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Double-zone methanol reactor: performance comparison with different coolants

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Methanol is one of the most important raw materials in refining and chemical industries with a global demand continuously increasing around the world. Currently, different commercial methanol reactors are available; existing different configurations, described in open literature, are conceived to increase both productivity and yield. Within this context, a reactor configuration with a double-zone on shell-side (double-zone methanol reactor - DZMR) has been proposed in literature, such a DZM reactor can work with different shell-side coolants; yet, relevant performance with different coolants has not been analysed so far.

For this reason, the aim of this work is to compare different coolants water and diathermic oil, both exchanging sensible heat only) fluxed in a small-scale DZMR for methanol production from syngas: specific consumption of coolants is compared at fixed reactor geometry, coolant velocity, gas phase temperatures, and then fixed methanol throughput.

Results show that a lower flow rate of water is needed compared to that of oil. For the same productivity of 38 kg/h of methanol, 129 kg/h of water per kg/h of methanol are required against 165 kg/h of oil per kg/h of methanol. A deeper economic analysis is suggested to compare the profitability related to both coolants in a small-scale DZMR.

* 1. Introduction

Methanol (MeOH) is one of the most important base chemicals, used for the production of formaldehyde (26.9 %), olefins and propylene (19.3 %), methyl-tertiary-butyl-ether and tert-amyl methyl ether (9.7 %), gasoline blending (8.5 %), and biodiesel (3.5 %) (Dalena et al., 2018; Suseno and Umar, 2018). It can be conveniently, and relatively safely, stored and transported (it is a hydrogen carrier). Conventionally, methanol is produced from syngas (CO)/ H2)/ CO2) mixture) obtained by steam hydrocarbons reforming (i.e., steam methane reforming) or hydrocarbons partial oxidation. Since 2020, global methanol consumption has raised to 100 Mt (MethanolPrice, 2024), with the forecast to achieve approximately 150 Mt by 2026 and around 500 Mt by 2050 (Jitrwung et al., 2025).

Different reactor technologies are available for methanol industrial production; major technologies are proposed by process licensors as Air Liquide, Linde, Topsoe, Johnson Matthey, Casale and Toyo Eng. (Manenti and Bozzano, 2016). Such technologies are of shell-and-tube type, shell-and-coil type, shell-and-plate type, with the catalyst allocated either on shell-side or on tube/coil/plate-side. Each technology presents pros and cons and, in any case, each technology is aimed to maximize the chemical conversion and selectivity.

Other reactor configurations have been investigated and proposed in the literature to improve the methanol yield by optimization of cooling, intermediate addition of reactants, flow pattern and product removal (Hastadi et al., 2022). In particular, among them, membrane reactors for water or methanol removal have been studied (Farsi et al., 2012; Bazmi et al., 2024; Samimi et al., 2018): the thermodynamic limitation is overcome and the single-pass carbon conversion is increased. Similarly, fluidized bed reactors with sorbents (e.g. zeolites) to adsorb mainly water (Abashar and Al-Rabiah, 2018) and/or CO (Leonzio, 2020) have been proposed along with the adiabatic and plate water-cooled reactor (APW) suggested by Rahmatmand et al. (2019) for product removal and ensuring an increase of production of 12.2 % compared to the conventional former-Lurgi type. Moreover, in other configurations, reactors and reactants are split into multiple stages to optimise feed concentration and amount of catalyst along the length of the reactor (Hastadi et al., 2022). Also, different gas flow patterns have been investigated in the literature to improve performances (Eksiri et al., 2020; Dehghani et al., 2021).

Within this context, a double-zone methanol reactor (DZMR) has been investigated in Leonzio et al. (2025), where performances of such DZMR, cooled by diathermic oil, are evaluated. In particular, this reactor is of shell-and-tube type, with catalyst inside the tubes and coolant on the shell-side; the shell is divided into two zones in fluid communication each other and located in series along the longitudinal axis of the reactor. Overall, the DZMR configuration allows installing different shell-side thermal conditions on the two zones and it is found that the highest performances are obtained when the first shell-side zone (comprising the entry of reactants) works in non-isothermal conditions and the second shell-side zone (comprising the exit of products) works in isothermal conditions, ensuring a methanol production of 2600 tMeOH/tsyngas and a methanol yield and carbon conversion of 41 %. Specifically, the present paper investigates the performance of a small-scale DZMR with different coolants on the shell-side, such as water (as liquid water) and diathermic oil (at the same geometry, productivity, gas temperature and coolant velocity), through simulations by means of the commercial software Aspen Plus.

* 1. Mathematical modeling
		1. Description of the double-zone methanol reactor

The shell-and-tube type, double-zone methanol reactor object of this study has two shell-side zones arranged in series along the longitudinal axis, as shown in Figure 1; the reactor has a vertical layout, with the first and second shell-side zones respectively placed at top and bottom. The catalyst (Cu/ZnO/Al2O3) is loaded into tubes where the syngas is flowing, while the diathermic oil (Therminol 66) or water, used as coolant, is flowing on the shell-side and is removing the reaction heat. Baffles are also installed on shell-side to support the tubes and make the shell-side flow tortuous.

The two zones are in fluid communication via a peripherical duct surrounding the tube bundle and delimited by the shell. In particular, the peripherical duct has an annular shape and surrounds only the second zone. A second fraction of cooling oil or water, respectively in the oil-cooled or water-cooled configuration, is fed into the peripherical duct: consequently, such a second fraction of coolant flows across only one shell-side zone and undergoes partial heat exchange with the tube-side fluid.

Overall, the syngas and a first fraction of coolant are fed in the first zone and move downstream in a co-current way, respectively on tube- and shell-side. At outlet of the first zone, the first fraction of coolant is mixed with a second fraction of coolant in the peripherical duct, so to form the overall coolant flow rate. The coolant flows downstream in the duct. At the shell bottom, at exit of the peripherical duct, the coolant reverses its direction and flows upwardly in the second shell-side zone in a counter-current direction relative to the gas.



*Figure 1 Conceptual scheme of the double-zone methanol reactor (DZMR)*

* + 1. Modelling of the double-zone methanol reactor

The double-zone methanol reactor is modelled by Aspen Plus software, as shown in Figure 2, as two in-series plug flow reactors, of different tube length, both with 44 tubes with an outside diameter of 25.4 mm. In the first zone the tube length is 0.6 m whereas in the second zone the tube length is 2.4 m so that the DZMR tube has an overall length of 3 m. The shell internal diameter is 260.3 mm, the baffle span is 200 mm and the average longitudinal cross area for the shell-side coolant, between two adjacent baffles, is 0.011 m2. The reaction occurs at 6 MPa(a) on tube-side and the catalyst is characterized by a density and void fraction respectively of 1140 kg/m3 and 0.387 (Bisotti et al., 2022). The reactor is designed to have the optimal yield at the maximum heat transfer rate, minimum pressure drops and dead zones. The process feed is syngas at an overall flow rate of 126 kg/h with a temperature and pressure respectively of 240 °C and 6 MPa(a). The feed stoichiometric number ([H2]-[CO2]/[CO2]+[CO]) is set to 2.0 ([H2] of 73%, [CO] of 9% and [CO2] of 18%) as required for methanol synthesis to have the maximum yield (Fajimi et al., 2024). The major reactions in methanol synthesis are the following (see Eqs. 1-3) (Graaf et al., 1998):

$$CO\_{2}+H\_{2} \leftrightarrow CO+ H\_{2}O ∆H\_{298}^{0}= 41.2 kJ/mol\_{CO\_{2}} (1)$$

$$CO+2∙H\_{2} \leftrightarrow CH\_{3}OH ∆H\_{298}^{0}= -90.7 kJ/mol\_{CO} (2)$$

$$CO\_{2}+3∙H\_{2} \leftrightarrow CH\_{3}OH+ H\_{2}O ∆H\_{298}^{0}= -49.5 kJ/mol\_{CO\_{2}} (3)$$

The adopted kinetic model is that suggested by Graaf et al. (1998) and it is implemented in Aspen Plus as described in Kiss et al. (2016) while, the Soave−Redlick−Kwong (SRK) equation of state (EoS) is considered for the thermodynamic model because it shows a better agreement with experimental data against other potential thermodynamic models (Ostadi et al., 2020).

In the DZMR configuration cooled by oil, the second fraction of the oil is injected into the peripherical duct to cool down the oil exiting the first zone. In particular, the first oil fraction at the inlet and outlet of the first zone has a temperature respectively of 210 °C and 230 °C, while the second fraction of oil is at 215 °C at the inlet of the duct. The mixing between the first fraction and the second fraction in the duct leads to an overall oil flow rate having a temperature of 220 °C at inlet of the second zone. Accordingly, non isothermal shell-side conditions are installed in the first zone. On the contrary, due to a small increase (max 5 °C) of oil temperature, isothermal shell-side conditions are installed in the second zone. The overall heat transfer coefficient is evaluated by considering empirical correlations for both tube and shell sides after fixing the overall oil velocity to 0.2 m/s (Adeyanju and Manohar, 2009). By fixing the reactor geometry and average shell-side velocity, the flow rate of the coolant oil (or water) corresponds to a dependent variable.

In the DZMR configuration cooled by water, it is assumed that sensible heat only is exchanged with the syngas in both the first and second zone and the water pressure is set to operate below the saturation condition. To install in the first zone same operating temperatures of the oil case study (e.g. an inlet and outlet temperature respectively of 210 °C and 230 °C), the water pressure is set to 3.062 MPa(a). Imposing in the first zone the same thermal duty exchanged in the oil case study, the overall heat transfer coefficient is evaluated and required first fraction coolant flow rate is obtained in Aspen Plus through a design specification. For the second zone, a second fraction of cold water at 215 °C is added into the annular duct so to have an overall average water velocity of 0.2 m/s in the second zone, as for the oil case study. The overall heat transfer coefficient is obtained by imposing the same heat exchanged in the oil-based solution. At the outlet of the second zone, the cooling water is at a temperature of 220 °C.



*Figure 2 DZMR in Aspen Plus environment: A) diathermic oil is used as a coolant; B) water is used as a coolant*

* 1. Results and discussion

Firstly, it is interesting to report the calculated duty exchanged in both zones when diathermic oil is used as coolant: 15.28 kW and 15.95 kW are released in the first and second zone respectively. These data are in agreement with the reference conditions reported in Leonzio et al. (2025). From these values, the overall heat transfer coefficients relative to the first and second zone of the water-cooled reactor configuration can be inferred: these coefficients are respectively equal to 149 W/m2K and 169 W/m2K. Such overall heat transfer coefficients allow installing gas temperatures as those installed in the oil case study and are in agreement with literature (Bisotti et al., 2022; Chen et al., 2011).

Under these operating conditions, the computational model allows verifying that, for both oil and water case studies, the temperature peak achieved by process gas in the first zone is in all cases lower than the maximum value of 300 °C, beyond which sintering and deactivation phenomena of the catalyst may occur (Twigg et al., 2003).

Figure 3 and Figure 4 show the flow rate profiles calculated or each process gas species, related to the first (Figure 3A and Figure 4A) and second (Figure 3B and Figure 4B) zone, respectively for the oil-cooled and water-cooled reactor. The profiles given in Figure3 and Figure 4 for the oil-cooled and water-cooled DZMR are the consequence of same gas temperatures installed in both zones. In particular, for both case studies, in the first zone there is a continuous production of methanol and consumption of CO and H2; H2O production is strongly increasing along the tube length until the temperature peak is reached, after that along the tube length the H2O is decreasing due to the water gas shift reaction. It is to be underlined that the CO2 decreases along the tube till to the temperature peak is reached, then the CO2 increases due to the water gas shift reaction. are supported by the work of De Maria et al. (2013). In the second zone, the flow rates of CO, CO2 and H2 are decreasing along the tube length while CH3OH and H2O flow rates are increasing. The gas temperature profile related to the second zone is monotonic: because no discontinuity points in the profiles arise.

B)

*Figure 3 Flow rate profiles along the oil-cooled DZMR length: A) first zone; B) second zone*

*Figure 4 Flow rate profiles along the water-cooled DZMR length: A) first zone; B) second zone*

A comparison of coolant flow rates for oil-based and water-based reactor configurations is reported in Table 1. As said, the model is based on exchange of sensible heat only (i.e., no water boiling). For the same amount of methanol production (e.g. 38 kgMeOH/h), a lower amount of cooling water is needed compared to that of oil. Specific consumption for water and oil is respectively of 129 kg/h per kg/h of MeOH and 165 kg/h per kg/h of MeOH, corresponding to a difference of 21% between the two coolants).

The lower consumption of water, especially in the first zone of the reactor, is due to higher specific heat capacity of water compared to that of oil at a fixed amount of exchanged heat (e.g. at 10 °C the specific heat capacities of oil and water are respectively of 1528 J/kgK and 4200 J/kgK).

Table 1: Comparison of DZMRs cooled by diathermic oil and water (exchange of sensible heat only)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Coolant  | Diathermic oil | Water |  |  |
| Methanol production (kg/h) | 38 | 38 |  |  |
| Coolant consumption (kg/h) | 6263 | 4888 |  |  |
| Specific cooling consumption (kg/kgMeOH) | 165 | 129 |  |  |
| Overall released heat (kW) | 31.23 | 31.23 |  |  |

Results show that for a small-scale DZMR, the water-based configuration requires a coolant flow rate lower than the oil-based configuration by 20% approx. Such a difference can be important for selecting the proper coolant and optimizing the operating expenditure of a small-scale methanol synthesis unit, as for local or on-site small methanol productions. However, for the comparison given in Table 1, it must take into account that the oil-based DZMR works with a low shell-side operating pressure (0.3 to 0.5 MPa abs), whereas the water-based DZMR works with a high shell-side operating pressure (>3 MPa abs). This may have an important impact on capital costs of a small-scale methanol unit.

It is important to underline that, in this study, a water-based DZMR with boiling water, as done for most part of industrial methanol reactors, is not considered due to the small-scale unit.

Finally, as a continuation of the present study, a detailed economic analysis should be done to evaluated the methanol production cost and the economic breakeven point of the synthesis unit for the water-based and the oil-based DZMR configurations.

* 1. Conclusions

In this work, the process performance of an innovative methanol reactor (e.g. a double-zone methanol reactor - DZMR) is analyzed for two different shell-side coolants, such as diathermic oil and water, exchanging sensible heat only. Given the reactor geometry, coolant temperatures, average coolant velocity and methanol production, the flow rate of the two different coolants is calculated. Results show that, for a small-scale DZMR, cooling water requires a flow rate of 21% lower than the required flow rate of cooling oil, for the same methanol production, which may lead to a lower operating expenditure. However, use of water as a coolant requires a higher operating pressure on shell-side. A subsequent, detailed economical comparison between the water-based and oil-based DZMR configurations may reveal the best coolant for small-scale methanol synthesis units.

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References

Abashar, M., Al-Rabiah, A., 2018. Investigation of the efficiency of sorption-enhanced methanol synthesis process in circulatingfast fluidized bed reactors. Fuel Process. Technol. 179, 387–398

Adeyanju, A.A. and Manohar, K., 2009. Theoretical and Experimental Investigation of Heat Transfer in Packed Beds, Research Journal of Applied Sciences 4 (5) 166-177

Bazmi, M., Gong, J., Jessen, K., Tsotsis, T. 2024. Waste CO2 capture and utilization for methanol production via a novel membrane contactor reactor process: Techno-economic analysis (TEA), and comparison with other existing and emerging technologies, Chemical Engineering & Processing: Process Intensification 201, 109825

Bisotti, F., Fedeli, M., Prifti, K., Galeazzi, A., Dell’Angelo, A., Manenti, F., 2022. Impact of Kinetic Models on Methanol Synthesis Reactor Predictions: In Silico Assessment and Comparison with Industrial Data Ind. Eng. Chem. Res. 61, 2206−2226

Chen, L., Jiang, Q., Song, Z., Posarac, D. 2011. Optimization of Methanol Yield from a Lurgi Reactor. Chem. Eng. Technol. 34,817−822

Dalena, F., Senatore, A., Basile, M., Knani, S., Basile, A., Iulianelli, A. 2018, Advances in Methanol Production and Utilization, with Particular Emphasis toward Hydrogen Generation via Membrane Reactor Technology. Membranes, 8, 98

De María, R., Díaz, I., Rodríguez, M., Sáiz, A. 2013. Industrial Methanol from Syngas: Kinetic Study and Process Simulation, International Journal of Chemical Reactor Engineering, 11(1) 469–477

Dehghani, Z., Rahimpour, M.R., Shariati, A., 2021. Simulation and multi-objective optimization of a radial flow gas-cooled membrane reactor, considering reduction of CO2 emissions in methanol synthesis, Journal of Environmental Chemical Engineering 9, 104910

Eksiri, Z., Mozdianfard, M.R., Mirvakili, A., Rahimpour, M.R., 2020. Two-dimensional modeling investigation of themodern methanol plate reactors, Chemical Engineering Research and design, 162, 212-227.

Fajimi, L.I., Chrisostomou, J., Oboirien, B.O., 2024. A techno economic analysis (TEA) of a combined process of torrefaction and gasifcation of lignocellulose biomass (bagasse) for methanol and electricity production, Biomass Conversion and Biorefnery, 14:12501–12516

Farsi, M., Jahanmiri, A., 2012. Dynamic modeling of a H2O-permselective membrane reactor to enhance methanol synthesis from syngas considering catalyst deactivation, J. Nat. Gas Chem. 21, 407–414.

Graaf, G. H., Stamhuis, E. J., Beenackers, A. A. C. M. 1988. Kinetics of Low-Pressure Methanol Synthesis. Chem. Eng. Sci. 43, 3185−3195.

Hastadi, K.F., Bhatelia, T., Patel, J., Webley, P.A., Pareek, V.K., Shah, M.T., 2022. Packed bed methanol reactor with flow diverters, Chemical Engineering & Processing: Process Intensification 175, 108916

Jitrwung, R., Krekkeitsakul, K., Teerananont, N., Thongyindee, P., Patthaveekongka, W., Areeprasert, C., 2025. Utilization of CO2 and recycling of methanol Residue from the refining process for production of Bio-Methanol, Carbon Resources Conversion 8, 100302

Kiss, A.A., Pragt, J.J., Vos, H.J., Bargeman, G., de Groot, M.T., 2016. Novel efficient process for methanol synthesis by CO2 hydrogenation, Chemical Engineering Journal 284, 260–269

Leonzio, G. 2020. Analysis and optimization of a methanol reactor with the adsorption of carbon monoxide and water, Renewable Energy, 146, 2744-2757

Leonzio, G., Manenti, G., Bozzini, M.M., Baratti, R., Manenti, F., 2025, Analysis of a methanol synthesis reactor operating in non-isothermal cooling conditions, to be submitted to Fuel Journal.

Manenti, F., Bozzano, G., 2016, Efficient methanol synthesis: Perspectives, technologies and optimization strategies, Progress in Energy and Combustion Science, 56, Pages 71-105

MethanolPrice, 2024, available at: <https://www.methanol.org/methanol-price-supply-demand/>, accessed on 9.10.2024

Ostadi, M.; Paso, K. G.; Rodriguez-Fabia, S.; Øi, L. E.; Manenti, F.; Hillestad, M. 2020. Process Integration of Green Hydrogen: Decarbonization of Chemical Industries. Energies, 13, 4859.

Rahmatmand, B., Rahimpour, M.R., Keshavarz, P., 2019. Introducing a novel process to enhance the syngas conversion to methanol over Cu/ZnO/Al2O3 catalyst, Fuel Processing Technology 193,159–179

Samimi, F., Karimipourfard, D., Rahimpour, M.R., 2018. Green methanol synthesis process from carbondioxide via reverse water gas shift reaction in a membrane reactor, Chemical Engineering Research and design, 140, 44–67

Suseno, T., Umar, D.F. 2021 Prospect of coal-based methanol market in Indonesia, IOP Conf. Ser.: Earth Environ. Sci. 882 012073

Twigg, M.V., Spencer, M.S., 2003. Deactivation of copper metal catalysts for methanol decomposition, methanol steam reforming and methanol synthesis, Topics in Catalysis 22, 3–4