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MODELING OF A TUBULAR FIXED-BED REACTOR FOR THE PRODUCTION OF DIMETHYL ETHER USING ALUMINA CATALYST

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ABSTRACT

A model to predict the behavior of an adiabatic tubular fixed-bed reactor for the production of dimethyl ether using alumina catalyst was developed. The steady state model incorporates the reaction rate kinetic expression obtained from literature into the model equations. The models were integrated numerically using Fourth-order Runge-Kutta method incorporated into a computer simulator (MATLAB 7.7 code). Model predictions are compared with data obtained from the literature under the same operating conditions and a good agreement is obtained with a variation ranging from 0.5% to 2.7%. The simulation results show that the production of dimethyl ether is greatly affected by parameters such as temperature, and feed flow rate with optimum yield of DME at a catalyst bed height of 2-4m at a temperature of 557 to 570K.

Keywords: Fixed-bed reactor, Natural gas, Methanol dehydration, Modeling, Simulation, Dimethyl ether, Alumina catalyst.

Contribution/ Originality

This study contributes in the existing literature by developing model equations that is used in predicting/simulation of functional parameters for optimum yield of DME. Unlike other works which assume isothermal condition, this study assumes an adiabatic condition and could be adopted for simulation of industrial DME plant.

1. INTRODUCTION

Natural gas is used for DME production, and Nigeria is blessed with this raw material, making DME usage in Nigeria a very attractive choice. With the use of DME as fuel for both diesel engines and domestic use, pollution can be controlled to a very large extent because it does not produce pollutants as compared to diesel fuels. Dimethyl ether (DME) is the simplest ether having the chemical formula of CH_3OCH_3. DME is a colorless gas at an ambient condition; its vapor pressure is about 0.6 MPa at 25°C, DME is easily to liquefied under low pressure [1]. Its physical properties are similar to those of propane and butane, which are the principal constituents of liquefied petroleum (LP) gas. Since its physical and chemical characteristics are very similar to those of LP gas, it is an easy substitute for LP gas that can be put to household use for cooking and home heating. DME is not only an easy substitute for LP gas, but also a very clean substitute for diesel fuel because a DME-fueled diesel car emits neither soot nor particulate matters and it has a very high cetane number of 50-60, while that of diesel is between 40-55 [2]. DME can be distributed and stored by using LP gas handling technology, which means DME does not need costly LNG tankers or LNG terminals. Once natural gas is converted to DME, it will provide a new competitive route to transport natural gas as compared to the LNG chain. DME is now used for a spray propellant (paints, agricultural chemicals, cosmetics, etc.) by replacing chlorofluorocarbon which is a greenhouse gas. Approximately 150,000 tons/year of DME are produced worldwide. Since DME is decomposed in a troposphere in dozens of hours, it does not cause ozone layer depletion [3]. A toxicity study of DME has confirmed that its toxicity is very low, similar to LP gas, far much lower than Methanol [1]. DME does not corrode any metal. DME is produced from synthesis gas obtained from natural gas or biomass. This work focuses on the production of DME from natural gas. The natural gas is first converted to synthesis gas through autothermal reforming of methane. The syngas produced passes through a series of reactions to form methanol. Methanol is then dehydrated in the presence of a catalyst to form the product of interest which is dimethyl ether. The synthesis of DME begins with the production of syngas through the reforming of methane. The syngas produced is then used for the production of methanol in a fixed bed catalytic reactor. DME synthesis is carried out in a shell and tube reactor whose tubes are loaded with alumina catalyst. Methanol is first heated up to a temperature of 533K by passing it through a heat exchanger. The feed enters as a fluid stream into the tubes of the reactor at a pressure of 1820kPa. The tubes are filled with spherical alumina catalyst with a void fraction of 0.4 to allow for the passage of the fluid reactant. The conversion of methanol to DME takes place on the surface of the catalyst leading to an exothermic system. The heat generated as a result of the reaction taking place in the tubes is removed by passing cooling water through the shell side of the reactor [4]. Heat removal from this reactor is very vital to prevent equilibrium conversion of the product formed and also to prevent catalyst deactivation due to increasing temperature. The reaction is exothermic, so the products are heated up to about 300°C before leaving the reactor. The reactor effluent is cooled and then throttled to a pressure of about 10.4 bars before it is fed to the first distillation column. The effluent is made up of DME, water and unreacted methanol. In this column, DME is separated as distillates while the other components come out as the bottom product. The bottom product is then throttled to a pressure of about 7.4 bars before being fed to a second distillation column. In this column, methanol is the distillate while water is the waste product. The methanol obtained is then compressed to a pressure of about 18 bars and recycled back to mix with the methanol at the reactor inlet. Like LPG, DME is stored in the liquid state under relatively low pressure of 0.5bar [5]. Considerable works have been done on the production of DME and few of them are cited in what follows. Takashi, et al. [1] developed an innovative way for direct DME synthesis from synthesis gas. In their work, they used a homogenous slurry reactor with the catalyst present as fine powder slurry in inert high-boiling-point oil. Natural gas was processed in an auto-thermal reformer in the presence of steam. The syngas formed was pumped to the slurry reactor. The reactor temperature was controlled, not letting the temperature exceed 300^{0}C. Shahrokhi and Baghmisheh [6] have simulated dynamic behavior of a fixed-bed reactor for methanol and DME production in a one-reactor system and proposed an optimizer for maximizing the production rate. Cho and Park [7] have analyzed one-step DME synthesis from syngas in a shell and tube type fixed bed reactor with consideration of heat and mass transfer between catalyst pellets and reactants in the gas phase. They did not consider the temperature at which catalyst decay begins. Yoon and Song [8] have conducted simulations using a one-dimensional steady-state model of a heterogeneous catalyst bed. They have simulated the reactor under steady-state conditions and compared the simulation results with the data obtained from a pilot-scale reactor. Moreover, they considered the effectiveness factor for the catalyst pellets and obtained temperature and concentration profiles along the reactor catalyst bed height.

The objective of the current study is to develop model equations that predict the change in the concentration of methanol, DME, and water along the reactor catalyst bed height; and the temperature of the reactor along the reactor catalyst bed height as the reaction proceeds; and to investigate the effect of operating parameters on the production of DME through methanol dehydration. This is achieved by first developing mathematical models describing the reactors using the principle of conservation of mass and energy.

2. REACTOR MODEL DEVELOPMENT

Figure 1 shows the hypothetical representation of a catalytic shell and tube fixed-bed reactor for the production of DME. The feed is introduced into the tube side of the reactor after being heated in a heat exchanger. The reaction is highly exothermic, for this reason; hence cooling water is passed through the shell side of the reactor to remove the heat of reaction as the reaction proceeds.

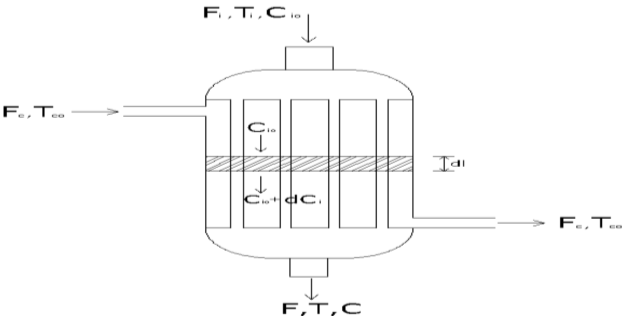

Figure-1. Hypothetical representation of a catalytic shell and tube fixed-bed reactor

Considering the mass and heat transfer occurring in the differential control volume ($A_R dl$) where A_R is the uniform cross sectional area of the control volume and dl is the height of the control volume with inlet and outlet concentration of components i as C_i, and ($C_i + dC_i$) respectively, where F_i and F are the inlet and outlet flow rates of species *i* respectively in m^3/s; C_i and C_{io} are the inlet and outlet concentrations of species i respectively in mol/m^3; F_c is the flow rate of coolant in m^3/s; T_{ci} and T_{co} are inlet and outlet temperatures of the coolant in ^oC; V_R is the volume of the reactor in m^3; A_R is the cross-sectional area of the reactor in m^2; L_R is the length of the reactor in *m*.

2.1. Model Assumptions

The following assumptions were made to develop the mathematical model for the production process of DME via methanol dehydration in a catalytic shell and tube reactor.

- A one-dimensional pseudo homogenous system is assumed.
- Radial variation of both temperature and concentration are neglected.
- Internal and external diffusions are not taken into account.
- The reactor operates under steady state condition.
- An open loop response system is assumed.
- Catalyst effectiveness factor is taken to be unity

The component mass balance equation is obtained by applying the principle of conservation of mass as:

$$U_o \frac{dc_i}{dl} = (r_i)\varepsilon \qquad (1)$$

where r_i is the rate of reaction of component *i*, ε is the void fraction, U_o is the fluid superficial velocity, and *i* represents components A, B, and C.

In terms of components A, B, and C, equation (1) for each component with *i* = A, B, C becomes:

$$U_O \frac{dC_A}{dl} = (r_A)\varepsilon \qquad (2)$$

$$U_o \frac{dc_B}{dl} = (r_B)\varepsilon \qquad (3)$$

$$U_o \frac{dc_C}{dl} = (r_C)\varepsilon \qquad (4)$$

By applying the principle of conservation of energy to the elemental volume in Figure 1, the energy balance equation is obtained as:

$$\frac{\partial T}{\partial l} = \frac{(\Delta H_i)(r_i)A_R}{F_i \rho_f C_{p_f}} - \frac{UO_H}{F_i \rho_f C_{p_f}}(T - T_w) \qquad (5a)$$

Equation (5a) can be written as: ``

$$\frac{\partial T}{\partial l} = X(r_i) - Y(T - T_w) \qquad (5b)$$

where $x = \frac{(\Delta H_i) A_R}{F_i \rho_f C_{p_f}}$, and $Y = \frac{U O_H}{F_i \rho_f C_{p_f}}$ (6)

Equations (2), (3), (4) and (5) are the model equations that describe the changes in concentration of the various components and the temperature in the reacting system along the height of the reactor.

2.2. Kinetic Reaction Model

The DME synthesis involves the dehydration of methanol on the surface of the catalyst. This reaction is reversible and exothermic. The kinetic model [9] was used in this work, as follows: The chemical reaction involved during the production of DME using the indirect method is mainly the dehydration of methanol. It is an exothermic and equilibrium reaction. The kinetic model [9] is as follows:

$$2A \leftrightarrow B + C \qquad (7)$$

With a heat of reaction given as: $\Delta H = -23.4 kJ/mol$

where *A* isCH_3OH (methanol), *B* is CH_3OCH_3 (dimethyl ether), *C* is H_2O (water).
The kinetic rate expressions for the components are as follows:

$$r_A = \frac{k\, K_A^2 \left(C_A^2 - {}^{(C_B C_C)}/_{K_{eq}} \right)}{(1 + 2(K_A C_A)^{0.5} + K_C C_C)^4} \qquad (8)$$

$$r_B = K_A^2 C_A^2 - k C_B \qquad (9)$$

$$r_C = K_A^2 C_A^2 - k C_C \qquad (10)$$

where k is the kinetic rate constant, $m^3/kmol.s$; K_i is the adsorption constant of species i, $m^3/kmol$; K_{eq} is the equilibrium constant, C_i is the concentration of species i, $kmol/m^3$.

The reversible reaction equilibrium constant K_{eq}, in the rate equation is determined using equation (11):

$$ln(K_{eq}) = 0.86 \log T + \frac{3138}{T} + 1.33 \times 10^{-3} T - 1.23 \times 10^{-5} T^2 + 3.5 \times 10^{-10} T \qquad (11)$$

The chemical reaction rate constant (k) is a function of temperature and is generally determined using the Arrhenius relations [4].

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \qquad (12)$$

Where k_o is the chemical reaction kinetic pre-exponential constant and E the activation energy, and values depicted in Table1.

While the catalytic surface reaction adsorption equilibrium constant (K) for component B and component C also is a function of temperature and is generally determined using the Arrhenius relations [4, 5] as:

$$K_i = K_{i0} \exp\left(\frac{-Ei}{RT}\right) \tag{13}$$

where K_{io} is the catalytic surface equilibrium adsorption pre-exponential constant and subscript i represents component B and component C and the values depicted in Table 1.

2.3. Pressure Drop along the Reactor Catalyst Bed Height

The pressure drop across the reactor length due to the flow of fluid is estimated using the Ergun Equation [5].

$$\frac{\Delta P}{L} = \frac{150\mu\,(1-\varepsilon)^2 U_o}{\varepsilon^3 d_p^2} + \frac{1.75(1-\varepsilon)\rho U_o^2}{\varepsilon^3 d_p} \tag{14}$$

Where ΔP is the pressure drop across the reactor, L is the height of the catalyst bed, μ is the fluid velocity, ε is the void fraction, U_o is the fluid superficial velocity, d_p is the catalyst particle diameter, ρ is the density of the fluid.

2.4. Operating Parameters

The kinetic parameters, physical properties of the feed, reactor dimensions and operating conditions of the reactor which are part of the numerical parameter incorporated into the model equations (2), (3), (4), and (5) and correlation required to integrate numerically the mass and energy balances equations are presented in Table 1 and 2.

Table-1. Kinetic Parameters [4]

	k_0	E	[5]
k	$3.7e^{10}$	-105000	
K_{CH_3OH}	$7.9\ e^{-4}$	70500	
K_{H_2O}	$0.84\ e^{-1}$	41100	

Table-2. Properties of feed, catalyst and operating conditions [2, 4, 5, 10]

Property	Value	Reference
FEED		
Molecular weight (kmol/kg)	32.04	[10]
Boiling point (K)	338.4	
Density of fluid at a temperature of 533K (kg/m^3)	14.38	
Specific heat capacity (kJ/kmol.K)	67.08	
Catalyst		
Name of catalyst	Alumina (Al_2O_3)	[2]
Voidfraction	0.4	
Catalyst diameter (m)	0.0054	
Bed density (kg/m^3)	780	
Length of catalyst bed (m)	6	
Specific heat capacity (kJ/kmol.K)	104	
operating conditions		
Number of tubes	2000	[4]
Tube diameter (m)	0.09	
Reactor length (m)	8	[5]
Reactor internal diameter (m)	4	
Temperature (K)	533	
Pressure (bar)	18.2	
Fluid superficial velocity (m/s)	0.278	
Feed volumetric flow rate (m^3/s)	3.5	
Molar volume of feed (m^3/kmol)	2.228	
Molar feed flow rate (kmol/s)	1.586	
Space time (s)	28.72	

2.5. Solution Technique

In order to solve the mass and energy balance equations, the initial values for the pressure of methanol, partial pressures of DME and water P_A, P_B, P_C respectively, and their concentrations C_A, C_B, and C_C respectively, as well as the temperature of the feed at the entry of the reactor ($z = 0$) are summarized in Table 3.

Table-3. Boundary conditions [Seyyed and Mohammad [11]]

Boundary condition	Value	
$P_A(z = 0)$	1820kPa	[11]
$P_B(z = 0)$	0	
$P_C\ (z = 0)$	0	
$C_A(z = 0)$	0.448kmol/m^3	
$C_B\ (z = 0)$	0	
$C_C(z = 0)$	0	
T (z = 0)	533K	

The mass and energy balance equations corresponds to a system of ordinary differential equations. These equations were integrated numerically using the Fourth-order Runge-Kutta technique. The algorithm is used to develop a MATLAB program (MATLAB 7.7 CODE) to solve the model equations.

3. RESULTS AND DISCUSSION

Table 4 shows the comparison between data obtained from literature and prediction from model equations (2), (3), (4), and (5), indicating that the predicted data agree reasonably well with the data obtained from literature [Farsi, et al. [4]].

Table-4. Comparison of model prediction results with literature data [Farsi, et al. [4]]

	Model Prediction	Literature Data [4]	% Deviation
DME molar flow rate (kmol/hr)	2519.5	2506	0.5
Methanol molar flow rate (kmol/hr)	940.3	937.7	2.7
Methanol conversion (%)	87.86	85.75	2.4
Temperature (K)	636.32	644	1.2

The result shows a deviation ranging from 0.5 to 2.7 percent which implies that model is reasonable.

3.1. Variation of Methanol, DME and Water Concentration along the Reactor Height

Figure 2 shows the variation of the methanol (feed) concentration and the products (DME and water) with the reactor catalyst bed height, indicating that the concentration of methanol decreases as the height of the reactor increases, while the concentrations of DME and water increases as the height of the reactor height increases. The reaction occurs rapidly from the reactor inlet and becomes steady at about 2-4m from the inlet. About 87% of the feed is converted to the products, DME and water. A substantial amount of the feed is converted to the desired product. The mole fraction of DME in the product is 0.67. The reaction occurs rapidly from the reactor inlet and becomes steady at about 2-4m from the inlet. This is made possible by the selectivity of the alumina catalyst used. Its selectivity is in favour of DME production. This is very important because water production in the course of the reaction.

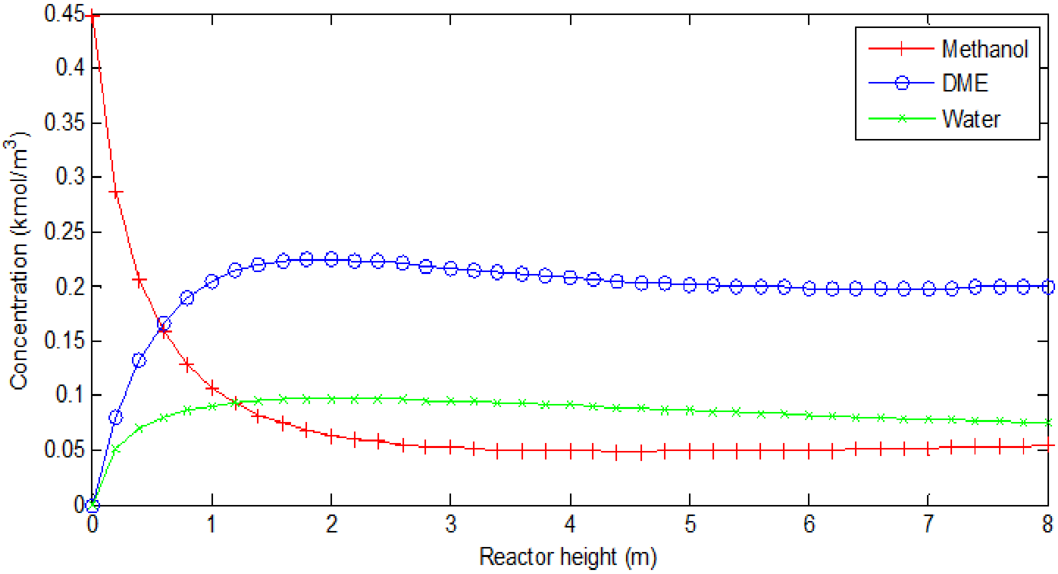

Figure-2. Variation of methanol, DME, and water concentration along the reactor height

Leads to catalyst poisoning, therefore the amount of water produced is kept at its minimum, and meanwhile, the reactor effluent is collected quickly to prevent build up of water in the system [12].

3.2. Volumetric Feed Flow Rate

Figure 3 shows the effect of volumetric flow rate on the concentration of the feed along the length of the reactor. For the DME production process, the amount of methanol that exited the reactor is 0.0749kmol/m^3, giving a conversion of 87.7% at a volumetric flow rate of 3.5m^3/s. It was noticed that when the feed flow rate was reduced, the amount of methanol that exited the reactor was also reduced giving a higher conversion. When the flow rate was increased, the amount of methanol that exited the reactor was increased, giving a lower conversion. This implies that the volumetric feed flow rate has a large effect on the production of DME. This is because the higher the feed flow rates the smaller the space time, and this means the reactant spends lesser time with the catalyst to be converted to product, resulting to a smaller conversion. Therefore, the feed flow rate is indirectly proportional to the conversion of the reactant. At a feed flow rate of 3.01m^3/s, the methanol concentration at the exit of the reactor is 0.0154kmol/m^3 giving a conversion of 96.6%. When the flow rate was increased to 3.27m^3/s, the resulting methanol concentration at the reactor exit is 0.0365kmol/m^3 91.9%.

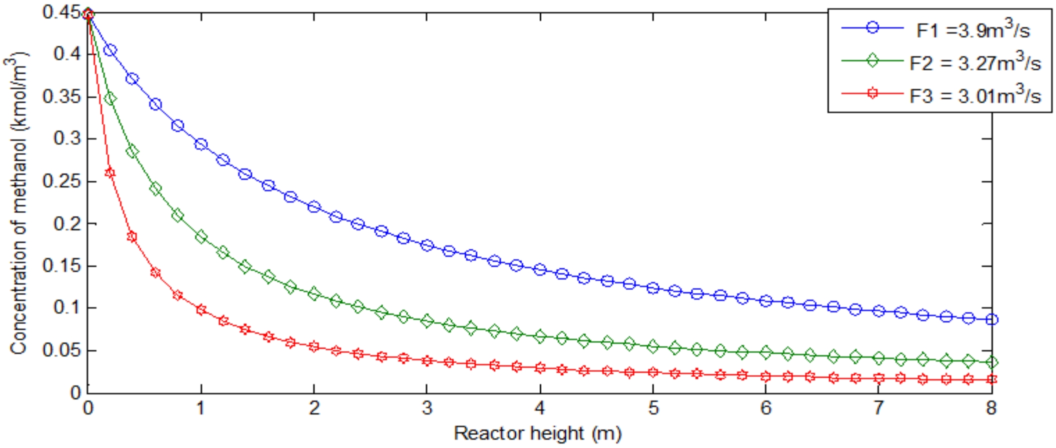

Figure-3. Effect of volumetric flow rate on feed concentration along reactor

An increase in the methanol flow rate from 3.27 to 3.9kmol/m^3 gave a methanol of 0.0871kmol/m^3 at the exit of the reactor resulting in a conversion of 80.5%.

3.3. Temperature

Figure 4: shows the effect of inlet temperature on the outlet concentration of DME. At low inlet temperature of 363K, the reaction increases gradually along the bed height, giving a concentration of 0.1351kmol/m^3 DME at the exit of the reactor at a temperature of 430K. Increasing the inlet temperature to 453K shows a rapid yield of DME at the first 1m of the reactor, and subsequently, a sluggish increase is observed all through the rest of the reactor length; leading to a concentration of 0.1715 kmol/m^3 of DME and an exit temperature of 541K

Subsequent increase in the inlet temperature shows a very rapid production rate that reaches a maximum and then declines gradually and becomes steady with negligible change in the concentration with increasing temperature. This trend is noticed because the production process involves a reversible exothermic reaction. More so, the catalyst starts deactivating due to high temperature and accumulation of water within its pores.

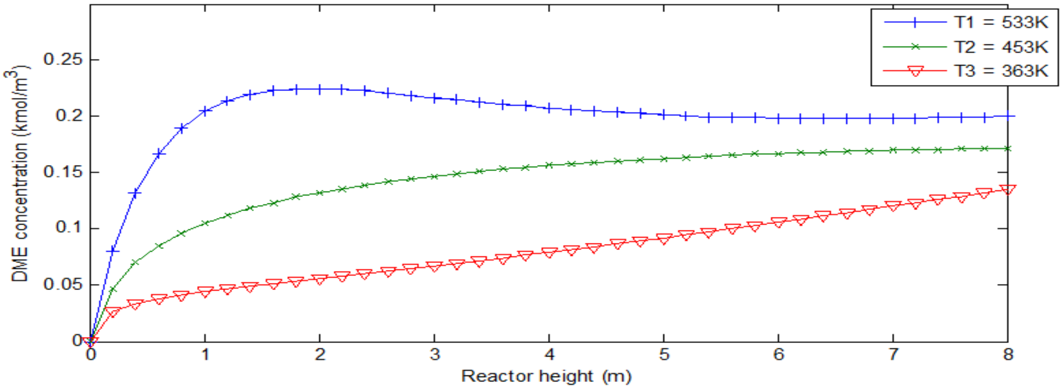

Figure-4. Effect of inlet temperature on the outlet concentration of DME

4. CONCLUSION

Model equations of a tubular fixed-bed reactor for the production of DME through methanol dehydration were developed using the principle of conservation of mass and energy. The models predict the change in the concentration of methanol, DME, water and the temperature progression along the reactor catalyst bed height, as the reaction proceeds. The kinetic parameters for the model were obtained from literature and the model predictions were validated with data obtained from literature operating under the process operating conditions.

The results of model prediction agree reasonably literature data with a percentage deviation ranging from 0.5% to 2.7%. Simulation results indicate that feed volumetric flow rate, and inlet temperature of feed are major process variables that affect the performance of the reactor with optimum yield of DME at a catalyst bed height of 2m. The sensitivity analysis made on the operational parameters showed that the conversion of methanol increased with temperature, reaching an optimum temperature of about 560-575K. It was also noticed that the feed volumetric flow rate greatly affects the conversion of methanol. Increasing the flow rate led to a lower conversion of methanol, and reducing the flow rate increases the conversion of methanol.

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Nomenclature

A_R	**Cross-sectional area of reactor**	***M***
C_i	Concentration of species i	*kmol/m³*
C_{p_f}	Specific heat capacity of the fluid	*kJ/kmol.K*
C_{p_s}	Specific heat capacity of the catalyst	*kJ/kmol.K*
F	Molar flow rate	*m³/s*
ΔH_i	Heat of reaction of the system	*kJ/kmol*
L_R	Height of the reactor	*M*
O_H	Circumference of the cross section of the reactor	*M*
r_i	Rate of reaction of species i	*mol/m³.s*
T	Temperature	*K*
U_o	Superficial velocity	*m/s*
U	Heat transfer coefficient	*W/m².K*
V_R	Volume of the reactor	*m³*
V_f	Volume of the reactor occupied by the fluid	*m³*
V_s	Volume of the reactor occupied by the catalyst	*m³*
Greek letters		
ρ_s	Density of catalyst	*kg/m³*
ρ_f	Density of fluid	*kg/m³*
z	Dimensionless space	
ε	Void fraction	
Subscripts		
A	Methanol	
B	Dimethyl ether	
C	Water	
F	Fluid	
R	Reactor	
S	Catalyst	