates the effect of those parameters on methanol production and hydrogen utilisation. Important considerations are highlighted for the different operating maps that are crucial for a cost-effective design and operation.

2. Process Description

Methanol synthesis from syngas is based on three reactions: the CO and CO₂ hydrogenation reactions and the Reverse Water Gas Shift reaction (Graaf et al., 1990):



It is an overall exothermic reaction conducted between 473 - 573 K due to the activation of the Cu-based catalyst at this temperature level and at temperatures higher than 553 K, catalyst sintering could take place (Bozzano and Manenti, 2016). Most industrial-scale methanol synthesis processes are conducted at pressures between 50-100 bar (Schittkowski et al. 2018). The relation between the added hydrogen and the contained carbonaceous components is described by the Stoichiometric Number:

$$S.N. = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \quad (4)$$

where [H₂], [CO] and [CO₂] refer to the molar flows of the reactants. A stoichiometric correlation has the value of 2, whereas the optimum case for maximum methanol production is slightly above the stoichiometric (Bozzano and Manenti 2016). Figure 1 illustrates the conventional methanol synthesis loop.

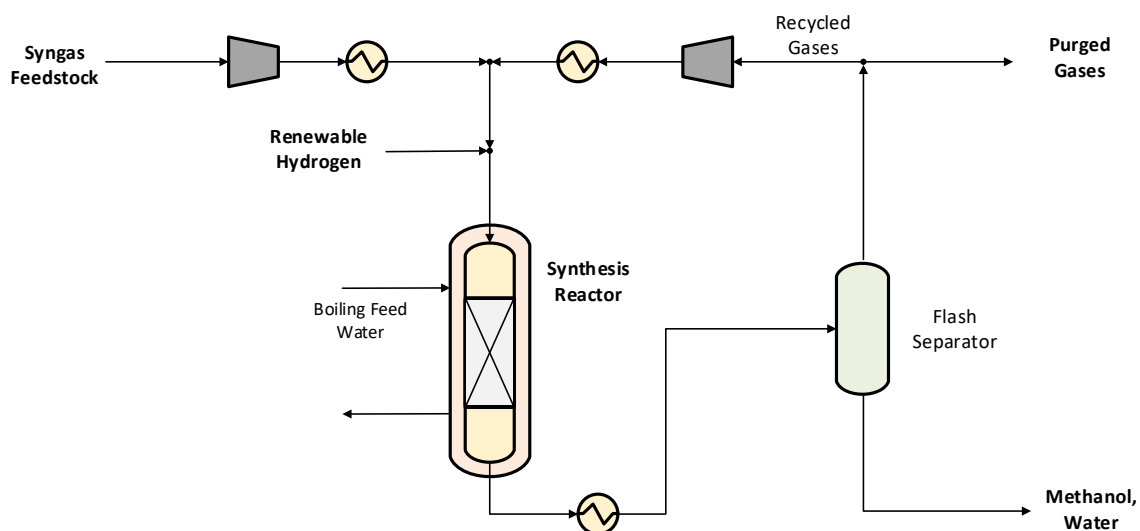


Figure 1: Methanol synthesis loop

The carbonaceous feed is mixed with renewable hydrogen in a certain stoichiometry, and the mixture is inserted in the reactor. The synthesis reactor is a shell-and-tube reactor, where the reactions take place inside the tube, which is loaded with the catalyst. Since the reaction is exothermic, heat is released and should be efficiently removed to prevent increase of the temperature inside the tube (reaction zone). In order to regulate the reactor

temperature, boiling feed water is fed in the shell side (operating as a boiler, isothermal cooling operation), whose cooling temperature is regulated through pressure manipulation (Luyben, 2010). The reactor outlet is cooled and consecutively flashed into gaseous and liquid products. The liquid products, mainly methanol and water, are fed into distillation columns to purify the methanol product. The gaseous phase, that contains the unreacted hydrogen and the carbonaceous gaseous components, is purged (up to a certain ratio) to avoid accumulation of inert components, which among others would result in increased compression costs. The recirculated stream is finally mixed with the fresh syngas and fed to the reactor.

3. Modelling Description and Methodology

The mathematical model of the methanol reactor is a one-dimensional (axial direction) pseudo-homogeneous model. A pseudo-homogeneous model neglects the temperature and concentration gradients between the solid catalyst and the gaseous phase in contrast to a heterogeneous model. This simplification reduces significantly the computational effort without having strong deviations between the two modelling approaches (Manenti et al., 2011). The developed model consists of a set of equations that represent the mass balances of each component, the energy balances of the reaction zone and reactor wall as well as the pressure drop (Ergun equation) (Bozzano and Manenti, 2016). The steady-state model equations are shown in Table 1. The set of equations is inserted as equality constraints and solved using the IPOPT software library within the CasADi open-source software tool (Andersson et al., 2019). The other unit equipment related to the methanol synthesis flowsheet (heat exchangers, compressors and flash separator) was modelled using equations from past literature works (Lovik, 2001).

Table 1: Equations used in the methanol synthesis model

		Equations
Component Mass Balances	CO	$\frac{M}{A_{cs}} \frac{\partial m_{CO}}{\partial z} = MW_{CO}(-r_{CH_3OH} + r_{H_2O})$
	CO ₂	$\frac{M}{A_{cs}} \frac{\partial m_{CO_2}}{\partial z} = MW_{CO_2}(-r_{H_2O})$
	H ₂	$\frac{M}{A_{cs}} \frac{\partial m_{H_2}}{\partial z} = MW_{H_2}(-2r_{CH_3OH} - r_{H_2O})$
	CH ₃ OH	$\frac{M}{A_{cs}} \frac{\partial m_{CH_3OH}}{\partial z} = MW_{CH_3OH}r_{CH_3OH}$
	H ₂ O	$\frac{M}{A_{cs}} \frac{\partial m_{H_2O}}{\partial z} = MW_{H_2O}r_{H_2O}$
	N ₂	$\frac{M}{A_{cs}} \frac{\partial m_{N_2}}{\partial z} = 0$
	CH ₄	$\frac{M}{A_{cs}} \frac{\partial m_{CH_4}}{\partial z} = 0$
Energy Balances	Reaction Zone	$\frac{M}{A_{cs}} c_{p,mix} \frac{\partial T_{bulk}}{\partial z} = \frac{4U}{d_{tube}} (T_{wall} - T_{bulk}) + \rho_{cat}(1 - \varepsilon_b) \sum_j^{N.R.} (-\Delta H_j^{reac}) r_j$
	Wall	$k_{shell} \frac{\partial T_{wall}}{\partial z} = h_o A_{shell} (T_{sat} - T_{wall}) + h_i A_{shell} (T_{wall} - T_{bulk})$
Pressure Drop	Ergun Equation	$\frac{\partial P}{\partial z} = - \left(1.75 + 150 \left(\frac{1 - \varepsilon_b}{Re} \right) \right) \frac{u^2 \rho_{gas}}{d_p} \left(\frac{1 - \varepsilon_b}{\varepsilon_b^3} \right)$

Additionally, specific functions to calculate several properties of the reactive mixture are included, in such way that properties are a function of the respective mesh node conditions (e.g., temperature, pressure, composition, etc.). The properties calculated with those specific functions are: density (ρ), gas thermal conductivity, viscosity (μ), gas mixture heat capacity (c_p), as well as the wall thermal conductivity (k_{shell}) and the heat transfer coefficients: outer (h_o), inner (h_i), wall (h_w), overall (U). The reaction kinetics mechanism is based on the kinetic model presented by Graaf et al. (1990).

The specific characteristics and assumptions of the methanol reactor are illustrated in Table 2. A mixture of steelworks off-gases is used as feedstock for the production of methanol after drying of the initial contained

moisture (Bampaou et al., 2021). The mixture contains CO and CO₂, which are the main reactants used for the synthesis as well as a large amount of inert components such as nitrogen and methane. The low amount of contained H₂ implies that the feed mixture requires conditioning to achieve the certain stoichiometries required by methanol synthesis. This amount of required hydrogen is the main focus of this work since it is the most expensive component during methanol synthesis. In this work, the efficient H₂ utilisation is among others described with the term MtH:

$$MtH = \frac{\text{Mass flow of produced Methanol}}{\text{Mass flow of added Hydrogen}} \quad (5)$$

which illustrates how efficiently each added hydrogen molecule is utilised within the loop for the production of a methanol unit. The higher the MtH term, the better the hydrogen utilisation within the methanol loop.

Table 2: Characteristics and assumptions of the methanol synthesis reactor

Characteristics	Value	Reference	Characteristics	Value	Reference	
Feed composition, wt. %	CO: 23.6;	(Bampaou et al., 2021).	Catalyst heat capacity, J/kg·K	5,000	(Askari et al., 2008)	
	CO ₂ : 31.8;		Shell tube thickness, m	1.98·10 ⁻³	(Manenti et al., 2011)	
	H ₂ : 0.5;		Shell tube material			
	CH ₃ OH: 0.0; H ₂ O: 0.0; N ₂ : 42.96; CH ₄ : 1.09		Shell tube heat capacity, J/kg·K	500	(Kim, 1975)	
			Density, kg/m ³	7,700	(Kim, 1975)	
Catalyst density, kg/m ³	1770	(Manenti et al., 2011)	Reactor length, m	5	Assumption	
Catalyst particle diameter, m	5.47·10 ⁻³	(Manenti et al., 2011)	Reactor diameter, m	0.025	Assumption	
			Bed voidage, -	0.30	Assumption	

4. Results and Discussions

Figure 2 illustrates the influence of each respective operating parameter on hydrogen consumption per methanol production unit. The base case represents methanol synthesis conducted at Stoichiometric Number: 1.9, operating pressure: 80 bar, cooling temperature: 514 K, mass flow: 0.002 kg/s/tube, inlet temperature: 510 K and no recycling. For the subsequent sensitivity analysis, one specific parameter was varied each time and the rest were kept constant in order to investigate its influence on the overall performance for a single-tube operation.

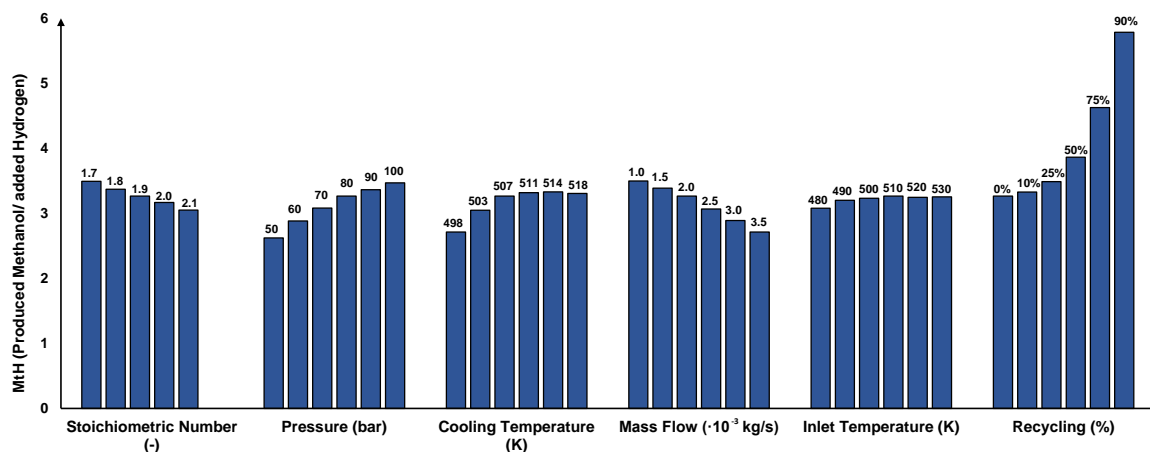


Figure 2: Influence of operating parameters on the required hydrogen per methanol production unit: Stoichiometric Number (1.7-2.1); Pressure (50-100 bar); Cooling Temperature (498-518 K); Inlet Mass Flow per tube (0.001-0.0035 kg/s); Inlet Temperature (480-530 K); Recycling (0-90 %)

As illustrated by Figure 2, the higher the stoichiometric number the more hydrogen is needed per produced methanol. This means that when operating at high stoichiometric numbers, provision for hydrogen recycling should be taken into consideration. Operation at lower stoichiometric numbers, on the other hand, would be beneficial for the efficient hydrogen utilisation and require lower amounts of fresh hydrogen by electrolysis.

Higher pressures, favour methanol production since it results on higher carbon conversion; which is also dictated by the reaction stoichiometry. However, for higher operating pressures, higher compression costs for both the feed and the recycle stream are needed. In other words, if choosing to operate at higher pressures, the revenues of the higher methanol conversion have to surpass the additional, associated compressions costs.

Cooling temperature should on one hand, be high enough to promote the synthesis reaction, while on the other hand should maintain the reaction zone under 553 K, to avoid catalyst sintering and the formation of hot spots. Cooling above 511 K does not entail additional advantages for the efficient hydrogen utilisation. Regarding the inlet temperature, operating at 510 K seems to be optimal for hydrogen utilization and operation above 510 K would increase the associated heat demands with no substantial hydrogen utilisation benefits.

The total mass flow per tube plays a major role on the efficient hydrogen utilisation; the lower the total mass flow per tube, the better the utilisation rates of hydrogen. Mass flow per tube could be an important optimisation parameter, since it would directly affect the efficiency as well as the associated pressure drop. Higher mass flows result in higher pressure drop based on the Ergun Equation (Table 1). Based on the current findings, operating with multiple tubes and lower mass flowrates per tube would increase the total system efficiency and could prove economically beneficial for higher-scale systems. Methanol production with multi-tube reactors is a common practice in industrial scale systems and an optimal tube design could further facilitate the economic viability of the process.

Finally, recycling of the unreacted off-gases has a strong influence on the required hydrogen by electrolysis. Operating at 90 % recycling ratio would result in a M_{tH} value of 6 compared to 3 of the no recycling case (base case), meaning that almost half of the fresh hydrogen amounts are required per produced methanol unit. The importance of recycling can also be seen in Figure 3, where the required feedstock and hydrogen are illustrated for the production of $2 \cdot 10^{-4}$ kg MeOH/s/tube for each case. Recycling 50 % of the residual off-gases could result in 10 % less hydrogen requirements and 90 % recycling results in 40 % less feedstock and hydrogen requirements. For this reason operating with a recycling loop could prove economically beneficial since it would result in lower demands for produced hydrogen by electrolysis. Also due to the lower required syngas feedstock, the total methanol yield (produced methanol to the CO and CO₂ of the feedstock) is increased from 42 % to 68 %.

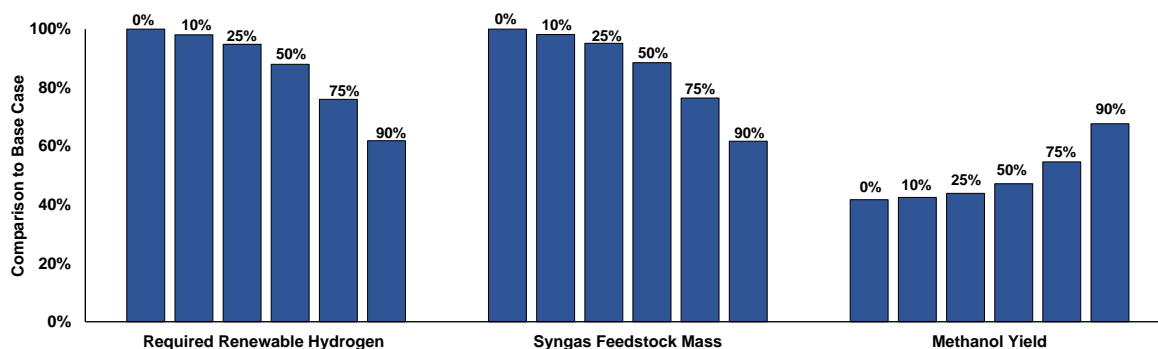


Figure 3: Feed and hydrogen requirements for the production of $2 \cdot 10^{-4}$ kg MeOH/s/tube for recycling 0-90 %

5. Conclusions

In this work, methanol synthesis from steelworks off-gases was investigated using the CasADi modelling software tool. The focus of this work is the efficient hydrogen utilisation, since it is the most expensive component in this process. Critical operating parameters such as operating pressure, inlet and cooling temperature, stoichiometric number and recycling were assessed for their influence on hydrogen utilisation. Results showed that substantial benefits could be attained if operating at certain conditions: higher operating pressures, lower stoichiometric numbers and mass flows per tube, and inlet and cooling temperatures up to 510 K could reduce the required hydrogen per produced methanol. Especially, recycling could lead to 40 % less hydrogen demands that could prove critical for the efficient hydrogen utilisation and subsequently for the economic performance. The findings of this work will be further utilised in a cost optimisation study that takes into consideration the above operating and design parameters for diverse electricity prices and economic conditions. In addition,

alternative flowsheet configurations that could further improve the hydrogen utilisation rates and the economic sustainability of the process will also be investigated.

Nomenclature

$A_{cs/shell}$ – Cross-sectional/in-between area, m^2	P – Pressure, bar
$C_{p,shell/mix}$ – Shell/gas mixture heat capacity, $J/kg \cdot K$	r_i – Reaction rate of component i , $kmol/kg_{cat} \cdot s$
d_{tube} – Tube diameter, m	Re – Reynolds number, -
d_p – Catalyst particle diameter, m	$T_{sat/wall/bulk}$ – Saturation/wall/bulk temperature, K
$h_{i/o}$ – Inner/outer heat transfer coefficient, $W/(m^2 \cdot K)$	U – Overall heat transfer coefficient, $W/(m^2 \cdot K)$
k_{shell} – Wall thermal conductivity, $W/(m \cdot K)$	u – Superficial fluid velocity, m/s
M – Total mass flow, kg/s	z – Reactor length, m
m_i – Mass fraction of component i	ΔH_j – Heat of reaction j , J/kmol
MW_i – Molecular weight of component i , kg/kmol	ϵ_b – Bed void fraction, -
$N.R.$ – Number of reaction, -	$\rho_{cat/gas}$ – catalyst/gas mixture density, kg_{cat}/m^3

Acknowledgements

The work described was developed within the project entitled “Integrated and intelligent upgrade of carbon sources through hydrogen addition for the steel industry”, (i³upgrade, GA No. 800659) that has received funding from the Research Fund for Coal and Steel of the European Union. The sole responsibility of the issues treated in this paper lies with the authors; the Commission is not responsible for any use that may be made of the information contained therein.

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