Design of thermally coupled shell and tube reactor

Tatpong Krachaeh

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By	Mr. Tatpong Krachaeh
Field of Study	Petrochemical Engineering
Advisor	Assoc.Prof.Dr. Duangkamol Na-Ranong

Accepted by the School of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

Thesis Committee

Duangkamol

____________________________________Chairman
(Assoc.Prof.Dr. Duangkamol Na-Ranong)

TEERAPORN

___________________________________Committee
(Asst. Prof. Dr. Teeraporn Suteewong)

Kriangsak

___________________________________Committee
(Assoc. Prof. Dr. Kriangsak Kraiwattanawong)

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Abstract

Currently, the growing of ethylene (C_2H_4) and ethane (C_2H_6) demand forced the licensors to make the alternative processes and resources to produce ethylene. The most common process to produce ethane and ethylene are the steam and thermal cracking process. Oxidative coupling reaction of methane (OCM) is a one of alternative process for ethylene and ethane production. However, OCM should be operated at low concentration of oxygen to avoid undesired reactions by use membrane reactor. For dry reforming of methane reaction (DRM), methane is reacted with carbon dioxide that is by-product from OCM reaction, which was mainly global warming agent. Hence, to examine behavior and improve performance under practical assumption, the dual-membrane reactor was considered. The model for PBR and dual-mem brane reactor were developed as two-dimension mole balance model. Kinetics model and parameter was reported from previously literature. The simulated results of OCM and DRM for both reactors obtained at temperature 1023-1103 K and pressure 1.224-1.007 atm. Results showed that for OCM, performance at same reactor length selectivity and yield of all products except hydrogen of dual-membrane reactor were more than PBR. For DRM, yield and selectivity of carbon monoxide and hydrogen of DMR at same length of methane were lower than PBR.

Keywords: Dual-membrane reactor, Oxidative coupling of methane, Dry methane reforming, Reactor integration, Integrated process structure

เรื่อง	การออกแบบเครื่องปฏิกรณ์แบบเชลล์และท่อ
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บทคัดย่อ

ในปัจจุบันการเติบโตของอุปสงค์ของเอทิลีน (C_2H_4) และอีเทน (C_2H_6) ได้ผลักดันให้มีการพัฒนากระบวนการผลิตและเสาะหาแหล่งวัตถุดิบใหม่สำหรับการผลิตเอทิลีน โดยทั่วไปกระบวนการผลิตอีเทนและเอทิลีนมักมาจากกระบวนการแตกตัวด้วยไอน้ำและความร้อน กระบวนการเปลี่ยนมีเทนเป็นเอทิลีน (OCM) เป็นหนึ่งในวิธีการทางเลือกสำหรับการผลิตอีเทนและเอทิลีน อย่างไรก็ตาม OCM ควรปฏิบัติการภายใต้ความเข้มข้นของออกซิเจนที่ต่ำ เพื่อหลีกเลี่ยงปฏิกิริยาที่ไม่พึงประสงค์ โดยใช้เครื่องปฏิกรณ์แบบเมมเบรน สำหรับปฏิกิริยาการเปลี่ยนมีเทนเป็นก๊าซสังเคราะห์ DRM มีเทนจะทำปฏิกิริยากับคาร์บอนไดออกไซด์ซึ่งเป็นผลิตภัณฑ์ที่ไม่พึงประสงค์จากปฏิริยา OCM ซึ่งเป็นสาเหตุหลักของสภาวะโลกร้อน ดังนั้นเพื่อที่จะศึกษาพฤติกรรมและพัฒนาประสิทธิภาพของเครื่องปฏิกรณ์ภายใต้สมมติฐานอย่างง่าย เครื่องปฏิกรณ์แบบเมมเบรนจึงถูกนำมาพิจารณา สมการดุลโมลและพลังงานของเครื่องปฏิกรณ์แบบเบดบรรจุถูกพัฒนาเป็นแบบสองมิติ และสำหรับเครื่องปฏิกรณ์แบบเมมเบรนคู่ แบบจำลองถูกพัฒนาแบบสองมิติ แบบจำลองจลนพลศาสตร์และพารามิเตอร์ได้ถูกรายงานรายงานไว้ในวรรณกรรมก่อนหน้า ผลจากการจำลองการเกิดปฏิกิริยา OCM และ DRM สำหรับเครื่องปฏิกรณ์ทั้งสองแบบถูกจำลองที่อุณหภูมิ 1023-1103 K และความดัน 1.224-1.007 atm ผลปรากฎว่าสำหรับปฏิกิริยา OCM ประสิทธิภาพของเครื่องปฏิกรณ์ที่ความยาวเท่ากัน ค่าการเลือกเกิด และสัดส่วนผลได้ร้อยละของผลิตภัณฑ์ทั้งหมดยกเว้นไฮโดรเจนของเครื่องปฏิกรณ์แบบเมมเบรนคู่มีค่ามากกว่าเครื่องปฏิกรณ์แบบเบดบรรจุ สำหรับปฏิกิริยา DRM สัดส่วนผลได้ร้อยละและค่าการเลือกเกิดของคาร์บอนมอนอกไซด์และไฮโดรเจนของเครื่องปฏิกรณ์แบบเมมเบรนคู่มีค่าน้อยกว่าของเครื่องปฏิกรณ์แบบเบดบรรจุ

คำสำคัญ: เครื่องปฏิกรณ์แบบเมมเบรนคู่, ปฏิกิริยาการเปลี่ยนมีเทนเป็นเอทิลีน, ปฏิกิริยาการเปลี่ยนมีเทนเป็นก๊าซสังเคราะห์, การรวมเครื่องปฏิกรณ์, โครงสร้างกระบวนการแบบบูรณาการ

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Tatpong Kracheah

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NOMENCLATURE

Latin symbols

a	Wall area [m^2]
Ac	Cross sectional area [m^2]
C	Concentration [mol/m^3]
C_c	Mole concentration of carbonate [mol/m^3]
Cp	Heat capacity [kJ/(mol·K), J/(kg·K)]
D	Diameter [m]
d	Diameter or equivalent diameter [m]
D_c	Diffusivity of carbonate [m^2/s]
$D_{eff,r}$	Effective radial diffusion coefficient [m^2/s]
D_k	Knudsen diffusion coefficient [m^2/s]
Ea	Activation energy [kJ/mol]
F	Mole flow rate [mol/s], Faraday constant [C/mol]
G	Mass flux [$g/cm^2 \cdot s$]
g_c	Conversion factor
H	Membrane thickness [m]
J_{co_2}	Flux of CO_2 [mol/m/s]
K	Reaction coefficient [mol/ (g-cat ·s ·Pa^{-x})]
k	Reaction coefficient [mol/ (g-cat ·s ·Pa^{-x})]
l	Length of reactor in axial direction [m]
m	Order of reaction
M	Molecular weight [kg/mol]
M_c	Molecular weight of carbonate mixture [kg/mol]
n	Order of reaction
P	Pressure [Pa]
r	Reaction rate [$mol/m^3 \cdot s$]
R	Gas constant [J/mol·K]
S	Selectivity
T	Temperature [K]
V	Volume [m^3]

X	Conversion
Y	Yield
z_c	Ion charge of carbonate
Z_{h*}	Ion charge of electron hole
H	Membrane thickness [m]
J	Flux or membrane permeability [mol/(m^2 s)]

Greek symbols

$\emptyset$	Void fraction
δ	Effective membrane thickness [m]
ε	Membrane or packed bed porosity [–]
μ	Dynamic viscosity [Pa·s]
ρ	Density [kg/m^3]
τ	Membrane tortuosity [–]

Subscripts

h^*	Electron hole
V^{**}	Oxygen vacancy
i	Component index
j	Reaction index
l	Axial direction
m	Membrane
p	Particle, pore
r	Radial direction
S, s	Shell: Shell 1 (OCM), Shell 2 (DRM)
T,t	Tube
Gas	Gas
K	Knudsen diffusion

CHAPTER I

INTRODUCTION

1.1 Background

Currently, the growing of ethylene (C_2H_4) and ethane (C_2H_6) demand forced the licensors to make the alternative processes and resources to produce ethylene. The most common process to produce ethane and ethylene are the steam and thermal cracking process. The steam and thermal cracking process make product by cracking heavier fractions of C-C and C-H bonds, which from petroleum refineries. Oxidative coupling reaction of methane (OCM) is a one of alternative process for ethylene and ethane production even though it has highly exothermic while reaction occurs. The OCM reaction was highly exothermic reaction with temperature 900–1200 K [1]. In this reaction, methane (CH_4) is reacted with oxygen (O_2) then produce ethylene and ethane including with undesired product such as carbon dioxide (CO_2) and water. Therefore, natural gas was a suitable resource for producing ethylene due to the component of natural gas is mainly composed of methane and economical relatively feedstock [2]. For utilized of highly exothermic from OCM, Dry reforming of methane reaction (DRM) that highly endothermic and reversible reaction was considered. In DRM reaction, methane is reacted with carbon dioxide that is by-product from OCM reaction [3]. The product from DRM reaction is synthesis gas that use wide range and facilely. In previous, the confidence to design the reactor to maximize the utilization of the heat of reaction and improve conversion, yield, and selectivity have been developed continuously [4].

In this study, behavior of oxidative coupling methane (OCM) and dry reforming of methane (DRM) in PBR and dual-membrane reactor. Performance of PBR were investigated in order to evaluate conversion of methane (X), selectivity (S), and yield (Y) in coupled thermally shell and tube reactor.

1.2 Objectives

To study the effect of operating conditions in shell side and tube side that related to behavior of OCM and DRM reaction in reactor and reactor performance in term of conversion of methane (X), selectivity (S), and yield (Y).

1.3 Scopes of Work

1.3.1 Develop two-dimension dual membrane reactor model.

1.3.2 Investigate behavior of each reaction under assumption isothermal and non-isothermal.

1.4 Expected Outputs

1.4.1 Coupling of OCM and DRM is one of coupling of highly exothermic and highly endothermic reaction in dual-membrane reactor that have trend to use by-product from OCM worthily. The information obtained from this study will be useful in the design of reactor for coupling of OCM and DRM.

CHAPTER II

LITERATURE REVIEW

2.1 Oxidative coupling reaction of methane (OCM)

The OCM process is partial oxidation of methane to produce ethane and ethylene in gas phase, subsequently. This reaction was discovered in 1980s for direct conversion of natural-gas that consisting of methane, to produce value-add chemicals[5] such as ethane, ethylene, and C_{2+}. The product from this reaction can be used to produce polymer such as polyethylene or other polymers. First of all, methane reacts with oxygen to produce ethane and water. Subsequently, ethane will react and transformed into ethylene or higher hydrocarbon. One of problem is a slightly increase of oxygen concentration can cause the reaction shift and generate carbon dioxide. Therefore, the type of oxygen feed be considered[4].

2.1.1 Catalyst for oxidative coupling reaction of methane (OCM)

Commonly catalysts for oxidative coupling reaction of methane were metal oxide catalyst. The oxide catalyst can be pure or modified by used transition metals. The catalyst can prepare by different synthesis conditions such as precipitation, impregnation, sol-gel, and flame spray pyrolysis. Modifications with other oxides, metals or chloride salt along with vary pressure, temperature, and space velocity for reaction shift toward to improved ethylene and ethane selectivity, yield, methane conversion, and to limit catalyst deactivation[6].

Pure or unmodified metal oxide catalysts have low selectivity, low yield, and low catalytic lifetime. The modified metal oxide catalysts was developed to improve these properties[6]. However, Godini et al.[6] studied about properties of catalyst for different preparation method by used 5 wt.%Na_2WO_4/1.9 wt.%Mn/SiO_2 catalyst prepared by sol–gel and impregnation methods. Reaction conditions were 825 ˚C and 2.5 methane/oxygen ratio. The method that used to prepare the catalyst effect to properties of catalyst. The different preparation method effect to properties of catalyst such as conversion, selectivity, and yield significantly.

From the Gao et al.'s[7] report studied the reactions that carried out with $BaCO_3$ by used methane/oxygen ratio of 4, methane and varying operating temperature around 740-860 ˚C. The report showed that the operating temperature effected to conversion and selectivity significantly. However, the study from Rane et al.[8] that studied the effect of temperature on CH_4 conversion for Li/CaO, Na/CaO and Cs/CaO catalyst when the Metal/CaO ratio was 0.1 and reactor operated at 700–750 ˚C, methane/oxygen ratio of 4, showed the effect from temperature that cause to conversion and selectivity but also depends on type of catalysts.

2.1.2 Kinetics data

The kinetics data was based on La_2CO_3/CaO catalyst [9]. These reaction equations consist of 10 stoichiometric reactions that occur in gas phase.

Step 1: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (2.1)

Step 2: $2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O$ (2.2)

Step 3: $CH_4 + O_2 \rightarrow CO + H_2O + H_2$ (2.3)

Step 4: $CO + 0.5O_2 \rightarrow CO_2$ (2.4)

Step 5: $C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$ (2.5)

Step 6: $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$ (2.6)

Step 7: $C_2H_6 \rightarrow C_2H_4 + H_2$ (2.7)

Step 8: $C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$ (2.8)

Step 9: $CO + H_2O \rightarrow CO_2 + H_2$ (2.9)

Step 10: $CO_2 + H_2 \rightarrow CO + H_2O$ (2.10)

The OCM reaction rate were as follows:

$$r_i = \frac{k_{0,j}e^{-(\frac{Ea}{RT})}P_c^{m_j}P_{O_2}^{n_j}}{(1+K_{j,CO_2}e^{-\Delta H_{ad,CO_2}/RT}P_{CO_2})^2} \text{ j = 1, 3-6} \tag{2.11}$$

$$r_2 = \frac{k_0 e^{-(\frac{Ea}{RT})}(K_{O_2}e^{-\Delta H_{ad,O_2}/RT}P_{O_2})^{n_2}P_{CH_4}^{m_2}}{(1+\left(K_{O_2}e^{-\frac{\Delta H_{ad,O_2}}{RT}}P_{O_2}\right)^n + K_{CO_2}e^{-\Delta H_{ad,CO_2}/RT}P_{CO_2})^2} \tag{2.12}$$

$$r_7 = k_{0,7}e^{-(\frac{Ea.7}{RT})}P_{C_2H_6} \tag{2.13}$$

$$r_8 = k_{0,8}e^{-(\frac{Ea.8}{RT})}P_{C_2H_6}^{m_8}P_{H_2O}^{n_8} \tag{2.14}$$

$$r_9 = k_{0,9}e^{-(\frac{Ea.9}{RT})}P_{CO}^{m_9}P_{H_2O}^{n_9} \tag{2.15}$$

$$r_{10} = k_{0,10}e^{-(\frac{Ea.10}{RT})}P_{CO_2}^{m_{10}}P_{H_2}^{n_{10}} \tag{2.16}$$

2.2 Dry reforming reaction of methane (DRM)

Carbon dioxide is one of pollutants that caused from industry, which even though no effects to human health but effect to global warming[10]. However, the carbon dioxide was one of reactant for DRM to produce synthesis gas.

From DRM reaction, Methane and carbon dioxide in gas phase were convert to synthesis gas and give high concentration of carbon monoxide that was used as reactant to methanol production in Fisher-Tropsch process or produce liquid transport fuel. This reaction was endothermic reaction and reversible. DRM reaction usually operated at high temperature around 900-1273 K[11] and low pressure condition due to the reaction has equilibrium as showed as eq. 2.17.

2.2.1 Catalyst for Dry reforming reaction of methane (DRM)

Catalyst for dry reforming reaction of methane (DRM) usually used the catalyst that made from metals such as Ni-based catalyst, Pt-based-catalyst, Ru-based catalyst, Rh-based catalyst, Pd-based catalyst, Co-based catalyst, and Ir-based catalyst. Difference of types of metal, the promoters, and the method that used to prepare the catalyst led to difference behavior. The most popular catalyst was nickel-based catalyst.

The problem for nickel-based catalyst was the carbon deposition that reduced the catalytic activity. Fortunately, this problem was partially reduced by adding promoters such as potassium and calcium oxides. However, the types of support effects to the activity of catalyst significantly that was reported by S.-E. Park et al.[11]

The mechanism of DRM consist of four steps were as follows[11]:

1. **Dissociative adsorption of methane**

   Rate determining step was this step that the methane (CH_4) adsorbed on the top of metal atom as CH_3 (complete tetravalency). Whereas some of methane dissociative adsorbed between two metal atoms as CH_2 (bridged adsorption)

2. **Dissociative adsorption of CO_2**

   Dissociative adsorption of CO_2 tends to adsorb on metal-support interface and can occurs in three ways:

   1. C-only coordination
   2. C-O coordination
   3. O-only coordination

   These ways were depend on the surface structure and defects. However, only C-O coordination and O-only coordination were useable for DRM.

3. **Hydroxyl groups formation**

   Hydrogen from metal active site migration to support. Then, the hydroxyl groups form on the surface of support at temperature below 1073 K.

4. **Intermediate's oxidation and desorption**

   Oxygen on surface of metal site react with S-CH_x groups and toward into S-CH_xO or S-CO. Then, S-CH_xO will form/or decomposition into carbon monoxide and hydrogen. After that, both of them will desorb.

However, the kinetics depends on types of catalyst and the mechanism can change with temperature[12].

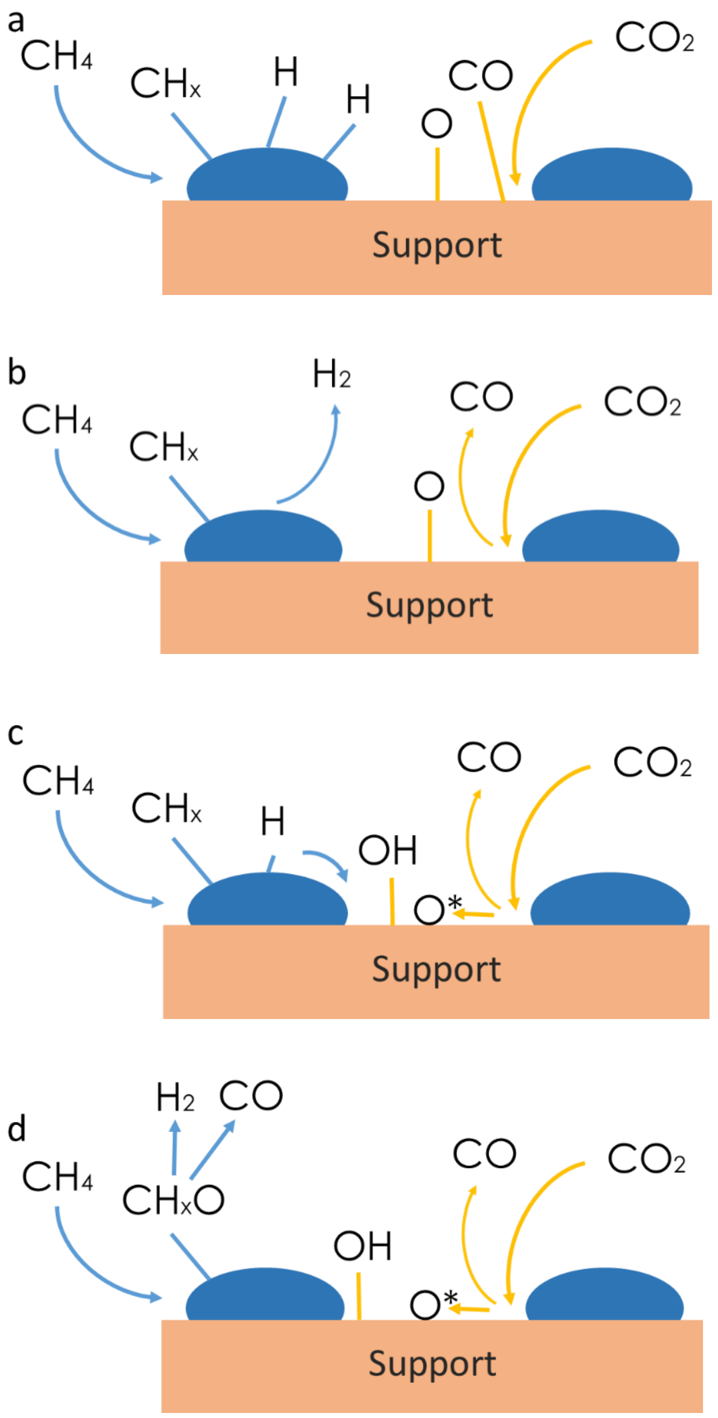

Figure 2.1 Reaction steps for the dry reforming of methane (DRM): (a) Dissociative adsorption of CO2 on the metal and metal-support interface, respectively. (b) Fast desorption of CO and hydrogen. (c) Formation of surface hydroxyls and oxygen spillover. (d) Surface hydroxyls and oxygen species oxidize hydrogen depleted S-CH_x species and formation of CO and H_2.

2.2.2 Kinetics data

The kinetics data that based on $Ni/La/Al_2O_3$ catalyst was reported by Unni Olsbye et al.[3]

Main reaction: $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ ($\Delta H_{298K} = +247$ kJ/mol) (2.17)

The DRM reaction rate were as follows:

$$r = \frac{kP_{CH_4}P_{CO_2}}{(1 + K_1P_{CH_4} + K_2P_{CO})(1 + K_3P_{CO_2})}\left(1 - \frac{P_{H_2}^2P_{CO}^2}{K_{eq}P_{CH_4}P_{CO_2}}\right) \tag{2.18}$$

2.3 Reactor design for OCM

Since the OCM was discovered in 1980s, many types of catalyst were developed to improve selectivity, yield, and conversion. Development of various reactor types also used to improve all of above performance of OCM process. Many concept design of reactors was developed such as multiphase reactor, heat management options, distributed O_2 feeding, and integration of product separation[4].

2.3.1 Multiphase reactor

The concepts of multiphase reactor was classified by the different phase of fluid (gas phase) and catalyst. For example, the multiphase reactors were fixed bed reactors, fluidized bed reactors, and bubble column reactors. Catalyst that usually used for fixed bed reactor and fluidized bed reactor was present in form of solid phase, while catalyst for bubble column reactor present in form of liquid phase[4].

For fixed bed reactors, Ching Thian Tye et al.[9] studied a one-dimensional model for the oxidative coupling of methane (OCM) reactor by change assumption for system such as isothermal, adiabatic, and non-isothermal and used kinetic model based on La_2O_3/CaO catalyst. The adiabatic and non-isothermal gave the results that increasing temperature along reactor length that cause low selectivity and yield due to series of reactions.

2.3.2 Heat management options

OCM reaction was exothermic reaction. This is a reason for packed bed reactor, the external cooling was necessary via wall-tube heat exchanger. For any fixed bad reactors, hotspot formation was a critical problem that must be considered[4].

2.3.3 Distributed O_2 feeding

This concept was used to avoid undesired reaction such as combustion reaction, which changing methane or C_{2+} toward to carbon dioxide or carbon monoxide by control concentration of oxygen. Reactor that used this concept, usually membrane reactor such as dense ceramic membrane reactor[13].

In 1997 one of distributed O_2 feeding concept was reported, Y. K. Kao et al.[13] studied OCM reaction and compare the performance of OCM in fixed bed reactor (FBR) and dense ceramic membrane reactor (DMR) that filled with Li/MgO catalyst. Both reactor operated at temperature 750 ˚C. The feed consist of 70% of methane and 30% of oxygen. Y. K. Kao et al.[13] reported that for dense ceramic membrane reactor, the oxygen concentration is uniform at low level due to dense ceramic membrane reactor limiting mole flux of oxygen that pass through. Therefore, undesired product was lower than FBR that means more selectivity than fixed bed reactor at same yield. The main reason that make FBR has lower selectivity of ethylene and ethane than DMR at same yield was methane and oxygen were fed together into the entrance of FBR. Hence, undesired reaction such as combustion of methane was easily to occur due to high ratio of oxygen.

2.3.4 Integration of product separation

The distributed O_2 feeding improve C_2 selectivity by limiting the rate of undesired reaction. But the integration of product separation is another idea to improve C_2 selectivity by separate the produced C_2 before they have a chance to change into carbon dioxide or carbon monoxide. Anna Lee Tonkovich et al.[14] studied the OCM process based on this idea by used simulated countercurrent moving-bed chromatographic reactor (SCMCR) and operate at temperature near 1000 K with a Sm_2O_3 catalyst. They separate the produced C_2 by used solid adsorbents. The problem for this idea was the temperature of operating for reaction and adsorption that are very different (~800°C and ~100°C, respectively). Hence, the reactor that reaction occurs should separate from the reactor that adsorption occurs.

2.4 Reactor design for DRM

Due to the catalyst that used for DRM usually used solid catalyst, the reactor that used for DRM was packed bed reactor or membrane reactor[10]

2.4.1 Packed bed reactor for DRM

In traditional, the packed bed reactor was a common type of reactor that used for heterogeneous catalysts and gas phase reaction[10].

2.4.2 Membrane reactor for DRM

The concept of membrane reactor for DRM was to separate hydrogen (H_2) that form by DRM reaction. Due to this reaction was a gas phase reaction and reversible as showed as equation 2.17. If hydrogen split out by membrane, the partial pressure of hydrogen inside reactor will decrease and the reaction will shift toward to product further. This idea has possibility to give high conversion and high yield even though the operating temperature was low. This means the using energy was reduced. Notwithstanding, the material that used to construct the reactor should be considered. The below table showed about the main features of membrane for implementing reactors[15].

Table 2.1 Main features of membrane for implementing reactors.

Type of membrane	Material	Selectivity	Permeability
Dense	Metallic electrolytes	High (H_2, O_2)	Low to moderate
Porous	Macroporous Mesoporous Microporous	Nonselective Low to moderate Can be very selective	High Moderate to high Moderate
Composite	Glass-metal Ceramic-metal Metal-metal	Can be very selective	Moderate

CHAPTER III

EXPERIMENTAL

3.1 Reactor model

Reactor designed as packed bed and dual-membrane reactor that fill with heterogeneous catalyst. For dual-membrane reactor, OCM reaction occurred at first shell side and DRM reaction occurred at second shell side. In practically, the reactor was considered as packed bed shell and tube reactor that operated under isothermal, non-isothermal, and isobaric.

The model was developed based on steady state, ideal gas, pseudo-homogeneous, and two-dimension PBR model. The behavior of OCM and DRM reaction this reactor was simulated by used mole balance (Eq.3.1).

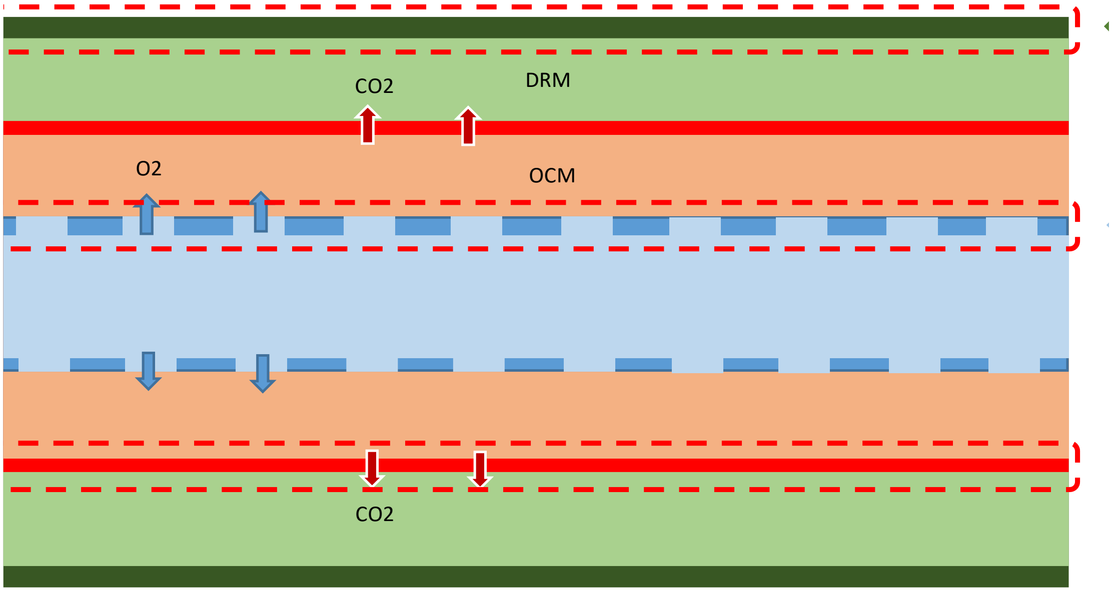

Figure 3.1 The two-dimension dual membrane reactor that used to simulate.

For dual-membrane reactor, it was divided into 3 zone that was separated by porous membrane (Shell 1) and molten carbonate composite membrane. In tube side (blue zone), oxygen was fed at this zone, then oxygen will diffuse from tube through the porous membrane into OCM zone (orange zone). For OCM zone, feed consist of methane, nitrogen, and carbon dioxide. At this section, 10 of reactions were occurred and produced ethane and ethylene. However, undesired reactions such as combustion also occur and produced carbon dioxide. To eliminate carbon dioxide from this section, the molten carbonate composite membrane was considered. Carbon dioxide will pass through the membrane by driving force into DRM section (green zone). For DRM zone, this zone needs to operate at low pressure due to DRM reaction has equilibrium limit. To give more synthesis gas yield the molten carbonate composite membrane was considered.

3.1.1 Mole balance for 2-Dimesion isothermal packed bed reactor

For mole balance of 2-Dimesion packed bed reactor, the equation that used, as showed as equation 3.1.

$$\frac{\partial C_i}{\partial l} = \frac{1}{U_l}\left[D_{eff,L}\left[\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r}\frac{\partial C_i}{\partial r}\right] + \sum_j r_{ij}\right] \tag{3.1}$$

3.1.2 Mole balance for 2-Dimension isothermal dual membrane reactor

For mole balance of 2-Dimesion isothermal dual-membrane reactor, the equation that used, as showed as equation 3.1.

Boundary conditions for dual-membrane reactor

Equation of oxygen flux permeability for porous membrane.

$$-D^t_{eff,r}\left.\frac{\partial C^t_i}{\partial r}\right|_{r=R^{Internal-t}} = D^s_{eff,r}\left.\frac{\partial C^s_i}{\partial r}\right|_{r=R^{External-OCM}} \tag{3.3}$$

Equation of carbon dioxide flux permeability for dense-ceramic membrane.

$$J_{co_2} = -\frac{\varepsilon_{MC}}{\tau_{MC}}\frac{\frac{C_C D_C}{H}(\sigma_{h^\bullet} + \sigma_{V^{\bullet\bullet}})RT\ln\frac{P''_{CO_2}}{P'_{CO_2}} + \frac{\sigma_{h^\bullet}}{2}RT\ln\frac{P''_{O_2}}{P'_{O_2}}}{RT(\sigma_{h^\bullet} + \sigma_{V^{\bullet\bullet}}) - 2\frac{\varepsilon_{MC}\tau_{SO}}{\tau_{MC}\epsilon_{SO}}Z_{h^\bullet}Z_C C_C D_C F^2} \tag{3.4}$$

Equation of flux for all species at wall of Shell-2

$$\left.\frac{\partial C^s_i}{\partial r}\right|_{r=R^{DRM-W}} = 0$$

3.1.3 Energy balance for 2-Dimesion isothermal packed bed reactor

For energy balance of 2-Dimesion adiabatic packed bed reactor, the equation that used, as showed as equation 3.6.

$$\frac{\partial T}{\partial l} = \frac{1}{C \cdot C_p . Ul}[\lambda_{eff,r}\left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right] + \sum_j [r_{ij}(-\Delta HR_j)]] \tag{3.6}$$

Boundary conditions for packed bed reactor

Equation of heat transfer at the wall of reactor.

$$\lambda^s_{eff,r} \left.\frac{\partial T^s_i}{\partial r}\right|_{r=R^{DMR-W}} = 0 \tag{3.7}$$

3.1.4 Energy balance for 2-Dimension isothermal dual membrane reactor

For energy balance of 2-Dimesion dual-membrane reactor, the equation that used, as showed as equation 3.6.

Boundary conditions for packed bed reactor

Equation of heat transfer at the porous membrane.

$$\lambda^s_{eff,r} \left.\frac{\partial T^t_i}{\partial r}\right|_{r=R^m} = \left[h^m + \sum_i K_i \, \Delta C_i C_{P_i}\right] \Delta T^{t-OCM} \tag{3.8}$$

Equation of heat transfer at the molten carbonate composite membrane.

$$\lambda^s_{eff,r} \left.\frac{\partial T^t_i}{\partial r}\right|_{r=R^m} = \left[h^m + \sum_i K_i \, \Delta C_i C_{P_i}\right] \Delta T^{OCM-DRM} \tag{3.9}$$

Equation of heat transfer at the wall of reactor was shown at equation 3.7.

3.2 Kinetics model

3.2.1 Dry reforming reaction of methane (DRM)

From DRM reaction, Methane and carbon dioxide were convert to synthesis gas. The kinetics data that based on Ni/La/Al_2O_3 catalyst was reported by Unni Olsbye et al.[3] and reaction and rate equations was showed in page 15.

3.1.5 Oxidative coupling reaction of methane (OCM)

From OCM reaction, the kinetics data was based on La_2CO_3/CaO catalyst [9]. These data consist of 10 stoichiometric reactions that occur in gas phase and reaction and rate equations was showed in page 11-12, respectively. Methane (CH_4) react with oxygen (O_2) to convert into ethane (C_2H_6). There are first three reaction that are reaction which methane was converted. The selective reaction is second reaction and fifth reaction. Non-selective reaction are first and third reaction due to these reaction form carbon dioxide (CO_2) and carbon monoxide (CO).

3.3 Evaluation of reactor performance

Table 3.1 Calculation of Reactor performance of OCM and DRM

Parameter	OCM	DRM
Conversion (X)	$X_{CH_4,OCM} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}}$	$X_{CH_4,DRM} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}}$
Selectivity (S)	$S_i = \frac{F_i}{F_{all\ product}}$	$S_i = \frac{F_i}{F_{all\ product}}$
Yield (Y)	$Y_i = \frac{F_i}{F_{CH_4,in}}$	$Y_i = \frac{F_i}{F_{CH_4,in}}$

3.4 Solution approach

3.4.1 Two-dimension packed bed reactor

For two-dimension packed bed reactor, setting mole balance equation and auxiliary equation. Subsequently, solve PDE equation by used Matlab. In isobaric and isothermal case, setting PDE equation to solve only the mole balance but for isobaric and non-isothermal case, setting PDE equation to solve the mole balance and energy balance.

Feeding and operating conditions for one-dimension packed bed reactor

For OCM packed bed reactor, the feeding and operating conditions was showed as follows.

Table 3.2 Feeding and operating conditions for one-dimension OCM packed bed reactor.

Feed	component	Conc.	unit
Shell1-OCM	CH_4	6	mol/m3
	O_2	6	mol/m3
	N_2	6	mol/m^3
Conditions	T	1023-1103	K
	v	0.000004	m^3/s

For DRM packed bed reactor, the feeding and operating conditions was showed as follows:

Table 3.3 Feeding and operating conditions for one-dimension DRM packed bed reactor.

Feed	component	Conc.	unit
Shell2-DRM	CH_4	6	
	CO_2	2.5	mol/m^3
			mol/m^3
	N_2	6	mol/m^3
Conditions	T	1023-1103	K
	v	0.000004	m^3/s

3.4.2 Two-dimension dual-membrane reactor

For two-dimension dual-membrane reactor, setting mole balance equation and auxiliary equation. Mole balance was reform from partial differential equation into numerical form by using numerical method. Then, solving all equations by programing on Matlab. Strategies for programing of 2-D dual-membrane reactor were showed as follow.

Feeding and operating conditions for two-dimension dual-membrane reactor

For dual-membrane reactor, the feeding and operating conditions was showed as follows:

Table 3.4 Feeding and operating conditions for two-dimension dual-membrane reactor.

Feed	component	Conc.	unit
Tube	O_2	6	mol/m^3
	N_2	6	mol/m^3
	P	102262.2	Pa
Shell1-OCM	CH_4	6	mol/m^3
	CO_2	2.5	mol/m^3
	N_2	6	mol/m^3
	P	123566.8	Pa
Shell2-DRM	CH_4	6	mol/m^3
	N_2	6	mol/m^3
	P	102262.2	Pa
Conditions	T	1023-1103	K
	v	0.000004	m^3/s

Table 3.5 summarizes data of reactor structure such as reactor length, reactor tube diameter, reactor shell-1 diameter or membrane thickness.

Table 3.5 Reactor structure design data for dual-membrane reactor

Reactor	Diameter	value	unit
	d,t	0.007	m
	d,ocm	0.015	m
	d,drm	0.020	m
	del,m	0.200	mm
	del,pm	3.000	mm
	L	0.350	m

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Model validation

Oxidative coupling of methane (OCM)

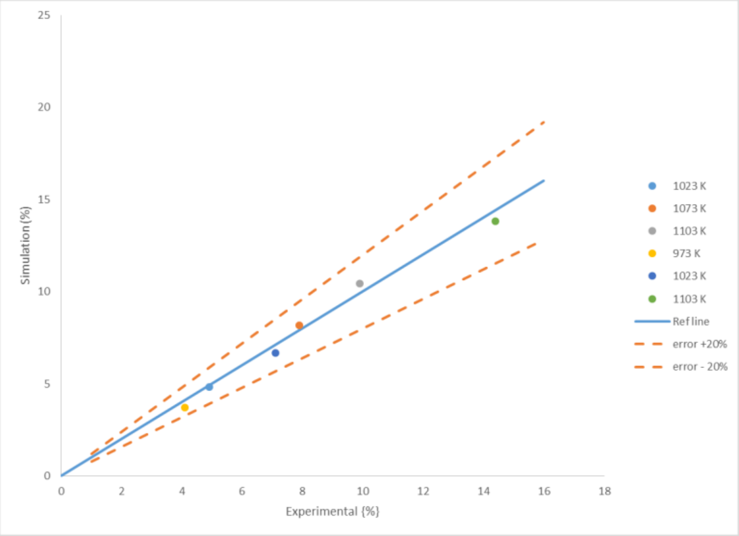

Figure 4.1. Parity plots of methane conversion (X).

Figure 4.1. shows the parity plot between simulation in this work and experimental from Tye, C. T., in term of conversion of methane with the derivative around ±20%.

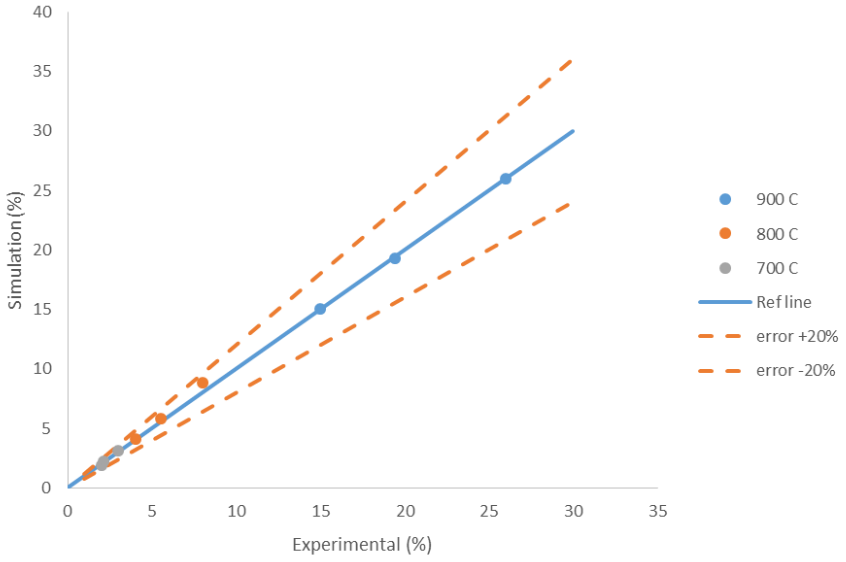

Figure 4.2. Parity plots of yield of carbon monoxide (YCO).

Figure 4.2. shows the parity plot between simulation in this work and experimental from U. Olsbye, in term of conversion of methane with the derivative around ±20%.

4.2 Oxidative coupling reaction of methane packed bed reactor (OCM-PBR)

Isothermal

For two-dimension packed bed reactor for OCM, the model is developed to be practical under isothermal and isobaric assumption. This reactor was operated at 1023-1103 K and 1.224 atm.

From Figure 4.3., the graph that plot between conversions of methane that used as reactant for OCM and reactor length. Methane and oxygen was decreased rapidly until run out of oxygen at reactor length around 0.0082 m. While oxygen was running out, methane consumption rate also stopped. Products from OCM reaction is carbon dioxide, carbon monoxide, hydrogen, water, ethane, and ethylene. The effect of temperature that use to operate, was shown in the graph. If temperature increase, conversion of methane will increase due to this reaction was depended on partial pressure. Increasing temperature will cause pressure inside reactor increase.

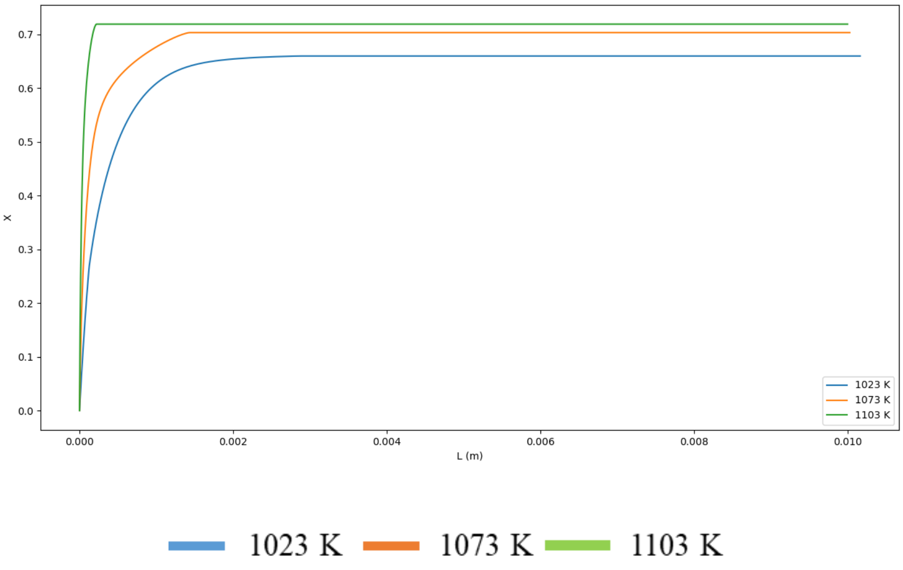

Figure 4.3. Conversion of methane along reactor length (m) for OCM-PBR

The graph that plots conversion of methane versus reactor length. This graph showed that the methane conversion can reached to around 0.7 rapidly and still hold at this conversion until the end of the reactor. Due to the concentration of another reactant (oxygen) was nearby zero. As shown in Figure 4.4. (b), yield of ethane was rapidly increased and then slowly decreased due to ethane can decompose to ethylene and hydrogen. All of above also can explain about Figure 4.4. (a), (d), which have same trend due to ethylene and hydrogen was product from ethane reactant. However, yield of carbon monoxide that rapidly increase and decrease because carbon monoxide was react with oxygen to produce carbon dioxide and water gas shift reaction was occurred. Selectivity of products that was interested such as synthesis gas and C_2 (ethylene and ethane) was showed as Figure 4.4. (e-h). These graphs showed the trend as same as yield of products except selectivity of hydrogen, which decrease when temperature increase.

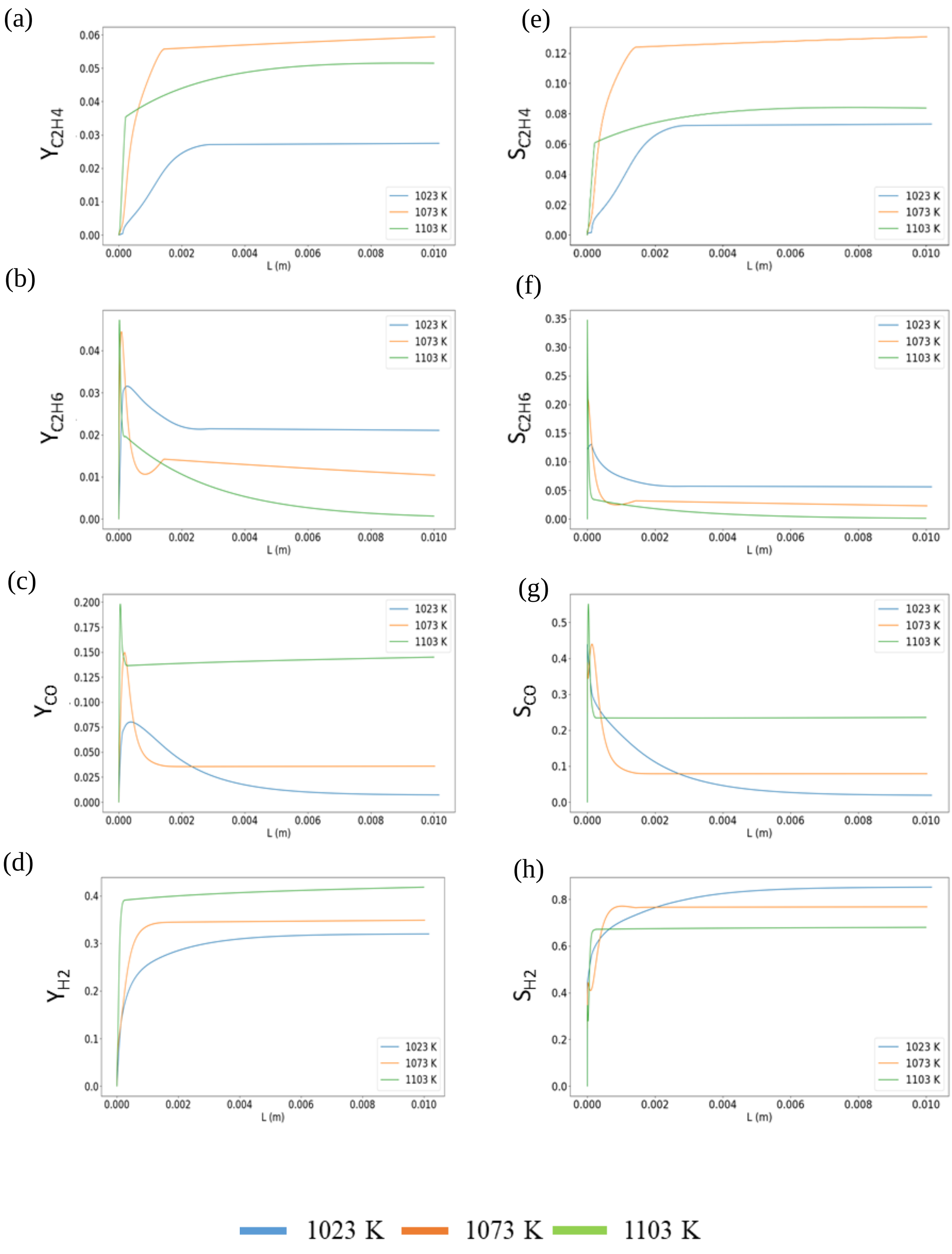

Figure 4.4. Performance of isothermal packed bed reactor for OCM reaction operated at 1023 – 1103 K and 1.224 atm.

Adiabatic

For the adiabatic OCM reaction, if temperature increase, the conversion of methane and C2 selectivity will increase due to the exothermic reaction however, in OCM adiabatic. If temperature increase, the conversion of methane and product selectivity will decrease due to the endothermic reaction. The effect of this DRM reaction temperature is less on yield and selectivity, so the temperature can be lower to achieve the same yield and selectivity. (It shouldn't be too lower to the reaction doesn't occur).

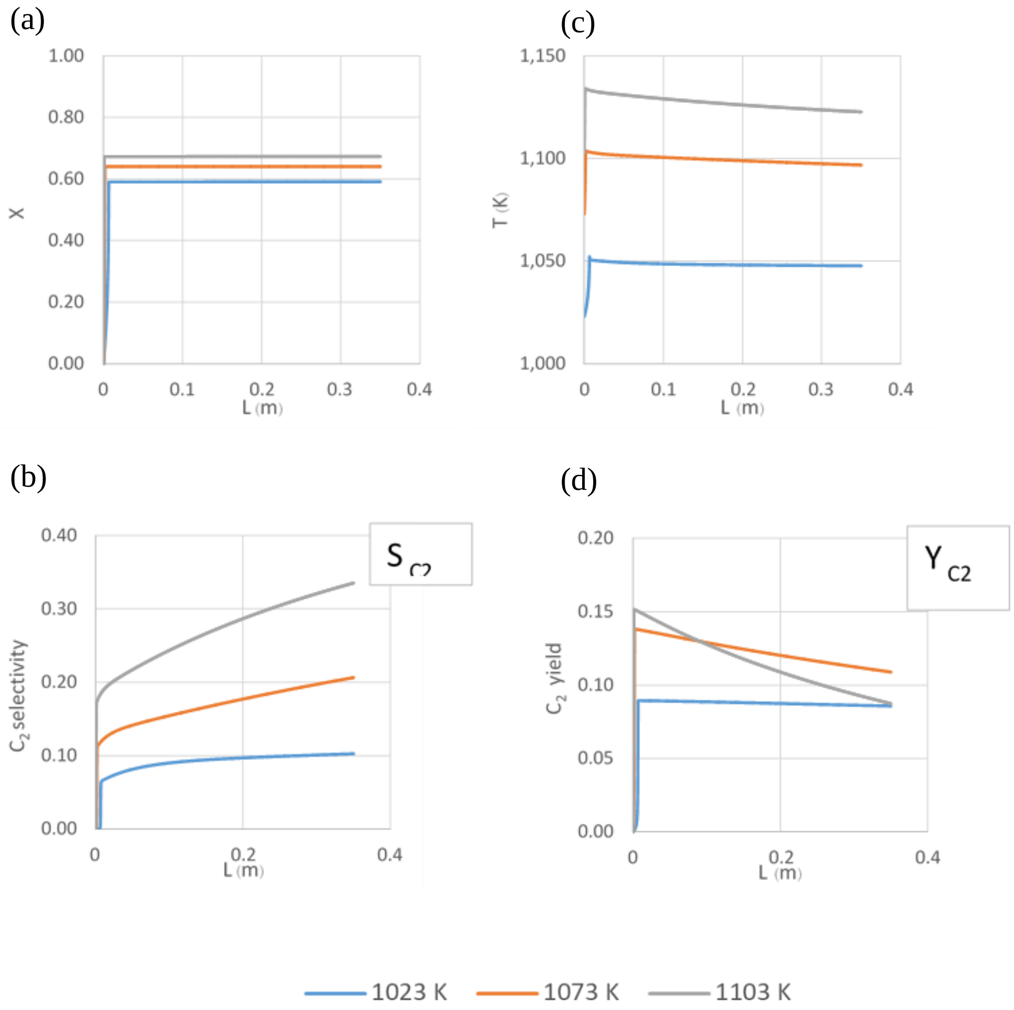

Figure 4.5. Performance of adiabatic packed bed reactor for OCM reaction operated at 1023 – 1103 K and 1.224 atm.

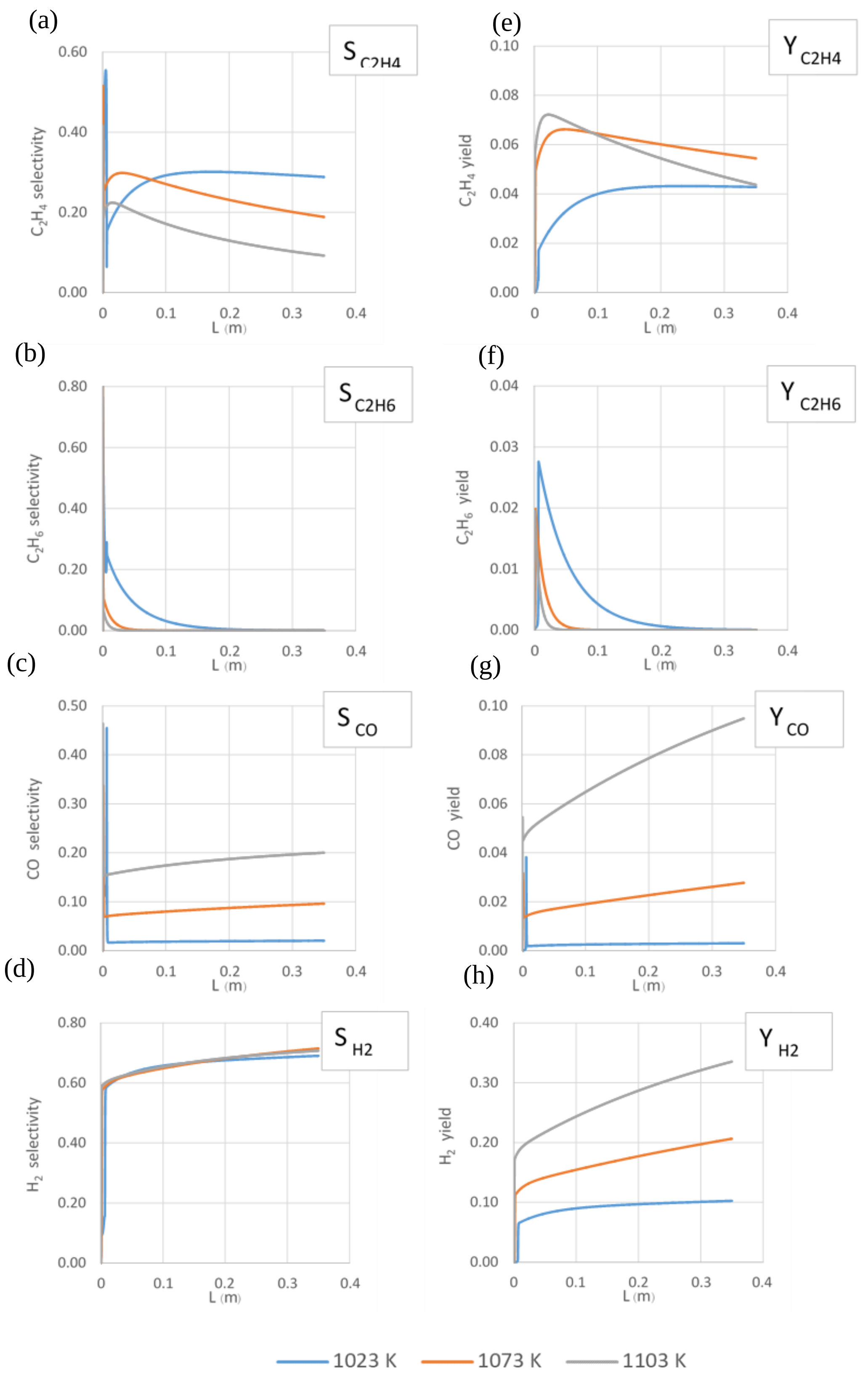

Figure 4.6. Performance of adiabatic packed bed reactor for OCM reaction operated at 1023 – 1103 K and 1.224 atm (con.)

4.3 Dry reforming of methane packed bed reactor (DRM-PBR)

Isothermal

For two-dimension packed bed reactor for DRM, the model was developed under practical, assumption isothermal and isobaric. This reactor was operated at 1023-1073 K and 1.0067 atm.

Figure 4.7. shows graph that plot between conversions of methane at difference temperature along the packed bed reactor length. Concentration of reactants were decreased until the reaction reached equilibrium at reactor length around 0.02 m. The effect of temperature that use to operate, was shown in the graph. If temperature increase, conversion of methane will decrease due to this reaction was depended on partial pressure. Increasing temperature will cause pressure inside reactor increase. Therefore, this reaction should be operated at low temperature.

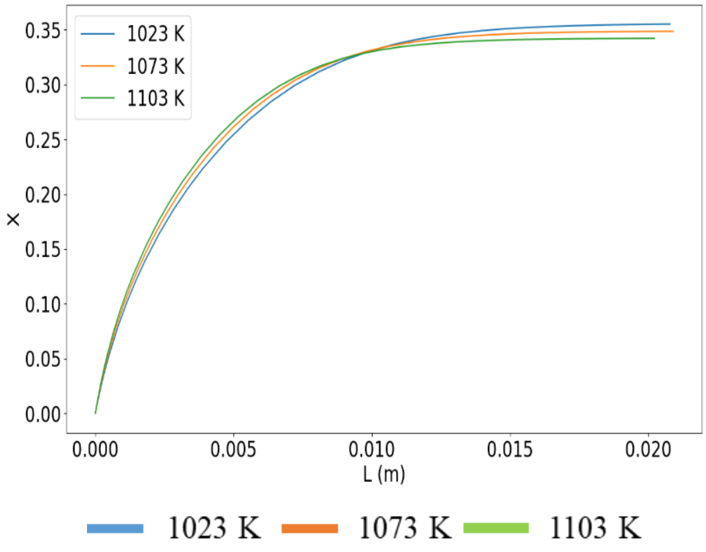

Figure 4.7. Conversion of methane along reactor length (m) for DRM-PBR at T 1023-1103K

Conversion of methane was showed in Figure 4.7. Conversion was rapidly increased then hold at conversion around 0.35 due to limitation of DRM reaction equilibrium. In the same way, yield and selectivity of carbon monoxide and hydrogen also have trend as same as conversion of methane along the packed bed reactor length for DRM and hold on when reaction reached to equilibrium.

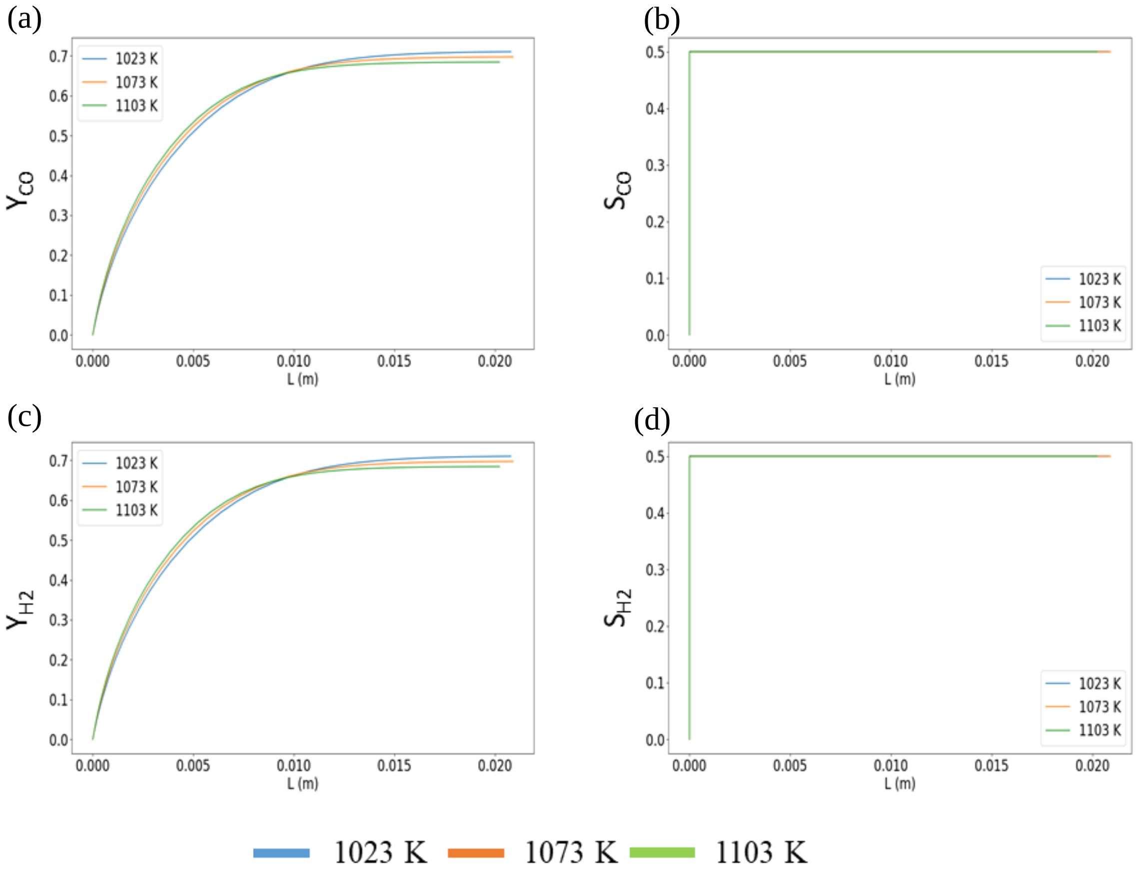

Figure 4.8. Performance of isothermal packed bed reactor for DRM reaction operated at 1023 – 1103 K and 1.0067 atm.

Adiabatic

The gradual decreasing of ethane may be due to the decomposition of ethane that convert to ethylene rather than the oxidation of ethane. The increasing of hydrogen and carbon monoxide yield at 1023 K and 1073 K was not much different, while at 1103 K was higher than both lower temperatures. At 1103 K the noticeable decreasing of ethylene maybe be due to steam reforming and oxidation, as it can produce higher hydrogen. In addition, the selectivity of hydrogen at different temperatures was increased at the initial length and then will be constant.

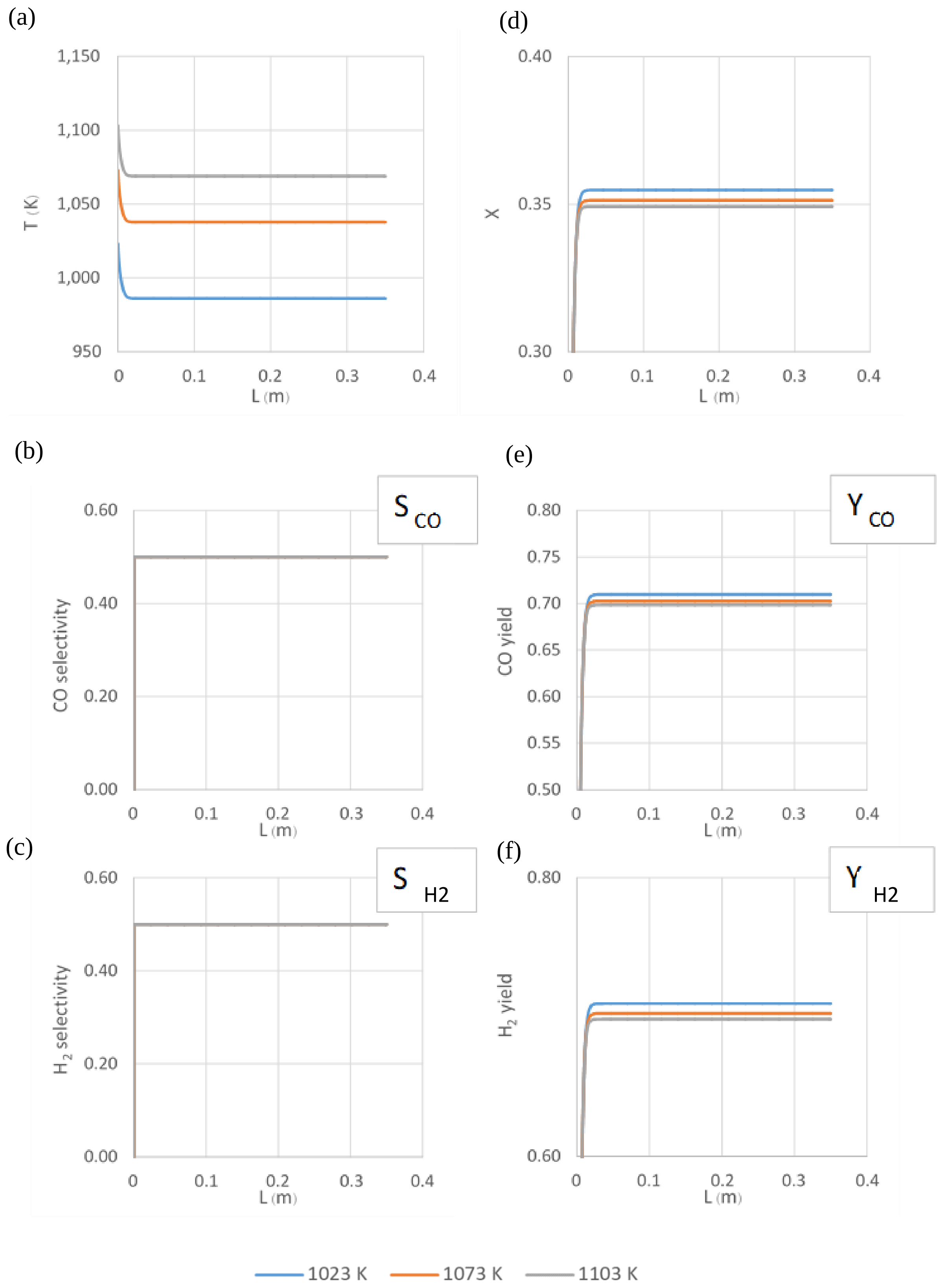

Figure 4.9. Performance of adiabatic packed bed reactor for DRM reaction operated at 1023 – 1103 K and 1.0067 atm.

4.4 Dual-membrane reactor

For dual-membrane reactor, the model was developed for two dimensions under practical assumption, isothermal, non-isothermal, and isobaric. Results that simulated from this model was divided into 2 sections for OCM and DRM.

4.4.1 Oxidative coupling of methane section

Adiabatic

For non-isothermal dual-membrane reactor of OCM, graph (a) was plotted between conversions of methane and reactor length (m). Conversion of methane increased slightly due to limitation of oxygen molar flux. However, when inlet temperature increase conversion will increase and also C_2 yield. For graph that plotted between temperature (K) and reactor length (m), temperature inside reactor decrease due to heat transfer to DRM with CO_2 that pass through molten carbonate composite membrane and heat transfer between OCM section and DRM section that separate by membrane. Subsequently, the heat transfer will use to drive DRM reaction at DRM section.

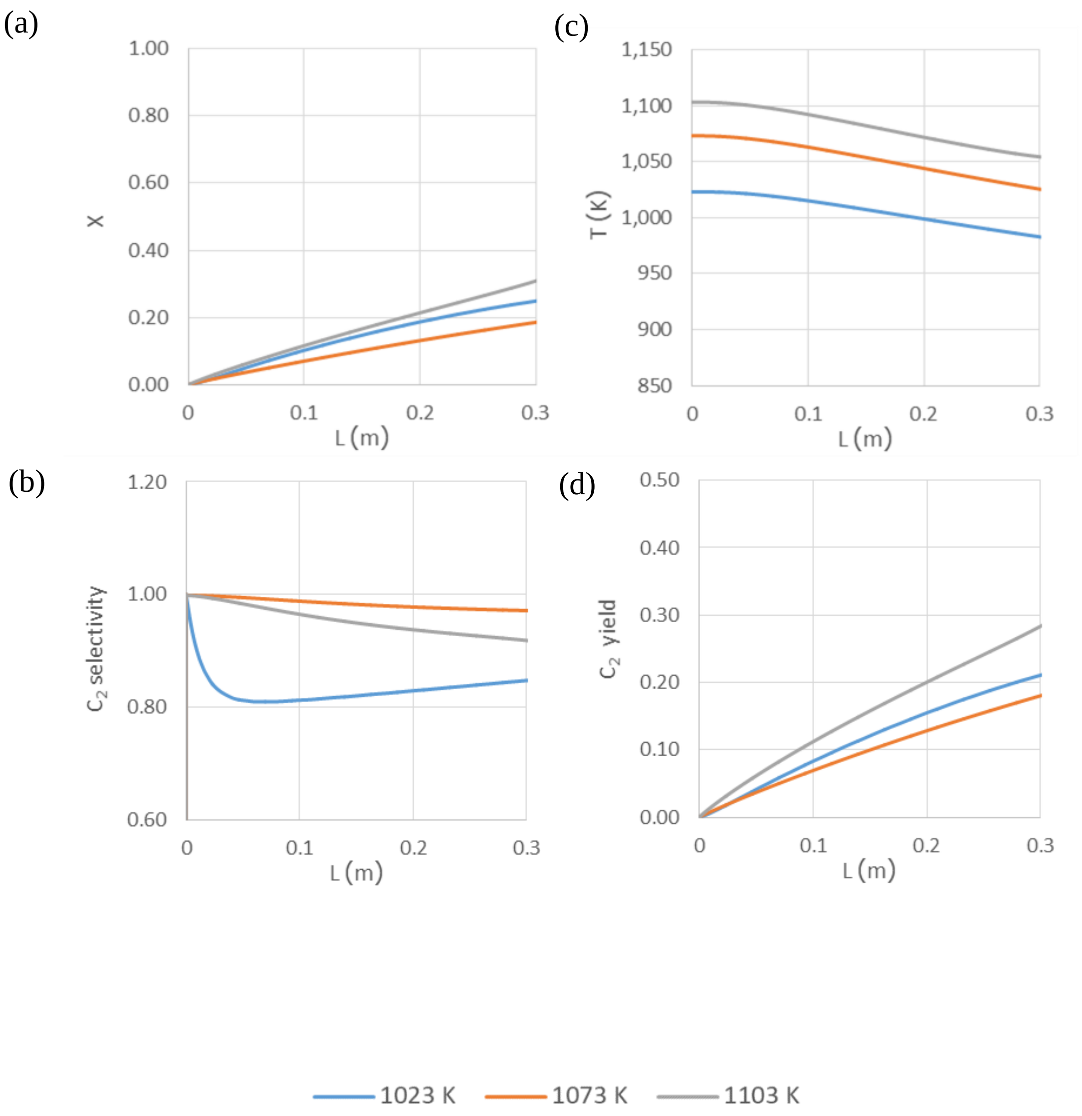

Figure 4.10. Performance of adiabatic dual-membrane reactor OCM section operated at 1023-1103 K and 1.224 atm.

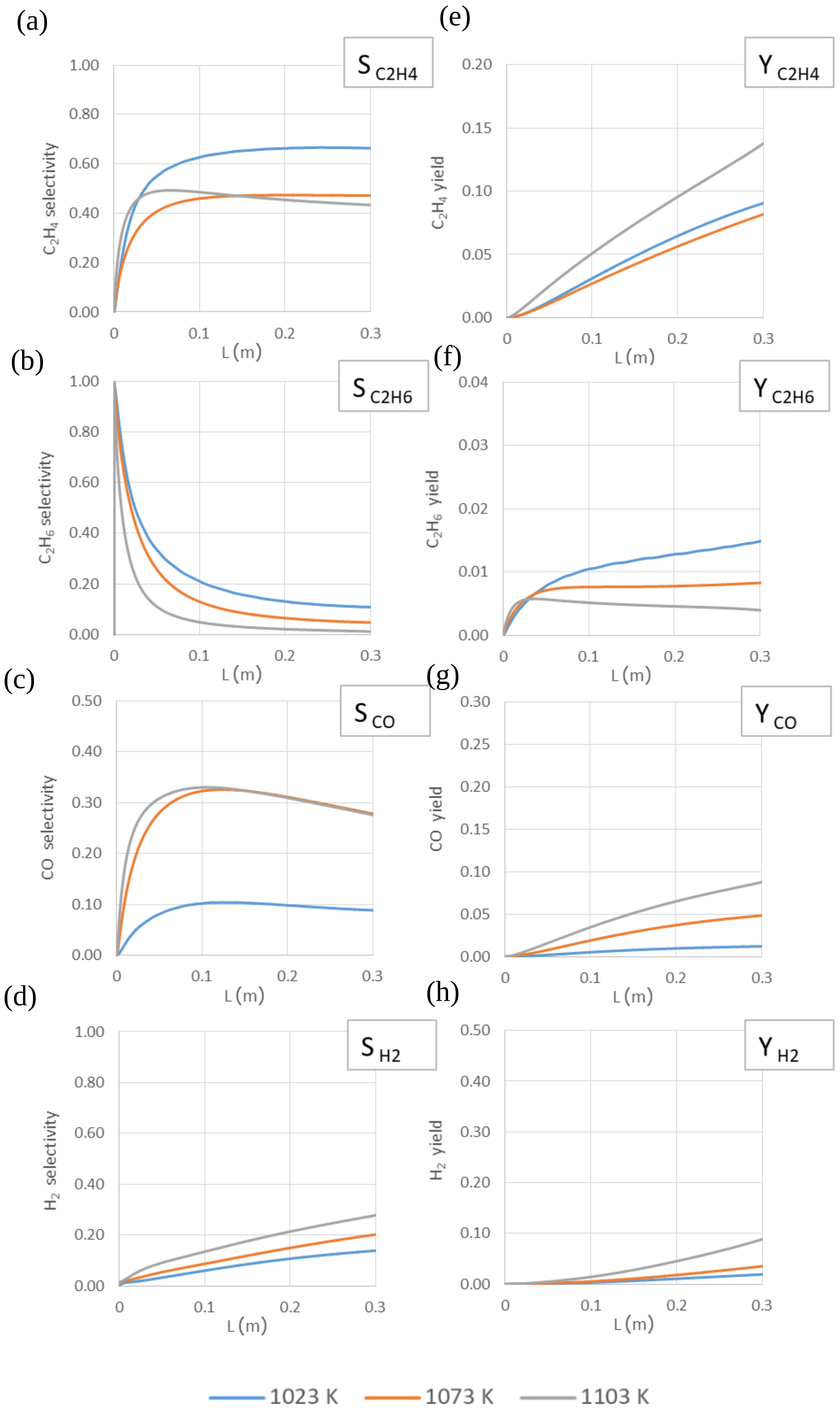

Figure 4.11. Performance of dual-membrane reactor OCM section operated at 1023-1103 K and 1.224 atm (con.)

4.4.2 Dry reforming of methane section

Adiabatic

For non-isothermal dual-membrane reactor of DRM, increasing of inlet temperature cause conversion and yield increase. However, temperature decrease due to this reaction is an endothermic reaction. When temperature decrease reaction equilibrium will change and cause methane conversion and yield of product decrease.

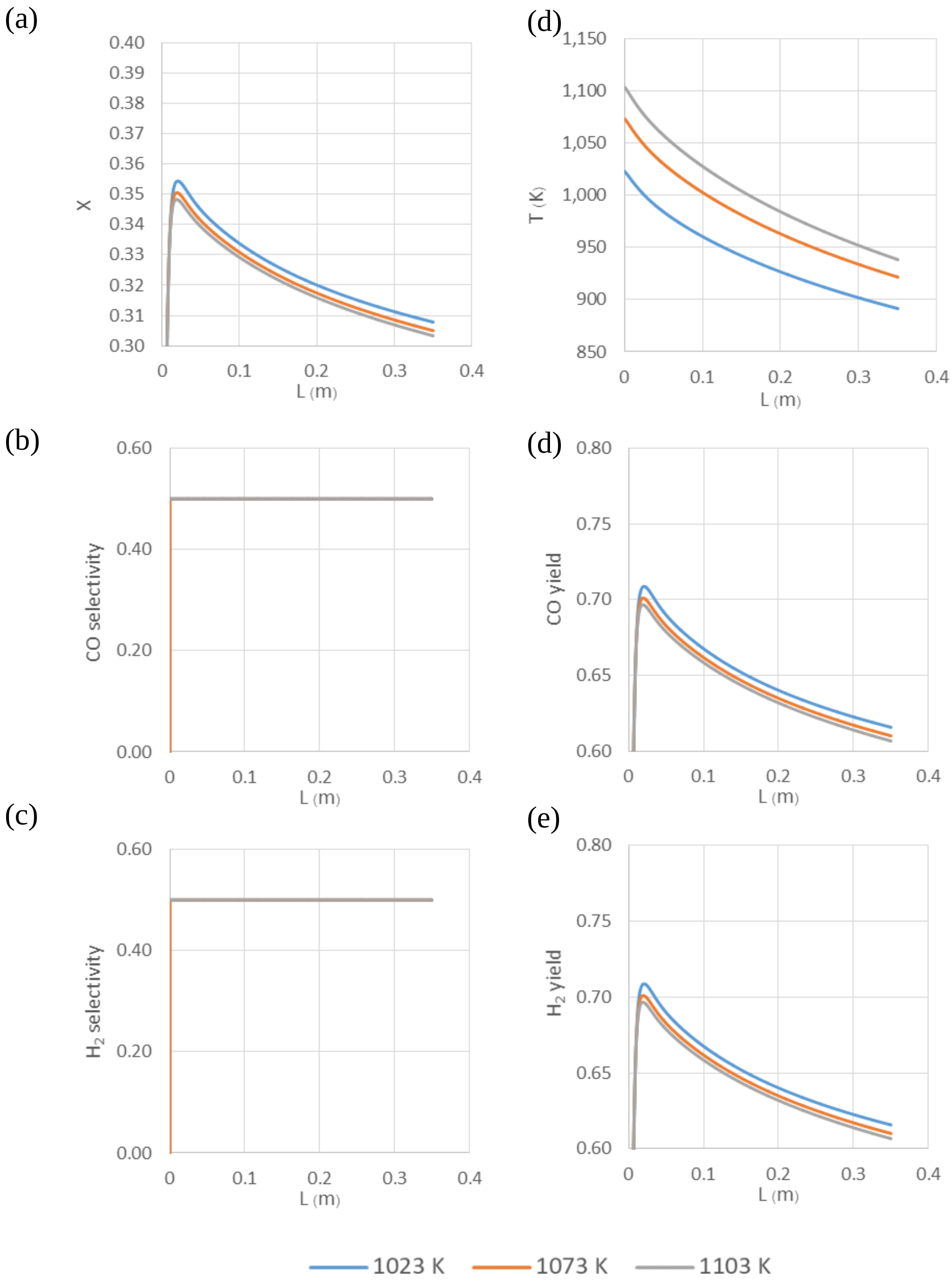

Figure 4.12. Performance of isothermal dual-membrane reactor DRM section operated at 1023-1103 K and 1.007 atm.

4.5 Comparing results of PBR and dual-membrane reactor adiabatic Oxidative coupling of methane reaction section

Comparisons of performance of packed bed reactor and dual-membrane reactor for oxidative coupling reaction of methane were showed as Figure 4.16. (a-d) that consist of conversion (a), and selectivity (b), temperature (c), and yield for products (d). From Figure 4.16. (a), which was plotted between conversion of methane (X) and reactor length (m), indicated that PBR have conversion more than DMR at same reactor length. Due to dual-membrane reactor was gradually dosing oxygen through porous membrane. Therefore, rate of methane consumption was lower than PBR. For temperature as shown in Figure 4.16. (c)., temperature inside PBR increase rapidly due to at the inlet partial pressure of oxygen and methane was at high level but for dual-membrane reactor temperature was decrease due to heat transfer to DRM section and reaction rate of OCM occurred slowly.

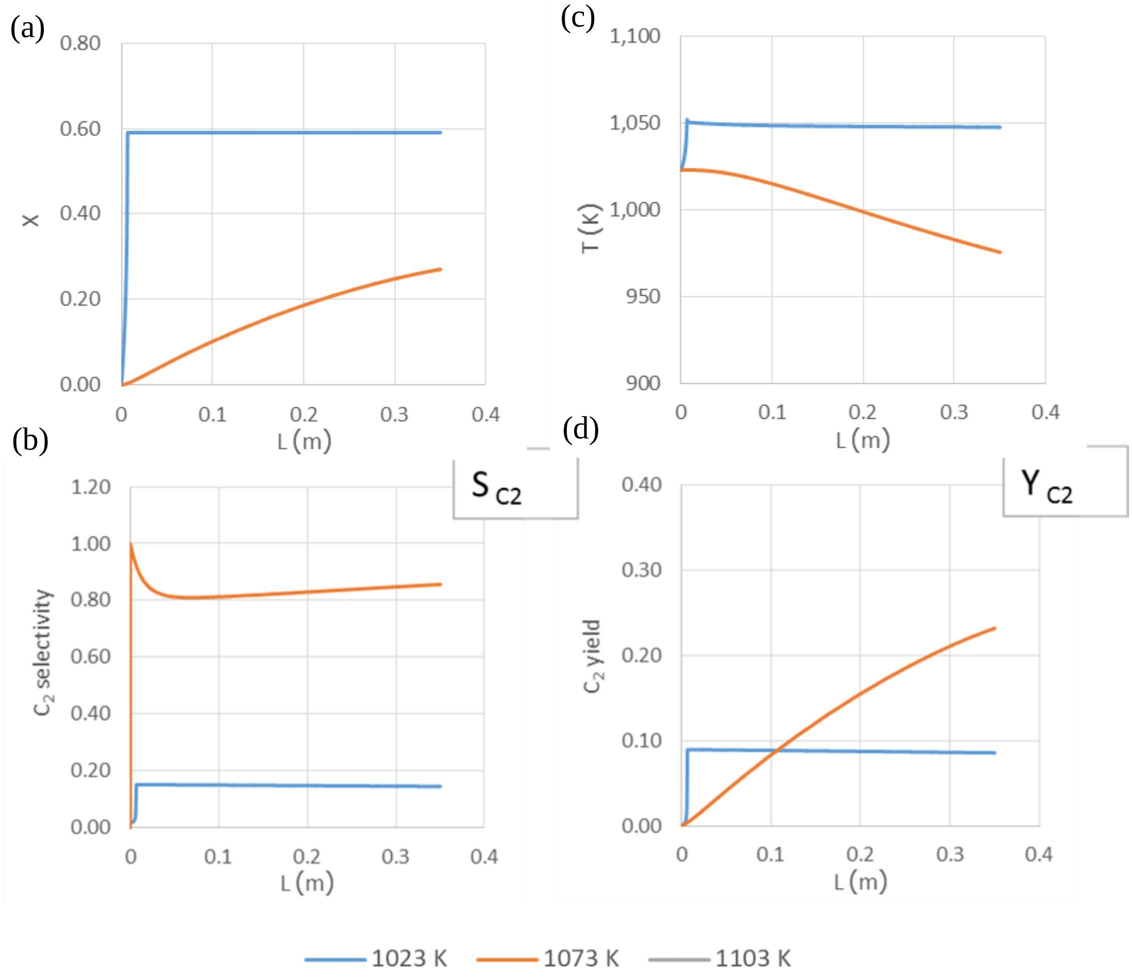

Figure 4.13. Compared performance of PBR and DMR for OCM along reactor length (m) at 1023 K.

For comparison of selectivity of PBR and dual-membrane reactor for OCM reaction with reactor length was shown in Figure 4.17 (a-d). Graphs of selectivity of ethylene, ethane, and carbon monoxide, Figure 4.17 (a-c), showed that selectivity of dual-membrane reactor was higher than PBR due to for dual-membrane reactor used dosing method that made oxygen concentration at low level, which made incomplete combustion of methane to ethane production cause easily. In the same way, selectivity of carbon monoxide of dual-membrane reactor that more than because oxygen concentration was not enough to cause oxidative reaction with carbon monoxide for carbon dioxide production. However, selectivity of hydrogen of PBR was more than PBR because of ethane has possibility to react with oxygen then produce ethylene and water but for dual-membrane reactor in ethylene production reaction was mainly produced from ethane decomposition. Figure 4.17 (h) that showed about selectivity of hydrogen, which PBR was more than dual-membrane reactor due to water gas shift reaction. This behavior able to describe by Figure 4.17 (c). Selectivity of carbon monoxide rapidly increase at primary period then also rapidly decrease because carbon monoxide reacts with water to carbon dioxide and hydrogen production.

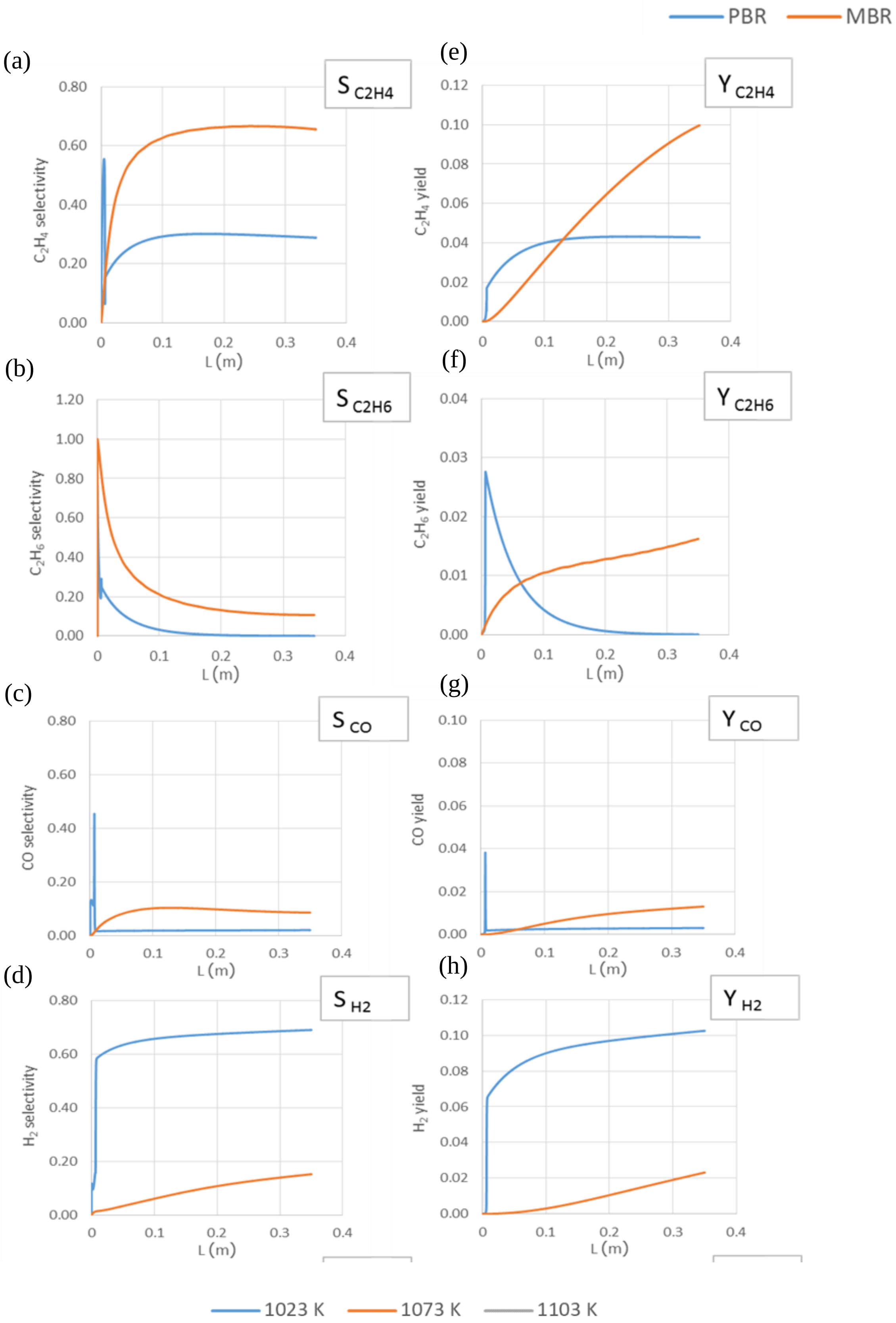

Figure 4.14. Compared performance of PBR and DMR for OCM along reactor length (m) at 1023 K (con.)

Dry reforming of methane reaction section

Figure 4.18. (a-e) showed about graphs that plotted between conversion of methane, temperature, yield, and selectivity of synthesis gas with reactor length. At same reactor length conversion of methane of PBR is higher than dual-membrane reactor due to limitation of molar flux of carbon dioxide that passed through molten carbonate composite membrane. These limitation cause rate of methane consumption for dual-membrane reactor is lower than PBR and also effect to yield of carbon dioxide and hydrogen in same trend. For selectivity of carbon dioxide at same length, dual-membrane reactor has selectivity lower than PBR due to temperature of dual-membrane reactor still decrease due to non-catalytic reaction of OCM occurred.

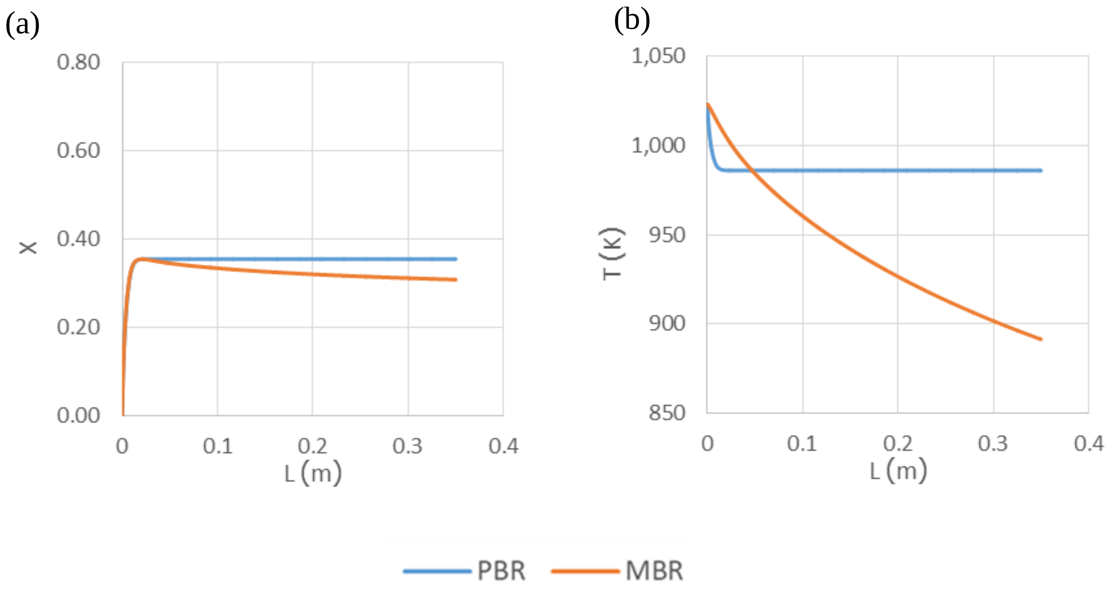

Figure 4.15. Compared performance of PBR and DMR for DRM along reactor length (m)

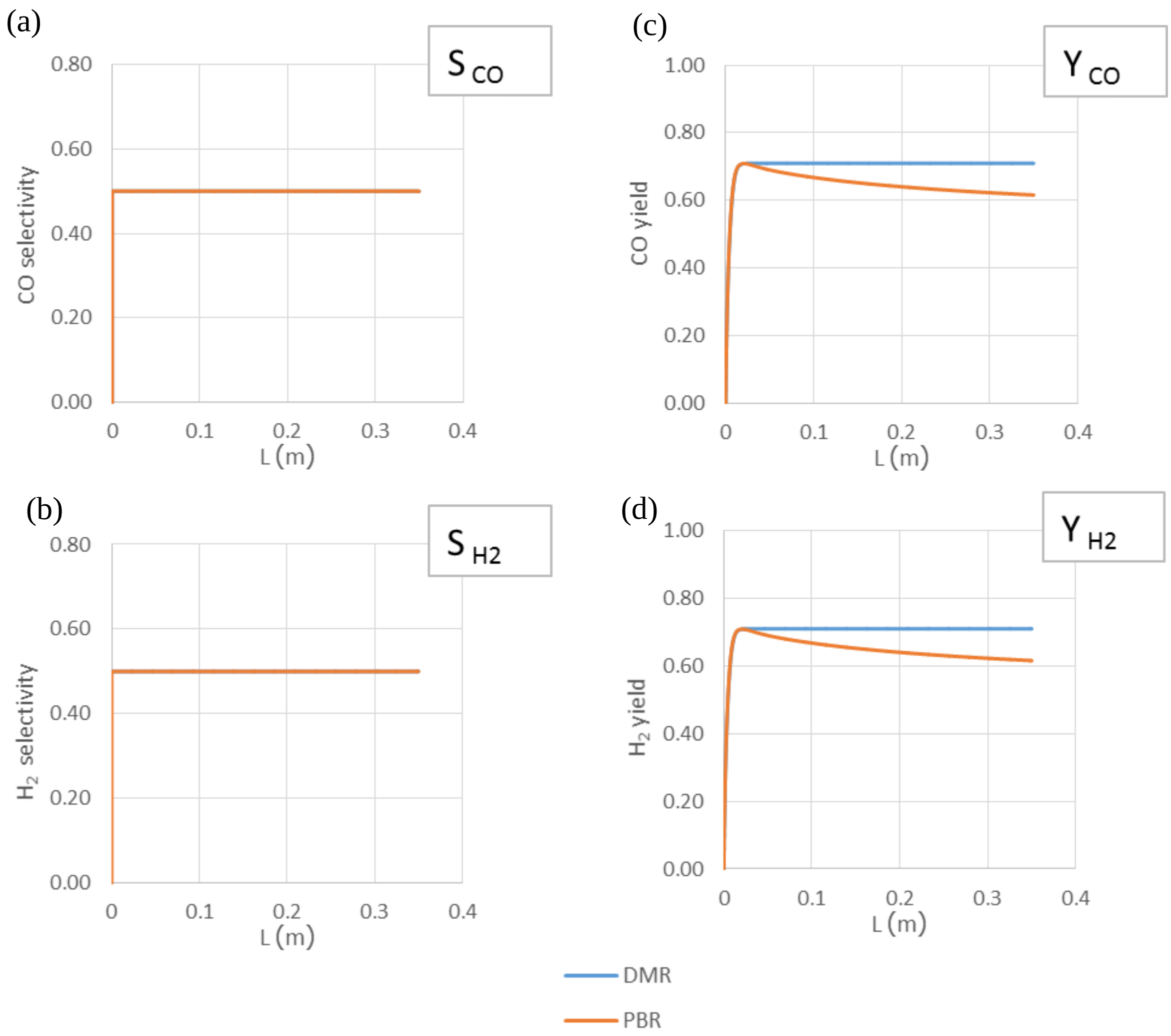

Figure 4.16. Compared performance of PBR and DMR for DRM along reactor length (m) (con.)

4.6 Comparing results of dual-membrane reactor for adiabatic with constant and vary membrane thickness

For MBR-2, this reactor was varied membrane thickness along reactor length until remain 33% of initial membrane thickness but for MBR-1, this reactor was operated at constant membrane thickness along reactor length. However, Figure indicated that thickness of membrane not effect to performance of dual-membrane reactor significantly for both reaction (OCM and DRM).

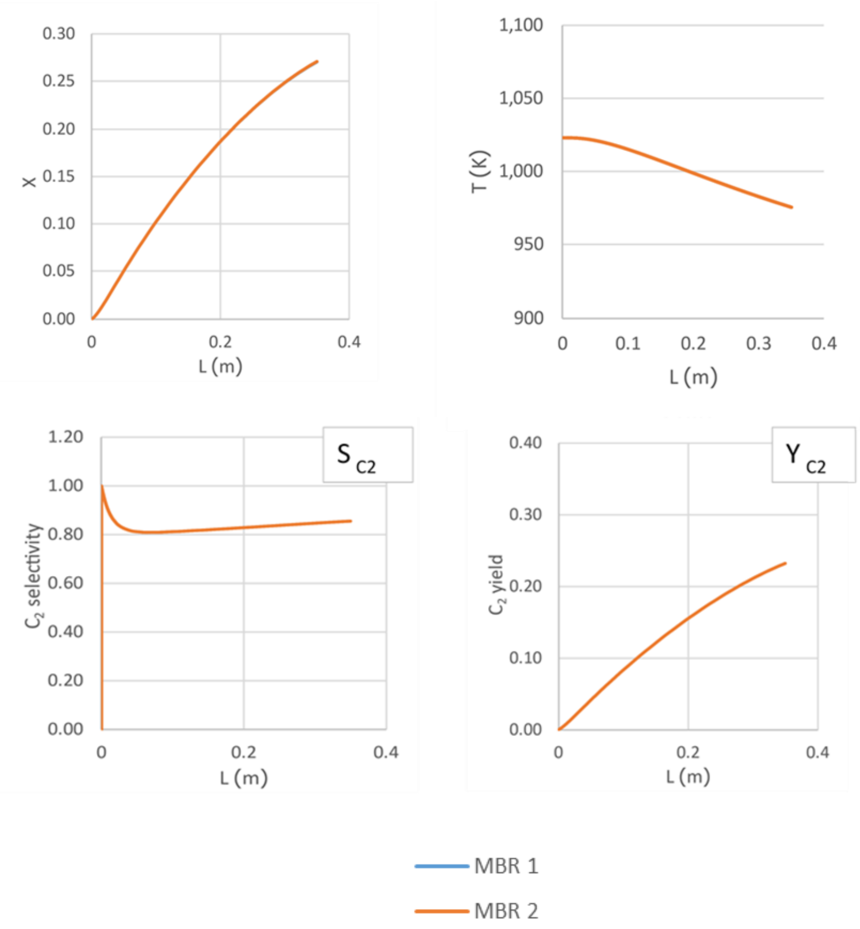

Figure 4.17. Compared performance of dual-membrane reactor for adiabatic OCM with constant and vary membrane thickness along reactor length (m)

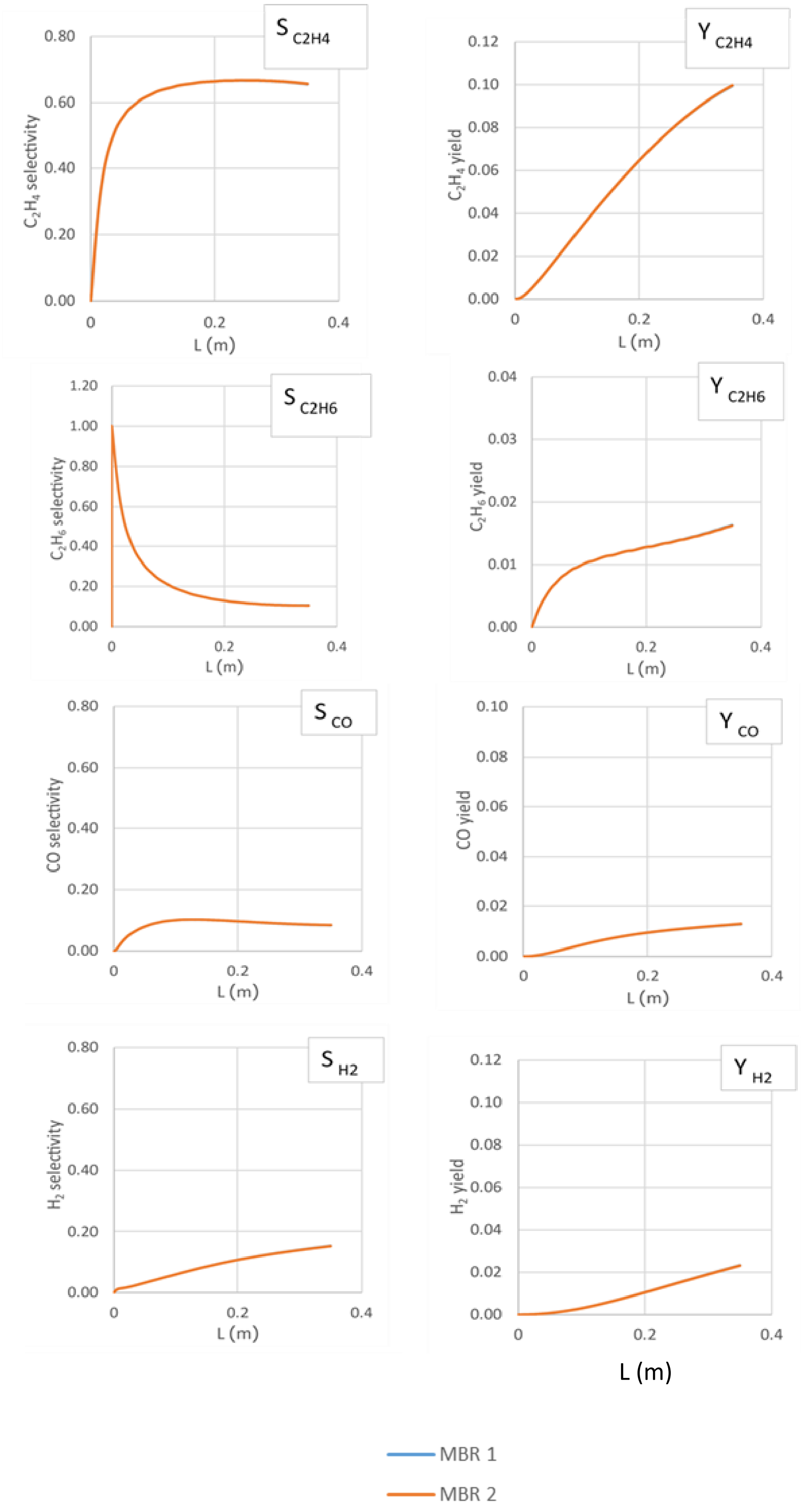

Figure 4.18. Compared performance of dual-membrane reactor for adiabatic OCM with constant and vary membrane thickness along reactor length (m) (con.)

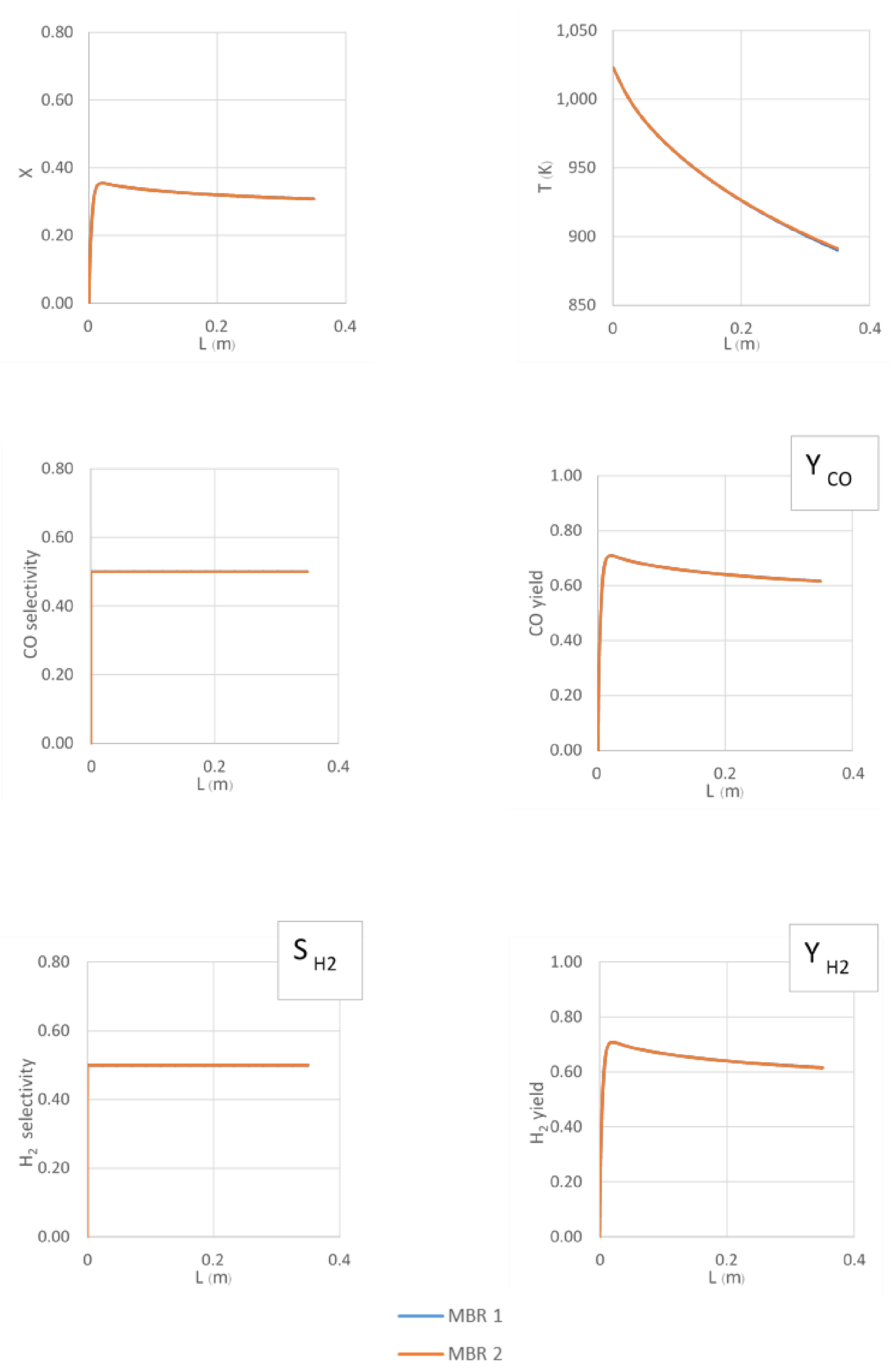

Figure 4.19. Compared performance of dual-membrane reactor for adiabatic DRM with constant and vary membrane thickness along reactor length (m)

CHAPTER V

CONCLUSION

In comparisons of performance of PBR and DMR for OCM reaction at same reactor length, dual-membrane reactor has selectivity and yield of ethane, ethylene, and carbon monoxide more than packed bed reactor by used advantage of porous that able to limit mass flux of oxygen to control oxygen concentration at low level that able to avoid undesired reactions. For DRM, selectivity of carbon dioxide and hydrogen of dual-membrane reactor has selectivity lower than PBR due to temperature of dual-membrane reactor decrease because non-catalytic reaction of OCM occurred.

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APPENDIX

Appendix A: Results of isothermal dual-membrane reactor

APPENDIX A: Results of isothermal dual-membrane reactor

Dual-membrane reactor

For dual-membrane reactor, the model was developed for two dimensions under practical assumption, isothermal, non-isothermal, and isobaric. Results that simulated from this model was divided into 2 sections for OCM and DRM.

Oxidative coupling of methane section

Isothermal

From Figure 4.20. that showed conversion of methane along the reactor length at difference inlet temperature, methane conversion increases as like as linear at low conversion due to concentration of oxygen was limited by flux of oxygen, which passed through porous dense ceramic membrane. Hence, at the outlet stream mole flow rate of methane still no differences from inlet significantly. However, conversion was affected from temperature, which was operated. When temperature increase conversion of methane will increase due to pressure inside reactor will increase and also cause molar flux of oxygen that pass through porous membrane increase.

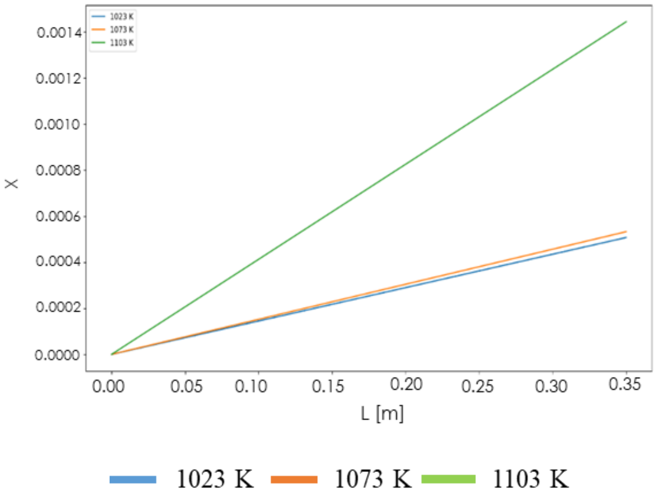

Figure 4.20. Conversion of methane along reactor length (m) for membrane reactor for OCM at T 1023-1103K

For yield of interested products was plotted along reactor length as showed as Figure (b-e). The results of yield of ethane, ethylene, and carbon monoxide have same trend, which increased along with reactor length. However, trend of yield of hydrogen still increases but while reactor length was increasing, slope of increasing rate decreased due to reverse water gas shift reaction occurred.

As shown in Figure 4.21. (e-h), Selectivity of ethane rapidly increase at first period due to oxygen was dossed at low concentration that cause incomplete combustion reaction of methane easily, then produce ethane as first interested product. Subsequently, selectivity of ethane decreased because products such as carbon monoxide, hydrogen, and especially ethylene that was produced from ethane decomposition and incomplete combustion reaction. All of above also used to explain about Figure 4.21. (a) and (c-d), which were graph of selectivity of ethylene, carbon monoxide, and hydrogen, respectively.

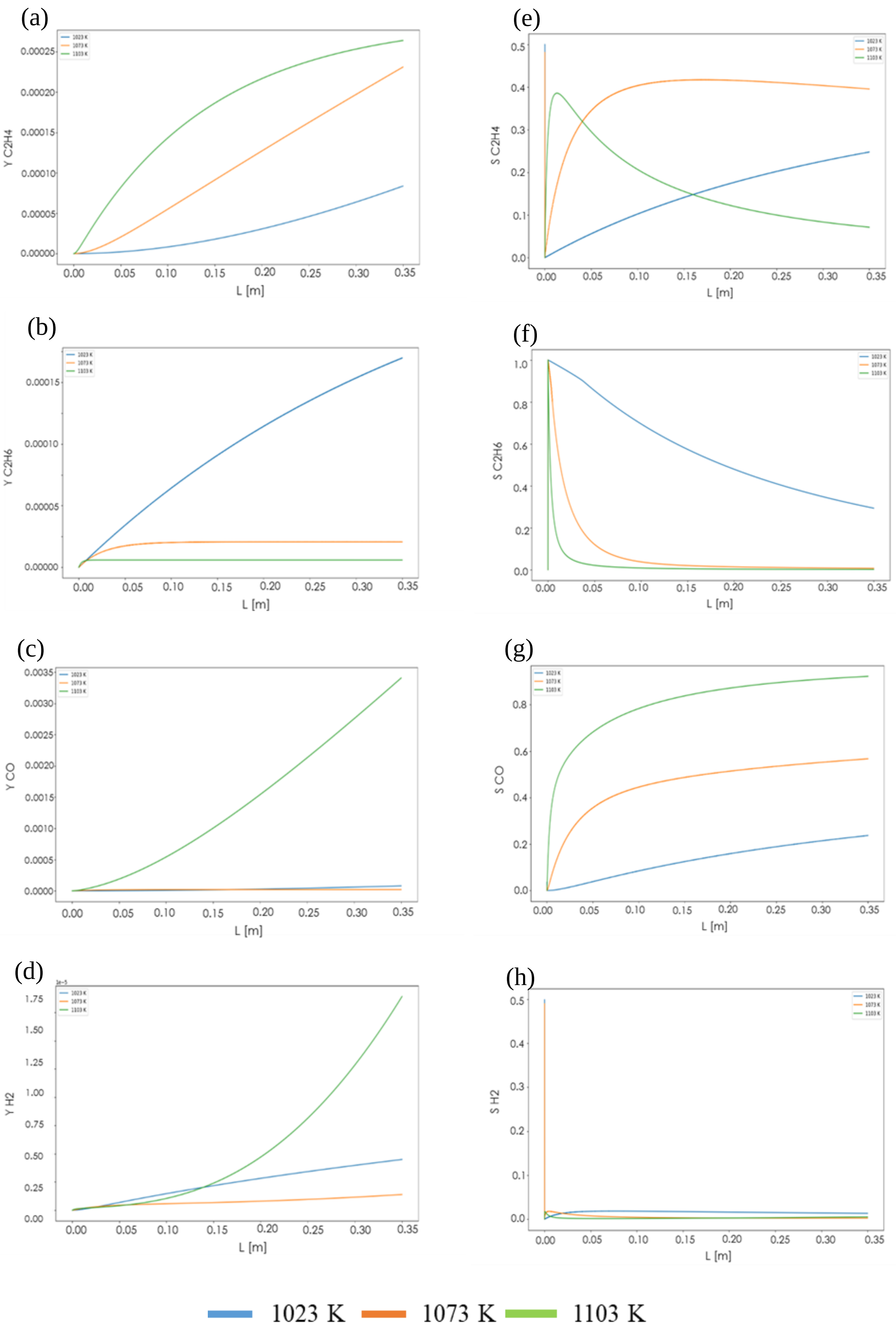

Figure 4.21. Performance of isothermal dual-membrane reactor OCM section operated at 1023-1103 K and 1.224 atm.

4.4.2 Dry reforming of methane section

Isothermal

As shown in Figure 4.22. (a), This graph showed conversion of methane along the reactor length, methane conversion increase at low conversion after it reached to equilibrium due to concentration of carbon dioxide that was limited by permeability of molten carbonate composite membrane pass through membrane and go into DRM section. Hence, at the outlet conversion of methane increase slightly. However, this condition have an advantage, which able to increase rate of production of synthesis gas due to Le Chatelier's principle. Yield of hydrogen and carbon monoxide increase along reactor length as showed as Figure 4.14. (a-c).

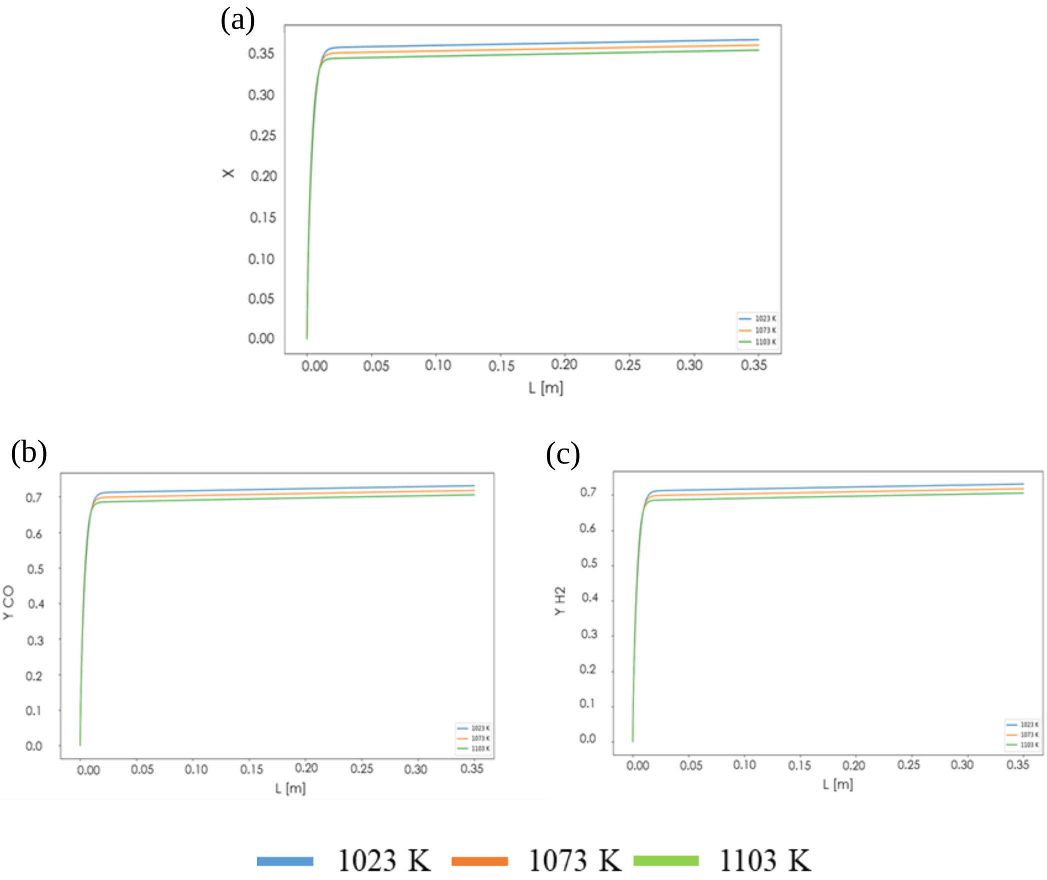

Figure 4.22. Performance of isothermal dual-membrane reactor DRM section (operated at 1023-1103 K and 1.007 atm)

BIOGRAPHY

Name: Tatpong Krachaeh

Date of Birth: April 30, 1999

Address: 4/1572, Sub-district Khlong Luang Phaeng, District Mueang
Chachoengsao, Chachoengsao Province, 24000

E-mail: tatpong.krachaeh@gmial.com, 60010373@kmitl.ac.th

Academic Background: Undergraduate of Bachelor of Engineering
Department of chemical Engineering, Faculty of Engineering
King Mongkut’s Institute of Technology Ladkrabang