Computation of effectiveness factor for methanol steam reforming over Cu/ZnO/Al₂O₃ catalyst pellet

Abayomi O. Olatunde¹ · Olaosebikan A. Olafadehan¹ · Mohammed A. Usman¹

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Abstract

A mathematical model was developed for a diffusion–reaction process in a spherical catalyst pellet contained in a heterogeneous packed bed reactor. The model developed was solved to predict the effectiveness factor and also to perform sensitivity analysis for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst a source of hydrogen fuel. The method of orthogonal collocation was used to solve the resulting differential equation. At temperature below 473 K the effect on intra-particle diffusion limitation is reduced to the minimum indicated by the effectiveness factor being almost equal to one but as the temperature increases above 473 K there is considerable increase in the diffusion limitation effect. The effects of thermal conductivity, diffusion coefficient, catalyst size and surface temperature on effectiveness factor for the reaction process were also considered. Result indicates that catalyst size of 1.623×10^{-4} m eliminates the effect of intra-particle diffusion resistance in the pellet. The variation of effectiveness factor with Thiele modulus, showing the asymptotic values, using power law and Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetics, was predicted. The two reaction kinetics had almost the same magnitude of effectiveness factor at different Thiele modulus which indicates that they can adequately predict the reaction process.

Keywords Isothermal · Langmuir–Hinshelwood–Hougen–Watson · Power law · Effectiveness factor · Steam reforming

Abbreviations

$A_{j,k}$	Orthogonal collocation matrix representing first derivative	NR	Number of interior collocation points in the radial direction
AAD	Absolute average deviation	n	Power rate order, dimensionless
$B_{j,k}$	Orthogonal collocation matrix representing second derivative	Re	Reynolds number, dimensionless
C_i	Concentration of species i within the catalyst pellet, mol/m ³	R	Radius of catalyst pellet, m
C_s	Concentration of species i at the outer surface of catalyst pellet, mol/m ³	$\bar{R}_i$	Dimensionless reaction rate of species i
$\bar{C}_i$	Dimensionless concentration of species i	R_u	Universal gas constant, J/(mol K)
c_{pi}	Specific heat capacity of species i , J/(kg K)	$(-r'_i)$	Rate of disappearance of species i , mol/(kg cat s)
$(D_e)_i$	Effective diffusion coefficient of species i in the particle, m ² /s	$(-r'_i)_s$	Rate of disappearance of species i , at the pellet surface mol/(kg cat s)
E	Activation energy, J/mol	$-r'_M$	Reaction rate of methanol at the catalyst outer surface, mol/(kg cat s)
F_{M0}	Molar flow rate of methanol in the feed, mol/s	r	Radial distance of pellet, m
NC	Number of components	SD	Standard deviation
		T	Temperature within catalyst pellet, K
		T_c	Temperature in the centre of the catalyst pellet, K
		T_s	Temperature at the outer surface of catalyst pellet, K
		$\bar{T}$	Dimensionless temperature within the catalyst pellet
		t	Time, s
		W	Weight of catalyst, kg

✉ Abayomi O. Olatunde
 aolatunde@unilag.edu.ng

¹ Department of Chemical and Petroleum Engineering,
 University of Lagos, Lagos, Nigeria

X_M	Fractional conversion of methanol, dimensionless
y_i	Mol fraction of component i , dimensionless

Greek symbols

β_l	Heat of reaction parameter with respect to reaction, l , dimensionless
γ	Arrhenius number, dimensionless
σ	Dimensionless radial distance
ϵ_p	Void fraction of the particle, dimensionless
η	Non-isothermal effectiveness factor, dimensionless
λ_e	Effective thermal conductivity of pellet, W/(m K)
ρ_p	Density of catalyst particle, kg/m ³
Φ	Thiele modulus, dimensionless
$\Delta H_{rxn, l}$	Heat of reaction per mole of component, with respect to reaction l , J/mol
$\Delta H_{f, 298 K}^0$	Standard heat of formation at 25 °C, J/mol

Subscripts

c	Centre condition
i	Species
l	Stoichiometric reaction using power law and LHHW
L	Langmuir–Hinshelwood–Hougen–Watson
M	Methanol
p	Particle
PL	Power law
s	Catalyst outer surface
S	Steam

Introduction

The use of hydrogen fuel as a major source of fuel in the near future has gained a tremendous recognition in the past few years [1]. It is now being used as an energy carrier in fuel cells and mobile vehicles because it is a clean fuel that does not emit carbon dioxide when burned or used. It can be stored as a liquid or gas, and has been described as a long replacement of fossil fuels [1]. While several works have been done on economical ways of producing hydrogen from hydrocarbons such as alcohols, gasoline, natural gas and many other ways [2, 3], steam reforming of methanol has been preferred because of the advantage of high energy density, availability and safe handling, and lack of inter-carbon bonds in methanol, hence relatively low reforming temperatures (433–573 K). In addition, steam reforming of methanol produces limited CO, typically less than 5000 ppm and a higher hydrogen fraction in the reformat compared to that of partial oxidation of methanol. Methanol is rich in

hydrogen as the ratio of carbon to hydrogen is 1:4 compared to other candidates of hydrogen production [4]. Therefore, methanol is often converted into a hydrogen-rich gas before it is fed to the fuel cell stack, and steam reforming (SR) of methanol is suitable for this process.

Many investigators have proposed the reaction network for modelling this process, with the kinetic expressions given, based on their extensive experimental studies [4–14]. However, in addition to the kinetics, estimation of the effect of intra-particle diffusion resistance in catalyst particles is also significant in the design of the catalytic reformer. These will generally have to be included in any realistic model of a reactor and explicitly explained. Major works have not been done in the literature on the effect of intra-particle diffusion resistance on this complex reaction system, thus the need to study this.

The objective of this study was to numerically compute non-isothermal effectiveness factor in a spherical catalyst pellet for catalytic steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst. Thus, a computational procedure using the method of orthogonal collocation was presented for the numerical solution of the governing differential mass and energy balance equations with a view to estimate the concentration profiles of key components (methanol and hydrogen) and temperature profile inside the catalytic pellet using the non-linear power law and highly non-linear LHHW kinetics of the steam reforming of methanol, and thus computing the non-isothermal effectiveness factor. The effects of reaction kinetics, catalyst size, thermal conductivity, diffusion coefficient and surface temperature on effectiveness factor were considered. The kinetics for the steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst used in this study was obtained by Lee et al. [4] in a regime of intra-particle diffusion limitations, as external mass and heat transfer resistances were negligible during the catalytic steam reforming of methanol [1, 4, 13, 15], and thus appropriate for use in this investigation.

Development of mathematical model

The steady-state mass and energy balance equations for a spherical catalyst pellet are given by the following equations, respectively:

$$\frac{(D_e)_i}{\rho_p} \left(\frac{d^2 C_i}{dr^2} + \frac{2}{r} \frac{dC_i}{dr} \right) = [-r'_i(C_i, T)] \quad i = \text{CH}_3\text{OH}, \text{H}_2\text{O}, \quad (1)$$

$$\frac{\lambda_e}{\rho_p (\Delta H_{rxn, l})} \left(\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right) = [-r'_l(C, T)] \quad , \quad (2)$$

where $[-r'_i(C_i, T)]$ is the rate of disappearance of species i [=] kmol/(kg cat s) and $(D_e)_i$ the effective diffusivity of component i , which is often approximately constant inside a catalyst particle and l is the number of reaction.

In Eqs. (1) and (2), it was assumed that external mass and heat transfer resistances were negligible while the resistances to mass and heat transfer inside the catalyst (i.e., intra-particle resistance) were significant.

These equations are subject to the following boundary conditions:

- (i) At the pore centre,

$$r = 0, \quad \frac{\partial C_i}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0. \quad (3)$$

- (ii) At the pore mouth,

$$r = \frac{d_p}{2} = R, \quad C_i = (C_i)_s, \quad T = T_s. \quad (4)$$

The following dimensionless variables are defined:

$$\bar{C}_i = \frac{C_i}{(C_i)_s}, \quad \bar{T} = \frac{T}{T_s}, \quad \sigma = \frac{r}{R},$$

$$\bar{R}_i(\bar{C}_i, \bar{T}) = \frac{[-r'_i(C_i, T)]}{(-r'_i)_s[(C_i)_s, T_s]}. \quad (5)$$

Combining Eqs. (1) to (5), we have the following equation:

$$\bar{T} = 1 + \beta_l(1 - \bar{C}), \quad (6)$$

where $\beta_l = \left[\frac{(-\Delta H_{rxn,l})(D_e)_l(C_i)_s}{\lambda_e T_s} \right]$ is a heat of reaction parameter with respect to reaction l , which characterizes the potential for temperature gradients inside the particle.

Equation (1) in dimensionless form yields:

$$\frac{d^2 \bar{C}_i}{d\sigma^2} + \frac{2}{\sigma} \frac{d\bar{C}_i}{d\sigma} - \phi^2 \bar{R}_i(\bar{C}_i, \bar{T}) = 0 \quad i = \text{CH}_3\text{OH}, \text{H}_2\text{O}, \quad (7)$$

where $\phi = \left\{ R \sqrt{\frac{\rho_p [(-r'_i)_s ((C_i)_s, T_s)]}{(D_e)_i (C_i)_s}} \right\}$ is called the Thiele modulus, and $\bar{R}_i(\bar{C}_i, \bar{T})$ is the dimensionless rate of reaction of species i , normalized with respect to the reaction rate at the external conditions.

The boundary conditions of Eq. (7) are $\bar{C}_i = 1$ at $\sigma = 1$ and $\frac{d\bar{C}_i}{d\sigma} = 0$ at $\sigma = 0$.

The developed model Eqs. (6) and (7) can now be applied to any reaction system or network.

Application of the model to the reaction kinetics

The steam reforming of methanol on a commercial Cu/ZnO/Al₂O₃ catalyst to produce hydrogen was considered. This reforming reaction was studied at atmospheric pressure and in a temperature range between 433 and 533 K by [4]. The main reaction is

The chief products of steam reforming of methanol are hydrogen and carbon dioxide with a small amount of CO, usually less than 1%, as a by-product [16–18]. However, Lee et al. [4] obtained a power rate law and Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expressions for the reforming reaction by fitting the rate expressions to their experimental data. An excellent fitting of the data by the LHHW expression indicated that the dehydrogenation of the adsorbed methoxy to the adsorbed oxymethylene is the rate-determining step, and that adsorption of all reacting species other than methoxy and hydrogen on the active sites was negligible.

The power-law expression obtained for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst was of the form given by Lee et al. [4]:

$$(-r'_M) = k_0 \exp\left(-\frac{E_1}{R_u T}\right) p_M^{\alpha_1} (A + p_{H_2})^{\alpha_2} [=] \text{ mol/(kg cat s)}, \quad (9)$$

where $k_0 = 2.19 \times 10^9 \text{ mol Pa}^{0.083}/(\text{kg cat s})$, $E_1 = 1.03 \times 10^5 \text{ J/mol}$, $\alpha_1 = 0.564$, $\alpha_2 = -0.647$ and $A = 1.16 \times 10^4 \text{ Pa}$.

The LHHW rate expression obtained for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst had the form given by Lee et al. [4]:

$$(-r'_M) = \frac{k_{01} \exp\left(-\frac{E_2}{R_u T}\right) K_1 \frac{p_M}{\sqrt{p_{H_2}}}}{\left(1 + K_1 \frac{p_M}{\sqrt{p_{H_2}}}\right) \left(1 + \sqrt{K_2 p_{H_2}}\right)} [=] \text{ mol/(kg cat s)}, \quad (10)$$

where

$$k = k_{01} \exp\left(-\frac{E_2}{R_u T}\right)$$

$$= 3.13 \times 10^{10} \exp\left(-\frac{1.11 \times 10^5}{R_u T}\right) [=] \text{ mol/(kg s)},$$

$$K_1 = K_{01} \exp\left(-\frac{\Delta H_1}{R_u T}\right)$$

$$= 1.186 \times 10^{-4} \exp\left(\frac{2.0 \times 10^4}{R_u T}\right) [=] \text{ Pa}^{-0.5},$$

$$K_2 = K_{02} \exp \left(-\frac{\Delta H_2}{R_u T} \right) \\ = 6.34 \times 10^{-10} \exp \left(\frac{5.0 \times 10^4}{R_u T} \right) [=] \text{Pa}^{-1}.$$

To estimate the non-isothermal effectiveness factor of the catalyst particle, the intra-particle concentration profiles of the reacting species that affect the reaction rate should be determined. The concentration profiles depend on the effective diffusivities of the reacting species and on the reaction rate. However, the components identified in the steam reforming of methanol are methanol (M), steam (S), carbon dioxide (C), hydrogen (H₂) and nitrogen (N₂). Carbon monoxide was neglected in the reforming mixture since its concentration was insignificant. Moreover, the reaction rate for the steam reforming of methanol was found to depend on the partial pressures of methanol and hydrogen, as evident in Eqs. (11) and (12); therefore, the concentration profiles of the two components (methanol and hydrogen) are needed to evaluate the non-isothermal effectiveness factor of the catalyst particle. Using the modified Maxwell–Stefan equation to formulate the multicomponent diffusion in the catalyst [19, 20], we have

$$\bar{C}_{H_2} = 1 + \frac{3(D_e)_M(C_M)_s}{(D_e)_{H_2}(C_{H_2})_s} (1 - \bar{C}_M), \quad (11)$$

$$\bar{C}_{CO_2} = 1 + \frac{(D_e)_M(C_M)_s}{(D_e)_{CO_2}(C_{CO_2})_s} (1 - \bar{C}_M), \quad (12)$$

$$\bar{C}_S = 1 - \frac{(D_e)_M(C_M)_s}{(D_e)_S(C_S)_s} (1 - \bar{C}_M), \quad (13)$$

where $(D_e)_M$ and $(D_e)_{H_2}$ are the respective effective diffusivities of methanol and hydrogen in the catalyst, and $(C_M)_s$ and $(C_{H_2})_s$ the dimensionless concentrations of methanol and hydrogen at the external surface of the catalyst. Equation (11) shows that there is a mutual relation between concentration profile of methanol and hydrogen inside a catalyst particle, which is in agreement with Schneider [19, 20] relation.

The non-isothermal effectiveness factor, η , of the catalyst is given by

$$\eta = \frac{3}{\phi^2} \frac{d\bar{C}_M}{d\sigma} \bigg|_{\sigma=1}. \quad (14)$$

Hence, to estimate the effectiveness factor by Eq. (14), it is necessary to solve governing Eq. (7) to obtain the dimensionless concentration profile of methanol inside the catalyst

pellet, $\bar{C}_M(\sigma)$, and then obtain the dimensionless temperature profile inside the catalyst pellet via Eq. (6).

Since all the reacting species (methanol, M, steam, S, carbon dioxide and hydrogen) involved in the steam reforming of methanol are in the gaseous phase, ideal gas law, $p = C R_u T$, is applied to the reaction rate of disappearance of methanol, Eq. (9), to obtain

$$(-r'_M) = k_0 \exp \left(-\frac{E_1}{R_u T} \right) (C_M R_u T)^{\alpha_1} \left(\frac{A}{R_u T} + C_{H_2} R_u T \right)^{\alpha_2}. \quad (15)$$

Applying ideal gas law to LHHW rate expression (10), we have

$$(-r'_M) = \frac{k_{01} \exp \left(-\frac{E_2}{R_u T} \right) K_1 \sqrt{R_u T} \left(\frac{C_M}{\sqrt{C_{H_2}}} \right)}{\left[1 + K_1 \sqrt{R_u T} \left(\frac{C_M}{\sqrt{C_{H_2}}} \right) \right] \left(1 + \sqrt{K_2 C_{H_2} R_u T} \right)}. \quad (16)$$

Rendering the power rate law model and LHHW rate expression for the steam reforming of methanol in dimensionless forms, and using the respective expressions obtained in Eq. (9), we have the following equations for the power rate law model and LHHW rate expression, respectively:

$$\frac{d^2 \bar{C}_M}{d\sigma^2} + \frac{2}{\sigma} \frac{d\bar{C}_M}{d\sigma} - \phi_{PL}^2 \exp \left[-\frac{\gamma_{PL}}{1 + \beta(1 - \bar{C}_M)} \right] \left[\frac{A}{R_u T_s \bar{T}} + R_u (C_{H_2})_s T_s \bar{C}_{H_2} \bar{T} \right]^{\alpha_2} (\bar{C}_M \bar{T})^{\alpha_1} = 0, \quad (17)$$

$$\frac{d^2 \bar{C}_M}{d\sigma^2} + \frac{2}{\sigma} \frac{d\bar{C}_M}{d\sigma} - \frac{\phi_L^2 \exp \left[-\frac{(\gamma_L + \gamma_1)}{1 + \beta(1 - \bar{C}_M)} \right] \bar{C}_M \sqrt{\frac{\bar{T}}{\bar{C}_{H_2}}}}{(DEN1)(DEN2)} = 0, \quad (18)$$

where

$$\gamma_{PL} = \frac{E_1}{R_u T_s}, \quad (19)$$

$$\beta = \frac{(-\Delta H_{rxn})(D_e)_M(C_M)_s}{\lambda_e T_s}, \quad (20)$$

$$\phi_{PL} = R \sqrt{\frac{\rho_p k_0 (R_u T_s)^{\alpha_1}}{(D_e)_M (C_M)_s^{1-\alpha_1}}}, \quad (21)$$

$$\phi_L = R \sqrt{\frac{\rho_p K_{01} K_{01}}{(D_e)_M} \left[\frac{R_u T_s}{(C_{H_2})_s} \right]^{0.5}}, \quad (22)$$

$$DEN1 = 1 + K_{01} \sqrt{\frac{R_u T_s}{(C_{H_2})_s}} (C_M)_s \exp \left[-\frac{\gamma_1}{1 + \beta(1 - \bar{C}_M)} \right] \bar{C}_M \left(\frac{\bar{T}}{\bar{C}_{H_2}} \right), \quad (23)$$

$$DEN2 = 1 + \sqrt{K_{02} R_u (C_{H_2})_s T_s \exp \left[-\frac{\gamma_2}{1 + \beta(1 - \bar{C}_M)} \right] \bar{C}_{H_2} \bar{T}}, \quad (24)$$

$$\gamma_L = \frac{E_2}{R_u T_s}, \quad (25)$$

$$\gamma_i = \frac{\Delta H_i}{R_u T_s}, \quad i = 1, 2. \quad (26)$$

The boundary conditions of Eqs. (17) and (18) are $\bar{C}_M = 1$ at $\sigma = 1$ and $\frac{d\bar{C}_M}{d\sigma} = 0$ at $\sigma = 0$.

$\bar{T}$ and $\bar{C}_{H_2}$ are as given in Eqs. (6) and (11), respectively.

The Ergun equation was used to calculate the pressure drop through the catalyst beds. It is represented as follows:

$$\Delta P = \left(\frac{150}{Re} + 1.75 \right) \frac{\rho_f u_o^2}{d_p} \left(\frac{1 - \epsilon_p}{\epsilon_p^3} \right) L,$$

where ΔP is the pressure drop, Re is the Reynolds number, ρ_f is the density of the fluid, u_o is the superficial velocity, d_p is the catalyst pellet diameter, ϵ_p is the bed voidage and L is the length of the packed bed.

Numerical method of solution

Orthogonal collocation

The numerical method adopted for the solution of the developed models for the catalytic steam reforming of methanol with a view to predicting the key component concentration profile inside the pellet and thus computing non-isothermal effectiveness factor values is the orthogonal collocation method [21, 22].

Parameters and operating conditions used for the computation

In the computational procedure of this study, the effective diffusivity values of methanol and hydrogen in the catalyst were estimated using the modified Maxwell–Stefan equation [19] and the cross-linked pore model [23], recommended by Haugaard and Livbjerg [24] based on experimental comparison of the pore-diffusion models. The respective effective diffusivities of methanol, $(D_e)_M$, hydrogen, $(D_e)_{H_2}$, carbon dioxide, $(D_e)_{CO_2}$, steam, $(D_e)_S$, are given by

$$(D_e)_M = \frac{\epsilon_p}{\tau} \left(\frac{y_S - y_M}{D_{M-S}} + \frac{y_{CO_2} + y_M}{D_{M-CO_2}} + \frac{y_{H_2} + 3y_M}{D_{M-H_2}} + \frac{y_{N_2}}{D_{M-N_2}} + \frac{1}{(D_K)_M} \right)^{-1}, \quad (27)$$

$$(D_e)_{H_2} = \frac{\epsilon_p}{\tau} \left(\frac{y_M + y_{H_2}}{3D_{H_2-M}} + \frac{y_S + y_{H_2}}{3D_{H_2-S}} + \frac{y_{CO_2} - y_{H_2}}{3D_{H_2-CO_2}} + \frac{y_{N_2}}{D_{H_2-N_2}} + \frac{1}{(D_K)_{H_2}} \right)^{-1}, \quad (28)$$

$$(D_e)_{CO_2} = \frac{\epsilon_p}{\tau} \left(\frac{y_{H_2} - 3y_{CO_2}}{D_{CO_2-H_2}} + \frac{y_M + y_{CO_2}}{D_{M-CO_2}} + \frac{y_S - y_{CO_2}}{D_{CO_2-S}} + \frac{y_{N_2}}{D_{CO_2-N_2}} + \frac{1}{(D_K)_{CO_2}} \right), \quad (29)$$

$$(D_e)_S = \frac{\epsilon_p}{\tau} \left(\frac{y_M - y_S}{D_{M-S}} + \frac{y_{CO_2} + y_S}{D_{S-CO_2}} + \frac{y_{H_2} + 3y_S}{D_{S-H_2}} + \frac{y_{N_2}}{D_{S-N_2}} + \frac{1}{(D_K)_S} \right), \quad (30)$$

where ϵ_p is the porosity of the catalyst, τ the tortuosity of pores in the catalyst, y_i the mole fraction of component i , D_{i-j} the diffusivity for a binary mixture of i and j , and $(D_K)_M$, $(D_K)_{H_2}$, $(D_K)_{CO_2}$ and $(D_K)_S$ the Knudsen diffusivities of methanol, hydrogen, carbon dioxide and steam, respectively. The tortuosity factor, τ , is a parameter, which corrects deviations of the real pore structure from the ideal cylindrical straight pores. $\tau = 3$ was assumed, a theoretical value for a random pore system [23]. The binary diffusivity was estimated by the method of Reid et al. [26]. The Knudsen diffusivity of component i is given by Smith [25]:

$$(D_K)_i = 97\bar{r} \sqrt{\frac{T_{rxn}}{M_i}} [=] \text{ m}^2/\text{s}, \quad (31)$$

where $\bar{r}$ is the mean pore radius [=] m, T_{rxn} the reaction temperature [=] K and M_i the molecular weight of species i .

The effective diffusivities, $(D_e)_M$, $(D_e)_{H_2}$, $(D_e)_{CO_2}$ and $(D_e)_S$, are seen to depend on the mole fractions of all components of the reaction mixture at a point in the catalyst. Schneider [19, 20] has shown that the change of the effective diffusivity along the pores in the catalyst is not very marked even under strong diffusion limitations, and that the effective diffusivity evaluated at the outer surface of a catalyst particle can be used throughout the particle without introducing any serious error into the concentration profile.

Effectiveness radial thermal conductivity computation [27]:

$$\frac{\lambda_e}{\lambda_f} = \alpha + \beta \text{Pr Re}. \quad (32)$$

For metal spheres:

$$\alpha = 13, \quad \beta = 0.11,$$

$$0.021 < \frac{d_p}{d_i} < 0.086,$$

$$\text{Pr} = \frac{C_{pf}\mu}{\lambda_f} = \frac{48.9926 \times 2.71E - 4}{3.08E - 2} = 0.4311, \quad (33)$$

$$\text{Re} = \frac{d_p G}{\mu} = \frac{3.62E - 4 \times 3.42}{2.71E - 4} = 4.5744, \quad (34)$$

$$\frac{\lambda_e}{\lambda_f} = [13 + 0.118 \times 0.4311 \times 4.5747], \quad (35)$$

$$\lambda_e = 0.4071 \text{ W/mK}.$$

Results and discussion

The results of the study are presented and discussed in this section. The case study depicts the results of the effect of intra-particle diffusion resistance on methanol steam reforming on a commercial Cu/ZnO/Al₂O₃ catalyst using power rate law and LHHW kinetics, respectively (Tables 1 and 2).

Effect of temperature on effectiveness factor

Figure 1 shows the effect of change in surface temperature on effectiveness factor of steam reforming of methanol on a commercial Cu/ZnO/Al₂O₃ catalyst. At temperature below 473 K, the effect on intra-particle diffusion limitation is reduced to the minimum indicated by the effectiveness factor being almost equal to one. At this point, almost all the catalyst surfaces are available for reaction. As the

Table 1 The geometric, kinetic and parameters used for the steam reforming of methanol on a commercial Cu/ZnO/Al₂O₃ catalyst

Physical properties and bed characteristics	Value	Unit
Fluid density	57	(kg/m ³)
Catalyst density	2400	(kg/m ³)
Catalyst pore mean radius	8×10^{-9}	(m)
BET area	66	(m ² /g)
Specific heat of the fluid	48.9927	(J/mol K)
Specific heat of the catalyst	1904	(J/kg K)
Thermal conductivity of the fluid	3.30×10^{-2}	(W/m K)
Superficial velocity	1.30	(m/s)
Methanol partial pressure in feed	0.01519875	(MPa)
Hydrogen partial pressure in feed	0.00506625	(MPa)
Steam partial pressure in feed	0.03033975	(MPa)
Nitrogen partial pressure in feed	0.0506625	(MPa)
Reaction temperature	523	(K)
Reactor tube diameter	6.80×10^{-3}	(m)
Particle radius	1.8125×10^{-4}	(m)
Thermal conductivity of the catalyst	0.4071	[W/(m K)]
Thermal conductivity of the bulk fluid	3.30×10^{-3}	[W/(m K)]
Void fraction in the bed	0.47	
Void fraction in particles	0.47	
Mass velocity	3.42	(kg m ² s ⁻¹)
Viscosity	2.70×10^{-4}	(Pa s)
Kinetic parameters		
Heat of reaction (523 K)	57,939.52	(J/mole)
Dimensionless number		
Reynolds number	4.5744	
Prandtl number	0.4311	

These values of constants and parameters were taken from the experimental work of Lee et al. [4] and Peppley et al. [9] and to which the simulation results were compared

Fig. 1 Effect of surface temperature on effectiveness factor for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst

Table 2 Calculated values of Knudsen and effective diffusion coefficients of species for the reaction system

Species	Knudsen diffusion coefficient (m ² /s)	Effective diffusion coefficient (m ² /s)
Methanol	3.14×10^{-6}	4.91×10^{-7}
Hydrogen	1.25×10^{-5}	1.96×10^{-6}
Carbon dioxide	2.67×10^{-6}	4.191×10^{-7}
Steam	4.18×10^{-6}	6.55×10^{-7}

temperature increases above 473 K, there is considerable increase in the diffusion limitation effect. This implies that at temperature above 473 K, effect of intra-particle diffusion

resistance becomes predominant providing only small area of the catalyst for reaction with most of the reactions taking place very close to the outer surface of the catalyst. The trend is in agreement with Lee et al. [4] with an absolute average deviation (AAD) of 0.111 and standard deviation (SD) of 0.131.

Effectiveness factor and Thiele modulus plot of both kinetics

Figure 2 shows the variation of effectiveness factor, η , with Thiele modulus, ϕ , for the power law kinetics of the reaction process. The reaction being endothermic, both concentration and temperature profiles decrease towards the centre of the pellet. For large values of the Thiele modulus, the rate of reaction is much greater than the rate of diffusion; thus, the

Fig. 2 Effectiveness factor versus Thiele modulus using power kinetics for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst

effectiveness factor is much less than unity, and the process is said to be diffusion-limited, that is, the surface reaction is rapid and that the reactant is consumed very close to the external pellet surface and very little penetrates into the interior of the pellet. However, when the diffusion rate is much larger than the reaction rate, the effectiveness factor is near unity and the process is said to be reaction-limited, and a significant amount of the reactant diffuses well into the pellet interior without reacting. From the plot, it can be seen that the internal diffusion effectiveness factor is approximately equal to 1.0 when the Thiele modulus is lower than 1.1, which means majority of the reactants diffuse quickly into the catalyst centre and the effect of internal diffusion can be neglected. When the value of Thiele modulus increased

from 1.3 to 3.4, the value of the internal diffusion effectiveness factor decreased from 0.8332 to 0.507, which indicates that the effect of internal diffusion resistance is pronounced. At Thiele modulus greater than 4.0, the internal diffusion effectiveness factor is very small which means severe intra-particle diffusion resistance meaning most of the catalyst is not being utilized.

Figure 3 shows the power law and Langmuir–Hinshelwood (LHHW) kinetics superimposed, it is seen that there is only a slight difference in the values of the effectiveness factor variation with Thiele modulus for both the power law and LHHW kinetics for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst, indicating that the two reaction kinetics can be used to predict the reaction process. Figure 4

Fig. 3 Effectiveness factor versus Thiele modulus for both power law and LHHW kinetics for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst

Fig. 4 Effectiveness factor versus Thiele modulus using LHHW kinetics for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst at different heat of reaction parameter

shows the variation of the values of effectiveness factor with Thiele modulus at different heat of reaction parameter, β , using power law kinetics for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst. The plot shows decrease in the magnitude of effectiveness factor as β decreases from -0.01 to -0.8 , all having very close values of effectiveness factor at different Thiele modulus. This is because the reaction being endothermic, the temperature decreases toward the centre of the pellet and since the rate decreases with drop in temperature, the effect of the heat-transfer resistance is diminished thus resulting in the closeness of the non-isothermal η profiles for various values of heat of reaction parameter for methanol, β . Therefore, the decrease in temperature (and of course the reaction rate) in going into the pellet is indicative of the little significance of the mass transfer.

Effect of diffusion coefficient and thermal conductivity

Figures 5 and 6 show the effect of diffusion coefficient and thermal conductivity on effectiveness factor respectively. From Fig. 5, as the diffusion coefficient increases, the effectiveness factor becomes limited by surface reaction effect and thus increasing the effectiveness factor. At a diffusion coefficient of $4.60 \times 10^{-7} \text{ m}^2/\text{s}$, the effectiveness factor is 0.6571; at $7.50 \times 10^{-7} \text{ m}^2/\text{s}$, the effectiveness factor increases by almost 30% to 0.6691. Increasing the diffusion coefficient to $1.50 \times 10^{-6} \text{ m}^2/\text{s}$ shows a small increase of about 0.5% to 0.6721. Further increase in diffusion coefficient does not show appreciable increase in the value of effectiveness factor. This is because for endothermic reaction which is

Fig. 5 Effect of diffusion coefficient variation on effectiveness factor for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst

Fig. 6 Effect of thermal conductivity variation on effectiveness factor for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst

the reaction we are considering, temperature and concentration gradients both reduce the reaction rate below that evaluated at surface conditions. The decrease in rate going into the pellet for endothermic reaction means that the mass transfer is of little importance which thus makes the diffusion coefficient to have minimal effect on effectiveness factor. Therefore, operating with the diffusion coefficient of $1.50 \times 10^{-6} \text{ m}^2/\text{s}$ for this reaction process will reduce to minimal value the effect of intra-particle diffusion resistance. As shown in Fig. 6, as the thermal conductivity increases, the diffusion effect becomes the limiting effect and thus decreasing the effectiveness factor. At thermal conductivity of $0.204 \text{ W/m}^2\text{K}$, the effectiveness factor is 0.6598; at $0.4071 \text{ W/m}^2\text{K}$, the effectiveness factor decreases by almost 1.2% to 0.6521. Increasing the thermal conductivity to $1.080 \text{ W/m}^2\text{K}$ shows a small decrease of about 1.1%

to 0.644. Further increase in thermal conductivity does not show appreciable change in the value of effectiveness factor. This is because the effective thermal conductivities of catalyst pellets are very low. For endothermic reaction, there is a decrease in temperature and diffusion rate into the pellets as stated earlier. Thus, the effect of heat transfer resistance is diminished which then makes the effect of effective thermal conductivity on the effectiveness factor not to be pronounced. Therefore, operating with the thermal conductivity $1.080 \text{ W/m}^2\text{K}$ will reduce to minimal value the effect of intra-particle diffusion resistance in the reaction process.

Effect of catalyst size

Figure 7 presents the effect that change in catalyst size will have on the magnitude of effectiveness factor. As the catalyst

Fig. 7 Effect of catalyst size on effectiveness factor

Fig. 8 Variation of pressure drop in the reactor with catalyst size

size increases, the effectiveness factor decreases. At the catalyst size of 8.41×10^{-4} m, the effectiveness factor is 0.3954, decreasing the catalyst size to 2.36×10^{-4} m the value of effectiveness factor increased to 0.6522. The catalyst size of 1.623×10^{-4} m was able to produce effectiveness factor of 1, thus removing the effect of intra-particle resistance on the catalyst with minimal pressure drop of 8% which is still within the allowed 10% pressure drop for fixed bed reactor [28]. This shows that catalyst size of 1.623×10^{-4} m is still acceptable for the reaction process as it is still with accepted pressure drop value. This effect is very important in the design and optimization of the reactor. Figure 8 shows the variation of pressure drop with catalyst size at reactor length of 0.00635 m considered for the reaction process. The pressure drop varies linearly with catalyst size with the difference from the initial value still less than 10%.

Figure 9 shows the concentration profiles of the reactant (methanol) at different Thiele moduli, 1.2, 2.2, 3.4, 4.6, 5.0 and 5.9 inside the catalyst pellet using the power law kinetics. At Thiele modulus of 1.2, the intra-particle diffusion resistance has no major effect on the rate of reaction per pellet. Almost all the entire volume of the catalyst is reacting at the same rate as about 80% of the methanol is able to diffuse quickly into the centre of the catalyst pellet. At Thiele modulus of 2.2, the effect of intra-particle diffusion started becoming predominant with almost 60% of the reactant being converted before diffusing to the centre of the catalyst pellet. When the Thiele modulus is 3.4, 75% of the reactant was converted at the surface of the catalyst pellet before reaching the centre. While for large Thiele moduli of 4.6, 5.0 and 5.9, by the time reactant gets to the centre

of the catalyst pellet, almost 97% of it has been converted. This is in agreement with Fig. 2. For these large values of Thiele moduli, the rate of reaction is greater than the diffusion rate; thus, the effectiveness factor is much less than unity and the process is said to be diffusion limited, that is, the surface reaction is rapid and the reactant is consumed very close to external pellet surface and very little penetrates into the interior of the pellet. Figure 10 depicts the temperature profile at different Thiele moduli inside the catalyst pellet. The temperature drops are minimal at different Thiele moduli which shows that the reaction process is isothermal. This may be due to the endothermic nature of steam reforming process and also because of slow heat transfer into the reactor from the external heating system [29, 30]. Thus, to increase heat transfer into the process, internal heating of the system can be adopted which can increase the temperature in the catalyst and leads to increase in the rate of conversion [30], or by combining endothermic steam reforming with exothermic combustion part of methanol which supplies the required heat [29].

Figure 11 shows the partial pressure of the key components inside the catalyst pellet. The two reactants methanol and steam partial pressure decreases from the outer catalyst surface to the centre of the catalyst as they reacted to form the products carbon dioxide and hydrogen. The products have their partial pressure increase from the centre of the pellet to the outer surface. Table 3 depicts the effect of molecular diffusion and Knudsen diffusion on the overall effective diffusivity inside the catalyst pellet. The molecular diffusivity is greater than Knudsen diffusivity which shows that the diffusion of the

Fig. 9 Dimensionless concentration profiles of methanol at different Thiele modulus along the radial distance within the catalyst pellet

Fig. 10 Temperature of methanol at different Thiele modulus along the radial distance within the catalyst pellet

Fig. 11 Partial pressure of reactants and products inside the catalyst pellet for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst

Table 3 Molecular, Knudsen and effective diffusion coefficients of methanol inside the catalyst pellet

Molecular diffusion coefficient (m ² /s)	Knudsen diffusion coefficient (m ² /s)	Effective diffusion coefficient (m ² /s)
2.07×10^{-2}	3.14×10^{-6}	4.91×10^{-7}

reactants into the catalyst pellet is more of molecular diffusion than Knudsen diffusion. This is due to the smaller size of the methanol particles which allow easy passage of the reactants into the catalyst pellet.

Conclusions

A mathematical model was developed for a diffusion–reaction process in a spherical catalyst pellet contained in a non-isothermal heterogeneous packed bed reactor. The model developed was solved to predict the non-isothermal effectiveness factor and also to perform sensitivity analysis for steam reforming of methanol on Cu/ZnO/Al₂O₃ catalyst, a source of hydrogen fuel. Results show that reducing the catalyst size to 1.623×10^{-4} m eliminates the effect of intra-particle diffusion effect. An increase in diffusion coefficient leads to an increase in the effectiveness factor while increase

in thermal conductivity leads to a decrease in effectiveness factor. Both power law and the developed LHHW kinetics for steam reforming of methanol on $\text{Cu/ZnO/Al}_2\text{O}_3$ were able to predict the reaction process adequately. Also at temperature below 473 K, the effect on intra-particle diffusion limitation is reduced to the barest minimum.

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