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A numerical performance study of a fixed-bed reactor for methanol synthesis by CO₂ hydrogenation

Daulet Izbassarov ^{a,*}, Judit Nyári ^a, Bulut Tekgül ^a, Erkki Laurila ^a, Tanja Kallio ^b, Annukka Santasalo-Aarnio ^a, Ossi Kaario ^a, Ville Vuorinen ^a

^a Department of Mechanical Engineering, Aalto University, FI-00076, Espoo, Finland

^b Department of Chemistry and Materials Science, Aalto University, FI-00076, Espoo, Finland

HIGHLIGHTS

- A novel computational tool is presented for CO₂ and H₂-based methanol synthesis.
- Aspen Plus (1D) and OpenFOAM (1D/2D) fixed-bed reactor simulations are performed.
- Maximum methanol yield is found to be limited by 1D solution.
- The isothermal random and staggered configurations outperformed the in-line system.

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ABSTRACT

Synthetic fuels are needed to replace their fossil counterparts for clean transport. Presently, their production is still inefficient and costly. To enhance the process of methanol production from CO₂ and H₂ and reduce its cost, a particle-resolved numerical simulation tool is presented. A global surface reaction model based on the Langmuir-Hinshelwood-Hougen-Watson kinetics is utilized. The approach is first validated against standard benchmark problems for non-reacting and reacting cases. Next, the method is applied to study the performance of methanol production in a 2D fixed-bed reactor under a range of parameters. It is found that methanol yield enhances with pressure, catalyst loading, reactant ratio, and packing density. The yield diminishes with temperature at adiabatic conditions, while it shows non-monotonic change for the studied isothermal cases. Overall, the staggered and the random catalyst configurations are found to outperform the in-line system.

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Introduction

Methanol production via CO_2 hydrogenation is a highly contemporary topic due to its CO_2 mitigation and excess electricity storage potential [8]. CO_2 can be captured and utilized from industrial emissions [38] or directly from air [7]. Such a technology is currently considered crucial to achieve CO_2 neutrality or even CO_2 negativity [15]. CO_2 can be used to produce building materials, fuels and chemicals. Most of the

* Corresponding author.

E-mail address: daulet.izbassarov@aalto.fi (D. Izbassarov).

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CO₂-based synthetic fuels are produced by hydrogenation which provides their energy content [16]. However, to achieve a minimum carbon neutrality of these compounds, hydrogen should be of non-fossil origin. One of the most established H₂ production processes is biomass gasification [6,9]. Moreover, water electrolysis with renewable electricity is another emergent technology for H₂ production [4]. Hydrogen is a valuable product for the chemical industry, and a long-term storage material for renewable electricity [2]. However, utilization of hydrogen as a transportation fuel [14,44] is also known to pose certain challenges including unfavorable storage [17,33], transportation and fueling conditions [25]. Meanwhile, methanol is a versatile compound that can serve as a raw material for the chemical and petrochemical industries [34]. Furthermore, its role as pure fuel or fuel additive is increasing [21], and its growing recognition in the marine industry makes methanol production from CO₂ and hydrogen an intriguing topic [40].

Currently, methanol is almost solely produced from natural gas, except for China where inexpensive coal is the main raw material [8]. Methanol synthesis from CO₂ and H₂ works similarly to natural gas-based synthesis meaning that the same reactions take place at similar conditions, and is usually carried out in a fixed-bed reactor [37]. A summary of experiments studying the rate equations of kinetic models under different conditions is presented by Bozzano and Manenti [8]. Langmuir-Hinshelwood-Hougen-Watson The developed (LHHW) type kinetic models often differ in the source of carbon provided for the formation of methanol. This is due to the uncertainty in the origin of the carbon molecule in the methanol compound as some consider either only carbon monoxide [45,49] or carbon dioxide [41,48] providing the carbon molecule, while others consider both of them [13,26]. The most frequently used kinetic models were proposed by Graaf et al. [13] and Vanden Bussche and Froment [48].

The performance of the methanol synthesis reactor strongly depends on the fluid flow and its interaction with the catalyst material as shown in Fig. 1. Several approaches have been proposed to study the methanol synthesis in a fixed-bed reactor. One common numerical model is the onedimensional approach, i.e. the plug flow reactor model. 1D models can be classified into two types as pseudohomogeneous and heterogeneous models. In the first model, the fixed-bed is treated as a pseudo-continuum. On the other hand the heterogeneous model treats both the gas and pellet phases explicitly. Manenti et al. [28] concluded that results obtained by both models are similar when the operating conditions are in the conventional region. Note that most of the previous contributions address steady-state and pseudohomogeneous models while only few works considered dynamic modeling [29]. Comprehensive summary of the 1D models can be found in the review by Bozzano and Manenti [8]. Several studies extended the 1D models to 2D [3,36,43]. Solsvik and Jakobsen [43] studied the effect of various closures for mass diffusion on the pellet and the reactor levels. They found that the difference between various closures were minor on both levels. Petera et al. [36] simulated different phenomena occurring in the catalyst and the reactor. They studied the mechanism of hot spot formation due to incidental reduction in the size of the catalyst. Arab et al. [3] compared the performance of a conventional fixed-bed reactor to a monolithic one. It was found that both reactors performed similarly at low space velocity (SV), while the latter one outperformed at high velocities.

Another approach is to use computational fluid dynamics (CFD) simulations. Within a CFD framework, a fixed-bed can be modeled by the effective continuum approach or by an actual particle-resolved simulation. In the first method, the full-size reactor can be taken into account, while the latter one enables only reduced-length reactor simulations. However, the latter approach provides more detailed information regarding local transport phenomena inside the bed by taking into account the actual geometry of the catalyst particles. Moreover, it is found that at small tube-to-particle diameter ratios, the effects of the inhomogeneous structure become important and the plug flow model predictions become questionable. Thus, there is a growing interest in the particle-resolved simulations [19].

Despite advances in coupled CFD simulations with reaction kinetics [10,19], CFD studies on methanol synthesis in fixed-bed reactors are scarce. Mirvakili et al. [30] investigated the effect of flow mal-distribution on the performance of an industrial reactor. Redondo et al. [39] studied the performance of various tubular and tube-cooled reactors. Both of the studies utilized the effective continuum approach. Recently, the particle-resolved approach was used by Karthik and Buwa [22] where they studied the selection of optimal geometry of the catalyst. In the aforementioned studies, the conventional LHHW kinetics was coupled with CFD. It is evident that there is a gap in understanding the effects of flow dynamics on methanol synthesis reactor. Thus, in the present study, particle-resolved CFD simulations coupled with LHHW



Fig. 1 – Schematic of the methanol synthesis reactor used in the present work. The contours represent velocity magnitude with the scale ranging from 0 (white) to $7.4U_i$ (black) where U_i is the average inlet velocity.

kinetics are performed to study the performance of the methanol synthesis reactor under various conditions. The main objectives of the present work are to 1) present a novel computational tool for methanol synthesis, 2) validate and verify the tool with available numerical and experimental data, 3) study the performance of the fixed-bed reactor for a range of parameters via the developed computational tool.

Mathematical formulation

Governing equations and discretization

The reacting flow is described by the compressible Navier-Stokes equations. The continuity, momentum, species and energy equations are given by:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \mathbf{0},\tag{1}$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \left[\mu (\nabla \mathbf{u} + \nabla \mathbf{u}^{\mathrm{T}}) - \frac{2}{3} \mu \nabla \cdot \mathbf{u} \mathbf{I} \right], \qquad (2)$$

$$\frac{\partial \rho \mathbf{Y}_{k}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{Y}_{k}) = \nabla \cdot (\rho \mathbf{D} \nabla \mathbf{Y}_{k}) + \dot{\omega}_{k}, \qquad k = 1, ..., n_{s}, \tag{3}$$

$$\frac{\partial \rho h_t}{\partial t} + \nabla \cdot (\rho \mathbf{u} h_t) = \frac{\partial p}{\partial t} + \nabla \cdot \left(\frac{\lambda}{c_p} \nabla h_s\right) + \dot{\omega}_h, \tag{4}$$

where **u**, *p*, Y_k, *h*_s, ρ , μ , λ , *c*_p, $\dot{\omega}_k$, $\dot{\omega}_h$ are the velocity, the pressure, the mass fraction of specie *k*, the sensible enthalpy, the density, the viscosity, the thermal conductivity, the heat capacity, the reaction rate of species *k* and the heat release rate, respectively. Above, *h*_t is the total enthalpy defined as *h*_t = *h*_s + 0.5|**u**|², I is the identity tensor and *n*_s is the number of species. For all species, the diffusion coefficient is $D = \lambda/(\rho c_p)$ as Lewis number is considered to be equal to unity. Note that the species formation/consumption rate ($\dot{\omega}_k$) and the heat source ($\dot{\omega}_h$) are defined only on the catalytic walls and can be written as:

$$\dot{\omega}_{k} = \rho_{cat} M W_{k} \sum_{i=1}^{n_{f}} \sum_{j=1}^{n_{r}} \frac{A_{i} \alpha_{jk} r_{ij}}{V_{i}},$$
(5)

$$\dot{\omega}_h = \sum_{k=1}^{n_s} \Delta h_{f,k}^0 \dot{\omega}_k,\tag{6}$$

where ρ_{cat} is the catalyst density, MW_k is the molecular weight and $h_{f,k}^0$ is the enthalpy of formation of species k, A_i is the area of face i of the catalytic wall, V_i is the volume of the cell adjacent to face i, α_{jk} is the stoichiometric coefficient of component k and r_{ij} is the reaction rate of reaction j. The catalyst density is defined as $\rho_{cat} = m_{cat}/A_{geometric}$, where m_{cat} and $A_{geometric}$ are mass and geometric area of the catalyst, respectively. Note that ρ_{cat} is used to redefine the reaction rate in terms of a molar flux, which was proposed earlier by Kuroki et al. [24]. Above, n_r and n_f represent the number of reactions and faces of a catalytic wall. Finally, the density of the mixture is calculated using ideal gas law.

The flow equations (Eqs. (1)-(4)) are solved by the pressure implicit splitting of operators (PISO) algorithm within the finite-volume OpenFOAM 6 [51] framework. Similar to our

previous works [20,46], the flux limited Gamma scheme of Jasak et al. [18] is used to discretize the convective terms, while the diffusion terms are approximated using central differences. Finally, a second order implicit scheme is utilized for temporal discretization.

Kinetic model

Α

In this paper, formation of methanol is considered both from CO_2 and CO. The popular model of Graaf et al. [13] is updated with equilibrium constants from Lim et al. [26] and experimental data of An et al. [1]. Methanol production occurs by hydrogenation of CO_2 and CO with a Cu/Zn/Al/Zr catalyst [8]. The mechanism is based on three main reactions:

(R1)
$$CO + 2H_2 \rightleftharpoons CH_3OH$$
, $\Delta H_{298K} = -90.2kJ/mol$ (7)

$$(R2) \quad CO_2 + 3H_2 \!\rightleftharpoons\! CH_3OH + H_2O, \quad \Delta H_{298K} = -48.8 kJ/mol \eqref{R2} \eqref{R2$$

$$(\text{R3}) \quad \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}, \quad \Delta\text{H}_{298K} = +41.3 \text{kJ/mol} \qquad \text{(9)}$$

Formation of by-products, e.g. dimethyl ether, is not considered here due to their negligible concentration [47].

Following Kiss et al. [23], the rate expression can be written in a generic form.

$$r = \frac{AB}{C},$$
 (10)

$$\mathbf{A} = \mathbf{a} T^n \exp\left(\frac{-E_a}{\mathbf{R}T}\right),\tag{11}$$

$$\mathbf{B} = \mathbf{B}_1 \left(\prod f_i^{b_i} \right) - \mathbf{B}_2 \left(\prod f_j^{b_j} \right), \tag{12}$$

$$\mathsf{C} = \left(\mathsf{C}_{i}\left[\prod f_{j}^{c_{j}}\right]\right)^{m} \tag{13}$$

where A, B, C are the kinetic term, the driving force and the adsorption term, respectively. The rate equations for R1, R2 and R3 are:

$$\begin{split} r_{1} &= \frac{k_{1}K_{CO}\left[f_{CO}f_{H_{2}}^{1.5} - f_{CH_{3}OH} / \left(f_{H_{2}}^{0.5}K_{eq_{1}}\right)\right]}{\left(1 + K_{CO}f_{CO} + K_{CO_{2}}f_{CO_{2}}\right)\left[f_{H_{2}}^{0.5} + \left(K_{H_{2}O} / K_{H_{2}}^{0.5}\right)f_{H_{2}O}\right)\right]}, \quad (14)\\ r_{2} &= \frac{k_{2}K_{CO_{2}}\left[f_{CO_{2}}f_{H_{2}}^{1.5} - f_{CH_{3}OH}f_{H_{2}O} / \left(f_{H_{2}}^{1.5}K_{eq_{2}}\right)\right]}{\left(1 + K_{CO}f_{CO} + K_{CO_{2}}f_{CO_{2}}\right)\left[f_{H_{2}}^{0.5} + \left(K_{H_{2}O} / K_{H_{2}}^{0.5}\right)f_{H_{2}O}\right)\right]}, \quad (14)$$

$$r_{3} = \frac{k_{3}K_{CO_{2}}\left[f_{CO_{2}}f_{H_{2}} - f_{H_{2}O}f_{CO}/K_{eq_{3}}\right]}{\left(1 + K_{CO}f_{CO} + K_{CO_{2}}f_{CO_{2}}\right)\left[f_{H_{2}}^{0.5} + \left(K_{H_{2}O}/K_{H_{2}}^{0.5}\right)f_{H_{2}O}\right)\right]},$$
(16)

where *f* corresponds to fugacity [Pa] and the reaction rate *r* is in [mol/(g_{cat} s)]. All coefficients are in the form of Eq. (11) with n = 0. All the constants are given in Table 1. Note that the ideal gas assumption is used in the present work, thus partial pressure is used instead of fugacity. To facilitate comprehensive validation of the method, the LHHW kinetic model is

Table 1 – Constants for the reactions R1, R2 and R3.					
Coefficient	Expression				
k ₁	$4.0638 imes 10^{-6} \exp(-11695/RT)$	kmol/kg _{cat} • s • Pa			
k ₂	$1.5188 imes 10^{-33} \exp(-266010/RT)$	kmol/kg _{cat} • s • Pa			
k ₃	$9.0421 imes 10^8 exp(-112860/RT)$	kmol/kg _{cat} • s • Pa ^{0.5}			
K _{CO}	$8.3965 imes 10^{-11} \exp(118270/\text{RT})$	Pa^{-1}			
K _{CO2}	$1.7214 imes 10^{-10} \exp(81287/RT)$	Pa^{-1}			
$K_{\rm CO}/K_{\rm eq_1}$	$3.5408 \times 10^{12} \exp(19832/RT)$	Ра			
K_{CO_2}/K_{eq_2}	$2.5813 \times 10^{10} \exp(26788/RT)$	Pa			
K_{CO_2}/K_{eq_3}	$6.1221 \times 10^{-13} \exp(125226/RT)$	Pa^{-1}			
$K_{\rm H_2O}/K_{\rm H_2}^{0.5}$	$4.3676 \times 10^{-12} exp(115080/RT)$	$Pa^{-0.5}$			

implemented both in the Aspen Plus® and the OpenFOAM. The details of implementation in the Aspen Plus® can be found in Ref. [32] based on the work of Kiss et al. [23] and An et al. [1]. Here, the following commonly used simplifications are assumed: (1) only surface reaction are considered, (2) catalyst deactivation is insignificant, (3) side reactions are negligible and (4) diffusion inside the pellets is instantaneous. Moreover, the catalytically active surface area is not taken into account, but instead the geometric one is used.

Results and discussion

Validation

Plug flow reactor

Firstly, the LHHW kinetic model implementation is validated. The validation is done with a plug flow reactor against data available in the literature. Within the plug flow reactor model, the flow is assumed to be steady, frictionless, and onedimensional. Diffusion in the radial and axial directions is neglected. Basically, uniform distribution of pellets and constant velocity inside the reactor is assumed. Kiss et al. [23] and An et al. [1] studied the problem numerically and experimentally, respectively. The reactor is assumed to be isothermal and characterized by radius r = 6 mm and length L = 500 mm. The reactor is fed with a composition of inlet mole fractions $R = H_2$:CO₂ = 3. Simulations are performed for temperature and space velocity sweeps at fixed pressure p = 5 MPa. In the T sweep, the space velocity is kept constant at $SV = 6 \text{ m}^3/\text{kg}_{cat}$ h, while the temperature is varied in the range T = 483-543 K. In the SV sweep, the temperature is fixed at T = 523 K, while the space velocity is changed between $SV = 1-10 \text{ m}^3/\text{kg}_{cat}h$. CO_2 conversion (X_{CO2}) and CH₃OH yield (Y_{CH_{3OH}) are defined as}

$$X_{CO_2} = \frac{Y_{CO_{2,i}} - Y_{CO_{2,o}}}{Y_{CO_{2,i}}}, \ Y_{CH_3OH} = \frac{Y_{CH_3OH,o}MW_{CO_2}}{Y_{CO_2,i}MW_{CH_3OH}},$$
(17)

where subscripts i and o denote inlet and outlet of the reactor, respectively. Table 2 presents CO₂ conversion and CH₃OH yield for the space velocity and temperature sweeps. As can be seen in the table, there is a good agreement between the Aspen Plus® data of Kiss et al. [23] and the present results obtained by both OpenFOAM and Aspen Plus®, thus indicating the accurate implementation of the kinetic model. In general, the maximum absolute deviation is found to be approximately 5% for the present data, which is consistent with findings of An et al. [1] and Kiss et al. [23].

Flow over single cylinder

Next, the flow solver is validated for a non-reacting heat transfer problem. Accordingly, 2D simulations of laminar flow over a stationary isothermal cylinder are performed. The mesh is generated using **snappyHexMesh** utility, a built-in utility within the OpenFOAM. The base mesh consists of hexahedral cells, while near the cylinder surface a body conforming boundary layer mesh is used. The size of the computational domain is $45d \times 20d$, where *d* is the diameter of the cylinder. The cylinder is positioned 15*d* away from the inlet. Air flow (N₂:O₂:Ar = 78:21:1%, v/v) with uniform velocity (U) and constant temperature ($T_i = 293.15$ K) is imposed at the inlet. The outlet pressure is fixed at p = 101,325 Pa, while the cylinder surface temperature is kept constant at $T_w = 303.15$ K. Symmetry boundary conditions are applied on top and bottom boundaries.

First, a grid independence study is performed at $\text{Re} = \rho \text{UD}/\mu = 100$ on three different meshes: M0, M1, M2 with the grid size in the boundary layer 0.01d, 0.0068d, 0.0046d, respectively. A summary of the results (drag and lift coefficients, Strouhal number and average Nusselt number) are presented in Table 3. The drag coefficient is defined as $C_d = 2F_d/\rho U^2 d$ where F_d is the drag force, the lift coefficient as $C_l = 2F_l/\rho U^2 d$ where F_l is the lift force, the Strouhal number as St = fd/U, where f is vortex shedding frequency, the Nusselt number as $Nu = qd/k(T_w - T_i)$, where q is the heat flux on the surface of cylinder. Note that $\langle Nu \rangle$ denotes surface- and time-averaged Nusselt number. The M1 is chosen for the simulations.

Next, simulations are performed for different Reynolds numbers, i.e. Re = 10, 20, 40 and 100. Comparison of the local pressure coefficient $C_p = 2(p - p_i)/\rho U^2$ and Nu with the data from the literature are shown in Fig. 2. As can be seen, there is a good agreement with the data in the literature.

Flow over in-line and staggered tube banks

Finally, the method is validated on a more challenging nonreactive heat transfer problem. Two different configurations are considered, i.e. in-line and staggered tube banks. The inline and the staggered cases have 81 and 77 cylinders, respectively. The size of the computational domain for both cases is $18d \times 22d$, where *d* is the cylinder diameter. Moreover, the center-to-center distance between two cylinders in longitudinal and transverse directions is 2*d* for both cases. The mesh used for the in-line configuration has 697,536 cells while for the staggered case the mesh has 675,312 cells, with the grid size near the cylinder taken as 0.005*d* for both cases. The boundary conditions are the same as in the previous section.

Table 2 – Comparison of current simulations with data of An et al. [1] and Kiss et al. [23]: CO_2 conversion and CH_3OH yield. SV and T sweeps are done at fixed T = 523 K and SV = 6 m³/kg_{cat}h, respectively.

		Conversion/Yield	An et al. [1]	Kiss et al. [23]	Aspen Plus	OpenFOAM
SV [m³/kg _{cat} h]	1	X _{CO2}	0.262	0.2428	0.2417	0.2428
		Y _{CH₃OH}	0.193	0.1548	0.1532	0.1547
	2	X_{CO_2}	0.26	0.2428	0.2417	0.2428
		Y _{CH₃OH}	0.191	0.1548	0.1532	0.1547
	4	X _{CO2}	0.256	0.2421	0.2409	0.2424
		Y _{CH₃OH}	0.18	0.1544	0.1527	0.1545
	6	X _{CO2}	0.25	0.2398	0.2381	0.2406
		Y _{CH₃OH}	0.166	0.153	0.1511	0.1534
	8	X_{CO_2}	0.243	0.2362	0.2341	0.2376
		Y _{CH₃OH}	0.153	0.1509	0.1488	0.1517
	10	X _{CO2}	0.23	0.2321	0.2297	0.2340
		Y _{CH₃OH}	0.134	0.1485	0.1462	0.1496
T [K]	483	X _{CO2}	0.17	0.1244	0.1184	0.1252
		Y _{CH₃OH}	0.11	0.1152	0.1096	0.1159
	503	X _{CO2}	0.225	0.1957	0.1902	0.1984
		Y _{CH₃OH}	0.155	0.1597	0.1549	0.1618
	523	X _{CO2}	0.255	0.2398	0.2381	0.2406
		Y _{CH₃OH}	0.178	0.153	0.1511	0.1534
	543	X _{CO2}	0.25	0.2404	0.2396	0.2404
		Y_{CH_3OH}	0.14	0.1058	0.1045	0.1058

Table 3 – Grid convergence for non-reacting flow over cylinder at $Re = 100$.						
Mesh	Number of cells	C _d	Cl	St	$\langle Nu \rangle$	
M0	50,440	1.3557	±0.3224	1.6865	5.1452	
M1	102,132	1.3585	±0.3289	1.6865	5.1298	
M2	211,946	1.3610	±0.3356	1.7133	5.1130	

Temperature $((T_w - T_i)/T_w)$ distribution for the in-line and the staggered configurations are shown in Fig. 3. Comparison of the average Nusselt number with an empirical correlation [52] and numerical simulations [27,50] is presented in Table 4. The results are in good agreement especially with numerical solution of Wang et al. [50] and Lo and Su [27]. The difference between the empirical correlation and current results are 13% and 17% for the in-line and staggered configurations,

respectively. We note that the observed deviations are within the accuracy of the correlation which is approximately 25%. Finally, as expected the heat transfer is enhanced in staggered configuration.

Methanol production in 2D fixed-bed

The method is finally applied to study methanol production in a two-dimensional fixed-bed as depicted in Fig. 4. The computational domain is chosen with size of $42 \text{ mm} \times 12 \text{ mm}$, while the morphology of the bed is described by three different configurations, i.e. in-line, staggered and random. Loose and dense packings are considered in this work as shown in Fig. 4. Data used for different configurations are shown in Table 5. For dense packing, one more random case (polydispersed) is considered where the diameter of cylinders



Fig. 2 – Validation of non-reacting single cylinder case. Comparison of local pressure coefficient and Nusselt number for non-reacting flow over cylinder at Re = 10, 20, 40 and 100.



Fig. 3 – Validation of non-reacting in-line and staggered tube banks. Temperature fields for (left) the in-line and (right) the staggered arrangements at Re = 20.

Table 4 – Comparison of the $\langle Nu \rangle$ for flow past a tube in a bank at Re = 20.							
Configuration	Zhukauskas [52]	Wang et al. [50]	Lo and Su [27]	Present			
Staggered	3.45	4.08	4.07	4.03			
In-line	3.07			3.46			

vary in the range of 0.72 mm $\leq d \leq$ 1.68 mm. Note that the total area of the cylinders is same in both random cases.

Following previous simulations [23] and experimental data [1], the base line parameters are defined as T = 523 K, p = 5 MPa, $R = H_2$:CO₂ = 6 and SV = 6 m³/kg_{cat}h. Note that, Kiss et al. [23] performed only isothermal 1D cases whereas here both Aspen Plus® (1D) and OpenFOAM (1D/2D) are used. Also, both adiabatic and isothermal reactors are considered in the current work.

At the inlet, fully developed velocity profile is imposed, while no-slip conditions are assumed at the walls. Mean inlet velocity (U_i) is chosen so that its value is equivalent to a cylindrical tube (D = 12 mm) with same SV resulting in Reynolds number Re = $\rho U_i D/\mu$ = 1000. For pressure, zero-gradient boundary condition is imposed at the inlet and the walls and fixed pressure condition is used for the outlet. Fixed values of T_i and R for temperature and species are imposed at the inlet, respectively. For all variables, except pressure, zero-



Fig. 4 – Schematic illustration of a catalytic fixed-bed reactor with various packed configurations. The CO_2 and H_2 enter from the left while they exit from the right end of the domain. The loose and dense packings consist of 42 and 64 cylinders, respectively.

Table 5 – Dimensions of loose and dense packing configurations. Below, S stands for center-to-center distance between cylinders, which is same in the longitudinal and the transverse directions for the in-line and staggered cases, R represents randomly generated distance, N_{cvl} is total number of cylinders (*d*) and Φ is the solid volume fraction.

	Configuration	L _u [mm]	L _b [mm]	S [mm]	d [mm]	N _{cyl} [-]	Φ [%]	Mesh
Loose	In-line	12	12	1.8	1.2	42	33	437,577
	Staggered	12	12	1.8	1.2	42	33	437,778
	Random	12	12	R	1.2	42	33	460,162
Dense	In-line	12	11.1	1.4	1.2	64	54	503,998
	Staggered	12	11.1	1.4	1.2	64	54	507,071
	Random	12	14.4	R	1.2	64	42	501,472

gradient conditions are imposed at the outlet. Adiabatic and isothermal boundary conditions are applied for the temperature on the reactor walls. Note that ideal isothermal condition is assumed, i.e., the temperature inside the reactor is constant.

Velocity and methanol distribution

First, velocity and methanol distributions are studied for the in-line, the random and the staggered configurations assuming adiabatic boundary conditions. Distribution of nondimensional streamwise velocity U/Ui and methanol mass fraction fields are depicted in Fig. 5. The flow direction is from left to right. Detailed inspection reveals different zones in the fixed-bed region. In the downstream of cylinders, stagnant/ reverse flow zones are noticed. Moreover, it is clear that the flow has preference towards zones with less resistance creating channels in interstitial regions and in the vicinity of the walls. Flow accelerates in the channels reaching maximum up to a factor of $U/U_i = 5$ for random configuration. Note that these features are consistent with previous observations [11]. For the in-line configuration, the main flow shows preference in horizontal direction thus is similar to straight channel flow. As a result, the main flow does not reach some parts of the surface of cylinders. On the other hand, the staggered case is more similar to a periodical convergingdiverging channel flow. Flow physics results in larger effective surface area (compared to the in-line case) exposed to the flow. In the random case, the flow moves in more tortuous channels due to non-uniform local porosity.

Significant interplay between instantaneous velocity and methanol fields can be observed as shown Fig. 5. Aforementioned regions inside the bed significantly affect the reaction rates by influencing residence time distribution, i.e., the residence time is high in the zero/back flow regions, while it is short in the high speed channels. As a result, in all the configurations, high local methanol mass fraction is observed in the wake regions, while it is low in the channel regions. It is clear that the in-line configuration shows the poorest performance, due to relatively small interaction of the reactants with the catalytic surface. There are large regions of unreacted flow in the channels especially in the vicinity of the upper and the lower walls. Moreover, the regions with reacted flow in the wake regions have only minor contribution to the overall performance. As can be seen both staggered and random configurations have stronger interaction of catalyst with reactants.

Bed configuration effects

Next, the effect of bed configuration on the mean mass fraction and temperature is studied. Fig. 6 shows mean mass fraction profiles of reactant (CO₂), products (CH₃OH, CO) and temperature along the adiabatic and isothermal reactors. Note that, due to space consideration other components are not shown. Moreover, all the mass fraction profiles provided in the paper are averaged in time and space. As can be seen the solution for random and staggered cases are similar while the in-line case shows the poorest performance. The CO₂ starts reacting in the inlet of porous media and its value is decreasing along the reactor. On the other hand, mass fraction of products (CH₃OH and CO) is increasing along the reactor. Note that production of CO is unwanted and would be recycled in the experiment. It is clear that the isothermal reactor outperforms the adiabatic one. For adiabatic case, mass fraction profiles of CH₃OH and CO are comparable, while for isothermal one methanol is produced almost 3 times more than carbon monoxide. Temperature increases along the reactor due to exothermicity of the methanol synthesis reactions. Similarly, the temperature profile follows closely for random and staggered cases, while the values are smaller for the in-line case.



Fig. 5 – Loosely packed catalytic fixed-bed reactor. Instantaneous (left) non-dimensional streamwise velocity (U/U_i) and (right) CH₃OH mass fraction field distributions in an adiabatic reactor for (top) the in-line, (middle) the random and (bottom) the staggered configurations. (SV = 6 m³/kg_{cat}h, p = 5 MPa, $R = H_2$:CO₂ = 6, Re = 1000, T = 523 K).



Fig. 6 – Loosely packed catalytic fixed-bed reactor. Effects of the configuration on the mean mass fraction profiles of CH_3OH , CO, CO₂ and T for (top row) adiabatic and (middle row) isothermal reactors. For bottom row, red and black colors represent results for adiabatic and isothermal reactors, respectively. The axial position of the bed is between 0 and 0.012 m. (SV = 6 m³/kg_{cat}h, p = 5 MPa, $R = H_2$:CO₂ = 6, Re = 1000, T = 523 K). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 7 – Loosely packed catalytic fixed-bed reactor. Effects of the configuration on the CH₃OH (\Box) and CO (\bigcirc) yield for (left) adiabatic and (right) isothermal reactors. (SV = 6 m³/kg_{cat}h, p = 5 MPa, $R = H_2$:CO₂ = 6, Re = 1000, T = 523 K).

Next, CH_3OH and CO yield values are compared for the three configurations as shown in Fig. 7. As expected, 1D results of OpenFOAM and Aspen Plus® are in good agreement. However, 1D results show higher values than corresponding

2D data. By definition the 1D case is insensitive to configuration as local flow inhomogeneities are neglected, i.e., perfect mixing. On the other hand, the 2D case has regions with unreacted flow. As a result, the in-line configuration clearly



Fig. 8 – Loosely packed catalytic fixed-bed reactor. Effects of the inlet temperature on the mean profile of T for adiabatic and isothermal reactors. Red and black colors represent results for adiabatic and isothermal reactors, respectively. The axial position of the bed is between 0 and 0.012 m. (SV = 6 m³/kg_{cat}h, p = 5 MPa, $R = H_2$:CO₂ = 6, Re = 1000). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

shows the poorest performance. Note that there is a significant difference between adiabatic and isothermal reactors. For adiabatic reactor, CH₃OH and CO yields are comparable, whereas for isothermal reactor, CH₃OH yield is approximately three times larger than corresponding CO one. It proves that isothermal condition is important for best performance. Hereafter, the random configuration is used unless otherwise stated.

Temperature effects

Next, the effect of inlet temperature is studied for the random configuration. For this purpose, computations are conducted by varying the inlet temperature in the range of 473 K $\leq T_i \leq$ 573 K while the other parameters are same as in the base case. The temperature range is in agreement with

experimental study of An et al. [1]. Profiles of mean temperature along the adiabatic and the isothermal reactors are plotted in Fig. 8. Moreover, CH₃OH and CO vield values are presented in Fig. 9. For the adiabatic case, methanol production decreases with temperature, while it shows nonmonotonic trend for isothermal one. On the other hand, amount of CO increases with temperature for both reactors. It can be observed that within the range studied in here, the most favorable temperature is 473 K for the adiabatic case, while it is 523 K for the isothermal one. Carefully inspecting the temperature profiles could explain the deviation, cf. Fig. 8. Temperature increases in the adiabatic reactor at $T_i = 473$ K and 523 K while it decreases at 573 K. The overall trend could be explained by the fact that methanol synthesis is mainly exothermic reaction (increases temperature), i.e., increase in the temperature deteriorates the equilibrium (decreases methanol production). While the reverse water-gas shift reaction is endothermic (decreases temperature), thus having the opposite effect. It is worth noting that in the isothermal case the temperature inside the reactor is constant. On the other hand, for adiabatic case the temperature is a balance of exothermic and endothermic reactions. At $T_i=473$ K, the methanol synthesis dominates over the reverse water-gas shift reaction thus having high values of methanol and temperature. The temperature along the adiabatic reactor approaches optimal value for the isothermal case ($T_i = 523$ K) but reaches only 512.8 K. On the other hand, at $T_i = 573$ K the reverse water-gas shift reaction is more dominant resulting in higher CO production and decrease in the T along the adiabatic reactor. Moreover, it is observed that both isothermal and adiabatic reactors show similar performance at $T_i = 573$ K. This could be attributed to only a small change in temperature along the bed. Note that increasing temperature beyond $T_i =$ 573 K may lead to catalyst deactivation such as catalyst sintering or obstruction of active sites [42].

Pressure effects

Then we examine the effects of pressure by varying p = 2.5, 5 and 10 MPa for the random configuration while keeping the other parameters same as in the base case. The results are shown in Figs. 10 and 11. The CH₃OH yield is favored by increase of pressure for both reactors which could be attributed



Fig. 9 – Loosely packed catalytic fixed-bed reactor. Effects of the inlet temperature on the CH₃OH (\Box) and CO (\bigcirc) yield for (left) adiabatic and (right) isothermal reactors. (SV = 6 m³/kg_{cat}h, p = 5 MPa, R = H₂:CO₂ = 6, Re = 1000).



Fig. 10 – Loosely packed catalytic fixed-bed reactor. Effects of the pressure on the mean profile of T for adiabatic and isothermal reactors. Red and black colors represent results for adiabatic and isothermal reactors, respectively. The axial position of the bed is between 0 and 0.012 m. ($SV = 6 \text{ m}^3/\text{kg}_{cat}$ h, $R = H_2$:CO₂ = 6, Re = 1000, T = 523 K). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

to rise in reactants concentration. At p = 2.5 MPa, solution is similar for both adiabatic and isothermal conditions due to the almost constant temperature inside the reactor, cf. Fig. 10. At higher pressures, the differences in CH₃OH and CO yield between adiabatic and isothermal conditions increases due to higher bed temperature in the former case [5]. While in isothermal conditions the bed temperature stays at constant $T_i = 523$ K regardless the change in pressure, for the adiabatic case it increases with pressure, cf. Fig. 10. As it has been discussed in the *Temperature effects* subsection higher temperatures in adiabatic conditions lead to a decrease in CH₃OH yield, cf. Fig. 9. Note that, the CO formation is insensitive to pressure variation in the adiabatic case, while it diminishes in the isothermal one. This could be attributed to enhanced CO conversion to methanol at constant temperature. Even though high pressure enhances methanol production, it poses a safety issue for the reactor.

Space velocity effects

Here, the effect of the space velocity on the reactor efficiency is studied. The space velocity is varied between 6 and 600 m³/ kg_{cat}h while keeping the other parameters as in the base case. The results are plotted in Fig. 12. Increase of SV leads to decrease in the yield of both CH_3OH and CO. Increase in SV could be attained by either increasing the feed speed or decreasing the mass of catalyst. Both methods were tested for the 1D case and identical solutions were obtained. In case of increased feed, the residence time decreases which leads to decreasing mass of catalyst results in diminished methanol production. Although not shown here, it is observed that the mean temperature decreased with SV for the adiabatic case, which could be attributed to the reduction in the methanol yield.

Reactants ratio effects

Another important parameter the inlet reactants ratio R is studied at R = 3, 6, 9 and 12. The results are plotted in Fig. 13. Note that stoichiometric number is optimal at R = 3. Thus, increasing R leads to excess H_2 in the feed and increase of CO and CH₃OH yield. Moreover, it is found that the temperature increases with the reactants ratio. As expected, the isothermal case outperforms by producing more methanol and less CO. Overall, the current results for the isothermal case are in agreement with data in literature [1,23,35].

Packing density effects

Finally, simulations are performed to investigate the effects of packing density. For this purpose, dense packing with in-line ($\Phi = 54\%$), staggered ($\Phi = 54\%$) and random ($\Phi = 42\%$) configurations are considered. The details of the configurations are mentioned above and can be seen in Table 5.

Instantaneous contours of methanol mass fraction for ordered and random packings in adiabatic regime are shown in Fig. 14. As mentioned earlier, in addition to regular random case one more polydispersed case is considered with varying size of diameters. Moreover, CH_3OH and CO yield values for



Fig. 11 – Loosely packed catalytic fixed-bed reactor. Effects of the pressure on the CH₃OH (\Box) and CO (\bigcirc) yield for (left) adiabatic and (right) isothermal reactors. (SV = 6 m³/kg_{cat}h, R = H₂:CO₂ = 6, Re = 1000, T = 523 K).



Fig. 12 – Loosely packed catalytic fixed-bed reactor. Effects of the space velocity on the CH₃OH (\Box) and CO (\bigcirc) yield for (left) adiabatic and (right) isothermal reactors. (p = 5 MPa, $R = H_2$:CO₂ = 6, Re = 1000, T = 523 K).



Fig. 13 – Loosely packed catalytic fixed-bed reactor. Effects of the reactants ratio $R = H_2$:CO₂ on the CH₃OH (\Box) and CO (\bigcirc) yield for (left) adiabatic and (right) isothermal reactors. (SV = 6 m³/kg_{cat}h, p = 5 MPa, Re = 1000, T = 523 K).

both adiabatic and isothermal cases are plotted in Fig. 15. Overall performance is similar to the loose packing cases observed in Figs. 5 and 7, i.e., the in-line case shows lowest yield values. It is especially evident in Fig. 14, where unreacted flow is observed near the top and bottom walls for the in-line case. Moreover, the yield values of densely packed systems are higher than corresponding loose packings, reaching values of the 1D approach except the in-line case. Indeed, densely packed system leads to more uniform distribution of the species in the bed, thus approaching 1D case. Freund et al. [12] mentioned that the critical aspect ratio of tube-to-particle diameter, below which the plug flow model becomes inadequate, is around 10. In the current work, the average aspect ratio is 10 for all the cases, thus approaching the plug flow model results. Moreover, Mousazadeh et al. [31] validated their 2D simulations with same aspect ratio against plug flow



Fig. 14 – Densely packed catalytic fixed-bed reactor. Instantenous methanol mass fraction fields for random (uniform and polydispersed), in-line and staggered configurations in the adiabatic reactor. The flow goes from left to right. (SV = 6 m³/ kg_{cat}h, p = 5 MPa, $R = H_2$:CO₂ = 6, Re = 1000, T = 523 K).



Fig. 15 – Densely packed catalytic fixed-bed reactor. Effects of the configuration on the CH₃OH (\Box) and CO (\bigcirc) yield for (left) adiabatic and (right) isothermal reactors. Poly stands for the polydispersed case. (SV = 6 m³/kg_{cat}h, *p* = 5 MPa, R = H₂:CO₂ = 6, Re = 1000, T = 523 K).

model. Overall, it is observed that the yield values increases with packing density approaching its upper limit set by 1D approach.

Conclusions

The LHHW kinetic model was coupled with OpenFOAM solver and Aspen Plus® for CO₂ and hydrogen-based methanol synthesis in a fixed-bed reactor. The implementation of the kinetic model was validated for the plug flow reactor and the results were found to be in a good agreement with experimental [1] and numerical [23] data. Next, the flow solver was validated against heat transfer over single and tube bank problems. Finally, the method was applied to a more challenging problem for two-dimensional fixed-bed reactor with cylindrical pellets. The effects of packing density, bed configuration, temperature, pressure, reactant ratio, and space velocity on adiabatic and isothermal fixed-bed reactors were examined. The overall findings can be summarised as:

- The OpenFOAM (1D/2D) and the Aspen Plus® (1D) results were compared. In overall, results obtained from both 1D and 2D simulations showed similar trend for the effects of temperature, pressure, reactant ratio, and space velocity. However, due to perfect mixing assumption, the 1D model was insensitive to the variation of bed configuration and packing density.
- 2. The difference between the 1D and the 2D cases were pronounced at loose packing conditions. The methanol yield values obtained from 2D simulations were generally smaller than the ones in the 1D case. However, the yield values converged to the corresponding 1D values with packing density. It was observed that the maximum methanol yield values were limited by quantities obtained from 1D simulations.
- 3. The in-line, the staggered, and the random configurations were compared for 2D case. It was found that the in-line

arrangement led to the poorest performance due to the limited interplay between reactants and the catalytic surface. Moreover, the staggered and the random configurations showed similar performance.

- 4. Both isothermal and the adiabatic reactors were considered. The isothermal reactor generally outperformed the corresponding adiabatic one due to exothermicity of the methanol synthesis reaction resulting in higher CH₃OH and lower CO yield.
- 5. Overall, it was observed that the methanol yield increased with the pressure, the catalyst loading and the reactant ratio. The yield decreased with temperature for the adiabatic case, while it showed non-monotonic trend for the isothermal case.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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