

Energy-Process Integration of the Gas-Cooled/Water-Cooled Fixed-Bed Reactor Network for Methanol Synthesis

Flavio Manenti*, Andres R. Leon-Garzon, Giulia Bozzano

^aPolitecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy
flavio.manenti@polimi.it

The paper deals with the techno-economical assessment of the gas-cooled/water-cooled fixed-bed reactor network for methanol synthesis. The study is the extension of the first-principles model for the water-cooled reactor already proposed in our prior work (Manenti et al., 2011a). Here, the optimisation is extended to the steam generation and the reactor length ratio. As a result, basing on the integrated optimisation of energy and process yield, we propose to significantly revise the common design. The traditional water/gas-cooling reactor length ratio could be significantly reduced with consequent simultaneous increase in methanol production and steam generation as well, however preserving safety and operational ranges. The economic benefit deriving from the proposed design for a medium-scale process is estimated in more than 1.7 M€/y.

1. Introduction

Even though many improvements have been made since its first commercial implementation in 1923 and a series of new production technologies are being developed (Lange, 2001), methanol is still largely produced from natural gas, specifically via syngas (CO and H₂ mixture) obtained by means of steam reforming operations (Olah et al., 2009). Some technologies are available from Lurgi, Topsoe, Davy Process Technology, Casale, Air Products to quote a few of societies, and the most common technology consists of a couple of reactors: (1) gas-cooled reactor (GAC) and (2) water-cooled (WAC) shell-tube boiler-reactor. Since the WAC reactor is considered the key section for the overall reacting system, many authors focused their attention on its optimal design and operation, neglecting the GAC portion of the reacting system. For instance, Chen and co-workers (Chen et al., 2011) studied the WAC reactor and the related boiling system to optimise the yield in methanol synthesis. They obtained a methanol yield improvement estimated in about 7 %. Similarly, our prior works investigated the steady-state optimal configuration of WAC reactor (Manenti et al., 2011a), its dynamic behaviour subject to possible syngas composition and inlet flow variations (Manenti et al., 2013), and the simultaneous control of the methanol production and hot-spot temperature position along the axial coordinate (Manenti et al., 2012). A one-dimensional steady-state heterogeneous model is proposed for the WAC reactor (Vakili and Eslamloueyan, 2012) for the direct dimethyl-ether synthesis using a dual-step technology. Nowadays, the use of a 7/3 WAC/GAC reactor length ratio is well consolidated and close to the optimal design especially of the water-cooled reactor since the target is the maximisation of methanol production. Nevertheless, it is mandatory to account for two aspects that can significantly improve the total revenue of the methanol synthesis process without any additional cost: (1) the optimisation of the overall WAC/GAC reactor network: rather than optimizing only the sole WAC reactor, it is possible to exploit the integrated model of the WAC/GAC network to perform an overall design optimisation to maximise the methanol yield; (2) the integration of energy production as medium pressure steam within the optimisation procedure (Cucek et al., 2010) according to the general energy policies also adopted in other closest fields (Klemeš et al., 2010). The methanol synthesis reactor network is described in Section 2. The mathematical modelling for WAC and GAC reactors is briefly reported in Section 3. The nonlinear programming problem to improve

methanol yield and steam generation is described in Section 4 together with the numerical results and economic considerations.

2. Chemical process

As mentioned above, methanol synthesis is usually based on a series of two fixed-bed tubular reactors (Mayra and Leiviska, 2009), although several other configurations have been proposed by Velardi and Barresi (2002) and later extended by Rahimpour et al. (2010). Following the process flow direction of Figure 1, the syngas is fed to the shell side of the gas-cooled reactor, where it is pre-heated by the hot process stream flowing in the fixed-bed tube bundle. The pre-heated syngas is then fed to the catalytic bed for methanol conversion and specifically to the tube side of the WAC reactor. Please note that different technologies may have the catalyst in the shell side (e.g., Davy Process technology), but they are not considered for the sake of simplicity and conciseness. The syngas fed to the fixed-bed of the catalytic tube bundle is partially converted into methanol along the first reactor. The methanol synthesis is particularly exothermic and the shell side is filled of boiling water to preserve the desired operating conditions of the WAC reactor. The intrinsic intensified nature of modern methanol process allows combining the methanol conversion to the medium pressure steam generation. As discussed elsewhere (Manenti et al., 2011a), phenomena occurring within in the first part of the water-cooled reactor are kinetic limited, whereas the thermodynamic equilibrium is usually achieved after 1-2 m along the longitudinal axis. In correspondence with this point, the maximum temperature, called the temperature hot-spot, is achieved. The hot-spot is one of the most important parameters to improve the process efficiency and to preserve the catalyst integrity and process safety (Manenti et al., 2011b) and some special techniques to monitor it are required (Manenti et al., 2012). The outflow of the WAC reactor is fed to the tube side of the GAC reactor where the methanol synthesis continues. GAC temperature profile is controlled exchanging with the fresh inlet syngas to be pre-heated in countercurrent in the shell side. The GAC reactor outflow is then sent to the downstream process where the methanol is recovered and the unreacted syngas is recycled back unless a purge system to remove by-products, and accumulations of incondensable gas.

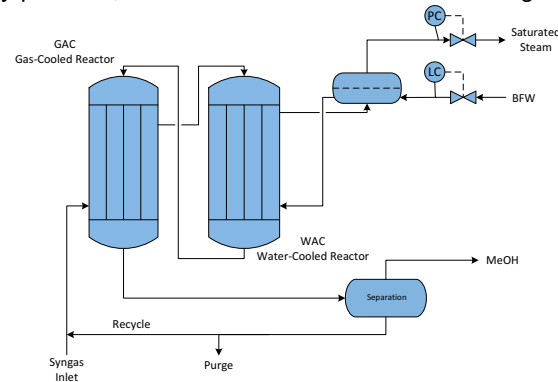
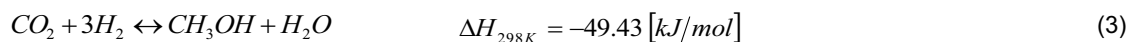
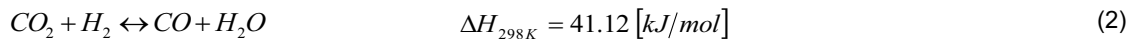
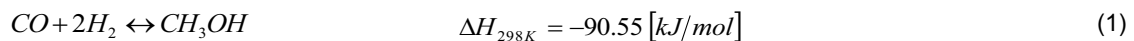


Figure 1: Methanol synthesis loop with water/gas-cooled (WAC/GAC) reactors.

Methanol is produced from syngas from three main reactions:



These reactions are not independent and any one of them can be expressed as a linear combination of the others as indicated elsewhere. Rather than using the chemical species, as in the typical mathematical modelling of chemical reactors, the chemical elements C, H, and O must be considered to reduce the size of the resulting numerical system (Manenti et al., 2013). Exothermic reactions (1) and (3) are favoured at low temperature despite the reaction rate; moreover, it is necessary to operate at high pressure (for instance 80 bar) to improve the equilibrium conversion exploiting the reduction in the number of moles. Typically, the synthesis of methanol is conducted over commercial Cu/ZnO/Al₂O₃ which has an estimated life of 3-4 years. Since catalyst deactivation occurs at temperatures above the 550 K, the operating range

of temperature is 484 K to 540 K. Typical feed composition is: CO = 0.046; CO₂ = 0.094; H₂ = 0.659; H₂O = 0.0004; CH₃OH = 0.005; N₂ = 0.093; CH₄ = 0.1026.

3. Mathematical modelling

The integrated modelling of the overall reactor network for methanol synthesis can be reasonably modelled taking into consideration three systems: the WAC reactor, the GAC reactor, and the preliminary phase separation for syngas recycle. The mathematical model developed for the simulation of the methanol production loop is based the assumption of negligible axial and radial diffusion, constant radial velocity, constant temperature and pressure profiles within the catalytic pellet, negligible catalyst deactivation and side reactions, and catalytic particle efficiency using modified Thiele modulus:

$$\phi_i = \frac{r_p}{3} \sqrt{\frac{k'_j (k_j^{eq} + 1)}{D_{i,eff}^j k_j^{eq}}}, \quad \eta_{li} = \frac{1}{\phi_i} \frac{(3\phi_i \coth(3\phi_i) - 1)}{3\phi_i} \quad (4)$$

where ϕ_i , ϕ_i is the modified Thiele modulus; r_p is the radius of catalytic pellets; k'_j is the pseudo-first-order constant of the j -th reaction; k_j^{eq} is the equilibrium constant of the j -th reaction; $D_{i,eff}^j$ is the effective diffusivity of the j -th component of the mixture as specified by Lommerts et al. (2000). The linearized kinetics required to achieve k'_j for methanol and water are, respectively:

$$r'_{CH_3OH} = k'_j \left(C_{H_2} - \frac{C_{CH_3OH}}{k_{CH_3OH}^{eq}} \right), \quad r'_{H_2O} = k'_j \left(C_{H_2} - \frac{C_{H_2O}}{k_{H_2O}^{eq}} \right) \quad (5)$$

and are obtained by replacing the r , k_{eq} , k_{eq} and concentration values calculated at the integration step. The kinetic laws adopted were already proposed elsewhere (Graaf et al., 1988):

$$r_1 = \frac{k_1 K_{CO} \left[f_{CO} f_{H_2}^{1.5} - \frac{f_{CH_3OH}}{f_{H_2}^{0.5} K_{P1}} \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) \left[f_{H_2}^{0.5} + \left(\frac{K_{H_2O}}{K_{H_2}^{0.5}} \right) f_{H_2O} \right]} \quad (6)$$

$$r_2 = \frac{k_2 K_{CO_2} \left[f_{CO_2} f_{H_2} - \frac{f_{CO} f_{H_2O}}{K_{P2}} \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) \left[f_{H_2}^{0.5} + \left(\frac{K_{H_2O}}{K_{H_2}^{0.5}} \right) f_{H_2O} \right]} \quad (7)$$

$$r_3 = \frac{k_3 K_{CO_2} \left[f_{CO_2} f_{H_2}^{1.5} - \frac{f_{CH_3OH} f_{H_2O}}{f_{H_2}^{1.5} K_{P3}} \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) \left[f_{H_2}^{0.5} + \left(\frac{K_{H_2O}}{K_{H_2}^{0.5}} \right) f_{H_2O} \right]} \quad (8)$$

The GAC and WAC reactors are modelled assuming that concentration and temperature gradients between the gas and solid phase are negligible, significantly simplifying the numerical solution and reducing the computation effort without losing in accuracy (Manenti et al., 2011a). Constitutive equations for the WAC reactor model are:

Mass balance:

$$\frac{M}{A_{int}} \frac{d\omega_i}{dz} = MW_i \rho_{cat} (1 - \varepsilon_b) \sum_j^{NR} v_{ij} \eta_j r_j \quad (9)$$

Energy balance:

$$\frac{M c_{p,mix}}{A_{int}} \frac{dT_c}{dz} = -\pi \frac{d_{int}}{A_{int}} U (T_{shell} - T_{bulk}) + \rho_{cat} (1 - \varepsilon_b) \sum_j^{NR} (-\Delta H_j^{rxn}) \eta_j r_j \quad (10)$$

Ergun equation:

$$\frac{dP}{dz} = - \left(1.75 + 150 \left(\frac{1 - \varepsilon_b}{Re} \right) \right) \frac{u^2 \rho_{\text{gas}}}{d_p} \left(\frac{1 - \varepsilon_b}{\varepsilon_b^3} \right) \quad (11)$$

Equations are the same for GAC reactor, but the additional energy balance to characterise the coolant gas flowing in countercurrent is needed:

Energy balance:

$$\frac{M c_{p_{\text{mix}}}}{A_{\text{int}}} \frac{dT_c}{dz} = - \pi \frac{d_{\text{int}}}{A_{\text{int}}} U (T_c - T_{\text{shell}}) \quad (12)$$

Finally, the preliminary separation for the syngas recycle consists of a simple flash drum separator, the total (13) and component mass balances (14)-(16) are:

$$F = V + L \quad (13)$$

$$F z_i = V y_i + L x_i \quad (14)$$

$$\sum_{i=1}^N y_i = 1 \quad (15)$$

$$\sum_{i=1}^N x_i = 1 \quad (16)$$

Given flash separator conditions, the solution is found adopting the method proposed by Rachford and Rice (1952):

$$f(V/F) = \sum_{i=1}^N \frac{z_i (K_i - 1)}{\frac{V}{F} (K_i - 1) + 1} = 0 \quad (17)$$

where K_i are the K-values of an appropriate equation of state:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \quad (18)$$

4. Energy-process optimisation

Basing on the integrated model of the WAC/GAC reactor network, including separation and recycle, it is possible to optimise the methanol synthesis by selecting certain degrees of freedom. In this specific case, the interesting parameter to optimise is the WAC/GAC reactor length ratio, which is roughly assumed equal to 7/3 (2.333) for the industrial best practice in many cases. This ratio comes from a one-dimensional optimisation where the WAC/GAC ratio is the only degree of freedom and the target is the maximisation of methanol yield (from now, process optimisation). This optimisation is performed by assuming the inlet syngas flow rate that matches the final methanol production and the shell temperature of WAC reactor that matches the specifications of the steam generation (simulation data reported in Manenti et al., 2011a). Actually the ratio obtained from this optimisation is rather close to the industrial best practice (2.125) as it is possible to see from the temperature profiles reported in Figure 2, where the discontinuity in correspondence to 5 m indicates the end of WAC reactor and the beginning of GAC reactor. No relevant variations are appreciated for the methanol yield profile of Figure 3.

Conversely, the use of the integrate model here proposed allow to account not only for process optimisation, but also for energy optimisation since the syngas pre-heating in GAC reactor and the steam generated in WAC reactor enter the same optimisation procedure. Thus, keeping constant certain operating conditions as above (feed properties) for calculation consistency, the optimal ratio is calculated solving a multi-dimensional problem with the WAC/GAC ratio and the shell temperature of WAC reactor as degrees of freedom and a boundary value problem as differential-algebraic set of constraints:

$$\begin{array}{l} \max \\ \text{WAC / GAC ratio} \\ \text{WAC shell temp} \end{array} y_{CH_3OH} \quad (19)$$

s.t.: WAC and GAC models (DAEs)

$$\max_{\substack{\text{WAC/GAC ratio} \\ \text{WAC shell temp}}} y_{CH_3OH} + F_{STEAM} \quad (20)$$

s.t. : WAC and GAC models (DAEs)

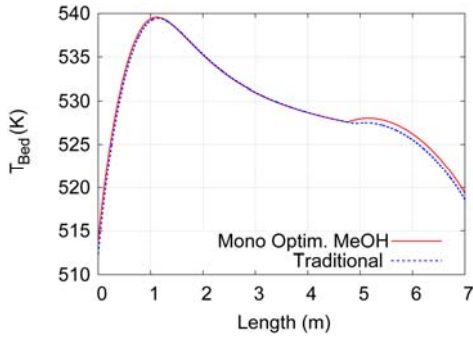


Figure 2: Temperature profiles adopting traditional (dashed) and optimal (solid) WAC to GAC reactor length ratio.

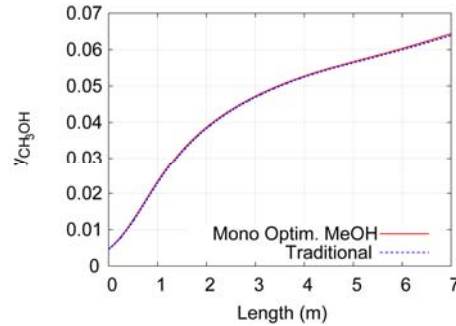


Figure 3: Methanol molar fraction profile adopting traditional (dashed) and optimal (solid) WAC to GAC reactor length ratio.

In the former case, the target is still the process optimisation (maximisation of methanol yield), whereas in the latter case the target is, at the same time, the maximisation of methanol yield and steam generation (energy-process optimisation). Comparing the temperature profiles of Figure 4 obtained for the process optimisation with respect to the traditional process optimisation, it is apparent that the WAC/GAC length ratio dramatically drops to 1.141 radically changing the network and increasing the methanol yield, as shown in Figure 5. This emphasises the importance of considering the overall reactor network in the optimal design of methanol synthesis process. The ratio further decreases to 1.121 when the energy-process optimisation is solved. The relevant differences of the temperature profiles with respect to the traditional optimal case lead to a relevant increase in the methanol yield: + 0.4 % of molar fraction on a total of 6.4 % outflowing the tube bundle of GAC reactor. Table 1 shows the economic comparison of different configurations of the reactor network obtained by solving the process optimisation and the energy-process optimisation. The comparison is provided with respect to the optimal traditional case. An additional revenue of 3.68 % for the process optimisation and 3.79 % for the energy-process optimisation for a medium-capacity methanol plant.

Table 1: Economic comparison.

	Traditional case	Process optimisation	Energy-process optimisation
Total revenue (€/y)	45,844,592	47,532,036	47,583,417
Methanol fraction (mol)	0.1823	0.1894	0.1897
Energy from steam (MW)	6.034	6.141	6.143

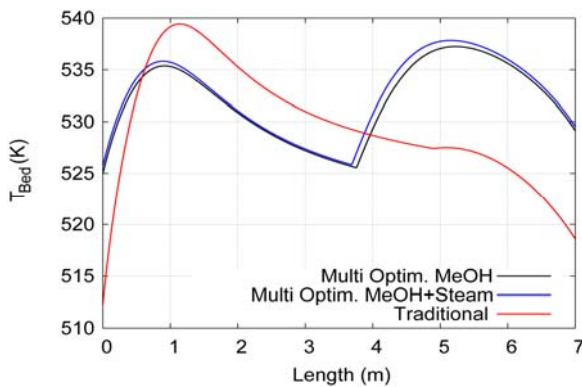


Figure 4: Temperature profiles of the WAC/GAC reactor network. Comparison between the traditional case and the process and energy-process optimisations.

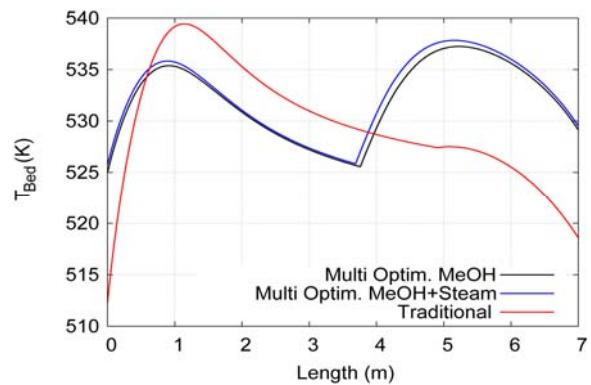


Figure 5: Methanol molar fraction profile of the WAC/GAC reactor network. Comparison between the traditional case and the process and energy-process optimisations.

5. Conclusions

This work showed the possibility to increase the methanol yield and, at the same time, the steam generation by means of the model-based integrated energy-process optimisation. Specifically, the mathematical model for the overall reactor network of the methanol synthesis, including the water-cooled reactor, the gas-cooled reactor, and the preliminary separation is developed and implemented as set of differential-algebraic constraints (leading to the boundary value problem due to the syngas preheating) in the optimisation procedure. The energy-process optimisation for a medium-size methanol plant leads to 1.7 M€/y of additional profit.

References

- Chen, L., Jiang, Q.Z., Song, Z.Z., Posarac, D., 2011. Optimization of Methanol Yield from a Lurgi Reactor. *Chemical Engineering & Technology*, 34, 817-822.
- Čuček, L., Lam, H.L., Klemeš, J.J., Varbanov, P.S., Kravanja, Z., 2010. Synthesis of regional networks for the supply of energy and bioproducts. *Clean Technologies and Environmental Policy*, 12, 635-645.
- Graaf, G.H., Stamhuis, E.J., Beenackers, A., 1988. Kinetics of Low-pressure Methanol Synthesis. *Chemical Engineering Science*, 43, 3185-3195.
- Klemeš, J.J., Varbanov, P.S., Pierucci, S., Huisingh, D., 2010. Minimising emissions and energy wastage by improved industrial processes and integration of renewable energy. *Journal of Cleaner Production*, 18, 843-847.
- Lange, J.P., 2001. Methanol synthesis: a short review of technology improvements. *Catal. Today*, 64, 3-8.
- Lommerts, B.J., Graaf, G.H., Beenackers, A., 2000. Mathematical modeling of internal mass transport limitations in methanol synthesis. *Chemical Engineering Science*, 55, 5589-5598.
- Manenti, F., Cieri, S., Restelli, M., 2011a. Considerations on the steady-state modeling of methanol synthesis fixed-bed reactor. *Chemical Engineering Science*, 66, 152-162.
- Manenti, F., Cieri, S., Restelli, M., Bozzano, G., 2013. Dynamic Modelling of the Methanol Synthesis Fixed-Bed Reactor. *Computers & Chemical Engineering*, 48, 325-334.
- Manenti, F., Cieri, S., Restelli, M., Lima, N.M.N., Zuniga Linan, L., 2011b. Dynamic Simulation of Lurgi-type Reactor for Methanol Synthesis. *Chemical Engineering Transactions*, 24, 379-384.
- Manenti, F., Cieri, S., Restelli, M., Lima, N.M.N., Zuniga Linan, L., Bozzano, G., 2012. Online Feasibility and Effectiveness of a Spatio-temporal Nonlinear Model Predictive Control. The Case of Methanol Synthesis Reactor. *Computer Aided Chemical Engineering*, 30, 867-871.
- Mayra, O., Leiviska, K., 2009. Modelling in methanol synthesis, *Chemical Engineering Transactions*, 17(1-3), 1413-1418.
- Olah, G.A., Goepfert, A., Surya Prakash, G.K., 2009. *Beyond Oil and Gas: The Methanol Economy*. Wiley-VCH, Weinheim, Germany.
- Rachford, H.H., Rice, J.D., 1952. Procedure for Use of Electrical Digital Computers in Calculating Flash Vaporization Hydrocarbon Equilibrium. *Trans. AIME*, 4, 195.
- Rahimpour, M.R., Bayat, M., Rahmani, F., 2010. Dynamic simulation of a cascade fluidized-bed membrane reactor in the presence of long-term catalyst deactivation for methanol synthesis. *Chemical Engineering Science*, 65, 4239-4249.
- Vakili, R., Eslamloueyan, R., 2012. Optimal design of an industrial scale dual-type reactor for direct dimethyl ether (DME) production from syngas. *Chemical Engineering and Processing*, 62, 78-88.
- Velardi, S.A., Barresi, A.A., 2002. Methanol synthesis in a forced unsteady-state reactor network. *Chemical Engineering Science*, 57, 2995-3004.