Modelling and Optimization of an intensified water electrolysis integrated tri-reforming coupled methanol production process

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Abstract. Mitigating greenhouse gas emissions (GHG) is a crucial global endeavour due to its significant impact on climate change. Fossil fuel fired power plant-based CO_2 emissions to fuel conversion can counter GHG emissions while also mitigating fuel shortage. CO_2 to methanol conversion pathway via the tri-reforming (TR) process is a useful valorization strategy which can achieve the aforementioned goals. The TR process primarily utilizes steam reforming of methane (SRM), dry reforming of methane (DRM) and partial oxidation of methane (POX) to convert waste CO_2 to syngas using co-reactants such as methane, oxygen and steam and this syngas can be converted to methanol. In this paper, the water electrolysis (WE) integrated tri-reforming coupled methanol production (TRMP) process has been advanced via novel process modifications and optimized. In this process, O_2 and H_2 from the WE unit are supplied to the tri-reforming (TR) and methanol production (MP) units respectively. The following process modifications were implemented: (a) throughput of the WE unit is increased and excess oxygen is routed to support the combustion of the purge stream (b) CO_2 flow from the combusted purge stream is sent to the TR reactor as recycle, and (c) the excess electrolyzer hydrogen counters the excess CO_2 load of the process due to recycling. Process optimization has been executed using Component object model (COM) interface aided Aspen Plus-Python integration leading to implementation of the differential evolution algorithm. Results clearly demonstrated that the implemented process modifications worked synergistically to bring significant improvements in process metrics, namely, the CO_2 valorization and profit generating potential of the process.

1 Introduction

Anthropogenic GHG emissions are significantly contributing to climate change today [1]. CO_2 is one of the major greenhouse gases. Olah *et al.* [2] proposed methanol economy where they suggested methanol and DME (dimethyl ether) as safer energy carriers than hydrogen which is highly volatile and difficult to handle. Thus, in this paper, CO_2 (sourced from a power plant running on fossil fuel) to methanol conversion pathway (using green

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hydrogen and natural gas) has been considered. Song and Pan [3] proposed the concept of the TR process to convert CO_2-rich flue gas from a power plant (running on fossil fuel) into syngas over a nickel-based catalyst. The TR process utilizes CH_4 as a co-reactant to convert CO_2 (via DRM reaction, Equation 1), H_2O (using SRM reaction, Equation 2) and O_2 (using POX reaction, Equation 3) (main reactions) to syngas which can be utilized for methanol production [4]. Zhang *et al*. [5] designed and optimized a TRMP process to valorize flue gases (originating from a conventional natural gas-fired power plant) to methanol. Ren *et al*. [4] conducted experiments on the TR process operating at higher pressures using a Nickel based catalyst to achieve close to thermodynamic equilibrium conversions. Dwivedi *et al*. [6] proposed integration of a WE unit and a power plant (operating on oxy-fuel combustion technology; led to reduced N_2 content in flue gas which increased the partial pressure of reactants) to the conventional TRMP process to improve the process metrics. Li *et al.* [7] conducted an experimental study proposing WE integrated oxidative dry reforming process that involves DRM and POX occurring in the plasma catalytic reforming (PCR) unit for syn-gas production (high energy efficiency while avoiding catalyst damage via sintering and coking) over a Ni-based catalyst. Shi *et al*. [8] improved the WE integrated TRMP process by two primary modifications: (i) utilizing captured CO_2 (using amine absorption technology) in lieu of flue gases arising from an oxy-fuel combustion based power plant, (ii) the WE unit output oxygen was routed to the TR process to promote the POX reaction and reducing energy requirements of the TR reactor. We have advanced the original process of Shi *et al*. [8] with the following process modifications: (i) increasing the throughput of the WE unit and using the additional O_2 output to combust the combustible components of the process's purge stream, (ii) recycling the CO_2 of the combusted purge stream to the TR reactor and corresponding H_2 production from the WE unit routed to the MP unit to counter the increased CO_2 load, and (iii) process optimization has been conducted using Differential evolution algorithm on the process using Aspen plus-python integration achieved through COM.

2 Process flow description and modification

2.1 Process A (base case)

This section describes our base case (Process A) i.e., Shi et al. [8] process, which is WE integrated TRMP process aimed at conversion of CO_2 (captured from flue gases via amine absorption) to methanol. Figure 1(a) shows the process flow diagram (PFD) of process A. PENG-ROB property method was employed for thermodynamic property prediction for this process [5]. The captured CO_2 feed stream (cost: 138.056 USD/ton, inflated from a cost of 86.4 USD/tonne in 2013 [8] for year 2024, inflation rate: 4.35%) is obtained via separation from coal fired power plant-based flue gases using amine absorption technology. A pre-reformed natural gas stream (devoid of C_{2+} hydrocarbons and methane enriched) is fed to the TR reactor along with steam (excess steam from pre-reformer product gases shown as a separate stream for clarity) and the captured CO_2 stream. Note that, the composition and flowrate of natural gas feed stream is same as the process of Shi et al. [8]. Oxygen, coming from the WE unit, is also sent to the TR reactor. The produced syngas is then dehydrated, mixed with H_2 (coming from the WE unit), compressed and sent to the MP reactor. The produced methanol is separated from

unconverted gases (using a flash separator) which are recycled and part of it is combusted (using air and utilized to preheat the feed streams) and then purged to avoid any inert build-up. The separated impure methanol stream is then purified using the purification unit (flash separator and distillation column).

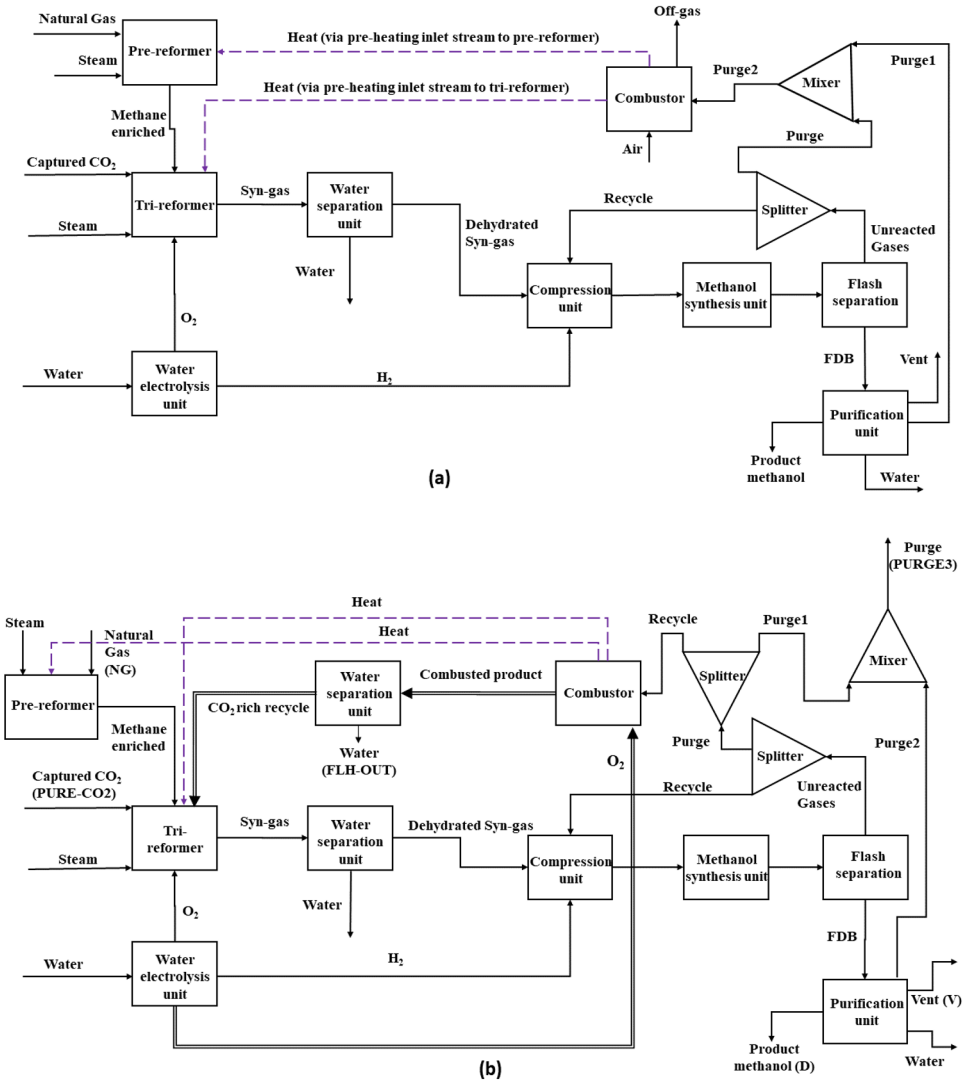

Fig. 1. **(a)** PFD of the WE integrated TRMP process (process A) [8], **(b)** PFD of the improved WE integrated TRMP process (process B) (with process modifications implemented as an improvement to process A, as described in Section 2.2).

2.2 Process A^{Opt} and B (improved processes)

Process A is optimized to create Process A^{Opt} (refer sections 3.1 and 3.2 for detailed optimization procedure). Several process modifications were made to the original process

(process A) (Figure 1 (a)) to create process B (Figure 1 (b)). Firstly, the production rate of the WE unit was increased to route the additional amount of oxygen produced to combust purge streams in the combustor in place of air in process A. This oxygen stream is sourced from a WE unit where co-produced hydrogen is supplied to the MP reactor. The utilization of oxygen for purge stream combustion eliminated the nitrogen content of the purge stream, enabling its recycling to the tri-reformer. This is in contrast to process A, where air was utilized for the combustion of the purge stream which generated nitrogen-containing flue gases which were unfit for recycling. Note that, the recycling of the combusted purge stream was done (after purging a small part of it) to the TR process after separation of water via flash separator leading to it being primarily CO_2. The additional co-produced hydrogen by the WE unit is sent to the MP unit via increased throughput of the stream. This countered the additional CO_2 load of the overall process due to CO_2 recycling which in turn enhanced the CO_2 conversion potential of the process (also refer Section 4.2 for additional details). The modelling and simulation of these processes was carried out using process simulator Aspen Plus V11. Subsequently, these processes were optimized as described in the sections ahead.

2.3 Process reactors: pre-reforming and tri-reforming (TR) reactors

The pre-reforming reactor primarily converts non-methane (ethane and higher hydrocarbons) in the natural gas stream to methane using steam input. The TR reactor produces syngas from a mixture of CO_2, O_2, H_2O and CH_4. The main TR reactions were DRM (Equation 1), SRM (Equation 2), and POX (Equation 3) and some side reactions (Equations 4-9) [3,4]. The pre-reforming and TR reactors were operated at 1046°C, 2400 kPa and 550°C, 2619 kPa in this study [8]. The TR reactor was simulated using an equilibrium reactor model (RGibbs) which calculates equilibrium composition by Gibbs free energy minimization [5].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \; [\Delta H^\circ = 247.3 \; kJ/mol] \quad [1]$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \; [\Delta H^\circ = 206.3 \; kJ/mol] \quad [2]$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \; [\Delta H^\circ = -35.6 \; kJ/mol] \quad [3]$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \; [\Delta H^\circ = -880 \; kJ/mol] \quad [4]$$

$$CH_4 \leftrightarrow C + 2H_2 \; [\Delta H^\circ = 74.9 \; kJ/mol] \quad [5]$$

$$2CO \leftrightarrow C + CO_2 \; [\Delta H^\circ = -172.2 \; kJ/mol] \quad [6]$$

$$C + CO_2 \rightarrow 2CO \; [\Delta H^\circ = 172.2 \; kJ/mol] \quad [7]$$

$$C + H_2O \leftrightarrow CO + H_2 \; [\Delta H^\circ = 131.4 \; kJ/mol] \quad [8]$$

$$C + O_2 \rightarrow CO_2 \; [\Delta H^\circ = -393.7 \; kJ/mol] \quad [9]$$

2.4 Process reactors: methanol production (MP) reactor

The MP reactor was modelled using the reactor module RPlug (plug flow reactor model, operated isothermally) with the MP reactions (Equations 10 and 11) implemented

via a Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model (utilized Aspen Plus specific kinetic parameters [9]). The reactor model used in this study was validated with experimental results in our previous study [10] and we have utilized the kinetic expressions, parametric values of the kinetic model, catalyst properties mentioned in that study. The aforementioned studies [9-10] can be referred to greater details of this model.

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \; [\Delta H^\circ = -49 \text{ kJ/mol}] \quad [10]$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \; [\Delta H^\circ = -41 \text{ kJ/mol}] \quad [11]$$

3 Procedures undertaken for process evaluation and optimization

3.1 Introducing process metrics

Process A (taken as base case) was enhanced to two improved processes: Process A^{opt} (optimized base case) and Process B (enhanced via process modifications and optimized). The process modifications employed to develop process B have been described in section 2. Gross margin (GM) (Equation 13 and 15) and Net percentage of CO_2 valorized (NPCV) (Equation 14 and 16) were the evaluation parameters used to evaluate the processes which have been used in our previous study [10]. Note that, GM_P and $NPCV_P$ are predicted parameters obtained from the reduced section of the processes, i.e. the entire processes excluding the purification section. GM_F and $NPCV_F$ are the final values of the process evaluation parameters ascertained from the complete process including the purification section. GM_P is predicted by assuming a recovery (Equation 12) of 99.5 % of methanol from the FDB stream (Figure 1 (b)), thus excluding the purification section. $NPCV_P$ is predicted by assuming all the combustible components (CH_4, CO, CO_2 excluding CH_3OH) from the FDB stream are purged out after combustion if applicable.

While GM evaluates the profit creation potential of the processes, NPCV assists us in the evaluation of their CO_2 conversion potential respectively. GM calculates revenue from selling the produced methanol while also including raw material costs (captured CO_2, natural gas stream, and hydrogen costs). Note that, only process A^{Opt} involves selling of excess oxygen (WE generated oxygen leftover after consumption in TR reactor) produced by WE unit and its selling price is included but not shown in gross margin formulas (Equation 13 and 15, mainly representing process B) for brevity. On the other hand, in process B, excess oxygen is sent to the combustor to support combustion of purge streams. NPCV considers direct CO_2 emissions from the processes while also considering CO_2 emissions arising from combustion of any uncombusted components (thus uses factors such as 2.74, 1.57 and 1.375 which converts methane, CO and methanol emissions to equivalent CO_2 emissions on a mass basis) purged from the processes such as unconverted CH_4, CO, and CH_3OH.

The prices considered for natural gas, product methanol, and green hydrogen (produced using an electrolyzer utilizing renewable electricity) are 0.1099 USD/kg (monthly cost for each month in 2024, averaged for the year) [11], 0.679 USD/kg [12] and 4 USD/kg [13] respectively.

$$R_{CH3OH} = (m_{CH3OH}^{D} x\ 100)/\ m_{CH3OH}^{FDB} \quad [12]$$

$$GM_P(\$/hr) = ((R_{CH3OH}/100)*\ 0.679*m_{CH3OH}^{FDB})-(0.1099\ *m_{NG})-(4*m_{Hydrogen})-(0.138056*m_{CO2}) \quad [13]$$

$$NPCV_P(\%) = ((m_{CO2}^{PURE\text{-}CO2} + m_{CO2}^{NG})-(m_{CO2}^{PURGE} + m_{CO2}^{FDB})-2.75*(m_{CH4}^{PURGE} + m_{CH4}^{FDB}) - 1.57*(m_{CO}^{PURGE} + m_{CO}^{FDB}) - 1.375*(m_{CH3OH}^{PURGE})*100)/(m_{CO2}^{PURE\text{-}CO2} + m_{CO2}^{NG}) \quad [14]$$

$$GM_F(\$/hr) = (0.679*\ m_D) - (0.1099\ *m_{NG}) - (4*m_{Hydrogen}) - (0.138056*m_{CO2}) \quad [15]$$

$$NPCV_F(\%) = ((m_{CO2}^{PURE\text{-}CO2} + m_{CO2}^{NG})-(m_{CO2}^{PURGE3} + m_{CO2}^{V}) - 2.75*(m_{CH4}^{PURGE3} + m_{CH4}^{V}) - 1.57*(m_{CO}^{PURGE3} + m_{CO}^{V}) - 1.375*(m_{CH3OH}^{PURGE3} + m_{CH3OH}^{V})*100)/(m_{CO2}^{PURE\text{-}CO2} + m_{CO2}^{NG}) \quad [16]$$

where, m_i^j = mass flow rate (kg/h) of component 'i' in the stream 'j' and m_i = mass flow rate (kg/h) of stream 'i'.

3.2 Optimization – Problem formulation

In this paper, we have chosen the differential evolution algorithm (to target a global optimum) for optimization. It is implemented for optimization of the processes simulated in Aspen Plus by Aspen Plus-Python integration achieved using the Component Object Model (COM) interface. This interface has been utilized previous by researchers for process optimization [14]. This study employs DE to optimize processes A (leading to process A^{Opt}) and B, in order to maximize NPCV (objective function) while satisfying the inequality constraint of maintaining GM ≥ 30923 USD/h (equivalent to gross margin of Shi et al. [8]process, GM_P, Table 1), while also satisfying the in-built model equations for the process flowsheet in Aspen Plus which act as equality constraints.

Objective function: Maximize $NPCV_P$
Decision variables:

1. O_2 flow to the TR reactor
2. H_2 flow to the MP reactor
3. Natural gas flow rate to the pre-reformer

Constraints:

1. $GM_P \geq 30923$ USD/h
2. Process model equations implemented in Aspen Plus (material balances, energy balances, equilibrium relationships, enthalpy balances, kinetic equations etc.)

3. $O_2/CH_4 \leq 0.55$ (refer section 4.1)
4. $O_2/CH_4 \geq 0.25$ (refer section 4.1)

4 Result and Discussion

4.1 Procedure conducted to achieve the optimal feed flow rate.

The process models (reduced) utilized for optimization via sensitivity analysis in Aspen Plus were reduced section of the processes. From the reduced process models, GM and NPCV values were predicted using Equation 13 and 14 from the bottom stream of flash separation section. Before conducting optimization on the process model, its results were validated by accurate prediction (errors ≤ 5.15 %) of GM and NPCV for the process of Shi et al. [8] as reported in Table 1. Note that, in Process A^{opt}, lower and upper bounds of 0.25 and 0.55 were set on the O_2/CH_4 ratio to ensure no carbon formation [15] and to avoid occurrence of the complete oxidation of methane reaction [10], respectively.

Table 1. Comparison between predicted and actual values of Gross margin and NPCV for the process of Shi et al. [8] and our process model utilized for optimization

Process metrics	**Predicted values (GM_P) (our optimization model)**	**Predicted values (GM_P) [8]**	**Final values (GM_F) [8]**	**Error (%) (between GM_P (our model) and GM_P [8])**	**Error (%) (between GM_P (our model) and GM_F [8])**
Gross margin ($/h)	30424	30923	30868	1.61	1.44
NPCV (%)	60.82	59.99	57.84	1.38	5.15

Table 2. Optimal values of co-feed flow rates and respective values of predicted and final process evaluation parameters (Initial CO_2 feed flow to TR reactor = 675 kmol/hr) from the reduced and complete process models.

	Input stream flow rates (kmol/h)						
Process	**Natural gas**	**Oxygen**	**Hydrogen**	**GM_P ($/hr)**	**$NPCV_P$ (%)**	**GM_F ($/hr)**	**$NPCV_F$ (%)**
A^{opt}	2595	1230	3910	30947	79.36	31274	79.12
B	2582	1423	3914	31100	94.22	31399	94.8

4.2 Sensitivity Analysis

Figure 2 shows how hydrogen input from electrolyzer acts synergetically with CO_2 recycle to improve the process. Effectively, GM_p and $NPCV_p$ on the y axis, CO_2 recycle fraction on parametric axis, hydrogen flow rate from WE unit from 0 to optimal rate (over and above fixed value, refer Figure 2). Note that, the constraint on GM_P is implemented to locate the optimum (Figure 2). This shows the synergetic interaction between the integration of the water electrolyis unit and CO_2 recycle. Increased hydrogen flow rate leads to decrement in the GM (profitability) because of the intake of expensive green hydrogen

while simultaneously increasing the NPCV for utilization of hydrogen to counter the recycled CO_2 to improve the CO_2 conversion potential (NPCV) of the process.

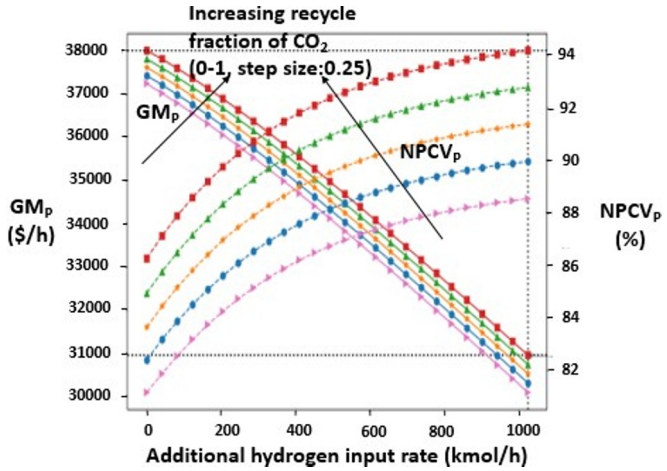

Fig. 2. Effect of CO_2 recycle fractions (25%, 50%,75%,100%) on process metrics (GM_P, $NPCV_P$) when additional hydrogen input rate* to the process B has been varied

(* additional hydrogen over and above the fixed value of 2888.84 kmol/hr calculated based on hydrogen flow rate corresponding to oxygen flowrate to the TR reactor)

5 Conclusion

This study focused on developing and optimizing an improved WE integrated TRMP process designed by Shi et al. [8]. This was done in two phases. In the first phase, the original process (process A) was optimized (termed process A^{opt}). In the second phase, the original process was advanced using the aforementioned process modifications and optimized (termed process B). This resulted in an improvement of 36.79 % in NPCV in process A^{opt} over A and 63.9 % in process B over A. This demonstrated higher profit and CO_2 valorization potentials of the improved processes. The industrial application of this process is in development of a production plant of methanol (viable both as a chemical and fuel) produced from waste CO_2 (released from a fossil fuel based power plant) which targets CO_2 mitigation objective while also producing a valuable product. More detailed profitability and CO_2 valorization potential calculations are needed to further establish the results in future work.

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