MODELING OF DIMETHYL ETHER SYNTHESIS FROM METHANOL IN FIXED BED REACTOR

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree
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By

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented by me in the seminar report entitled "**MODELING OF DIMETHYL ETHER SYNTHESIS FROM METHANOL IN FIXED BED REACTOR**", in partial fulfilment of the requirements for the award of degree of Master of Technology in Chemical Engineering with specialization in "Industrial Safety and Hazard Management", submitted to Department of Chemical Engineering, Indian Institute of Technology, Roorkee; is an aunthetic, Department of Chemical Engineering, IIT Roorkee. The matter embodied in this project work has not been submitted for the award of any other degree

Date :

Place : IIT , Roorkee SAKSHAMA PURI

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The extraordinary property of DME made it an alternative to LPG, natural gas and diesel. DME has attracted attention of many researchers from industrial purposes. Methanol dehydration carried out in adiabatic fixed bed reactor is production process of DME synthesis. In present work, the reactor is preceded by feed preheater has been simulated under unsteady state conditions. Non linear Partial differential equation was solved considering it to one dimension pseudo homogenous model. Validation of model was done on comparing simulation results with experimental data.

For model simulation, adiabatic fixed bed reactor was packed with 1.5 mm γ-Al_2O_3 pellets as catalyst. The process occurred in the temperature range of 543-603 K at atmospheric pressure. Also, the effect of WHSV, temperature, and flow rate on conversion of methanol was monitored. By adding water to methanol feed, catalyst deactivation take place rapidly. Hence, the results were obtained considering pure methanol as a feed.

Keywords: Catalytic dehydration, Fixed bed reactor, Catalyst deactivation, Weight hourly space velocity (WHSV) and Industrial reactor

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A	cross-sectional area of bed,(m^2)
Ci	molar concentration of component i ($kmol.m^{-3}$)
Cp	specific heat of the gas at constant pressure ($kJ.\ kg^{-1}.K^{-1}$)
dp	catalyst diameter (m)
ΔH_r	Heat of reaction ($kJ.kmol^{-1}$)
k	rate constant of dehydrogenation reaction ($mol.m^{-3}\ .\ Pa^{-1}\ .s^{-1}$)
Keq	reaction equilibrium constant for methanol dehydration reaction ($mol.m^{-3}$)
P	total pressure (Bar)
r	rate of methanol disappearance ($kmol.kg^{-1}.h^{-1}$)
T	temperature (K)
u	superficial velocity of fluid phase ($m.h^{-1}$)
ν_i	Stoichiometric coefficient
z	distance along bed height (m)
ρ	Gas phase density ($kg.m^{-3}$)
ε	dense-phase voidage, dimensionless,(void fraction)
ρ_b	Catalyst bed density, ($kg.m^{-3}$ **)**

Subscripts

b	bubble phase
M	Methanol
W	Water
i	chemical species
s	at surface catalyst
o	inlet conditions

CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

Synthesis from coal or natural gas has attracted many countries in latest years. Amongst them is DME ; which has made great effect on society. Dimethyl sulphate can also be prepared using DME . During combustion process of DME no pollutants such as CO , hydrocarbons and other particulates.DME has properties more of similar to LPG, hence it can easily be stored and transported. Neither powder or soot is being emitted by car using DME as a fuel ,hence it can be used as a good replacement for diesel . Dimethyl Ether , which is also referred as methoxymethane. It is colourless gas with ether like smell, volatile, with zero toxic level. It is useful precursor to other organic compound. DME has a property of being used as an aerosol propellant to replace chlorofluorocarbon. Its physical and chemical properties can be summarised as follows:

- DME has higher centane number and low auto ignition temperature.

- Contains C-O along with C-H bond. It doesn’t include any C-C bond having 38%oxygen, therefore, products on combustion like CO, other hydrocarbons are less.

- DME has more latent heat of evaporation on comparing it with natural gas, hence quite affordable to NOx reduction.

- DME boils at-25 °C, more than that of LPG and liquefies at 0.54 MPa.

1.2 APPLICATIONS

1.2.1 Feedstock

DME is used for the production of methylating agent consuming thousands tons of DME on addition of sulphur trioxide.

- $CH_3OCH_3 + SO_3 \rightarrow (CH_3O)_2SO_2$ ....(1)

Using carbonylation technology which is related to Monsanto acetic acid process, DME is converted to acetic acid.

- $(CH_3)_2O + 2\ CO + H_2O \rightarrow 2\ CH_3CO_2H$.........................(2)

1.2.2 Fuel

DME can be manufactured from lignocellulosic biomass and is developed as second generation synthetic biofuel.

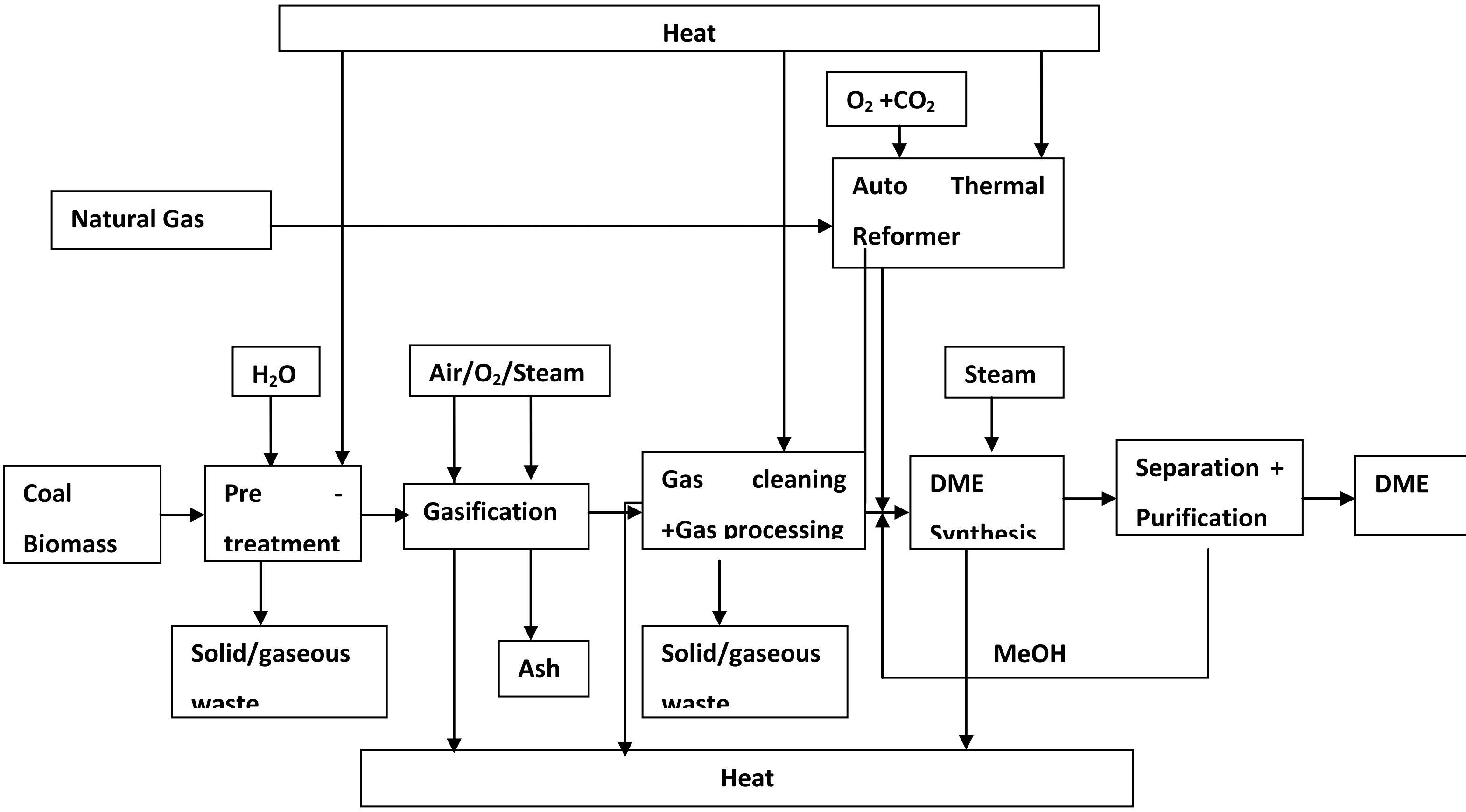


Figure1.1 Illustrates processes from various raw material to DME

1.2.3 Refrigerant

DME can also be used as refrigerant with ASHRAE refrigerant with designation R-E170. It is also used with refrigerating blend like butane and propene.

1.2.4 Treating Warts

Mixing propane with DME can be used to treat warts by freezing them.

1.3 PRODUCTION

Mainly two processes are defined for the preparation of DME, indirect and direct processes. Two step process or indirect process is generally performed in adiabatic packed bed reactor in presence of acidic catalyst. The other process known as direct process or single step in this DME is produced directly from synthesis gas using bifunctional catalyst.

INDIRECT PROCESS

$$2CH_3OH \longleftrightarrow CH_3OCH_3 + H_2O \text{..................................}(3)$$

DIRECT PROCESS

$$3CO + 3H_2O \longleftrightarrow CH_3OCH_3 + CO_2 \text{...............................}(4)$$

On comparing both the processes: direct process is more advantageous mainly of following reasons:

- DME synthesis in single step process is the low value thermodynamic process than methanol synthesis.
- As production of methanol is done along with DME using same reactor. methanol and DME are produced in same vessel, hence cost to purify methanol is negligible.

Approximately 50,000 tons of DME were produced in 1985 in Western Europe via methanol dehydration. Producing DME on large scale commercially is done by catalytic dehydration of methanol using fixed bed reactor **[Makarand et al. 1992].** Production can also be done using any of the reactor amongst packed bed. Its advantageous to use slurry reactor as it has property of removing heat from coil.**[Guo J .W et al. 2000].**

1.4 CATALYST USED

The reactions occurs reversibly and exothermically. Besides this, the catalyst used in the process deactivates when charged at temperature above 270° C. This deactivation should not be done hence operated at lower value of conversion per pass so that temperature should not exceed above 270°C, leading to increase the cost of installing the process. Continuing with it, the pressure drop should be very low by keeping small catalyst size of 4mm. Generally equation 1 is governed by acidic catalyst and equation 2 is governed by $Cu/ZnO/Al_2O_3$.

1.4.1 CATALYST PREPARATION

In preparing commercial catalyst, Cu-Zn catalyst was needed for synthesis process of methanol and γ - Al_2O_3 was used as a catalyst for dehydration of methanol. Cu-Zn was mixed with γ - Al_2O_3 in ratio 1:1. This mixture of catalyst was required in preparing DME for finding condition suitable for yielding high amount of DME. CO precipitation method was also used for the preparation of catalyst used in DME synthesis. $Cu(NO_3)_2.3H_2O$ and $Zn(NO_3)_2.6H_2O$ separate solutions were prepared. Adding this mixture to prepare sodium carbonate. Adding few drops of $Cu(NO_3)_2$-$Zn(NO_3)_2$ slowly till pH becomes 7. Precipitation was carried out. Filter the precipitate when it cools. Maintaining the ratio as 1:1 the precipitate produced was added to γ-Al_2O_3. Distilled water was added to this mixture and was blended and again filtered. The catalyst was dried overnight in oven at temp of 1050° C. This process goes same while preparing another catalyst named 2. γ--Al_2O_3 was mixed together with Na_2CO_3 while precipitating. Same steps are followed for making catalyst 2.

Results obtained experimentally proved that Cu-ZnO-ZrO_2/Al-modified H-Mordenite was a appropriate catalyst for preparing DME from synthesis gas and the appropriate ratio of methanol synthesis catalyst (Cu-ZnO-ZrO_2) to methanol dehydration catalyst (Al-modified H-Mordenite) was 2:1. At this condition, DME synthesis and CO conversion were around 82% and 68%. Hence stability of this catalyst was noticed without noticeable reduction in selectivity and conversion. Researchers advised that catalyst should not have any form of sulphur or sodium. Considering this catalyst was prepared using Cu and Zn solution that are free from sodium or sulfate ions. In many process adding thermal stabilizer is suggested that includes Zr, Al, Ti, Si, Ca and Mg. Thermal stability increases on increasing quantity of stabilizer. Precipitation is followed by calcinations for decomposition of carbonates to form oxides. The catalyst gets reduced before synthesis process and reducing it by passing reducing gas(H_2 in N_2) over the catalyst. There is absence of H_2O in off gas.

Also, effect of various other operating conditions were investigated like temperature, feed flow rate , pressure to obtain an optimum bi functional catalyst. Optimum temperature was calculated to be as 250° C. Conversion of synthesis gas can be increased on increasing the temperature till 270 °C. However, selectivity of DME was reduced at higher temperature. Considering pressure, on increasing pressure conversion of synthesis gas increases while DME synthesis remains constant. However, on increasing the feed flow rate, CO conversion was reduced along with selectivity.

Today, production process of DME is carried out using dehydration of methanol and is conducted in fixed bed reactor. Operating heterogeneous process loss of catalyst occurs on passage of time. In indirect process using γ-Al_2O_3, water plays an important role in catalyst deactivation **[Jun K-W et al. 2003].**

One of the advantages in producing DME by single step is that the reaction can be forwarded at higher temperature and lower pressure. If the reaction is highly exothermic or endothermic there is a problem related to catalyst sintering or reaction extinguishing **[Fogler Scott H. 2000].** The perfect reactor for this process is fluidized bed reactor **[Ray Y.C et al. 1987, Petukhov Y et al.2003].** Better heat removal occurs in fluidized bed bas catalyst particles move in bed of catalyst. However , loss of catalyst can take place due to collision between reactor wall and catalyst particles.

1.4.2 CATALYST MEMBRANE PREPARATION

Membranes of catalyst were prepared following methods of communicating vessels. Lower part of it was connected by the flexible polyurethane tube. In vertical portion it was supported using tubular. Lower part has solution mixed with isopropanol. Level variation was done in F -4SF .Movement speed was 0.5 cm/s and contact period was 80 sec. After one run, membrane was kept for 10 min at 25°C so that remaining solvent can evaporate.

Drying the tubes so that it gets hardened in oven 40 °C for 6hrs and 100°C for 4hrs. The quality of this composite membrane was predicted by gas permeability with respect to nitrogen and oxygen.

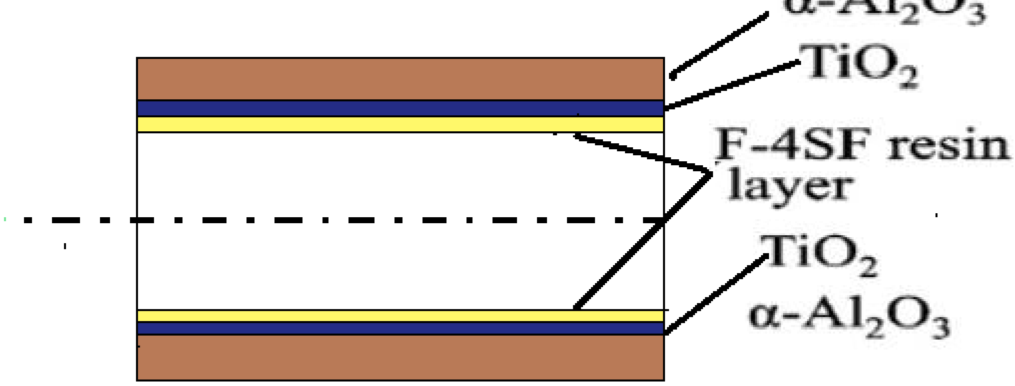


Figure 1.2. catalytic ceramic membrane (F -4SF)

1.4.3 CATALYTIC MEMBRANE REACTOR(CMR)

The below figures shows the representation of CMR and process diagram shows the supply of feed and outlet products. It consists of shell having dimension as inner dia = 12.75 mm, outer dia= 16mm. Inside housing membrane was covered on either side with O- rings. It consists of two inlet valve (V1 and V3) and two outlet valves(V2 and V4). Inlet of (methanol\vapor) with nitrogen were supplied from V1 and V3. This reactor was used in experimental study for determining methanol conversion.

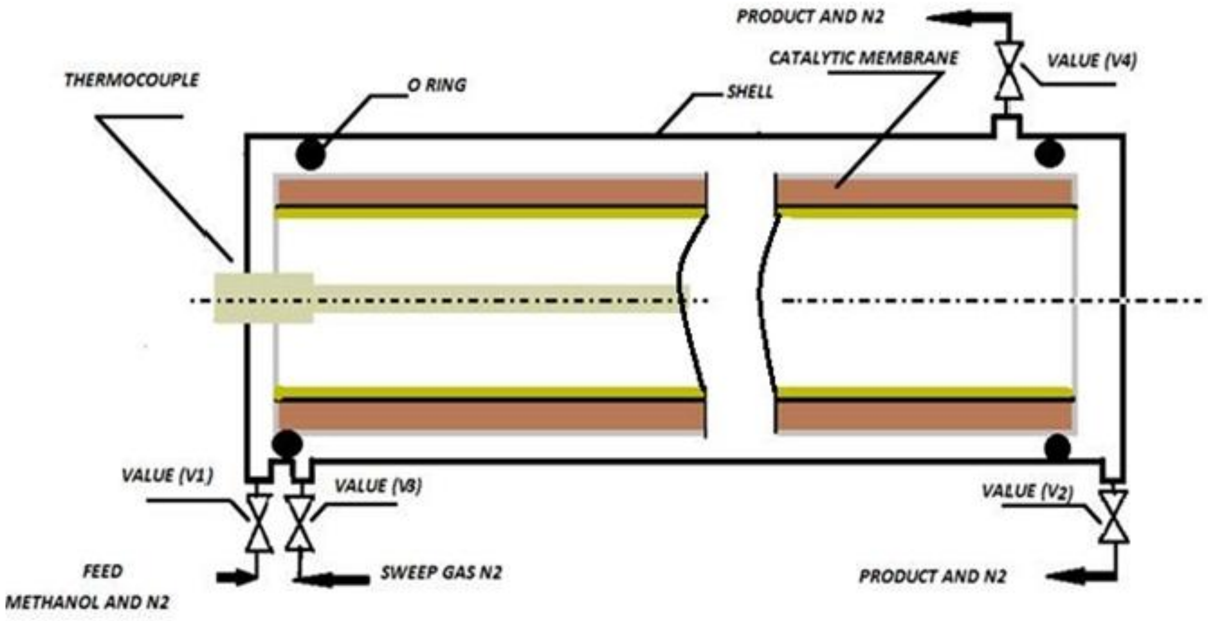


Figure 1.3. Illustrating a catalytic membrane reactor.

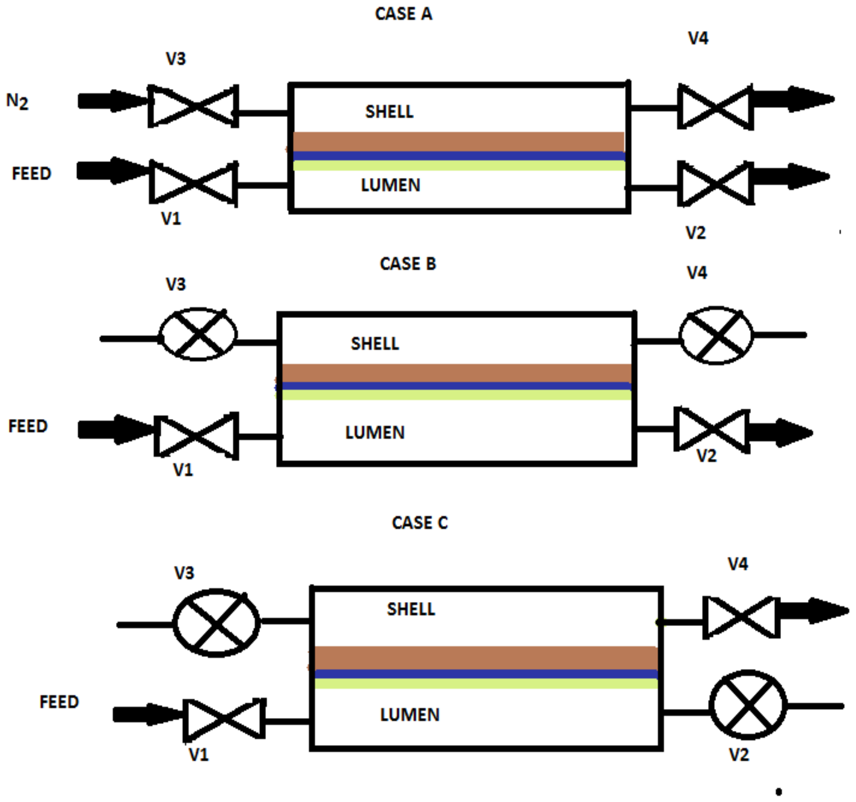


Figure 1.4. Different modes for supply of feed and outlet products

1.5 OTHER METHOD FOR DME SYNTHESIS

Production of DME can be done using syngas as feed for which Eucalyptus wood is important source. Following are the reaction occurring parameters: P= (2MPa), temperature (230 °C -270 °C), gas flowing in range of 50-100 mL/min, catalyst having weight in range of 3-5 gm with catalyst ratio (1:1).

DME synthesis process is shown. It has a gas cylinder for providing syngas as feed ; glass reactor of height 120mm was placed inside the furnace.

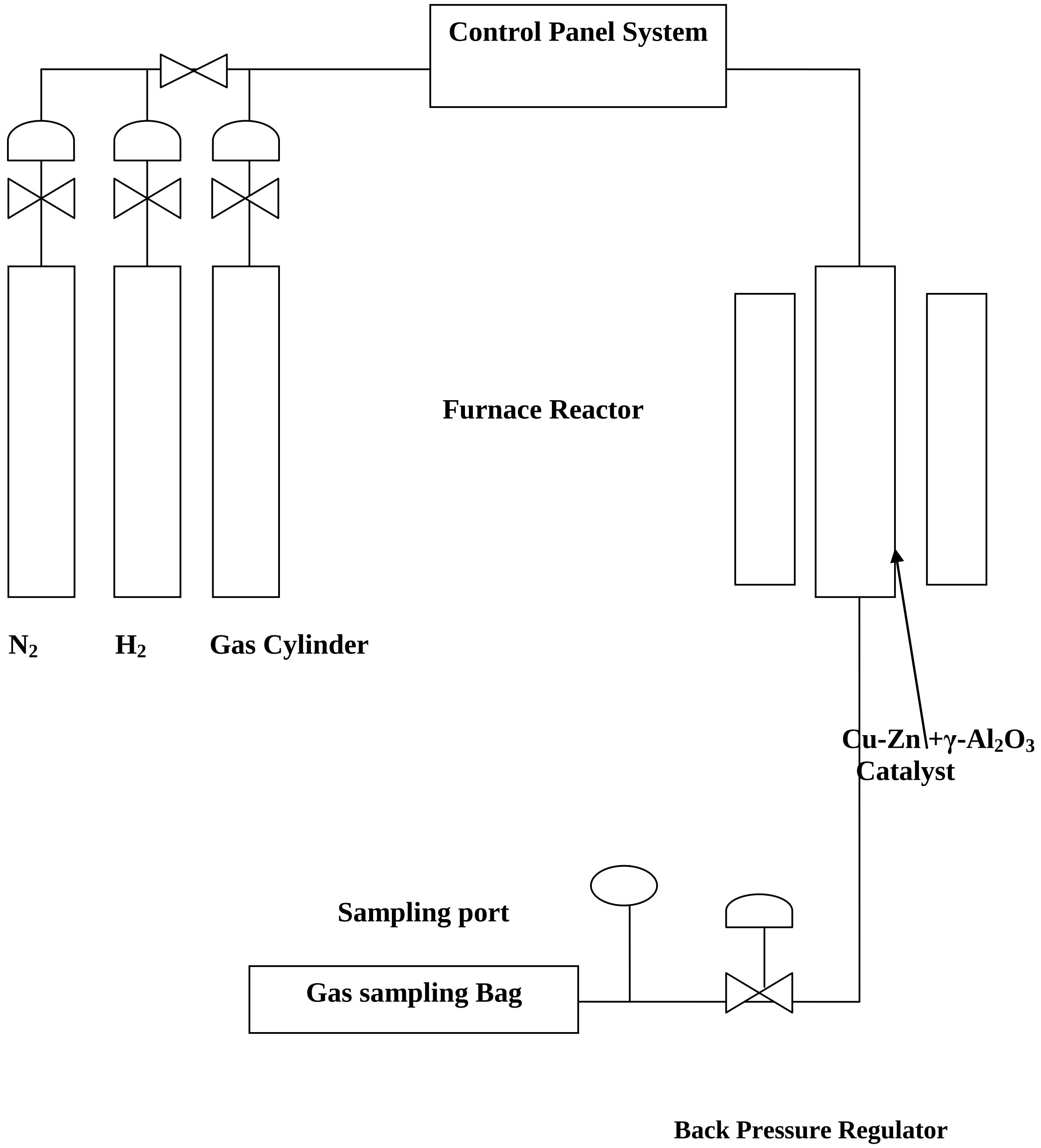


Figure 1.5. Representation of DME synthesis from syngas

Figure 1.5 shows representation of synthesis of DME synthesis from syngas schematic diagram of DME synthesis process. 3-5 gram Cu-Zn+ γ-Al_2O_3 catalyst was filled in middle. Before DME synthesis could start, reduction of catalyst was carried using H_2/N_2 at 230°C for complete 1 hour. Gas flow rate was kept at 100ml/min at 1 atm. Flow rate of gas was encountered by gas control unit(GCU). Back pressure unit was placed for controlling conditions at which system operates. After catalyst is reduced Completion , DME synthesis process was started. Gas was collected in gas sampling bag and analysed. From results yield of DME with conversion in CO can be estimated.

Table 1.1 shows the comparison between various reactors for DME synthesis at various operating conditions. Results showed that fixed bed reactor working isothermally gives maximum conversion of CO. Very less conversion could be seen in shell and tube type heat exchanger.

In present thesis we are considering adiabatic fixed bed reactor working at different inlet temperature and finding the optimum conditions to obtain maximum methanol conversion.

Type of Reactor	**Operating Temp(K)**	**Pressure at which reactor operates (MPa)**	**Conversion in CO**	**Loading of Catalyst (g)**	**H_2/CO**	**Dia of Reactor (m)**	**Height of (m)**	**Reference**
Fixed bed	503-543	4	17%	108	2.6	0.015	1.1	Wang et al
Fixed- bed tubular reactor	533	4.3	82-67.7%	1200	2	0.032	2	Li et al
Isothermal fixed bed reactor	548	4	95%	-	2	0.0064	0.1524	Erena et al
Shell tube type fixed bed reactor	553	5	39.85%	7850	1.5	0.03	1.6	Song et al
Internal recycle type reactor	523	5	-	-	-	-	-	Ng et al
Back mixed slurry reactor	473-623	5.27	50-60%	-	-	-	-	Brown et al
Fluidized bed	523	6	92.08%	800	1.4	0.003	2	Lu Wen Zhi et al

Table 1.1 : Reactor Comparisons

CHAPTER 2

LITERATURE REVIEW

A lot of modeling and simulation along with experimental work has been done on process naming direct process and indirect process in preparation of DME using various reactor configuration. Simulating packed bed reactor is not an easy work to perform as many non linear partial differential equations are evaluated with many algebraic relationships.

Hosseini and Khosravi Nikou (2012) One dimensional heterogeneous model for methanol dehydration to DME production using γ- Al_2O_3 as a catalyst was modeled in adiabatic fixed bed reactor. Temperature and conversion graph were plotted. Using this reactor model, temperature from temperature-conversion graph keeping rate constant at various inlet temperature was calculated. Pressure along with effect of mass flow rate was investigated. Results showed that maximum conversion was obtained at optimum operating condition was 81.36 %.

Volkov et al. (2012). The dehydration of methanol in vapour phase with the use of CMR was not investigated previously. Production of membrane was by adding F-4SF resin onto inside surface of membrane. This CMR was further used in different modes of supply of feed with outlet products . Amongst those three configurations, the maximum conversion of methanol was 36.4% having selectivity of DME of 100% was demonstrated.

Javier et al. (2011). The kinetic model proposed by him completely fits the experimental results for CO_2 conversion and product yield with the evolution of time using CuO-ZnO-Al_2O_3/γ-Al_2O_3 bifunctional catalyst. Catalyst deactivation is slower for DME synthesis from syngas. It was seen; the presence of having CO_2 concentration term, measure depletion of methanol rate of reaction with preparation of paraffin. In DME synthesis from syngas ; water plays an important role, it effects reaction rate and coke deposition. On further study of parameters , suitable conditions were selected for maximizing the production of DME and minimizing catalyst deactivation. The conditions were as follows:

Temperature :270 °C, pressure 40 bar and H_2/CO_2 ratio in feed as 4/1.

Liang et al. (2011) In an isothermal fixed bed reactor, methanol Dehydration to produce DME over Al_2O_3 was investigated. The experiments were conducted at temperature interval of 513-613 K , with LHSV in range of 0.9-2.1 h^{-1}, keeping pressure range from 0.1 to 1 MPa. Experimentally, changes made in operating conditions for dehydration of methanol dehydration were noticed. Using Langmuir Hinshelwood different intrinsic kinetic equation was formed . 67.21kJ/mol of activation energy was liberated . Hence the developed model with kinetic equations was valid.

Vakili et al. (2011) . As DME is used because of it is friendly to the environment, Generally DME is prepared by process also referred as indirect process for production of DME. But a new method is defined known as direct DME synthesis which is more advantageous than indirect process due to its economical superiority.

In new process, both generation and methanol dehydration occur at same instant using hybrid catalyst hence purification unit of methanol was not considered. Main objective evaluated by **R. Vakili** was optimizing conditions at which reactor operates to obtain maximum DME production along with benzene mole fraction in outlet stream. Using these results, reactor performance would become better by changing production rate or products along with flow rate. Hence reducing the operating cost and increasing net profit of plant.

Fatemen et al. (2010) Production of DME was done using syngas in a micro channel, using hybrid catalyst mixture. Operating conditions were 60 bar pressure and 210-300 °C temperature. The graph for temperature was evaluated after measuring along with simulating values from reactor. As micro channel reactor provided best operating conditions isothermally. Hence, various parameters effecting selectivity with respect to product formation and production of DME can be studied. But problem using γ-Al_2O_3 , as it is inactive catalyst for dehydration process. At lower value for DME equilibrium, value for conversion of CO along with production rate of DME was initiated by high value for temperature as well as pressure. Maximum value for conversion of CO was obtained when H_2 having large quantity of syngas was used.

Eslamloueyan et al. (2010) DME production was done using heat exchanger with packed bed reactor. Before feed was entered in the reactor, it was heated inside exchanger by using heat that was provided from the exit products. Products were sent to purify in purification unit for DME and water and methanol was separated from DME. Methanol that was not used during the process was sent back inside the reactor. Equations were developed for modeling of both reactor as well as feed pre heater. **Eslamloueyan** studied, heterogeneous model one dimensionally at steady state.

Jalil et al. (2010) As DME is clean alternative fuel for diesel engine because of lesser emission of NOx, low carbon particles, low engine noise with low smoke production. Synthesis of DME can also take place from syngas using catalysts that contains Cu/Zn for production of methanol along with γ- Al_2O_3 as methanol dehydration of methanol catalyst. Various conditions for reaction to occur were investigated. Temperature, reaction pressure, feed flow rate, catalyst weight and GHSV effects DME production. It was found that, maximum yield of DME was obtained at 280° C, at 2M Pa. Reaction was carried out for 5 hour. CO conversion at this condition was 2.52% and H_2 conversion was 3.11%. Both Cu-Zn and γ- Al_2O_3 catalyst were compared and it was found that Cu-Zn gave DME yield for DME on comparing it with other catalyst . hence, Cu-Zn gave maximum DME production with better conversion for CO and H_2.

Yingying et al. (2010) New technical improved method was put forward for processing DME that contained both synthesis and dehydration for methanol processed in fixed bed reactor. Operating conditions i.e. pressure ,temperature, feed ratio with space velocity on CO conversion. DME yield and CO conversion increases monotonically with increase in pressure. Considering for the conversion of CO, it was found that initially it increases and becomes constant after the ratio for H_2/CO becomes equal to 2or more than 2. Coming to the yield in DME, initially increases then suddenly it decreases for an increased value of space velocity. These situations were placed to obtain have maximum conversion for CO along with the selectivity for DME. Temperature at which the reaction occurs was set in range of 270-280° C for which the ratio for H_2/CO was set above 2 and space velocity more than 1000 and less than 1300.

Fazlollahnejad et al. (2009) One dimensional heterogeneous plug flow model was designed for modeling of fixed bed- reactor operating adiabatically for dehydration of methanol to using catalyst for production of DME. Comparison between experimental values of temperature and conversion profile were done with the predicted model.. Reactor was enclosed with 1.5 mm γ-Al_2O_3 pellets and operated in range of 543- 603 K at 1 atm. Also, effects of WHSV and temperature on methanol conversion were monitored. According to the results, reactor was enclosed with 1.5 mm γ-Al_2O_3 pellets acting as dehydration catalyst and operated in a temperature range of 543-603 K working at an atmospheric pressure. Adding to this, what causes change in conversion was investigated including WHSV with temperature .According to the results, at 603K with WHSV of 72.87 h^{-1} the maximum conversion was seen.

Erene et al. (2008) Investigated the operating condition on deposition of coke and noticed the deactivation o f metallic function from coke.

Raoof et al. (2008) Dehydration of methanol to DME was carried out in adiabatic fixed bed reactor working adiabatically using γ-Al_2O_3 **.** If change in temperature occurs from 233 to 303 °C of reactor, conversion in methanol values could be seen and was noticed. According to the output, temperature has great effect on methanol conversion. Also, conversion of mixture of methanol with water and pure methanol versus time was studied and catalyst deactivation with water was monitored. Using feed as a pure methanol ,catalyst deactivates slowly. While when water is mixed with methanol, deactivation of γ- alumina increase. Hence loss in catalyst was noted to be 12 times more than that occurred while using pure methanol as a feed. So, a model was predicted that was completely dependent on temperature for production of DME from methanol whose values matches with experimental data.

Moradi et al. (2008) monitored effect for composition of syngas with WHSV for the production of DME from indirect process and concluded that feed composition dominates the other operating conditions

Aguayo et al. (2007) A kinetic model was proposed for production of DME using single step from (H_2+CO), and with hydrogen and carbon dioxide and various parameters were calculated for CuO-ZnO-Al_2O_3/γ- Al_2O_3. Model developed was correct as it fits experimental values with those obtained after simulation being run on fixed bed reactor operating isothermally. The important step for modeling are synthesis from (H_2+CO) , dehydration occurring in methanol also with reaction for water gas shift. One of the advantage for carrying out methanol dehydration which leads to production of DME and methanol as 60%

and 5% from CO. Temperature and pressure was kept at 270°C and 30 bar. Generally at higher temperature hydrocarbons are mainly formed.

Luan et al. (2007) deactivated catalysts can be regenerated by redox cycle method in single step using catalyst like Cu-Zn-Al_2O_3 . Many researchers have studied how operating conditions effected CO conversion and selectivity for DME.

Moradi (2007) Using single step DME synthesis from syngas, operating conditions was determined. Bi functional catalyst was prepared by mixing commercial methanol catalyst and dehydration catalyst. Slurry reactor was taken for production process of DME from syngas at different operating conditions which were determined experimentally according to Taguchi algorithm. Various operating conditions were: H_2/CO mole fraction in feed varied from 0.26 to 1.5, pressure from 10 to 50 bar, temperature from 200 to 240 °C, weight ratio of methanol catalyst to dehydration catalyst from 0.67 to 4. Various experiments were conducted in slurry reactor with speed equal to 1600rpm and space velocity equal to 500ml/gcath. Considering the experimental results, optimum conditions that were chosen as : T= 240 °C, P= 33.3 bar, H_2/CO =1.5 and weight ratio of methanol catalyst to dehydration equal to 3.

Lee et al. (2006) considered steady state model for analysing performance of fixed bed reactor for preparing DME.

Nasehi et al.(2006) considering steady state conditions and simulated adiabatic reactor for synthesis of DME using methanol dehydration process and expressed that both one and two dimension model was approximately similar

Shahrokhi et al. (2005) modeled, simulated unsteady condition on fixed bed reactor using syngas as feed to prepare methanol. Further, optimized the model to produce maximum quantity of methanol for final production of DME.

Zhi et al. (2004) The process is highly exothermic for methanol production. Choosing fluidizes bed reactor to operate was better option regarding heat and mass transfer. Different mechanism for production of DME with new kinetic model equations was proposed. Reactor performance was estimated for the production of DME by carrying out experiments, resulting in higher value for CO conversion and production of DME while using fluidized bed reactor rather than slurry reactor. For simulation of DME synthesis both P-P model and P-M model was defined. On comparing simulated results with experiment results it was seen P-M model has better production for DME than P-P model. Hence in further study various parameters effecting P-M model was studied.

Lu et al. (2004) predicted best model for DME production using fluidized bed reactor: includes both the phases (Dense and bubble)

As there is issue for reaction equilibrium limit occurring at high temperature along with low catalyst performance at les value of temperature. Hence **Omata et al(2003)** defined production process for DME with syngas to overcome above issue. Optimization of reaction with genetic algorithm as well as neutral network was performed to have maximum value of CO conversion.

Modeling of isothermal fixed bed reactor was proposed by **Jahanmiri and Eslamloueyan (2002)** and simulated the production of methanol. Optimal temperature was calculated along shell side to obtain maximum methanol conversion. Considering fixed bed researcher worked on DME synthesis process.

Kunii et al. (1991) plug flow being considered in bubble phase is valid, but gets confused whether modeling dense would be valid. Considering it to be either P-M model or can be P-P model.

For simulating synthesis of methanol **Wagialla et al. (1991)** defined P-M model whereas simulation process for polyethylene synthesis defined by **Fernandes and Lona (2001)** used P-P model. Other researchers **Kunii and Levenspiel (1969,1991)** inference ,on increasing ratio for bed height with diameter above 10, changes plug flow in dense phase. Flow type can be predicted in dense phase by using this principle : u_0/umf should have value in range of 3-11, at this condition dense phase of gas flowing reversibly may happen researchers defined ratio for bed height w.r.t diameter near to 40 and u_0/umf in range of 2-8.

Hence what type of flow should be assumed was determined on comparing simulated results with those of experimental results**.**

Jorgensen (1986) presented modeling and control of fixed bed reactor.

Velasco et al. (1999) Used adiabatic packed bed reactor to investigate the optimal inlet temperature along with deactivation of catalyst. Isothermal optimal conditions were studied by Dixit and Grant for temperature. Mainly, optimization of tubular reactor has been incorporated for reaction which are reversible in nature and liberate heat during the process. Optimal temperature profile was calculated by **Mansson et al.** along the ammonia synthesis reactor using optimal control theory that resulted in the maximization of ammonia in effluent stream of the reactor.

Ng et al. (1999) Kinetic equations using catalyst for the production of DME from methanol**.** $CuO/ZnO/Al_2O_3$ for methanol forming and γ-Al_2O_3 for dehydration were investigated to work at 250°C with 5MPa using recycle type reactor. Vanden Bussche and Fragment defined combined kinetic model for production of DME using methanol and for methanol. Beric and Levec investigated model for dehydration of methanol. Results with different values for CO_X:H_2 ratio and weight of catalyst was measured. Deactivation of catalyst at high space velocity was monitored.

Gorazd Bercic and Janez Levec (1993) they developed both one -dimensional heterogeneous as well as pseudo homogenous model for an adiabatic fixed bed reactor. Conversion process for methanol and temperature profile shown by model generated by them were measured with to experimental values from the reactor. Enclosing the reactor with 3mm γ-Al_2O_3 and temperature range was 290 -400°C. Rate controlling step was intraparticle mass transport.

CHAPTER 3

MODELING STUDY

The **objective** of present work is to develop a mathematical model for simulation of production process for DME using adiabatic fixed bed reactor from methanol. Equations were derived for mass and energy balance for this reactor using suitable assumptions. Model validation is done by comparing simulating values with those of experimental values. To extend the model for variation of temperature and DME concentration with time. In this thesis work, model equations are simulated using MATLAB software.

The reaction equation for methanol dehydration is as follows:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O..........(5) \qquad \Delta H_{298} = -23.4 kJ/mol$$

Many researchers studied and explained various different kinetics for methanol dehydration performed on acidic catalyst. Some of them are shown in table 3.1 from different literature.

Equations	**Catalyst**	**Reference source**
$-r_m = \dfrac{k_1 P_M^{0.5}}{P_M^{0.5} + k_2 P_w}$	Al_2O_3	Kallo and Knozinger (1967)
$-r_m = \dfrac{k K_M P_M^{0.5}}{1 + K_M P_M^{0.5} + K_W P_W}$	Al_2O_3	Figueras et al (1971)
$-r_m = \dfrac{k K_M P_M}{(1 + 2\sqrt{K_M P_M} + K_W P_W)^2}$	Acidic ion exchange resin	Klusacek and Schneider (1982)
$r_m = \dfrac{k_s \times K_M^2 (C_M^2 - (C_w \times C_E)/K)}{(1 + 2\sqrt{K_M C_M} + K_w Cw)^4}$	γ -Al_2O_3	Bercic and Levec(1992)
$-r_m = \dfrac{k[P_M^2 / P_W - (P_D / K_{eq})]}{(1 + K_M P_M + K_W P_W)^2}$	HZSM-5	Lu et al.(2004)

Table 3.1. List of published kinetic model equations by different researchers

3.1 Reaction Kinetics

Production of DME is generally known as dehydration process for methanol. A large amount of heat is liberated and reaction occurs at equilibrium condition. Synthesis of DME became centre of interest for many scholars. Rate equations being defined by Beric and Levec (1993) has been considered in this study.

$$r_m(T,C_i) = \frac{k_s \times K_M^2 (C_M^2 - (C_w \times C_E)/K)}{(1+2\sqrt{K_M C_M} + K_w Cw)^4} \text{.............}(6)$$

This equation gives the result more approximate to the experimental values.

Where:

ks= reaction rate constant ,(kmol/kghr)

r_m= rate of disappearance, (kmol /kg hr)

K_i =adsorption constant, (m^3/kmol)

K=thermodynamic equilibrium constant.

T=Temperature (K)

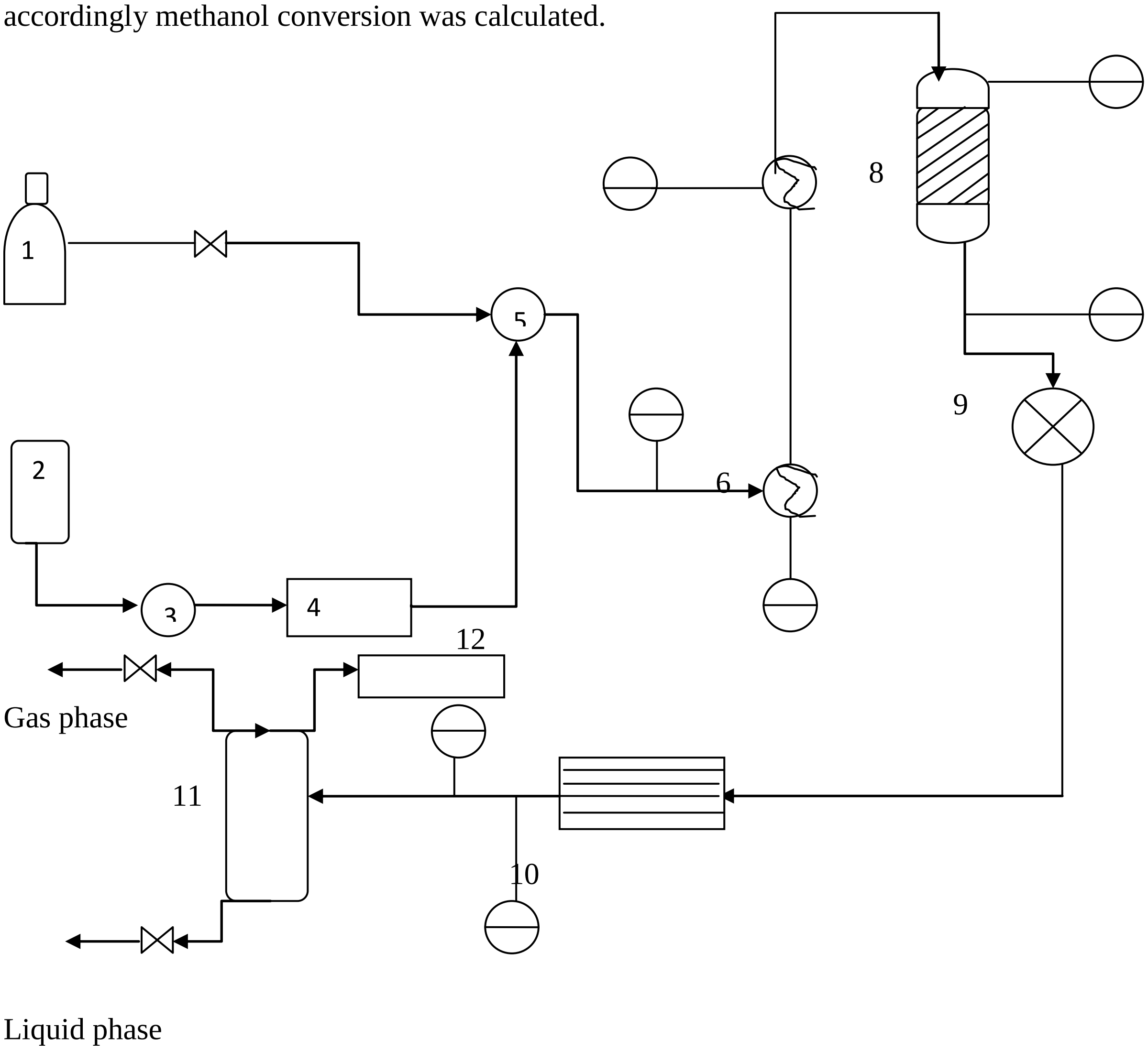
$$\ln(K) = 0.86\log T + \frac{3138}{T} + 1.33\times10^{-3}T - 1.23\times10^{-5}T^2 + 3.5\times10^{-10}T \text{........}(7)$$

Using equation 7, one can easily find out thermodynamic equilibrium constant.

$$k_s = 5.35\times10^{13}\exp(-17280/T) \text{.............}(8)$$
$$K_M = 5.39\times10^{-4}\exp(8487/T) \text{................}(9)$$
$$K_w = 8.47\times10^{-2}\exp(5070/T) \text{..................}(10)$$

3.2 Process Description

The diagram below shows the schematic representation for DME synthesis. Methanol (free from other content)from methanol storage tank enters at various flow rates ranging from 44 g.h^{-1} to 1021 g.h^{-1} . it was heated initially before it could enter the reactor. After this heating process the methanol was transferred to adiabatic fixed bed reactor. Thermocouple was used for temperature measurement at different sections inside catalyst bed .Heat exchanger was installed following the reactor so as to reduce the temperature of the outlet products by passing these products to air cooler. The outlet product were passed through air cooler and double pipe heat exchanger to lower down the temperature of product. Gas-liquid separator separates the cooled product. A back pressure regulator was placed to set the pressure. The final product were analysed by gas chromatograph. The unreacted methanol was measured, accordingly methanol conversion was calculated.



1: N_2 cylinder; **2**: methanol feed tank **;** **3**: dosing pump ;**4**: flow meter ;**5**: mixer ; **6**: evaporator **7**:preheater ;**8**: adiabatic fixed bed reactor ;**9**: air cooler ;**10**: condenser ;**11**: liquid gas separator ;**12** : back pressure regulator

Figure 3.1. A diagram showing preparation of DME using methanol experimentally

3.3 Modeling a Reactor

Considering this present study, pseudo homogenous model for one dimension process has been developed and simulated to operate at both the conditions: steady and dynamic conditions in adiabatic fixed bed reactor. The model is designed to have both mass and energy equations. basic. In this work dispersion model cannot be encountered mainly because of following reason

- As d_p / d_{tube} <1 [**Fazlollahnejad et al. 2009]**
- L_{tube}/d_{tube} <50 [**Fazlollahnejad et al. 2009]**

Various assumptions for defining mathematical model are : [**Fazlollahnejad et al. 2009]**

- The reactor is assumed to be plug flow with ideal gas property
- It should not be allowed for the heat to transfer from reactor to the environment.
- Reactor operates at isobaric condition
- Negligible radial gradients in concentration and temperature.
- Diffusion in catalyst pores is negligible.
- Uniform temperature within catalyst (Biot number =0.0125) **[Farsi et al. 2011]**

Based on above assumptions derived mass and energy balance for the gas phase can be written as:

$$\varepsilon \frac{dC_i}{dt} = u \frac{dC_i}{dz} + \eta_o v_i r_m (T^b, C_i^b) \rho_b \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

$$\rho_g C_{pg} \varepsilon \frac{dT}{dt} = -u\rho C_p \frac{dT}{dz} + \eta_o v_i r_m (T^b, C_i^b)(-\Delta H_r) \rho_b \ldots\ldots\ldots(12)$$

Initial and boundary values for the above equations are as follows:

Boundary condition :

$$C_{Z=0} = C_{0,}$$
$$T_{Z=0} = T_0$$

Initial condition:

$$C_{Z,t=0} = C_i^{ss}$$
$$T_{Z,t=0} = T_i^{ss}$$

Effectiveness factor can be defined by:

$$\eta = \frac{V^{-1}\int_V r_M(T, C_i)\,dV}{r_M(T^b, C_i^b)} \text{.....................(13)}$$

η is assumed to be 1, as catalyst particles are small enough to have variation of temperature and concentration. Thus, this factor does not play important role on temperature of reactor and methanol conversion.

Parameter	**values**
T(K)	573-603
P(Pa)	101325
Mass flow rate (kg/hr)	0.469
Feed : Pure Methanol is charged	

Table 3.2. Feed specifications

Parameter	**value**
Density of bed (kg/m^3)	693.96
Reactor diameter(m)	0.01905
Length of reactor(m)	0.25
Catalyst particle diameter(mm)	1.5
Reactor height (cm)	90
WHSV^{-1}	63.4-79.8
Void fraction	0.6

Table 3.3. Equipment and catalyst parameters

3.4 Equations used

- Heat of Reaction (kJ/kmol)

$$\Delta H_R = \Delta H_{298,f} + \int_{298}^{T} C_p dT \text{.............}(14)$$

- Specific Heat of fluid (kJ/kgK)

$$C_P = A + BT + CT^2 + DT^{-1} \text{....................}(15)$$

- Gas phase density (kg/m^3)

$$\frac{\rho_1}{\rho_2} = \frac{T_2}{T_1} \text{................}(16)$$

CHAPTER 4

RESULT AND DISCUSSION

Using operating conditions and feed specifications defined in table **3.2** and table **3.1**, equations 11 and 12 were simulated using **MATLAB s**oftware. Results were obtained after simulating mass and energy equations. PDE's were converted into ODE using finite difference method. Then these ODE's were solved in MATLAB by 4th order Runge Kutta method to obtain steady state condition.

4.1 Simulation when reactor operates at steady state

Simulation results of steady state have been shown. Considering adiabatic plug flow reactor, and simulation has been carried out for one dimensional pseudo homogenous model. Following results were obtained.

Temperature varying with reactor length is shown. When the feed temperature is increased from 543 -603 K, reaction rate increases as it is exothermic reaction and hence equilibrium state is assumed to reach faster.

Figure 4.1 to 4.6 shows the best operating temperature at which we can get maximum methanol conversion.

Figure 4.1 shows the variation of temperature along the length of reactor, as the experimental values are not much closer to the simulated results by **Fazlollahnejad M et al** as well as simulation being done using MATLAB. Hence temperature 543 K is not considered to be the optimum temperature for feed inlet. At this temperature error of 0.648 was noticed which is quite large according to the numerical method being used. Hence the model suggested by both in present work and **Fazlollahnejad** is not appropriate to work at thus temperature.

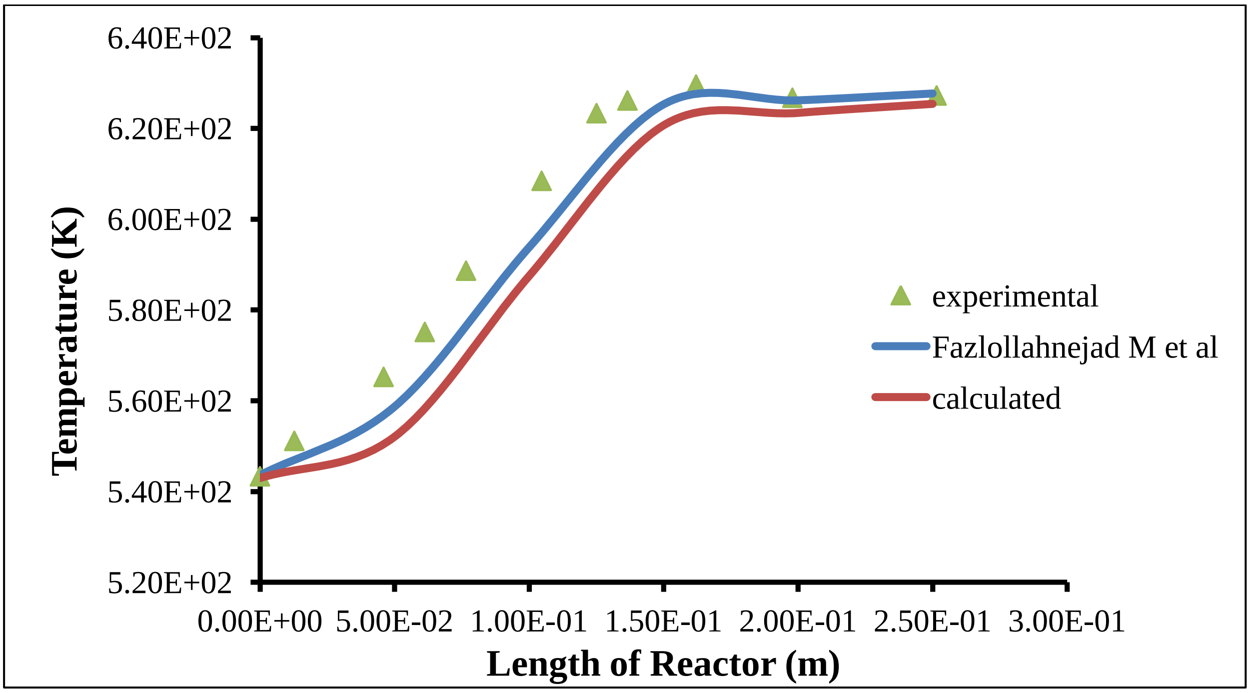


Figure 4.1. Variation of temperature along the length of reactor (p=1atm and WHSV =45.33h^{-1})

.

Figure 4.2 illustrates the simulation result when inlet temperature was 573K. In the this graph , it is clearly predicted that present work values match up closely to the experimental result along with the simulation results by **Fazlollahnejad M et al**. Hence this temperature could be considered appropriate as reaction to start with, but simulation result with 603 K will be noticed. But more parameters are also considered for finding optimum temperature.

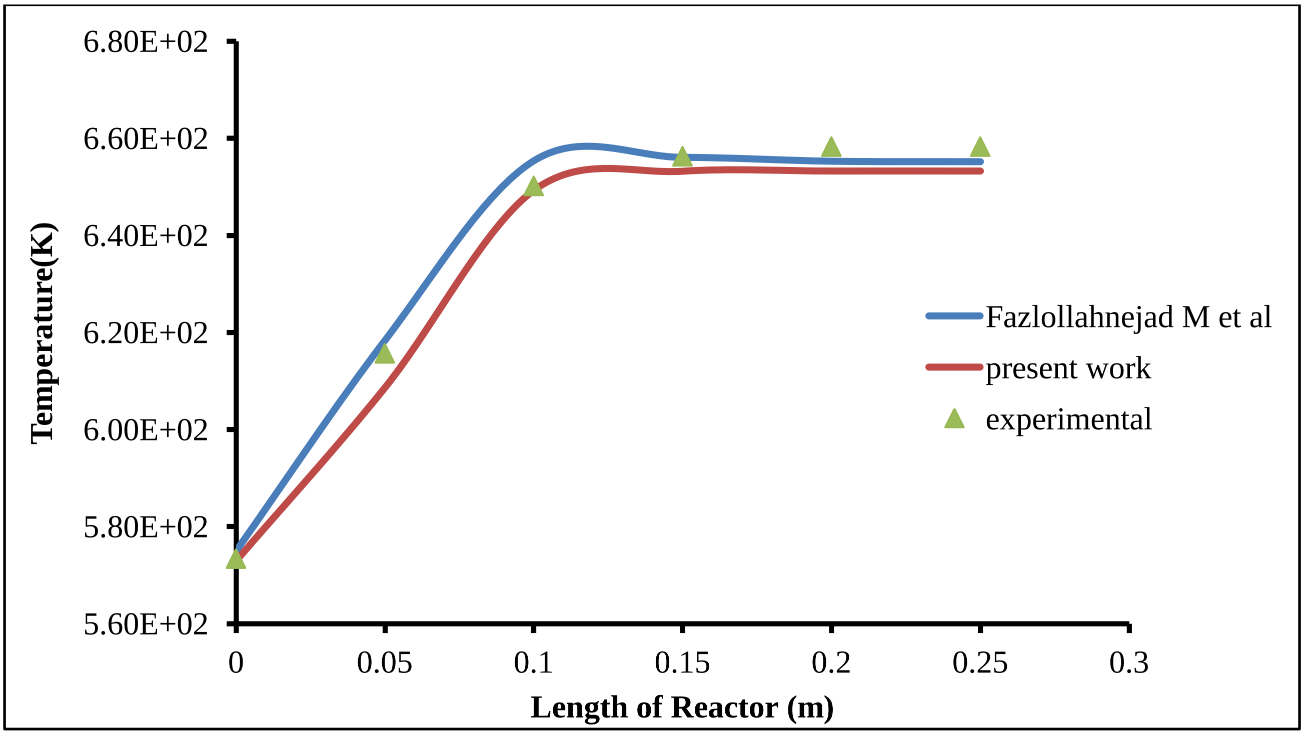


Figure 4.2. Variation of temperature along the length of reactor (p=1atm and WHSV = 63.5 h^{-1})

.

In **figure 4.3**, the graph obtained by simulation in present work is almost similar to the values obtained by experimental values. But as the length increases there is wide gap between present work as compared **Fazlollahnejad**. As the reason to the gap might be **Fazlollahnejad et al** solved the modeling equation considering values of heat of equation to be constant as the length of reactor varies.

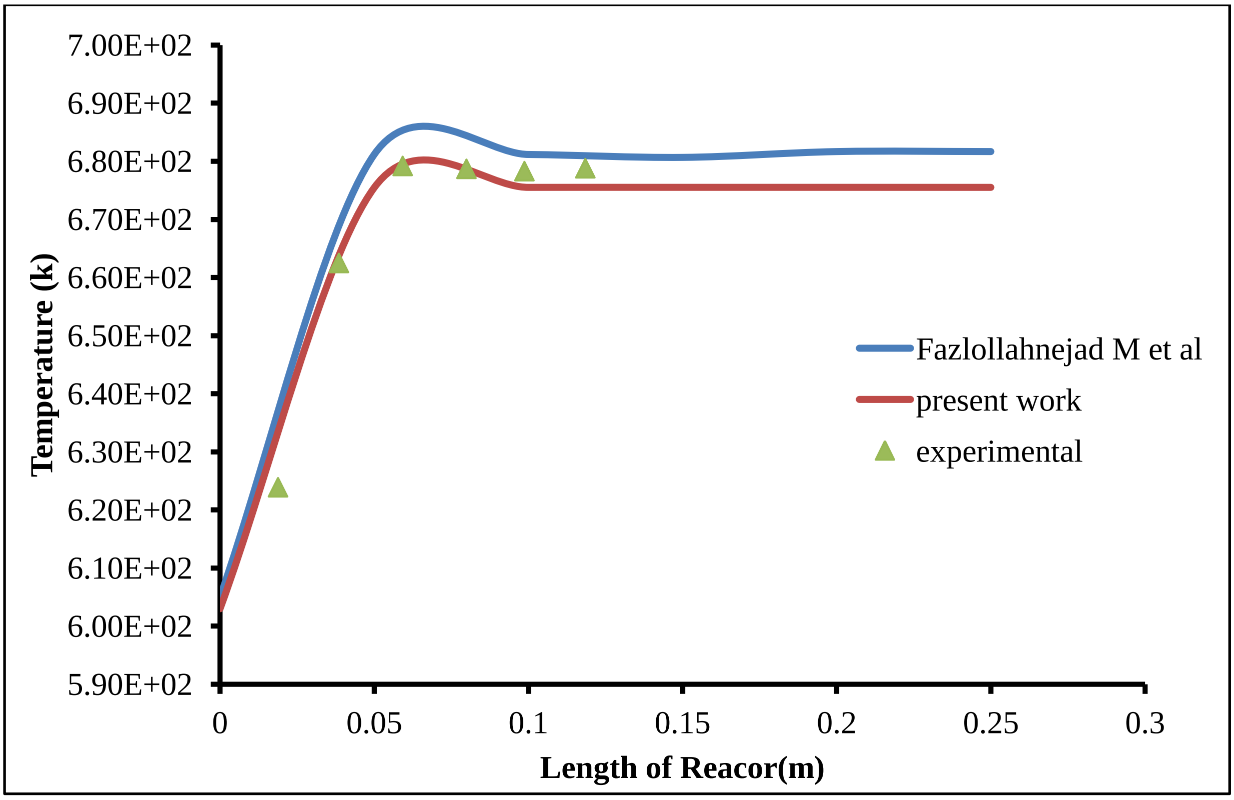


Figure 4.3. Variation of temperature along the length of reactor (p=1atm and WHSV = 79.8h^{-1})

As the temperature range for the process was 543-603 K. Three temperature conditions were set for the simulating process. At 603 K, both the results by **Fazlollahnejad M et al** and results generated using MATLAB are closer to experimental results. Hence this could be possible inlet feed temperature. But temperature effect on MeOH conversion is to be noticed.

Figure 4.4 illustrates how methanol conversion changes along the rector length when operated at temperature at feed temperature of 543 K. It can be seen that in present study on simulating the conversion is attained slowly whereas, in study by Fazlollahnejad et al , it attains much higher value for conversion.

Maximum conversion attained is 82% in present study working at WHSV of 45.33 h^{-1} .

Results were also simulated by changing inlet temperature with different WHSV values.

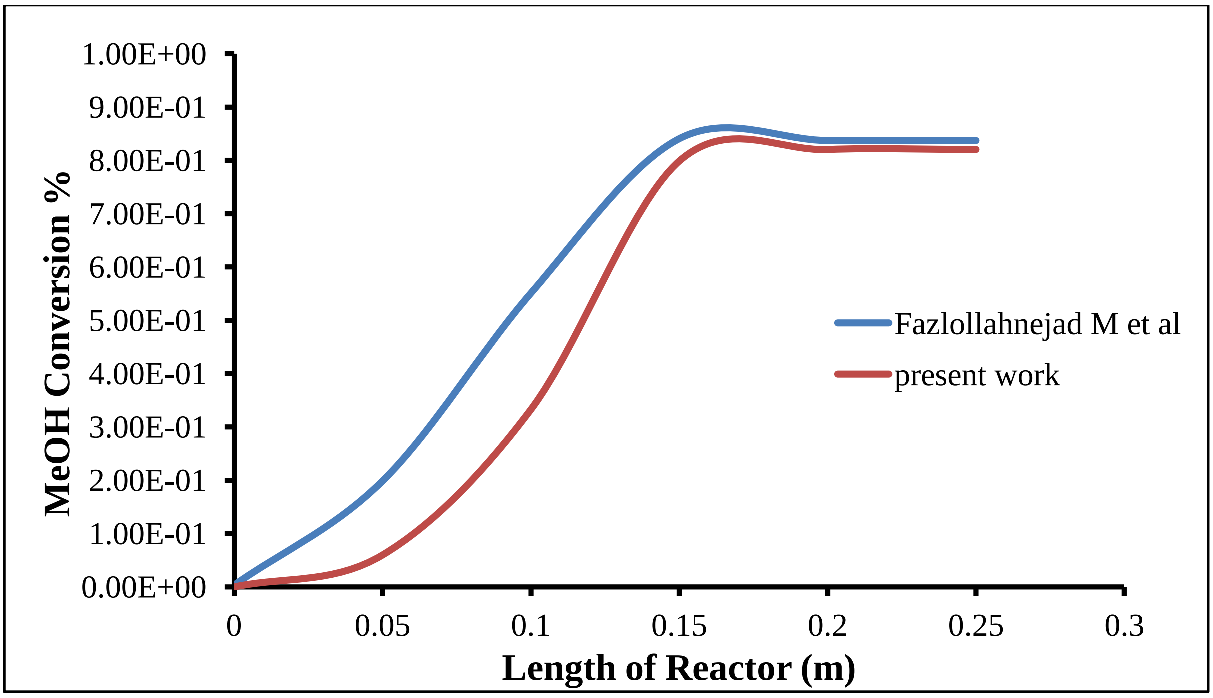


Figure 4.4. Methanol conversion *versus* length of reactor (T=543 K, p=1atm,WHSV =45.33h^{-1})

Figure 4.5 demonstrates conversion of methanol as it enters the reactor at inlet feed temperature of 573 K with WHSV of 63.5. Results closely matched up with the experimental data and output given by **Fazlollahnejad M et al.** But at 0.1 m it suddenly increases and reach to maximum value of 87%

Whereas conversion predicted by experiment was nearly 85%.

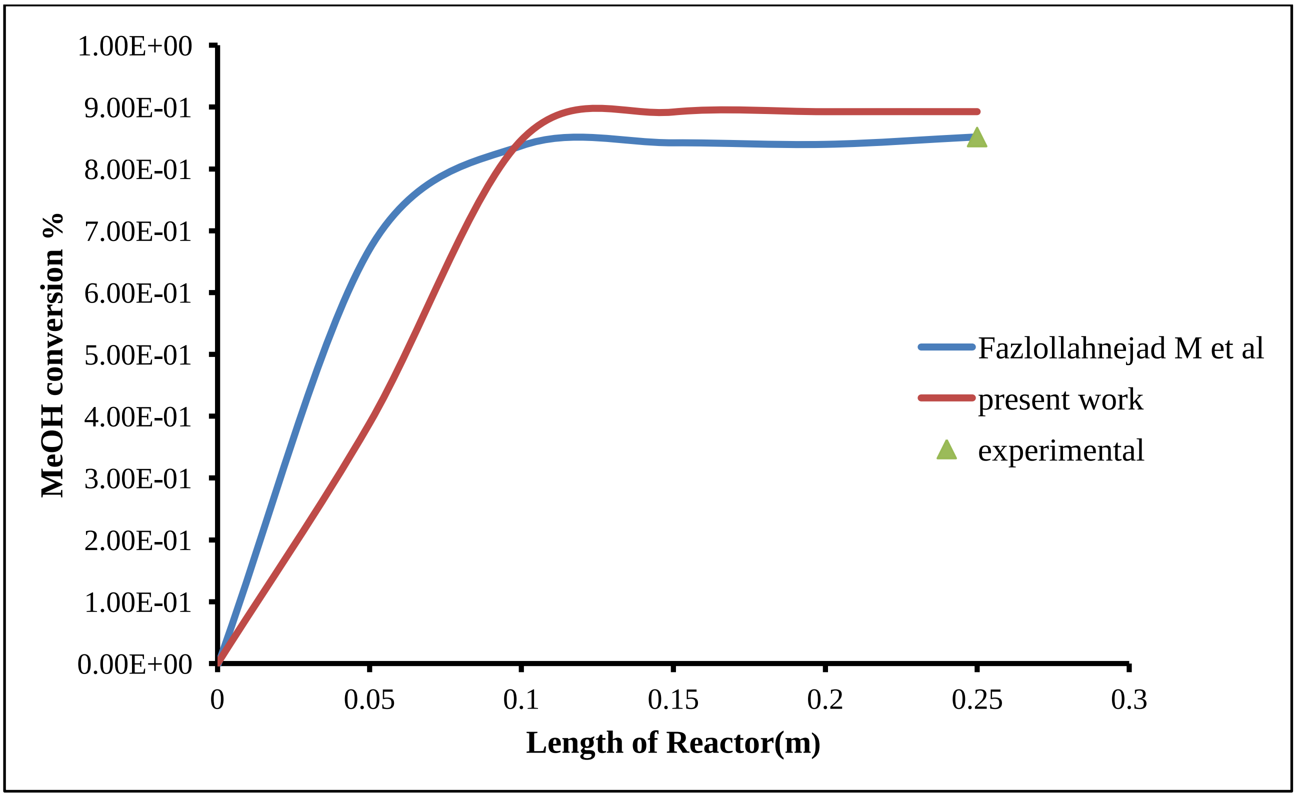


Figure 4.5. Methanol conversion *versus* length of reactor(T=573 K, p=1atm,WHSV =63.5h^{-1})

Figure 4.6 illustrates the conversion at optimum temperature 603 K. Inlet temperature of 603 K with WHSV of 79.8 h^{-1}

In **figure 4.6.** this is the best output obtained by simulating the model using MATLAB.

Results are very close to the experimental data and maximum conversion attained was 89% .

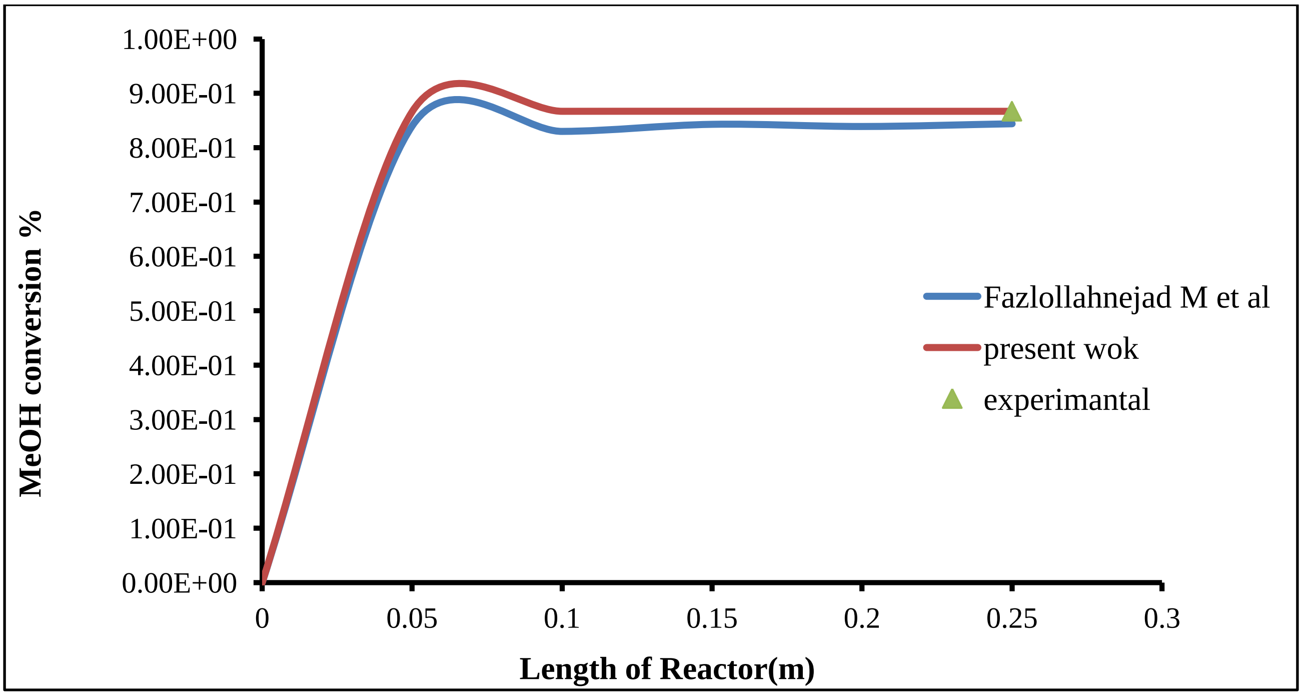


Figure 4.6. Methanol conversion *versus* length of reactor (T=603 K, p=1atm,WHSV =79.8h^{-1})

As we obtain the optimum temperature at which the reactor could be operated. Hence we found mole fraction of DME along the length of reactor.

Figure 4.7 illustrates the mole fraction of DME in gaseous phase at optimum temperature of 603 K. At the end of the reactor where equilibrium is prevailed the mole fraction of DME obtain is 0.42. as the reaction starts methanol is immediately converted into DME and moles of DME remains constant.

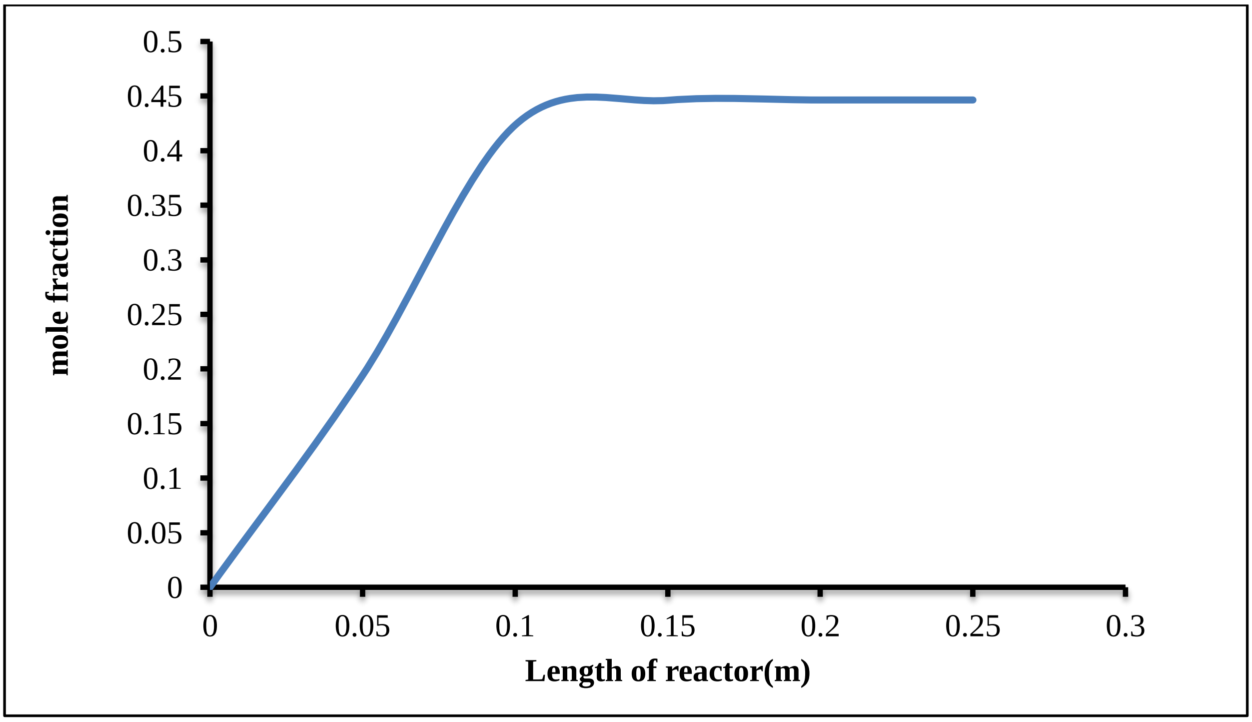


Figure 4.7. DME mole fraction at T=603 K

Figure 4.8 illustrates the molar flow rate of reactants and product at steady state operating condition.

As we are considering pure methanol in the feed, it decreases as the reaction proceeds to form water and DME and remains constant. Considering methanol it decreases linearly but after a while it increase and then remains constant, due to recycled methanol from the output product.

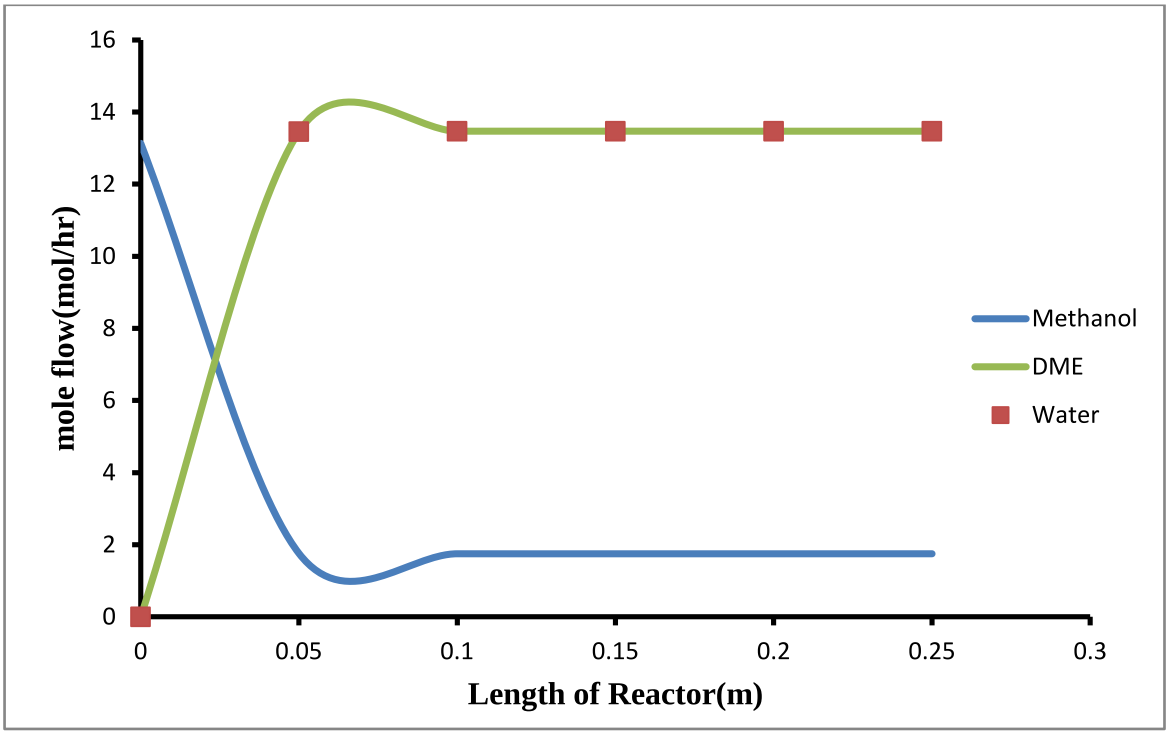


Figure 4.8. Molar flow rate of MeOH, DME, and Water along the length of reactor

Figure 4.9 shows maximum yield of DME at feed temperature of 603 K in percentage.

Using :

$$\text{Yield \%} = \frac{moles\ of\ product\ formed}{moles\ of\ reactant\ used} \text{ x } 100$$

Maximum yield obtained is 45 % but it decreases and the reaction proceeds forward and remains constant at value of 42%. Hence reactor optimum length is 0.07 m.

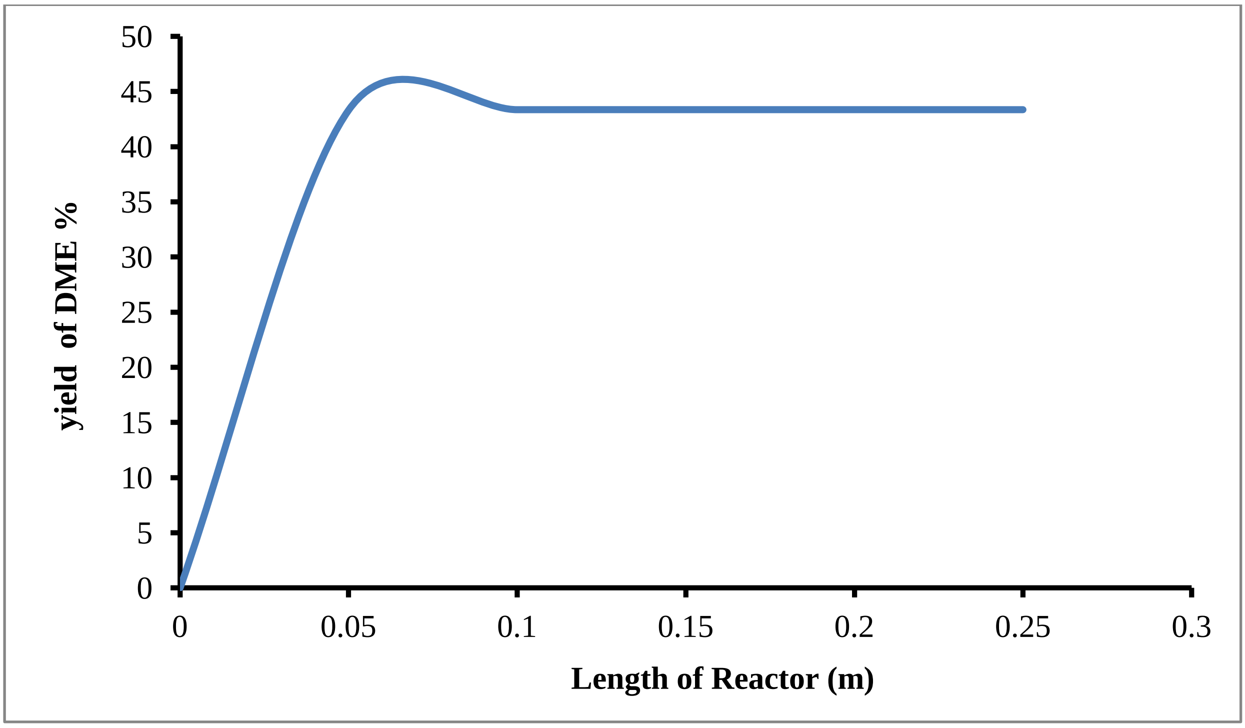


Figure 4.9. Percentage yield of DME

4.2 Dynamic Simulation

Figure 4.10 represents the 3D view of methanol concentration (kmol/m^3) with reactor length and with time.

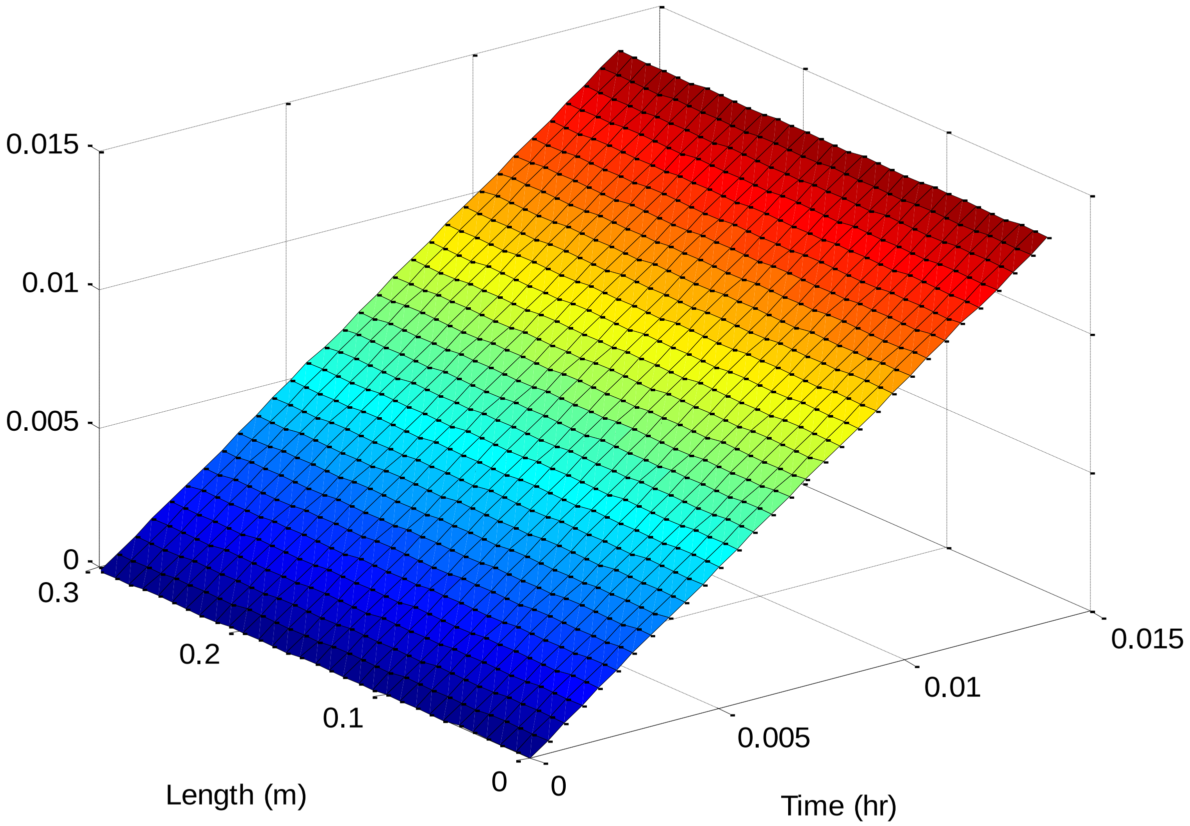


Figure 4.10. Methanol concentration with reactor length and time

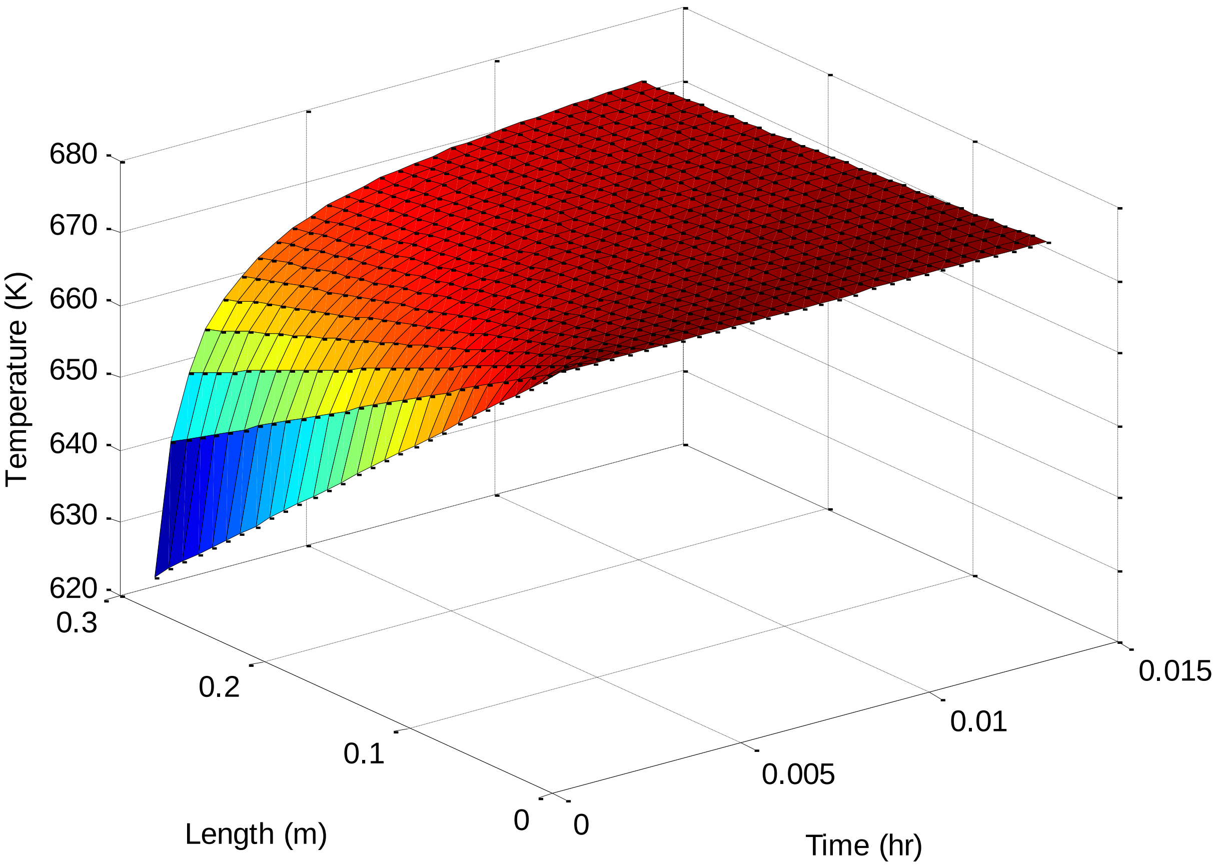


Figure 4.11 . Dynamic Temperature profile

4.3 Effect of Temperature :

Dehydration process for methanol is exothermic in nature. Therefore, when temperature was increased upto a limit, fluctuation in rate of reaction was seen. It varies directly with temperature, but talking about conversion its value lowers down. Hence, temperature should be lowered down when the system is not close to equilibrium

4.4 Pressure Effect:

Pressure does not have any effect on methanol dehydration as the reaction is in equilibrium. Pressure could only effect reaction rate only. According to different researchers maximum attainable pressure for the process could be not more than 5 atm.

4.5 Flow Rate Effect:

Flow rate has considerable effect on the conversion. As flow rate varies inversely with the residence time. Therefore, more time is required to reach equilibrium at higher flow rates. Hence, for high flow rates maximum conversion occurs at the exit of reactor.

4.6 Effect of WHSV:

WHSV plays an important role in conversion of methanol. Gas velocity varies directly with WHSV, if gas velocity increases contact time for reactant decreases but mass transfer increases. Resulting in increase of methanol conversion while decrease in WHSV.

CHAPTER 5

SUMMARY AND CONCLUSION

A one dimensional pseudo homogenous model is developed to simulate the adiabatic fixed bed reactor. The model is solved for both steady and unsteady state. The axial temperature and conversion profile are predicted by the model. Also, effect of WHSV on methanol conversion in different inlet feed temperatures are considered. The results show that maximum conversion of methanol is 89% at 603 K, 87 % at 573 K and 82% at 543 K. Therefore, according to the obtained results, maximum conversion is obtained at 605 K with WHSV of 79.8 h^{-1} .

Hence operating temperature is calculated to be 603 K. Therefore, on increasing the temperature methanol conversion increases negligibly, but selectivity with respect to DME decreases.

The comparison of simulation results and the experimental data shows that the proposed model is best suitable at feed temperature of 603 K.

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