Experimental and Simulation Analysis of Hydrogen Production by Partial Oxidation of Methanol

[1]Umair Sikander* and [2]Arshad Hussain
[1,2] *School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), Sector H-12, Islamabad 44000, Pakistan.*
umair.sikandar@scme.nust.edu.pk*

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Summary: Partial oxidation of methanol is the only self-sustaining process for onboard production of hydrogen. For this a fixed bed catalytic reactor is designed, based on heterogeneous catalytic reaction. To develop an optimized process, simulation is carried out using ASPEN HYSYS v 7.1. Reaction kinetics is developed on the basis of Langmuir Hinshelwood model. 45:55:5 of CuO: ZnO: Al_2O_3 is used as a catalyst. Simulation results are studied in detail to understand the phenomenon of partial oxidation of methanol inside the reactor. An experimental rig is developed for hydrogen production through partial oxidation of methanol. Results obtained from process simulation and experimental work; are compared with each other.

Keywords: Partial oxidation of methanol, Hydrogen production, Process simulation, Fixed Bed Catalytic Reactor, Heterogeneous Catalytic Reactions.

Introduction

Nowadays extensive attention has been paid to using hydrogen as an energy carrier for its high efficiency and very low to zero pollution [1]. The biggest advantage of hydrogen fuel is versatility; it can be used in combustion engines, as a propellant, an explosive, a source of electricity (PEM-Fuel Cells) [2]. Major problem in using hydrogen as a fuel source is its storage [3]. Not only it is the lightest gas and escapes easily, it is also highly flammable and can easily catch fire by a high friction giving it enough temperature to reach its flash point [4]. This work is focused on addressing the issues of producing hydrogen economically and safely.

An alternate method of on-board production of hydrogen by Partial Oxidation of Methanol (POM) using a fixed Bed Catalytic Reactor (FBCR) [5] is devised in this work. Methanol is the third commodity chemical after ethylene and ammonia; with a production capacity in excess of 25 million tons, much superior to the actual overall demand [6]. It also has the leading candidate because all other fuels require high processing temperatures and produce unacceptable amounts of CO [7]. Hydrogen can be produced from methanol by three different methods [8].

Cracking [9]

$$CH_3OH \rightleftharpoons 2H_2 + CO \quad \Delta H = 92KJ/mol \qquad (1)$$

Steam Reforming [10]

$$CH_3OH+H_2O \rightleftharpoons 3H_2+CO_2 \; \Delta H = 49.4KJ/mol \qquad (2)$$

Partial Oxidation [11]

$$CH_3OH+(1/2)O2 \rightleftharpoons 2H_2+CO_2 \Delta H=-192.2KJ/mol \; (3)$$

Among these methods partial oxidation is the only process which is exothermic and thus self-sustaining. Also it has the advantage to use oxygen directly from air.

For POM a ratio of 1:2 of oxygen to methanol is fed to the reactor in vapor phase where the reaction takes place in the presence of a catalyst. 45:55:5 of CuO: ZnO: Al_2O_3 is used as a catalyst [12]. High concentrations of H_2 and CO_2 were obtained with only the traces of unwanted by-products. Perkin Elmer GC with TCD detector is used for the product analysis. All the experimental work and calculations are made on a pilot scale. Reaction kinetics and process design is studied thoroughly and an optimized process design is developed.

This work is further extended by conducting process simulation using Aspen HYSYS v7.1 which is the novelty of this work. Effects of process variables are analyzed in detail by process simulation.

Results and discussion

Simulation Results

Simulation results are helpful for the optimization of POM process. Simulation also provides an insight of the reactor to have a better

*To whom all correspondence should be addressed.

understanding about the POM process. Results obtained by HYSYS simulation are plotted by the Aspen-HYSYS tool. These results are discussed below:

Rate of Hydrogen Production

Fig. 1 shows that production rate of hydrogen is increasing along the reactor length till 11cm and after that hydrogen production rate is decreased. This result shows that optimized reactor length is 11cm for POM. It is also notable that the point from which production rate of hydrogen is decreasing production rate of methanol is increasing. This implies that if reactor length is further increased, backward reaction will accelerate and the product gained from such reactor will be of much lower conversion.

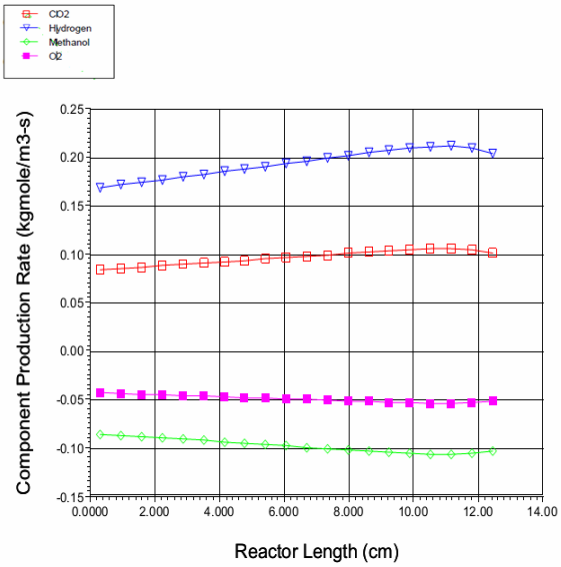

Fig. 1: Compound Production rate VS Reactor Length.

Rate of Reaction vs Reactor Length

Rate of reaction based on %age conversion of methanol, increases along the reactor length as shown in Fig. 2. When reactants are introduced in reactor there is a pressure drop and temperature difference which results into a slow reaction rate which gradually increases. POM is an exothermic reaction as the reaction proceeds there is some increase in temperature which in turn increases the rate of reaction. In the later part backward reaction is taking place at a higher rate, thus there is a decrease in rate of reaction.

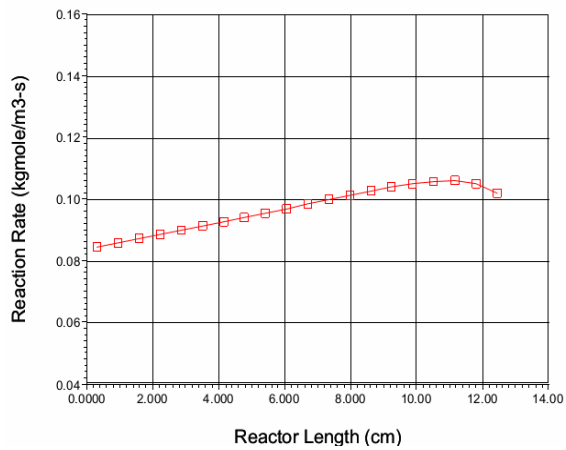

Fig. 2: Reaction rate VS reactor length.

Change in Heat Capacity of the Overall System

Along the reactor, heat capacity is being reduced as shown in Fig. 3. It means that compounds of lower heat capacity are being produced. Since hydrogen has a fairly low heat capacity than methanol the plotted graph confirms that hydrogen is being produced and methanol is being consumed along the reactor. This plot also leads to another discussion of efficient heat supply to the reactor. At the end of the reactor heat capacity is low so all the heat present at this region would be consumed by the catalyst and it will be at higher temperature in this region. Thus the goal of uniform temperature will not be achieved. For this a differential model of heat transfer should be developed to get an idea of point to point energy requirement in the reactor.

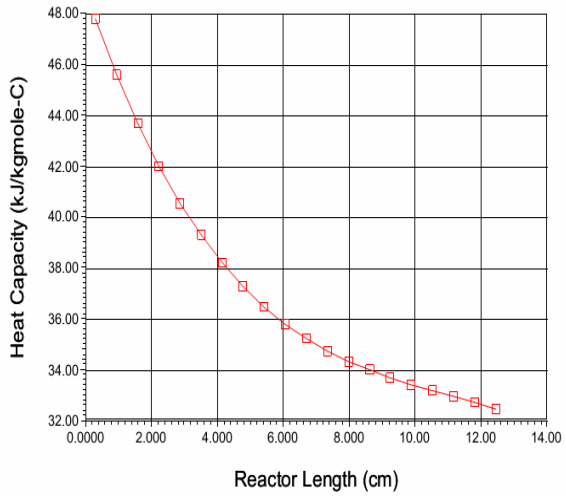

Fig. 3: Heat Capacity VS Reactor Length.

Pressure Drop in the Reactor

Fig. 4 shows the pressure drop along the reactor. From this graph pressure drop at any particular length

can be found and incorporating these values of ΔP/l in Ergun Equation superficial critical velocity of any compound at any point inside the reactor can be calculated.

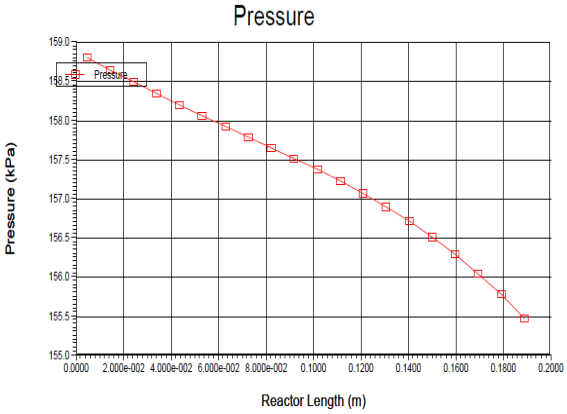

Fig. 4: Pressure VS Reactor Length.

Catalyst Characterization

Catalyst was characterized with SEM for morphological and surface properties. JEOL JEX-2300 was used under an accelerating voltage of 20kV. The magnifications used were 5000X and 50,000X. The particles were found to be micrometer sized fine powder having spheroids and discs of 0.1-0.5 µm. There were some aggregates present but overall the catalyst had uniform size distribution and was found as highly porous structure as evident from the Figs. 5 and 6.

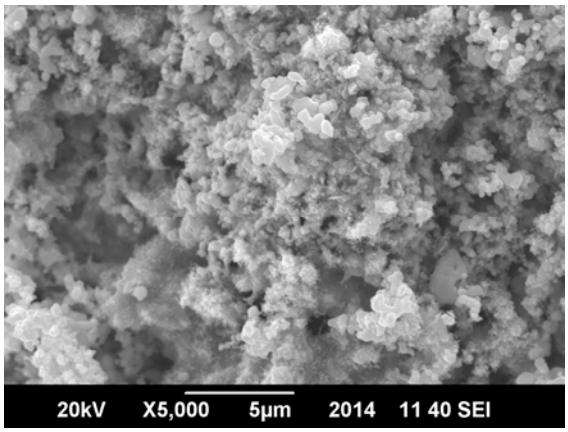

Fig. 5: SEM micrograph of catalyst at X5000.

Jeol JSM-6460 Energy Dispersive Spectroscope (EDS) was used for compositional analysis. The compositional ratio of Cu, Zn and Al was found concurrent with the desired mixing ratios (Fig. 7, Table-1).

Table-1: Catalyst quantitative mass percentages from EDS.

Element	Composition Theoretical (Mass %age)	Composition Actual (Mass %age)
Al	3.1	2.4
Cu	43.6	41.5
Zn	53.3	56.06

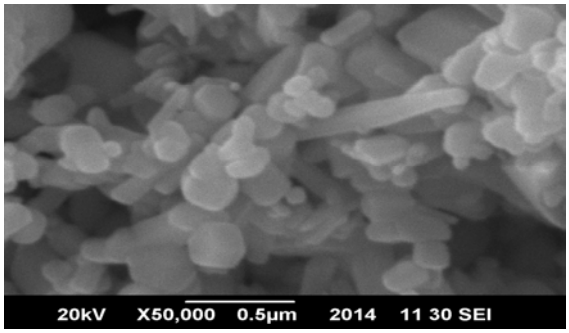

Fig. 6: SEM micrograph of catalyst at X50,000.

Experimental Results

From Gas chromatographic analysis, undesirable fraction of water is also present in the product mixture. This can only be possible by the complete oxidation reaction of methanol in spite of partial oxidation. Complete oxidation reaction is given in Eq. 4.

$$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O \qquad (4)$$

It means that methanol being consumed not only produces hydrogen but is also producing water with it; as a side reaction. This side reaction decreases the overall molar conversion of POM to 63.3%. While designing the process, care should be taken that side reactions must be avoided as much as possible. In the case of POM, catalyst plays this very role. Results obtained indicate the importance of catalyst as it is the property of catalyst only to direct the reaction on the desired path and reduce the chances of possible side reactions.

Process Simulation

Simulation of POM is carried out using ASPEN HYSYS v7.1. A complete dynamic model is created using this tool and FBCR is designed along with reaction kinetics to investigate the behavior of the reactor under different process conditions. Hydrogen is closest to the ideal gas in its properties; therefore Peng Robinson fluid package is taken which considers the gases to be ideal in nature. After selecting the components and fluid package reaction kinetics are defined. HYSYS has the provision to choose a type of reaction from a list available. POM is a heterogeneous catalytic reaction [11] so same reaction type is taken.

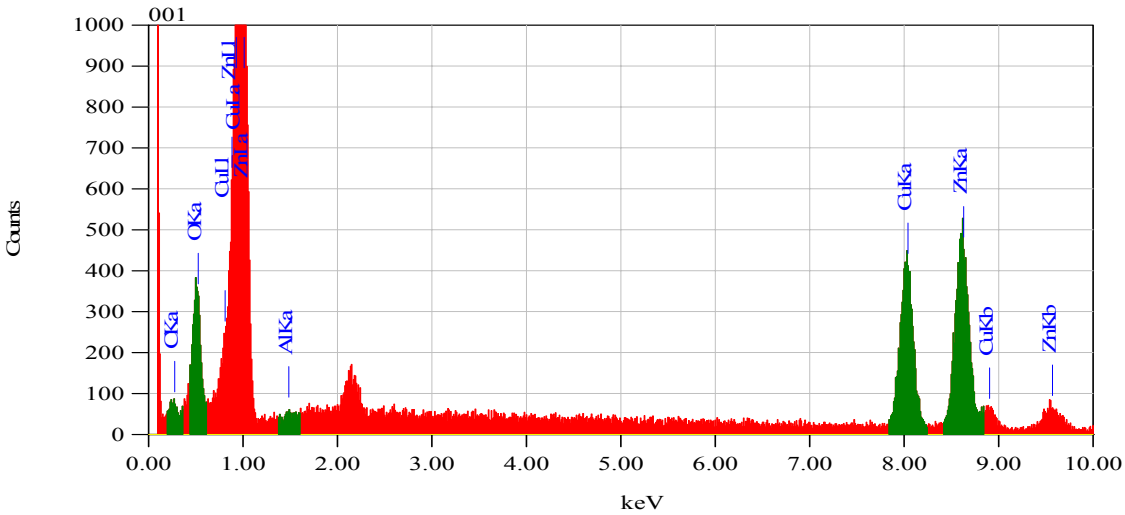

Fig. 7: EDS Compositional spectra of catalyst

Reaction Kinetics

In HYSYS heterogeneous catalytic reactions are based on Langmuir Hinshelwood (LH) model. For POM various mechanisms are proposed in literature based on Langmuir Hinshelwood model. The most promising results are however reported by Lin *et al*. [13] and suggest that reaction take place according to the following mechanism.

(Adsorption)

$$O_2 + 2S \rightleftharpoons 2OS \quad (5)$$

(Surface reaction)

$$2CH_3OH + OS \rightleftharpoons 2CH_3OS + H_2O \quad (6)$$

(Desorption)

$$2CH_3OS + H_2O \rightleftharpoons CH_3OH + 2H_2 + CO_2 + 2S \quad (7)$$

(Overall)

$$2CH_3OH + O_2 \rightleftharpoons 4H_2 + 2CO_2 \quad (8)$$

It is to be noted that methoxide is produced on the surface reaction step (Eq. 6) which in return produce hydrogen and carbon dioxide on the desorption step. Formation of methoxide is of utmost importance in POM as hydrogen is liberated on its decomposition. This implies that rate controlling step in this model is surface reaction where methanol is being decomposed.

Rate equation in this mechanism is obtained from an extended Langmuir Hinshelwood Hougen Watson (LHHW) model. This model is based on the concept that rate controlling step must be focused while developing rate equation for any heterogeneous catalytic reaction. The rate of reaction according to LHHW model is calculated by Eq. 9.

$$r = \frac{k_R\,[O_2]^{\frac{1}{2}}[CH_3[OH]]^2}{\left[1 + K_{ad}[[O_2]]^{\frac{1}{2}} + \frac{[CH_3OH]^{\frac{1}{2}}[H_2][CO_2]^{\frac{1}{2}}}{K_{de}[H_2O]^{\frac{1}{2}}}\right]^2} \quad (9)$$

When all the parameters in the above equation are specified in HYSYS, heat of reaction calculated by the software is -192 kJ/mol(as shown in Fig. 8). Reaction is then saved in the reaction set ‘Rxn-1’ which can now be invoked where needed.

Simulation Environment

The complete process is defined in the simulation environment after setting parameters. Now two material streams are taken for methanol and oxygen respectively. A mixer ‘Mix-100’ is attached which mixes the two reactants according to the proportion of 2:1 and provide us with a single stream ‘mixed reactants’. This stream is then pre heated to 200°C using a heater ‘E-100’. Finally reactants are introduced to horizontal reactor ‘FBCR’ from the bottom. Product stream is taken from the top of the reactor. As POM is an exothermic reaction, heat is evolved, and to maintain the temperature inside the reactor a cooling line is attached to the reactor. Process flow diagram is depicted in Fig. 9.

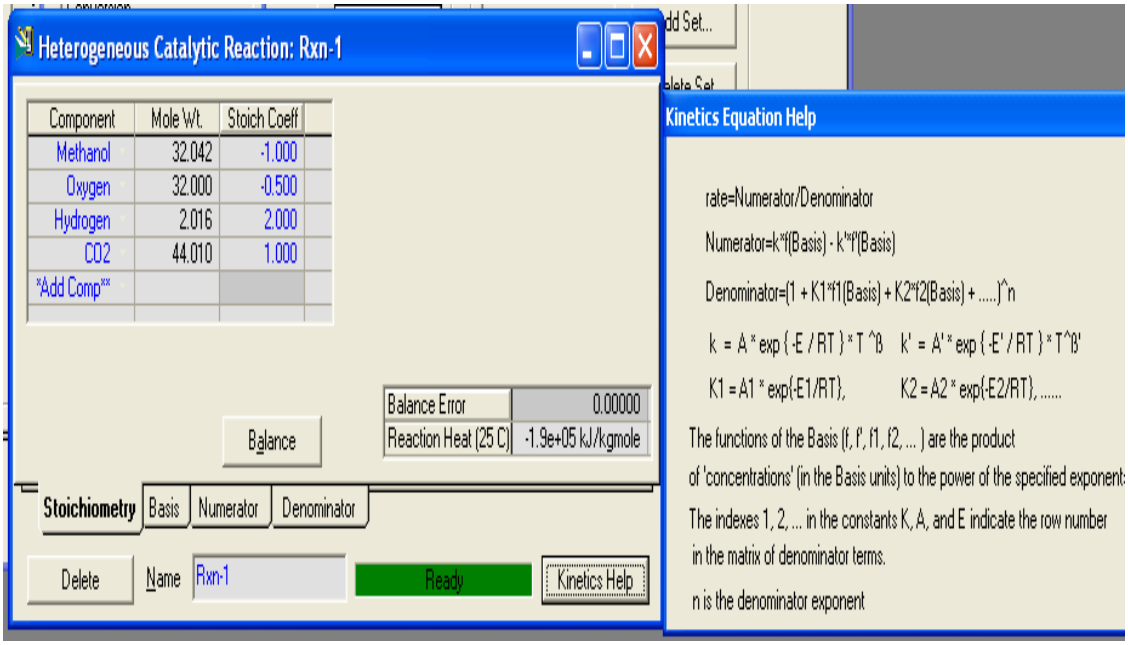

Fig. 8: Defined heterogeneous catalytic reaction.

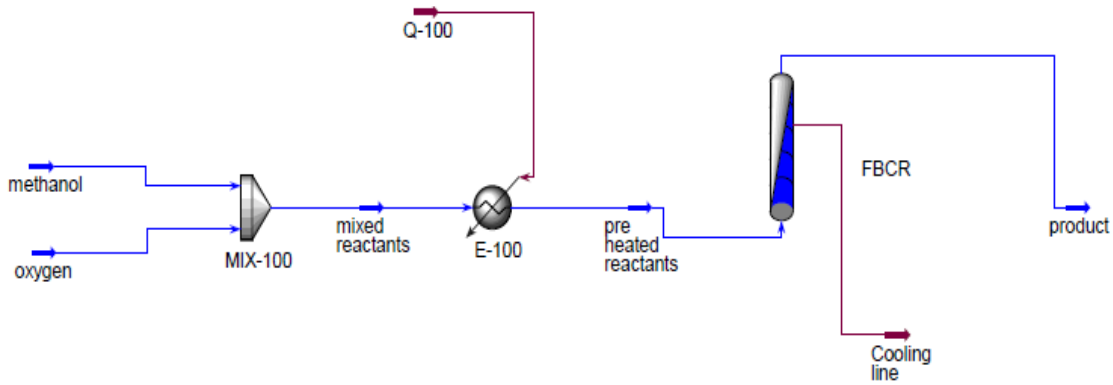

Fig 9: Simulation process flow diagram.

Reactor Design

Plug Flow Reactor (PFR) model is chosen for reactor design to carry out the POM reaction. For 60% conversion FBCR volume is calculated by equation (10) [14].

$$V_R = (1-\varepsilon_B)\left(\frac{R\,T\,N_f}{\eta k_R P}\right)\int_{1-conv N_f}^{N_f}\frac{dN_f}{N_f} \qquad (10)$$

By putting the vales

k_R	=	19.6	(as defined in 'Rxn-1')
ε_B	=	0.2	
R	=	8.314 dm^3.kPa/mol.K	
T	=	473K	
N_f	=	0.06mole	
η	=	0.94	
P	=	150 kPa	

The calculated volume of the reactor is 0.0126 dm^3.

Particle diameter is set to be 1mm and since all the catalyst particles are spherical in shape; particle sphericity is set as 1. Density of the particle is given 5.8 kg/cm^3.After setting all the reactor parameters reaction set 'Rxn-1' is recalled.

Calculations are made by the HYSYS according to design parameters on the POM reaction. Simulation results into an 89% conversion of methanol (set as a base component) as shown in Fig. 10.

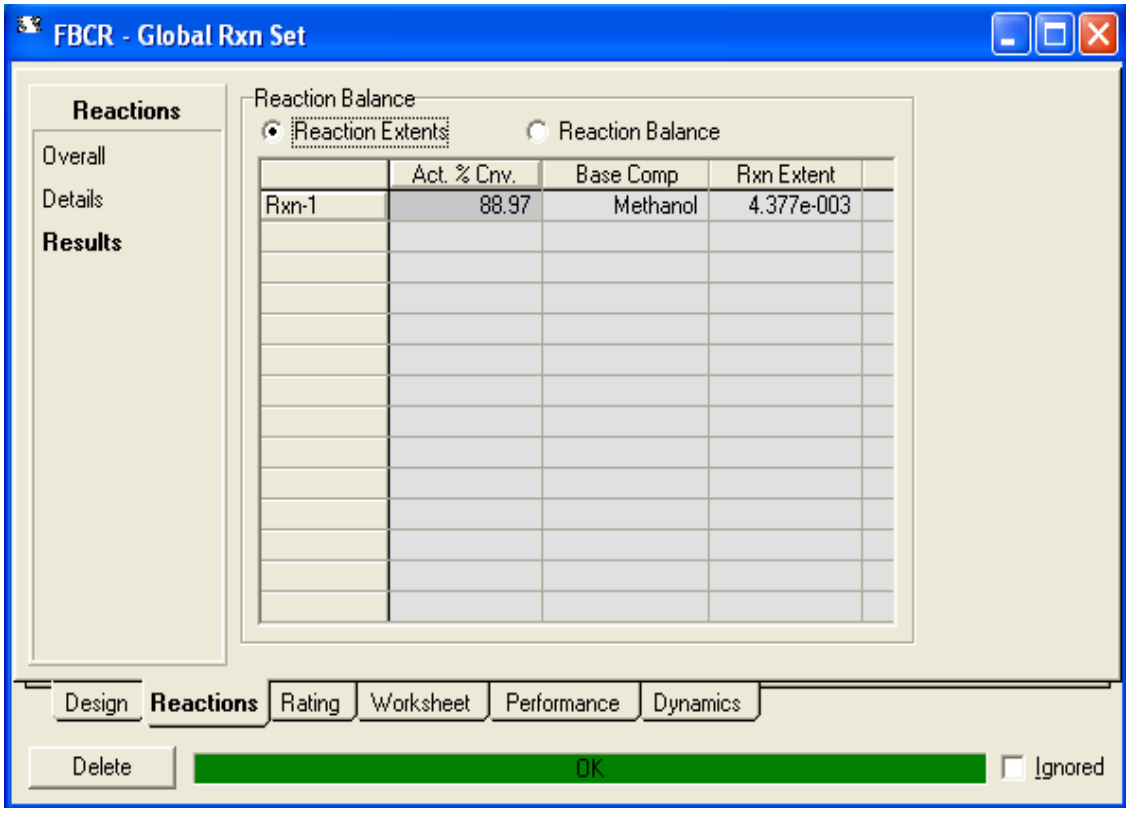

Fig. 10: Percentage conversion of methanol.

Pressure drop calculated on the basis of Ergun Equation is 3.501 kPa, which is well within the allowed range. After running the simulation 0.6278 mole fraction of hydrogen in the product feed stream is obtained. Detailed simulation process worksheet is shown in Table-2.

Table-2: Simulation process worksheet.

Component mole fraction	Methanol Stream	Oxygen Stream	Mixed Reactants	Product Stream
Methanol	1.000	-	0.667	0.038
Oxygen	-	1.000	0.333	0.0195
Hydrogen	-	-	-	0.6278
Carbon dioxide	-	-	-	0.3139

Experimental Setup

Experimental Rig

An experimental rig is designed and fabricated for the production of hydrogen by POM. Commercial grade Oxygen cylinder is used with a dual pressure regulator. Oxygen line is then attached with a gas flow meter of range 0.1 – 10 liters per minute. By adjusting flow rate, calculated oxygen at required pressure is fed to reactor. Methanol is kept in a tank located at the bottom of the rig. An electric heater is fitted inside the methanol tank for its vaporization. Compound pressure gauge and thermocouple are installed within the tank for continuous monitoring of tank pressure and temperature. Methanol tank has a drain valve and pressure relief valve for safety aspects. Methanol flow rate is controlled with a needle valve.

Single pass column of stainless steel is used as fixed bed catalytic reactor. Reactor column is filled with 45:55:5 of CuO: ZnO: Al_2O_3 catalyst (procured from Sigma-Aldrich) according to the required loading for maintaining the desired void fraction inside the column. Reactor is held vertically and thermocouple is installed to monitor the inside. Reactor is fully wrapped with heating tape to keep the column at temperature (210°C) required for POM.

Synthesis of Hydrogen Gas

Methanol is heated up to 80°C by using electric heater. When pressure inside the methanol tank reaches 1.5bar needle valve opens and methanol vapors are fed to the reactor. Flow rate is maintained at 0.7 liters per minute by flow meter fitted on the methanol line. Oxygen is then mixed with methanol at 1.5 bar (adjusted by pressure regulator) and at flow rate of 0.3 liters per minute (by a flow meter attached). Mixed reactants are then introduced to the reactor bottom which is kept at a temperature of

210°C. At this point heating tape must be switched off, since POM is an exothermic reaction temperature inside the reactor is now self-maintained. Reaction product leaving from the top of the reactor is analyzed with Perkin Elmer GC with 5A Mol Sieve Column and TCD detector. Argon gas is used as a mobile phase for GC analysis. Molar concentrations of different reaction product are calculated by the chromatogram as shown in Table-3.

Table-3: Molar %age from GC-TCD analysis.

Compound	No. of moles	Molar %age
Hydrogen	1.975	41.48
Oxygen	0.468	9.8
Water	0.81	16.67
Carbon dioxide	1.34	28.14
Methanol	0.168	3.52

Comparison between simulation and experimental results

Both simulation and experimental designs are identical in dimensions and process flow rates it is advantageous to give a comparison to calculate a deviation between the results of two processes. Comparison between experimental and simulation results is carried out in the form of percentage experimental yield. Losses are not included in the process simulation thus theoretical yield of hydrogen mole fraction is calculated on the basis of simulation results from Fig. 11.

Mole fraction of hydrogen from simulation model=0.67

For experimental result mole fraction of hydrogen is calculated from the Table-3.

Moles of hydrogen = 1.975

Total moles = 4.761

Mole fraction of hydrogen by experimental data = 0.42

$$\%\text{age Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} = 0.42/0.67 = 61\%$$

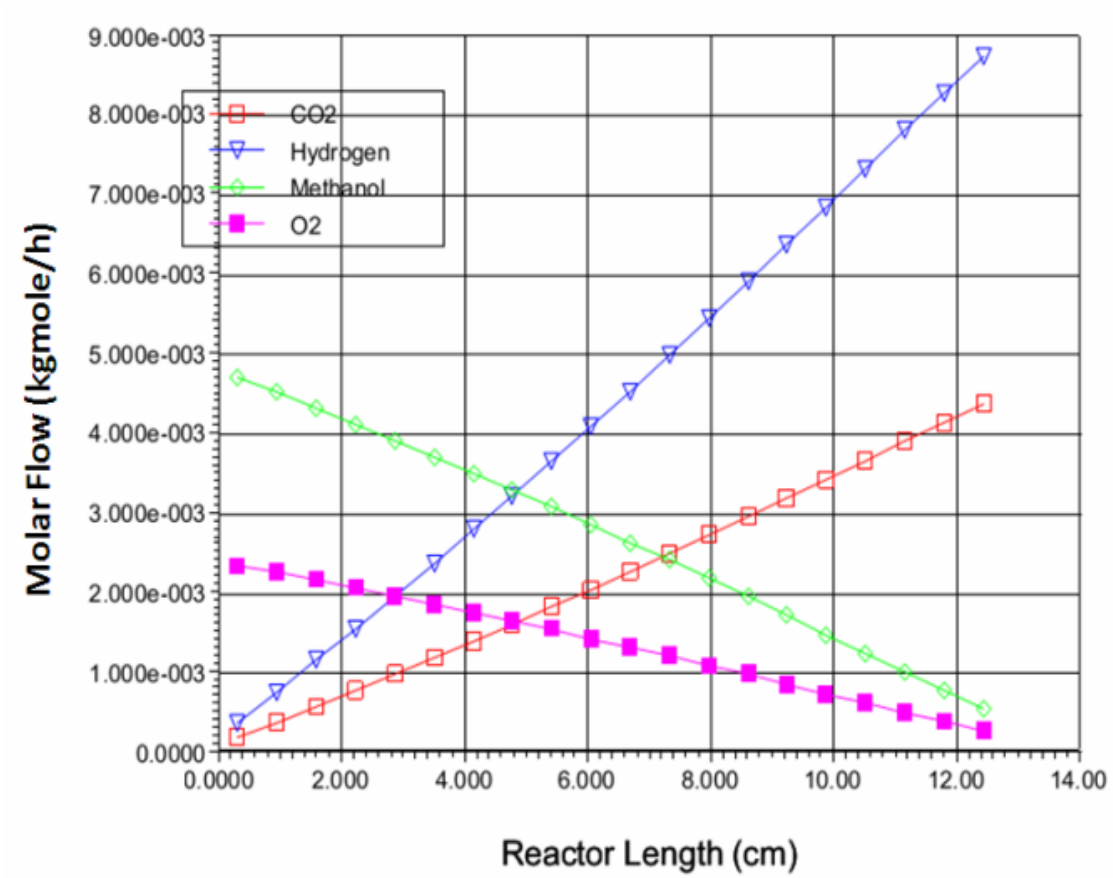

Fig. 11: Mole Fraction Vs Reactor Length.

Conclusion

Process selectivity of POM depends enormously on the nature of catalyst. Reaction is sensitive to the process conditions. Optimized process design is of high importance as number of side reactions are likely to happen even with a slightest change in operating conditions. Comparison between simulation and experimental processes, results into a yield of 61%. Thus the results discussed here not only validate the two processes but also give us the detail insight on the partial oxidation of methanol process. Design constraints and assumptions are also validated by these results.

Nomenclature

k_R	=Reaction rate constant
K_{ad}	=Adsorption Constant
K_{de}	=Desorption Constant
[X]	=concentration of X
V_R	= Volume of the reactor
ε_B	=Void fraction
R	=Ideal gas constant
N_f	=Molar flow
T	=Operating temperature
η	=Effectiveness factor (based on reaction kinetics)
k	=Reaction rate constant
P	=Pressure

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