

# **Design and Production of Hydrogen from Methanol**



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In

Energetic Materials Engineering

BY

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## **Dedication**

This piece of work is dedicated to all the Engineers and researchers of  
this world

## Acknowledgements

The following study is the effort undertaken by me under the sublime guidance of Almighty **ALLAH**, the most beneficent and merciful who gave me the will to complete my work.

I offer my gratitude to last prophet **Muhammad (P.B.U.H.)** who has given the lesson of “To seek knowledge is obligatory for every Muslim male and female.”

I wish to express my sincere gratitude and respect to my supervisor Dr. Arshad Hussain for his ideas and knowledge; he has imparted me during the conduction of this work. His support, guidance and encouragement is most appreciated.

I would like to take this opportunity to thank all my teachers and friends in the Department of Chemical Engineering at (SCME) for their time, help and kindness.

Acknowledgements are incomplete without the reference of my parents whose prayers were incessant and enabled me to reach this stage.

## **Abstract**

Hydrogen is the fuel of future. It has found its uses as an alternate energy source either by direct combustion or by electricity generation through fuel-cell. Hydrogen being the lightest gas has storage problems and risk hazards. In order to overcome these challenges idea of on-board production of hydrogen is popular among researchers. For on-board production of hydrogen process of partial oxidation of methanol is proposed and discussed in this work. For partial oxidation of methanol a fixed bed catalytic reactor is designed. In order to explain the method in detail computer aided modeling and simulation of process is carried out using Aspen-HYSYS V7.1 tool. Simulation studies are focused to optimize the process for best possible conversion of methanol to desired product hydrogen. By simulation various parameters and response of fixed bed reactor is studied in detail. Reaction kinetics is explained on the basis of Langmuir Hinshelwood model in this work. In order to make the whole process reliable experimental rig is also designed for physical production of hydrogen by partial oxidation of methanol. Results from both simulation and experimental work are analyzed and compared with each other.

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# Chapter 1

# Introduction



*“If we had a hydrogen economy worldwide, every nation on earth could create its own energy source to support its economy, and the threat of war over diminishing resources would just evaporate.”*

Dennis Weaver

**Hydrogen** is the chemical element with atomic number 1. It is represented by the symbol **H**. With an average atomic weight of 1.00794 amu (1.007825 amu for hydrogen-1), hydrogen is the lightest element and its monatomic form ( $H_1$ ) is the most abundant chemical substance, constituting roughly 75% of the Universe's baryonic mass. Non-remnant stars are mainly composed of hydrogen in its plasma state.

At standard temperature and pressure, hydrogen is a colorless, odorless, tasteless, non-toxic, nonmetallic, highly combustible diatomic gas with the molecular formula  $H_2$ . Naturally occurring atomic hydrogen is rare on Earth because hydrogen readily forms covalent compounds with most elements and is present in the water molecule and in most organic compounds. Hydrogen plays a particularly important role in acid-base chemistry with many reactions exchanging protons between soluble molecules.

## 1.1 History

Henry Cavendish (a British scientist) was the first one to discover Hydrogen in 1766 by reacting Zinc metal with hydrochloric acid. Sixteen years after this discovery in 1783 a French physicist Jacques Alexander Cesar Charles launched a manned Hydrogen balloon; this was the first time Hydrogen was used as a fuel. Later on in 1845 Sir William Grove (Father of Fuel Cell) created a “gas battery” on practical scale based on the fuel cell effect.

On commercial scale Hydrogen was first used by NASA in 1958 for their space programs. Currently NASA is using liquid Hydrogen primarily as a propellant and as a fuel for fuel cells. Practical hydrogen-air fuel cell was first built by Francis T. Bacon in 1959; it was a 5-kilowatt system.

The Hydrogen Economy Miami Energy Conference (THEME) was the first international conference on hydrogen energy organized in 1974 by the University of Miami. The scientists and engineers who attended the THEME conference formed the International Association for Hydrogen Energy (IAHE). World's first solar powered hydrogen production plant became operational in 1990 at Solar-Wasserstoff-Bayen, Germany. NECAR was the first hydrogen powered fuel-cell vehicle surfaced in 1994. Later on in 1995 Chicago Transit Authority unveiled their three hydrogen fuel-cell buses. Iceland proposed their 2030 hydrogen economy plan in 1998. First hydrogen fueling station was opened at German cities of Hamburg and Munich in 1999. U.S. Energy Secretary Spencer Abraham announced over \$350-million devoted to hydrogen research and vehicle demonstration projects in 2004 [1].

## 1.2 Hydrogen as an Energy Source

Hydrogen is without doubt the best source of energy available and saying that it's the oldest source of energy is not wrong; since we have been getting energy from sun as far as we could remember, which is merely a fire-ball of hydrogen gas and fusion reaction is taking place.

Hydrogen is now considered as the most appropriate alternate energy source based on its calorific value. 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) etc. Hydrogen possesses so enormous power that the biggest bomb produced till today is hydrogen-bomb and it is said that 3 hydrogen-bombs are enough to completely destruct the whole earth. On the other hand scientists also believe that if we can control a fusion reaction, it can solve the world energy crisis infinitely.

Exploring hydrogen for its use in PEM-Fuel cells is the current interest of energy scientists and engineers.

### 1.3 Challenges

#### 1.3.1 Risks & Hazards

In 1937 the *Hindenburg*, a dirigible inflated with hydrogen gas, erupted into flames while landing in Lakewood [1]. This accident raised another debate among the scientists regarding the safety issues involved with use of hydrogen energy. Hydrogen being the lightest gas has its storage limitations. As it easily escape between the interstices present in the material of container make it almost impossible to store hydrogen for a long period of time. R&D is still in progress addressing to this issue. Material scientists are trying to develop such a material that can hold hydrogen without any leakages and have the capacity to sustain appreciable pressure.

Hydrogen storage also raise the safety concerns since hydrogen is highly flammable it can easily catch fire by a mere spark of a kitchen lighter or even by a high friction giving it enough temperature to reach its flash point. Concentration of fuel is also important for the possible flammability and hydrogen has a wide flammable range in terms of its concentration. In reference to other fuels it has the highest flammability range as shown in fig-1.1.

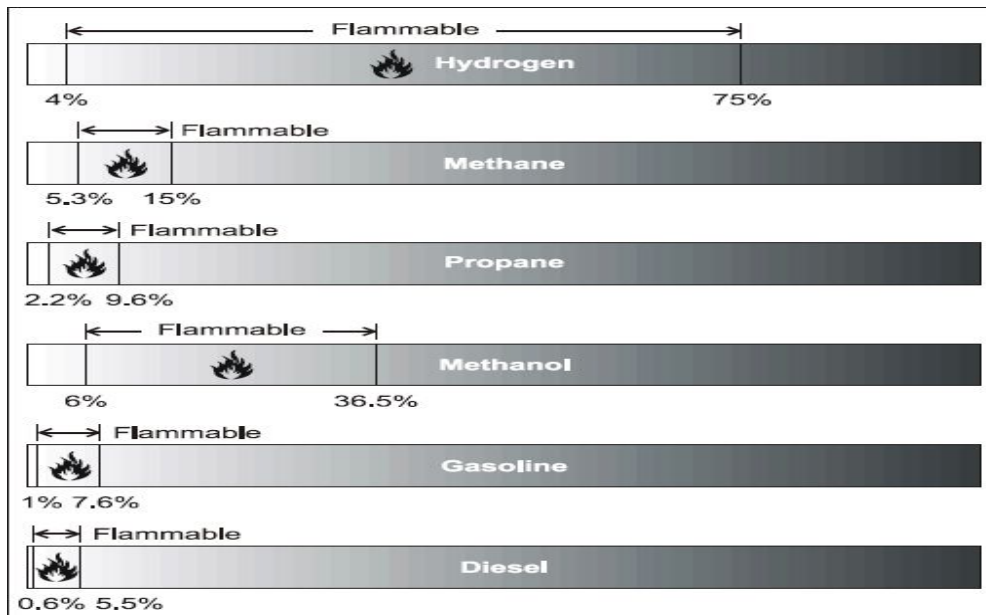


Figure 1-1: Flammability Ranges of Comparative Fuels at Atmospheric Temperature [2]

Not only hydrogen is highly flammable it has the tendency of explosion; between the concentrations of 15-59% with air it is a potential bomb [2]. A study has shown that the concentration of hydrogen leaking from an invisible cavity of hydrogen container can reach 18% in five minutes which is considerably in the explosion range and can generate a shockwave which in return can explode the whole container [3].

Hydrogen has the lightest density which means it occupies large volume. In order to supply sufficient amount of hydrogen as a fuel it has to be stored under high pressure, which in return increase the risk hazard. At high pressure the leakage of gas increased and so is the collision of molecules which in return increase the temperature of the gas taking it closer the self-explosion range, a slight stimuli can result into fatal consequences.

### **1.3.2 Challenges in Production**

Hydrogen can be produced by a number of ways like electrolysis of water, coal gasification (FT-process), oxidation of hydrocarbons. Some other methods are recently explored but have not yet gained enough popularity.

Electrolysis of water without doubt produce hydrogen in its purest form but it is also the most expensive method to produce hydrogen and on the grounds of economy it makes the whole process non-feasible. Also in terms of energy it becomes a closed loop as we are providing electrical energy in the first place to produce hydrogen which can then be used as a source of hydrogen.

All other processes are economically feasible but have a drawback of producing carbon-oxides (CO, CO<sub>2</sub>). These oxides not only affect the performance of the process but also a major environmental concern.

Keeping all these problems in view researchers and scientists are trying to develop methods which can effectively and economically produce hydrogen on large scale.

## 1.4 Scope of Study

This work is focused on addressing the issues of producing hydrogen economically and safely. The biggest problem is on-board storage and handling of hydrogen gas. Therefore an alternate method of on-board production of hydrogen is devised in this work. So we no longer have to store hydrogen rather we are able to there and then produce hydrogen for its further use. Variability in the production of hydrogen is also considered so that we can produce hydrogen in variable proportions depending upon its use.

All the work and calculations are made on a pilot scale so it can easily be upgraded to industrial scale. Places where limited amount of hydrogen is required like in fuel-cells or in combustion engines the process devised is sufficient to fulfill the requirements.

Reaction kinetics and process design are studied thoroughly and an optimized design is selected for the process. Parameters and variables are also considered in the design and their effects on the whole process are examined and compared with the reported work.

Work is further extended to a whole new dimension of process simulation which is the novelty of this work. Process simulation make the model dynamic and enable us to study the variable effect in more detail and to draw the dynamic profiles of transport phenomenon and heat & mass transfer more extensively. By simulation we can also improve and optimize the design to our requirements.

# Chapter 2

# Process Selection

## 2.1 Different methods of producing Hydrogen

Hydrogen can be produced by a number of methods. Some commonly used methods are:

- Steam reforming of hydrocarbons
- Coal gasification / Coal carbonization
- Electrolysis of water
- Oxidation of hydrocarbons

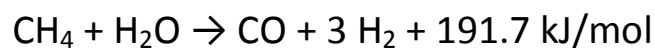
Some other new unconventional methods for producing hydrogen are:

- Plasma Reforming
- Photocatalytic water splitting
- Bio-hydrogen routes
- Enzymatic hydrogen generation
- Bio catalyzed electrolysis

These processes are still in their initial phases and have failed to produce any ground-breaking results; therefore, our focus is majorly on the processes with promising results.

### 2.1.1 Steam reforming of hydrocarbons

This process is the most dominant source of hydrogen. Highest process efficiency of natural gas (CH<sub>4</sub>) up to 80%. It is an endothermic process in which natural gas reacts with steam at high temperature of 700-1100 °C to yield syngas.



The main drawbacks of this process are its endothermicity and reaction is occurring at a very high temperature; we constantly have to provide energy to the process.

Use of methane to produce hydrogen also raise a logical question that why use a conventional energy source to produce another conventional energy source, why don't find an alternative.

### 2.1.2 Coal gasification

Coal gasification is one of the oldest methods to produce hydrogen on a large scale. This process has played a vital role in WWII. This process however critically depends on the grade and purity of the coal also the product is a mixture of  $H_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$ . Process efficiency is very low.

### 2.1.3 Electrolysis of water

Approximately 5% of industrial hydrogen is produced by electrolysis. In this process water is electrolyzed between two electrodes using a catalyst; Zirconium is normally used as a catalyst. Water is ionized and hydrogen is collected from anode. By electrolysis 99.99% pure hydrogen can be collected but it is also the most expensive method since a lot of energy is required for the ionization of water, even more than what we get from hydrogen.

### 2.1.4 Oxidation of hydrocarbon

Oxidation of hydrocarbon means reacting a hydrocarbon with oxygen at a given conditions. In case of complete oxidation  $CO_2$  &  $H_2O$  are the products which are not required here. However, by partial oxidation we get  $H_2$  and  $CO_2$ . This process has the advantage of exothermicity which makes the process self-sustaining and the reported yield of this process up to 96%. The only drawback of this process is its high selectivity.

Process	Advantages	Disadvantages
Steam reforming	Proven technology, industrial production capacity, high efficiency	Endothermicity, high formation of $CO$ , energy demanding
Coal gasification	Cheap raw product	Low efficiency, energy demanding, very high selectivity on the basis of raw material



Electrolysis of water	Highest efficiency, simple process	Most expensive, consume more energy than delivered
Partial oxidation	Exothermicity hence self-sustaining, high efficiency, economically more effective, capability to generate hydrogen on-board,	High selectivity, complex reaction mechanism,

Table 2-1 Comparative study of different processes

Method of partial oxidation is most advantageous and hence selected.

## 2.2 Selection of raw material

Partial oxidation method can be applied on various hydrocarbons, so the selection of suitable hydrocarbon for partial oxidation is of utmost importance. Factors to be considered in the selection of suitable raw material are:

- Tendency to give maximum %age yield
- Ease of availability
- Cheap material
- Must be synchronized with the process

On the basis of these factors Methanol is the most suitable raw material. Since it 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 [4]. Also methanol has the highest hydrogen atom over unit molar mass than any other material making it the most suitable material for hydrogen production.

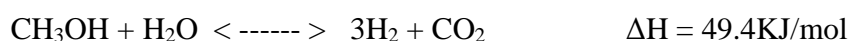
### 2.3 Detail description of partial oxidation of Methanol (POM)

Hydrogen can be produced from methanol by three different methods

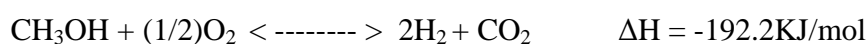
(i) Cracking



(ii) Steam Reforming



(iii) Partial Oxidation



Among these methods partial oxidation is the only process which is exothermic. 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. Feed ratio and pressure is important and it must be greater than the reactor pressure drop otherwise a back pressure will be generated which can cause catastrophic damages.

Reactor is filled with catalyst; since selectivity of reaction is very important catalyst plays the most vital role in this process. A solid catalyst is used in this process, as our reactants are in vapor phase a heterogeneous catalytic reaction take place in the reactor producing H<sub>2</sub> and CO<sub>2</sub>.

Different type of reactors like tubular, multi-tubular, wash-coated, gyratory reactors etc. can be used for POM. Among them single tubular packed bed reactor also called fixed bed catalytic reactor (FBCR) is the most suitable. In it reactor column is filled with catalyst and reactant vapors are allowed to pass through the voids between the catalyst surfaces.

A heterogeneous catalytic reaction takes place on the surface of the catalyst. First reactants are adsorbed on the surface of the catalyst making an activated complex which in return reacts to produce the H<sub>2</sub> and CO<sub>2</sub>. The products are then desorbed from the surface of the catalyst. Rate of

adsorption and desorption are the reaction rate determining factors. Reaction kinetics is based on the Langmuir Hinshelwood model (see chapter 3).

To provide appropriate activation energy to methanol reactor is heated to a temperature range of 200-250 °C. Heat transfer is a complex phenomenon in FBCR as heat is not distributed uniformly rather eddies are produced due to the porosity of the catalyst. Heat conduction capacity of catalyst is important while calculating energy balance.

FBCR is designed to provide the proper retention time for the reaction to take place. POM is reversible reaction so care is taken that reactor must not be over designed because backward reaction may speed up resulting into lower product yield. It is a continuous process so that reaction cannot achieve its equilibrium state otherwise at equilibrium both forward and backward reaction will be occurring which is highly undesirable. Selectivity of catalyst towards forward reaction is also important and must be considered while selecting the catalyst.

## 2.4 Selection of Catalyst

Catalyst is a substance used in small quantity as compared to the reactants, in order to accelerate the reaction without being consumed. Catalyst is not being consumed during the reaction however it might change its physical state. Catalyst is used not only to accelerate the reaction sometimes it is used even to initiate the reaction. Catalyst is specific in its function.

In partial oxidation of methanol catalyst plays the most important role as the whole reaction is taking place on catalyst surface. During POM number of side reactions are also taking place which are undesirable and also it is a reversible reaction so in this case catalyst not only accelerates reaction in forward direction but it also prevent side reactions and backward reaction to take place. This feature is called *selectivity*.

A number of materials had yet been used by researchers as a catalyst like Pt, Pd, Rh, Au, Cu etc. among those Copper (Cu) with ZnO has proven to be very effective and easily available. We in this project have used oxide of Cu (CuO) with ZnO as a catalyst. It is advisable to use catalytic

oxides in an oxidation reaction because there are likely chances that in spite of desired reaction the oxidation of catalyst may occur and the oxygen supplied be consumed undesirably.

Earlier work by Velu et. al. from Ceramics Technology Department, National Industrial Research Institute of Nagoya [5] suggested that 45:55 of Cu-ZnO has yielded the maximum conversion. During POM CO is also produced which decays the catalyst after a short period of time in order to overcome this drawback a small quantity of alumina (  $\text{Al}_2\text{O}_3$  ) is also added with the catalyst.  $\text{Al}_2\text{O}_3$  works as a stabilizer and the reported results say that catalyst does not deactivate even after the 110hr operation. Aluminum also does have an inhibiting effect in POM resulting into a slightly lower yield. A ratio of 45:50:5 of Cu-ZnO- $\text{Al}_2\text{O}_3$  has reported maximum yield with only traces of CO [5]. For this work the same ratio is been used

Particle size of the catalyst directly affects the available surface area, smaller the size larger be the surface area. As POM reaction is a surface phenomenon rate of reaction is very much dependant on the surface area. Smaller particles of few microns are used in this project. Size of catalyst also raise another complexity in the process; as we reduce the size of the particle the bed become more closely packed and so pressure drop is increased. To overcome this, an optimized bed size and particle size is adjusted to provide the appropriate bed porosity with void fraction of 0.2 (see Chapter 3).

## 2.5 Selected process Attributes

<b>Process</b>	<b>Partial Oxidation</b>
<b>Raw Material</b>	<b>Methanol</b>
<b>Type of Reactor</b>	<b>Single-Tubular Fixed Bed Catalytic Reactor with heating facility</b>
<b>Catalyst</b>	<b>45:50:5 CuO-ZnO-Al<sub>2</sub>O<sub>3</sub></b>

Table 2-2 Process Attributes

# Chapter 3

# Process Design

### 3.1 Process Design

POM is based on heterogeneous catalytic reaction in an FBCR, which is a complex process and requires a comprehensive designing. Ultimate goal of process design is to calculate the volume of the reactor. FBCR volume is calculated by the equation

$$V_R = - (1 - \varepsilon_B) \left( \frac{R T}{k} \right) \int_{N_f}^1 c^{n} \frac{dN_f}{N_f} \quad (3.1.1)$$

Where:

- $V_R$  = Volume of the reactor
- $\varepsilon_B$  = Bed porosity of the reactor
- $R$  = Ideal gas constant
- $N_f$  = Molar flow
- $T$  = Operating temperature
- $\eta$  = Effectiveness factor (based on reaction kinetics)
- $k$  = Reaction rate constant
- $P$  = Pressure

These are the parameters involved in the reactor design, have to be calculated individually and then incorporated in eq (3.1.1) to calculate the required volume. An interesting notable fact here is that if bed porosity and effectiveness factor here are taken to be constant unity the equation resembles to the plug flow reactor performance equation. This fact strengthens the concept that FBCR is based on plug flow reactor.

### 3.2 Bed Porosity

Bed porosity is also called void fractions. It is the factor that denotes empty space (voids) in the reactor for the flow of reactants through the catalyst. Bed porosity is defined as the volume of voids per volume of reactor and is calculated from the equation:

$$\epsilon_B = (1 - \rho_B / \rho_P) \quad (3.2.1)$$

Where:

$\rho_P$  = Density of the particle

$\rho_B$  = Density of the bed

$\epsilon_B$  is adjusted to be 0.2

On the basis of 0.2 void fractions we now have to calculate the bed density for catalyst loading.

From eq (2)

$$\rho_P = (1 - \epsilon_B) \rho_B$$

$$\rho \text{ of CuO} = 6.31 \text{ g/cm}^3$$

$$\rho \text{ of ZnO} = 5.61 \text{ g/cm}^3$$

$$\rho \text{ of Al}_2\text{O}_3 = 3.95 \text{ g/cm}^3$$

Catalyst used is in the ratio of 45:50:5

So

$$\rho_P = \frac{\text{CuO} \times 45 \quad \text{nO} \times 5 \quad \text{O} \times 5}{1}$$

$$\rho_P = 5.842 \text{ g/cm}^3$$



And

$$\rho_B = (1 - 0.2) 5.842$$

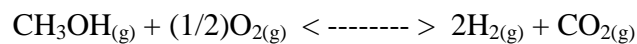
$$\rho_B = 4.6736 \text{ g/cm}^3$$

This means that for void fraction of 0.2 we must load 4.67 gm of catalyst per cubic cm volume of the reactor.

### 3.3 Molar Flow

Molar flow of reactants is very important in POM. Methanol and oxygen must be fed in their stoichiometric ratio or else there will be a complete oxidation resulting into water and carbon dioxide as the products.

Stoichiometry of reactants must be maintained according to the reaction eq:



From this eq it is clear that methanol and oxygen must be kept in the ratio of 2:1

Base component in this process is methanol so we apply material balance on the basis of methanol.

In order to keep a proper supply of methanol 0.04 mole/min feed of methanol is assumed.

$$\text{Methanol feed} = 0.04 \text{ mole}$$

Since oxygen is in ratio of 1:2 to methanol

$$\text{Oxygen feed} = 0.02 \text{ mole}$$

Both our reactants are in gaseous phase so we have to calculate the volumetric feed rate of reactants

**For Methanol**

As we know

$$1 \text{ mole} = 22.4 \text{ l} \quad (\text{at STP})$$

$$0.04 \text{ mole} = 22.4 \times 0.04$$

$$= 0.91$$

Methanol is fed in form of vapors and for that we have to heat the methanol thus our operating conditions varied from STP.

To vaporize methanol it is heated to the temperature of 80 °C and to overcome the back pressure it is kept at 1.5 bar pressure.

Operating conditions are

$$80 \text{ }^\circ\text{C} \text{ and } 1.5 \text{ bar}$$

Flow rate of methanol at operating conditions is calculated as

$$\frac{1}{1} = \frac{1}{1}$$

$$\frac{1}{9} = \frac{1.5}{5}$$

$$V_2 = 0.7$$

$$\text{Flow rate of methanol} = 0.7 \text{ lpm}$$

**For Oxygen**

Feed rate of oxygen stoichiometrically is 0.02 mole/min

Again

$$1 \text{ mole} = 22.4 \text{ l} \quad (\text{at STP})$$

$$0.02 \text{ mole} = 0.02 \times 22.4$$

$$= 0.448 \text{ l}$$

Oxygen is also fed at a pressure of 1.5 bar but at normal temperature

So again using Gas law:

$$\frac{1}{1} = \frac{1}{1}$$

$$\frac{1}{9} = \frac{1.5}{9}$$

$$V_2 = 0.3$$

$$\text{Flow rate of oxygen} = 0.3 \text{ lpm}$$

$$\text{Total flow rate of reactants in} = 0.3 + 0.7$$

$$= 1 \text{ lpm}$$

**3.4 Effectiveness Factor**

Effectiveness factor ( $\eta$ ) is a dimensionless factor. It actually tells the story that how reaction is taking place. Effectiveness factor is based on geometry of the catalyst and tells us how effectively catalyst is being used in the process and is very much dependant on rate of reaction.

For different geometrical shapes different equations of effectiveness factor are used. Some of these equations are:

Sphere	$\eta = \frac{1}{\Phi} \left[ \frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right]$
Cylinder	$\eta = \frac{1 I_1(2\Phi)}{\Phi I_0(2\Phi)}$
Slab	$\eta = \frac{\tanh \Phi}{\Phi}$

[6]

Where

$\Phi$  = Thiele Modulus

As our catalyst is spherical in shape we used the equation

$$\eta = \frac{1}{\Phi} \left[ \frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right] \quad (3.3.1)$$

### 3.3.1 Thiele Modulus

Thiele Modulus is a dimensionless factor and is defined as the ratio of rate of reaction to the rate diffusion of reactants into the catalyst particle [7]. Thiele modulus is the key factor in the whole designing process as it relates the rate of reaction to the efficiency of catalyst to the volume of the reactor. POM is a surface phenomenon and hence the rate of diffusion is ignored here as there is no diffusion of reactant gases into the catalyst particle. We are now concerned with the rate of reaction only.

### 3.3.2 Reaction Rate

POM is a heterogeneous catalytic reaction. There are several models of solving heterogeneous rate equations the most effective and promising model is however Langmuir Hinshelwood (LH) model.

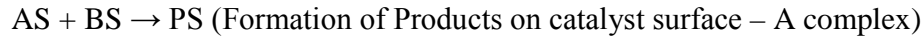
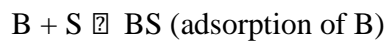
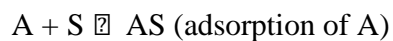
Langmuir Hinshelwood model is based on the fact that reaction occurs in three steps.

- (i) Adsorption of reactants on the surface of catalyst
- (ii) Reaction occurring on the surface of catalyst
- (iii) Desorption of products from the surface of catalyst

According to LH model the rate expression is given as

$$\frac{\text{kinetic factor} \times \text{rate of reaction}}{\text{adsorption} + \text{desorption} + \text{expression}}$$

### Basic Reaction Steps



On the basis of this the rate equation is given as

$$\frac{K C_A C_B}{1 + K_1 C_A + K_2 C_B}$$

Where:

R = Rate of Equation

K' = reaction constant

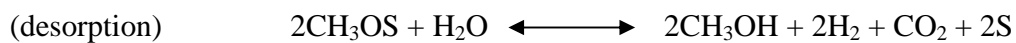
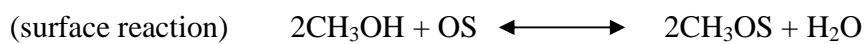
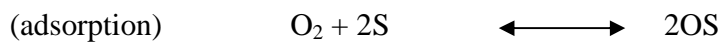
K<sub>1</sub> = Adsorption-Desorption constant of A

K<sub>2</sub> = Adsorption-desorption constant of B

$C_A$  = Concentration of A

$C_B$  = Concentration of B

For POM various mechanisms are proposed in literature based Langmuir Hinshelwood model. The most promising results are however reported by Lin et. al[8]. He proposed that reaction take place according to the mechanism.



It is to be noted that methoxide is produced on the surface reaction step 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 the decomposition of it. This implies that rate controlling step in this model is surface reaction where methoxide is being produced.

Rate equation in this mechanism is obtained from the Langmuir Hinshelwood Hougen Watson model which is an advanced model of LH. This model is based on the concept that rate controlling step must be focused while developing rate equation for any heterogeneous catalytic reaction.

Equation for the rate of reaction for the above mechanism according to LHHW model is calculated to be as

$$r = \frac{k_1}{1 + \frac{k_2}{k_3}}$$

Where:

$k_R$  = Reaction rate constant

$K_{ad}$  = Adsorption Constant

$K_{de}$  = Desorption Constant

$[X]$  = concentration of X

Rate of reaction is determined from the above rate equation at different values of reactant concentrations and is then plotted against the concentration of reactant per unit volume of the reactor.

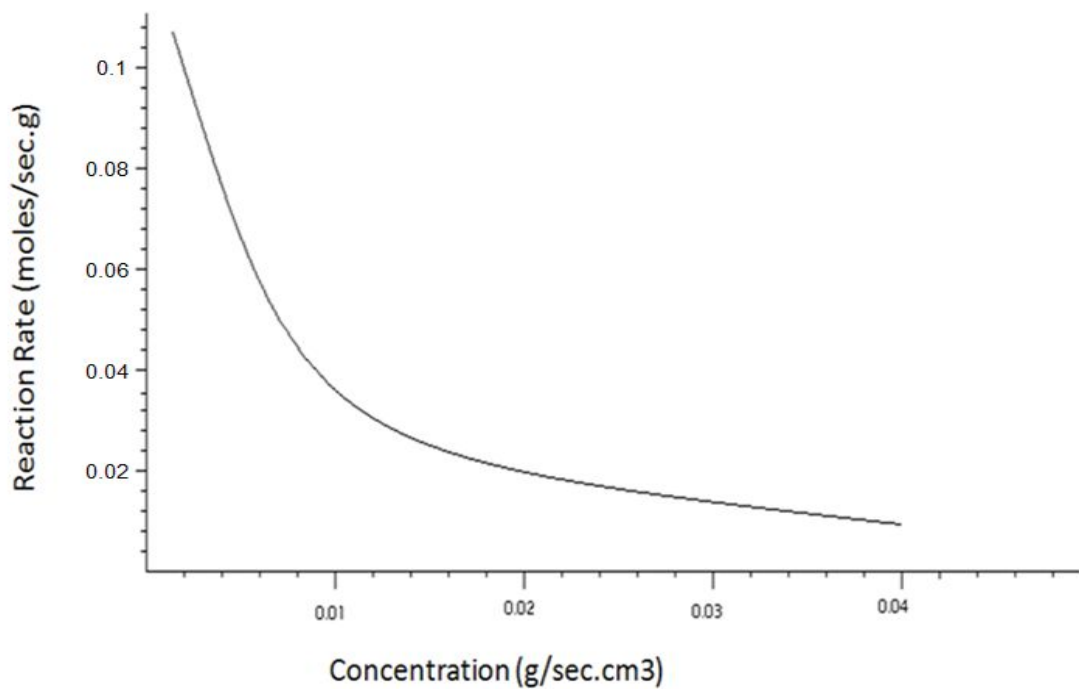


Figure 3-1 Rate of Reaction at different concentrations

According to our given flow rate of reactants the rate of reaction is calculated from this graph

From figure 3.1.1  $r = 0.04$  (moles/sec.g)

As our process is a surface phenomenon Thiele modulus is also the same

So

$$\Phi = 0.04$$

And now from this value of effectiveness factor is calculated using the eq 3.3.1

$$\eta = 0.94$$

### 3.4 Reactor Volume

Using the above equations volume of reactor can finally be calculated from eq 3.1.1

$$V_R = - (1 - \epsilon_B) \left( \frac{R}{k} \right) \int_{N_f}^1 c^{n\nu} N_f \frac{dN_f}{N_f}$$

By putting the vales

$$\epsilon_B = 0.2$$

$$R = 8.314 \text{ l KPa/mol.K}$$

$$T = 473\text{K}$$

$$N_f = 0.06 \text{ mole}$$

$$\eta = 0.94$$

$$P = 150 \text{ KPa}$$

And for 60% conversion



Volume of reactor is calculate to be

$$0.1166 \text{ dm}^3$$

Reactor is constructed in the form of vertical cylinder for the dimensions of reactor we fixed the length to dia ratio to be 7

$$L/d = 7$$

$$V = \frac{\pi}{4} d^2 L = 1.166 \times 10^{-4}$$

By putting  $L/d = 7$

$$\text{Length of reactor} = L = 0.1938\text{m} = 0.6358\text{ft} = 7.6\text{in}$$

$$\text{Dia of reactor} = d = 0.0276\text{m} = 0.0905\text{ft} = 1\text{in}$$

# Chapter 4

## Process Simulation using ASPEN\_HYSYS V7.1

Simulation is the imitation of the real-world process or system. For simulation a model is first developed based on the characteristics of the process. Computer simulation has now become a useful tool to understand the behaviors of various processes under different conditions. By simulation we cannot only study behaviors of our system but can also optimize our model for our desired results.

## **4.1 ASPEN HYSYS**

Aspen HYSYS is a market-leading chemical process modeling tool for conceptual design, optimization and performance monitoring. Aspen HYSYS is a core element of AspenTech's aspenONE® Engineering applications. HYSYS has a built in library of commonly used compounds along with their properties which make the simulation easy and effective.

## **4.2 Simulation and Modeling of POM**

Simulation of POM is carried out using latest HYSYS v7.1. A complete dynamic model is created using this tool and FBCR is designed along with reaction kinetics to observe the behavior of the reactor under different conditions. Parameters calculated in Chapter 3 are incorporated in this model to get the optimized results. Step by step modeling of the POM is given as:

### **Step-I**

Components and appropriate fluid package is taken. Components are taken from the master component list of HYSYS as shown.

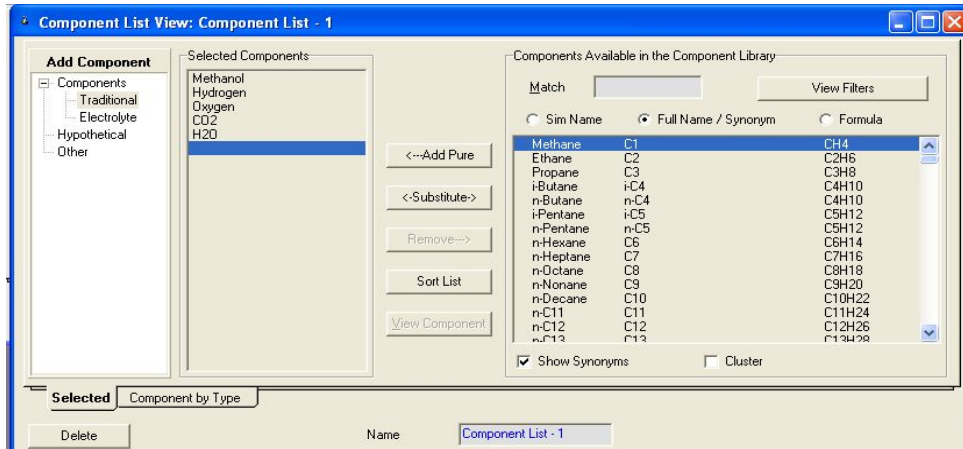


Figure 4-1 Selected components List

Since Hydrogen is closest to the ideal gas in its properties Peng Robinson fluid package is taken which consider gases to be ideal in nature and an extensive thermodynamic properties are included in this package.

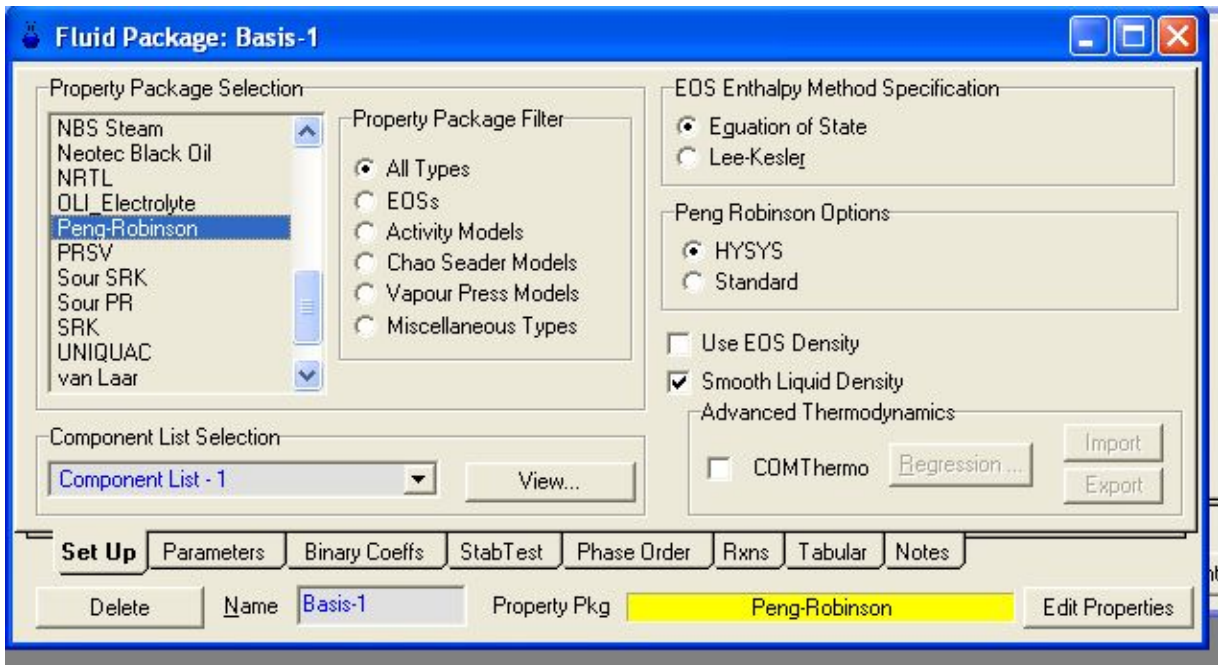


Figure 4-2 Selected fluid package

**Step II**

After selecting the components and fluid package reaction kinetics is defined. HYSYS has the provision to choose a type of reaction from a list available. POM is a heterogeneous catalytic reaction so same reaction type is taken.

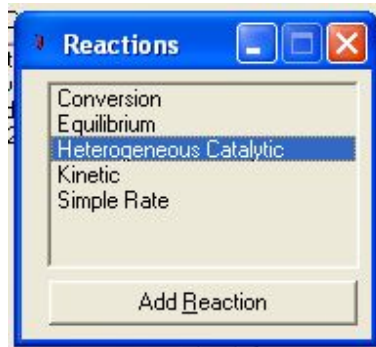


Figure 4-3 Selected reaction type

In HYSYS heterogeneous catalytic reactions are based on LH model which is the same model on which reaction kinetics of POM were calculated during process design (see Chapter 3). Reaction kinetics for the model are defined here using the same parameters calculated earlier.

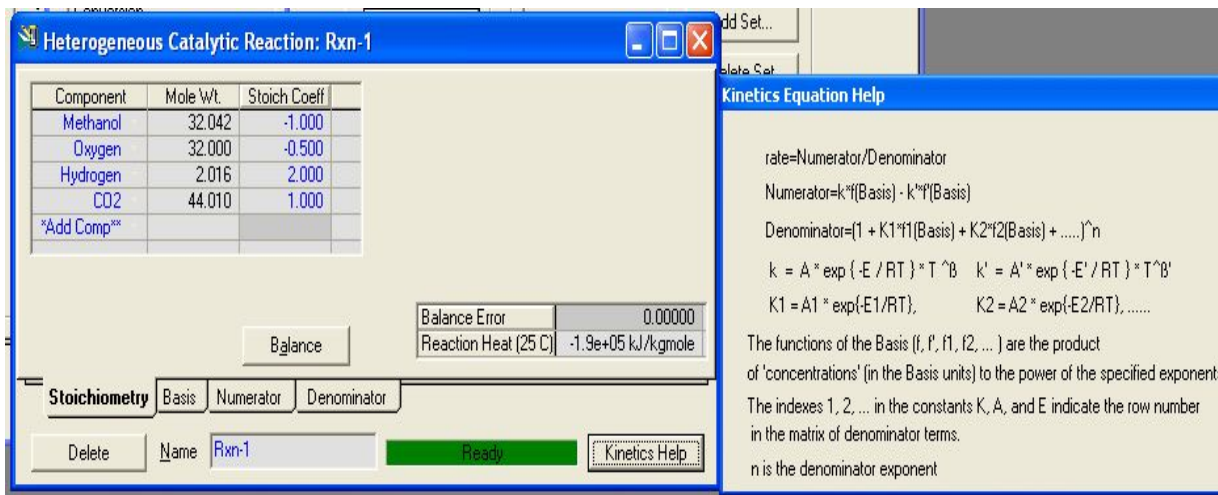


Figure 4-4 Defined heterogeneous catalytic reaction

When all the parameters are defined the reaction tab turns to the 'Ready' mode. Reaction is then saves in the reaction set 'Rxn-1' which can now be called where needed.

**Step-III**

After setting these parameters we then entered into the simulation environment. Now two material streams are taken for methanol and oxygen respectively. A mixer 'Mix-100' is attached which mix the 2 reactants according to the proportion of 2:1 and provide us with a single stream 'mixed reactants'. This stream is then pre heated to the desired temperature of 200 °C using a heater 'E-100'. And now finally our reactants are introduced to horizontal FBCR from bottom. Product stream is taken from the top of the reactor. As POM is an exothermic reaction, heat is evolved. To maintain the temperature inside the reactor a cooling line is also attached to the reactor. Complete process flow diagram is as:

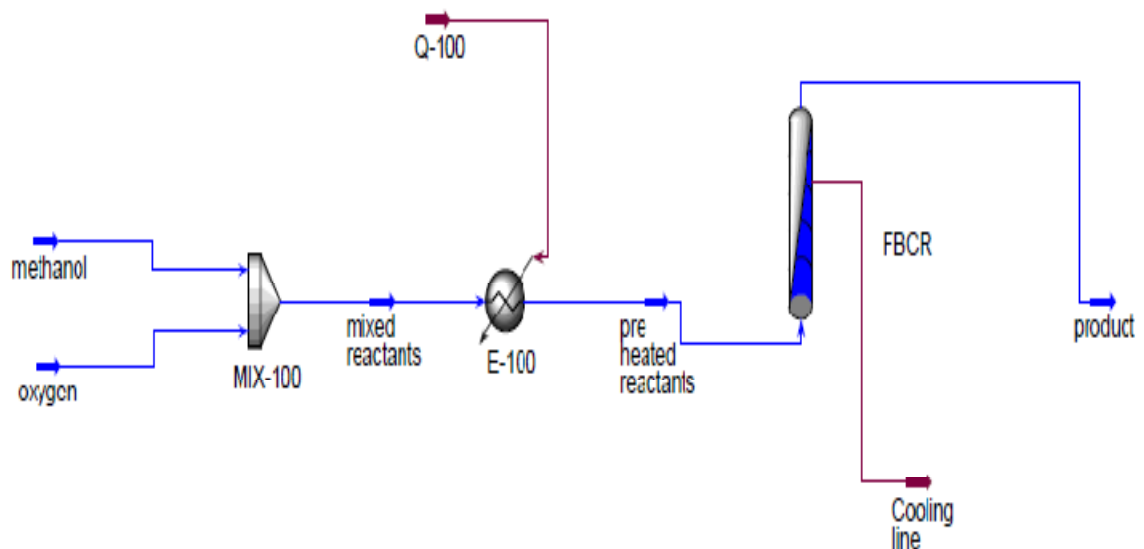


Figure 4-5 Simulation process flow diagram

**Step-IV**

FBCR is now designed to carry out the POM reaction. Plug Flow Reactor (PFR) model is chosen from the equipment pellet for this. Fixed Bed Catalytic Reactor is based on the performance equation of PFR and PFR model and PFR model in HYSYS also has the provision to define the catalyst data. These arguments justify the decision of selecting PFR model.

At first material streams of ‘pre-heated reactants’ and ‘products’ is attached with the reactor along with the energy stream of ‘cooling line’.

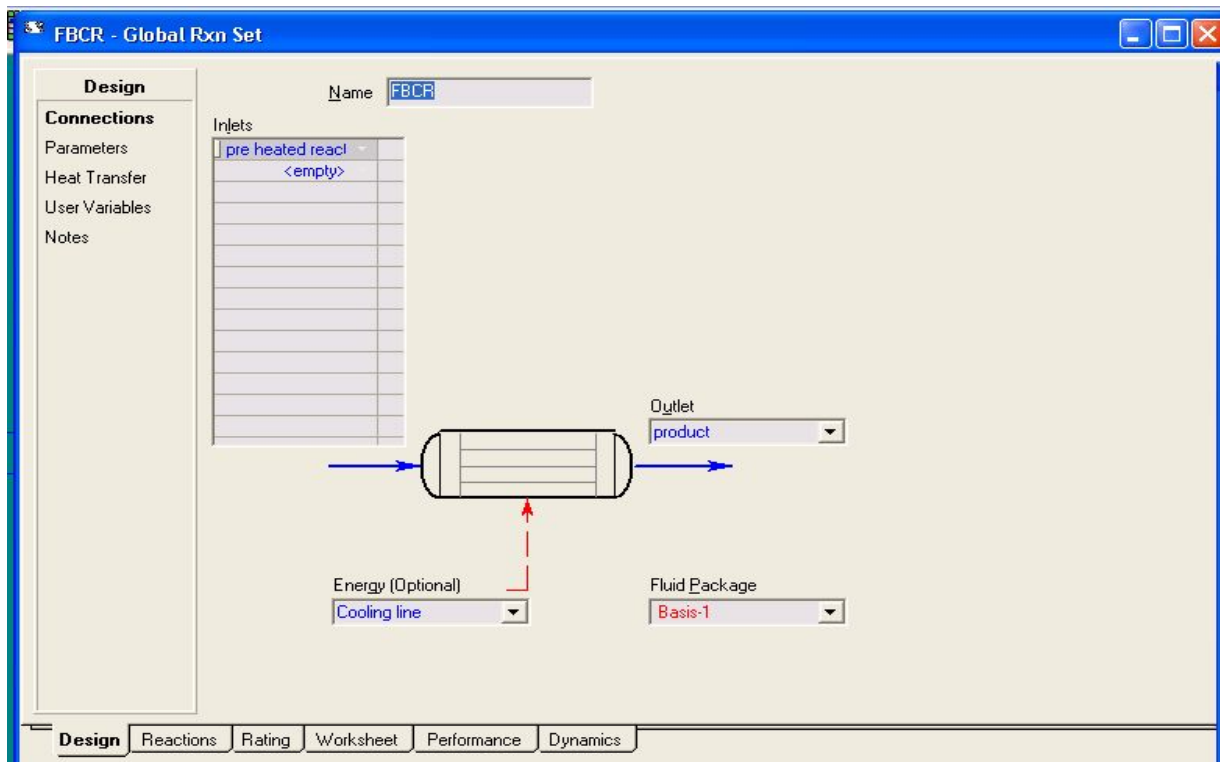


Figure 4-6 Material & Energy streams in FBCR

**Step-V**

Dimensions of reactor are now defined according to the calculated volume of reactor in Chapter 3. Length of the reactor is given to be 0.194 m and the diameter is defined to be 0.0276 m. volume of reactor thus calculated by HYSYS is  $1.16 \times 10^{-4} \text{ m}^3$ , which is same as calculated earlier. FBCR is a single pass tubular reactor; so number of tubes is set to be 1. POM is a surface reaction phenomenon therefore; in the column of tube packing void fraction is set to 0.2.

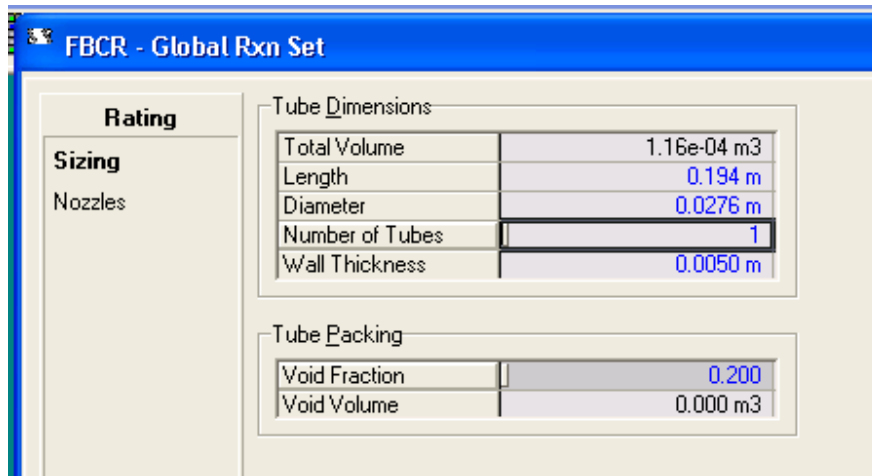


Figure 4-7 FBCR design parameters

Once the void fraction is adjusted  $< 1$  HYSYS automatically asks for the catalyst data. Particle diameter is set to be 1mm and since we have assumed that all the catalyst particles are sphere in shape; particle sphericity is set as 1. Density of the particle is given  $5.8 \text{ kg/cm}^3$  according to the calculations done in Chapter 3. HYSYS calculated the bulk density equals to  $4.7 \text{ kg/cm}^3$ , which is the same as calculated earlier.



Catalyst Data	
Particle Diameter	0.00100 m
Particle Sphericity	1.000
Solid Density	5.8 kg/m <sup>3</sup>
Bulk Density	4.7 kg/m <sup>3</sup>
Solid Heat Capacity	250.000 kJ/kg-C

Figure 4-8 Catalyst data

### Step-VI

After setting all the reactor parameters reaction set 'Rxn-1' is called. Rxn-1 comprises of POM reaction which was already defined in Step-II.

**Reactions**

Overall  
**Details**  
 Results

Reaction Details

Reaction: Rxn-1 [View Reaction...]

Specifics:  Stoichiometry  Basis

Stoichiometry

Comp	MWt	Coeff
Methanol	32.04	-1.0
Oxygen	32.00	-0.5
Hydrogen	2.016	2.0
CO2	44.01	1.0
<empty>		

Balance Error: 0.0000  
 Reaction Heat (25 C): -1.925e+005 kJ/kgmole

Design **Reactions** Rating Worksheet Performance Dynamics

Delete [OK] Ignored

Figure 4-9 Reaction set in FBCR

FBCR now understand that Rxn-1 reaction is taking place inside the reactor. Simulator key pressed to activate the simulation. Calculations are made by the HYSYS according to our design parameters on the POM reaction based upon the Peng Robinson fluid package. The status bar is turned to green with an “OK” message. This is a confirmatory report that reactor design is proper and simulation is now working effectively.

**Step-VII**

For further confirmation Pressure drop is calculated by the HYSYS using famous Ergun Equation.

$$\Delta P/L = \frac{150 \mu u_o}{(\phi_s dp)} \times \frac{(1-C_b)^2}{C_b^3} + \frac{1.75 \rho u_o}{(\phi_s dp)} \times \frac{(1-C_b)}{C_b^3}$$

Pressure drop calculated by HYSYS is 3.501 KPa, which is well within the allowed range.

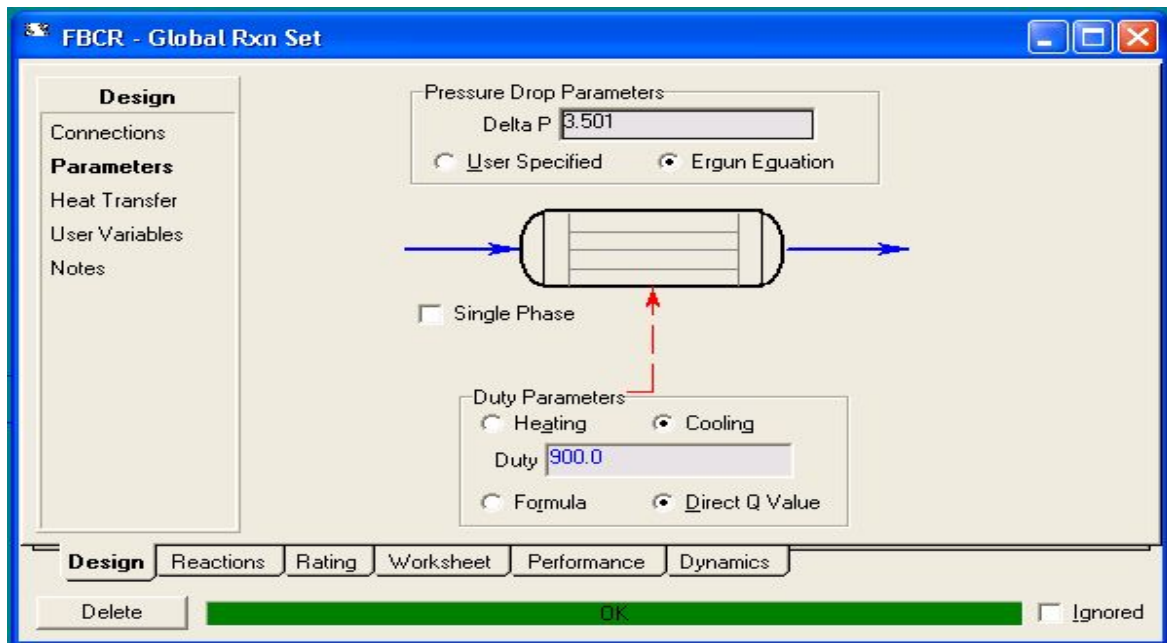


Figure 4-10 Pressure drop in FBCR

### 4.3 Simulation Results

Model is now fully defined and results are obtained from the simulation. Flow sheet of the model is given as

The screenshot shows the 'Workbook - Case (Main)' window with the 'Compositions' tab selected. The table displays the composition of various streams. The 'mixed reactants' stream has a mole fraction of 0.6667 for Methanol and 0.3333 for Oxygen. The 'product' stream has a mole fraction of 0.0389 for Methanol and 0.6278 for Hydrogen. The 'methanol' stream has a mole fraction of 1.0000 for Methanol. The 'oxygen' stream has a mole fraction of 1.0000 for Oxygen. The 'pre heated reac' stream has a mole fraction of 0.6667 for Methanol. The 'New' stream has a mole fraction of 0.0000 for Methanol, 0.0000 for Oxygen, and 0.0000 for Hydrogen. The 'H2O' and 'MEAmine' streams have mole fractions of 0.0000 for Methanol, 0.0000 for Oxygen, and 0.0000 for Hydrogen.

Name	mixed reactants	product	methanol	oxygen	pre heated reac	** New **
Comp Mole Frac (Methanol)	0.6667	0.0389	1.0000	0.0000	0.6667	
Comp Mole Frac (Oxygen)	0.3333	0.0195	0.0000	1.0000	0.3333	
Comp Mole Frac (Hydrogen)	0.0000	0.6278	0.0000	0.0000	0.0000	
Comp Mole Frac (CO2)	0.0000	0.3139	0.0000	0.0000	0.0000	
Comp Mole Frac (H2O)	****	****	****	****	****	
Comp Mole Frac (MEAmine)	****	****	****	****	****	

Material Streams: MIX-100, E-100  
 Fluid Pkg: All  
 Include Sub-Flowsheets  
 Show Name Only  
 Number of Hidden Objects: 0  
 Horizontal Matrix

Figure 4-11 Simulation process work sheet

After running the simulation we obtain 0.6278 mole fraction of hydrogen in the product feed stream which is a confirmation that hydrogen is being produced and also the mole fraction of methanol is reduced from 0.667 mole fraction in mixed reactants stream to 0.0389 mole fraction in product stream shows that methanol is being consumed for the production of hydrogen.

Detailed ASPEN Tech auto generated report of model is given in Annex-A.

# Chapter 5

# Experimental

# Work

For physical production of hydrogen by POM an experimental rig is developed. The experimental setup is a pilot scale unit capable to carry out the POM at the desired temperature and pressure conditions.



Figure 5-1 Experimental rig

## 5.1 Parts of Experimental Rig

Laboratory scale experimental rig comprises of following parts

- Oxygen Cylinder
- Methanol tank
- Gas Purger
- Electric Heater
- Thermocouple
- Drain Valve
- Needle Valve
- Compound Pressure Gauges
- Pressure relief valve
- Gas flow meters
- Pneumatic connectors
- Fixed bed catalytic reactor
- Heating tape
- Gas container
- Control Panel
- Stand for rig

## 5.2 Experimental Setup

Commercial grade Oxygen cylinder is used with a dual pressure regulator. By regulator pressure of oxygen supplied to the rig can be adjusted. Oxygen line is then attached with a gas flow meter of range 0.1 – 10 liters per minute, thus by using flow meter calculated oxygen at required pressure is supplied.

Methanol is kept in a tank located at the bottom of the rig. Tank is filled with liquid methanol up to the required mark. For vaporizing methanol in to gaseous state electric heater is attached

inside the tank. Thermocouple is also attached with the tank for continuous monitoring and control of tank temperature. For measuring the pressure of methanol vapors a compound pressure gauge is used. Methanol tank also have a drain valve and pressure relief valve for safety aspects. Methanol line is controlled with a needle valve and for flow adjustment another flow meter of the range 0.2 to 2 liters per minute is used.

Single pass column of stainless steel is used for fixed bed catalytic reactor. Column of calculated specifications is made and filled with catalyst according to the required loading for maintaining the desired void fraction inside the column. Filter paper and metal gauze sheets are used for holding the catalyst inside the column whereas allowing gaseous compounds to pass through the column. Both sides of the reactor are properly sealed to avoid any gas leakages along the column.

Reactor is held vertically with the stand using a holder. Thermocouple is attached with reactor for measuring and maintaining the temperature inside the reactor. Reactor is then fully wrapped with heating tape to provide heat to the reactor for keeping the column at temperature required for POM reaction to take place.

Gas pycnometer is used for collecting product gas sample attached at the outlet of reactor. Product gas is stored in the pycnometer for further analysis by GC or by any other analytical technique.

Control panel is used for controlling temperature inside methanol tank and reactor. Thermocouples and heaters are attached to a PID controller for automated adjustment of temperatures at both points.

Complete experimental setup is insulated by glass wool for preventing any heat loss during the process. Pneumatic connectors are used to attach gas supply lines with flow meters.

### 5.3 Experimental Procedure

1. Methanol tank is filled with methanol up to the required level and tank is fully sealed for preventing any gas leakages.
2. Temperature is then adjusted at 80 °C from control panel for methanol heating using electric heater. Care should be taken that heater must be fully immersed inside methanol.
3. When temperature raises methanol begin to vaporize and start exerting pressure on the walls of container. Pressure inside the tank is measured by the pressure gauge.
4. Within the mean while reactor is also heated using heating tape. Reactor temperature is maintained at 210 °C using thermocouple. 210 °C is the required temperature for POM reaction.
5. When pressure inside the methanol tank reach 1.5 bar needle valve is opened to supply methanol. Flow rate is maintained at 0.7 liters per minute using flow meter attached along the methanol line.
6. Oxygen from O<sub>2</sub> cylinder is then purged to the methanol at pressure 1.5 bar (adjusted by pressure regulator) and flow rate of 0.3 liters per minute (adjusted by a flow meter attached).
7. Mixed reactants are then introduced to the FBCR from bottom which is kept at a temperature of 210 °C. Care should be taken that reactor is fully sealed to avoid any leakages.
8. While reactant gas is introduced temperature of FBCR must be kept constant as POM is sensitive to temperature conditions.
9. At this point heating tape must be switched off, since POM is an exothermic reaction temperature inside the reactor is now self-maintained.
10. A rise in temperature at this point in the reactor temperature itself is a confirmatory test that POM is successfully occurring inside the reactor as all the other possible reactions are endothermic in nature.
11. Product gas leaving from the top of the reactor is stored in pycnometer for further analysis. product gas must be collected for 4 to 5 minutes so that a reasonable pressure is maintained inside the pycnometer; necessary for gas analysis specially when analyzing the sample using Gas Chromatography.



12. Collected gas is then analyzed using GC with TCD detector.

## 5.4 Product Gas Analysis

Ultimate goal of product gas analysis is to verify the production of hydrogen gas. Not very analytical techniques are available for hydrogen gas analysis as it is the lightest compound present many fine analytical techniques fails to identify the presence of hydrogen gas. However Gas Chromatography (GC) is a technique that can effectively analyze hydrogen gas provided that proper column along with proper detector is available for sample analysis.

GC comes with various detectors like Flame Ionization Detector (FID), Electron Capturing Detector (ECD), Mass Spectrometer (MS) Detector, Thermal Conductivity Detector (TCD) etc. among these only TCD detector is capable of detecting hydrogen gas.

For our product analysis Perkin Elmer GC with 5A Mol Sieve Column and TCD detector is used. Argon is used as a carrier gas and resultant Gas Chromatograph obtained is

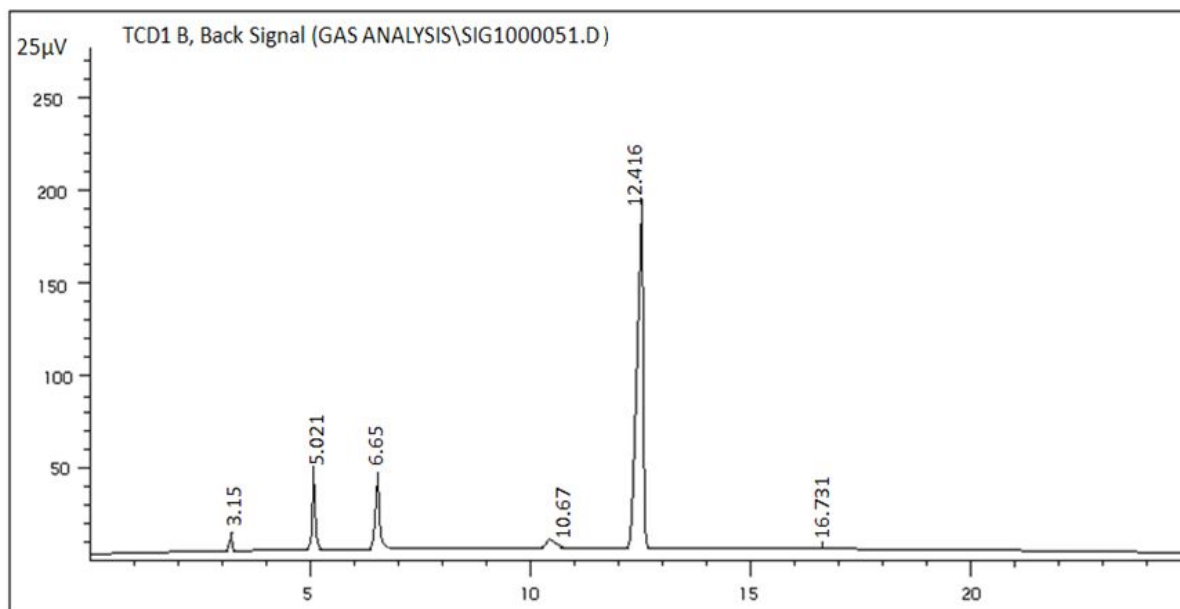


Figure 5-2 GC-TCD analysis of product mixture

Explanation of peaks obtained in chromatogram is as follows

<b>Retention Time</b>	<b>Compound</b>	<b>Wt %age</b>
3.15	Hydrogen	3.95
5.021	Oxygen	14.98
6.65	Water	14.58
10.67	Methanol	5.4
12.416	Carbon dioxide	59.01
16.731	Impurity	2.08

Table 5-1 wt %age from GC-TCD analysis

Weight percentages obtained from chromatogram are then converted into their respective mole percentages and the results obtained after calculation are:

<b>Compound</b>	<b>No. of moles</b>	<b>Molar %age</b>
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

Table 5-2 Molar %age from GC-TCD analysis

# Chapter 6

# Results &

# Discussion

After performing simulation and experimental production of hydrogen by POM various results are obtained. These results are discussed here along with comparisons between simulation and experimental observations and with reported literature data.

### **6.1 Results of process simulation**

As discussed in detail in chapter 4 the process simulation was carried out using Aspen-HYSYS V7.1. Simulation model provides the results which are helpful in the optimization of the process. Simulation also tell us 'the inside the reactor' phenomenon. These results help us in getting a better understanding about the POM process. Results obtained from simulation by HYSYS are in graphical form plotted by the Aspen-HYSYS tool.

### 6.1.1 Compound Production rate Vs Reactor Length

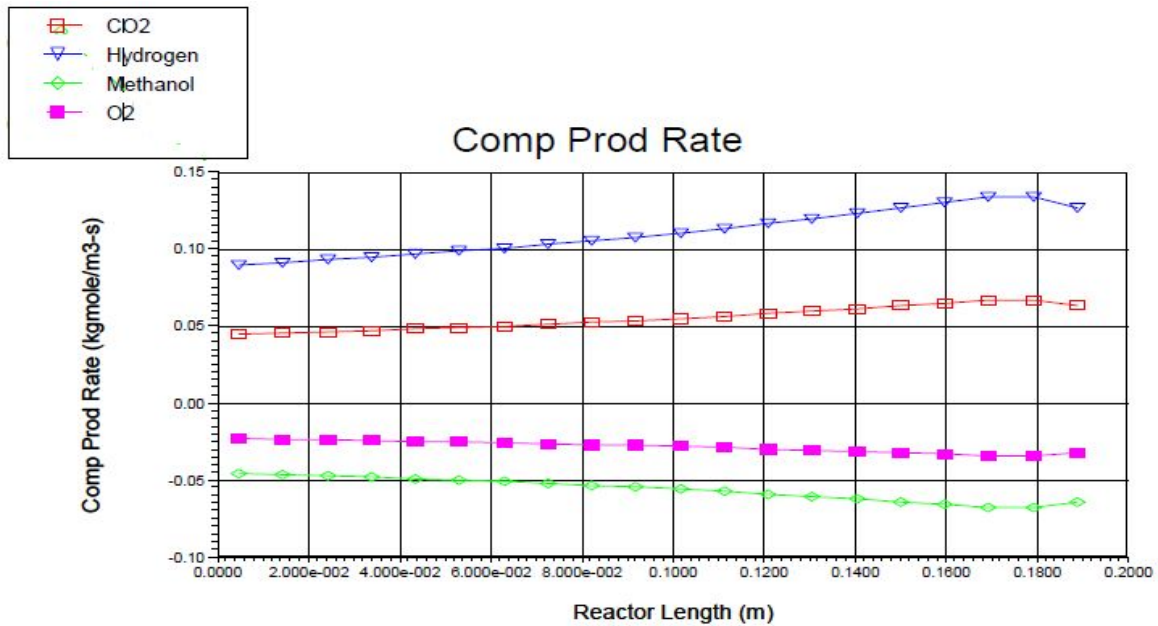


Figure 6-1 Compound Production rate Vs Reactor Length

The plotted graph shows that production rate of hydrogen is in increasing trend along the reactor length till the length of 0.18 m and after that hydrogen production rate is decreased. This result implies that optimized reactor length is 0.18 m for POM. It is also notable that the point from which production rate of hydrogen is decreasing production rate of methanol is increasing which means that now backward reaction is speeding up and if we design the reactor of greater length backward reaction will start to occur and the product gained from such reactor will be of much lower conversion.

### 6.1.2 Heat Capacity Vs Reactor Length

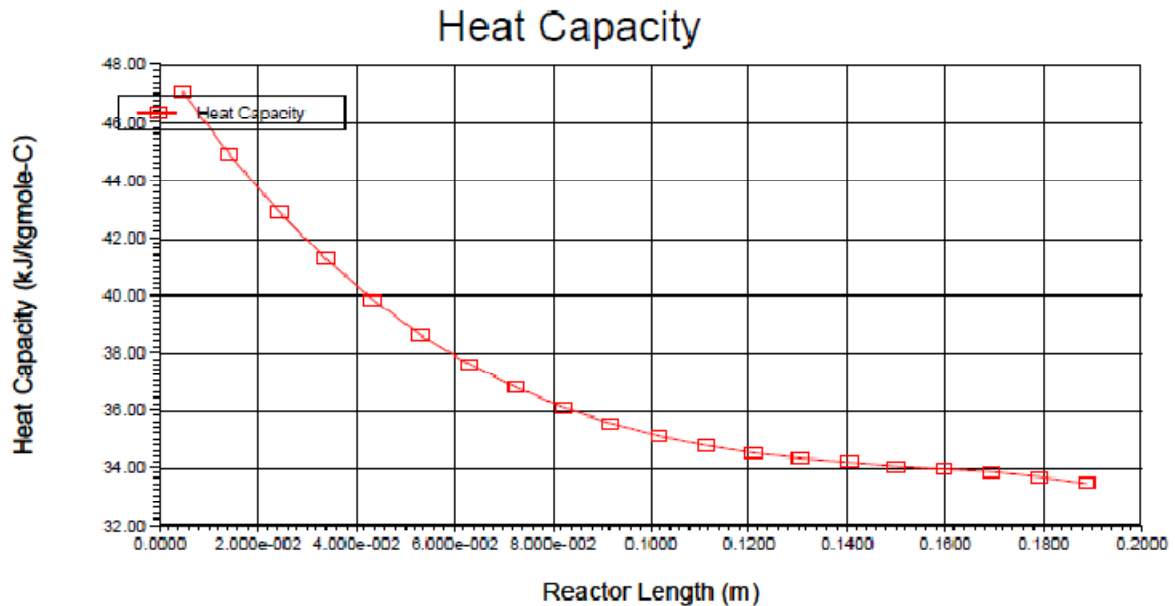


Figure 6-2 Heat Capacity Vs Reactor Length

Along the reactor heat capacity is being reduced which shows that compounds of lower heat capacity are being produced. Since hydrogen has a fairly low heat capacity than methanol the plotted graph proves that hydrogen is being produced and methanol is being consumed along the reactor. The plot also gives rise to another discussion of efficient heat supply to the reactor. As at the end of the reactor heat capacity is low so all the the heat present at this region would be consumed by the catalyst and thus temperature of catalyst will be higher at this region and the goal of uniform temperature will not be achieved. For this a differential model of heat transfer has to be produced to get an idea of point to point energy requirement in the reactor.

### 6.1.3 Mole Fraction Vs Reactor Length

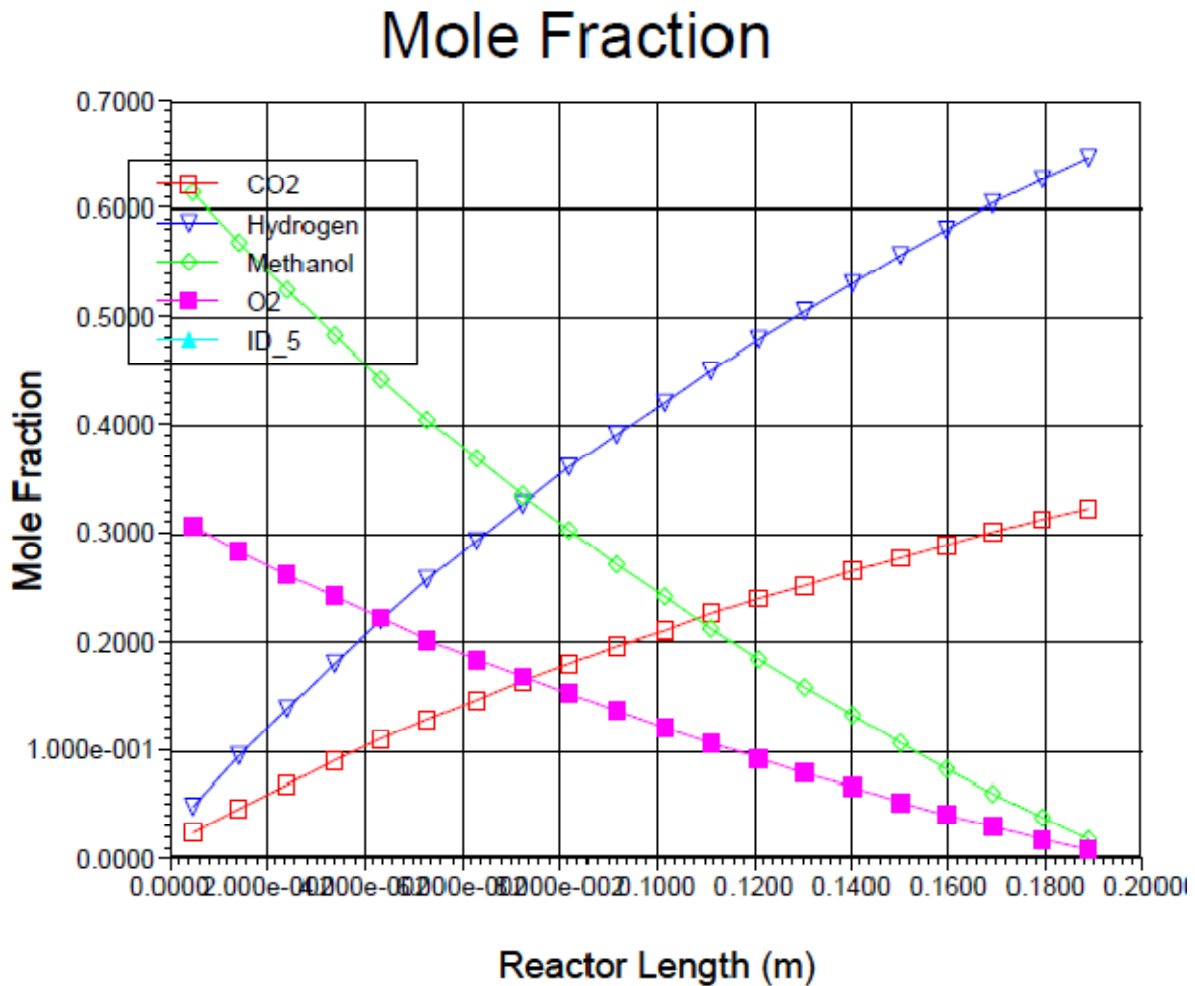


Figure 6-3 Mole Fraction Vs Reactor Length

This graph shows the production of hydrogen. Initially the mole fraction is 0.66 methanol and 0.33 oxygen which is the mole fraction of reactants being introduced to the reactor. Along the reactor length mole fraction of methanol is almost zero and mole fraction of hydrogen is increased from 0 to 0.67. mole fraction of hydrogen is increased at the highest rate the reason is simple that hydrogen is the lightest material and have highest no. of moles per unit weight. The slope (either increasing or decreasing) of carbon dioxide is the lowest only because it is the heaviest material present in POM process.

### 6.1.4 Pressure Vs Reactor Length

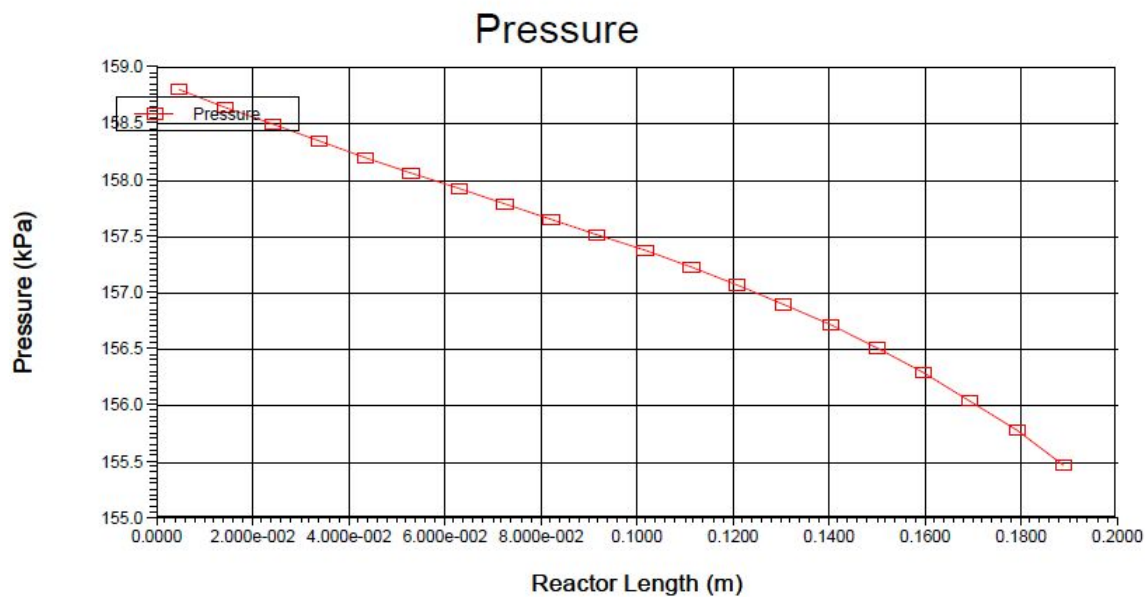


Figure 6-4 Pressure Vs Reactor Length

This plot shows the pressure drop at any point in the reactor. Now from this graph we have the pressure drop and length and by incorporating these values of  $\Delta P/l$  in Ergun Equation we can have the superficial critical velocity of any compound at any point inside the reactor, which is an important factor while studying the fluid dynamics.



## 6.2 Results of Experimental Work

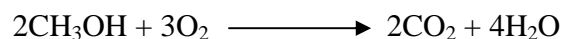
Experimental work carried out on the FBCR is discussed in detail in Chapter 5. Results obtained by the analysis of product gas from GC are really interesting.

### 6.2.1 Presence of excess Oxygen

It is notable that Oxygen is present in excess quantity as compared to methanol. This implies that methanol is the limiting reactant and all the calculations must be based on methanol.

### 6.2.2 Presence of water in product mixture

From GC analysis fraction of water is also found in the product mixture which is undesirable. This can only be possible by the complete oxidation reaction of methanol in spite of partial oxidation. Complete oxidation reaction is given as:



It means that methanol being consumed not only produce hydrogen but is also producing water with it as a side reaction. In this case %age conversion of methanol to hydrogen must be carried calculated by considering this side reaction as well.

Mathematical calculation of methanol conversion is given as

Basis: 100gm of product gas

Wt of product gas according to GC analysis is given as

Hydrogen	-	3.95gm
Water	-	14.58gm
Carbon dioxide	-	59.01gm
Oxygen	-	14.98gm

Methanol	-	5.4gm
Impurities	-	2.08gm

By dividing each component by its molecular weight no. of moles calculated are

Hydrogen	-	1.975
Water	-	0.81
Carbon dioxide	-	1.34
Oxygen	-	0.468
Methanol	-	0.168

By POM to produce 2 moles of hydrogen we require methanol = 1mole

And to produce 1.975 moles we require methanol = 0.9875mole

By complete oxidation to produce 4 moles of water methanol require = 2mole

For 0.81 moles of water methanol require = 0.405mole

Un reacted methanol = 0.168

Total methanol In = 0.168 + 0.9875 + 0.405

= 15605

%age conversion for POM =  $\frac{09875}{1.5605} \times 100 = 63.3\%$

This result shows that side reactions do have their importance in the process and affects the %age yield of the desired product. 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. Result obtained signifies the importance of catalyst once again as it is the property of catalyst only to direct the reaction on the desired path and reduce down the chances of possible side reactions.

### 6.3 Comparison between simulation and experimental results

In order to validate the simulation model on more practical grounds and comparing the experimental process with the ideal behavior a comparison between mole fraction of hydrogen from the two methods is carried out.

Mole fraction of hydrogen from the simulation is obtained from the figure

$$\text{Mole fraction of hydrogen from simulation model} = 0.67$$

For experimental result mole fraction of hydrogen is calculated from the table . for this pupose mole fraction of water is neglected and mole fraction only by POM is calculated.

From table

$$\text{Moles of hydrogen} = 1.975$$

$$\text{Moles of oxygen} = 0.468$$

$$\text{Moles of carbon dioxide} = 1.34$$

$$\text{Moles of methanol} = 0.168$$

$$\text{Total moles} = 3.951$$

$$\text{Mole fraction of hydrogen by experimental data} = 0.51$$


$$\% \text{age Yield} = \frac{\text{Actual yield}}{\text{t e ratical yield}} = .51/.67 = 74\%$$

## 6.4 Conclusion

Comparison between simulation model and experimental data results into a %age yield of 74% which is considered as a high yield. Thus the results discussed here not only validate the two processes with each other but also give us the detail insight on the partial oxidation of methanol process.

Design constraints and assumptions are also validated by these results as on the basis of those design factors both simulation model and experimental process are able to give appreciable results.

# Annex – A

1	 <b>LEGENDS</b> Burlington, MA USA	Case Name: PART OXI 123.HSC
2		Unit Set: SI
3		Date/Time: Sun Jul 15 17:14:36 2012
4		
5		

## Plug Flow Reactor: FBCR

### CONNECTIONS

#### Inlet Stream

13	STREAM NAME	FROM UNIT OPERATION
14	pre heated reactants	Heater E-100

#### Outlet Stream

17	STREAM NAME	TO UNIT OPERATION
18	product	

#### Energy Stream

21	STREAM NAME	TO UNIT OPERATION
22	Cooling line	

### PARAMETERS

#### Physical Parameters

27	Type : Ergun Equation	Pressure Drop: 3.501 kPa
----	-----------------------	--------------------------

#### Heat Transfer : Cooling

30	Type : Direct Q Value	Energy Stream : Cooling line	Duty : 900.0 kJ/h *
----	-----------------------	------------------------------	---------------------

#### Dimensions

33	Total Volume: 1.159e-004 m3	Length: 0.1938 m *	Diameter: 2.760e-002 m *	Number of Tubes: 1 *
34	Wall Thickness: 5.000e-003 m *	Void Fraction: 0.2000 *	Void Volume: 2.319e-005 m3	

#### Reaction Info

37	Reaction Set: Global Rxn Set	Initialize From: Re-init
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#### Integration Information

40	Number of Segments: 20 *	Minimum Step Fraction: 1.0e-06 *	Minimum Step Length: 1.9e-07 m
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#### Catalyst Data

43	Particle Diameter: 1.000e-003 m *	Particle Spericity: 1.0000 *	Solid Density: 5.842 kg/m3 *
44	Bulk Density: 4.674 kg/m3	Solid Heat Capacity: 250.0 kJ/kg-C *	

#### User Variables

### RATING

#### Sizing

##### Tube Dimensions


52	Total Volume 1.159e-004 m3	Length 0.1938 m *	Diameter 2.760e-002 m *	Number of Tubes 1 *	Wall Thickness 5.000e-003 m *
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##### Tube Packing

54	Void Fraction 0.2000 *	Void Volume 2.319e-005 m3
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#### Nozzle Parameters

57	Base Elevation Relative to Ground Level 0.0000 m	Diameter 2.760e-002 m *	Length 0.1938 *
58		product	pre heated reactants
59	Diameter (m)	5.000e-002	5.000e-002
60	Elevation (Base) (m)	0.0000	0.0000
61	Elevation (Ground) (m)	0.0000	0.0000

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## Plug Flow Reactor: FBCR (continued)


### Conditions

	Length (m)	Temperature (C)	Pressure (kPa)	Vapour Fraction	Duty (kJ/h)
13	0.005	185.9	158.81	1.0000	45
14	0.015	160.6	158.65	1.0000	45
15	0.024	137.4	158.50	1.0000	45
16	0.034	116.5	158.35	1.0000	45
17	0.044	98.09	158.21	1.0000	45
18	0.053	82.23	158.07	1.0000	45
19	0.063	69.05	157.93	1.0000	45
20	0.073	58.69	157.80	1.0000	45
21	0.082	51.21	157.66	1.0000	45
22	0.092	46.70	157.52	1.0000	45
23	0.102	45.20	157.38	1.0000	45
24	0.111	46.80	157.23	1.0000	45
25	0.121	51.50	157.07	1.0000	45
26	0.131	59.30	156.91	1.0000	45
27	0.141	70.09	156.72	1.0000	45
28	0.150	83.78	156.52	1.0000	45
29	0.160	100.0	156.30	1.0000	45
30	0.170	118.0	156.05	1.0000	45
31	0.179	135.7	155.78	1.0000	45
32	0.189	146.8	155.48	1.0000	45

	Length (m)	Enthalpy (kJ/kgmole)	Entropy (kJ/kgmole-C)	Inside HTC (kJ/h-m2-C)	Overall HTC (kJ/h-m2-C)
35	0.005	-127189	161.08	---	---
36	0.015	-128251	159.46	---	---
37	0.024	-129149	157.71	---	---
38	0.034	-129898	155.98	---	---
39	0.044	-130508	154.34	---	---
40	0.053	-130989	152.85	---	---
41	0.063	-131349	151.53	---	---
42	0.073	-131593	150.43	---	---
43	0.082	-131727	149.56	---	---
44	0.092	-131753	148.96	---	---
45	0.102	-131674	148.64	---	---
46	0.111	-131493	148.58	---	---
47	0.121	-131210	148.80	---	---
48	0.131	-130829	149.26	---	---
49	0.141	-130353	149.93	---	---
50	0.150	-129789	150.77	---	---
51	0.160	-129148	151.71	---	---
52	0.170	-128460	152.64	---	---
53	0.179	-127794	153.38	---	---
54	0.189	-127368	153.44	---	---

### Flows

	Length (m)	Molar Flow (kgmole/h)	Mass Flow (kg/h)	Volumetric Flow (m3/h)	Heat Flow (kJ/h)
59	0.005	0.008	0.24	0.183	-974.5
60	0.015	0.008	0.24	0.180	-1020
61	0.024	0.008	0.24	0.176	-1065
62	0.034	0.009	0.24	0.174	-1110

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## Plug Flow Reactor: FBCR (continued)

### Flows

	Length (m)	Molar Flow (kgmole/h)	Mass Flow (kg/h)	Volumetric Flow (m3/h)	Heat Flow (kJ/h)
13	0.044	0.009	0.24	0.171	-1154
14	0.053	0.009	0.24	0.170	-1199
15	0.063	0.009	0.24	0.170	-1244
16	0.073	0.010	0.24	0.170	-1289
17	0.082	0.010	0.24	0.172	-1334
18	0.092	0.010	0.24	0.176	-1379
19	0.102	0.011	0.24	0.181	-1424
20	0.111	0.011	0.24	0.188	-1469
21	0.121	0.012	0.24	0.198	-1514
22	0.131	0.012	0.24	0.209	-1559
23	0.141	0.012	0.24	0.224	-1604
24	0.150	0.013	0.24	0.241	-1649
25	0.160	0.013	0.24	0.260	-1694
26	0.170	0.014	0.24	0.282	-1739
27	0.179	0.014	0.24	0.305	-1784
28	0.189	0.014	0.24	0.323	-1829


### Segment Overall Reaction Rates (kgmole/m3-s)

	Length (m)	Rxn-1
32	4.845e-003	4.503e-002
33	1.454e-002	4.591e-002
34	2.423e-002	4.681e-002
35	3.392e-002	4.773e-002
36	4.361e-002	4.868e-002
37	5.330e-002	4.967e-002
38	6.298e-002	5.070e-002
39	7.268e-002	5.180e-002
40	8.237e-002	5.297e-002
41	9.206e-002	5.422e-002
42	0.1017	5.558e-002
43	0.1114	5.704e-002
44	0.1211	5.861e-002
45	0.1308	6.030e-002
46	0.1405	6.208e-002
47	0.1502	6.392e-002
48	0.1599	6.570e-002
49	0.1696	6.716e-002
50	0.1793	6.749e-002
51	0.1890	6.387e-002

### Component Production Rates (kgmole/m3-s)

	Length (m)	Methanol	Oxygen	Hydrogen	CO2
55	4.845e-003	-4.503e-002	-2.252e-002	9.006e-002	4.503e-002
56	1.454e-002	-4.591e-002	-2.296e-002	9.182e-002	4.591e-002
57	2.423e-002	-4.681e-002	-2.341e-002	9.362e-002	4.681e-002
58	3.392e-002	-4.773e-002	-2.387e-002	9.546e-002	4.773e-002
59	4.361e-002	-4.868e-002	-2.434e-002	9.736e-002	4.868e-002
60	5.330e-002	-4.967e-002	-2.483e-002	9.933e-002	4.967e-002
61	6.298e-002	-5.070e-002	-2.535e-002	0.1014	5.070e-002
62	7.268e-002	-5.180e-002	-2.590e-002	0.1036	5.180e-002



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## Plug Flow Reactor: FBCR (continued)

### Component Production Rates (kgmole/m3-s)


Length (m)	Methanol	Oxygen	Hydrogen	CO2
8.237e-002	-5.297e-002	-2.648e-002	0.1059	5.297e-002
9.206e-002	-5.422e-002	-2.711e-002	0.1084	5.422e-002
0.1017	-5.558e-002	-2.779e-002	0.1112	5.558e-002
0.1114	-5.704e-002	-2.852e-002	0.1141	5.704e-002
0.1211	-5.861e-002	-2.931e-002	0.1172	5.861e-002
0.1308	-6.030e-002	-3.015e-002	0.1206	6.030e-002
0.1405	-6.208e-002	-3.104e-002	0.1242	6.208e-002
0.1502	-6.392e-002	-3.196e-002	0.1278	6.392e-002
0.1599	-6.570e-002	-3.285e-002	0.1314	6.570e-002
0.1696	-6.716e-002	-3.358e-002	0.1343	6.716e-002
0.1793	-6.749e-002	-3.374e-002	0.1350	6.749e-002
0.1890	-6.387e-002	-3.193e-002	0.1277	6.387e-002

### Transport

Length (m)	Viscosity (cP)	Molecular Weight	Mass Density (kg/m3)	Heat Capacity (kJ/kgmole-C)	Surface Tension (dyne/cm)	Z Factor
4.845e-003	1.463e-002	30.85	1.291	47.113	---	0.9945
1.454e-002	1.428e-002	29.73	1.316	44.899	---	0.9941
2.423e-002	1.396e-002	28.68	1.340	42.970	---	0.9938
3.392e-002	1.368e-002	27.67	1.361	41.305	---	0.9935
4.361e-002	1.345e-002	26.72	1.379	39.879	---	0.9932
5.330e-002	1.328e-002	25.81	1.390	38.671	---	0.9932
6.298e-002	1.318e-002	24.95	1.394	37.658	---	0.9932
7.268e-002	1.316e-002	24.12	1.389	36.818	---	0.9934
8.237e-002	1.322e-002	23.33	1.372	36.130	---	0.9938
9.206e-002	1.338e-002	22.58	1.345	35.576	---	0.9944
0.1017	1.361e-002	21.85	1.306	35.137	---	0.9951
0.1114	1.392e-002	21.15	1.255	34.796	---	0.9958
0.1211	1.427e-002	20.48	1.196	34.537	---	0.9966
0.1308	1.467e-002	19.83	1.129	34.343	---	0.9974
0.1405	1.515e-002	19.20	1.057	34.197	---	0.9981
0.1502	1.558e-002	18.60	0.9823	34.083	---	0.9986
0.1599	1.595e-002	18.02	0.9084	33.982	---	0.9991
0.1696	1.632e-002	17.46	0.8380	33.875	---	0.9995
0.1793	1.664e-002	16.93	0.7759	33.733	---	0.9998
0.1890	1.676e-002	16.46	0.7329	33.505	---	1.000

### Component Mass Flowrates (kg/h)

Length (m)	Methanol	Oxygen	Hydrogen	CO2
4.845e-003	0.1516	0.0757	0.0008	0.0083
1.454e-002	0.1455	0.0726	0.0015	0.0167
2.423e-002	0.1392	0.0695	0.0023	0.0253
3.392e-002	0.1328	0.0663	0.0031	0.0341
4.361e-002	0.1263	0.0631	0.0039	0.0430
5.330e-002	0.1197	0.0598	0.0048	0.0521
6.298e-002	0.1129	0.0564	0.0056	0.0615
7.268e-002	0.1060	0.0529	0.0065	0.0710
8.237e-002	0.0989	0.0494	0.0074	0.0807
9.206e-002	0.0916	0.0458	0.0083	0.0907
0.1017	0.0842	0.0420	0.0092	0.1009
0.1114	0.0766	0.0382	0.0102	0.1113

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## Plug Flow Reactor: FBCR (continued)

### Component Mass Flowrates (kg/h)


Length (m)	Methanol	Oxygen	Hydrogen	CO2
0.1211	0.0687	0.0343	0.0112	0.1221
0.1308	0.0607	0.0303	0.0122	0.1332
0.1405	0.0524	0.0262	0.0132	0.1446
0.1502	0.0438	0.0219	0.0143	0.1563
0.1599	0.0350	0.0175	0.0154	0.1684
0.1696	0.0261	0.0130	0.0166	0.1807
0.1793	0.0170	0.0085	0.0177	0.1931
0.1890	0.0085	0.0042	0.0188	0.2049

### Component Mass Fractions

Length (m)	Methanol	Oxygen	Hydrogen	CO2
4.845e-003	0.6415	0.3203	0.0032	0.0350
1.454e-002	0.6155	0.3073	0.0065	0.0707
2.423e-002	0.5890	0.2941	0.0098	0.1071
3.392e-002	0.5620	0.2806	0.0132	0.1442
4.361e-002	0.5345	0.2669	0.0167	0.1820
5.330e-002	0.5064	0.2528	0.0202	0.2206
6.298e-002	0.4777	0.2385	0.0238	0.2600
7.268e-002	0.4484	0.2239	0.0275	0.3003
8.237e-002	0.4184	0.2089	0.0313	0.3414
9.206e-002	0.3877	0.1936	0.0351	0.3836
0.1017	0.3563	0.1779	0.0391	0.4268
0.1114	0.3240	0.1618	0.0432	0.4711
0.1211	0.2908	0.1452	0.0473	0.5166
0.1308	0.2567	0.1282	0.0516	0.5635
0.1405	0.2216	0.1106	0.0560	0.6117
0.1502	0.1854	0.0926	0.0606	0.6614
0.1599	0.1482	0.0740	0.0653	0.7125
0.1696	0.1102	0.0550	0.0701	0.7647
0.1793	0.0720	0.0360	0.0749	0.8171
0.1890	0.0359	0.0179	0.0794	0.8668

### PROPERTIES

Name	pre heated reactants	product		
Molecular Weight	32.03	16.46		
Molar Density (kgmole/m3)	3.951e-002	4.453e-002		
Mass Density (kg/m3)	1.266	0.7329		
Act. Volume Flow (m3/h)	0.1868	0.3225		
Mass Enthalpy (kJ/kg)	-3933	-7740		
Mass Entropy (kJ/kg-C)	5.058	9.324		
Heat Capacity (kJ/kgmole-C)	49.63	33.50		
Mass Heat Capacity (kJ/kg-C)	1.550	2.036		
Lower Heating Value (kJ/kgmole)	4.254e+005	1.686e+005		
Mass Lower Heating Value (kJ/kg)	1.328e+004	1.024e+004		
Phase Fraction [Vol. Basis]	---	---		
Phase Fraction [Mass Basis]	4.941e-324	2.122e-314		
Partial Pressure of CO2 (kPa)	0.0000	50.39		
Cost Based on Flow (Cost/s)	0.0000	0.0000		
Act. Gas Flow (ACT_m3/h)	0.1868	0.3225		
Avg. Liq. Density (kgmole/m3)	27.61	27.03		
Specific Heat (kJ/kgmole-C)	49.63	33.50		

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## Plug Flow Reactor: FBCR (continued)


### PROPERTIES

Name	pre heated reactants	product		
Std. Gas Flow (STD_m3/h)	0.1745	0.3396		
Std. Ideal Liq. Mass Density (kg/m3)	884.2	444.9		
Act. Liq. Flow (m3/s)	---	---		
Z Factor	0.9949	---		
Watson K	8.695	11.78		
User Property	---	---		
Partial Pressure of H2S (kPa)	0.0000	0.0000		
Cp/(Cp - R)	1.201	1.330		
Cp/Cv	1.208	1.332		
Heat of Vap. (kJ/kgmole)	4.772e+004	1.709e+004		
Kinematic Viscosity (cSt)	11.84	22.87		
Liq. Mass Density (Std. Cond) (kg/m3)	773.0	---		
Liq. Vol. Flow (Std. Cond) (m3/h)	3.058e-004	---		
Liquid Fraction	0.0000	0.0000		
Molar Volume (m3/kgmole)	25.31	22.46		
Mass Heat of Vap. (kJ/kg)	1490	1039		
Phase Fraction [Molar Basis]	1.0000	1.0000		
Surface Tension (dyne/cm)	---	---		
Thermal Conductivity (W/m-K)	3.198e-002	0.1068		
Viscosity (cP)	1.499e-002	1.676e-002		
Cv (Semi-Ideal) (kJ/kgmole-C)	41.32	25.19		
Mass Cv (Semi-Ideal) (kJ/kg-C)	1.290	1.531		
Cv (kJ/kgmole-C)	41.09	25.16		
Mass Cv (kJ/kg-C)	1.283	1.529		
Cv (Ent. Method) (kJ/kgmole-C)	---	---		
Mass Cv (Ent. Method) (kJ/kg-C)	---	---		
Cp/Cv (Ent. Method)	---	---		
Reid VP at 37.8 C (kPa)	---	---		
True VP at 37.8 C (kPa)	6.845e+004	---		
Liq. Vol. Flow - Sum(Std. Cond) (m3/h)	3.058e-004	0.0000		
Viscosity Index	---	---		

### DYNAMICS

#### Vessel Parameters: Initialize from Product

Single Phase: Not Activated		Lag Rxn Temperature: Not Activated	
Laminar Flow	Activated	Fixed Delta P	Not Activated
Flow Equation	Activated	PFR Elevation (m)	0 *
Pressure Flow Relation		Segmented Holdup Details	
Segment	Pressure-Flow K (kg/hr/sqrt(kPa-kg/m3))	View Holdup	
1.000	*	FBCR:Seg-1 Holdup	
2.000	*	FBCR:Seg-2 Holdup	
3.000	*	FBCR:Seg-3 Holdup	
4.000	*	FBCR:Seg-4 Holdup	
5.000	*	FBCR:Seg-5 Holdup	
6.000	*	FBCR:Seg-6 Holdup	
7.000	*	FBCR:Seg-7 Holdup	
8.000	*	FBCR:Seg-8 Holdup	
9.000	*	FBCR:Seg-9 Holdup	
10.00	*	FBCR:Seg-10 Holdup	

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## Plug Flow Reactor: FBCR (continued)

Segment	Pressure-Flow K (kg/hr/sqrt(kPa·kg/m <sup>3</sup> ))	View Holdup
11.00	*	FBCR:Seg-11 Holdup
12.00	*	FBCR:Seg-12 Holdup
13.00	*	FBCR:Seg-13 Holdup
14.00	*	FBCR:Seg-14 Holdup
15.00	*	FBCR:Seg-15 Holdup
16.00	*	FBCR:Seg-16 Holdup
17.00	*	FBCR:Seg-17 Holdup
18.00	*	FBCR:Seg-18 Holdup
19.00	*	FBCR:Seg-19 Holdup
20.00	*	FBCR:Seg-20 Holdup

### Overall Holdup Details

Phase	Accumulation (kgmole/h)	Moles (kgmole)	Volume (m <sup>3</sup> )
Vapour	0.0000 *	0.0000 *	0.0000 *
Liquid	0.0000 *	0.0000 *	0.0000 *
Aqueous	0.0000 *	0.0000 *	0.0000 *
<b>Total</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>

### Direct Q

SP	(kJ/h)	900.0 *	Max. Available	(kJ/h)	---
Min. Available	(kJ/h)	---			

### Heat Flow into the PFR: Cooling

### NOTES

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