

A STUDY ON MATHEMATICAL MODELING OF DIRECT SYNTHESIS OF  
DIMETHYL ETHER IN STRUCTURED MEMBRANE REACTORS

by

Hayrettin Hasan Köybaşı

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## ABSTRACT

### A STUDY ON MATHEMATICAL MODELING OF DIRECT SYNTHESIS OF DIMETHYL ETHER IN STRUCTURED MEMBRANE REACTORS

Catalytic transformation of CO<sub>2</sub> into dimethyl ether (DME) is modeled in a membrane microchannel reactor. The reactor geometry includes an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supported SOD membrane layer, capable of *in-situ* H<sub>2</sub>O removal, residing between a reaction channel and a parallel permeate channel. Reaction channels are washcoated with a physical mixture of Cu–ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA) and HZSM–5 catalysts, which are responsible for the synthesis and dehydration of methanol respectively. CO<sub>2</sub>-H<sub>2</sub> reactant mixture (H<sub>2</sub>/CO<sub>2</sub>=3) is dosed to the reaction channel at space velocity=6×10<sup>3</sup> ml gcat<sup>-1</sup> h<sup>-1</sup> whereas, pure H<sub>2</sub> at identical temperature and pressure, is fed to the permeate channel to sweep permeated steam. A steady-state isothermal reactor model based on the mass and momentum conservation equations is solved numerically using ANSYS software. Computed performance metrics show minimal deviation from the reported experimental data at 483–543 K, 30–50 bar. Incorporation of energy conservation to the model results in near-constant temperature profile and almost identical reactor performance, which validates isothermal operation. Owing to steam efflux from and H<sub>2</sub> influx to the reactive stream, membrane integration increases CO<sub>2</sub> conversion (~ 60%) and DME yield (~ 30%) by a factor of >3 compared to membraneless operation. The benefits become more significant at higher temperature and pressures. Sending sweep H<sub>2</sub> counter-currently offers superior H<sub>2</sub>O removal. Relative inlet velocity of the permeate inlet ( $v_{rat}$ ) affects membrane mass transfer dramatically. Adopting higher CZA/HZSM-5 mass ratio improves both performance metrics and the reactor capacity. With a ~7 m<sup>3</sup> reactor system, 2.76×10<sup>2</sup> tons of DME can be synthesized from 1×10<sup>3</sup> tons of CO<sub>2</sub> annually, provided that 1 MW electrolyzer provides the required H<sub>2</sub>.

## ÖZET

### MİMARİLİ MEMBRAN REAKTÖRLERDE DİMETİL ETER SENTEZİNİN MATEMATİKSEL MODELLENMESİ

$\text{CO}_2$ 'nin dimetil etere (DME) katalitik dönüşümü membranlı mikrokanal reaktörde modellenmiştir. Buharı ayrıştırabilen  $\alpha\text{-Al}_2\text{O}_3$  destekli SOD membran tabakası, reaktör mimarisinde reaksiyon ve süpürme kanalları arasında bulunmaktadır. Reaksiyon kanalları, sırasıyla metanolün oluşumu ve dehidrasyonundan sorumlu  $\text{Cu-ZnO/Al}_2\text{O}_3$  (CZA) ve HZSM-5 katalizörlerinin fiziksel karışımıyla kaplanmıştır.  $\text{CO}_2\text{-H}_2$  gaz karışımı ( $\text{H}_2/\text{CO}_2=3$ ) reaksiyon kanalına  $6 \times 10^3 \text{ ml g}_k^{-1} \text{ sa}^{-1}$  boşluk hızıyla gönderilmiş, eşit sıcaklık ve basınçtaki  $\text{H}_2$  gazı ise membrandan süzülen buharı uzaklaştırmak üzere süpürme kanalına beslenmiştir. Kütle ve momentum korunum denklemlerini baz alan izotermal yatışkın hal modeli ANSYS programında numerik olarak çözülmüştür. Hesaplanan performans metrikleri, 483–543 K ve 30–50 bar aralığında literatürde belirtilen deneysel verilerden minimal sapma göstermektedir. Enerji korunum denklemlerinin modele eklenmesiyle elde edilen neredeyse sabit sıcaklık profili ve değişmeyen reaktör performansı, izotermal koşulların geçerliliğini tasdik etmektedir. Membran entegrasyonu reaksiyon karışımına  $\text{H}_2$  girişi ve  $\text{H}_2\text{O}$  çıkışı sağladığından,  $\text{CO}_2$  dönüşümünü ( $\sim \%60$ ) ve DME verimini ( $\sim \%30$ ) membransız sonuçlara göre en az üç kat artırmaktadır. Sıcaklık ve basıncın artırılması membran işlevini ve faydalarını daha belirgin hale getirmektedir. Süpürücü  $\text{H}_2$  gazını zıt yönlü beslemek daha üstün  $\text{H}_2\text{O}$  ayrımı sağlamaktadır. Süpürme kanalının oransal giriş hızı ( $v_{\text{rat}}$ ) membran kütle aktarımını önemli ölçüde etkilemektedir. Katalizör kütle oranını (CZA/HZSM-5) artırmak hem performans metriklerini hem de reaktör kapasitesini iyileştirmektedir. 1 MW'lık elektrolizörün gerekli hidrojeni sağlaması halinde,  $\sim 7 \text{ m}^3$ 'lük reaktör sistemi yıllık  $1 \times 10^3$  ton  $\text{CO}_2$ 'den  $2.76 \times 10^2$  ton DME sentezleyebilmektedir.

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## LIST OF SYMBOLS

$C_2$	Inertial resistance coefficient of the washcoat, $m^{-1}$
$c_{p,i}$	Heat capacity of species $i$ , $J\ kg^{-1}\ K^{-1}$
$c_{p,m}$	Heat capacity of gas mixture, $J\ kg^{-1}\ K^{-1}$
$D_{eff,i,m}$	Effective diffusivity of species $i$ in the mixture, $m^2\ s^{-1}$
$D_{i,j}$	Binary diffusion coefficient, $m^2\ s^{-1}$
$D_{i,m}$	Diffusion coefficient of species $i$ in the mixture, $m^2\ s^{-1}$
$D_{K,i}$	Knudsen diffusivity of species $i$ , $m^2\ s^{-1}$
$d_p$	Particle diameter (equalized to the thickness of the catalyst washcoat layer), $m$
$d_{pore}$	Average pore diameter, $m$
$f_i$	fugacity of species $i$ in the mixture, $bar$
$F_i$	Molar flow rate of the component $i$ , $mol\ s^{-1}$
$f_{pure,i}$	Fugacity of pure species $i$ , $bar$
$f_{pure,i}$	Fugacity of pure species $i$ , $bar$
$G_{f,i}$	Gibbs free energy of formation of species $i$ , $kJ\ mol^{-1}$
$H_{f,i}$	Enthalpy of formation of species $i$ , $kJ\ mol^{-1}$
$H$	Height of the microchannel, $m$
$I$	3x3 identity matrix
$\vec{J}_i$	Molar flux of species $i$ through the membrane, $mol\ m^{-2}\ s^{-1}$
$k_{cat}$	Thermal conductivity of the catalyst layer, $W\ m^{-1}\ K^{-1}$
$K_{D,rxn}$	Reaction equilibrium constant, $bar^{-2}$ (rxn=1, 3), $-$ (rxn=2,4)
$k_{eff,m}$	Effective thermal conductivity of gas mixture in the washcoat layer, $W\ m^{-1}\ K^{-1}$
$K_i, K'_i$	Adsorption/desorption equilibrium constant for species $i$ , $bar^{-1}$
$k_i$	Thermal conductivity of species $i$ , $W\ m^{-1}\ K^{-1}$
$k_m$	Thermal conductivity of gas mixture, $W\ m^{-1}\ K^{-1}$

$k_{rxn}$	Reaction rate constant, mol g <sub>cat</sub> s <sup>-1</sup> bar <sup>-1.5</sup> for rxn=1, 3; mol g <sub>cat</sub> s <sup>-1</sup> bar <sup>-1</sup> for rxn=2; mol g <sub>cat</sub> s <sup>-1</sup> bar <sup>-2</sup> for rxn=4
$k_w$	Thermal conductivity of the membrane layer, W m <sup>-1</sup> K <sup>-1</sup>
$L$	Length of the microchannel, m
$l_{edge}$	Edge length of a mesh cell, m
$M_i$	Molecular weight of species $i$ , kg mol <sup>-1</sup>
$M_m$	Average molecular weight of gas mixture, kg mol <sup>-1</sup>
$n_i$	Number of moles of species $i$ , mol
$N_g$	Number of gas phase species $i$ , –
$p$	Total pressure, bar
$p_{perm}^i$	Partial pressure of species $i$ in the permeate channel, Pa
$p_{rxn}^i$	Partial pressure of species $i$ in the reaction channel, Pa
$Perm_i$	Membrane permeability of species $i$ , mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup>
$R$	Gas constant (=8.314 J mol <sup>-1</sup> K <sup>-1</sup> )
$R_i$	Consumption/generation rate of species $i$ , mol m <sup>-3</sup> s <sup>-1</sup>
$r_{rxn}$	Rate of a reaction, kmol m <sup>-3</sup> s <sup>-1</sup>
$S_i$	Mass source term of species $i$ , kg m <sup>-3</sup> s
$S_{f,i}$	Entropy of formation of species $i$ , kJ mol <sup>-1</sup> , K <sup>-1</sup>
$T$	Temperature, K
$v_{rat}$	Ratio of permeate inlet velocity to the fixed reactive stream inlet velocity, –
$\vec{v}$	Velocity vector, m s <sup>-1</sup>
$W$	Width of the microchannel, m
$x, y, z$	Cartesian coordinates
$X_{CO_2}$	CO <sub>2</sub> conversion (defined in Equation (??))
$Y_{DME}$	DME yield (defined in Equation (??))
$Y_i$	Mass fraction of species $i$ , –
$y_i$	Mole fraction of species $i$ , –
$Z$	Compressibility factor of gas mixture, –

$\Delta G_{rxn}$	Gibbs free energy of reaction, $\text{kJ mol}^{-1}$
$\Delta H^\circ$	Standard enthalpy of reaction, $\text{kJ mol}^{-1}$
$\Delta H_{rxn}$	Heat of reaction, $\text{kJ mol}^{-1}$
$\varepsilon_{cat}$	Porosity of the washcoat layer, –
$\Phi_{i,j}$	Dimensionless parameter for the mixture of $i$ and $j$ , –
$\mu_i$	Viscosity of species $i$ , $\text{kg m}^{-1} \text{s}^{-1}$
$\mu_m$	Average gas mixture viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
$\rho_m$	Density of gas mixture, $\text{kg m}^{-3}$
$\rho_{cat}$	Density of the catalyst mixture, $\text{kg m}^{-3}$
$\rho_{CZA}$	Density of Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> , $\text{kg m}^{-3}$
$\rho_{CZA,mix}$	Density of CZA catalyst in the catalyst layer, $\text{kg m}^{-3}$
$\rho_{HZSM-5}$	Density of HZSM-5 catalyst, $\text{kg m}^{-3}$
$\rho_{HZSM-5,mix}$	Density of HZSM-5 in the catalyst layer, $\text{kg m}^{-3}$
$\left(\sum v\right)_i$	Sum of the atomic diffusion volumes for species $i$ , –
$\tau_{cat}$	Catalyst tortuosity, –

**LIST OF ACRONYMS/ABBREVIATIONS**

1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
CH <sub>3</sub> OH	Methanol
CH <sub>3</sub> OCH <sub>3</sub>	Dimethyl ether
CH <sub>4</sub>	Methane
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CO <sub>2</sub>	Carbon dioxide
CP	Porous catalyst phase
CZA	Cu-ZnO/Al <sub>2</sub> O <sub>3</sub>
DME	Dimethyl ether
FP	Fluid phase
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
HZSM-5	Zeolite socony mobil no. 5
MW	Molecular weight
NO <sub>x</sub>	Nitrogen oxides
RWGS	Reverse water-gas shift reaction

## 1. INTRODUCTION

Significant increase in global average temperatures driven by accumulation greenhouse gases such as  $\text{CH}_4$  and  $\text{CO}_2$  in the atmosphere, has the potential to cause major economic and environmental devastation. Countries around the world have pledged to reduce their  $\text{CO}_2$  emissions by increasing the share of renewable sources in their power grids. The strong motivation in gradual replacement of fossil-fuel based conventional energy infrastructure, drives significant interest in sustainable energy technologies.

Sunlight can be converted directly into renewable energy by photovoltaic systems. Alternatively, indirect transformation of solar energy can be accomplished by wind and hydro-power. Renewable energy can also be used in the production of so-called "green hydrogen". Challenges associated with  $\text{H}_2$  storage and handling can be addressed by its subsequent transformation into ammonia, methane, methanol or dimethyl ether [1].

Carbon capture and utilization technologies (CCU) not only offer sustainable methods to synthesize useful chemicals but they have the capability to utilize atmospheric  $\text{CO}_2$  as the carbon source.  $\text{CO}_2$  can be used as feedstock to synthesize various chemicals such as carbamic acids, polycarbonates, dimethyl carbonate, methanol and dimethyl ether [2]. Since the majority of fossil fuels are extracted to power transportation and energy generation, synthesis of alternative fuels from  $\text{CO}_2$  offers a major opportunity in sustainable future. Such a scenario would create a circular carbon economy where new oil and natural gas discoveries become redundant.

Dimethyl ether (DME) is a volatile organic compound with the formula  $\text{CH}_3\text{OCH}_3$ . It is transformed into liquid phase at pressures above 5 bar. DME shares similar characteristics with butane and propane, and it burns with visible blue flame. Molecular structure of DME is composed of C-O and C-H bonds, while lacking any C-C bond. It is considered as an extremely promising alternative fuel due to its ease of transportation and handling, non-toxicity, high cetane number, smokeless combustion and low combustion noise.

DME can be used in conventional compression-ignition engines, provided that fuel injection equipment is modified slightly for such application. On the other hand, its corrosiveness, low combustion enthalpy, low density/lubricity pose a challenge for its mainstream adoption [3]. In addition to being a potential fuel source, DME can also be used as a feedstock to synthesize various chemicals like dimethyl sulfate, methyl acetate and light olefins [4].

Table 1.1. Physical properties of dimethyl ether [5].

Molecular formula	C <sub>2</sub> H <sub>6</sub> O
Molar mass	46.07 g mol <sup>-1</sup>
Appearance	Colorless gas
Liquid density	667 kg m <sup>-3</sup>
Melting point	-141 °C, 132 K
Boiling point	-24 °C, 249 K
Solubility in water	71 g dm <sup>-3</sup> at (20 °C)
Vapor pressure	>100 kPa
Auto-ignition point	235°C, 508 K

Conventional DME synthesis is based on so-called indirect route, where methanol synthesis and dehydration reactions take place in separate reactors. Synthesis gas, a mixture of carbon oxides (CO + CO<sub>2</sub>) and hydrogen (H<sub>2</sub>), is transformed into methanol in the first reactor via metallic catalysts. Following the purification steps, methanol is dehydrated into DME in a second reactor containing solid acid catalyst. In an alternative approach called direct route, methanol synthesis and dehydration steps can be combined in a single reactor. Either bi-functional catalysts or physical mixtures of acidic and metallic catalysts can be used for this purpose. Direct route offers some advantages over the indirect approach. Since fewer reactors need to be installed, required capital investment is lower. Moreover, since methanol is converted and removed from the reactive mixture, thermodynamic limitations on methanol synthesis are minimized [5].

Due to exothermic nature of hydrogenation and dehydration reactions, temperature regulation plays a key role in DME synthesis. Catalyst deactivation and undesired side reactions become more significant at elevated temperatures. In addition, at higher temperatures, lower equilibrium conversions can be achieved. The requirement for facile temperature regulation is more relevant for the direct route, since combination of exothermic reactions lead to faster rate of heat generation. Temperature variation within reactor can reach up to  $\sim 40$  K when cooling-integrated fixed bed reactor is used. On the other hand, near isothermal conditions can be obtained with microchannel reactors. Volumetric intensification results in transport rates up to two orders of magnitude larger than those obtained with fixed bed reactors. A typical microchannel reactor involves parallel channels having dimensions between  $10^{-6}$  and  $10^{-3}$  m. Hence, compared to conventional packed bed geometries, surface area to volume ratio of microchannel reactors is  $\sim 10^3$  times higher. Additionally, the capacity of microchannel system can be varied easily by changing the number of microchannels [6].

Sourcing syngas from sustainable feedstocks such as biomass is a promising approach in DME synthesis. On the other hand, biomass-derived syngas has significantly higher  $\text{CO}_2$  content compared to syngas derived from steam reforming [7]. Presence of  $\text{CO}_2$  in the reaction mixture creates several undesired effects. High  $\text{CO}_2$  partial pressures lead accelerated RWGS reaction and subsequent steam generation. Being a side product of DME synthesis, accumulation of steam suppresses the rate of methanol dehydration thermodynamically. Furthermore, hydrothermal sintering of catalyst become more pronounced with high steam concentrations. Unless  $\text{H}_2\text{O}$  in the reaction media is removed effectively, DME synthesis via  $\text{CO}_2$  hydrogenation becomes impractical [8].

Several strategies can be adopted to avoid negative consequences of steam accumulation via selective *in-situ* steam removal [9]. Sorption-enhanced DME synthesis involves packing  $\text{H}_2\text{O}$  selective sorbent materials alongside catalyst particles. Due their small micropores blocking large molecules, zeolite materials such as 3A and 4A, offers high affinity and selectivity towards steam. On the other hand, since sorbent materials become saturated with  $\text{H}_2\text{O}$  as time progresses, adsorbent needs to be regenerated by the removal of adsorbed  $\text{H}_2\text{O}$ . *In-situ*  $\text{H}_2\text{O}$  removal can also be accomplished by the use of steam-selective membranes.

Unlike sorption enhanced process, adsorption-desorption cycles are not needed, hence, continuous operation is possible. Several membrane materials such as ZSM-5, MOR, sodalites and polymer nafion are proposed for steam removal applications. Among them, sodalite (SOD) materials offer moderate  $\text{H}_2\text{O}$  permeance and excellent permselectivity, preventing cross membrane transfer of  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ . Relatively low  $\text{H}_2\text{O}/\text{H}_2$  permselectivity of SOD membranes leads to another key benefit. The rate of methanol formation can be improved significantly by keeping high  $\text{H}_2$  content in the reaction mixture via cross membrane  $\text{H}_2$  transport [10]. For this purpose,  $\text{H}_2$  can be selected as sweep gas to maximize  $\text{H}_2$  concentration on the permeate side.

Integrating membranes to microchannel reactors combines the benefits of both volumetric and functional intensification. High surface area of microchannel reactors provides extended contact between fluids and membrane surface. Furthermore, temperature and flow rate of sweep gas can be easily manipulated to accomplish effective temperature regulation. Remarkable improvements in  $\text{CO}_2$  conversion and DME yield are reported upon adopting membrane-integrated micro-structured systems [11, 12]. It should be noted that, these studies involve  $\text{CO}_2$  containing syngas as feedstock. On the other hand,  $\text{CO}_2$  derived from air separation or carbon capture can also be used to synthesize DME. Moreover, clean  $\text{H}_2$  derived from renewable energy can be selected as the second raw material. Such an approach can lead to carbon neutral fuel production where solar energy is stored in DME molecule as chemical energy.

This thesis is composed of five main chapters, including Introduction. Detailed literature survey about DME synthesis and associated process intensification are presented in Chapter 2. Details about the reactor geometry and operating parameters, reaction network and kinetic model, membrane model and solution methodology is given in Chapter 3. In Chapter 4, reactor model and isothermal conditions are validated in the first two sections. Then, detailed discussion about the results of the parametric study is provided. Key conclusions obtained from this work and recommendations are provided in Chapter 5.

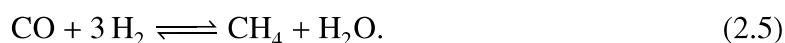
## 2. LITERATURE SURVEY

### 2.1. Dimethyl Ether Production

Syngas, a mixture of carbon oxides and hydrogen, derived mainly from hydrocarbons via reforming or gasification reactions, is used to synthesize DME. Catalytic reactions taking place in the synthesis [5, 13] can be listed as



Due to exothermic nature of methanol formation and DME synthesis reactions, unless effective cooling is applied, temperature of the reaction mixture increases. Such a situation may increase temperature above 573 K, resulting in undesired methanation reaction which can be expressed as



Currently, DME production can take place with two different approaches. The first one which is called two-step or indirect route, methanol synthesis (Reactions (2.1) and (2.3)) and methanol dehydration (Reaction (2.4)) occur in two separate reactors involving metallic and acidic catalysts, respectively. On the other hand, synthesis and dehydration of methanol take place in a single reactor simultaneously in the one-step or direct route. Combination of metallic and acidic functions is needed by using either bi-functional catalyst or a physical mixture of metallic and acidic catalysts. [5]. Key information derived from computational and experimental studies on both routes are presented in the following sections.

### 2.1.1. Indirect DME Production

Due to ease of product purification and high DME selectivity obtained at mild conditions, conventional DME synthesis involves two-step process. Properties of different dehydration catalysts is the main focus of studies involving two step synthesis. Operating temperature is typically varied within 380-720 K. On the other hand, due to reaction stoichiometry of Reaction (4), the effect of pressure has lower impact.

Additional parameters such as pressure, H<sub>2</sub>/CO ratio, effect of co-feeding CO<sub>2</sub> and space velocity are also investigated at operating conditions of 1-100 bar, 0.5-2.5 and 00-3000 h<sup>-1</sup> [14]. In these studies, CO conversion and DME yield are typically between 20-97% and 10-100% respectively. Apart from traditionally adopted fixed bed reactor, indirect route is also investigated for reactive distillation [15], catalytic membrane reactor [16] and Platelet Milli-reactor [17]. Furthermore, various solid acid catalyst such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [18–20], HZSM-5 [21, 22], HY zeolite supported by modified Cu-Mn-Zn [23], mordenite [24], and Nafion [25] are tested in the synthesis of DME from methanol. Kinetic expressions in the form of Langmuir-Hinshelwood [26] and Eley-Rideal [27] mechanisms are derived for DME synthesis from methanol. These studies commonly point out that the presence of H<sub>2</sub>O or DME slows the kinetics of Reaction (2.4) [15].

It is reported that 80% methanol conversion with no side product can be obtained above 573 K, when alumina impregnated SBA-15 (Al@SBA-15) catalyst is used in DME synthesis [25]. However, lower temperatures resulted in formaldehyde formation, with a yield of 20 % at 473 K. DME synthesis in a fixed bed reactor containing both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalysts yielded higher activity than using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> alone [28]. Additionally, stability of HZSM-5 is improved below 508 K. Production rate of 13.5 g<sub>DME</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> is observed at 508 K. A study conducted by Chen *et al.* [14] revealed that, co-feeding CO<sub>2</sub> enhances CO conversion. At CO<sub>2</sub>/CO=2, H<sub>2</sub>/CO=4, 473 K optimum reactor performance is achieved where 90% CO conversion is observed. Zhu *et al.* [29] created a two stage reaction system where Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalyst are stacked consecutively.

Optimal operating temperatures of methanol synthesis and dehydration stages are found as 543-553 and 508-518 K, respectively. Selecting  $H_2/CO > 2$  greatly enhances reactor performance. CO conversion increases from 10% to up to 52% whereas, the change in DME yield is from 10% to 52%. Increasing pressure to 80 bar boosted reactor performance where 78% CO conversion and 63% DME yield obtained compared to 30% and 21 % at 30 bar, respectively.

### 2.1.2. Direct DME Production and Process Intensification

Direct DME synthesis require bi-functional or hybrid catalyst which combine metallic function catalyzing methanol synthesis and acidic character dehydrating dehydrating methanol into DME. Consumption and removal of methanol from the reaction environment relaxes thermodynamic limitations on methanol synthesis process, leading to higher CO conversions. Due to reduction in the number of reactors, required capital investment is relatively lower in the direct route.

Catalytic investigations for the direct route generally focus on optimizing CO conversion and DME yield by varying the dehydration catalyst and its degree of acidity. Solid acid catalysts like  $\gamma\text{-Al}_2\text{O}_3$  [30–32],  $\text{SiO}_2\text{-Al}_2\text{O}_3$  [33, 34] and zeolites like HZSM-5 H-Y, H-Beta and H-Ferrierite [35–37] are studied. At operating conditions of 513-553 K, 1-70 bar,  $H_2/CO = 0.5\text{-}2$ , residence time =  $3\text{-}8 \text{ kg}_{\text{cat}} \text{ h kmol}^{-1}$ , CO conversions vary between 53% and 95%, and DME yield is in the range of 34-52%. In these studies, effect of Cu-ZnO/ $\text{Al}_2\text{O}_3$  mass ratio is also investigated, by varying this parameter between 1:1 and 3:1.  $\text{CO}_2$  can exist in synthesis gas in varying degrees based on the the production method. Certain studies focused on the impact of using  $\text{CO}_2$  on direct DME synthesis at operating conditions of 513-543 K,  $H_2/CO_2 = 2\text{-}10$  and 30-40 bar, resulting in 15-50%  $\text{CO}_2$  conversions and 9-25% DME yields. Catalysts used in these studies are  $\gamma\text{-Al}_2\text{O}_3$  [38], ZSM-5 [39] and HZSM-5 [40, 41]. Additional details on dehydration catalysts, and information related to the synthesis and characterization can be found in [13].

Apart from the properties of adopted catalysts, temperature regulation also plays a key role in direct DME synthesis. Due to exothermic reactions involved, equilibrium conversions decrease at elevated temperatures, which indicates potential drawbacks in the absence of a cooling system. At elevated temperatures, rate of Reaction (2) increases dramatically if CO<sub>2</sub> is present in the feed. Generated H<sub>2</sub>O suppresses methanol dehydration and exacerbates hydrothermal sintering of both methanol synthesis and dehydration catalysts [13, 31, 42]. Furthermore, Reaction (2.2) also consumes H<sub>2</sub>, whose partial pressure needs to be high to achieve satisfactory CO conversion. Therefore, CO<sub>2</sub> utilization via DME synthesis poses significant challenges.

Despite the strong correlation between the rate of heat removal from the catalyst bed and the reactor geometry, studies concerned about this aspect are limited. A microchannel reactor packed with a physical mixture of F51-8PPT (methanol synthesis) and ZSM-5 (methanol dehydration) catalysts, is investigated by Hu *et al.* [43]. Volumetric miniaturization and subsequent facile temperature regulation, improved DME yield three-folds and prevented catalyst deactivation. Hayer *et al.* performed both experimental and computational studies involving heat-exchange integrated microchannel reactor, packed with metallic (CZA) and solid acid ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5) catalysts [44–46]. Effects of temperature and pressure, feeding rate, stream composition and coolant inlet temperature on CO conversion and DME selectivity is investigated. Cooling integration and volumetric miniaturization enabled significant intensification of direct DME synthesis. McBride *et al.* compared layered and physical mixture arrangements of methanol synthesis and dehydration catalysts. A significant increase in DME productivity is observed when physical mixture is adopted over layered configuration. Catalysts can be incorporated into microchannel reactors by either packing them in particulate form or coating microchannels with a thin layer of catalyst. The latter strategy proved to be superior for various reaction systems [47, 48]. Wall-coated microchannel reactors offers heat transfer rates  $\sim 10^2$  higher compared to configurations involving packed particulate catalysts. Furthermore, transport resistances can be minimized and near ideal catalyst effectiveness can be observed [49–52]. A typical high-performance microchannel reactor involves washcoated channels with hydraulic diameters within  $10^{-6}$ - $10^{-2}$  m.

They are generally created from metallic substrates via micromachining techniques, having surface area-to-volume ratios up to  $10^4 \text{ m}^2 \text{ m}^{-3}$ . Combined with their high transport rates, microchannel reactors enables near-isothermal operation [53, 54].

Functional intensification of DME synthesis via *in-situ* steam removal is also extremely promising. In a conventional DME synthesis, steam generated from Reaction (2.4) is consumed by water gas shift reaction, leading to thermodynamic synergy between reactions. Furthermore,  $\text{H}_2$  is generated, which improves the rate of methanol synthesis. However,  $\text{CO}_2$  is also produced as a side product, leading to problematic  $\text{CO}_2$  emissions [8]. One-step DME synthesis via  $\text{CO}_2$  hydrogenation suffers from significant thermodynamic limitations. Steam generated via Reactions (2.1-2.2 and 2.4) accumulates within the reaction media and hinders both methanol formation and dehydration reactions [55]. Removal of  $\text{H}_2\text{O}$  from the reaction media relaxes the thermodynamic limitations and allow  $\text{CO}_2$  to be used as a feedstock in DME synthesis. Several studies [56–58] investigated incorporation of steam-selective adsorbents alongside catalyst particles. In this so-called sorption enhanced DME synthesis, equilibrium  $\text{CO}_2$  conversion and yield is easily surpassed. For the sorption process, typically, 3A, LTA zeolites are selected [9]. In an alternative approach, *in-situ* steam removal can also be accomplished via steam-selective membranes. Iliuta *et al.* [8] created one-dimensional isothermal unsteady state model to investigate direct DME synthesis in a membrane reactor containing CZA and HZSM-5 mixture. Superior DME yield and selectivity are obtained in the presence of a steam-selective membrane. Diban *et al.* [55] created a one-dimensional isothermal model to simulate lab-scale membrane reactor. Influence of  $\text{H}_2\text{O}$  permeance and  $\text{H}_2\text{O}$  permselectivity on reactor performance is elucidated. De Falco *et al.* [59] simulated an industrial scale fixed bed reactor surrounded by hydrophilic ZSM-5 membrane. Remarkable improvements in  $\text{CO}_2$  conversion and DME yield are observed compared to conventional reactor without a membrane.

This study aims to investigate direct DME synthesis in a membrane microchannel reactor. Unlike similar studies, Pure  $\text{CO}_2$  derived from air separation or carbon capture, and  $\text{H}_2$  produced via water electrolysis will be considered to be the feedstock of the reactor system.

A detailed two-dimensional mathematical model will be created to study the effects of various operating parameters on CO<sub>2</sub> conversion and DME yield. In addition, Validity of the mathematical model and isothermal operation will be tested. Finally a pilot scale reactor scheme will be sized based on H<sub>2</sub> production rate of a 1 MW water electrolyzer powered by renewable energy.



### 3. MATHEMATICAL MODELING

#### 3.1. Details of the Multifunctional Reactor

A simplified illustration of the membrane microchannel reactor system is presented in Figure 3.1. Rectangular reaction and permeate channels with identical dimensions of  $1.5 \times 10^{-1}$  m ( $L$ ),  $3 \times 10^{-4}$  m ( $H$ ), and  $6 \times 10^{-4}$  m ( $W$ ) m, are separated with  $1 \times 10^{-3}$  m thick  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supported SOD membrane layer. Unlike permeate channel, reaction channel is washcoated with  $5 \times 10^{-5}$  m thick catalyst layer which contains a physical mixture of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and HZSM-5. Rectangular cross-section is adopted since conventional micromachining techniques are more suitable to create such structures [60], whereas channel dimensions are selected considering the balance between pressure drop and transport rates [61]. The design is coherent with a previous work involving a microchannel reactor containing a membrane and washcoated catalyst layer [62].

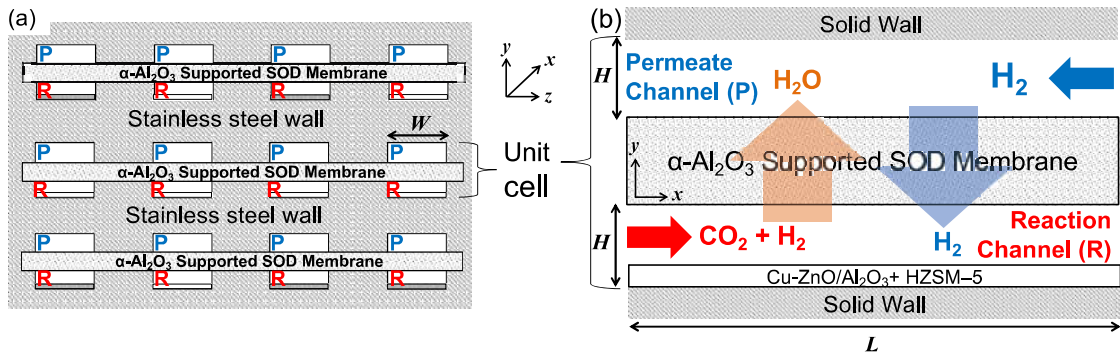


Figure 3.1. Simplified (not to scale) drawings of a multi-functional reactor block (left) and repeating unit cell (right).

Operating range of the reactor is determined based on the study of An *et al.* [63], which involves experimental investigation of DME synthesis via CO<sub>2</sub> hydrogenation. In this regard, a mixture of CO<sub>2</sub> and H<sub>2</sub> (H<sub>2</sub>/CO<sub>2</sub>=3) is dosed to the reaction channel with a space velocity of  $6 \times 10^3$  ml g<sub>cat</sub> h<sup>-1</sup>.

Based on the assumption of green H<sub>2</sub> via electrolysis of water driven by renewable (i.e. solar and/or wind generated) electricity [64], pure H<sub>2</sub> is fed to the permeate channel, which sweeps permeated H<sub>2</sub>O and a portion of it mixes with the reactive flow via cross-membrane transport. Such a H<sub>2</sub> feeding strategy resulted in superior reactor performances in previous studies [11, 12]. Inlet velocity magnitudes of the reaction and permeate channels are determined as  $2.2 \times 10^{-3}$  and  $2.2 \times 10^{-2}$  m s<sup>-1</sup> respectively, based on adopted space velocity and  $v_{\text{rat}}$  (Ratio of permeate inlet velocity to the fixed reactive stream inlet velocity) at default operation. Inlet temperature and pressure of both channels are kept identical, which are 523 K, 50 bar at default operation. A parametric study is conducted by varying a selected parameter within the range given in Table 3.1, and other parameters are kept at their default values.

Table 3.1. Operating parameters of the microchannel reactor system.

Parameter	Default value	Range
Temperature at the reaction channel inlet (K)	523	503–543
Pressure at the reaction channel inlet (bar)	50	30–50
Temperature at the permeate channel inlet (K)	Same as the reaction channel inlet	
Pressure at the permeate channel inlet (bar)	Same as the reaction channel inlet	
Molar inlet H <sub>2</sub> /CO <sub>2</sub> ratio	3	1–4
Reaction channel inlet velocity (m s <sup>-1</sup> )	$2.2 \times 10^{-3}$	-
Space velocity (ratio of the volumetric flow rate of reactants to the mass of catalyst) (ml g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	$6 \times 10^3$	-
Ratio of the permeate channel inlet velocity to the reaction channel inlet velocity ( $v_{\text{rat}}$ )	10	5–20
Mass ratio (CZA/HZSM-5) of catalysts	2	1–3
Relative flow direction	Counter-current	Co/counter-current

Reactor performance is measured by fractional CO<sub>2</sub> conversion and DME yield, whose respective definitions are given as [63]

$$CO_2 \text{ conversion } (X_{CO_2}) = (F_{in,CO_2} - F_{out,CO_2}) / (F_{in,CO_2}) \quad (3.1)$$

$$DME \text{ yield } (Y_{DME}) = 2 \times F_{out,DME} / (F_{in,CO_2}) \quad (3.2)$$

It should be noted that, cross-sectional surface averaged molar flow rates of the associated species are considered.

### 3.2. Reaction Network and the Kinetic Model

Physical mixture of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalysts situated within the porous catalyst layer is responsible for the transformation of CO<sub>2</sub> into DME. Reactions (2.1-2.3) are driven by Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>, whereas HZSM-5 catalyzes Reaction (2.4). Effect of methanation reaction and hydrothermal sintering of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst are not considered in the model considering their negligible effect below 573 K [30]. Additionally, HZSM-5 exhibits excellent hydrothermal stability up to 773 K [65]. High CO<sub>2</sub> inlet concentration promotes reverse Boudouard reaction ( $2CO = CO_2 + C(s)$ ,  $\Delta H^0 = -172 \text{ kJ mol}^{-1}$ ), and prevents formation of carbon species [38, 42]. Based on these considerations, catalyst deactivation is neglected in the simulations. Kinetic expressions postulated by [65, 66] are adopted to the reactor model as

$$r_{rxn = (2.1)} = \frac{k_{rxn} K_{CO_2} [f_{CO_2} f_{H_2}^{3/2} - f_{CH_3OH} f_{H_2O} / (f_{H_2}^{3/2} K_{D,rxn})]}{DEN = (1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [f_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) f_{H_2O}]} \quad (3.3)$$

$$r_{rxn = (2.2)} = k_{rxn} K_{CO_2} (f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_{D,rxn}) / DEN \quad (3.4)$$

$$r_{rxn = (2.3)} = k_{rxn} K_{CO} (f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (f_{H_2}^{1/2} K_{D,rxn})) / DEN \quad (3.5)$$

$$r_{rxn = (2.4)} = \frac{k_{rxn} (f_{CH_3OH}^2 - f_{CH_3OCH_3} f_{H_2O} / K_{D,rxn})}{1 + K'_{H_2O} f_{H_2O} + K_{CH_3OH} f_{CH_3OH}} \quad (3.6)$$

Presented kinetic expressions require estimation of reaction equilibrium constants, which can be computed via the Gibbs free energy of the pertinent reaction as

$$K_{D,rxn} = \exp(-\Delta G_{rxn}/RT). \quad (3.7)$$

Formation enthalpy and entropy of the reactive species are computed as a function of temperature, leading to Gibbs free energy of formation of species. Pertinent calculation steps can be showed as

$$\frac{H_{f,i}}{RT} = a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + \frac{b_1}{T} \quad (3.8)$$

$$\frac{S_{f,i}}{R} = a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + \frac{b_2}{T} \quad (3.9)$$

$$\frac{G_{f,i}}{RT} = \frac{H_{f,i}}{RT} - \frac{S_{f,i}}{R}. \quad (3.10)$$

Then, using reaction stoichiometry, Gibbs free energy of a reaction is obtained as

$$\Delta G_{rxn} = \sum_{i=products} n_i G_{f,i} - \sum_{i=reactants} n_i G_{f,i}. \quad (3.11)$$

Table 3.2. Thermodynamic data of the reactive species.

	$a_1$	$a_2(\times 10^3)$	$a_3(\times 10^6)$	$a_4(\times 10^9)$	$a_5(\times 10^{12})$	$b_1(\times 10^{-4})$	$b_2$
CO	3.58	-0.61	1.02	0.91	-0.90	-1.43	3.51
H <sub>2</sub>	2.34	7.98	-19.5	20.2	-7.38	-0.092	0.68
CO <sub>2</sub>	2.36	8.98	-7.12	2.46	-0.14	-4.84	9.90
H <sub>2</sub> O	4.20	-2.04	6.52	-5.49	1.77	-3.03	-0.85
CH <sub>3</sub> OH	5.72	-15.2	65.2	-71.1	26.1	-2.56	-1.50
CH <sub>3</sub> OCH <sub>3</sub>	5.31	-2.14	53.1	-62.3	23.1	-2.40	7.13

Thermodynamic constants used in Equations (3.8) and (3.9) are presented in Table 3.2, whereas computed reaction equilibrium constants in the operating temperature range is available in Table 3.3.

Table 3.3. Reaction equilibrium constants at different temperatures,  $K_{D,rxn}$

$rxn$	493 K	503 K	513 K	523 K	533 K	543 K
1	$5.15 \times 10^{-5}$	$3.89 \times 10^{-5}$	$2.97 \times 10^{-5}$	$2.28 \times 10^{-5}$	$1.77 \times 10^{-5}$	$1.38 \times 10^{-5}$
2	$6.70 \times 10^{-3}$	$8.13 \times 10^{-3}$	$9.78 \times 10^{-3}$	$1.17 \times 10^{-2}$	$1.39 \times 10^{-2}$	$1.63 \times 10^{-2}$
3	$8.10 \times 10^{-3}$	$5.04 \times 10^{-3}$	$3.19 \times 10^{-3}$	$2.05 \times 10^{-3}$	$1.34 \times 10^{-3}$	$8.91 \times 10^{-4}$
4	24.46	21.99	19.87	18.02	16.41	15.00

Since rate expressions are expressed in terms of component fugacities, Lewis law is adopted to estimate component fugacities as

$$f_i = y_i f_{pure,i}, f_{pure,i} = \exp\left[\left(b_i - \frac{a_i}{RT}\right) \frac{p}{RT} \ln(p)\right] \quad (3.12)$$

where Table 3.4 provides necessary constants for the pertinent species.

Table 3.4. The van der Waals coefficients of species needed in Equation (3.12).

	$a_i(\text{bar } L^2 \text{ mol}^{-2})$	$b_i(L \text{ mol}^{-1})$
CO	1.472	0.03948
H <sub>2</sub>	0.2453	0.02651
CO <sub>2</sub>	3.658	0.04286
H <sub>2</sub> O	5.537	0.03049
CH <sub>3</sub> OH	9.472	0.06584
CH <sub>3</sub> OCH <sub>3</sub>	5.69	0.07742

Temperature dependence of reaction rate constants and adsorption equilibrium constants are provided in the following tables.

Table 3.5. Temperature dependence of the rate constants ( $k_{\text{rxn}} = A \exp(B/RT)$ ) [63].

rxn	A	B	Unit*
1	$1.52 \times 10^{-33}$	$-2.66 \times 10^5$	$\text{mol g}_{\text{cat}} \text{s}^{-1} \text{bar}^{-3/2}$
2	$9.04 \times 10^8$	$-1.13 \times 10^5$	$\text{mol g}_{\text{cat}} \text{s}^{-1} \text{bar}^{-1}$
3	$4.06 \times 10^{-6}$	$-1.17 \times 10^4$	$\text{mol g}_{\text{cat}} \text{s}^{-1} \text{bar}^{-3/2}$
4	$1.90 \times 10^{-3}$	$4.08 \times 10^3$	$\text{mol g}_{\text{cat}} \text{s}^{-1} \text{bar}^{-2}$

Table 3.6. Adsorption equilibrium constants of the pertinent species [63].

$K_i = A \exp(B/RT)$	A	B	Unit*
$K_{CO}$	$8.40 \times 10^{-11}$	$1.18 \times 10^5$	$\text{bar}^{-1}$
$K_{CO_2}$	$1.72 \times 10^{-10}$	$8.13 \times 10^4$	$\text{bar}^{-1}$
$K_{H_2O}/K_{H_2}^{1/2}$	$4.37 \times 10^{-12}$	$1.15 \times 10^5$	$\text{bar}^{-1}$
$K'_{H_2O}$	8.35	$3.89 \times 10^{-5}$	$\text{bar}^{-1}$
$K_{CH_3OH}$	9.46	$1.13 \times 10^{-3}$	$\text{bar}^{-1}$

### 3.3. Membrane Model

Methodology outlined by Ji *et al.* [67] constitutes the basis of the membrane model whose domain is presented in Figure 3.2. A discontinuity in Navier-Stoke equations is created by a zero-thickness wall between channels to ensure that only user-defined source terms determine the mass transfer across channels. Mesh cells that neighbor zero-thickness wall are designated as source zone for permeate side and sink zone for the reaction channel. Mass transfer across membrane is implemented by defining source terms in these regions which are quantified by a user-defined function and integrated to the existing framework. Fick's Law is used to compute cross-membrane mass flux as

$$J_i = Perm_i(p_{rxn}^i - p_{perm}^i). \quad (3.13)$$

User-defined function (UDF) involves obtaining partial pressures of the permeable species ( $i=H_2$  or  $H_2O$ ) for a mesh cell in sink zone ( $p_{rxn}^i$ ) and neighboring mesh cell in the sink zone ( $p_{perm}^i$ ).

Multiplication of their difference by the membrane permeance yields cross-membrane mass flux in units of  $\text{mol m}^{-2} \text{s}^{-1}$ . Since source terms need to be defined in  $\text{kg m}^{-3} \text{s}^{-1}$ , molecular weight of the species and length of a mesh cell edge are also considered as

$$S_i = \frac{J_i M_i}{l_{\text{edge}}}. \quad (3.14)$$

A user defined memory (UDM) is defined to store the values of the source terms in cell centroid. Instead of calculating source terms for both sides of the zero-thickness wall, UDM is multiplied by -1 and defined as the source term in the neighboring mesh cell. This approach ensures that the total mass is conserved in the entire solution domain. Since mesh cells in the source zone are identical to those in the permeate channel apart from the source terms, intersection between permeate channel and source zone is defined as the interior boundary condition. The same condition is also applied to the surface between the sink zone and the reaction channel.

Steam permeance and permselectivity ( $S_{H_2O/i}$ ) are the two key properties of the membrane material. Due to very high ( $3.3 \times 10^3 \text{ m}^2 \text{ m}^{-3}$ ) membrane surface area per reactor volume, the former property is of secondary importance for a microchannel reactor. On the other hand, the slippage of reactants or methanol to the permeate channel could diminish the reactor performance significantly [55]. Based on these considerations membrane material is selected as SOD, which offers excellent permselectivities ( $S_{H_2O/CH_3OH}=233$ ,  $S_{H_2O/DME}=253$ ,  $S_{H_2O/CO_2}=22.6$ ). At 473 K,  $H_2O$  permeance and steam-hydrogen permselectivity ( $S_{H_2O/H_2}$ ) values are reported as  $6.5 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{ Pa}^{-1}$  and 4.6, respectively. On the other hand, steam permeance value is assumed as  $3.0 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{ Pa}^{-1}$  in the simulations based on three considerations. Membrane property data is not available for temperatures higher than 473 K which creates uncertainties for the system. Secondly, multicomponent nature of the reactant flow can lead to surface competitive adsorption and other detrimental factors resulting in poorer membrane performance [67]. Thirdly, since steam content in a mesh cell is limited, mass created in the source zone can be higher than mass disappearing in the sink zone at high permeance values.

As a result, increasing the number of iterations fails to decrease residuals of species conservation equations and continuity equation to an acceptable level.

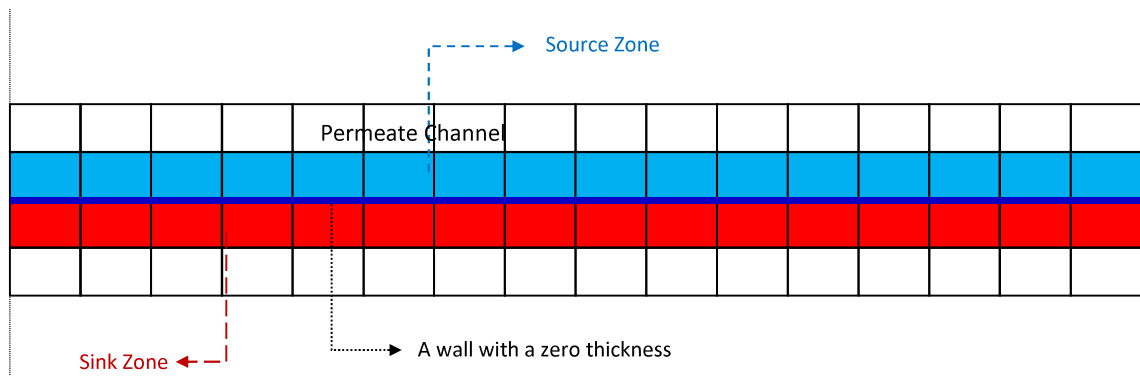


Figure 3.2. Implementation of the membrane model via zone partitioning.

### 3.4. Solution Methodology and Associated Equations

A two-dimensional (2D) steady state mathematical model involving catalytic reactions, membrane mass transfer, convective and diffusive transport of species and reactive transport within catalyst layer is created to simulate proposed membrane microchannel reactor illustrated in Figure 3.1.

In the case of adiabatic modeling (Section 4.2), convective heat transfer in fluid phases, inter-channel heat exchange through membrane, and heat transfer from catalyst layer are also considered. Relevant conservation equations are presented in Table 3.7. It should be noted that Equations (3.23-3.25) are not considered in the mathematical model unless adiabatic simulations are performed (Section 4.2).

Table 3.7. Reactor model equations (FP: Fluid phases in reaction and permeate channels, CP: Porous catalyst phase in reaction channels; ML: membrane layer between permeate and reaction channels).

Continuity equation	$\nabla \cdot (\vec{v}) = 0$	(3.18)
Momentum equation (FP)	$\nabla \cdot (\rho_m \vec{v} \vec{v}) = \nabla p + \nabla \cdot [\mu_m (\nabla \vec{v} + (\nabla \vec{v})^T) - \frac{2}{3} (\nabla \cdot \vec{v}) \mathbf{I}]$	(3.19)
Momentum equation (CP)	$\nabla \cdot (\rho_m \vec{v} \vec{v}) = \vec{F} - \nabla p + \nabla \cdot [\mu_m (\nabla \vec{v} + (\nabla \vec{v})^T) - \frac{2}{3} (\nabla \cdot \vec{v}) \mathbf{I}]$ $\vec{F} = (\frac{\mu_m}{\alpha} \vec{v} + \frac{C_2}{2} \rho_m  \vec{v}  \vec{v}); \alpha = \frac{d_p^2}{150} \frac{\epsilon_{cat}^3}{(1 - \epsilon_{cat})^2}; C_2 = \frac{3.5}{d_p} \frac{1 - \epsilon_{cat}}{\epsilon_{cat}^3}$	(3.20)
Species mass equation (FP)	$\nabla \cdot (\rho_m \vec{v} Y_i) = \nabla \cdot \vec{J}_i; \vec{J}_i = -\rho_m D_{i,m} \nabla Y_i$	(3.21)
Species mass equation (CP)	$\nabla \cdot (\rho_m \vec{v} Y_i) = \nabla \cdot \vec{J}_i + M_i R_i; \vec{J}_i = -\rho_m D_{eff,i,m} \nabla Y_i$ $R_{CO} = r_2 - r_3; R_{CO_2} = r_1 - r_2; R_{H_2} = -3r_1 - r_2 - 2r_3$ $R_{CH_3OH} = r_1 + r_3; R_{CH_3OCH_3} = r_4; R_{H_2O} = r_1 + r_2 + r_4$	(3.22)
Energy equation for FP	$\nabla \cdot (\rho_m c_{p,m} \vec{v} T) = \nabla \cdot (k_m \nabla T)$	(3.23)
Energy equation for CP	$\nabla \cdot (\rho_m c_{p,m} \vec{v} T) = \nabla \cdot (k_{eff} \nabla T) + \sum (-\Delta H_{rxn} r_{rxn})$	(3.24)
Energy equation ML	$\nabla \cdot (k_w \nabla T) = 0$	(3.25)

Gambit software (version 2.3.16) is used to create the solution domain representing the unit cell shown in Figure 3.1. The domain is discretized by square mesh cells, where the resulting mesh contains  $6 \times 10^5$  nodes,  $4.8 \times 10^4$  cells in the catalyst layer,  $2.28 \times 10^5$  cells in reaction channel,  $1.2 \times 10^4$  cells in source/sink zones, and  $2.76 \times 10^5$  cells in the permeate channel. Feed temperature, gas composition and velocity are defined as the conditions at the channel inlet. Outermost surfaces are defined as wall boundary condition and transport processes through these regions are nullified. The same boundary condition is applied to the zero-thickness wall, described in 3.2, except thickness of the membrane layer and thermal conductivity data are provided manually which are needed to compute the rate of heat conduction through membrane.

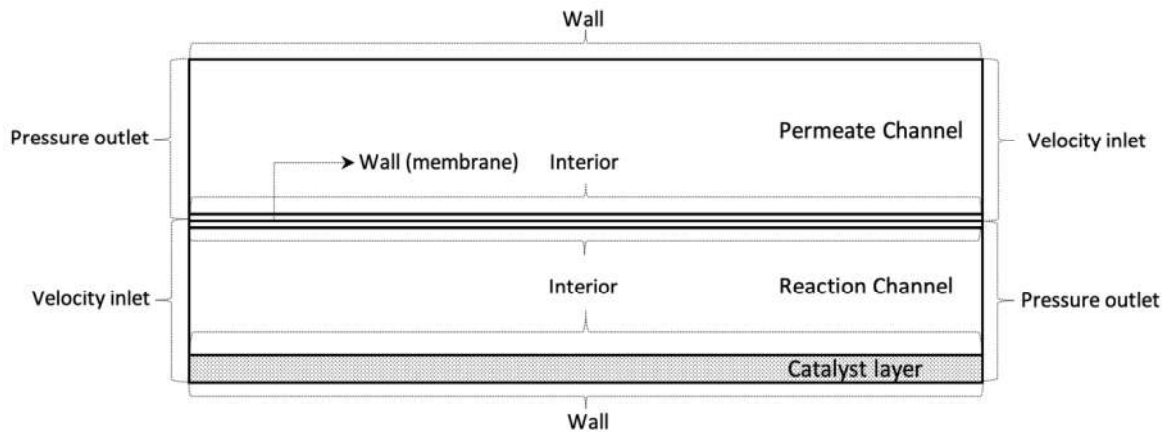


Figure 3.3. Description of the zones and boundary conditions in the solution domain.

Set of property correlations needed to quantify the physical properties of the gas mixture can be found in the literature [12]. These relations, along with the kinetic model (Section 3.2), and the membrane model (Section 3.3) are defined as user-defined functions (UDF) and integrated to the reactor model.

Obtaining flow fields inside the catalyst layer poses some challenges due to very small catalyst particle sizes, since particle-resolved CFD approach requires exact geometry of the porous region. Instead, porous nature of the layer is considered to influence pressure drop, effective thermal conductivity and mass diffusivity within the region. Catalyst layer acts the same way as the other fluid regions apart from the following features:

- Momentum conservation equation includes a momentum source term ( $\vec{F}$ ), formulated in Equation (3.20), to quantify pressure drop caused by the porous nature.
- Effective mass diffusivity of the species are considered to incorporate the effect of Knudsen diffusion within the pores.
- Effect of heat conduction is reflected in energy conservation equations whereas in other fluid regions, this effect is absent.
- Catalytic reactions take place based on the provided UDF.

Temperature, pressure and mixture composition data are processed within each mesh cell to obtain local rate of reactions. Reactive transport within the catalyst layer is modeled based on the quantification of effective mass diffusivity of the reactive species, . Since volumetric reaction rates need to be obtained, catalyst density data is needed. For CZA/HZSM-5=2 the density of the catalyst layer can be calculated as

$$\frac{1}{\rho_{\text{cat}}} = \frac{2/3}{\rho_{\text{CZA}}} + \frac{1/3}{\rho_{\text{HZSM-5}}}. \quad (3.15)$$

Then, density of CZA and HZSM-5 within the catalyst layer can be calculated as

$$\rho_{\text{CZA,mix}} = \frac{2\rho_{\text{cat}}}{3} \quad (3.16)$$

$$\rho_{\text{HZSM-5,mix}} = \frac{1\rho_{\text{cat}}}{3}. \quad (3.17)$$

For default catalyst ratio of CZA/HZSM-5=2, parameters related to catalyst density and physical properties (e.g. porosity, tortuosity) of the porous washcoat layer is presented in Table 3.8.

Table 3.8. Physical properties of the porous catalyst layer

Property	Value	Unit	Reference
$k_{\text{cat}}$	24.2	W m <sup>-1</sup> K <sup>-1</sup>	[10]
$\epsilon_{\text{cat}}$	0.61	-	[10]
$\tau_{\text{cat}}$	1.64	-	[10]
$d_{\text{pore}}$	1.14×10 <sup>-8</sup>	m	[10]
$\rho_{\text{CZA}}$	2.37×10 <sup>3</sup>	kg m <sup>-3</sup>	[10]
$\rho_{\text{HZSM-5}}$	7.7×10 <sup>2</sup>	kg m <sup>-3</sup>	[11]
$\rho_{\text{cat}}$	1.34×10 <sup>3</sup>	kg m <sup>-3</sup>	-
$\rho_{\text{CZA,mix}}$	8.95×10 <sup>2</sup>	kg m <sup>-3</sup>	-
$\rho_{\text{HZSM-5,mix}}$	4.47×10 <sup>2</sup>	kg m <sup>-3</sup>	-

## 4. RESULTS AND DISCUSSION

Effects of key operating parameters such as inlet temperature and pressure, flow direction of the permeate channel, molar inlet CO<sub>2</sub>/H<sub>2</sub> ratio, permeate channel inlet velocity and CZA/HZSM-5 mass ratio are studied in the following sections. When a particular parameter is investigated, others are kept at their default values reported in Table 3.1. In addition, validity of the mathematical model and isothermal conditions are tested. Finally, required number of reaction channels and the reactor volume are determined based on a CO<sub>2</sub> to DME pilot plant operated with 1 MW power input. Obtained results provide meaningful insights in designing and operating an actual system.

### 4.1. Model Verification

Experimental results reported by An *et al.* [63] are used to test the accuracy of the mathematical model. The aforementioned study involves feeding CO<sub>2</sub> and H<sub>2</sub> gas mixture (H<sub>2</sub>/CO<sub>2</sub>=3) at 483-543 K, 30-50 bar to a reactor containing CZA and HZSM-5 catalysts mixed physically with a mass ratio of 2:1. Space velocity (volumetric flow rate of the inlet gas divided by the catalyst mass) is reported as  $6 \times 10^3 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . A parity plot is presented in Figure 4.1, where deviations from the experimental results can be observed.

Both reactor configurations can operate without transport resistances [63,68] which, despite different reactor geometries, allows meaningful comparison. In addition, membrane mass transfer is disabled in the simulations to obtain coherent results. Investigation of Figure 4.1 reveals that the maximum difference between the experimental and predicted CO<sub>2</sub> conversion and DME yield are 5.3% and 8.5%, respectively. Therefore, the mathematical model which is comprised of employed assumptions, thermodynamic relations, property correlations and kinetic model (Equations (3.3), (3.4), (3.5), (3.6)) can be used reliably to predict the behaviour of an actual system.

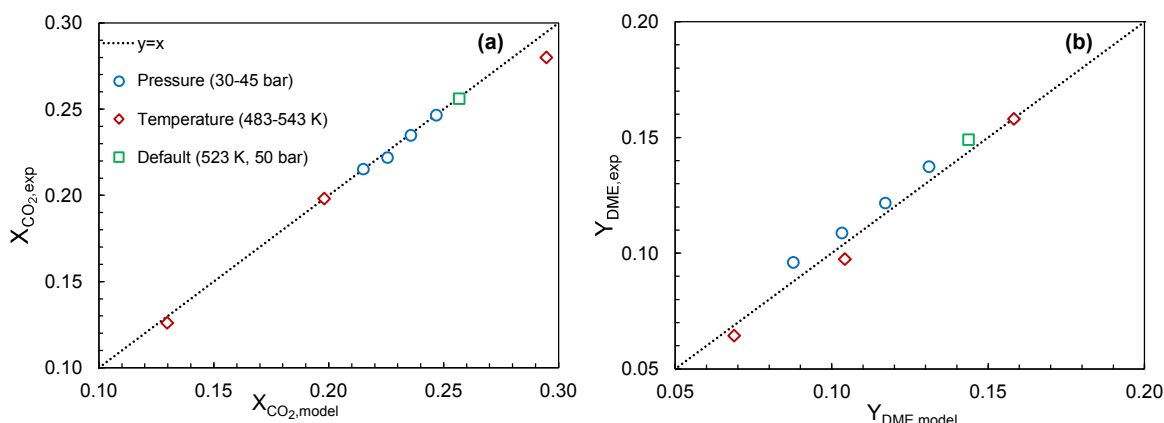


Figure 4.1. Comparison of the experimental and predicted CO<sub>2</sub> conversions and DME yields. Experimental data is taken from [63].

## 4.2. Validation of the Isothermal Conditions

Heat released by exothermic reactions can be managed effectively using microchannel reactors and near-isothermal conditions are achievable [53, 69]. Therefore, mathematical model assumes that the reactor operates isothermally. To test this assumption, energy conservation equations [68] for fluid and catalyst phases as well as conductive heat transfer through membrane layer are incorporated into the model. Heat fluxes across the outermost boundaries of a unit cell are disabled to ensure adiabatic operation.

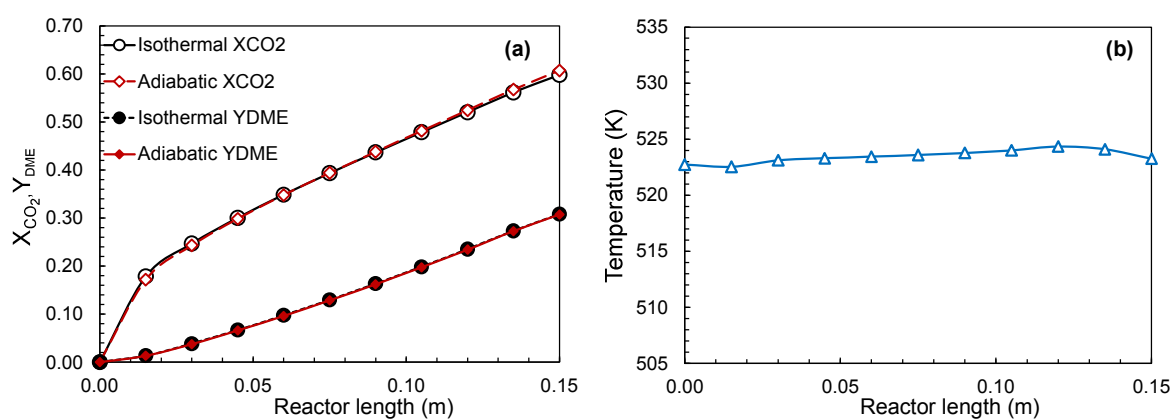


Figure 4.2. Variation of performance metrics under adiabatic and isothermal conditions (a), temperature of the gas mixture along the reactor length (b).

Evolution of CO<sub>2</sub> conversion, DME yield and mixture temperature along the reaction channel are presented in Figure 4.2. Due to negligible ( $<\pm 1$  K) temperature variation in adiabatic case, two configurations have almost identical CO<sub>2</sub> conversion and DME yield. The results point out facile temperature regulation via heat exchange between permeate and reaction channels despite the presence of both endothermic (Reaction (2.2)) and exothermic (Reactions (2.1), (2.3), (2.4)) reactions. Therefore, neglecting computationally expensive energy conservation equations is justified.

### 4.3. Impact of Inlet Temperature and Pressure

Membrane integrated and membraneless configurations are simulated at 503–543 K and 30–50 bar to investigate the influence of inlet temperature and pressure. Performance metrics are found to improve at increased temperature or pressure for both configurations (Figure 4.3). Since hydrogenation reactions involve products having fewer number of mole species compared to reactants, higher equilibrium conversions can be obtained by increasing the operating pressure. In addition, such a change would increase the reactant partial pressures and boost the rate of reactions. Due to dependence of rate constants on temperature, a similar promotion on reaction kinetics can be achieved by adopting higher inlet temperatures. Reactor performance is maximized at 543 K and 50 bar, resulting CO<sub>2</sub> conversion and DME yield of 73.3% and 34.5%, respectively with membrane integration, and 29.5% and 15.8%, respectively without a membrane. Additionally, incremental change on temperature or pressure produces much more dramatic improvements in the presence of a membrane. In terms CO<sub>2</sub> conversion and DME yield, a relatively flat trajectory is observed without a membrane, especially towards the reactor exit. On the other hand, as evident in increasing trends along the reactor, membrane allows reactor to preserve its performance due to relaxed thermodynamic limitations. Additionally, considering relatively high reactor performance at milder operating conditions, membrane integration offers a robust option to decrease energy consumption in overall process.

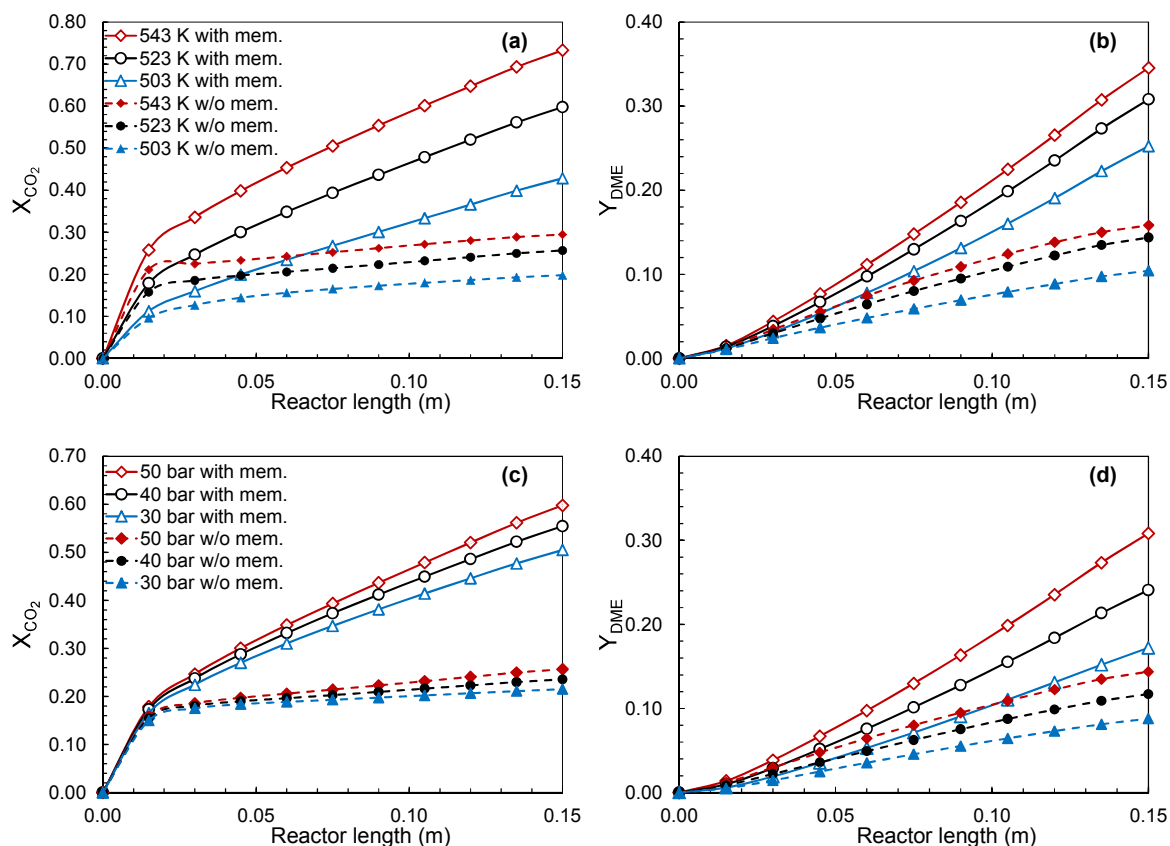


Figure 4.3. Influence of temperature/pressure on CO<sub>2</sub> conversion, DME yield with and without membrane integration.

#### 4.4. Impact of Flow Direction of the Permeate Channel

Evolution of concentration gradient between channels along the reactor can be manipulated by adopting either co-current or counter-current permeate flow. Comparison presented in Figure 4.4 reveals that, unlike nearly identical H<sub>2</sub> flow rate profiles, the behavior of H<sub>2</sub>O flow rate is strikingly different for these configurations. Steam content is higher for counter-current flow within the first  $\sim 7.5 \times 10^{-2}$  m of the reaction channel. However, since H<sub>2</sub>O continues to build-up in co-current configuration, H<sub>2</sub>O flow rate is significantly higher at the outlet of the reaction channel. As a result, average H<sub>2</sub>O flow rate is  $1.5 \times 10^{-8}$  mol s<sup>-1</sup>, which is higher than  $8.5 \times 10^{-9}$  mol s<sup>-1</sup> obtained when sweep gas fed counter-currently. The dissimilar H<sub>2</sub>O flow rate profiles lead to similar divergence in CO<sub>2</sub> conversion and DME yield trends. Even though these metrics are superior for co-current flow in the first  $1 \times 10^{-1}$  m, counter-current configuration leads to better results at the channel exit.

$\text{H}_2\text{O}$  and  $\text{H}_2$  flow rate profiles are also provided for membraneless case in Figure 4.4. In the absence of membrane,  $\text{H}_2$  flow rate in a reaction channel decreases due to Reactions (2.1-2.3), conversely,  $\text{H}_2$  permeated through membrane causes net increase in  $\text{H}_2$  content. Furthermore, SOD membrane is capable to decrease  $\text{H}_2\text{O}$  flow rate by a factor of  $\sim 7$  towards reactor exit. The beneficial effect of avoiding thermodynamic suppression due to steam build-up can be observed just after  $\sim 2 \times 10^{-2}$  m from the inlet. Up to three times higher  $\text{CO}_2$  conversion and DME yield can be obtained with the combined impact of cross-membrane  $\text{H}_2\text{O}$  and  $\text{H}_2$  transfer.

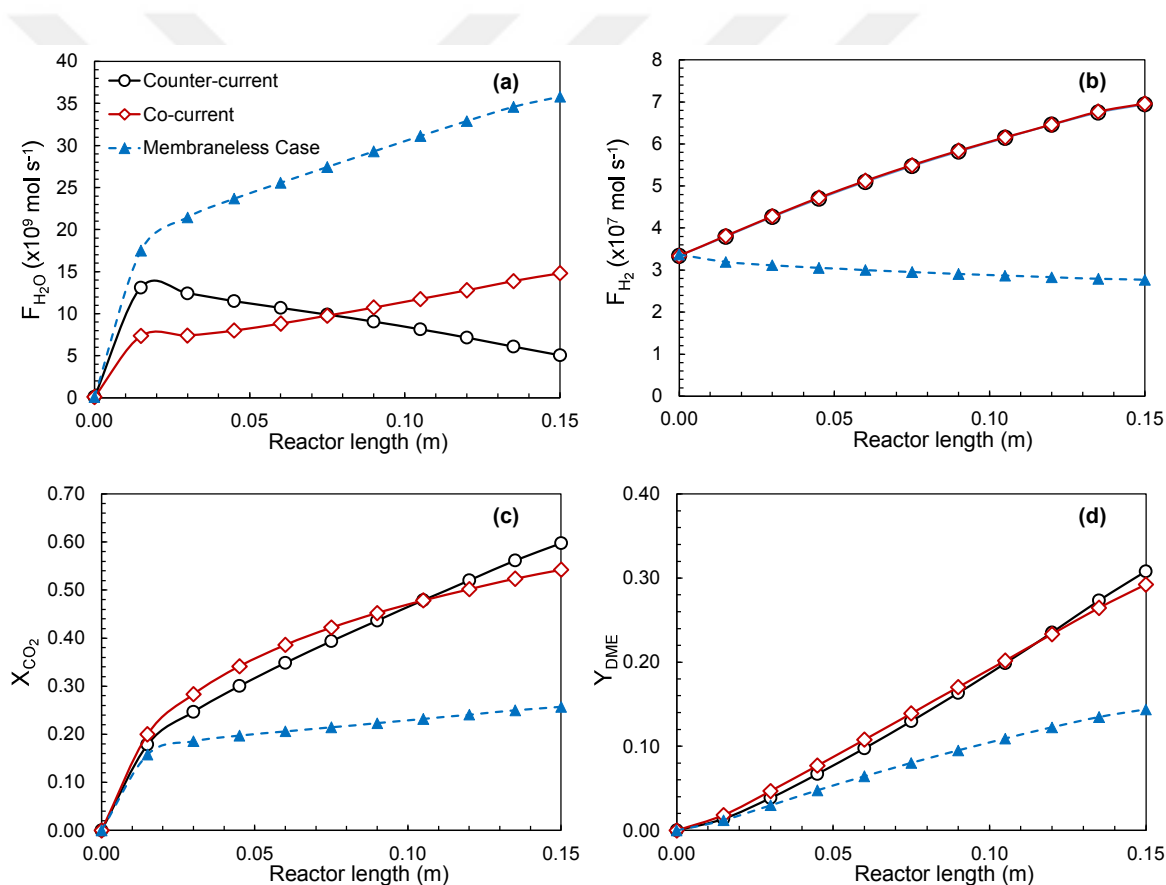


Figure 4.4. Comparison of co-current, counter-current and membraneless configurations in terms of performance metrics and flow rates of  $\text{H}_2\text{O}$  and  $\text{H}_2$  along the reactor.

#### 4.5. Impact of H<sub>2</sub>/CO<sub>2</sub> Feed Ratio

Considering the strong dependence of hydrogenation kinetics on H<sub>2</sub> partial pressure (Equations (3.3), (3.4), (3.5)), the effect of relative hydrogen content in the reaction channel is investigated by varying molar inlet ratio of H<sub>2</sub>/CO<sub>2</sub> within 1-4. When adopting higher H<sub>2</sub>/CO<sub>2</sub> ratios, inlet flow rate of CO<sub>2</sub> is decreased to accommodate additional H<sub>2</sub> to keep space velocity constant at  $6 \times 10^3 \text{ ml g}_{\text{cat}} \text{ s}^{-1}$  and vice versa. Examination of Figure 4.5 reveals that higher H<sub>2</sub>/CO<sub>2</sub> ratios lead to superior CO<sub>2</sub> conversion and DME yield. On the other hand, the difference is less remarkable within H<sub>2</sub>/CO<sub>2</sub>=3-4. Diminishing CO<sub>2</sub> content/partial pressure at higher H<sub>2</sub>/CO<sub>2</sub>, seems to suppress the rate of Reaction (2.2) despite higher H<sub>2</sub> concentration. Such a variation in inlet CO<sub>2</sub> flow rates is also responsible for the dependence of total amount of CO<sub>2</sub> consumed and DME produced in a reaction channel on H<sub>2</sub>/CO<sub>2</sub> ratio.  $1.4$ ,  $1.7$  and  $1.8 \times 10^{-8} \text{ mol s}^{-1}$  DME is synthesized and  $8.9$ ,  $6.7$  and  $6.1 \times 10^{-8} \text{ mol s}^{-1}$  CO<sub>2</sub> is consumed at H<sub>2</sub>/CO<sub>2</sub> of 1, 3 and 4, respectively. Considering the trade-off between the amount of CO<sub>2</sub> consumed and DME produced, optimal H<sub>2</sub>/CO<sub>2</sub> ratio should be determined based on a detailed techno-economic analysis.

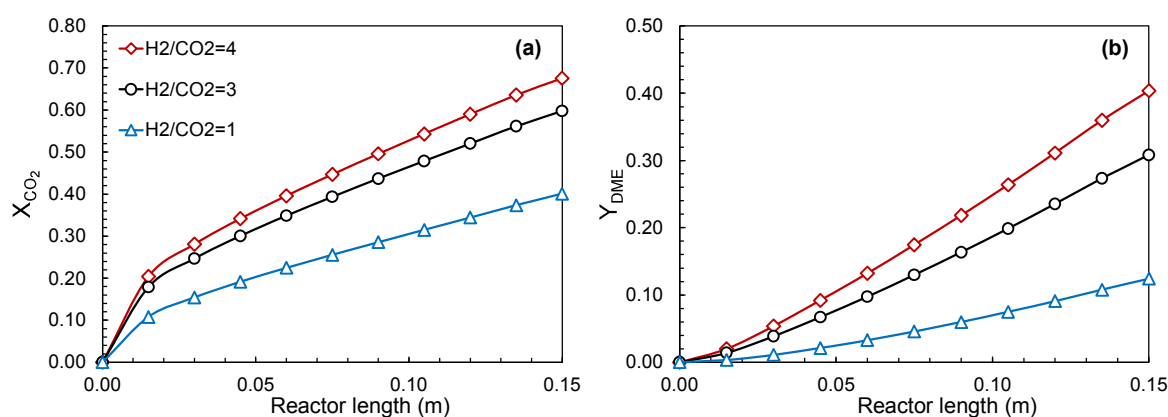


Figure 4.5. Influence of molar inlet H<sub>2</sub>/CO<sub>2</sub> ratio on reactor performance.

#### 4.6. Effect of the inlet velocity of the permeate stream

Magnitudes of inlet velocities of reaction and permeate channels at default operation are given in Table 3.1.

The ratio of these values, defined as ( $v_{rat}$ ), is varied between 5 and 20 to study the impact of sweep  $H_2$  flow rate. At low sweep  $H_2$  flow, membrane performance suffers since concentration of  $H_2O$  on the permeate side would approach to the values observed in the reaction channel. At the opposite extreme, concentration of  $H_2O$  in the sweep mixture would be negligible when very large quantities of  $H_2$  is sent to the permeate channel. In such a configuration, the influx of  $H_2$  towards the reactive mixture is also maximized due to conserved  $H_2$  concentration gradient between channels. As shown in Figure 4.6, increasing  $v_{rat}$  from 5 to 10, results in a remarkable improvement on cross-membrane mass transport. Consequently, both DME yield and  $CO_2$  conversion increases. On the other hand, considering the diminished improvement and the cost associated with conditioning and dosing additional  $H_2$ , increasing  $v_{rat}$  beyond 10 seems impractical.

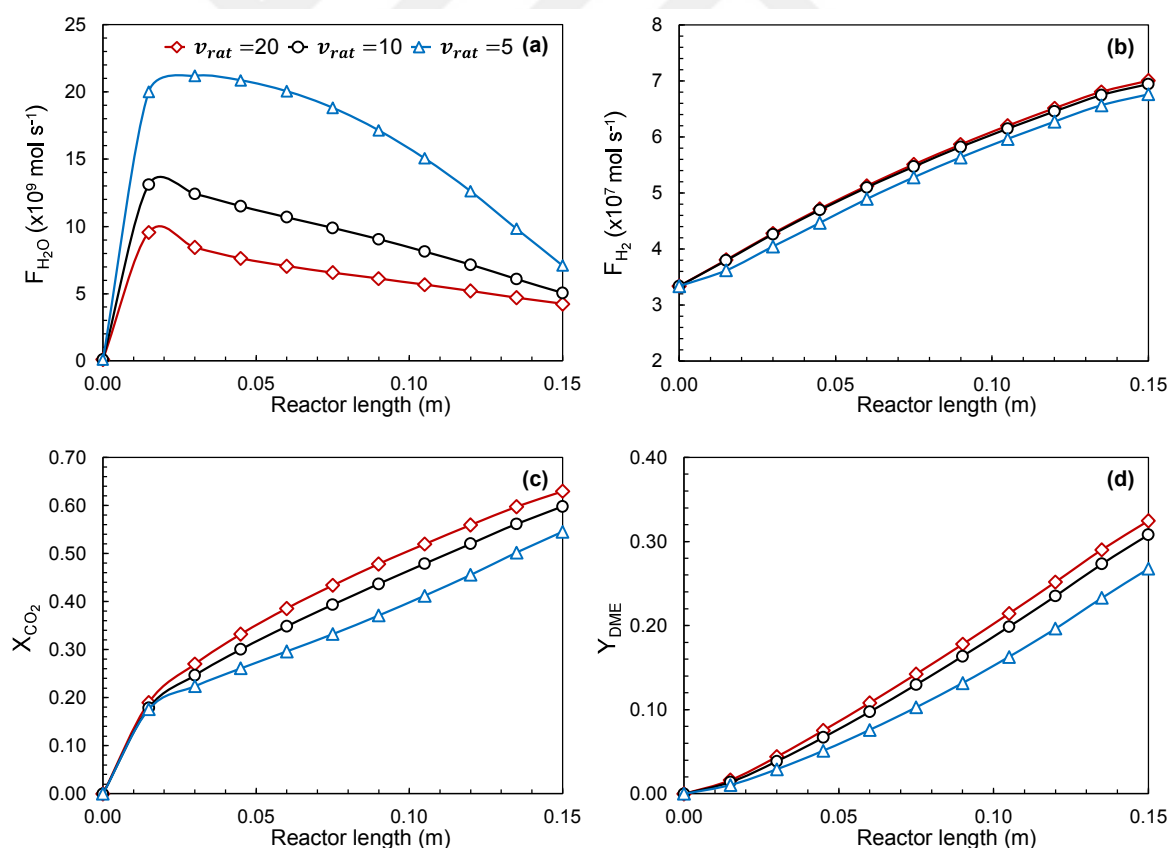


Figure 4.6. Evolution of  $CO_2$  conversion, DME yield and flow rates permeable species along the reactor at different  $v_{rat}$  values.

One can speculate that, rather than setting  $v_{\text{rat}}=10$ , a better reactor performance can be achieved by sending a portion of sweep  $\text{H}_2$  to the reaction channel. Such a configuration would lead to higher  $\text{H}_2/\text{CO}_2$  ratios whose benefits are reported in Section 4.5. To test this hypothesis, a new variable called  $\text{H}_2$  flow ratio, which is defined as the flow rate of  $\text{H}_2$  diverted to the reaction channel divided by the amount of  $\text{H}_2$  sent to permeate channel at default operation. In other words,  $\text{H}_2$  flow ratio of 0.9 implies that 10% of the original sweep  $\text{H}_2$  is fed to the reaction channel and the remaining 90% is kept at permeate side.

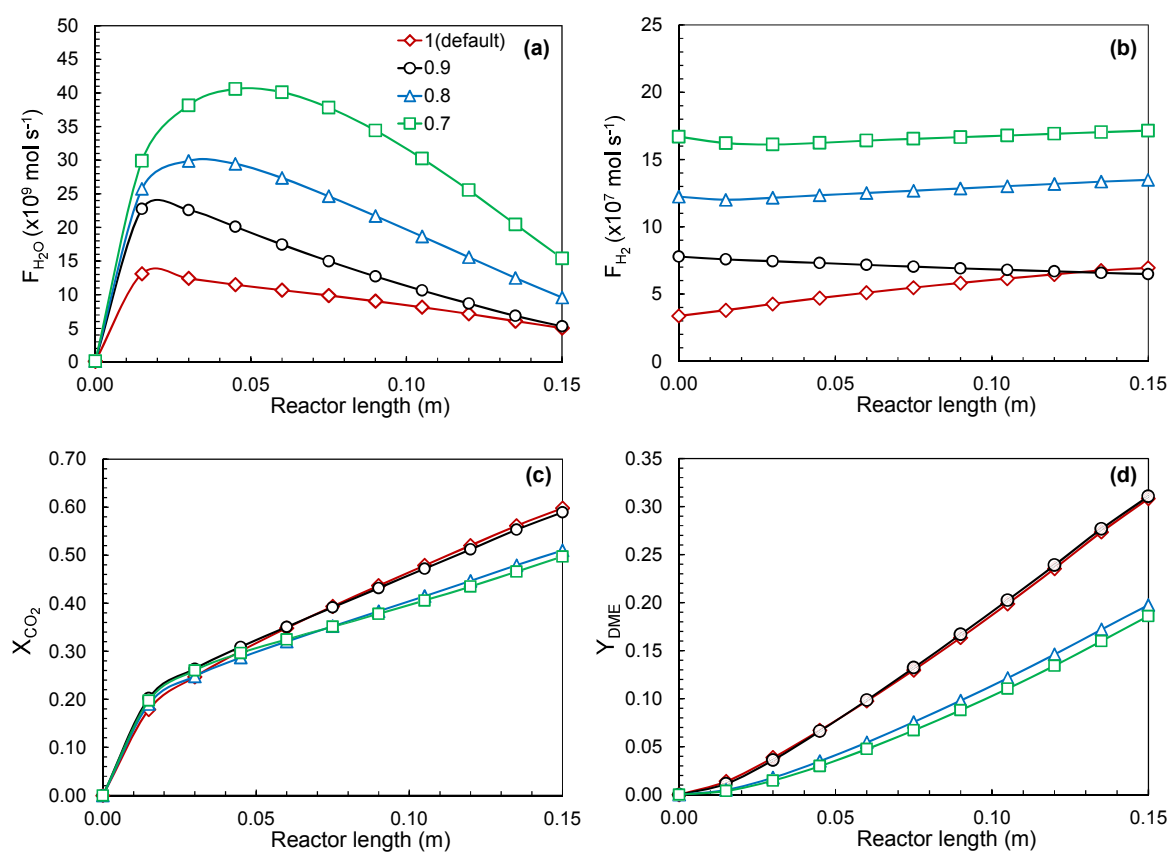


Figure 4.7. Effect of hydrogen flow ratio on performance metrics and flow rates of  $\text{H}_2\text{O}$  and  $\text{H}_2$  along the reactor.

Flow ratio is varied between 0.7 and 1 and the results are presented in Figure 4.7. When flow ratio is set to 0.7,  $\text{H}_2$  flow rate in the reactive mixture increases substantially and up to  $\text{H}_2/\text{CO}_2 \approx 30$  can be reached towards the reactor exit.

However, this configuration leads to significant accumulation of H<sub>2</sub>O due to unsatisfactory membrane performance linked to low  $v_{\text{rat}}$ . Similar reactor performances observed at flow ratios of 0.9 and 1, indicates a perfect balance between the competing effects of H<sub>2</sub>/CO<sub>2</sub> ratio and  $v_{\text{rat}}$ .

#### 4.7. Impact of Catalyst Ratio

Considering the dimensions of a reaction channel (Section 3.1), a single washcoated catalyst layer has a volume of  $4.5 \times 10^{-9} \text{ m}^3$  which can accommodate catalyst mixtures with various compositions. Relative rate of methanol formation and its dehydration can be manipulated by varying the relative amounts of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and HZSM-5 in the catalyst mixture. Densities of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and HZSM-5 are  $2.4 \times 10^3$  and  $7.7 \times 10^2 \text{ kg}^{-1} \text{ m}^3$  respectively, which implies total mass of catalyst would be higher as CZA/HZSM-5 is increased. Therefore, inlet flow rate of reactants are adjusted to keep space velocity constant at  $6 \times 10^3 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . Changing catalyst ratio from CZA/HZSM-5=1 to 3 increases converted CO<sub>2</sub> amount from 5.0 to  $7.7 \times 10^{-8} \text{ mol s}^{-1}$  even though the improvement in fractional CO<sub>2</sub> conversion remain insignificant (Figure 4.8). On the other hand, since rate of methanol dehydration depends on both partial pressure of methanol and the amount of dehydration catalyst, changing CZA/HZSM-5 creates two competing effects on DME yield. Since highest DME yield is obtained at CZA/HZSM-5=3 it can be deduced that, higher methanol partial pressures fueled by increased CZA content dominates the negative influence of diminished amount of dehydration catalyst. Considering these findings, it can be concluded that both reactor capacity and performance metrics can be optimized by choosing ideal catalyst composition.

#### 4.8. Sizing of Intensified CO<sub>2</sub> to DME Reactor System

Renewable energy can be utilized to produce so-called green hydrogen via water electrolysis, which is one of the key ingredients of a CO<sub>2</sub> to DME pilot plant [70]. Around 18 kg H<sub>2</sub>/h ( $\approx 2.5 \text{ mol H}_2 \text{ s}^{-1}$ ) can be synthesized with a 1 MW power input which is the power capacity adopted by many pilot projects.

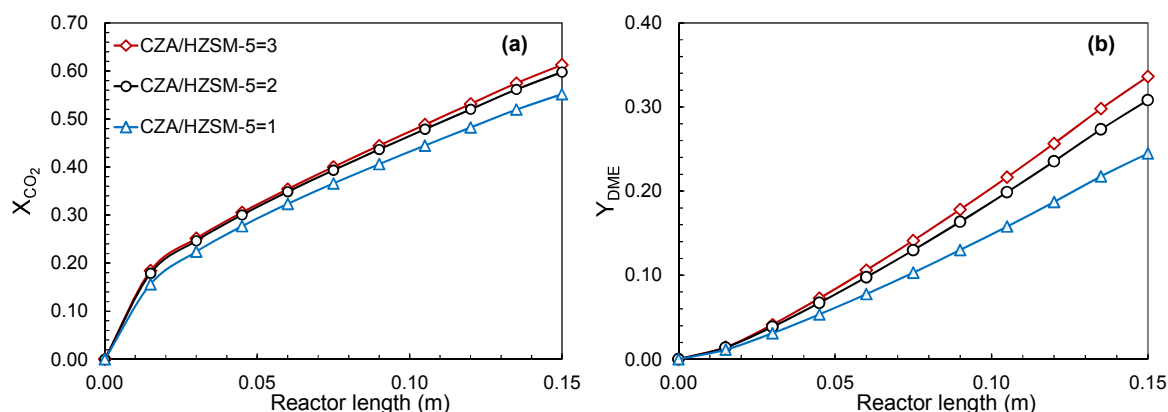


Figure 4.8. Effect of catalyst mass ratio on CO<sub>2</sub> conversion and DME yield.

The number of required unit cells can be estimated based on the H<sub>2</sub> consumption of a single cell assuming no H<sub>2</sub> is lost during separation and recycle stages. Based on this approach,  $1.1 \times 10^7$  reaction channels are needed. Assuming the thickness of the membrane layer and the horizontal distance between adjacent channels are  $1 \times 10^{-3}$  m, target capacity can be reached with eight compact reactor blocks (W&H $\approx$ 2.4 m, L= $1.5 \times 10^{-1}$  m) with a total volume of  $6.9 \text{ m}^3$ . Around  $1 \times 10^3$  tons of CO<sub>2</sub> can be converted into  $2.76 \times 10^2$  tons of DME, 35 tons of methanol and  $2.8 \times 10^2$  tons of CO annually based on such sizing. It should be noted that the present study focuses only on the reactor unit, and potential CO<sub>2</sub> emissions due to energy requirement of feed conditioning and product separation should be considered in a separate study.

## 5. CONCLUSION

### 5.1. Conclusions

Direct DME synthesis via CO<sub>2</sub> hydrogenation is investigated in a membrane microchannel reactor. A repeating unit cell contains a steam selective SOD membrane layer which is sandwiched between a reaction channel and a parallel permeate channel. The inner walls of a reaction channel are washcoated with a physical mixture Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalysts with a 3:1 mass ratio, where the former is responsible for methanol synthesis and the latter dehydrates methanol to DME. In default operation, H<sub>2</sub>-CO<sub>2</sub> gas mixture (H<sub>2</sub>/CO<sub>2</sub>=3) is fed to the reaction channel with a space velocity of  $6 \times 10^3$  ml gcat<sup>-1</sup> h<sup>-1</sup> and pure H<sub>2</sub> is dosed to the permeate channel to sweep permeated H<sub>2</sub>O. An isothermal steady state reactor model which considers two dimensional conservation of momentum, species mass transport, membrane mass transfer and reactive transport within the porous catalyst layer is solved using finite volume method under ANSYS platform. Validation of isothermal conditions is performed by incorporating energy conservation equations to the reactor model which resulted in near-constant temperature profile. The following are the other key conclusions obtained from this work:

- Reactor performance can be improved by increasing temperature or pressure. Membrane integration enhances CO<sub>2</sub> conversion and DME yield by a factor of > 3. Furthermore, reactor responds to changes in temperature and pressure more strongly when the membrane layer is present.
- Higher inlet H<sub>2</sub>/CO<sub>2</sub> ratios promote CO<sub>2</sub> conversion and DME yield. However, the highest amount of CO<sub>2</sub> is converted when H<sub>2</sub>/CO<sub>2</sub>=1.
- Membrane mass transfer and reactor performance depends strongly on the flow rate of the permeate channel which is quantified by the relative inlet velocity magnitude ( $v_{rat}$ ). However, the benefits becomes insignificant for  $v_{rat} > 10$ . Dosing a portion of sweep H<sub>2</sub> to the reaction channel does not lead to a better reactor performance due to diminished H<sub>2</sub>O removal capability dominating the positive impact of higher H<sub>2</sub>/CO<sub>2</sub> ratio.

- Counter-current flow configuration offers slightly superior H<sub>2</sub>O removal capability compared to co-current flow which affects reactor performance in a positive way.
- Both reactor capacity and performance metrics (CO<sub>2</sub> conversion and DME yield) can be altered by varying the CZA/HZSM-5 mass ratio. Reactor performance is maximized at CZA/HZSM-5=3.
- Eight microchannel reactor blocks having total a volume of 6.9 m<sup>3</sup> are capable of converting 1×10<sup>3</sup> tons of CO<sub>2</sub> a year into 2.76×10<sup>2</sup> tons of DME using H<sub>2</sub> input from 1 MW electrolyzer.

## 5.2. Recommendations

- Other methanol synthesis and/or dehydration catalysts can be modeled and the results can be compared with the CZA-HZSM-5 mixture.
- The impacts of membrane permeance and permselectivities can be investigated using different membrane materials.
- Volumetric miniaturization can be studied by varying the channel dimensions.
- A membrane model based on Maxwell-Stefan diffusion can be created to obtain a more realistic membrane simulation.
- The impact of catalyst deactivation can be studied by adopting an unsteady state reactor model and compatible kinetic expressions.

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