

COMPUTER-BASED INTENSIFICATION OF METHANOL SYNTHESIS PROCESS COMPRISING PLASMA REACTORS AND MEMBRANE REACTIVE SEPARATORS

F. Kapon^{1,2}, E. Delikonstantis², S.A. Theofanidis², A. Georgiadis², Georgios D. Stefanidis^{1*}

¹School of Chemical Engineering, National Technical University of Athens, Athens, Greece

²AristEng S.à r.l., Luxembourg City, Luxembourg (*gstefani@mail.ntua.gr)

Abstract

This work presents a complete and intensified conceptual process model for methanol (MeOH) production solely from steel mill off-gases, employing plasma reactors and membrane reactive separators (aka membrane reactors). Coke Oven Gas (COG) and Blast Furnace Gas (BFG) streams produced in integrated steel mills serve as feedstock in the process simulations. The design capacity is set by the hourly production of COG and BFG of a small size steel mill. CO₂ is captured from BFG upstream in a conventional amine-based absorber, followed by a plasma-assisted reactor where CO₂ is split to CO. Further downstream, CO is converted to MeOH into a catalytic membrane reactor where in-situ water removal enhances MeOH production. The reactor includes two concentric membranes, one for water (vapor) removal and the other for selective H₂ addition to the reaction zone. The amount of H₂ required for MeOH synthesis is reclaimed from COG. To intensify the H₂ reclaim, COG is firstly fed in a membrane reactor where catalytic partial oxidation of CH₄ to H₂ takes place; CH₄ is also a major component of COG. This reactor also includes two membranes, one for selective O₂ addition in the reaction zone and one for selective H₂ removal from the reactant mixture. The former is necessary to partially oxidize CH₄, sufficing the energy requirements for the endothermic reforming reactions. The process model is simulated using the Aspen Plus[®] V11 process simulator while membrane reactors are designed and simulated using the mathematical environment of MATLAB[®] to increase flexibility and ensure a novel, tailor-made as well as fit-for-purpose approach. Available experimental data is used to simulate the plasma-assisted CO₂ splitting unit.¹ The performance of the global process model is optimized as a whole and the operating window that intensifies MeOH productivity withing reasonable and feasible reactor design aspects is determined.

KEY WORDS: Process intensification, Conceptual process modeling, Optimization, Methanol, Steel mill off-gases valorization

INTRODUCTION

As the anthropogenic CO₂ emissions steadily rise (37.5Gt in 2022)² the necessity of capturing and utilizing CO₂ released from the industrial sector becomes more pressing. This particularly applies to steelmaking processes which account for ~11% of the total CO₂ emissions globally emitted.³ CO₂ conversion into value-added products can offer an extra source of revenue to carbon emitters and justify the investment in treating the exhaust gases.⁴ MeOH is among the top produced organic chemicals due to its broad range of applications, from building block of other chemicals to alternative fuel or fuel additive for increasing octane number.⁵ Current MeOH production is mostly reliant on fossil sources, thus it is highly carbon intensive⁵. Coal gasification and natural gas reforming are the main routes for generating syngas (CO and H₂) which reacts over a commercial Cu/ZnO/Al₂O₃ catalyst to yield MeOH.⁵ Direct CO₂ hydrogenation to MeOH suffers from catalyst deactivation due to water formation.⁵ Therefore, the two-step CAMERE process with prior CO₂ to CO conversion via reverse water gas shift (RWGS) has been proposed and demonstrated at pilot scale of 100 kg d⁻¹ MeOH capacity.⁶ Intensification of MeOH throughput has been investigated via deploying membrane reactors or catalytic sorbents which can shift the chemical equilibrium through in-situ water removal

(ISWR),⁷ while protecting the catalyst from deactivation. Further GHG emissions reduction can be attained by running the process with renewable electrical energy. For instance, plasma-driven CO₂ splitting has been successfully demonstrated at lab scale with a chemical looping scheme where O radicals are removed from the reaction zone by reacting with mixed metal oxides (i.e., CeO₂/Fe₂O₃), thus attaining 60% instantaneous CO₂ conversion and 29% average conversion.¹

METHODOLOGY

The conceptual plant-process design of this work, uses plasma-driven CO₂ splitting as the core of the process (purple box of Figure 1). CO₂ is captured from BFG upstream in a two-column liquid amine absorption unit and it is converted into CO. For the CO₂ absorption unit, the reaction model generated by ASPEN TECH was utilized and the whole system was tailored and optimized to the particular incoming flue gas stream from BFG (orange box of Figure 1). Both absorption unit and electrified plasma reactor were simulated in Aspen Plus. The latter is solely based on experimental data from Delikonstantis et al research.¹

The required H₂ for the downstream MeOH synthesis is simulated as a product of autothermal CH₄ reforming. The process is designed in an adiabatic membrane reactor following a one-dimensional (1-D) plug-flow non-isothermal model. The reaction scheme implemented in the simulations is the one proposed by De Groote and Froment⁸. A set of 4 reactions describes the chemical process: 1) Total oxidation of CH₄, 2) Partial steam CH₄ Reforming, 3) Water Gas Shift reaction and 4) Total Steam CH₄ Reforming. The Langmuir–Hinshelwood type reaction rate equations are followed for CH₄ reforming with Ni/Al₂O₃ catalyst, as proposed by Xu and Froment,⁸ and for CH₄ oxidation by Trimm and Lam using porous Pt/Al₂O₃ as catalyst.⁸ The reactor configuration includes three coaxial zones that are separated by two membranes (green box of Figure 1). Atmospheric air is fed to the central zone to supply oxygen (O₂) to the middle layer where CH₄ partial oxidation and reforming takes place. The two zones are separated by a perovskite oxygen-ion conducting permeable dense membrane La_{0.2}Ba_{0.8}Fe_{0.8}Co_{0.2}O_{3-δ}⁹ which is only permeable to O₂. Then, the pure O₂ stream comes in contact with the COG stream in the intermediate reaction zone. H₂O is also introduced in the intermediate zone for the reforming reactions. The required energy is provided by the CH₄ oxidation reaction along the entire length of the reactor, together with the energy carried by the pre-heated feed supply. From the reaction zone the produced H₂ can permeate the annular Pd-Ag-based membrane.

A similar reaction model approach is developed for MeOH synthesis following the mechanism proposed by Graff with a CuO/ZnO/Al₂O₃ catalyst.¹⁰ The system is simulated with a 1-D plug-flow non-isothermal model including three main chemical reactions: 1) CO hydrogenation, 2) reverse water-gas shift (RWGS), and 3) CO₂ hydrogenation. The MeOH synthesis reactor unit entails a jacketed dual-membrane reactor (yellow box in Figure 1), where annular membrane layers enable H₂ permeation and H₂O vapor removal, while external cooling is applied to control the operating temperature. H₂ produced by the upstream autothermal CH₄ reforming reactor, is fed to H₂ transfer zone of the MeOH membrane reactor together with a carrier gas (N₂), and it selectively diffuses through Pd-based membrane into the reaction zone, where it reacts with CO and CO₂ from the plasma reactor. The generated H₂O vapor is removed from the reaction zone via a hydroxy-sodalite membrane (H-SOD), and it reaches the axial zone of the tubular reactor where it is continuously displaced by a flow of sweep gas (i.e., N₂). Cooling water circulates in the reactor shell, to remove heat produced by the exothermic reactions in the catalytic tube. Owing, to the membrane-assisted H₂O-MeOH separation,

a simple physical separation of the liquid MeOH from the unreacted gases is designed at the reactor outlet.

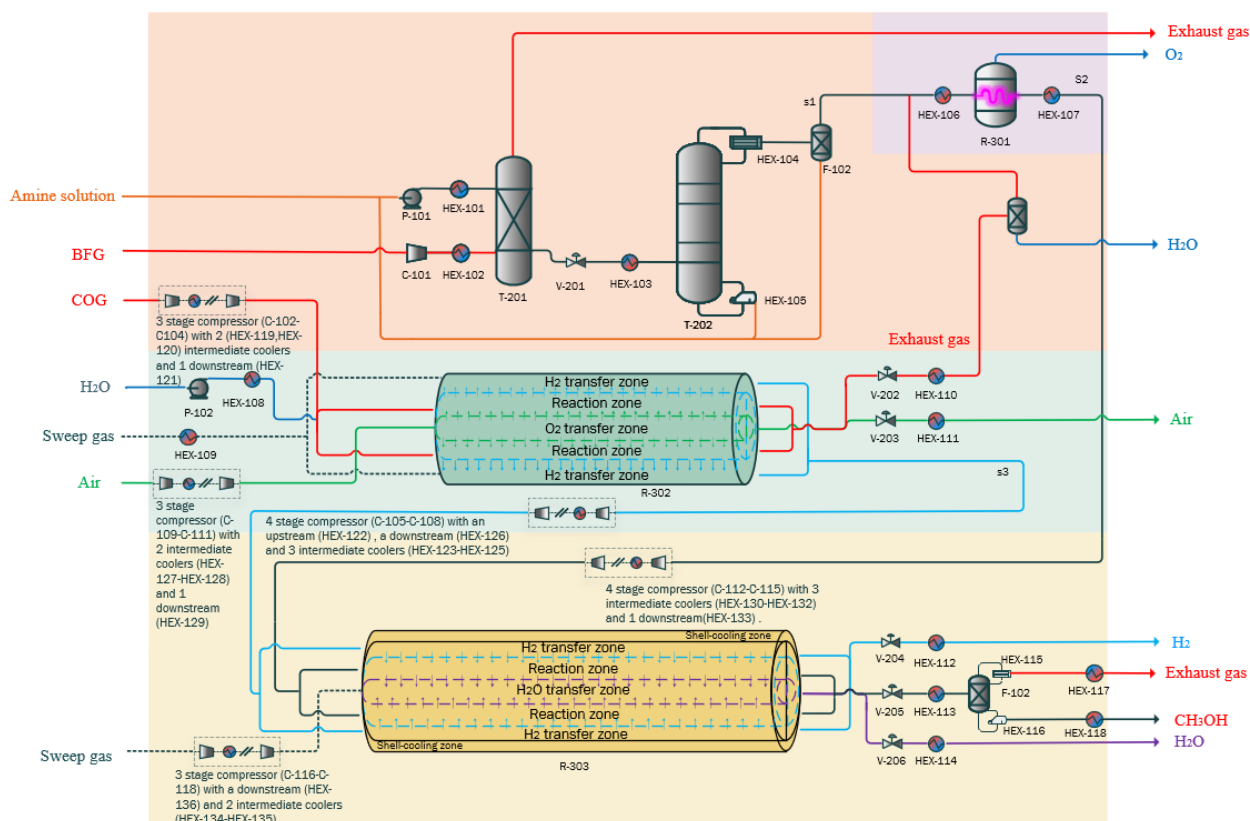


Figure 1: Process flow diagram of intensified MeOH production via plasma CO₂ splitting and membrane reactors: 1) CO₂ capture unit-orange box, 2) Partial oxidation of CH₄ in a membrane reactor- green box, 3) CO₂-to-CO conversion in a plasma-assisted reactor- purple box 4) MeOH synthesis in a membrane reactor- yellow box, Streams: Blast Furnace Gas-BFG, Coke Oven Gas-COG

For the one-dimensional mathematical model development, energy and mass balances of the three different zones of the membrane reactors are based on the following assumptions: 1) Radial temperature and concentration gradients are not considered in the simulations; 2) Carbon deposition on the catalytic surface is ignored, resulting in no catalyst deactivation (CH₄ reforming reactor); 3) Internal and external mass transfer resistance is ignored due to small particle size of the catalyst and small Damköhler number, respectively; 4) The membrane reactor is simulated in adiabatic and isobaric conditions (CH₄ reforming reactor); 5) The gas mixture is an ideal gas; 6) The membranes are considered to be completely selective; 7) Constant bed porosity; 8) Adjusted Soave–Redlich–Kwong (SRK) equation used for fugacity coefficients calculations (MeOH reactor); 9) Effectiveness factor: 0.6 (MeOH reactor).

RESULTS AND CONCLUSION

Since the CO₂ absorption unit is a well-established technology and the plasma reactor is solely based on experimental results the optimization procedure was centred on membrane reactors. Each design parameter was thoroughly chosen to serve dual objectives: maximizing CH₄, CO&CO₂ conversion and ensuring high product yields. Adjustments on the examined parameter ranges (inlet temperature, H₂O/CH₄ molar ratio (CH₄ reforming reactor), membrane diameters, operational pressure) were based on literature values, aligned with the reactive systems and membrane

performance. Additionally, the analysis revealed that (higher) alterations to certain parameters yielded negligible impacts on reactor performance, underscoring the attainment of an optimal performance (Air flow rate (CH₄ reforming reactor), H₂O/CH₄ molar ratio (CH₄ reforming reactor), Operational pressures, Inlet temperatures (MeOH reactor)).

Partial Oxidation of Methane in a dual membrane reactor

The designed reactor meets the required specifications of partial off-gasses valorisation of a commercial steel-mill industry with a length of 12 m and a perovskite-membrane diameter of 0.72 and Pd/Ag 1.78 m respectively.

The inlet temperature of the different zones of the adiabatic reactor is assumed to be the same. For this case, the temperature of 950 K is selected, at which the performance of the system in terms of both H₂ separation and CH₄ conversion typically reached a plateau. Air flow rate was set to 150 mol s⁻¹ while H₂O/CH₄ ratio was set to 2.5 respecting also the criteria. The central reactor channel hosting the O₂ and the annular reaction zone are operated at the same pressure, while the outer H₂ transfer membrane is at atmospheric pressure to provide a driving force for the H₂ permeance. An intermediate pressure of 25 bar is selected, as varying the operating pressure within the valid range does not notably impact the reactor outlet. Finally, the membrane's diameter selection was performed by defining the gas velocity as given by rule of thumbs while upholding high component permeability and reactor performance. The same procedure was also applied to size the membranes for the MeOH reactor.

The simulated axial flow rate profiles of the different species involved in the reforming process in Figure 2. CH₄ is almost entirely converted within the first 2/3 of the reactor length, hence CO₂ production shows a plateau in the final section. Similarly, most CO produced in the reforming reaction is converted before reaching the reactor outlet due to water gas shift reaction. Therefore, the gas flow exiting the reaction zone of the membrane reactor comprises mostly H₂O and CO₂. H₂ transfer is maximum at the beginning of the reactor, where the mass transfer driving force is the highest, and it substantially decreases in the final section of the reactor, where complete CH₄ conversion limits H₂ productivity and in turn its transfer. Hence, the H₂ throughput from the reforming reactor is 0.58 kg s⁻¹, and ~28% of the total energy required for the process is provided by CH₄ oxidation, whilst the remaining is supplied by the enthalpy of the inlet streams. Ultimately, the overall system is mainly endothermic: ~94 mol% of the CH₄ feed is consumed during the reforming reaction (endothermic), and ~6 mol% is consumed during the partial oxidation (exothermic).

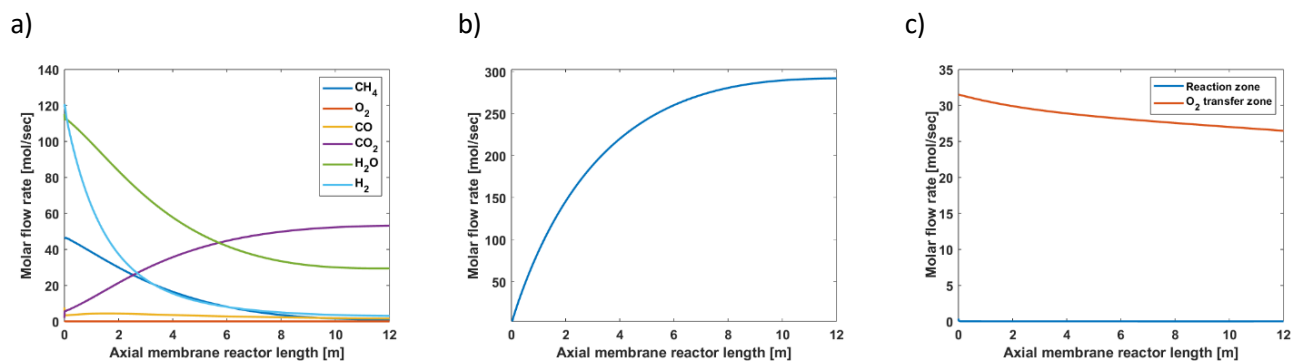


Figure 2: a) Flow rate profiles in the reaction zone of the partial oxidation of CH₄ membrane reactor b) H₂ flow rate profile in its transfer zone c) O₂ flow rate profiles in the reaction and O₂ transfer zone

Methanol synthesis in a dual membrane reactor

In order to meet the MeOH production requirements, the intensified reactor has a length of 50 m and the H-SOD and the Pd-based membranes have diameters of 0.90 m and 1.15 m, respectively.

The inlet temperature of the reaction zone was set at 563 K, the upper limit of the valid temperature range, sustaining a slightly higher yield. The feed H₂ stream coming from the CH₄ reforming section is heat up to 475 K after the compression unit. The effect of the specific inlet temperature is almost negligible. The inlet temperature to the H₂O transfer zone is set at 475 K, according to literature values.¹⁰ The synthesis reaction set is commonly performed at 50-100 bar¹¹, however, mechanical stability of the membrane system is key in this configuration, and the simulation is based on reaction pressure of 80 bar, which corresponds to MeOH yield higher than 40%. The H₂ transfer zone is designed to operate at the same pressure, whereas the H₂O permeation membrane operates at 40 bar to enhance mass transfer from the reaction zone, while minimizing mechanical instability of the membrane layer.

The resulting mass flow rates of the individual species in the reaction unit and other results are reported Figure 3. The 50 m long membrane reactor can attain 61.9% CO and 19.4% CO₂ conversion with 44.3% MeOH yield. Nonetheless, in the last 5 m the hydrogenation reaction slows down and a flatter trend is observed for the flow rates of both reactants and products. The pressure difference between the reaction zone and the internal H₂O removal layer drives a linear H₂O transfer. The high permeability of the Pd-based H₂ membrane causes the steep drop in H₂ flow rate in the outer reactor layer, and the H₂ flow rate steadily decreases in the reaction zone after an initial surge due to H₂ production via water gas shift. The reactor product stream consists of 97.3% MeOH and 2.7% H₂O, while the unreacted gases (i.e., CO, CO₂, and H₂) are physically separated. The reactor temperature is mostly affected by the exothermicity of the reaction and the mass transfer between reactants and products in the different layers. H₂O vapor produced in the reaction zone is constantly transferred to the inner zone, where the temperature shows a constant increase. Conversely, the temperature in the outer layer hosting the H₂, decreases along the axial direction of the reactor due to external cooling and H₂ depletion in favour of the reaction zone.

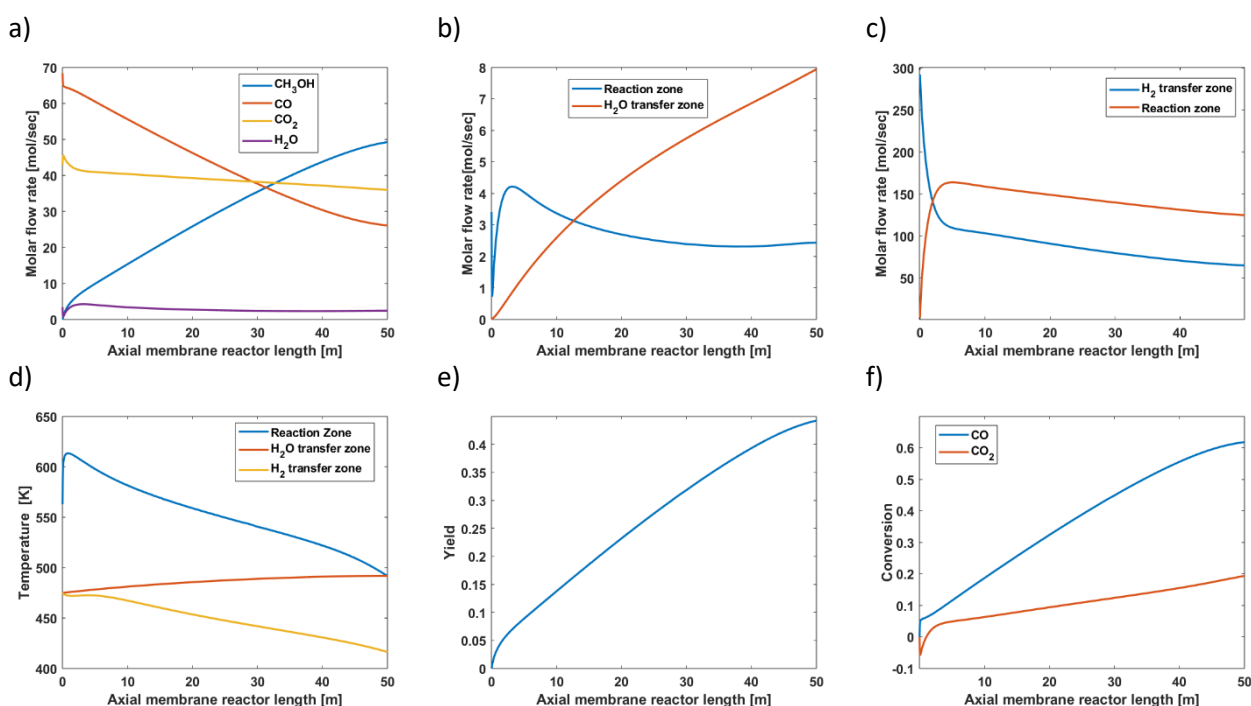


Figure 3: a) Flow rate profiles in the reaction zone d) Flow rate profiles of H₂O in the reaction zone and its transfer zone c) Flow rate profiles of H₂ in the reaction zone and its transfer zone d) Temperature profiles e) MeOH yield profile f) Conversion of CO and CO₂

This study proposes an intensified MeOH plant that can be deployed to valorise the flue gases of a steel making plant. CO₂ capture from a BFG stream is conducted via liquid amine absorption with overall capture efficiency of ~99%. The reclaimed CO₂ is split in plasma reactor with 60% conversion, where the following MeOH synthesis is conducted in a dual-membrane reactor with ISWR. H₂ is fed in the MeOH reactor, originating from COG, and further produced via catalytic CH₄ steam reforming (from CH₄ present in COG) in an adiabatic dual membrane reactor. The latter exploits selective permeation of the membrane layers to intensify O₂ supply from air (for CH₄ partial oxidation) and H₂ separation from the products. The energy required for the endothermic reforming process is supplied in-situ by the exothermic partial oxidation. The unit attains complete CH₄ conversion while almost all of the H₂ is transferred to the outer layer. The MeOH synthesis reactor performs ISWR via a H-SOD membrane that allows shifting the chemical equilibrium according to Le Chatelier principle, corresponding to MeOH productivity of ~1.6 kg·s⁻¹ (44.3% MeOH yield). Heat integration through pinch point analysis was also carried out to minimise utility requirements. The proposed plant design can represent a blueprint for separation-free processes deployed to integrate larger plants where copious waste streams can be upgraded.

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