Chemical Process Design Vol.1 No.1 (2022) 1-16

University of Sistan and Baluchestan

Chemical Process Design

Available online at http://cpd.usb.ac.ir/




# GTL Process Simulation and Sensitivity Analysis: Zero $CO_2$ Emission and Productivity Improvement

Alireza Behroozsarand*, Kamran Gasemzadeh

Renewable Energies Department, Faculty of Chemical Engineering, Urmia University of Technology, Urmia, 57155-419, Iran

ARTICLE INFO

***Article history:***
*Received: 2022-05-06*
*Received in revised form: 2022-07-03*
*Accepted: 2022-07-06*
*Published online: 2022-07-20*

***Keywords:***
*Gas-to-Liquids (GTL); Steam Methane Reforming (SMR); Tri-Methane Reforming (TMR); Sensitivity analysis*

***DOI:*** *10.22111/cpd.2022.42322.1000*

ABSTRACT

Refineries and petrochemical industries can transform some of their flare gas into noteworthy gasoil, gasoline, and LPG products by applying technology of gas-to-liquid (GTL). One of the main parts of GTL plant is the production of synthetic gas process. As the main objective of this study, two technology steam methane reforming (SMR) and tri-methane reforming (TMR) techniques have been used to simulate and analyze the proposed sensitivity of the new integrated GTL process. Therefore, four parameters have been studied in sensitivity analysis (SA) against changing the proportion of gas recovery to gas synthesis and amine subunits. SA results represented that raising recycle gas ratio has negative impact on SMR model productivity and has positive effect on TMR model productivity, especially between 0.0 to 0.7 ratios. Also, the decreasing trend of the syngas production rate in the SMR was much more severe and with a greater slope than the increase in the syngas production rate in the TMR. Therefore, on this basis, the final productivity in the integrated process also shows a significant increase about by using the TMR process (3835 kg/hr) versus the SMR process (3793 kg/hr).

## 1. Introduction

Natural gas (NG) steam reforming (SR) is the most widely used as manner of $H_2$ production in industrial scale. Also, by improving some industries, for example iron industries and several new petrochemical plants (olefin units), producing flare gas within $CH_4$ and $CO_2$ as greenhouse gases was one of main problem of world from environmental viewpoint. On the other hand, steam methane reforming (SMR) and carbon dioxide reforming or dry reforming (DR) combines to produce syngas for the synthesis of green fuels and valuable chemical products. However, this process requires high energy demand and there is a risk of carbon formation that would deactivate the catalyst [7]. In previous decade, to overcome this problems, Song et al. [40] suggested TRM process as a novel syngas production procedure.

Corresponding author. Tel.: +98 (441) 3554180; fax: +98 (441) 3554183.
E-mail address: a.behroozsarand@uut.ac.ir (A. Behroozsarand).

This process refers to simultaneous reforming of oxidative $CO_2$ steam from natural gas, which involves synergetic combination of DR, SR, and methane oxidations.

SMR: $CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (\Delta H^{\circ}_{298} = +206\ kJ.mol^{-1})$ (1)

Partial oxidation of methane (POM): $CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \quad (\Delta H^{\circ}_{298} = -36\ kJ.mol^{-1})$ (2)

DR of methane (DRM): $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (\Delta H^{\circ}_{298} = +247\ kJ.mol^{-1})$ (3)

Water gas shift (WGS): $CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H^{\circ}_{298} = -41.1\ kJ.mol^{-1})$ (4)

According to reaction equations 1 to 4, to improve the performance of this process, $O_2$ and $H_2O$ are used to decrease coke formation on the catalysts surface and the $H_2/CO$ ratio is maintained around 2 [26]. Since the modified reactions are endogenous and the reaction is oxidative degradation, the combination of these reactions saves energy because the heat generated by the POM is consumed in the modified reactions. [26]. Some advantages of the TMR process compared with other well-known types of reforming processes are: Higher energy efficiency owing to combination of endothermic and exothermic reactions. Controlling of synthesis gas ratio ($H_2/CO$) by regulating the feed composition. Minimizing coke formation via presenting of water and oxygen in reaction domain. One other hand, as mentioned before, the TRM process could be used to obtain synthesis gas with an $H_2/CO$ molar ratio of 2, which is suitable for the generation of methanol and the Fisher-Tropsch (FT) process [11]. Meanwhile, considerable regard has been pay off to global warming due to the greenhouse effect. The reduction and utilization of greenhouse gases such as $CO_2$ and methane ($CH_4$) are therefore becoming more important challenges. In recent years, regarding to literature, TRM process has been studied from both viewpoints; namely experimentally (catalyst field) and analytically (Process, simulation, optimization, and modeling fields). Recently, Kumar et al. studied tuning the metal-support interaction of methane tri-reforming catalysts for industrial flue gas utilization [28]. Chen et al. worked on techno-economic evaluation of $CO_2$-rich natural gas dry reforming for linear alpha olefins production [8].

Al-Yaeeshi et al. enhances the efficiency of the Fischer-Tropsch process through $CO_2$ injection. Syngas production in the reforming units is simulated for three cases; two cases for auto-thermal reforming (ATR) with varying steam flow rates and a case for SMR [2]. Al-Sobhi et al. studied techno-economic and environmental assessment of Gasoline produced from GTL and MTG processes [1]. Also, Mohammad Osat et al. reported an optimized conventional tri-reforming reactor to an energy efficient membrane reactor for hydrogen production [31]. In Table 1, summary of new literatures that have direct relation with TRM process has been listed.

**Table 1.** Summary review on TMR works from 2003 up to 2020

| Researchers | Year | Scope | Ref. |
|---|---|---|---|
| **Catalyst field** | | | |
| Pino, Lidia et al. | 2011 | Hydrogen production by methane tri-reforming process over Ni–ceria catalysts: Effect of La-doping | [33] |
| García-Vargas et al. | 2012 | Precursor influence and catalytic behavior of Ni/CeO2 and Ni/SiC catalysts for the tri-reforming process | [20] |
| Si, Lan-jie et al. | 2012 | Influence of preparation conditions on the performance of Ni-CaO-ZrO2 catalysts in the tri-reforming of methane | [39] |
| García-Vargas et al. | 2013 | Methane tri-reforming over a Ni/β-SiC-based catalyst: Optimizing the feedstock composition | [19] |
| Majewski, Artur J. Wood, Joseph | 2014 | Tri-reforming of methane over Ni@SiO2 catalyst | [30] |
| García-Vargas et al. | 2014 | Influence of alkaline and alkaline-earth cocations on the performance of Ni/β-SiC catalysts in the methane tri-reforming reaction | [22] |
| Pino, Lidia | 2014 | Hydrogen from biogas: Catalytic tri-reforming process with Ni/LaCeO mixed oxides | [34] |
| García-Vargas et al. | 2015 | Catalytic and kinetic analysis of the methane tri-reforming over a Ni–Mg/β-SiC catalyst | [21] |

| Researchers | Year | Scope | Ref. |
|---|---|---|---|
| Yoo, Jaekyeong et al. | 2015 | Hydrogen production by tri-reforming of methane over nickel–alumina aerogel catalyst | [42] |
| García-Vargas et al. | 2015 | Preparation of Ni–Mg/β-SiC catalysts for the methane tri-reforming: Effect of the order of metal impregnation | [23] |
| Díez-Ramírez, J. et al. | 2016 | Kinetic, energetic and exergetic approach to the methane tri-reforming process | [11] |
| Hossain, M. Anwar et al. | 2016 | Artificial neural network modeling of hydrogen-rich syngas production from methane dry reforming over novel Ni/CaFe2O4 catalysts | [25] |
| Nada H. Elsayed et al. | 2017 | Effect of silicon poisoning on catalytic dry reforming of simulated biogas | [14] |
| Martin Schmal, et al. | 2018 | Perspective of catalysts for (Tri) reforming of natural gas and flue gas rich in $CO_2$ | [38] |
| Camila Emilia Kozonoe et al. | 2019 | The Fe-Co-Cu supported on MWCNT as catalyst for the tri-reforming of methane –Investigating the structure changes of the catalysts | [27] |
| Chayene Gonçalves Anchieta et al. | 2019 | Effect of ionic liquid in Ni/ZrO2 catalysts applied to syngas production by methane tri-reforming | [3] |
| Z. A. Fedorova, M. M. Danilova, V. I. Zaikovskii | 2020 | Porous nickel-based catalysts for tri-reforming of methane to synthesis gas: Catalytic activity | [17] |
| Rohit Kumar, Kritagya Kumar, K. K. Pant, N. V. Choudary | 2020 | Tuning the metal-support interaction of methane tri-reforming catalysts for industrial flue gas utilization | [28] |
| **Process, simulation, optimization, and modeling fields** | | | |
| Lee, Seung-Ho et al. | 2003 | Tri-reforming of $CH_4$ using $CO_2$ for production of synthesis gas to dimethyl ether | [29] |
| Cho, Wonjun et al. | 2009 | Optimal design and operation of a natural gas tri-reforming reactor for DME synthesis | [9] |
| Arab Aboosadi, Z. and at al. | 2011 | Optimization of tri-reformer reactor to produce synthesis gas for methanol production using differential evolution (DE) method | [4] |
| Gangadharan, Preeti and at al. | 2012 | Evaluation of the economic and environmental impact of combining dry reforming with steam reforming of methane | [18] |
| Oyama, S. Ted et al. | 2012 | Dry reforming of methane has no future for hydrogen production: Comparison with steam reforming at high pressure in standard and membrane reactors | [32] |
| Zhang, Yishan et al. | 2013 | Process simulation and optimization of methanol production coupled to tri-reforming process | [43] |
| Farniaei, Mehdi et al | 2014 | Syngas production in a novel methane dry reformer by utilizing of tri-reforming process for energy supplying: Modeling and simulation | [15] |
| Rahnama, Hamid et al. | 2014 | Modeling of synthesis gas and hydrogen production in a thermally coupling of steam and tri-reforming of methane with membranes | [35] |
| Wu, Wei et al. | 2014 | Conceptual design of syngas production systems with almost net-zero carbon dioxide emissions | [41] |
| Khajeh, S. et al. | 2015 | Optimizing the fluidized-bed reactor for synthesis gas production by tri-reforming | [26] |
| Zhang, Yishan et al. | 2015 | A conceptual design by integrating dimethyl ether (DME) production with tri-reforming process for $CO_2$ emission reduction | [44] |
| Dwivedi, Abhishek et al. | 2016 | Sensitivity based optimization of the Tri-reforming based $CO_2$ valorization process | [12] |
| Chein, Rei-Yu et al. | 2017 | Parametric study on catalytic tri-reforming of methane for syngas production | [7] |
| Borja Hernandez, Mariano Martin | 2018 | Optimization for biogas to chemicals via tri-reforming. Analysis of Fischer-Tropsch fuels from biogas | [24] |
| Mohsen Sadeghi et al. | 2018 | Exergo-economic assessment and optimization of a syngas production system with a desired $H_2$/CO ratio based on methane tri-reforming process | [36] |
| Rei-Yu Chein, Wen-Hwai Hsu | 2018 | Thermodynamic analysis of syngas production via tri-reforming of methane and carbon gasification using flue gas from coal-fired power plants | [6] |
| M. Farsi, M. Fekri Lari, M. R. Rahimpour | 2019 | Development of a green process for DME production based on the methane tri-reforming | [16] |
| Dang Saebea et al. | 2019 | Process simulation of bio-dimethyl ether synthesis from tri-reforming of biogas: $CO_2$ utilization | [37] |
| Ahmad Taghizade Damanabi et al. | 2019 | Potential of tri-reforming process and membrane technology for improving ammonia production and $CO_2$reduction | [10] |
| Abhishek Dwivedi, Ravindra Gudi, Pratim Biswas | 2020 | An oxy-fuel combustion based tri-reforming coupled methanol production process with improved hydrogen utilization | [13] |
| Qianqian Chen et al. | 2020 | Techno-economic evaluation of $CO_2$-rich natural gas dry reforming for linear alpha olefins production | [8] |
| Ali AttiqAl-Yaeeshi et al. | 2020 | A simulation study on the effect of $CO_2$injection on the performance of the GTL process | [2] |

| Researchers | Year | Scope | Ref. |
|---|---|---|---|
| Al-Sobhi et al. | 2021 | Techno-economic and environmental assessment of Gasoline produced from GTL and MTG processes | [1] |
| Osat, Mohammad et al. | 2022 | Optimization and improvement of a conventional tri-reforming reactor to an energy efficient membrane reactor for hydrogen production | [31] |

In this work, a comparative study of TRM and SMR process to investigate syngas yield, $CO_2$ emissions and energy consumption is presented for new arrangement of GTL plant [5]. Moreover, recycle ratio value of recycled gas from FTS unit to amine and reforming units (SMR and TMR) in FTS unit has been selected as effective variable. Productivity, $CO_2$ conversion, methane conversion, $H_2$:CO ratio in syngas unit, and syngas productivity parameters of all integrated GTL plant has been chosen as dependent parameters. So, in sensitivity analysis section effect of effective variable on dependent parameters has been studied and reported.

## 2. Process Description

Process description of new sequence and optimal integrated proposed GTL process is briefly presented in Fig. 1(a). Regarding to our previous work results [4], this arrangement has higher productivity for a fixed amount of feed (natural gas), better thermal integration, improvement of equipment sizing (e. g. column) than traditional FT process that finally leads to economic development. Indeed, in this study, two scenarios have been evaluated and implied:

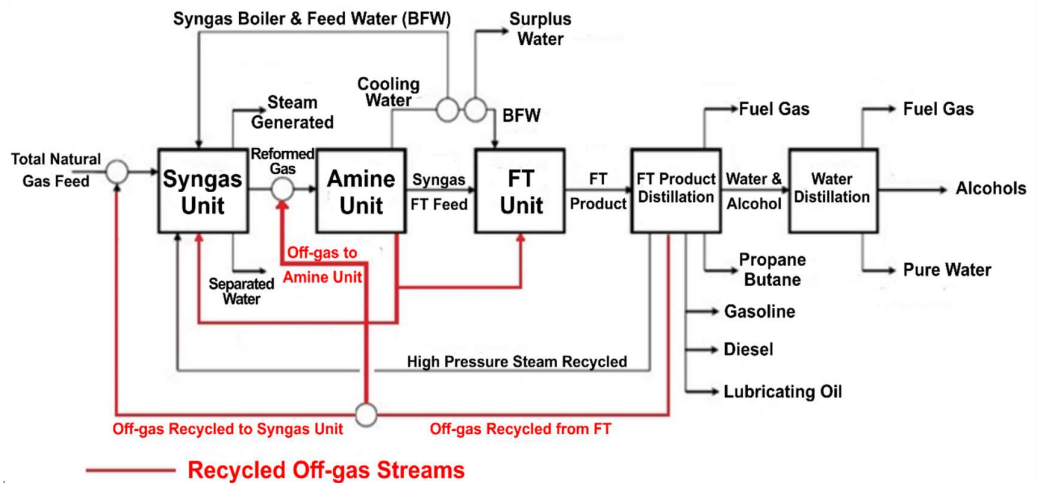
a) Optimization of recycle gas ratio value and position of recycled gas streams by using SMR technology for syngas production.
b) Optimization of recycle gas ratio value and position of recycled gas streams by using TMR technology for syngas production (Fig. 1(b)).

Decreasing of $CO_2$ exportation from FT process is significant point, because it improves the process economically and also it will be a step towards progress for the environment. In GTL process, carbon dioxide flow must be considered from two different and contradictory perspectives.

a) Environmentally view: carbon in the hydrocarbon feed is transformed to $CO_2$, which is undesirable
b) Productivity view: $CO_2$ is applied as feed for syngas producing in TMR process.

Therefore, for reducing or elimination of $CO_2$ emission, separation and using of separated $CO_2$ to feed stream can be progressed process efficiency. It is noted that because $CO_2$ can be carbon source of CO, therefore raising of $CO_2$ fraction in TMR feed can cause to more CO producing in water gas shift (WGS) reactors. In addition, if Fe catalyst as main catalyst of FT reaction used in GTL process, it is necessary that the ratio of $H_2$ to CO should be near 1. Conventionally, syngas production processes are auto thermal reactor (ATR) and partial oxidation (POX) and recommended ratio is between 2 and 3 for these processes. Therefore, for decreasing ratio, CO fraction must be increased or $H_2$ decreased in feed stream. One of the basic and simple methods to gain greater productivity of carbon monoxide is utilization of $CO_2$ mixing with feed stream. Indeed, $CO_2$ is one of FTS byproduct, so it is necessary separated to mix with synthesis gas unit feed stream. Moreover, as $CO_2$ is greenhouse gas that makes changing of climate, so reduction of $CO_2$ emission is very important in environmental viewpoint. Thus, recently $CO_2$ emission is monitored and controlled.

(a)




(b)

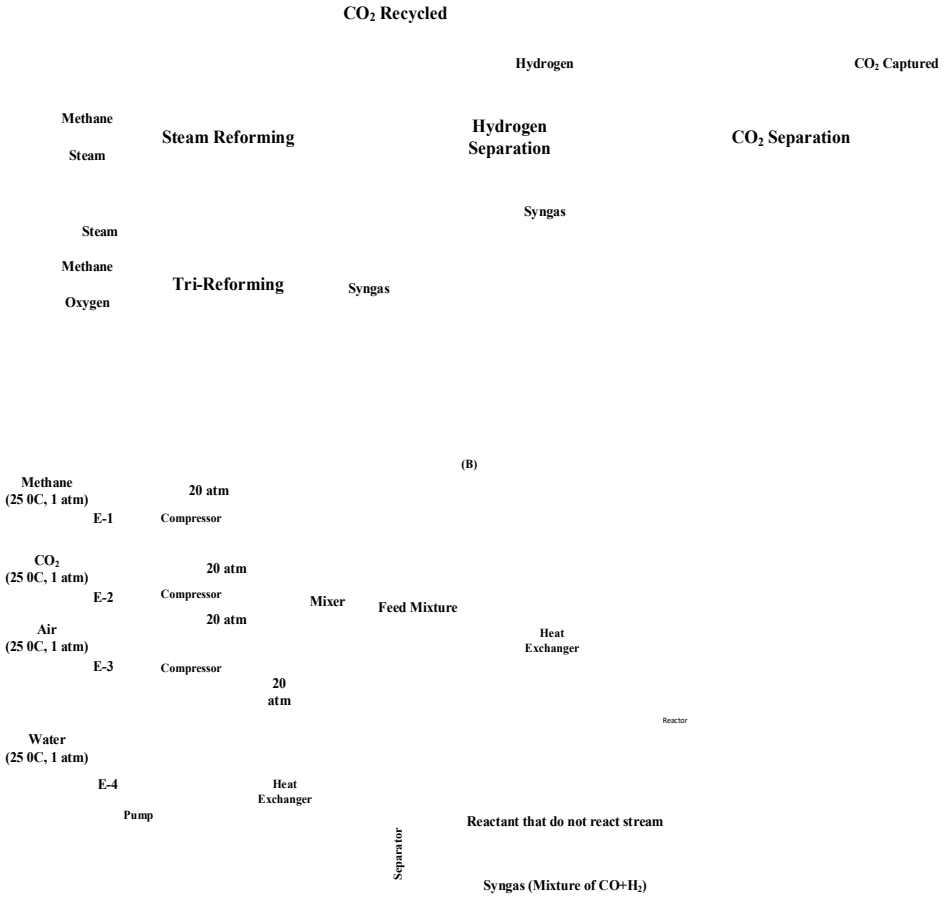



**Fig. 1.** Block flow diagram (BFD) of arrangement of (a) FT process and (b) tri-reforming processes

In our previous study [4], all light gas stream sent to amine unit and synthesis gas unit with optimized ratio of 13:87. In this evaluation, SMR technology is used for producing syngas production. But, according to equations 1 to 3, carbon dioxide can be applied as main feed in TMR technology, so it seems this technology can be very important and noteworthy options in GTL process. As our knowledge, there is no any publication about the FTS product using

TMR. As mentioned before, in synthesis gas production via reforming process, thermal energy is needed for the endothermic reactions. Therefore, main section of NG is applied as burner fuel in reformer. In this work, by proposing of TMR as process for producing FTS required syngas, this energy integration problem is resolved completely. In fact, in FTS unit based on fixed bed reactor, heat removal using saturated water, temperature of separation vessels, defined productivity is the main parameter for comparing of two methodologies. For calculating of mass flow of saturated water in role of reactor coolant, temperatures of reactor and FTS reactions generated heat were considered. In this study, in first step all units simulated singly and new proposed arrangement was exerted in all of GTL process. All gathered gases from various units such as distillation, amine, and others subunits divided into two groups:

1- Separated gas stream gas include of $CO_2$, $CH_4$, and $C_2H_6$ entitled Off-gas.
2- Separated gas stream gas include of $H_2$, CO, $CH_4$, $C_2H_6$, and $C_3H_8$ entitled recycle gas.

In the event of energy savings and environmental considerations, this gas is transferred out of the atmosphere to the atmosphere, leading to the process of hydrocarbon separation (Tail gas recovery (TGR)) where valuable products are separated. But the process uses recycled gases. Due to the new configuration considered here, this flow is distributed into two parts. The $1^{th}$ section is backed to the amine unit and the $2^{th}$ section to the synthesis gas unit. Hence, with consider to the component composition and flow rate of mixed recycled gas, there are two significant subjects:

1- Because size of an equipment such as heat exchanger, column, … has a direct relationship with the inlet flow rate, so it is not logical all recycled gas conducted to one unit such as amine unit.
2- Since $H_2$ and CO are products of the gas synthesis unit, total current recycling is not appropriate to the transformer while preparing $CO_2$ is necessary to adjust the $H_2$/CO ratio.

Therefore, considering these conflicting points, the optimal ratio between these currents should be used.

## 3. Simulation procedure and results analysis

### *3.1. Material and energy balance results*

The integrated GTL with all subunits (syngas, amine, FT, distillation, and water distillation plants) was simulated by applying the Aspen Hysys V.10 process simulator. Because list of components in subunits of integrated GTL are not similar, so two different fluid package have been selected for simulation: 1) Syngas and FT Units (Peng-Robison model); 2) Amine Unit (Amine Package model). Syngas, Amine, and FT subunits include of 22, 14, and 101 components, respectively. As mentioned previous section, two scenarios have been applied in simulation of GTL process. In first scenario, SMR process has been applied in syngas production and in second one TMR process has been used. All inputs such as natural gas properties (mass flow, temperature, pressure, and compositions) is the same for each case. Regarding to GTL process, natural gas stream can be divided into two parts: A): Natural gas as SMR and TMR feed and B): Natural gas as fuel gas for burners.

The ratio value of A/B is about 0.5995/0.4005 and 0.5538/0.4462 in cases of SMR and TMR, respectively. Hence, it can be concluded that considerable part of natural gas is used for heating system in two cases and this is a main disadvantage of SMR and TMR technologies. On the other hands, this ratio is better for TMR than SMR, so it can be predicted the achieved syngas productivity may be higher than SMR case. Moreover, the achieved H2 /CO ratio for case of SMR is around 1, while this ratio for case of TMR is 3.5. In general, there are three outlet streams in this unit:

1) Reformed gas (syngas) 2) high pressure steam (HPS) 3) Separated sour water

Summary of material and energy balance data of integrated GTL process in two model (SMR and TMR models) have been reported in Table 2.

**Table 2.** Specification of feed and product of syngas production, amine, FT, product distillation and water distillation units

| Stream Name | Natural gas to Synthesis gas (Feed and fuel) in TMR and SMR cases | Total Natural gas to Reformer in SMR case | Total Natural gas to Reformer In TMR case | Reformed Gas in SMR case | Reformed Gas in TMR case |
|---|---|---|---|---|---|
| Component | Mole (%) | Mole (%) | Mole (%) | Mole (%) | Mole (%) |
| Hydrogen | 0.00 | 3.78 | 53.83 | 35.72 | 74.78 |
| CO | 0.00 | 3.42 | 1.99 | 36.63 | 21.57 |
| $CO_2$ | 0.60 | 42.88 | 11.40 | 26.51 | 2.91 |
| con | 84.90 | 11.35 | 7.33 | 0.47 | 0.38 |
| $H_2O$ | 0.00 | 35.73 | 23.61 | 0.69 | 0.37 |
| Oxygen | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Nitrogen | 0.50 | 0.04 | 0.03 | 0.04 | 0.00 |
| Ethane | 9.20 | 2.01 | 1.14 | 0.00 | 0.00 |
| Propane | 3.50 | 0.58 | 0.45 | 0.00 | 0.00 |
| i-Butane | 0.40 | 0.03 | 0.02 | 0.00 | 0.00 |
| n-Butane | 0.70 | 0.13 | 0.14 | 0.00 | 0.00 |
| n-Pentane | 0.20 | 0.03 | 0.02 | 0.00 | 0.00 |
| i-Pentane | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 |
| n-Hexane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n-Heptane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n-Octane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n-Nonane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| n-Decane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $C_{10+}$* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Methanol | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ethanol | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1-Propanol | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Mass Flow (kg/hr) | 45000 | 318747 | 239994 | 251178 | 171009 |
| Actual Volume Flow ($m^3$/hr) | 1875 | 34103 | 53850 | 15866 | 23426 |
| T ($^0$C) | 21 | 590 | 522 | 42 | 40 |
| P (kPa) | 2800 | 2310 | 2310 | 1810 | 2150 |

| Stream Name | Recycle gas SMR | Recycle gas TMR | Stream Name | Recycle gas SMR | Recycle gas TMR |
|---|---|---|---|---|---|
| Component | Mole (%) | Mole (%) | Component | Mole (%) | Mole (%) |
| Hydrogen | 26.53 | 88.66 | i-Butane | 0.00 | 0.00 |
| CO | 22.40 | 3.30 | 1-Butene | 0.02 | 0.01 |
| $CO_2$ | 12.48 | 2.02 | 3M-1-butene | 0.01 | 0.00 |
| $H_2O$ | 0.00 | 0.00 | 1-Pentene | 0.02 | 0.01 |
| Methane | 29.25 | 4.25 | tr2-Pentene | 0.00 | 0.00 |
| Ethylene | 0.25 | 0.04 | 33M-1-butene | 0.01 | 0.01 |
| Ethane | 6.51 | 1.03 | 3M1C5= | 0.00 | 0.00 |
| Propane | 2.01 | 0.42 | 4Mtr2pentene | 0.00 | 0.00 |
| tr2-Butene | 0.04 | 0.01 | 1-Hexene | 0.00 | 0.00 |
| n-Butane | 0.39 | 0.16 | tr3-Hexene | 0.01 | 0.00 |
| i-Pentane | 0.04 | 0.03 | 44M1-pentene | 0.00 | 0.00 |
| n-Pentane | 0.03 | 0.02 | 3M1C6= | 0.00 | 0.00 |
| n-Hexane | 0.00 | 0.00 | n-Heptane | 0.00 | 0.00 |
| Mass Flow (kg/hr) | 257387 | 436028 | | | |
| Actual Volume Flow ($m^3$/hr) | 28687 | 200360 | | | |
| T($^0$C) | 31 | 29.4 | | | |
| P(kPa) | 1110 | 1110 | | | |

| Stream Name | Syngas to FT SMR | Syngas to FT TMR | Stream Name | Water-Alcohol SMR | Water-Alcohol TMR |
|---|---|---|---|---|---|
| Component | mole (%) | mole (%) | Component | Mole (%) | Mole (%) |
| Hydrogen | 38.52 | 87.30% | Hydrogen | 0.00 | 0.00 |

| | | | | | |
|---|---|---|---|---|---|
| CO | 36.52 | 7.06% | CO | 0.00 | 0.00 |
| $CO_2$ | 0.52 | 0.28% | $CO_2$ | 0.26 | 0.00 |
| Methane | 18.45 | 3.51% | $H_2O$ | 9.47 | 92.43 |
| $H_2O$ | 0.4 | 0.50% | Methanol | 83.02 | 7.14 |
| Oxygen | 0.00 | 0.00% | Ethanol | 7.21 | 0.37 |
| Nitrogen | 0.00 | 0.00% | 1-Propanol | 0.04 | 0.03 |
| Ethane | 4.01 | 0.83% | Mass Flow (kg/hr) | 1042 | 183.4 |
| Propane | 1.24 | 0.34% | Actual Volume Flow (m3/hr) | 1.338 | 0.1915 |
| i-Butane | 0.00 | 0.00% | T ($^0$C) | 45 | 45 |
| n-Butane | 0.24 | 0.13% | | | |
| n-Pentane | 0.02 | 0.02% | | | |
| i-Pentane | 0.03 | 0.02% | | | |
| DEAmine | 0.00 | 0.00% | | | |
| Mass Flow(kg/hr) | 287341 | 468017 | | | |
| Actual Volume Flow($m^3$/hr) | 23506 | 141618 | | | |
| T($^0$C) | 41 | 43.5 | | | |
| P(kPa) | 1750 | 1750 | | | |

| **Stream Name** | **C3-C4 SMR** | **C3-C4 TMR** | **Stream Name** | **C3-C4 SMR** | **C3-C4 TMR** |
|---|---|---|---|---|---|
| Component | mole (%) | mole (%) | Component | mole (%) | mole (%) |
| Hydrogen | 0.00 | 0.00 | n-Pentane | 0.05 | 0.83 |
| CO | 0.00 | 0.00 | n-Hexane | 0.00 | 0.00 |
| $CO_2$ | 0.00 | 0.68 | i-Butane | 0.02 | 0.02 |
| $H_2O$ | 0.00 | 0.00 | 1-Butene | 2.27 | 2.40 |
| Methane | 0.00 | 0.00 | 3M-1-butene | 0.71 | 3.07 |
| Ethylene | 0.00 | 0.08 | 1-Pentene | 0.09 | 2.20 |
| Ethane | 0.24 | 6.92 | tr2-Pentene | 0.00 | 0.10 |
| Propane | 42.18 | 21.03 | Methanol | 0.19 | 0.00 |
| tr2-Butene | 5.46 | 2.87 | Ethanol | 0.00 | 0.00 |
| n-Butane | 48.41 | 53.23 | 1-Propanol | 0.00 | 0.00 |
| i-Pentane | 0.37 | 6.57 | | | |
| Mass Flow(kg/hr) | 2270 | 782 | | | |
| Actual Volume Flow($m^3$/hr) | 4.38 | 1.498 | | | |
| T($^0$C) | 46 | 53.55 | | | |
| P(kPa) | 900 | 1140 | | | |

| **Stream Name** | **C5+ SMR** | **Stream Name** | **C5+ SMR** | **Stream Name** | **C5+ SMR** |
|---|---|---|---|---|---|
| Component | mole (%) | Component | mole (%) | Component | mole (%) |
| Hydrogen | 0.00 | tr2-Pentene | 1.12 | trans3C7= | 3.21 |
| CO | 0.00 | 33M-1-butene | 1.48 | 3Mcycpentene | 0.01 |
| $CO_2$ | 0.15 | 22-Mbutane | 0.19 | 244M2pentene | 0.03 |
| $H_2O$ | 0.01 | 3M1C5= | 0.46 | Ecyclopentan | 0.77 |
| Methane | 0.05 | 4Mtr2pentene | 0.63 | 25-Mhexane | 0.31 |
| Ethylene | 0.00 | 3-Mpentane | 0.43 | 23M1C6= | 0.09 |
| Ethane | 0.27 | 1-Hexene | 4.53 | Toluene | 0.08 |
| Propane | 0.65 | tr3-Hexene | 3.06 | tr3-Octene | 0.04 |
| tr2-Butene | 0.10 | 44M1-pentene | 0.98 | 23-Mhexane | 0.15 |
| n-Butane | 0.93 | Mcyclopentan | 0.02 | 112-MCC5 | 0.56 |
| i-Pentane | 5.76 | Benzene | 0.36 | 2M-3Epentane | 0.03 |
| n-Pentane | 5.93 | 3M1C6= | 1.44 | 2-Mheptane | 0.62 |
| n-Hexane | 6.99 | 33-Mpentane | 0.19 | Mcyclohexane | 1.35 |
| i-Butane | 0.00 | Cyclohexane | 0.02 | 1234-T-M-CC6 | 0.86 |
| 1-Butene | 0.04 | 2-Mhexane | 0.20 | 3-Ehexane | 0.20 |
| 3M-1-butene | 0.38 | 1-Heptene | 3.31 | 2-E-1-C6= | 0.44 |
| 1-Pentene | 2.69 | n-Heptane | 5.83 | 224-Mhexane | 0.09 |
| **Stream Name** | **C5+ SMR** | **Stream Name** | **C5+ SMR** | **Stream Name** | **C5+ SMR** |
| Component | mole (%) | Component | mole (%) | Component | mole (%) |
| tr4-Octene | 2.19 | trans-2-C10= | 0.91 | n-Dodecyl-BZ | 0.03 |
| n-Octane | 4.81 | 12-E-BZ | 2.52 | n-C17 | 0.39 |
| 22-Mheptane | 0.04 | 1-Undecene | 0.28 | 1-Heptadecen | 0.01 |
| 334-Mhexane | 0.13 | n-C11 | 2.50 | n-C18 | 0.29 |
| E-Benzene | 0.10 | 1-Dodecene | 0.90 | n-C19 | 0.24 |
| 1Mtr2n-PCC5 | 1.22 | n-C12 | 1.46 | n-C20 | 0.18 |
| m-Xylene | 0.19 | 135-E-BZ | 0.23 | n-C21 | 0.14 |
| 23-Mheptane | 0.08 | 1-Tridecene | 0.14 | n-C22 | 0.11 |

| | | | | | |
|---|---|---|---|---|---|
| 4-Moctane | 0.83 | 1-M-Naphtln | 0.02 | Cumene | 1.17 |
| 224-Mheptane | 0.87 | n-C13 | 1.28 | Indane | 0.05 |
| n-Nonane | 3.58 | 13MNaphthaln | 0.27 | Naphthalene | 0.04 |
| 1-Nonene | 0.39 | n-C14 | 0.92 | p-i-PStyrene | 0.41 |
| 245-Mheptane | 0.17 | Hex-M-Benz | 0.07 | Phenyl-CC6 | 0.11 |
| n-PBenzene | 0.40 | 1-Pentadecen | 0.07 | Methanol | 0.60 |
| 2-Mnonane | 0.92 | n-C15 | 0.68 | Ethanol | 4.49 |
| 1-Decene | 0.50 | n-C16 | 0.51 | 1-Propanol | 2.82 |
| n-Decane | 2.67 | 1-Hexadecene | 0.03 | | |
| Mass Flow(kg/hr) | 14036 | | | | |
| Actual Volume Flow($m^3$/hr) | 20.1 | | | | |
| T($^0$C) | 45 | | | | |
| P(kPa) | 100 | | | | |

| **Stream Name** | **C5+ TMR** | **Stream Name** | **C5+ TMR** | **Stream Name** | **C5+ TMR** |
|---|---|---|---|---|---|
| Component | mole (%) | Component | mole (%) | Component | mole (%) |
| Hydrogen | 0.01 | tr2-Pentene | 0.09 | trans3C7= | 3.79 |
| CO | 0.01 | 33M-1-butene | 2.25 | 3Mcycpentene | 0.01 |
| $CO_2$ | 0.10 | 22-Mbutane | 1.08 | 244M2pentene | 0.03 |
| $H_2O$ | 0.02 | 3M1C5= | 1.39 | Ecyclopentan | 0.90 |
| Methane | 0.05 | 4Mtr2pentene | 0.19 | 25-Mhexane | 0.37 |
| Ethylene | 0.00 | 3-Mpentane | 0.50 | 23M1C6= | 0.10 |
| Ethane | 0.10 | 1-Hexene | 0.71 | Toluene | 0.09 |
| Propane | 0.17 | tr3-Hexene | 0.49 | tr3-Octene | 0.05 |
| tr2-Butene | 0.01 | 44M1-pentene | 5.06 | 23-Mhexane | 0.17 |
| n-Butane | 0.27 | Mcyclopentan | 3.50 | 112-MCC5 | 0.66 |
| i-Pentane | 3.91 | Benzene | 1.09 | 2M-3Epentane | 0.03 |
| n-Pentane | 5.14 | 3M1C6= | 0.02 | 2-Mheptane | 0.74 |
| n-Hexane | 8.05 | 33-Mpentane | 0.41 | Mcyclohexane | 1.59 |
| i-Butane | 0.00 | Cyclohexane | 1.64 | 1234-T-M-CC6 | 1.01 |
| 1-Butene | 0.01 | 2-Mhexane | 0.22 | 3-Ehexane | 0.24 |
| 3M-1-butene | 0.01 | 1-Heptene | 0.02 | 2-E-1-C6= | 0.51 |
| 1-Pentene | 0.01 | n-Heptane | 0.23 | 224-Mhexane | 0.10 |
| **Stream Name** | **C5+ TMR** | **Stream Name** | **C5+ TMR** | **Stream Name** | **C5+ TMR** |
| Component | mole (%) | Component | mole (%) | Component | mole (%) |
| tr4-Octene | 2.58 | trans-2-C10= | 1.07 | n-Dodecyl-BZ | 0.03 |
| n-Octane | 5.67 | 12-E-BZ | 2.96 | n-C17 | 0.45 |
| 22-Mheptane | 0.05 | 1-Undecene | 0.33 | 1-Heptadecen | 0.02 |
| 334-Mhexane | 0.15 | n-C11 | 2.95 | n-C18 | 0.34 |
| E-Benzene | 0.12 | 1-Dodecene | 1.05 | n-C19 | 0.28 |
| 1Mtr2n-PCC5 | 1.44 | n-C12 | 1.72 | n-C20 | 0.21 |
| m-Xylene | 0.23 | 135-E-BZ | 0.27 | n-C21 | 0.16 |
| 23-Mheptane | 0.10 | 1-Tridecene | 0.16 | n-C22 | 0.13 |
| 4-Moctane | 0.98 | 1-M-Naphtln | 0.02 | Cumene | 1.38 |
| 224-Mheptane | 1.03 | n-C13 | 1.50 | Indane | 0.06 |
| n-Nonane | 4.22 | 13MNaphthaln | 0.32 | Naphthalene | 0.04 |
| 1-Nonene | 0.45 | n-C14 | 1.08 | p-i-PStyrene | 0.49 |
| 245-Mheptane | 0.19 | Hex-M-Benz | 0.08 | Phenyl-CC6 | 0.14 |
| n-PBenzene | 0.47 | 1-Pentadecen | 0.09 | Methanol | 0.37 |
| 2-Mnonane | 1.09 | n-C15 | 0.80 | Ethanol | 0.21 |
| 1-Decene | 0.59 | n-C16 | 0.60 | 1-Propanol | 0.27 |
| n-Decane | 3.14 | 1-Hexadecene | 0.03 | | |
| Mass Flow(kg/hr) | 13032 | | | | |
| Actual Volume Flow($m^3$/hr) | 18.55 | | | | |
| T($^0$C) | 45 | | | | |
| P(kPa) | 100 | | | | |

### *3.2. Sensitivity analysis formulation*

One of the most important parameters that have been considered in this study, is effect analysis of recycling of unreacted gas stream entitled “Recycle Gas (Table 2)” to process. This stream contains mainly $H_2$, CO, $CO_2$, $CH_4$,

and $C_2H_6$ components. So, concerning to stream composition, there are two options for recycling: 1) Amine and FT units, 2) SMR or TMR unit. As the target is final product productivity improvement, therefore, split ratio of "Recycle Gas" between Amine-FT units and SMR or TMR unit was selected as optimal value. According to previous work by authors [4], this value is 13:87. It should be noted that the total mas flow rate of input natural gas in all cases is remained constant (45000 kg/hr). In the following, concepts of productivity and split ratio are presented:

$$\text{Productivity(bbl / day)} = Q_{C_3} + Q_{C_4} + Q_{C_{5+}} + Q_{\text{Alcohol}} \quad (5)$$

where $Q_{C3}$, $Q_{C4}$, $Q_{C5+}$ and $Q_{\text{Alcohol}}$ are volume flow rate of $C_3$, $C_4$, $C_{5+}$ and alcohol components in products stream.

$$\text{Split ratio} = \frac{\text{Mass flow of recycle gas to SMR or TMR unit}}{\text{Total mass flow of recycle gas}} \quad (6)$$

As mentioned above, main aim of study is comparing of SMR and TMR technologies in GTL plant and investigation of recycle gas ratio effects on final productivity (Eq. 5), syngas productivity, methane conversion, $CO_2$ conversion, and $H_2$/CO ratio in syngas product.

### *3.3. GTL process analysis with using SMR and TMR processes*

#### *3.3.1. Final productivity*

As the target is productivity improvement, therefore, effect of split ratio of "Recycle Gas" between Amine-FT units and SMR or TMR unit was shown in Fig. 2. As indicated in this figure, increasing recycle gas ratio has negative effect on SMR model productivity and has positive effect on TMR model productivity especially between 0.0 to 0.7 ratios. But, the rate of reduction is more severe in SMR model. The maximum and minimum productivity values in SMR methodology are 3508 (ratio value is 0.05) and 227 (ratio value is 1.0), respectively. These values in TMR model are 3835 (ratio value is 0.1) and 3183 (ratio value is 0.0). It concluded that minimum ratio value has maximum productivity in both cases, so recycling of recycled gas in suitable method for improvement of final product in TMR method unlike SMR method.

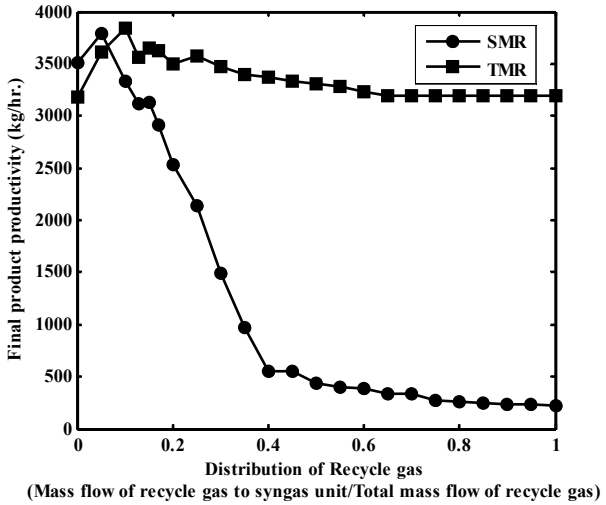



**Fig. 2.** Effect of ratio of recycle gas distribution on final product productivity (bbl/d)

#### *3.3.2. Syngas productivity*

Fig. 3 illustrates effect of recycle gas ratio on syngas productivity in both cases. According to this figure, by increasing of recycling flow to syngas unit, productivity of this unit is decreased on SMR mode and increased in TMR mode. It seems that probably main reason for increasing syngas productivity is role of $CO_2$ in TMR reactions as feed stock. On the other hands, in SMR reactions, $CO_2$ is take part in WGS reaction. Indeed, increasing mass flow of recycled gas to TMR process is similar to increasing of feed stream. Simulation results indicate that maximum values of syngas productivity in SMR and TMR processes are 183543 and 374943 (kg /hr).

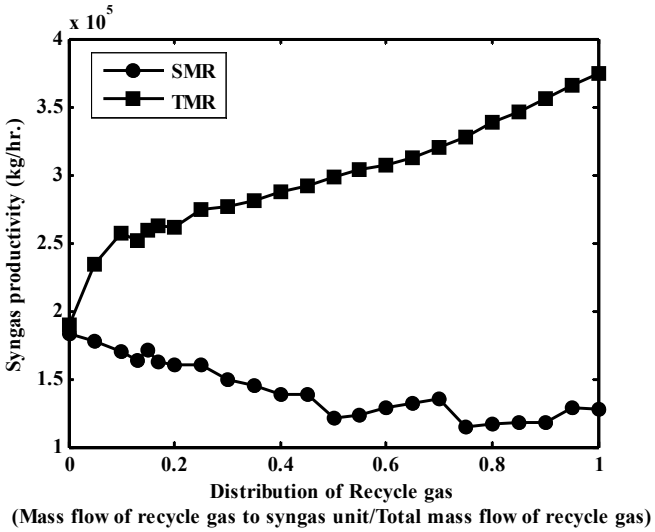



**Fig. 3.** Effect of ratio of recycle gas distribution on syngas productivity (kg/hr)

*3.3.3. ($H_2$/CO) in syngas products*

The ratio of $H_2$/CO in syngas product is one of most significant parameters in syngas production unit. The processes such as Fischer-Tropsch (FTS), Methanol, DME, and others, syngas is feed stock. So, its quality is main factor in process condition. For example, in GTL process, this ratio is different for Fe catalyst based on FTS and Cobalt catalyst based on FTS. If Fe catalyst is used for FTS process, the ratio of $H_2$/CO should be considered around 1, but for case of cobalt catalyst, this ratio should be achieved around 2 up 2.5. Increasing of $CO_2$ content of feed stream leads to more CO generation via WGS reaction. Therefore, for decreasing $H_2$/CO ratio, carbon monoxide weight fraction must be increased in feed stream. One of methods to obtain greater productivity of carbon monoxide is utilization of $CO_2$ mixing with feed stream [5]. Fig. 4(a) and Fig. 4(b) have been presented effect of recycle gas ratio on $H_2$/CO ratio in SMR and TMR, respectively.

*3.1.1. Methane conversion*

Methane conversion can be used as index of syngas plant performance. According to reaction lists of SMR and TMR (Eq.1 to Eq.4) and composition of recycle gas (29 mole% methane, 26 mole% $H_2$, 22.4 mole% CO, 12.48 mole% $CO_2$ in SMR and 4.25 mole% methane, 88.6 mole% $H_2$, 3.3 mole% CO, 2.0 mole% $CO_2$ in TMR), by focusing on methane fraction in recycle gas stream in SMR mode, it seems that increasing of recycle gas ratio makes the partial pressure of methane rise, SMR reaction (Eq.1) goes to producing more syngas product. On the other hands, high mole

fraction of hydrogen in recycle gas for TMR mode causes reverse reaction of SMR. Hence, increasing of methane conversion in SMR and decreasing of this parameter in TMR by increasing recycle gas ratio (Fig. 5) are reasonable.

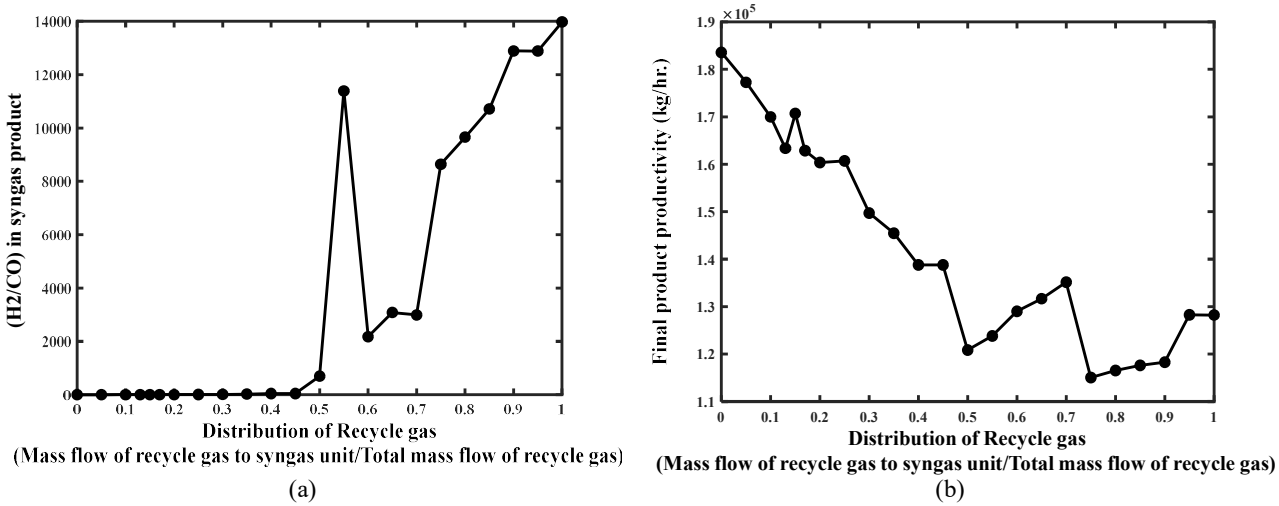



**Fig. 4.** Effect of ratio of recycle gas distribution on $H_2$/CO ratio; (a) SMR; (b) TMR

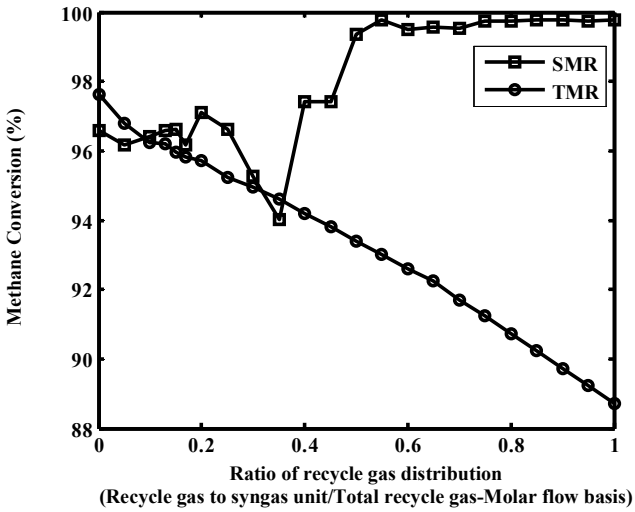



**Fig. 5**. Effect of ratio of recycle gas distribution on methane conversion

*3.1.2. Overall comparison of SMR and TMR Processes*

In sections 3.3.1, 3.3.2, 3.3.3, and 3.3.4 four parameters include of final product productivity, syngas productivity, $H_2$/CO ratio in syngas product, and methane conversion analysis versus recycle gas ratio have been investigated. Table 3 and Table 4 showed final results of sensitivity analysis of TMR and SMR models, respectively. According to reported results in these Tables, productivity as main comparing parameter between SMR and TMR in this study shows different trend in two cases. Indeed, final productivity has maximum value in ratios of 10% and 5% in TMR and SMR, respectively. Also, productivity has minimum value in ratios of 0% and 100% in TMR and SMR, respectively. It is evident that using of recycled gas to syngas unit has more advantage for TMR process than SMR, because minimum productivity is in 100% case of SMR. The important reason for this behavior of these two processes is that carbon dioxide has feed role in TMR, but in SMR, methane has main feed role, therefore recycle gas with $CO_2$ content can causes improving productivity value in TMR case.

**Table 3**. Results of sensitivity analysis of TMR process

| Min./Max. status | Ratio (Syngas/Total) (unit less) | Final productivity (kg/hr) | Syngas productivity (kg/hr) | $H_2/CO$ | $CH_4$ Conversion (%) |
|---|---|---|---|---|---|
| Min. case in Productivity<br>Min. case in Syngas Productivity<br>Max. case in $CH_4$ Conversion | 0 | 3183 | 189301 | 0.98 | 97.64 |
| Max. case in $H_2/CO$ | 0.05 | 3612 | 234198 | 0.99 | 96.78 |
| Max. case in Productivity | 0.1 | 3835 | 256591 | 0.98 | 96.24 |
| | 0.13 | 3565 | 251178 | 0.98 | 96.21 |
| | 0.15 | 3655 | 259007 | 0.98 | 95.97 |
| | 0.17 | 3629 | 261983 | 0.97 | 95.82 |
| | 0.2 | 3498 | 261497 | 0.97 | 95.71 |
| | 0.25 | 3578 | 274382 | 0.97 | 95.22 |
| | 0.3 | 3467 | 276353 | 0.96 | 94.95 |
| | 0.35 | 3395 | 280485 | 0.96 | 94.60 |
| | 0.4 | 3374 | 287437 | 0.95 | 94.18 |
| | 0.45 | 3332 | 292147 | 0.95 | 93.80 |
| | 0.5 | 3312 | 298810 | 0.95 | 93.38 |
| | 0.55 | 3282 | 304220 | 0.94 | 93.02 |
| | 0.6 | 3237 | 307546 | 0.94 | 92.58 |
| | 0.65 | 3196 | 312484 | 0.94 | 92.25 |
| | 0.7 | 3198 | 319940 | 0.94 | 91.69 |
| Min. case in $H_2/CO$ | 0.75 | 3198 | 327436 | 0.93 | 91.24 |
| | 0.8 | 3198 | 338366 | 0.93 | 90.73 |
| | 0.85 | 3198 | 346539 | 0.93 | 90.24 |
| | 0.9 | 3198 | 355979 | 0.93 | 89.73 |
| | 0.95 | 3198 | 365510 | 0.93 | 89.23 |
| Max. case in Syngas Productivity<br>Min. case in $H_2/CO$<br>Min. case in $CH_4$ Conversion | 1 | 3198 | 374943 | 0.93 | 88.72 |
| Minimum | 0 | 3183 | 189301 | 0.93 | 88.72 |
| Maximum | 1 | 3835 | 374943 | 0.99 | 97.64 |
| Average | 0.5 | 3371 | 294623 | 0.95 | 93.48 |

**Table 4.** Results of sensitivity analysis of SMR process

| Min./Max. status | Ratio (Syngas/Total) (unit less) | Final productivity (kg/hr) | Syngas productivity (kg/hr) | $H_2/CO$ | $CH_4$ Conversion (%) |
|---|---|---|---|---|---|
| Max. case in Syngas Productivity<br>Min. case in $H_2/CO$ | 0 | 3508 | 183543 | 1.24 | 96.59 |
| Max. case in Productivity | 0.05 | 3793 | 177259 | 2.61 | 96.17 |
| | 0.1 | 3330 | 169970 | 3.76 | 96.42 |
| | 0.13 | 3117 | 163362 | 3.93 | 96.59 |
| | 0.15 | 3130 | 170714 | 4.18 | 96.61 |
| | 0.17 | 2914 | 162883 | 5.10 | 96.16 |
| | 0.2 | 2535 | 160371 | 6.46 | 97.09 |
| | 0.25 | 2144 | 160726 | 9.09 | 96.62 |
| | 0.3 | 1489 | 149694 | 14.54 | 95.25 |
| Min. case in $CH_4$ Conversion | 0.35 | 968 | 145474 | 23.72 | 94.01 |
| | 0.4 | 553 | 138790 | 43.18 | 97.40 |
| | 0.45 | 553 | 138790 | 43.18 | 97.40 |
| | 0.5 | 433 | 120838 | 697.87 | 99.35 |

| | | | | | |
|---|---|---|---|---|---|
| | 0.55 | 398 | 123822 | 11389.41 | 99.76 |
| | 0.6 | 383 | 129002 | 2176.03 | 99.51 |
| | 0.65 | 343 | 131679 | 3084.63 | 99.55 |
| | 0.7 | 343 | 135165 | 2991.86 | 99.53 |
| Min. case in Syngas Productivity | 0.75 | 271 | 115057 | 8642.56 | 99.74 |
| | 0.8 | 258 | 116550 | 9655.63 | 99.75 |
| | 0.85 | 245 | 117637 | 10712.20 | 99.76 |
| Max. case in $CH_4$ Conversion | 0.9 | 232 | 118277 | 12890.12 | 99.77 |
| | 0.95 | 239 | 128268 | 12884.63 | 99.75 |
| Min. case in Productivity<br>Max. case in $H_2$/CO | 1 | 227 | 128236 | 13976.13 | 99.76 |
| Minimum | 0 | 227 | 115057 | 1.24 | 94.01 |
| Maximum | 1 | 3793 | 183543 | 13976.13 | 99.77 |
| Average | 0.5 | 1366 | 142874 | 3880.96 | 97.94 |

## 4. Conclusion

A comprehensive simulation and sensitivity analysis of an integrated GTL process by using SMR and TMR technology were developed. In all simulated cases, by changing recycling ratio of recycle gas to syngas unit and FTS unit, four parameters (final productivity, syngas productivity, $H_2$/CO ratio, and methane conversion) have been investigated, simultaneously. In this study, maximization of total productivity was considered as main parameter. Sensitivity analysis results represented that raising recycle gas ratio has negative effect on SMR model productivity and has positive effect on TMR model productivity, especially between 0.0 to 0.7 ratios. Moreover, the rate of productivity decline is more severe in SMR model.

## Nomenclature

| | | | |
|---|---|---|---|
| ATR | Autothermal | Q | Volume flow rate |
| FTS | Fischer Tropsch | SMR | Steam methane reforming |
| GTL | Gas to Liquid | Syngas | Synthesis gas |
| HPS | High Pressure Steam | TMR | Tri-methane reforming |
| NG | Natural gas | WGS | Water Gas Shift |

## References

[1] Al-Sobhi, S.A., Alnouss, A., Alhamad, M., 2021. Techno-economic and environmental assessment of gasoline produced from GTL and MTG processes, Computer Aided Chemical Engineering, 50, 1827-1832. https://doi.org/10.1016/B978-0-323-88506-5.50283-7

[2] Al-Yaeeshi, A.A., Alnouss, A., Mckay, G., Al-Ansari, T., 2020. A simulation study on the effect of $CO_2$ injection on the performance of the GTL process. Computers & Chemical Engineering, 136, 106768-106778. https://doi.org/10.1016/j.compchemeng.2020.106768

[3] Anchieta, C.G., Assaf, E.M., Assaf, J.M., 2019. Effect of ionic liquid in Ni/ZrO2 catalysts applied to syngas production by methane tri-reforming, International Journal of Hydrogen Energy, 44 (18), 9316-9327. https://doi.org/10.1016/j.ijhydene.2019.02.122

[4] Arab Aboosadi, Z., Jahanmiri, A.H., Rahimpour, M.R., 2011. Optimization of tri-reformer reactor to produce synthesis gas for methanol production using differential evolution (DE) method, Applied Energy, 88 (8), 2691-2701. http://dx.doi.org/10.1016/j.apenergy.2011.02.017

[5] Behroozsarand, A. and Zamaniyan, A., 2017. Simulation and optimization of an integrated GTL process. Journal of Cleaner Production, 142 (4), 2315-2327. https://doi.org/10.1016/j.jclepro.2016.11.045

[6] Chein, R.Y., Hsu, W.H., 2018. Thermodynamic analysis of syngas production via tri-reforming of methane and carbon gasification using flue gas from coal-fired power plants, Journal of Cleaner Production, 200, 242-258. https://doi.org/10.1016/j.jclepro.2018.07.228

[7] Chein, R.Y., Wang, C.Y., Yu, C.T., 2017. Parametric study on catalytic tri-reforming of methane for syngas production, Energy, 118, 1-17. http://dx.doi.org/10.1016/j.energy.2016.11.147

[8] Chen, Q., Wang, D., Gu, Y., Yang, S., Tang, Z., Sun, Y., Wu, Q., 2020. Techno-economic evaluation of CO2-rich natural gas dry reforming for linear alpha olefins production, Energy Conversion and Management, 205, 112348-112359. https://doi.org/10.1016/j.enconman.2019.112348
[9] Cho, W., Song, T., Mitsos, A., Mckinnon, J.T., Ko, G.H., Tolsma, J.E., Denholm, D., Park, T., 2009. Optimal design and operation of a natural gas tri-reforming reactor for DME synthesis. Catalysis Today 139 (4), 261-267. http://dx.doi.org/10.1016/j.cattod.2008.04.051
[10] Damanabi, A.T., Servatan, M., Mazinani, S., Olabi, A.G., Zhang, Z., 2019. Potential of tri-reforming process and membrane technology for improving ammonia production and CO2 reduction, Science of The Total Environment, 664, 567-575. https://doi.org/10.1016/j.scitotenv.2019.01.391
[11] Díez-Ramírez, J., Dorado, F., Martínez-Valiente, A., García-Vargas, J.M., and Sánchez, P., 2016. Kinetic, energetic and exergetic approach to the methane tri-reforming process. International Journal of Hydrogen Energy. http://dx.doi.org/10.1016/j.ijhydene.2016.04.229
[12] Dwivedi, A., Gudi, R., Biswas, P., 2016. Sensitivity based optimization of the Tri-reforming based CO2 valorization process, IFAC-PapersOnLine, 49 (7), 359-364. http://dx.doi.org/10.1016/j.ifacol.2016.07.362
[13] Dwivedi, A., Gudi, R., Biswas, P., 2020. An oxy-fuel combustion based tri-reforming coupled methanol production process with improved hydrogen utilization, International Journal of Greenhouse Gas Control, 93, 102905-102924. https://doi.org/10.1016/j.ijggc.2019.102905
[14] Elsayed, N.H., Elwell, A., Joseph, B., Kuhn, J.N., 2017. Effect of silicon poisoning on catalytic dry reforming of simulated biogas. Applied Catalysis A: General, 538, 157-164. https://doi.org/10.1016/j.apcata.2017.03.024
[15] Farniaei, M., Abbasi, M., Rahnama, H., Rahimpour, M.R., Shariati, A., 2014. Syngas production in a novel methane dry reformer by utilizing of tri-reforming process for energy supplying: Modeling and simulation, Journal of Natural Gas Science and Engineering, 20 (9), 132-146. http://dx.doi.org/10.1016/j.jngse.2014.06.010
[16] Farsi, M., Fekri Lari, M., Rahimpour, M.R., 2019. Development of a green process for DME production based on the methane tri-reforming, Journal of the Taiwan Institute of Chemical Engineers, 106, 9-19. https://doi.org/10.1016/j.jtice.2019.10.001
[17] Fedorova, Z.A., Danilova, M.M., Zaikovskii, V.I., 2020. Porous nickel-based catalysts for tri-reforming of methane to synthesis gas: Catalytic activity, Materials Letters, 261, 127087-127101. https://doi.org/10.1016/j.matlet.2019.127087
[18] Gangadharan, P., Kanchi, K.C., Lou, H.H., 2012. Evaluation of the economic and environmental impact of combining dry reforming with steam reforming of methane, Chemical Engineering Research and Design, 90 (11) 1956-1968. http://dx.doi.org/10.1016/j.cherd.2012.04.008
[19] García-Vargas, J.M., Valverde, J.L., De Lucas-Consuegra, A., Gómez-Monedero, B., Dorado, F., Sánchez, P., 2013. Methane tri-reforming over a Ni/β-SiC-based catalyst: Optimizing the feedstock composition, International Journal of Hydrogen Energy, 38 (11) 4524-4532. http://dx.doi.org/10.1016/j.ijhydene.2013.02.001
[20] García-Vargas, J.M., Valverde, J.L., De Lucas-Consuegra, A., Gómez-Monedero, B., Sánchez, P., Dorado, F., 2012. Precursor influence and catalytic behaviour of Ni/CeO2 and Ni/SiC catalysts for the tri-reforming process, Applied Catalysis A: General, 431–432, 49-56. http://dx.doi.org/10.1016/j.apcata.2012.04.016
[21] García-Vargas, J.M., Valverde, J.L., Díez, J., Dorado, F., Sánchez, P., 2015. Catalytic and kinetic analysis of the methane tri-reforming over a Ni–Mg/β-SiC catalyst, International Journal of Hydrogen Energy, 40 (28), 8677-8687. http://dx.doi.org/10.1016/j.ijhydene.2015.05.032
[22] García-Vargas, J.M., Valverde, J.L., Díez, J., Sánchez, P., Dorado, F., 2014. Influence of alkaline and alkaline-earth cocations on the performance of Ni/β-SiC catalysts in the methane tri-reforming reaction, Applied Catalysis B: Environmental, 148–149, 322-329. http://dx.doi.org/10.1016/j.apcatb.2013.11.013
[23] García-Vargas, J.M., Valverde, J.L., Díez, J., Sánchez, P., Dorado, F., 2015. Preparation of Ni–Mg/β-SiC catalysts for the methane tri-reforming: Effect of the order of metal impregnation, Applied Catalysis B: Environmental, 164 (3), 316-323. http://dx.doi.org/10.1016/j.apcatb.2014.09.044
[24] Hernandez, B. Martin, M., 2018. Optimization for biogas to chemicals via tri-reforming. Analysis of Fischer-Tropsch fuels from biogas, Energy Conversion and Management, 174, 998-1013. https://doi.org/10.1016/j.enconman.2018.08.074
[25] Hossain, M.A., Ayodele, B.V., Cheng, C.K., Khan, M.R., 2016. Artificial neural network modeling of hydrogen-rich syngas production from methane dry reforming over novel Ni/CaFe2O4 catalysts, International Journal of Hydrogen Energy, 41 (26), 11119-11130. http://dx.doi.org/10.1016/j.ijhydene.2016.04.034
[26] Khajeh, S., Arab Aboosadi, Z., Honarvar, B., 2015. Optimizing the fluidized-bed reactor for synthesis gas production by tri-reforming, Chemical Engineering Research and Design, 94 (2), 407-416. http://dx.doi.org/10.1016/j.cherd.2014.08.018
[27] Kozonoe, C.E., De Paiva Floro Bonfim, R., Brito Alves, R.M., Schmal, M., 2019. The Fe-Co-Cu supported on MWCNT as catalyst for the tri-reforming of methane – Investigating the structure changes of the catalysts, Fuel, 256, 115917-115930. https://doi.org/10.1016/j.fuel.2019.115917
[28] Kumar, R., Kumar, K., Pant, K.K., and Choudary, N.V., 2020. Tuning the metal-support interaction of methane tri-reforming catalysts for industrial flue gas utilization, International Journal of Hydrogen Energy, 45 (3), 1911-1929. https://doi.org/10.1016/j.ijhydene.2019.11.111
[29] Lee, S.H., Cho, W., Ju, W.S., Cho, B.H., Lee, Y.C., Baek, Y.S., 2003. Tri-reforming of CH4 using CO2 for production of synthesis gas to dimethyl ether, Catalysis Today, 87 (1–4), 133-137. http://dx.doi.org/10.1016/j.cattod.2003.10.005

[30] Majewski, A.J. Wood, J., 2014. Tri-reforming of methane over Ni@SiO2 catalyst, International Journal of Hydrogen Energy, 39 (24), 12578-12585. http://dx.doi.org/10.1016/j.ijhydene.2014.06.071
[31] Osat, M., Shojaati, F., Hafizi, A., 2022. Optimization and improvement of a conventional tri-reforming reactor to an energy efficient membrane reactor for hydrogen production, Chemical Engineering and Processing - Process Intensification, 175, 108933-108945. https://doi.org/10.1016/j.cep.2022.108933
[32] Oyama, S.T., Hacarlioglu, P., Gu, Y., Lee, D., 2012. Dry reforming of methane has no future for hydrogen production: Comparison with steam reforming at high pressure in standard and membrane reactors, International Journal of Hydrogen Energy, 37 (13), 10444-10450. http://dx.doi.org/10.1016/j.ijhydene.2011.09.149
[33] Pino, L., Vita, A., Cipitì, F., Laganà, M., Recupero, V., 2011. Hydrogen production by methane tri-reforming process over Ni–ceria catalysts: Effect of La-doping, Applied Catalysis B: Environmental, 104 (1–2), 64-73. http://dx.doi.org/10.1016/j.apcatb.2011.02.027
[34] Pino, L., Vita, A., Laganà, M., Recupero, V., 2014. Hydrogen from biogas: Catalytic tri-reforming process with Ni/LaCeO mixed oxides, Applied Catalysis B: Environmental, 148–149, 91-105. http://dx.doi.org/10.1016/j.apcatb.2013.10.043
[35] Rahnama, H., Farniaei, M., Abbasi, M., Rahimpour, M.R., 2014. Modeling of synthesis gas and hydrogen production in a thermally coupling of steam and tri-reforming of methane with membranes, Journal of Industrial and Engineering Chemistry, 20 (4), 1779-1792. http://dx.doi.org/10.1016/j.jiec.2013.08.032
[36] Sadeghi, M., Jafari, M., Yari, M., Mahmoudi, S.M.S., 2018. Exergoeconomic assessment and optimization of a syngas production system with a desired H2/CO ratio based on methane tri-reforming process, Journal of $CO_2$ Utilization, 25, 283-301. https://doi.org/10.1016/j.jcou.2018.04.009
[37] Saebea, D., Authayanun, S., Arpornwichanop, A., 2019. Process simulation of bio-dimethyl ether synthesis from tri-reforming of biogas: $CO_2$ utilization, Energy, 175, 36-45. https://doi.org/10.1016/j.energy.2019.03.062
[38] Schmal, M., Toniolo, F.S., Kozonoe, C.E., 2018. Perspective of catalysts for (Tri) reforming of natural gas and flue gas rich in CO2, Applied Catalysis A: General, 568, 23-42. https://doi.org/10.1016/j.apcata.2018.09.017
[39] Si, L.-J., Wang, C.-Z., Sun, N.-N., Wen, X., Zhao, N., Xiao, F.-K., Wei, W., Sun, Y.-H., 2012. Influence of preparation conditions on the performance of Ni-CaO-$ZrO_2$ catalysts in the tri-reforming of methane, Journal of Fuel Chemistry and Technology, 40 (2), 210-215. http://dx.doi.org/10.1016/S1872-5813(12)60011-5
[40] Song, C. Pan, W., 2004. Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired $H_2$/CO ratios, Catalysis Today, 98 (4), 463-484. http://dx.doi.org/10.1016/j.cattod.2004.09.054
[41] Wu, W., Yang, H.T., Hwang, J.J., 2014. Conceptual design of syngas production systems with almost net-zero carbon dioxide emissions, Energy, 74, 753-761. http://dx.doi.org/10.1016/j.energy.2014.07.042
[42] Yoo, J., Bang, Y., Han, S.J., Park, S., Song, J.H., Song, I.K., 2015. Hydrogen production by tri-reforming of methane over nickel–alumina aerogel catalyst, Journal of Molecular Catalysis A: Chemical, 410, 74-80. http://dx.doi.org/10.1016/j.molcata.2015.09.008
[43] Zhang, Y., Cruz, J., Zhang, S., Lou, H.H., Benson, T.J., 2013. Process simulation and optimization of methanol production coupled to tri-reforming process, International Journal of Hydrogen Energy, 38 (31), 13617-13630. http://dx.doi.org/10.1016/j.ijhydene.2013.08.009
[44] Zhang, Y., Zhang, S., Benson, T., 2015. A conceptual design by integrating dimethyl ether (DME) production with tri-reforming process for CO2 emission reduction, Fuel Processing Technology, 131 (3), 7-13. http://dx.doi.org/10.1016/j.fuproc.2014.11.006