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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Catalytic conversion modeling of methanol in dehydration reactor using Voronoi 3D pore network model

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Received 4 May 2021; accepted 20 June 2021 Available online 28 June 2021

KEYWORDS

Dimethyl Ether; Methanol; Effectiveness Factor; Fixed Bed Reactor; Pore Network; Voronoi model **Abstract** Dimethyl ether as a clean fuel has been attracted in the recent decade. It can be produced in the catalytic reaction of methanol dehydration. Modeling and simulation of the fixed-bed reactor for this process is desired to predict the reactor performance. A Voronoi 3-dimensional pore network model for the reactor is used to study the effect of pore space on the reactor performance. Considering the morphological structure of the pore space is one of the advantages of this model. In this study, pore network modeling was used to consider mass and heat transfer both in the reactor and catalyst scales. The effectiveness factor results for the catalyst scale are used for the reactor simulations and the effect of methanol temperature and concentration on reactor performance is studied. The results indicated that the reduction of flow rate increases reactants residence time in the reactor and consequently increases the amount of conversion. The inlet methanol concentration had a significant influence on the conversion and the methanol concentration in the middle of the reactor increased from 22 to 34 mol/m³ when its purity decreased from 99 to 97%.

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Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

1. Introduction

Dimethyl ether (DME) has been recognized as a green source of energy for various industrial applications. DME does not produce any sulfur oxide in burning, thus is regarded as safe fuel for the environment (Bakhtyari and Rahimpour, 2018; Barbarossa et al., 2019). Given that DME possesses several

https://doi.org/10.1016/j.arabjc.2021.103284

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| 7 | Concentration | M | Methanol |
|-------|---|----------------|---------------------------------|
| 0 | total concentration | W | water |
| | specific heat of fluid | α | thermal diffusivity |
| | reactor diameter | ΔH | heat of reaction |
| 1 | dispersion coefficient | ΔH | dimensionless heat of reaction |
| ,k | dispersion coefficient | Ebed | bed porosity |
| 1 | molecular diffusion coefficient | $\eta(C_M, T)$ | T) effectiveness factor |
| | particle diameter | ho | gas phase density |
| | thermodynamic equilibrium constant | $ ho_B$ | catalyst bed density |
| | reaction rate constant | Pe_k | Peclet number for k component |
| М | adsorption constant of methanol | Pe_h | heat Peclet number |
| , | adsorption constant of water | Pr | Prandtle number |
| | axial thermal conductivity | Т | temperature |
| | solids thermal conductivity | T_0 | inlet temperature |
| | fluid thermal conductivity | U | superficial velocity |
| | thermal conductivity of a quiescent bed | x | reactor longitudinal coordinate |
| d | tortuosity coefficient | L | catalyst bed height |
| | | υ | kinematic viscosity |
| ıbscr | <i>ipts</i> | Φ_k^2 | Thiele modulus |
| | DME | | |
| | Methanol, DME | | |

advantages, it can be utilized as a domestic fuel, in cars, and as fuel in power plants (Semelsberger et al., 2006). The common commercial method for mass production of DME is through dehydration of methanol over-acidic catalysis such as alumina, zeolites (Rezakazemi et al., 2017; Rezakazemi et al., 2012a, b; Riasat Harami et al., 2019), etc. (Hassanpour et al., 2010; Lu et al., 2004). The reaction kinetics has been studied at different conditions.

A kinetic model for the dehydration of methanol to DME on the performance of γ – Alumina is presented which considers a partial inhibition of active site activity. The selection of the best model is based on the Fisher test. The model that best fits the experimental data is the model that considers the exponential effect of water, methanol and DME (Sierra et al., 2013).

Modeling is one of the low-cost methods for predicting chemical processes (Ahmad et al., 2020; Babanezhad et al., 2021c; Cao et al., 2021a; Cao et al., 2021b; Fasihi et al., 2012; Hashemi et al., 2012; Nazem et al., 2018; Pelalak et al., 2021a; Pelalak et al., 2021b; Pelalak et al., 2021c) for this reason some of the researchers have attempted modeling and simulation of a catalytic packed bed of methanol dehydration reactor (Ahmadlou and Rezakazemi, 2018; Ali et al., 2020; Pishnamazi et al., 2020b). Naschi et al. (2006) simulated DME production in a fixed bed reactor and indicated that the difference between 1D and 2D modeling is not significant.

DME product has been used as a valuable input feed for various processes. In general, the conversion process of DME to olefins is an attractive option for the conversion of methanol to olefins due to the easier production of DME, higher reactivity, and moderate deactivation by HZSM-5 catalysts (Cordero-Lanzac et al., 2020). Also, the effect of different process variables affecting the recovery and reduction of used HZSM-5 zeolite catalyst during the conversion of DME to olefin in a fixed bed reactor has been studied (Cordero-Lanzac et al., 2018).

Mohammad et al. (2010) modeled and optimized the methanol to DME in an isothermal fixed-bed reactor. They showed that the higher DME production rate and methanol conversion in the optimized reactor. Fazlollahnejad et al. (Fazlollahnejad et al., 2009) and Bercic and Levec (1993) studied an adiabatic fixed-bed reactor for methanol dehydration to dimethyl ether, experimentally. For finding the conversion and temperature profile, they utilized a laboratory-scale reactor. They also considered a plug flow condition in reactor modeling to find concentration and temperature profile in the reactor length (Bercic and Levec, 1993).

In all of the previous studies, continuum modeling was used for the simulation of the reactor (Babanezhad et al., 2021a; Babanezhad et al., 2020a; Babanezhad et al., 2019; Babanezhad et al., 2020d; Babanezhad et al., 2020e; Cao et al., 2020; Nguyen et al., 2020b; Rezakazemi and Shirazian, 2018, 2019; Tian et al., 2020). But in this study, a pore network modeling is used to predict the reactor performance for the first time. Voronoi pore network model is employed for the simulation of catalytic methanol dehydration reactor.

Here, a method is proposed that models the random structure of a porous bed via the Voronoi pore network design. In this Voronoi pore network design, three structures related to porous geometries with cross fractures (granular), interconnected tubes (tubular), and fibers (filamentary) are modeled. Fluid flow is solved by this model and by a Voronoi pore network code. The porosity–permeability relationship for catalyst bed geometry is generally consistent with simple cubic, bodycentered and face-centered cubic models (Xiao and Yin, 2016).

In order to determine a porous bed, the Voronoi-Delaunay network method was used to divide the pore space between the catalyst grains. The modeled catalytic bed consists of a series of randomly spaced cylinders.

The geometry of the pore spaces in the reactor is found by considering the spatial position of the particles in the reactor. We used this information to construct a random packing model and to estimate the solid and void spaces in the packing, thus any assumption is avoided. In 1970, Finney (Finney and Bernal, 1970) measured the location of the center coordinate of particles in a random packing which has the same spheres. Mason (1971) employed Finney's results for the simulating of porous media, and later Mellor (1989) proposed a technique for extracting a network model of the pore space in the Finney packing. Dadvar and Sahimi modeled the deactivation of immobilized glucose isomerase in the packed-bed reactors by using Finny's data for constructing a 3D network of pores with distributed sizes and connectivity (Dadvar and Sahimi, 2003).

Here we are going to study the effect of the packed bed morphology on transport phenomena in the reactor and to find reactor performance. We obtained the effectiveness factor of pore network modeling in particle scale. In fact, in this study pore network modeling is used in two different scales, particle level, and reactor scale. In the particle scale pore network modeling is used to find the effectiveness factor for the catalysts at different conditions of concentration and temperature. These results are used to find temperature and concentration distribution along the reactor by considering the effect of pore spaces in transport mechanisms.

In previous studies like (Mohammad et al., 2010), the effect of convention and reaction terms were just regarded in reactor modeling without any attention to the pore spaces and their effect on reactor performance. Furthermore, in this modeling in mass and heat transfer equations the effect of dispersion term is also included.

In this paper first, the reactor pore network is explained. Then mass and heat transfer equations in the reactor are presented and the mathematical method for solving the equations is explained. Then the simulation results are presented. The results are summarized in the last session.

2. Reactor network modeling

A reactor of the packed bed is a kind of porous medium and any porous medium can be mapped to a pore network model. The most appropriate method for modeling a flow in a packed bed is to study the flow in its passageways and to present a model at the pore scale. To determine the structural model of the packed bed, it is necessary to know the x, y, and z coordinates for the spherical particle center and particle diameter. Knowing how the spheres are placed in the packed bed enables us to determine the size and how the empty spaces relate to each other, and in fact, to determine the network pattern of the flow inside the packed bed. For this purpose, it is necessary to first determine the packed bed structural units using Finney experimental information.

A Voronoi pore network is used to represent the pore spaces in the reactor. Finney's random packed bed data (Finney and Bernal, 1970) was used for constructing Voronoi pore network. It was placed 25,000 same spherical particles in an ellipsoidal-shaped container and measured the center spatial coordinates of about 7000 of them. This data is also used for modeling of immobilized glucose isomerase packed bed reactor by Dadvar and Sahimi (2003) where the details of Voronoi network construction are explained and therefore it is not repeated in this paper.

Without any assumption and approximation, by applying the Finney data (Finney and Bernal, 1970), we construct a random packing model of microporous particles to specify the solid and void space in the packing.

Since most reactors are cylindrical, in the present modeling we obtained the volume of the largest rectangular cube enclosed in an ellipsoid form as to Finney information as follows. The reason for considering the cubic form is to be able to have more particles in the reactor bed. The Lagrange multiplier method is used to determine the dimensions of the largest rectangular cube surrounded by the above elliptical volume. According to this method, the maximum or minimum values of the function V, V = f (X, Y, Z) can be obtained by solving the system of the following equations (considering the limit g (X, Y, Z) = 0):

$$\frac{\partial V}{\partial \mathbf{X}} + \gamma \ \frac{\partial g}{\partial X} = 0 \ \frac{\partial V}{\partial \mathbf{Y}} + \gamma \ \frac{\partial g}{\partial Y} = 0 \ \frac{\partial V}{\partial \mathbf{Z}} + \gamma \ \frac{\partial g}{\partial Z}$$
$$= 0 \ \mathbf{G}(\mathbf{X}, \mathbf{Y}, \mathbf{Z}) = 0$$
(1)

Using the Lagrange multiplier method, we calculated that the reactor contains around 1600 particles of Finney's random packing considering the particle sizes are 3 mm, the reactor size in different directions is:

X = 3.487 cm Y = 3.255 cm Z = 3.519 cm

To investigate the model validation, we are going to compare the results with the experimental data of Bercic and Levec (1993) which was obtained in a bed height of 700 mm. Since the height of the cubic packed bed is about Z = 3.519 cm, we consider this height to be repeated 16 times so that the reactor length could be similar to the Bercis and Levec's reactor (Bercic and Levec, 1993). Fig. 1 presents the schematic of the segments in the reactor.

After determining the position of the particles in the reactor, it is necessary to identify the closest quaternary groups of particles relative to each other that form a pyramid to determine the position of the vertices of the Voronoi cells inside them. For this purpose, the following steps have been performed for each particle:

(i). A particle is selected, which we call the central particle. (ii). The distance of the central particle from the other particles is determined using Eq. (2).

$$l_{i} = \left((x_{o} - x_{i})^{2} + (y_{o} - y_{i})^{2} + (z_{o} - z_{i})^{2} \right)^{1/2}$$
(2)

Where l_i is the distance between the center particle and the particle i, and x, y, and z show their coordinates, and the subtitles "o" and "i" represent the desired quantities for the center particle and the particle i, respectively.

(iii). The around particles of the central particle are numbered in the order of their distance from the "o" central particle.

(iv). The center particle and the ternary groups around it are selected in order of distance. It should be noted that the above ternary groups are selected as long as they are not on the same plate with the center particle and can form a pyramid, and these groups form the Delaunay network structural units with the center particle.

(v). If any point is selected in section (iii), first the vertical perpendicular plates of the sides are drawn and then the



Fig. 1 The scheme of reactors connection and Voronoi network.

intersection points of these plates are determined (point "v"). This point may or may not be one of the vertices of the Voronoi cell that forms around point "o". The distance from point "v" to points "o", and the other points in section (iii) are the same.

(vi). Point "v" can be known as a vertex of a Voronoi cell corresponding to point "o" if its distance is shorter than "o" or equal to its distance to all other random points. Steps (iv) to (vi) are repeated for the other ternary groups around "o". In this way, the coordinates of the vertices of the Voronoi cell that form around the point "o" are determined and calculated. Each of the Voronoi vertex is formed between which of the quaternary group of particles.

Steps (i) to (vi) are performed for all particles, In this way, the coordinates of the vertices of Voronoi cells that are located in the whole network are determined. It should be noted that in the construction of the Voronoi network, boundary conditions in the directions \times , y, z are considered periodically.

By performing the above steps, Voronoi cells are formed separately around each particle. Then we need to determine how these cells are arranged in the Voronoi network.

Given that in the Voronoi network, the vertices are the same nodes, thus the number of nodes that are connected in the whole network is determined.

After identifying the nodes that form a passageway, it is necessary to determine the exact characteristics of each path, i.e. its length, effective surface, and hydraulic radius.

The calculation of the path length is simple and is determined using Eq. (2) and by determining the two nodes on either side of each path. To calculate the effective crosssectional area, it is necessary to know that the effective cross-sectional area on the faces of the Delaunay pyramids is where the particles form closer together. Therefore, by considering the coordinates of the particles and their size, the crosssectional area can be calculated. For example, according to Fig. 2, by determining the coordinates of points A, B, and C, the length of the sides, i.e. a, b and c can be calculated and the perimeter and area of the triangle ABC can be obtained from the following Eqs (3) and (4):

$$P = \frac{1}{2}(a+b+c) \tag{3}$$

$$S' = \sqrt{P(P-a)(P-b)(P-c)}$$
 (4)

Where P is half the perimeter and S' is the area of the triangle.

The total area of the parts of the three circles inside the triangle is calculated as follows:

$$S^{\prime\prime} = \frac{\pi}{2}R^2 \tag{5}$$

where R is the radius of the spherical particles, and the cross-section of the passage path S is obtained from the following Eq. (6):

$$S = S' - S' \tag{6}$$

If the triangle is formed in the form of Fig. 2A (this condition occurs when the entered height on side "a" is less than the size of the radius of the particle), then the cross-sectional area of the sector part which is outside the triangle, i.e., S'' is added to the value of S' and S is obtained from the following Eq. (7):

$$S = S' - S'' + S'''$$
(7)

The cross section of the sector is obtained from the following Eq. (8):

$$S^{'''} = \frac{1}{2}R^2(\theta - \sin\theta) \tag{8}$$

The size of angle A or the calculation of drawn height from angle A on the BC side be determined.



Fig. 2 Schematic of the cross-section of the feed passage.

$$h = \frac{2S'}{a} \tag{9}$$

$$\cos\frac{\theta}{2} = \frac{h}{R} \tag{10}$$

$$\theta = 2\cos^{-1}\left(\frac{\theta}{2}\right) \tag{11}$$

where h is the size of the height and θ is the radian.

The Voronoi network cells are polyhedral that include one particle of the random packing so that each point within a polyhedron is nearer to that particle center than to the center of any other particle (Dadvar and Sahimi, 2003). In Voronoi network, the cell vertices, and the polyhedron sides represent the network nodes and bonds, respectively.

Based on the Finney's packing we found that the average length of the bonds is close to 86% of the particles diameters which is matched to Bryant et Al. (Bryant et al., 1993a). By using the spatial coordination of the vertices, the length of each bond can be estimated. Distribution of the bonds' lengths is presented in Fig. 3.



Fig. 3 Effective lengths distribution of the pores in the packed bed.

The effective radius of any pore is computed as hydraulic radius R_h :

$$R_{h} = \frac{P_{P}}{A_{P}} = 2 \frac{Wetted Perimeter}{Flow Cross Section}$$
(12)

The wetter perimeter is denoted by P', in Fig's. 2A and 2B is calculated from Eq. (13) and 14, respectively.

$$P' = 2P - 6R + \pi R - R\theta \tag{13}$$

$$P' = 2P - 6R + \pi R \tag{14}$$

Studies have shown that the cross sections in the catalytic bed of the present reactor are mostly in the form of Fig. 2B.

Fig. 4 indicates the distribution of the hydraulic radius, and a good agreement is observed between the results and the data of Bryant et al. (Bryant et al., 1993b).

The above calculations are performed separately for each path. In this way, we have determined the complete specifications of the passageways only using the coordinates of the particles in the bed, so that no assumptions have been made to simplify the shape of the network. During these calculations,



Fig. 4 Effective diameters distribution of the pores in the packed bed.

paths and nodes are numbered to determine which paths are interconnected, and which node is each path between, and which nodes are adjacent to each other.

Fig. 3 indicates that the lengths of flow path computed above are uniformly distributed between 0 and sphere radius. Indeed, 0 refers to the adjacent cells with nearly coincident geometric centers. It is also observed that several path lengths exceed the sphere radius. Here, the assumption of a regular lattice is not correct, because the structure of network is disordered. Also, the uniformity of the network coordination proposes that it is correct to postulate a lattice of uniform bond coordination in an unconsolidated random packing of spherical shape. However, the simplicial cell tessellation proposes that the natural value of the bond coordination in such a packing is four, which is less than the values usually assumed (Bryant et al., 1993a).

As shown in Figs. 3 and 4, the results are based on a sample of the structure of the γ – Alumina catalyst. Since the actual structure of the catalyst is not completely regular in the lattice, the effect of changes in the catalyst structure and connection of the pore network to each other, the effect of the catalyst particle size distribution and their random arrangement and the random flow path based on γ – Alumina catalyst have been determined (Based Figs. 3 and 4). Examined in Figs. 3 and 4. This model of pore network can also be used for distinct catalysts with porous structures of γ – Alumina. While continuous models are not able to determine the effect of catalyst bed structure on the conversion rate. This method can be used to make catalysts with a suitable structure to achieve the highest efficiency.

3. Models of mass and heat transport in the reactor

In this work, conversion of methanol to DME over γ – *Alumina* catalyst was studied. The reactor type is packed bed which is filled with porous alumina particles. The reaction is exothermic, and the reaction kinetics of the catalytic dehydration of methanol to DME may be expressed as:

$$2CH_3OH \leftrightarrow C_2H_6O + H_2O \tag{15}$$

As shown in Table 1, the catalyst characteristics and reactor conditions are shown in this research work.

Bercic and Levec stated that the reaction rate can be considered as follows (Bercic and Levec, 1993):

| Table 1 The catalyst specifications and reactor control | nditions. |
|---|-----------|
|---|-----------|

| Parameter | Value |
|--|-----------------------------------|
| Catalyst Spherical Diameter (mm) | 3 |
| Catalyst Bed Height (mm) | 700 |
| Catalyst Bulk Density (kg/m ³) | 882 |
| Catalyst Porosity | 0.4 |
| Input Temperature (K) | 551 and 561 |
| Feed Volumetric Flow (L/hr) | 6.74 and 4.34 |
| Pressure (bar) | 2.1 |
| Reactor Dimension in Voronoi Model | $3.487 \times 3.255 \times 3.519$ |
| (cm) | |
| Catalyst Numbers (grain) | 1588 |
| Catalyst | $\gamma - Alumina$ |

$$-r = K_s \frac{K_M^2 \left(C_M^2 - \frac{C_D C_M}{K}\right)}{\left(1 + 2\sqrt{K_M C_M} + K_W C_W\right)^4}$$
(16)

The kinetic constants and thermodynamics equilibrium constant are presented in Table 2.

For modeling of the packed-bed reactor, mass and heat transports due to convection, diffusion and reaction need to be taken into account. The contribution of convention term is considerable due to the flow field in the pore space of bed. Initially, the flow field inside the bed was determined. Then, the reactants and products concentration distributions inside the reactor at different locations were calculated. Laminar flow was assumed in order to calculate the flow fields as well as pressure in the Voronoi network.

The volumetric flow rate Q_{ij} in each bond ij of the network with an effective radius R_{ij} and length L_{ij} can be written as (Neeteson and Rival, 2015):

$$Q_{ij} = \left(\frac{\pi R_{ij}^4 \Delta P_{ij}}{8\mu L_{ij}}\right) \left(\frac{P_i + P_j}{2} \times \frac{1}{P_i}\right)$$
(17)

Which is Poiseuille's law with an extra correction factor $\left(\frac{P_i+P_j}{2} \times \frac{1}{P_i}\right)$ expressing the average pressure relative to the outlet pore pressure. This term is almost equal to one because the pressure difference of a pore is negligible. Therefore, Eq. (17) is simplified to:

$$Q_{ij} = \left(\frac{\pi R_{ij}^4 \Delta P_{ij}}{8\mu L_{ij}}\right) \tag{18}$$

At the steady state condition, we have:

$$\sum_{\{ij\}} \mathcal{Q}_{ij} = 0 \tag{19}$$

Eq. (19) is written for each node of the Voronoi network giving several linear equations. The concentration as well as temperature distribution in the bed can be obtained by solving:

$$\frac{d^2 C_k}{dx^2} - \frac{u_{ij}}{D_{k,a}} \frac{dC_k}{dx} - \frac{2\nu\eta(C_M, T)}{D_{a,k} R_{ij}\rho_S}(-r) = 0$$
(20)

Where subscripts k refer to methanol, DME and u_{ij} is the pore-scale fluid velocity calculated using the flow field, $u_{ij} = R_{ij}^2 \Delta P_{ij} / (8\mu L_{ij})$ and $\eta(C_m, T)$ is the effectiveness factor of the catalyst.

Since the concentration and temperature varies along the reactor length, we obtained the effectiveness factor in various temperatures and concentration. The effectiveness factor in various temperatures and concentration is summarized in Table 3.

| Table 2 The kinetic constants. | | | | |
|---|--|--------------|--|--|
| Kinetics parameters | Value | Unit | | |
| K _s (Bercic and Levec, 1993) | $5.35 \times 10^{13} \exp(\frac{-17280}{T})$ | [kmol/kg.hr] | | |
| K _M (Bercic and Levec, 1993) | $5.39 \times 10^{-4} \exp(\frac{8487}{T})$ | $[m^3/kmol]$ | | |
| K _W (Bercic and Levec, 1993) | $8.47 \times 10^{-2} \exp(\frac{5070}{T})$ | $[m^3/kmol]$ | | |
| K (Schiffino and Merrill, 1993) | $\exp(-1.7 + \frac{3220}{T})$ | | | |

 Table 3
 The effectiveness factor at various temperatures and concentration.

| | | | | | <i></i> |
|----------------|-------|-------|-------|--------|---------|
| $T(\circ K)$ | 550 | 575 | 600 | 625 | 650 |
| C _M | | | | | |
| 1 | 0.600 | 0.300 | 0.046 | 0.0193 | 0.0035 |
| 0.9 | 0.554 | 0.214 | 0.042 | 0.0155 | 0.0028 |
| 0.8 | 0.494 | 0.121 | 0.039 | 0.014 | 0.0017 |
| 0.6 | 0.490 | 0.118 | 0.038 | 0.013 | 0.0014 |
| 0.4 | 0.486 | 0.114 | 0.032 | 0.012 | 0.001 |
| 0.2 | 0.48 | 0.105 | 0.016 | 0.0015 | 0.0003 |
| 0.1 | 0.475 | 0.03 | 0.003 | 0.001 | 0.0001 |

Table 2 shows the effect of temperature changes on the effectiveness factor for different feed samples at different concentrations and temperatures. Catalyst effectiveness factor decreases with increasing feed temperature. These results show that the catalyst effectiveness factor is strongly dependent on temperature. The reason for these drastic changes is the dependence of velocity constant, thermodynamic equilibrium constant and methanol and water absorption coefficients on temperature, which affects the reaction kinetics. These constants are shown in Table 1. Also increasing the concentration of the input feed also increases the effectiveness factor of the catalyst. According to the reaction kinetics, increasing the water concentration reduces the reaction rate, so the trend of effectiveness factor changes in Table 2 is logical.

Water concentration in each segment can be obtains from the total balance in each pore.

$$C_W = C_0 - (C_M + C_E)$$
(21)

The following equation represents the temperature distribution in each bond:

$$\frac{d^2T}{dx^2} - \frac{u\rho_b \cdot C_p}{K_T} \cdot \frac{dT}{dx} - \frac{2\Delta H \cdot \eta \cdot (C_M, T)}{K_T \cdot R_{ij} \cdot \rho_S} (-r) = 0$$
(22)

The dispersion coefficient $D_{k,a}$ in each pore ij, is obtained by Taylor–Aris equation (Aris, 1956; Taylor, 1953):

$$D_{k,a} = D_{AB} + \frac{R_{ij}^2 \cdot u_{ij}^2}{48 \cdot D_{AB}}$$
(23)

where molecular D_{AB} is the diffusivity in pore ij, originate from the Chapman-Enskog kinetic theory and attempts to allow attractive and repulsive forces between the molecules (Babanezhad et al., 2021b; Babanezhad et al., 2020b; Babanezhad et al., 2020c; Nguyen et al., 2020a; Nguyen et al., 2020c; Pishnamazi et al., 2020a).

$$D_{AB} = \frac{0.00185.T^{1.5}}{P(\sigma_{AB})^2 \cdot \Omega_{D,AB}} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$
(24)

Where the collision integral $\Omega_{D,AB}$ is determined by the temperature and by $T^* = k_B T / \varepsilon_{AB} \cdot \varepsilon_{AB}$ and σ_{AB} are estimated by the following combining rule (Poling et al., 2001).

$$\frac{\varepsilon_{AB}}{k_B} = \sqrt{\frac{\varepsilon_A}{k_B} \frac{\varepsilon_B}{k_B}}$$
(25)

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \tag{26}$$

$$\Omega_{D,AB} = \frac{1.06036}{(T^*)^{0.1561}} + \frac{0.193}{exp(0.47535.T^*)} + \frac{1.03587}{exp(1.53.T^*)} + \frac{1.7648}{exp(3.89.T^*)}$$
(27)

Eq. (20) gives the Methanol and DME concentration in each bond of the reactor and Eq. (22) gives the temperature distribution in each bond of the packed-bed reactor. We derived an equation like Eq. (19) for each node of the Voronoi network to compute concentration and temperature distributions throughout the reactor.

But, S_{ij} denotes the effective cross-sectional area of the bonds ij. Moreover, J_{ij} denotes the flux of methanol and DME in the bonds. Also, h_{ij} is heat flux in the bonds including diffusion and convection and they are as follows:

$$\sum_{(ij,k)} J_{ij,k} S_{ij} = 0 \tag{28}$$

$$J_{ij,k} = -(D_{k,a})_{ij} \frac{dC_{i,k}}{dz} + C_{i,k} u_{ij}$$
⁽²⁹⁾

$$\sum_{i=1}^{n} h_{ij,k} S_{ij} = 0 \tag{30}$$

$$h_{ij} = -k_T \frac{dT_{ij}}{dx} + u\rho_b c_p T_i \tag{31}$$

Given that analytical solution for the Eqs. (20) and (22) is not available; we are not able to derive an analytical expression for J_{ij} and h_{ij} to use it in Eqs. (28), (30). So, we must resort to numerical solution for Eqs. (20), (22).

Here, it is vital to study an important point in Eqs (20), (22). In these equations, the surface area of the pore in the Voronoi network, considered as cylinder. Although as it is shown in Fig. 5 they are converging- diverging segments. This effect can be improved by the ratio α_{ij} which is the ratio of the true internal surface area S_{cd} of such a pore and its cylindrical surface area S_c :

$$\alpha_{ij} = \frac{S_{cd}}{S_c} = \frac{\left(a + b\sqrt{h^2} + (b - a)^2\right)}{2ah}$$
(32)

We add α_{ij} to Eqs. (20), (22). Therefore, rewrite these equations according below:

$$\frac{d^2 C_k}{dx^2} - \frac{u_{ij}}{D_{k,a}} \frac{dC_k}{dx} - \frac{2\nu\eta(C_M, T)\alpha_{ij}}{D_{a,k}R_{ij}\rho_S}(-r) = 0$$
(33)

$$\frac{d^2T}{dx^2} - \frac{u\rho_b C_p}{K_T} \frac{dT}{dx} - \frac{2\Delta H\eta(C_M, T)\alpha_{ij}}{K_T R_{ij}\rho_S}(-r) = 0$$
(34)

The Dimensionless form of equations (33), (21) and (34) are:

$$\frac{d^2 \overline{C}_k}{d\overline{x}^2} - P e_k \frac{d\overline{C}_k}{d\overline{x}} - \acute{\mathbf{E}}_{sk}^2 (-R) = 0$$
(35)

$$\bar{C}_W = 1 - \left(\bar{C}_M + \bar{C}_E\right) \tag{36}$$

$$\frac{d^2\bar{T}}{d\bar{x}^2} - Pe_h \frac{d\bar{T}}{d\bar{x}} - \bar{\Delta H}(-R) = 0$$
(37)



Fig. 5 The converging- diverging pore between two particles.

Where $\overline{C} = \frac{C}{C_0}$, $\overline{T} = \frac{T}{T_0}$, $\overline{x} = \frac{x}{L_{ij}}$ and R (dimensionless reaction rate) can be calculated using following equation:

$$-R = \frac{K_M^2 C_o^2 \left(\bar{C}_M^2 - \frac{\bar{C}_D \bar{C}_M}{\bar{K}}\right)}{\left(1 + 2\sqrt{K_M \bar{C}_M} + K_W \bar{C}_W\right)^4}$$
(38)

The dimensionless parameters in Eqs. (35) and (37) are:

$$Pe_k = \frac{u_{ij}L_{ij}}{D_{k,a}} \tag{39}$$

$$Pe_h = \frac{\rho C_p u_{ij} L_{ij}}{k_T} \tag{40}$$

$$\dot{E}_{sk}^{2} = \frac{2L_{ij}^{2} v K_{s} \alpha_{ij} \eta(C_{m}, T)}{D_{k,a} R_{ij} \rho_{s} C_{0}}$$
(41)

$$\bar{\Delta H} = \frac{2\Delta H L_{ij}^2 K_s \alpha_{ij} \eta(C_m, T)}{k_T R_{ij} \rho_s T_0}$$
(42)

Eqs. (35), (37) are nonlinear equations that can be solved by the following boundary conditions:

$$\bar{x} = 0 \qquad C_k = 1 \tag{43}$$

$$\bar{x} = 1 \qquad \frac{dC_k}{d\bar{x}} = 0 \tag{44}$$

$$\bar{x} = 0 \qquad \bar{T} = 1 \tag{45}$$

$$\bar{x} = 1$$
 $\frac{d\bar{T}}{d\bar{x}} = 0$ (46)

Eq. (35) denotes for Methanol and DME mass balance and Eq. (37) expresses the energy balance for each pore. These equations will be solved simultaneously for each pore and for each equation the finite difference method is used with one point in the pore. Considering 3 grid points in each bond which two of them are at the end points and one is in the middle. Therefore, equations (35) and (37) will be organized in the dimensionless form as follows for the middle grid. The schematic of grid point in one pore is shown in Fig. 6.

$$\bar{C_{k,2}} = \frac{-\dot{E}_{s,k}^2(-R_2)}{8} + \frac{(4+2Pe_k)}{8} \bar{C_{k,1}} + \frac{(4-2Pe_k)}{8} \bar{C_{k,3}} \quad (47)$$

$$\bar{T}_2 = \frac{-\dot{E}_{sh}^2(-R_2)}{8} + \frac{(4+2Pe_h)}{8} \bar{T}_1 + \frac{(4-2Pe_h)}{8} \bar{T}_3$$
(48)

If the equations (36) and (37) were linear then we could theoretically calculate the energy and flux but as a result of nonlinear characteristics of these equations the theoretical solution cannot be found, and they should be calculated with a numerical method.

If we write equations (29) and (31) using numerical method, then we have:

$$J_{ij,k} = -D_{k,i} \frac{C_{k,i} - C_{k,2}}{L_{ij}/2} + u_{ij}C_{k,i}$$
(49)

$$h_{ij} = -k_T \frac{T_i - T_2}{L_{ij}/2} + u\rho c_p T_i$$
(50)

where $C_{k,2} = \overline{C_{k,2}} C_0$ is the concentration in the middle of the pore and $T_2 = \overline{T_2} T_0$ is the temperature in the middle of the pore.

With substitution equation (47) and (48) in Eqs (49) and (50) for all of the grids we have a series of equations in which the concentration and temperature of grids are unknown. These equations were solved by using bi-conjugate gradient method and the concentrations and temperature in the grids are found. The parameters used in the simulation are presented in Table 4.

A FORTRAN program is developed to find the concentration and temperature distribution in the reactor.

4. Results and discussion

Fig. 7 shows methanol mole fraction distribution while the input temperature is 551 K and for two different flow rates, the results of simulation indicate that by increasing the flow rate, methanol mole fraction will increase at the reactor outlet which is due to decrease in methanol resident time. Therefore, the equilibrium conversion will be obtained in a longer length of the reactor.

Fig. 8 shows the effect of flow rate on temperature distribution in the reactor while the input temperature is 551 K. The results show that in low flow rate input, the resident time of methanol in contact with catalyst particles will increase. Therefore, the equilibrium conversion will be obtained in a shorter length of the reactor and finally the temperature in reactor length and the final temperature will increase.

The effect of the input feed temperature on methanol concentration distribution in the reactor is presented in Fig. 9. Increases in input temperature will increase the reaction rate



Fig. 6 The schematic of numbering the grids in each bond.

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| Table 4 The parameters used in the simulation. | | | | | | |
|---|-------------------------------|-------------------------------|---|---------------------------------|--|--|
| Parameter | Value | Unit | Parameter | Value | Unit | |
| C _p (Diep and Wainwright, 1987) ΔH _r (Schiffino and Merrill, 1993) d (Bercic and Levec, 1993) L (Bercic and Levec, 1993) | 110 -23.56 0.078 0.7 | kJ/kmol.K kJ/mol m m | k_T (Bercic, 1990) $ρ_B$ (Bercic and Levec, 1993) d_S (Bercic and Levec, 1993) ρ | 0.972 882 0.003 0.0825 | $ \begin{array}{c} kJ/h.m.K \\ (kg_{cat}kg_{cat}/m^3 \\ m \\ kmol/m^3m^3 \end{array} $ | |

and the equilibrium conversion will be obtained in a shorter length of the reactor.

The effect of inlet temperature on the temperature distribution inside the reactor is shown in Fig. 10 increase in inlet temperature will increase the reaction rate and therefore the temperature would also be higher along the reactor. Consequently, the final temperature due to equilibrium condition happens closer to the reactor inlet.



Fig. 7 Methanol mole fraction versus reactor length at $T_0 = 551$ K (Exp.Points (Bercic and Levec, 1993)).



Fig. 8 The simulated reactor temperature versus reactor length at $T_0 = 551$ K (Exp.Points (Bercic and Levec, 1993)).



Fig. 9 Methanol concentration versus reactor length at q = 4.34 L.h⁻¹ (Exp.Points (Bercic and Levec, 1993)).



Fig. 10 The simulated reactor temperature versus reactor length at $q = 4.34 \text{ L.h}^{-1}$ (Exp. Points (Bercic and Levec, 1993)).



Fig. 11 Methanol, DME, water concentration versus reactor length at $q = 4.34 \text{ L.h}^{-1}$, $T_0 = 551 \text{ K}$.



Fig. 12 Methanol concentration versus reactor length at $T_0 = 561$ K for $C_M = 0.99$ (--), $C_M = 0.98$ (--), $C_M = 0.97$ (--).

Fig. 11 presents the mole fraction distribution of DME and methanol through the reactor.

The effect of feed purity on mole fraction distribution in the reactor is studied in Fig. 12. If methanol includes some water at the reactor inlet, DME conversion will strongly reduce. The methanol concentration in the reactor is reduced or in other words the DME concentration would be less. Therefore, the equilibrium reactor length would increase. Increasing the concentration of inlet methanol causes an equilibrium reaction to be achieved in less length than the reactor (pink dashed line).

In the previous methods used in modeling, the dispersion term in the reactor is omitted, but in the network modeling method, the dispersion term is used to model the reactor. Also, the effect of catalyst effectiveness factor has been considered by considering its changes in relation to changes in concentra-



Fig. 13 Methanol equilibrium conversion (Experimental Data (Bercic and Levec, 1992; Diep and Wainwright, 1987; Hayashi and Moffat, 1982) versus temperature.

tion and temperature in the simulation. The obtained results show that the introduced method shows a very good prediction for the dehydration process of methanol in the catalytic reactor. Also, one of the most important features of the network model is that the model is able to predict fluid displacement in heterogeneous environments. The developed model was employed to understand the influence of critical characteristics of a porous medium. This is possible only if a pore-network model has been utilized. Extending the model to 3D porous media is feasible and easy. Therefore, since a comprehensive pore-network model of porous media has been developed, it can be employed to understand crucial related phenomena (Hekmatzadeh et al., 2016).

As shown in Fig. 13, for exothermic reactions, increasing the temperature has a negative effect. This reaction is reversed, and the methanol equilibrium conversion is reduced. Approximately 520 to 651 K can be known as the optimal operating temperature range. Equilibrium conversions that are calculated from the previously presented relationships and by showing each other the experimental data, the best equilibrium constant model is obtained. It is clear from Fig. 13 that our correlations and the proposed correlations by Bercic and Levec are more consistent with the experimental data than other correlations.

5. Conclusions

In the current research, a pore network mechanistic model based on three dimensional Voronoi was developed for simulation of a packed bed reactor. The model was implemented for understanding the effect of pore space on the performance of reactor in converting methanol through dehydration reaction. The model is capable to take into account the morphology of pore space in the catalytic chemical conversion. The pore network model was used to investigate both mass and

heat transfer in the reactor. The influence of temperature as well as concentration on the reactor performance was evaluated using the developed model, and it was revealed that flow rate has significant effect on the reaction yield. The results of the simulations showed that the input feed flow rate reduction causes that reactants spend more time in contact with catalyst and it is caused that equilibrium conversion is obtained in a shorter length of the reactor. Furthermore, the input feed temperature increase causes that the equilibrium conversion obtains in a shorter length of the reactor. Therefore, the input flow rate reduction and input feed temperature increase cause that the equilibrium conversion obtains in a shorter length of the reactor. The result of the simulation in different input methanol concentrations showed that the reduction of methanol concentration causes the equilibrium conversion reduction in two ways. First of all, the reduction of methanol concentration causes the reduction of effectiveness factor and secondly causes the reduction of $(C_M^2 - \frac{C_D C_M}{K})$ in reaction rate equation. Increasing the feed inlet temperature at constant concentra-

tions also reduces the catalyst efficiency. Increasing the purity of methanol in the feed increases the conversion percentage and increases the efficiency coefficient, thus increasing the production of DME. Using this simulation, the appropriate radius for the size of the pore network can be determined. The simulation result shows that with increasing the percentage of pore network obstruction, the efficiency coefficient decreases sharply. This result shows that the higher the connection rate in the pore network and the larger the connection number, the easier the transfer will be and the higher the conversion rate. while continuous models will not be able to detect the effect of catalyst particle structure on the conversion rate. This conversion can be used to build catalysts and create the right structure for them. An increase in the passageways the pore network are connected and an increase in the percentage of closed pore network has reduced the conversion of methanol (reduced DME production). Increasing the methanol flow rate to the reactor reduces the contact time of the reactants with the catalyst and as a result the desired conversion rate is longer length the reactor.

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.

Acknowledgements

Afrasyab Khan is thankful to the Russian Government and Institute of Engineering and Technology, Department of Hydraulics and Hydraulic and Pneumatic Systems, South Ural State University, Lenin prospect 76, Chelyabinsk, 454080, Russian Federation for their support to this work through Act 211 Government of the Russian Federation, contract No. 02. A03.21.0011.

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