

**Technical Analysis of Dehydrogenation  
Process of Liquid Organic Hydrogen  
Carriers (LOHC's) for Hydrogen  
Storage**



**By**

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2022**

# **Technical Analysis of Dehydrogenation Process of Liquid Organic Hydrogen Carriers (LOHC's) for Hydrogen Storage**



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**This work is submitted as an M.S. thesis in partial fulfillment of the  
requirement for the degree of**

**M.S. in Process Systems Engineering**

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**September 2022**

*I have devoted my thesis to their constant support,  
encouragement, and love in honor of my parents.*

## Acknowledgment

Praising ALLAH, whose worth cannot be adequately expressed by words, whose riches cannot be tallied by calculators, whose summit of intellectual understanding cannot be fully grasped by the deepest abysses of understanding, is due, his praise is due. His description is without limit, his eulogies are without edict, and his time is without end.

I want to thank and convey my profound gratitude to my research supervisor, **Dr. Iftikhar Ahmad**, for his unwavering support, supervision, and compassionate counsel in steering me in the correct way whenever he realized I needed it. Additionally, I would like to express my appreciation to committee members. **Dr. Erum Pervaiz and Dr. Muhammad Ahsan** for their insightful recommendations and assistance.

Additionally, I would like to express my gratitude to **Prof. Dr. Amir Azam Khan** (Principal School of Chemical and Materials Engineering) and **Dr. Erum Pervaiz** (HOD Department of Chemical Engineering) for providing a research-oriented environment in which I could effectively apply my skills in completing this research work.

Finally, I want to convey my heartfelt appreciation to my parents for their unwavering support and encouragement during my years of education, research and writing my thesis. Without them, this feat would not have been possible.

**Aizaz Yousaf**

## Abstract

Hydrogen as a clean-energy carrier has gained great attention in the current times while its storage, transportation and dehydrogenation are the stumbling blocks in fulfilment of a hydrogen backed clean economy. The efficiency of storage that is hydrogenation has been achieved significantly but dehydrogenation efficiency still needs improvement in order to increase the efficiency of the overall Hydrogen storage technique. Liquid organic hydrogen carrier (LOHC) could be one of the replacements, provided appropriate conditions are given for its storage, transportation and its dehydrogenation that is the removal of hydrogen from the LOHC thus contributing to the clean fuel idea in coming years. In this study, a parametric and simulation-based research was carried out for the storage and release of hydrogen for three different LOHC's. Specifically, the dehydrogenation reaction was assessed over three catalysts for the temperature range of 300–450 °C and a pressure range of 1–3 bar to select the best catalyst and LOHC under optimum operating conditions. Likewise, the effects of hydrogen addition in the feed mixture were also investigated as functions of operating conditions. Hydrogen addition in the feed not only reduced the percentage conversion but also enhanced catalyst's stability. It avoids the coke formation on the catalyst surface. The results were compared for maximum LOHC conversion in the required conditions. The optimum operating conditions selected for the dehydrogenation process were 360 °C and 1.8 bar. In order to perform the simulation, Aspen Plus simulation software was utilized to carry out different simulations under different temperature and pressure conditions. The conversion percentage trends were observed with increasing temperature and pressure on the graphs which shows their impact on the conversion percentage.

**Keywords:** Aspen Plus, Liquid Organic Hydrogen Carrier (LOHC), Dehydrogenation Process

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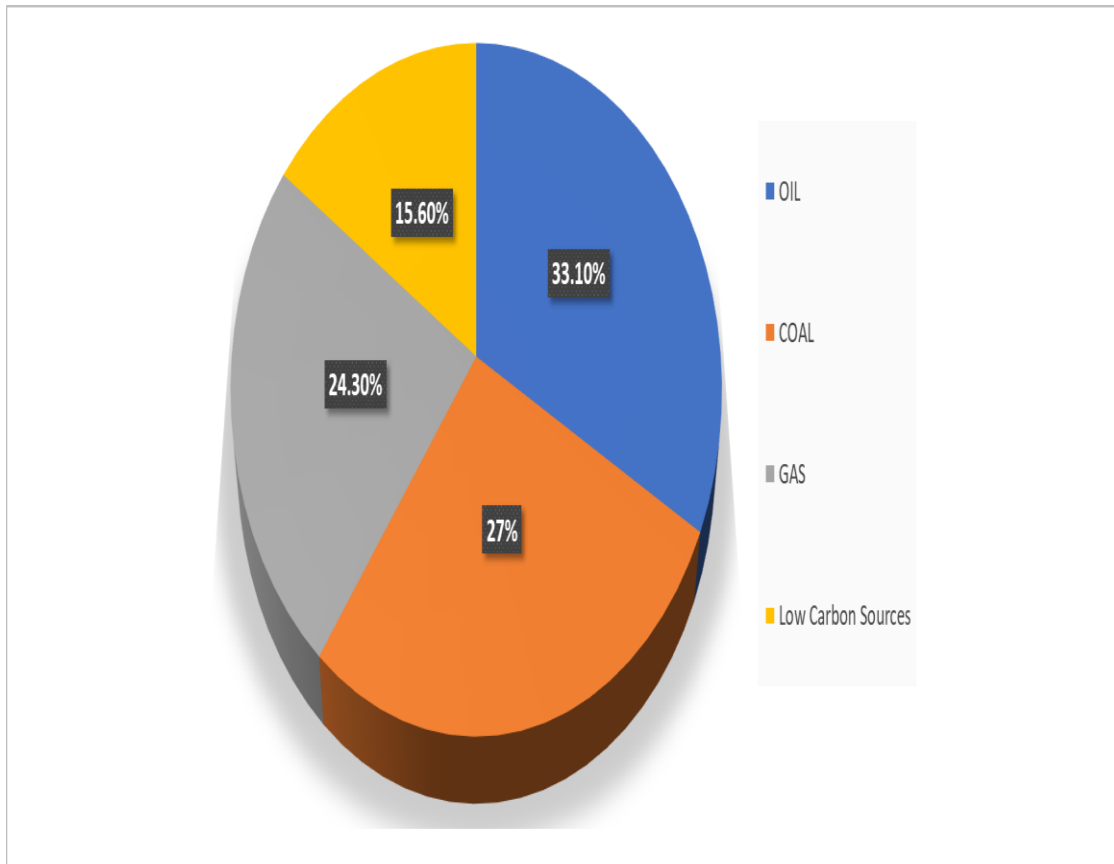
# Chapter 1

## Introduction

### 1.1 Background

Energy has become the irrefutable key ingredient in all spheres of the modern world, from household to transport, infrastructure, agriculture, and various industrial processes. Any nation's prosperity and growth greatly rely on an uninterrupted energy supply. The energy demand positively correlates with economic progress in a country. Due to the instability in prices coupled with the limited sources of energy production, there is a certain supply and demand gap. Therefore, the need for low-cost energy production is essential. In responding to the challenge of an energy shortage, a flexible approach is needed. The best way to increase energy resource productivity is to increase efficiency and fully utilize these resources by bringing innovation to existing practices. Rapid growth and development are observed in the renewable energy sectors that mostly use solar and wind energy. This is due to the increased energy demand by the constant increase in the world population. Fossil fuels that remain our primary source of power are on the verge of depletion are not environment friendly and are causing an increase in greenhouse gases which results in climate change and global warming.

According to the BP statistical review 2020 more than 80% of the Global energy demand is fulfilled by fossil fuels in which 33.1% is fulfilled from oil, 27% from coal and 24.3% from Gas. These all-fossil fuels are the main contributors to the global warming and are very rich in carbon emission which results in greenhouse gases. According to this report only 15.6% of the demand is fulfilled by low carbon sources which includes solar, Hydro and other renewable resources as shown in Figure 1. The uses of these low carbon emission fuels need to be increased whereas the fossil fuels need to be reduced to save our planet from global warming which results in climate changes and ultimately in huge disasters as recently the floods in Pakistan.

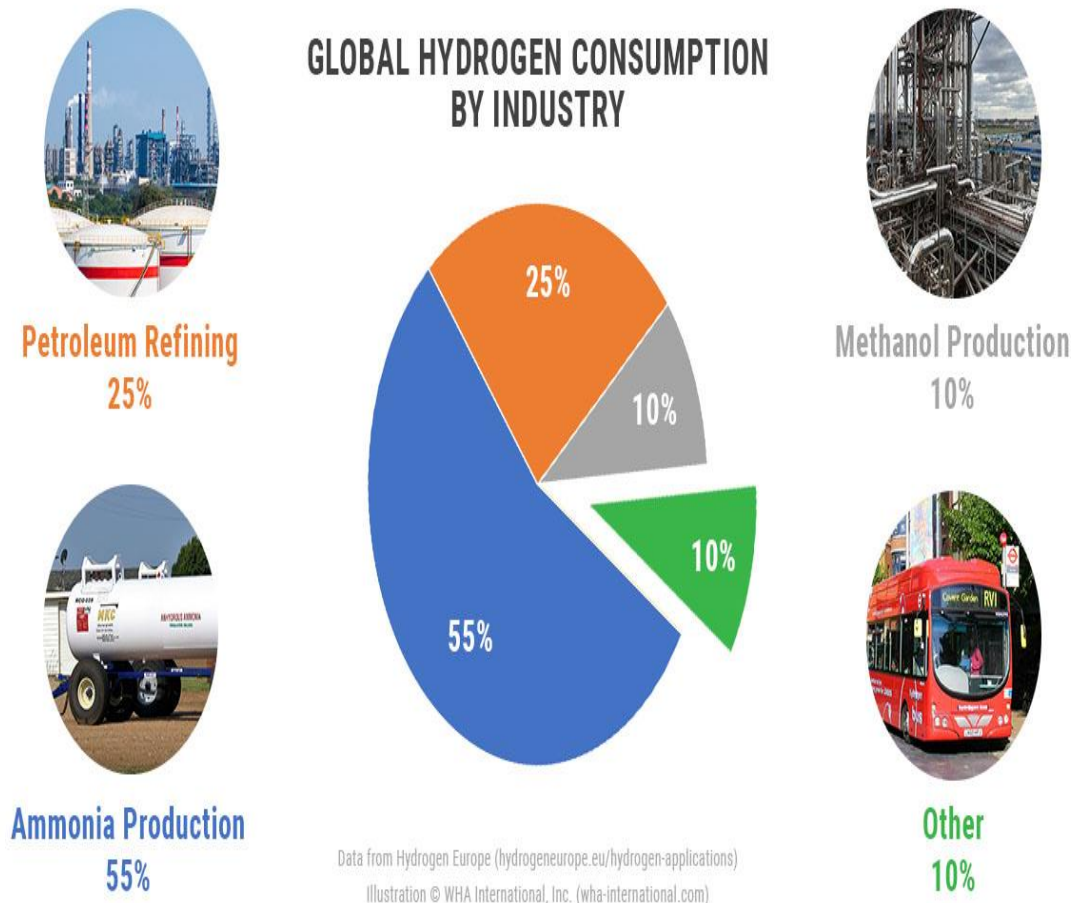


**Figure 1:** Global Primary Energy demand by Fossil fuels (BP statistical review 2020)

Therefore, another alternate energy efficient design and fuel was needed to avoid the greenhouse gases in order to make the environment friendly and reduces the damage to the global warming, because of the global warming many irregularities can occur in the natural cycle of climate which results in disasters like floods and can cause damages to human lives as well as the wild life. Hydrogen fuel is one of the alternatives, that has no carbon emissions and no greenhouse gases so its environmentally friendly.

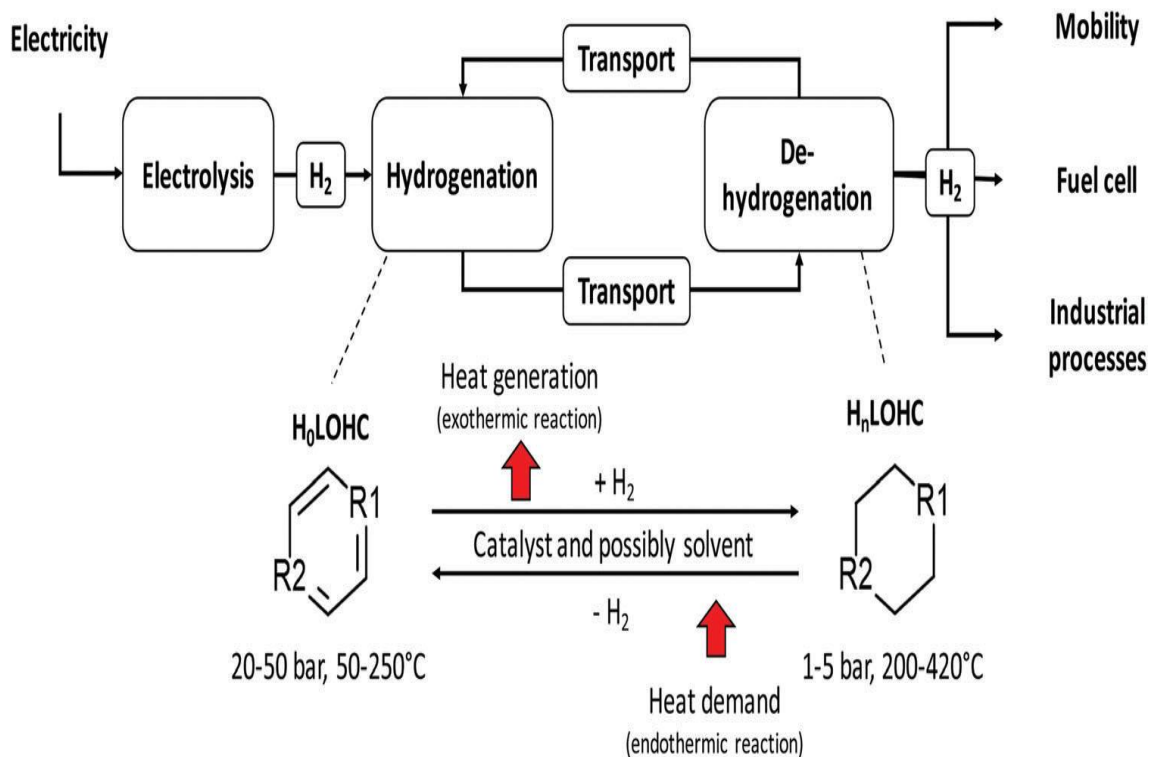
Hydrogen as a fuel has many uses, according to the global hydrogen consumption by industry about 25% is used by petroleum refining, 10% by methanol production and others whereas about 55% of the global hydrogen is used by ammonia

production.



**Figure 2:** Global Hydrogen Consumption by Industry

Hydrogen has less effect on the environment but it is gaseous in nature and is very difficult to transport it from one place to another in its original state (gaseous), therefore before transporting, it needs to be converted to liquid state and then removed in gaseous form at the required destination through dehydrogenation process. Hydrogenation process has achieved its efficiency but dehydrogenation needs improvement so as to achieve the highest efficiency to reduce hydrogen loss as a result of it.



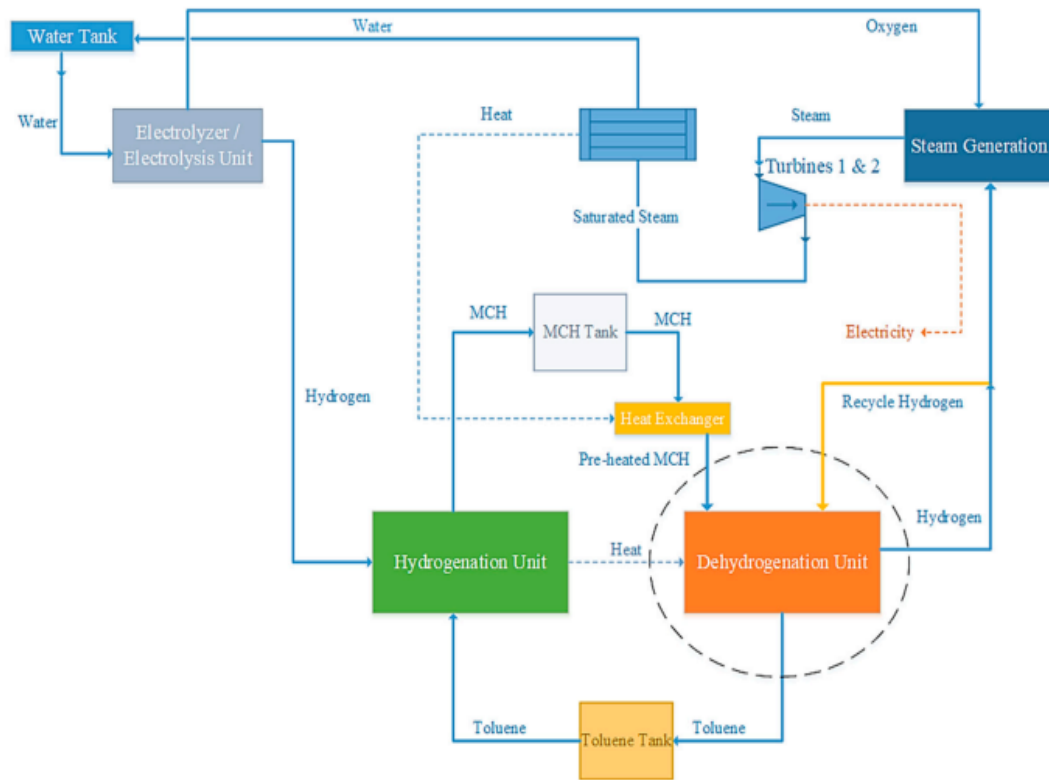
**Figure 3:** Schematic Flow diagram of Hydrogen stream cycle

Hydrogen stream cycle has three steps as shown in Figure 3

- a. Hydrogenation
- b. Transportation
- c. Dehydrogenation

Many researchers have worked on this and they have successfully achieved 99% efficiency in hydrogenation but dehydrogenation still needs more work as the required efficiency have not been achieved yet. Most of the hydrogen is wasted in dehydrogenation process, which needs to be retained.

There are many techniques available for hydrogenation and dehydrogenation processes but Liquid Organic Hydrogen Carrier (LOHC) technique is way more efficient and cheaper. In this process reversible cycle of hydrogenation and dehydrogenation takes place. LOHC absorbs hydrogen and is in liquid form, they are transported to their required destinations and dehydrogenated there, and is ready for applications purposes. The schematic flow diagram of the LOHC process is given in Figure 3.



**Figure 4:** Schematic Flow diagram of Liquid Organic Hydrogen Carrier (LOHC) Process

These reactions are carried out at different pressure and temperature parameters to make the process efficient and less hydrogen is wasted during the whole process. Dehydrogenation process needs improvement in order to save hydrogen and cost. The main focus of this study therefore was dehydrogenation process that is to determine the best operating parameters of temperature and pressure in order to increase its efficiency and also to determine the use of best catalyst for the reactions.

## 1.2 Theoretical Background

### 1.2.1 Liquid Organic Hydrogen Carrier (LOHC):

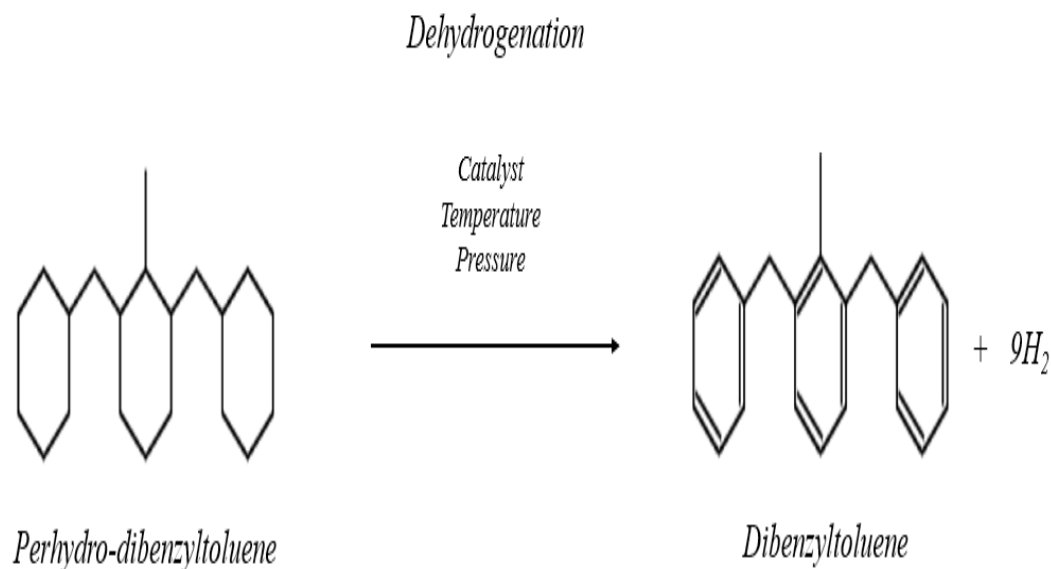
Liquid Organic Hydrogen carriers are organic compounds that can easily absorb and release hydrogen through chemical reactions. They are mostly in liquid form therefore the hydrogen is absorbed and are stored in liquid form. They can easily be

transported through tankers. During the dehydrogenation process at high temperatures, they are separated and hydrogen is converted back to gaseous form where its ready for its applications as a fuel. The LOHC's taken for this study are

- a. Methylcyclohexane
- b. PerhydroDibenzylToluene
- c. Pentinithiophene

### 1.2.2 Dehydrogenation Process:

Dehydrogenation process is the removal of hydrogen from a compound when the conditions of temperature and pressure are provided in the presence of catalyst.



**Figure 5:** Dehydrogenation reaction of LOHC

They are endothermic reactions, i.e., they need energy in order to break the bonds between the LOHC and hydrogen molecules. Different LOHC's needs varied energies in order to break their bonds. These LOHC's were selected because they can easily absorb and release hydrogen as compared to the others.



### **1.3 Thesis Outline**

The essential motivation and background of the research work were discussed in this chapter. Further, theoretical concepts of the dehydrogenation process and literature review are discussed in Chapter 2. This chapter also includes a summary of research work already carried out to develop the dehydrogenation process model and optimization tools, along with the objectives of this research. Flowsheet development of dehydrogenation process in Aspen Plus® along with description model development has been discussed in Chapter 3. In Chapter 4, results are discussed in details along with the graphs of percentage conversion vs temperature and the effects of pressure on conversion percentage. While the conclusions are given in the end of this thesis.

# Chapter 2

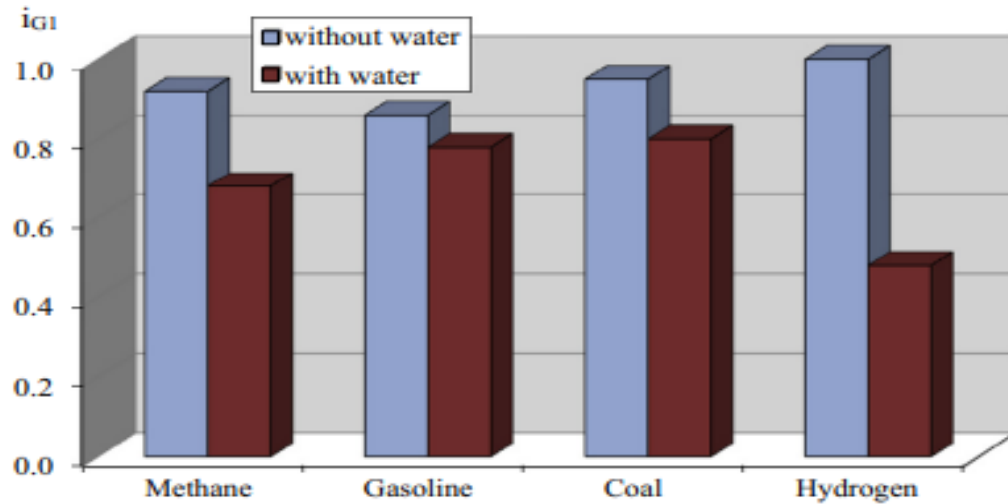
## Literature Survey and Objectives

### 2.1 Literature Survey

Conventional fuel-based power generation systems are the major contributors to global warming and climate changes in the modern era. To overcome these issues the research shift towards introducing the environmentally friendly fuels to fulfill the future fuel demand, for that purpose hydrogen as a fuel is quite feasible and friendly to the environment [1]. Hydrogen has been widely used as fuel in motor vehicles, different industries employed hydrogen for special purposes like metal alloying and different electronic industries utilized hydrogen beam for cleaning and also in fuel cells [2–5].

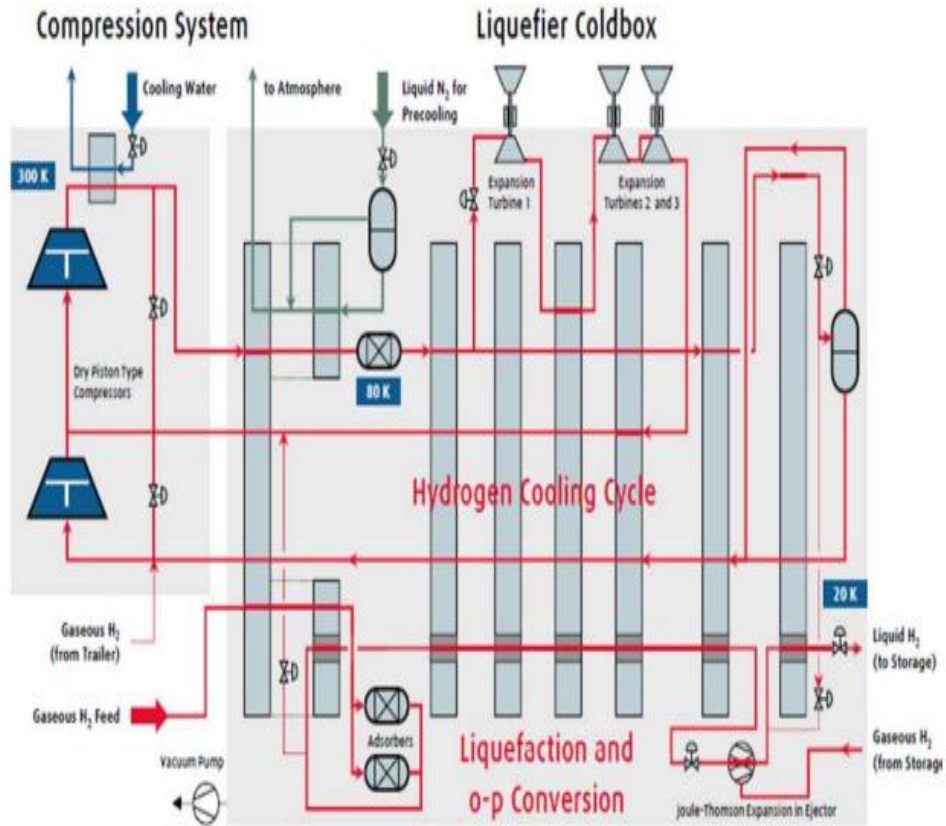
The applications of hydrogen cannot be ignored as it has the ability to replace the fossil fuels in future but the main hurdle is that hydrogen is gaseous in nature, its converted to liquid form through hydrogenation process for transportation and then removed through dehydrogenation process at the required destination. During the dehydrogenation some hydrogen can be lost as its converted back to gaseous form, so certain steps needed to be taken to avoid these losses. Many researchers have worked on its applications and also on its emissions, it was shown that it emits very low carbons to the air which is helpful in keeping the environment clean and avoiding the greenhouses that can trap heat in the atmosphere which results in global warming and climate changes and which ultimately results in climate disasters like floods.

The global environmental index has shown that hydrogen as a fuel is cleaner than other fossil fuels as shown in Figure 6 [6].



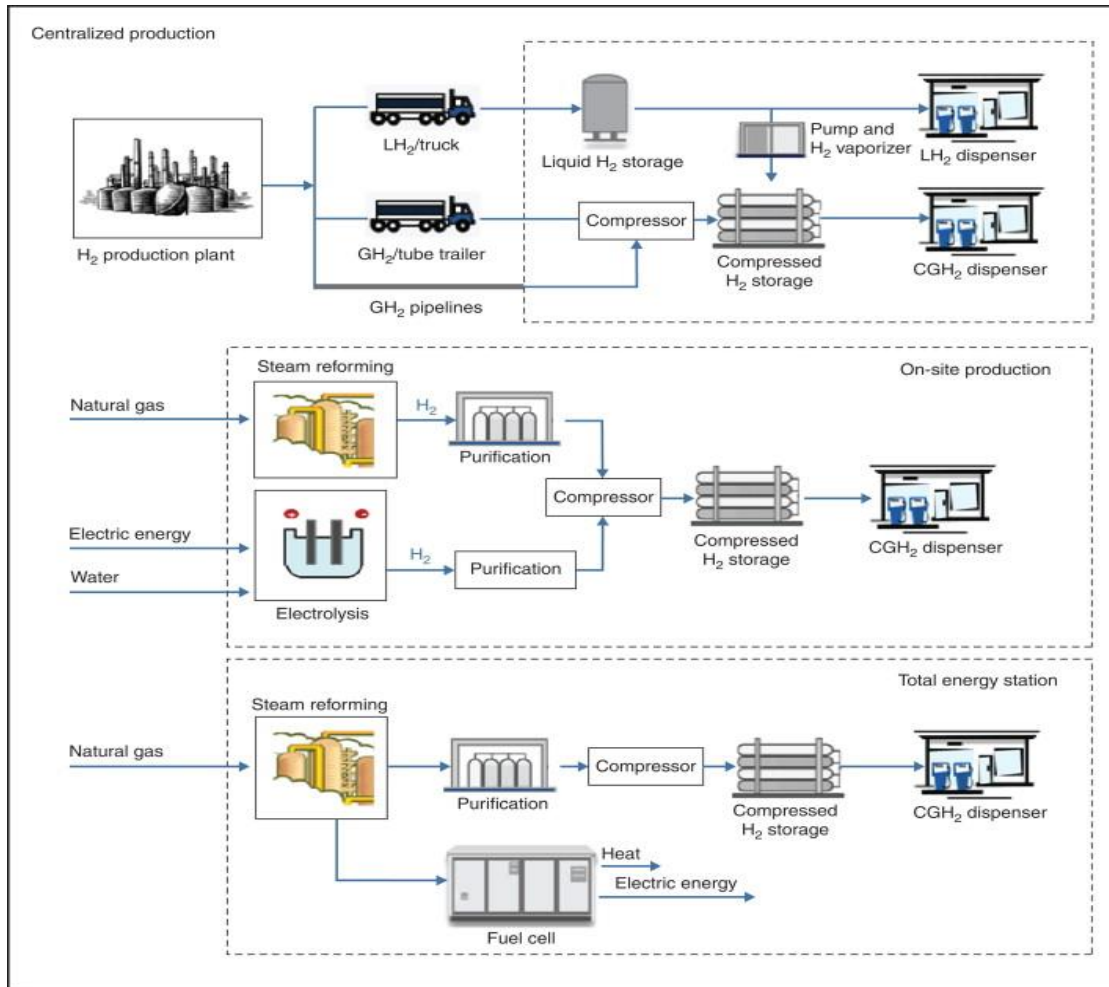
**Figure 6:** Normalized Pollution Index for the Fuels

There are many other hydrogen storage techniques available, i.e., liquefaction [7] in which huge amount of hydrogen are liquefied in central plants and then transported in trucks and carriage trains, although it has large volumetric density but a very large amount of electrical energy is consumed during liquefaction almost 4-10 kWh electricity is used to produce 1 kg of hydrogen [8], but it has two main drawbacks that due to the constant unavoidable heat influx to the storage vessels 2-3% of the hydrogen is evaporated and lost per day [9] and secondly high energy consumption as large amount of electricity is required for liquefaction. The hydrogen in gaseous form is first passed through the compression system which compresses the hydrogen gas and increase its density. Afterwards the hydrogen gas is passed through the liquefier cold box which liquefies the hydrogen. To exist as a liquid Hydrogen must be cooled to  $-252.87\text{ }^{\circ}\text{C}$  at atmospheric pressure and it's achieved in the liquefier cold box. Afterwards its collected and transported for application purposes as shown in the Figure 7.



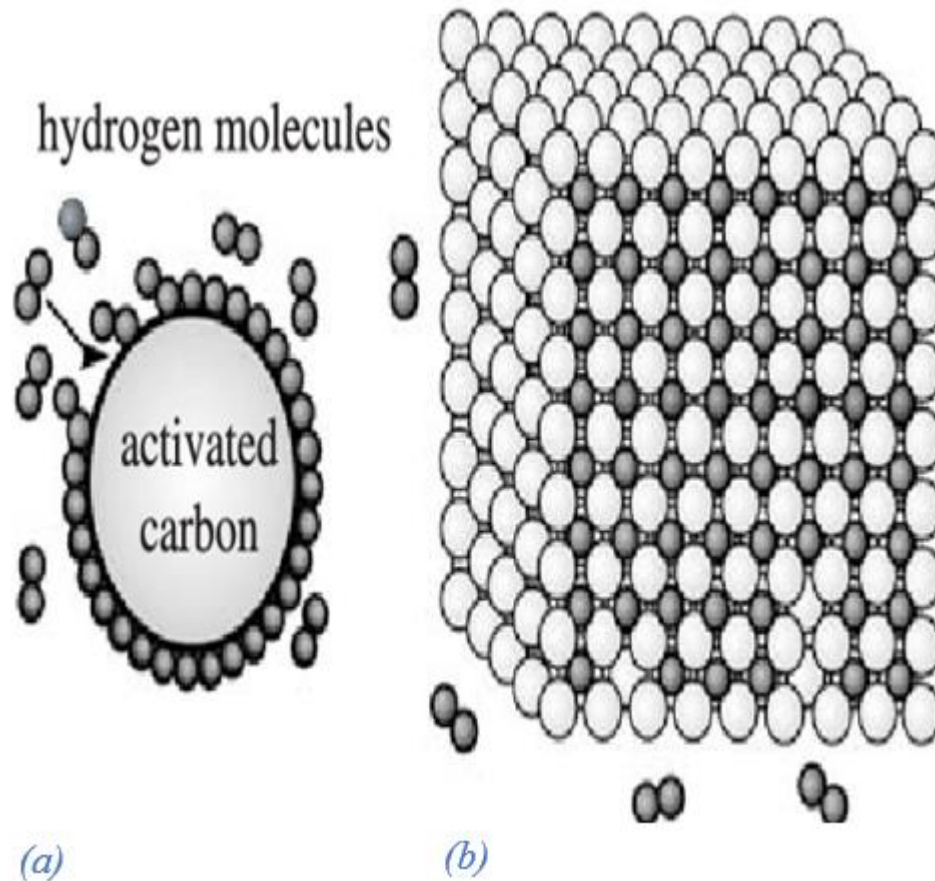
**Figure 7:** Diagram of liquefaction process of Hydrogen

Compression [10] is another technique which includes two types of compression, compressed gaseous hydrogen CGH<sub>2</sub> and material-based hydrogen. At an ambient temperature, gaseous hydrogen can be compressed and stored which has multiple practical applications. Back in 2010, 80% of refueling stations used this method [11]. However, this technique comes with a significant drawback, i.e., low volumetric density. The compressors mostly used for hydrogen compression are rotary compressors. They are compressed prior to refueling it to the vehicles so as to maximum hydrogen can be transferred in to the vehicle tanker so as to avoid frequent refueling of the vehicle and can work for more time. The flow diagram of compressed gaseous hydrogen is given in Figure 8.



**Figure 8:** Diagram of Compression technique process for Hydrogen

In material-based compression storage the atoms of hydrogen are tightly bound with atoms of other materials through physisorption, i.e., in which the molecular interaction between the adsorbate molecules and that of the adsorbent are governed by the van der Waals forces e.g., absorption in a metal organic framework or nanotubes [12] and chemisorption, i.e., the chemical bond between the adsorbate molecules and active sites on specific surface e.g., metal hydrides or LOHC's [13].



**Figure 9:** Physisorption and Chemisorption process of Hydrogen Storage

Absorption in a metal organic framework is a technique which involves the inclusion of sufficient surface area and pore volume and formation of high energy hydrogen binding sites on metal cluster or ligand [14], nanotubes e.g., Carbon nanotubes this technique depends upon the geometrical structure arrangements of the carbon nanotubes [15], arrangement of the tubes and the tube diameter [16], which makes the LOHC technique more feasible. In this technique the LOHC's are organic compounds that can easily react, absorb and release hydrogen. Secondly, it's less expensive as the existing carriage techniques can be used that are fuel tankers and carriage trains for transportation without any losses and secondly these are easily available and are cheaper. Different LOHC's are available such as toluene and N ethyl carbazole to carry liquid hydrogen from one place to another. The present research techniques are implemented widely but more parametric

studies are needed to make it more efficient in order to decrease the hydrogen wastage significantly in hydrogenation and dehydrogenation process.

A comparison of cost effectiveness and energy demand between these techniques [17] is given in the Table 1.

**Table 1.** Energy and cost demands of hydrogen-storage systems

<b>Description</b>	<b>Unit</b>	<b>LOHCs</b>	<b>Compressed Hydrogen Storage</b>	<b>LH Storage</b>
Energy demand	kWh x/kWh	1.1 %	3.5%	21%
Cost estimation	hyd €/kg hydrogen a	0.238	0.243	0.732

This system includes reversible cycle of hydrogenation and dehydrogenation in which hydrogenation can be achieved with max efficiency of 98% but there are still complications in unloading the hydrogen in dehydrogenation which means that most of the hydrogen is wasted during the release [18]. Many researchers have conducted experimental works on dehydrogenation using various catalysts in the absence of hydrogen like Usman et al., used 0.3 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> catalyst based on the power law kinetic model and in the absence of hydrogen the conversion was 97.5% [(19), Mizsey et al., used a sulfided, reforming catalyst on a spherical alumina support on the pilot plant scale system and yield of toluene was 98% [20] and Jothimurugesan et al., used 0.3 wt. % Pt-Re/Alumina catalyst [21] while in the presence of the hydrogen the catalyst activity and stability improves significantly.

The literature shows that performance of the dehydrogenation is mainly dependent on the temperature, pressure and use of suitable catalysts where kinetic data has not been studied and conversion reactors have been used to present the dehydrogenation process [22].

Catalytic dehydrogenation of LOHCs is very common these days because mostly the dehydrogenation is carried out through catalysis using fixed bed reactors like Dibenzyl Toluene [23]. Another technique for dehydrogenation is that the coupling of a hydrogen fueled Micro Gas Turbines with a reactor for the dehydrogenation process, which is quite desirable. In such a combined system, the excess exhaust enthalpy can be used to maintain the endothermal dehydrogenation reaction required for breaking the bonds without affecting the overall efficiency of the gas turbine [24].

Many researchers have studied the dehydrogenation process through experiments [25] but the simulation aspects need to be studied appropriately. According to the literature the dehydrogenation system and the percentage of LOHC conversion depends upon the temperature, pressure and use of suitable catalysts [26]. Changing these parameters results in change of percentage of LOHC conversion.

## 2.2 Objectives

- Developing an Aspen Plus model for dehydrogenation process.
- Technical analysis and simulation of dehydrogenation process using Aspen Plus.
- Assessment of three LOHC's for efficient dehydrogenation by changing temperature and pressure parameters and the catalyst

LOHC's	Catalysts
Methylcyclohexane (MCH)	0.3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>
PerhydroDibenzylToluene (PHDBT)	Sulfided Pt/Al <sub>2</sub> O <sub>3</sub>
Pentiniithiophene (PTH)	0.3 wt. % Pt + Re/Al <sub>2</sub> O <sub>3</sub>

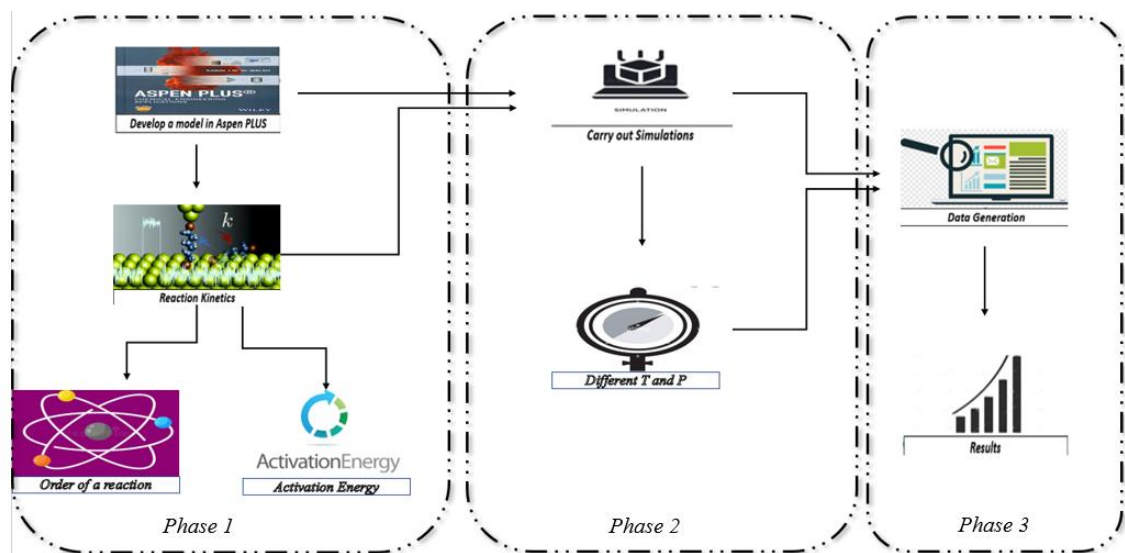


- Find out more efficient LOHC in terms of percentage conversion at specific temperature and pressure.
- Find out optimum temperature and pressure conditions for the process.

# Chapter 3

## Process Description and Simulation Method

### 3.1.4 Schematic Framework of the Overall process



**Figure 10:** Schematic framework diagram of the overall process

The overall process involves the three phases that are shown in Figure 10

#### 3.1.1 Phase 1:

In phase 1 we perform two tasks with the help of literature. First is developing a model for the dehydrogenation process in Aspen Plus simulation software. Second is determining the reaction kinetic parameters which involves order of the reaction 'n' and finding out the required Activation energies for the reactions and specific reaction rates from the literature.

### **3.1.2 Phase 2:**

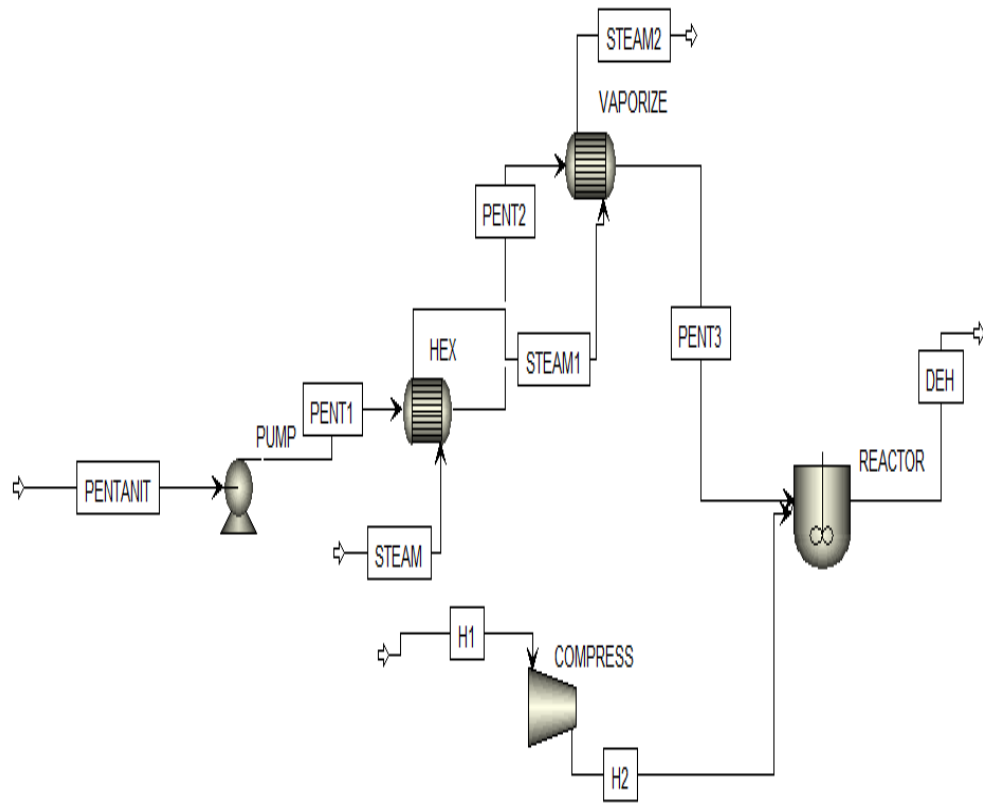
In phase 2 we carry out the simulations at temperature range from 300-450 °C and pressure 1, 1.8 and 3 bars for the three LOHC's individually. The temperature and pressure are changed after running each simulation one after the other.

### **3.1.3 Phase 3:**

In phase 3 data is generated as a result of simulations which shows the trends between temperature and conversion percentage of the feed and also effect of the pressure on the conversion percentage.

## **3.2 Process Description and Model Development**

Aspen Plus was used for the model making for dehydrogenation process of these LOHC's. The model consists of Pump through which the feed is passed at 25 °C temperature and pressure that variate at 1, 1.8 and 3 bar. After the pump, the feed and steam of temperature 700 °C is passed through a heat exchanger (HEX) where the temperature of the feed increases to 250 °C. Then the feed and the steam are passed through another vaporizer to get the required temperature for the feed that is 300-450 °C to enter the reactor. The feed entered into the reactor with a hydrogen stream whose weight ratio is H<sub>2</sub>/feed is 0.5 for the reaction to takes place and the feed conversion takes place. The H<sub>2</sub>/feed ratio is kept at 0.5 by combining the H<sub>2</sub> stream from the compressor before entering into the reactor. The temperature of the H<sub>2</sub> stream is also varied over the range 300-450 °C to get accurate results. The DEH stream is composed of H<sub>2</sub> and the correspondent LOHC. The H<sub>2</sub> is separated for application purpose and the LOHC is transferred again for hydrogenation. And the process is repeated for more transportation of H<sub>2</sub>. The process flow diagram created on Aspen Plus simulation software is given in Figure 11.



**Figure 11.** Process flow diagram of the dehydrogenation.

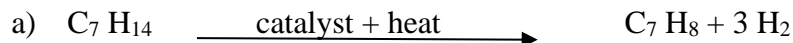
**Table 2:** Parameter and its vales for the dehydrogenation process model

<b>Parameter</b>	<b>Value</b>
No. of pumps	1
No. of compressors	1
No. of heat exchangers	2
RCSTR reactor	1
Feed T (PENT)	25 °C
Feed Pressure (PENT)	1,1.8 and 3 bar
Steam temperature	800 °C
Steam1 temperature	450 °C
Reactor temperature	300-450 °C
DEH Composition	LOHC + Gaseous H <sub>2</sub>
H <sub>2</sub> Temperature	200 °C
Feed temperature before reactor (PENT3)	300-450 °C
H <sub>2</sub> /Feed weight ratio	0.5
Fluid package	Peng-Robinson

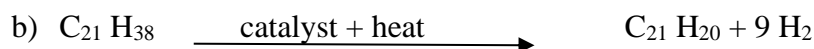
### 3.2.1 Balanced Chemical Reactions for the LOHC's:

The reaction takes place at different temperatures that ranges from 300 to 450 °C and pressure that are 1, 1.8 and 3 bars and the catalyst are also varied for different results. The

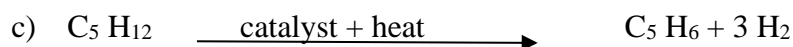
H<sub>2</sub>/feed ratio is also kept at 0.5. Different results occur at different parameters for different LOHCs. The reactions are given below



In this reaction one MCH dehydrogenate into three molecules of Hydrogen and one molecule of Toluene.



Similarly in this reaction one PHDBT dehydrogenate into nine molecules of Hydrogen and one Dibenzyltoluene.



In this one PTH dehydrogenate into three hydrogen molecules and one Methylthiophine.

### 3.2.3 Determination of rate of Chemical Equilibrium:

Chemical equilibrium expression tells us about both the concentration of the reactant as well as the product, Equilibrium constant is expressed as

$$K_{eq} = K_c \exp \left\{ \frac{-\Delta H}{R} \left( \frac{1}{T_r} - \frac{1}{T} \right) \right\}$$

If a reaction is;



The equilibrium constant K<sub>c</sub> is

$$K_c = \frac{[C]^k [D]^l}{[A]^m [B]^n}$$

### 3.2.4 Activation Energies and reaction rate constant 'k' for the reactions:

Activation Energy is the minimum amount of energy needed to activate or energize molecules or atoms so that they can undergo a chemical reaction or transformation. With

increase in temperature the molecules collide with more speed with each other and reaches the activation energy faster as compared to less temperature. These are different for varying reactants and catalysts, whereas reaction rate is the rate of the reaction in which the reactants are converted into products. Temperature has a direct effect on it, i.e., with increase in temperature this rate increases and vice versa. The activation energies and reaction rate constants 'k' for the three reactions are given in the table 3 and 4 with their corresponding catalysts [27-32].

**Table 3:** Activation Energies for the three reactions

<b>Activation Energy (Ea) in kJ /mol</b>			
<b>Catalyst</b>	<b>MCH</b>	<b>PHDBT</b>	<b>PTH</b>
0.3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>	100.6	117	79.7
Sulfided Pt/Al <sub>2</sub> O <sub>3</sub>	200	171	123.2
0.3 wt. % Pt + Re/Al <sub>2</sub> O <sub>3</sub>	51.9	149	100

**Table 4:** Reaction rate constants of reactions for the three reactions

<b>reaction rate constants of reaction 'k' in sec<sup>-1</sup></b>			
<b>Catalyst</b>	<b>MCH</b>	<b>PHDBT</b>	<b>PTH</b>
0.3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>	$1.65 \times 10^{-5}$	$3.5 \times 10^{-5}$	$5.6 \times 10^{-5}$
Sulfided Pt/Al <sub>2</sub> O <sub>3</sub>	$2.335 \times 10^{-6}$	$1.5 \times 10^{-5}$	$3.2 \times 10^{-5}$
0.3 wt. % Pt + Re/Al <sub>2</sub> O <sub>3</sub>	$1.336 \times 10^{-5}$	$2.1 \times 10^{-5}$	$4.9 \times 10^{-5}$

### 3.2.5 Determination of Order of Reaction 'n':

Order of a reaction is given by the rate law equation formula



$$\text{Rate} = K [\text{A}]^m [\text{B}]^n$$

$$\text{Order of a reaction} = m + n$$

In the table 4 the order of reactions 'n' for the three reactions calculated are given respectively

**Table 5:** Order of reactions 'n' for the three reactions

<b>LOHC Reaction</b>	<b>Order of reaction 'n'</b>
Methylcyclohexane	1
Perhydro Dibenzyltoluene	1
Pentiniithiophene	1

### 3.2.7 Determination of Conversion Percentage:

This is the equation through which we calculate the percentage conversion of the feed.

The conversion percentage is determined by the molar flows as mentioned below

$$\text{Conversion \%} = \frac{\text{total molar flow} - \text{molar flow after reaction}}{\text{Total molar flow}} \times 100$$



# Chapter 4

## Results and Discussion

The results of this research study have been divided into the following subsections MCH, PHDBT and PTH. In the graphs along the x axis is temperature in Celsius while along the y axis is the conversion of the feed at different pressures mentioned.

### 4.1 Methylcyclohexane (MCH)

For MCH conversion the graphs at different pressures and different catalysts are given below:

#### 4.1.1 Pressure (1 bar):

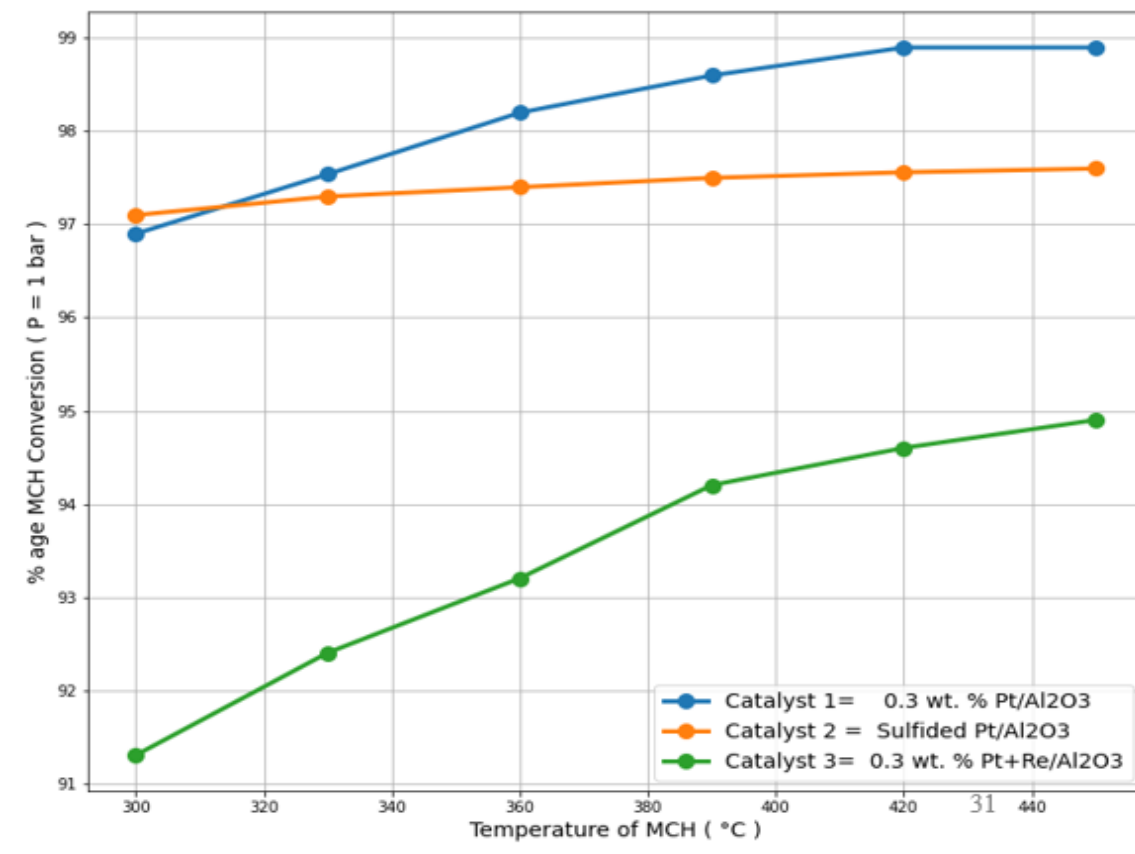
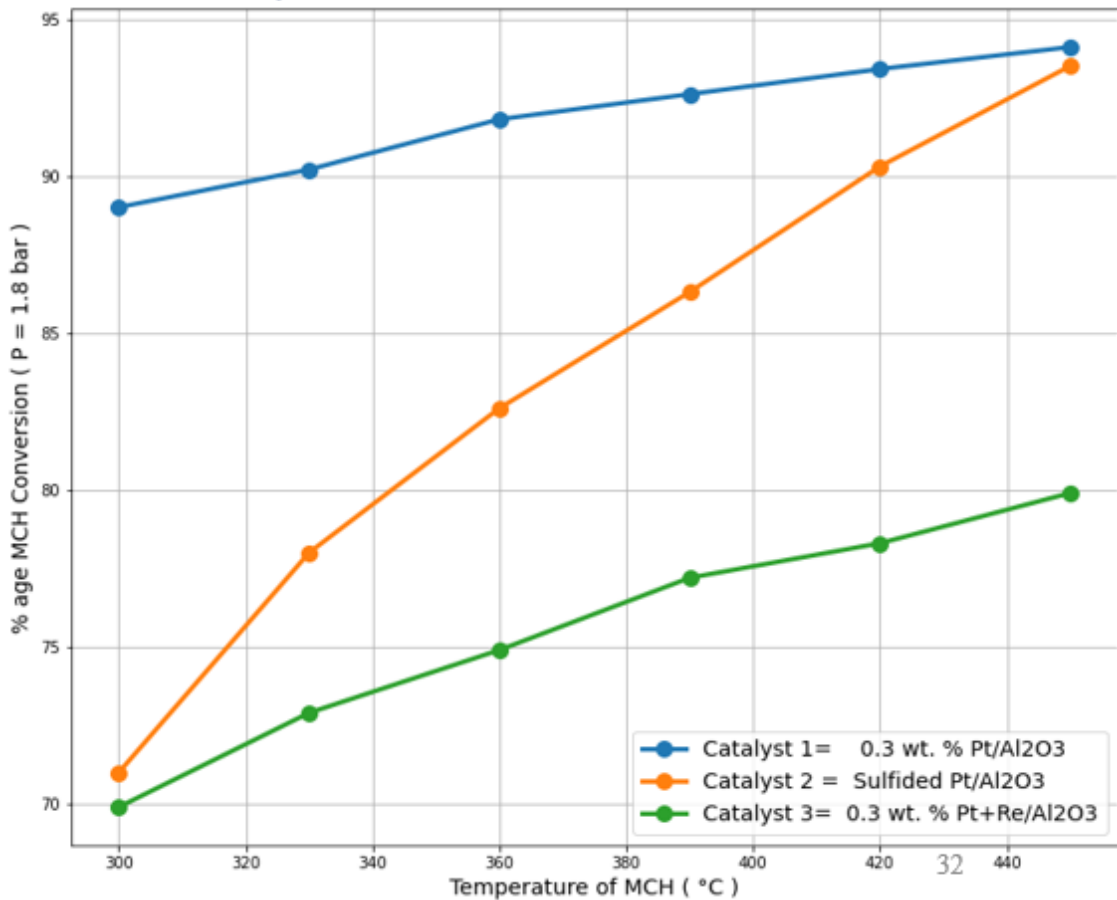


Figure 12. Catalysts effect on MCH conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 1$  bar.

In Figure 12 the trend for three catalysts is shown at temperature range from 300-450 °C. With increase in temperature the conversion increases. The catalyst 1 shows the maximum conversion i.e., 98.9% for MCH while catalyst 2 trend is a linear line i.e., the temperature has less effect on the conversion. Catalyst 3 conversion is relatively less as compared to the other two catalysts. At 317 °C the conversion of catalyst 1 and 2 are same as shown from the trend in Figure 1.

#### 4.1.2 Pressure (1.8 bar):



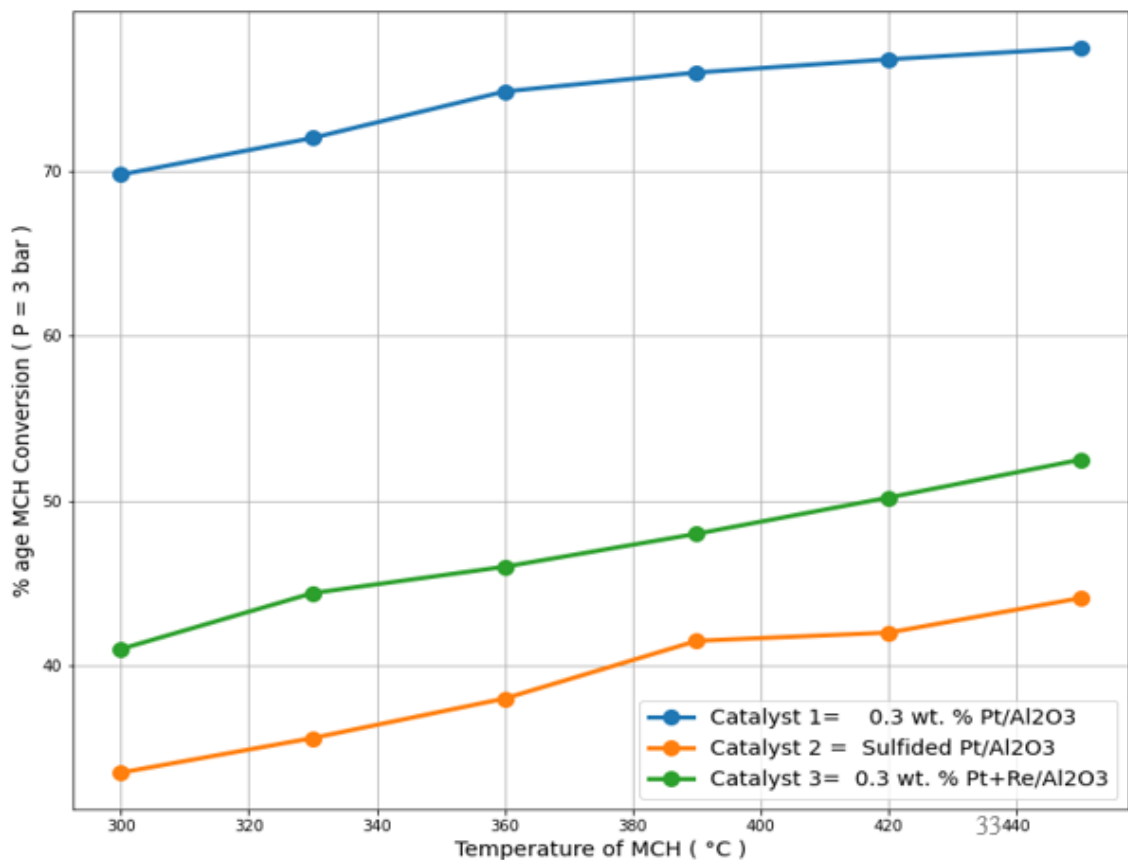
**Figure 13.** Catalysts effect on MCH conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 1.8$  bar.

In Figure 13 the same trend follows but catalyst 1 and 2 shows less difference between the conversions at 450 °C and catalyst 2 and 3 have less difference at 300 °C. Catalyst 2 has shown a very different trend at 1.8 bar pressure as compared to 1 bar. In this the conversion has a visible increase with varying temperature i.e., from 72% at 300 °C to 93

% at 450 °C, but still maximum conversion takes place at 450 °C for cat 1 i.e., 94.1%. for catalyst 3.

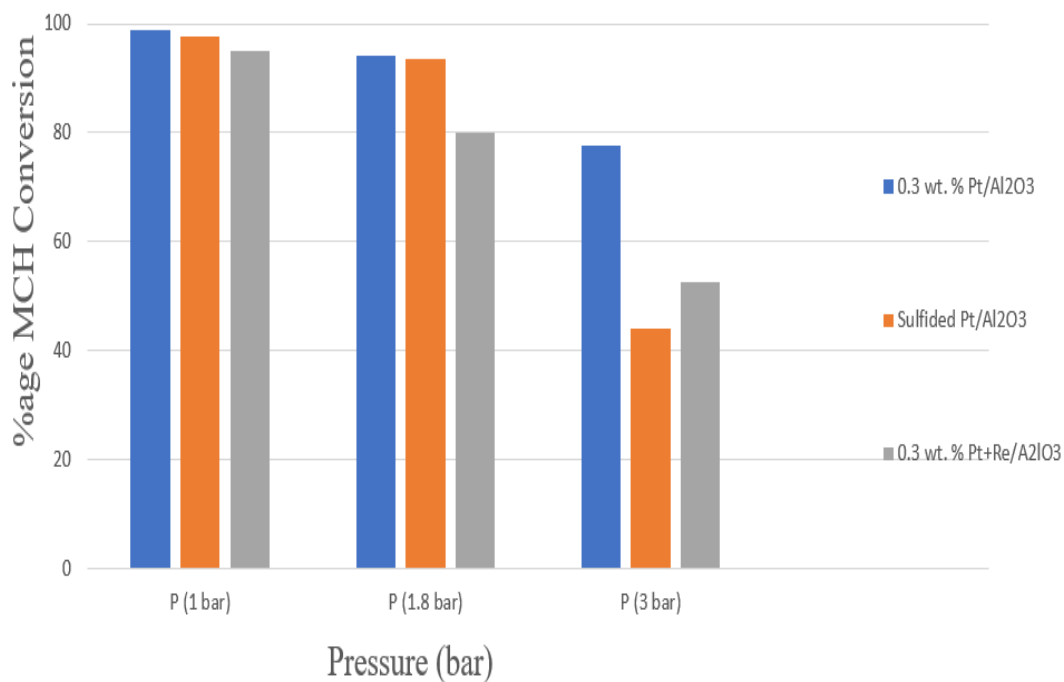
#### 4.1.3 Pressure (3 bar):

In Figure 14 at pressure 3 bar the trend changes again catalyst 1 shows more conversion than the other two i.e., 77.5% but as compared to Figure 1 and 2 the conversion is comparatively low. For catalyst 2 and 3 the conversion the trend is almost the same but the conversion is very low i.e., 44% for catalyst 2 and 52.5% for catalyst 3 at a 450 °C temperature. This shows that the catalyst activity and efficiency reduce with the increase in pressure because the conversion is less for all the three catalysts at 3 bar as compared to conversion at pressure 1 bar.



**Figure 14.** Catalysts effect on MCH conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 3$  bar.

#### 4.1.4 Effect of pressure on MCH conversion percentage:



**Fig 15:** Effect of pressure on %age MCH conversion

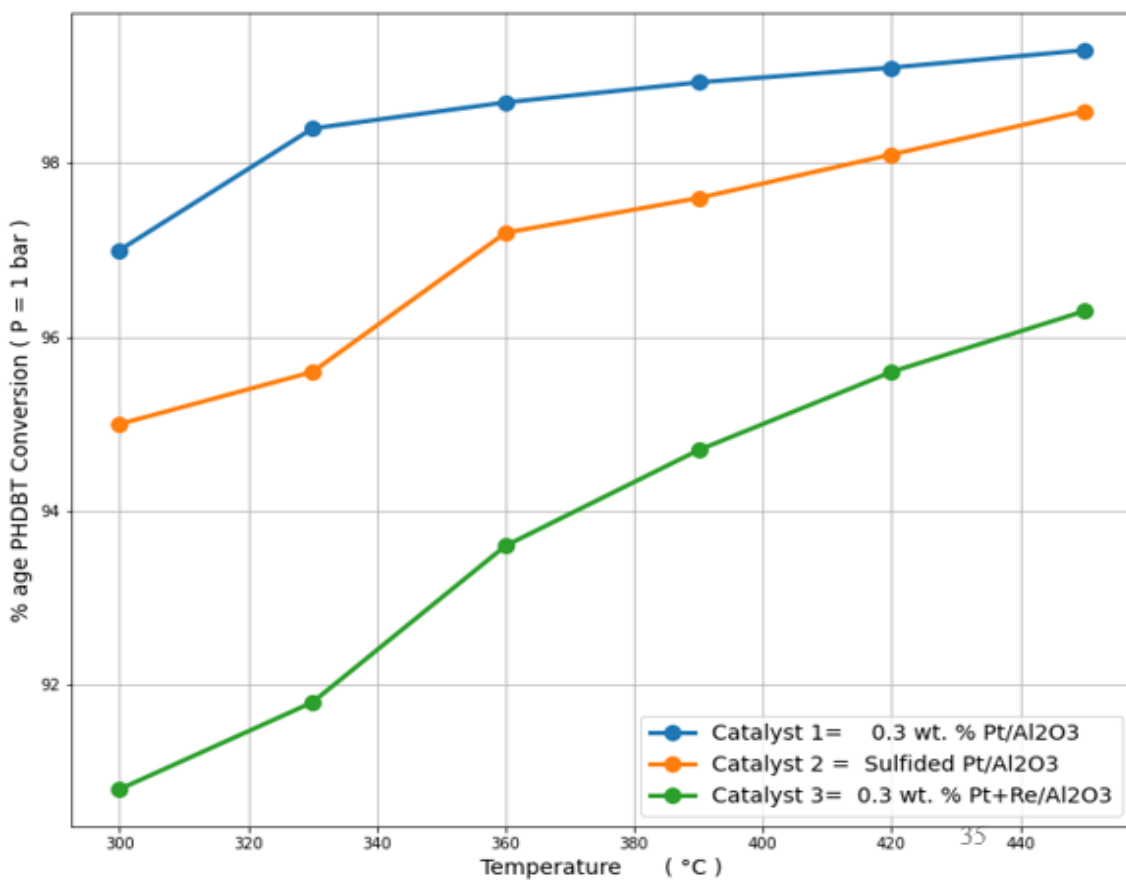
The graph in the Figure 15 shows the maximum MCH conversion percentage for the three catalysts at 450 °C at three pressures that are 1, 1.8 and 3 bar. It can be seen that with the increasing pressure the conversion percentage decreases comparatively. It means that with increasing pressure the catalyst activity become less and LOHC conversion percentage is less because the conversion is directly related to the catalyst stability and activity. At higher pressure the coke formation on the surface of the catalyst also occurs due to which additional H<sub>2</sub> stream is added to the reactor with the feed stream to avoid coke formation and increase the catalyst stability and activity.

## 4.2 PerhydroDibenzylToluene (PHDBT)

The graphs are given below and this Liquid Organic Hydrogen Carrier has more efficiency as compared to MCH.

### 4.2.1 Pressure (1 bar):

In the Figure 16 the conversion increases with the increase in temperature and the maximum conversion is at 450 °C i.e., 99.3%. The trend suggests that using this Liquid Organic Hydrogen Carrier the conversion is more as compared to the other's used, i.e., the conversion for catalyst 1 at 450 °C is 99.3% while for catalyst 2 is 98.6% and for catalyst 3 is 96.3%. these catalysts do not come close at any temperature so the difference is also more between these catalysts at their correspondent temperatures. The best catalyst is catalyst 1, i.e., commercial Pt/Al<sub>2</sub>O<sub>3</sub> which shows the maximum conversion at 450 °C.



**Figure 16.** Catalysts effect on PHDBT conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 1$  bar.

#### 4.2.2 Pressure (1.8 bar):

In Figure 17 the conversion is less because the pressure increases to 1.8 bar from 1 bar so the catalyst efficiency decreases. In catalyst 2 the conversion is almost uniform over the different temperatures. The conversion of catalyst 1 and catalyst 2 are almost the same at 450 °C i.e., for catalyst 1 the conversion is 95.8% and for catalyst 2 is 95.5%. catalyst 3 conversion is comparatively less than the other 2 and at 450 °C the conversion is 81.7%. This means that with the increase in temperature the catalyst is more active and unstable for which we add hydrogen with the feed before entering into the reactor to make it stable. But catalysts react differently to the increasing temperature and pressure due to which their performance varies.

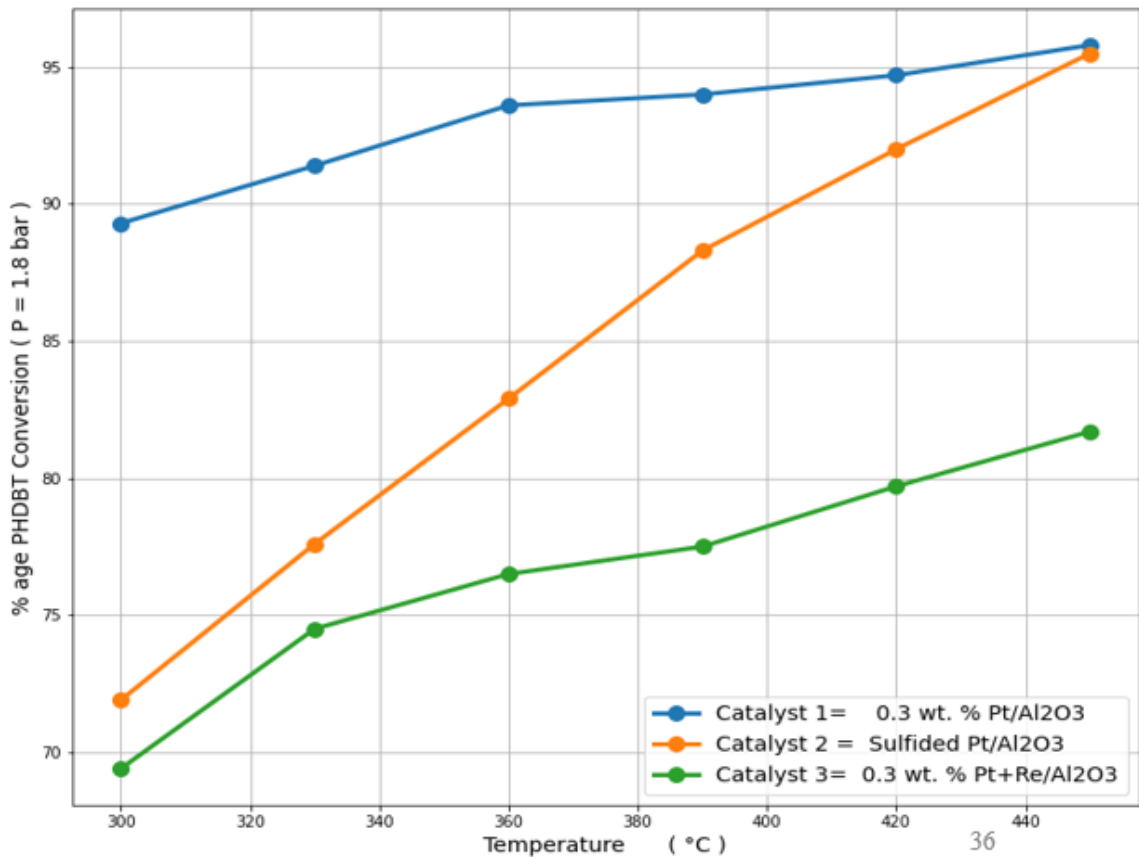
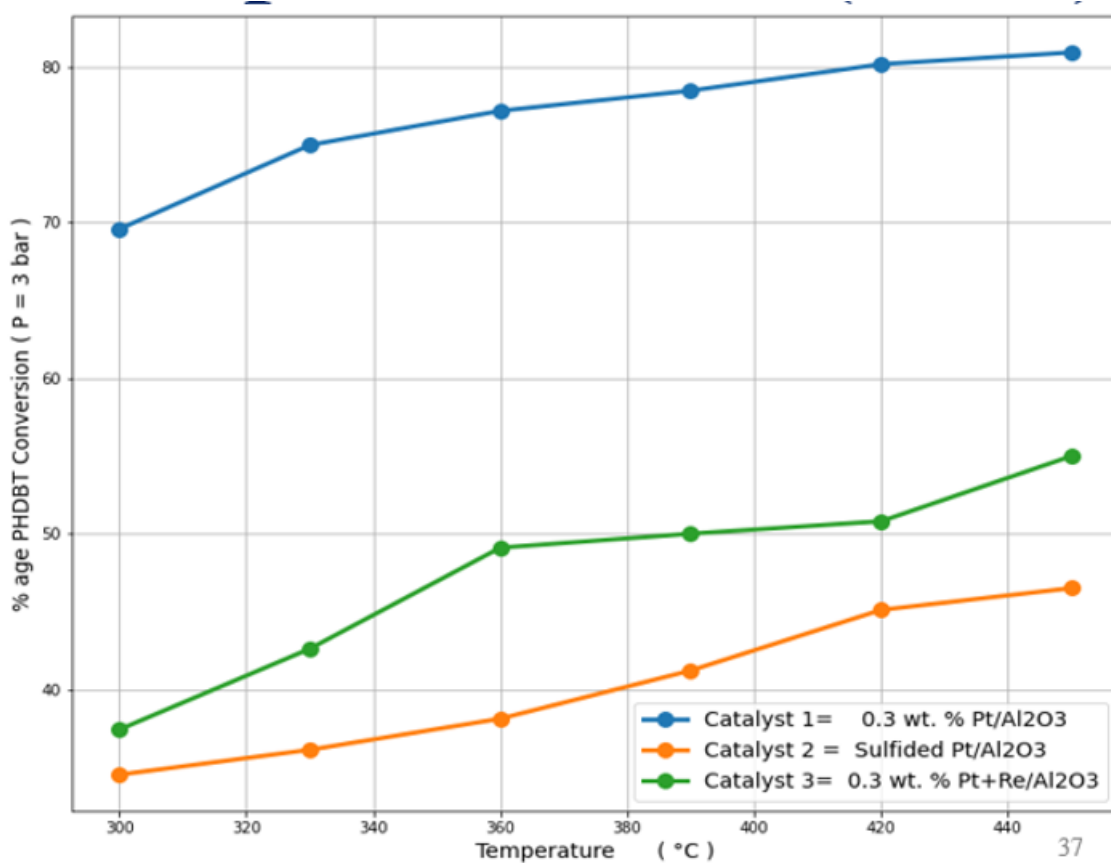


Figure 17. Catalysts effect on PHDBT conversion percentage at H<sub>2</sub>/MCH = 0.5, P = 1.8 bar.

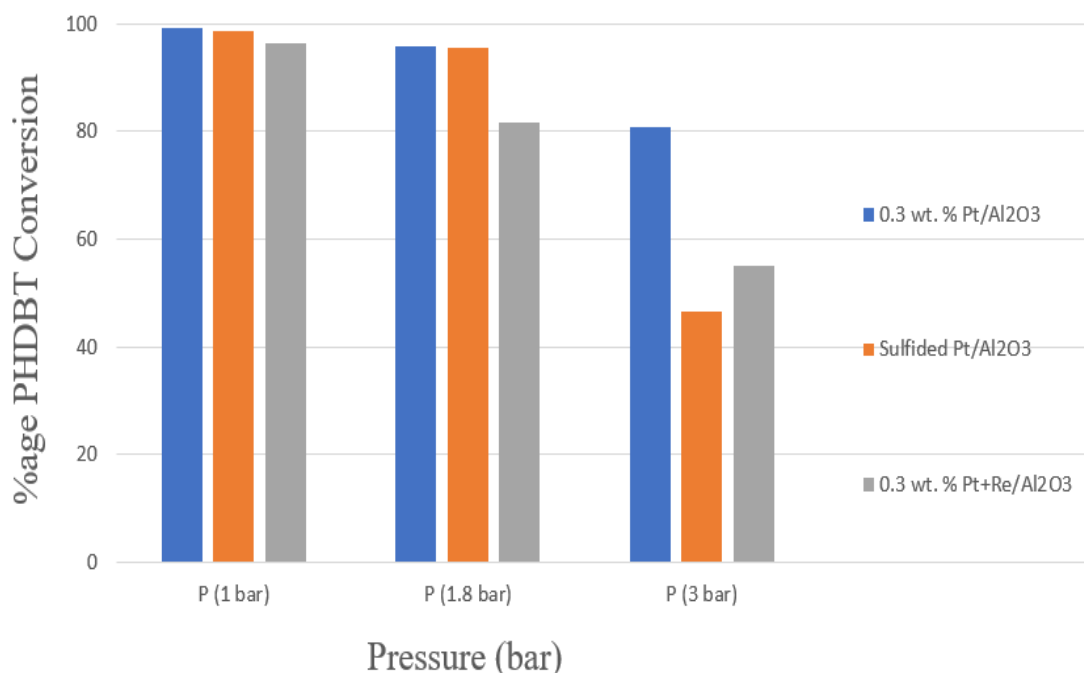
### 4.2.3 Pressure (3 bar):

In the Figure 18 as the pressure has increased conversion has decreased for the catalysts but still the trend is same as it gradually increases with temperature. The difference between the catalyst 2 and catalyst 3 is less over the correspondent temperatures while that of catalyst 3 is relatively greater. At 3 bars the catalyst 2 shows less conversion with this LOHC too as was shown with MCH. At 450 °C the conversion for catalyst 1 is 80.96%, for catalyst 2 is 46.5 % and for catalyst 3 is 55%. The catalyst 2 stability and effectiveness at 3 bar pressure has shown an abnormal trend as compared to the 1 and 1.8 bar pressure that is due to the coke formation on the surface of the catalyst.



**Figure 18.** Catalysts effect on PHDBT conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 3$  bar.

#### 4.2.4 Effect of pressure on PHDBT conversion percentage:



**Figure 19:** Effect of pressure on %age PHDBT conversion

The Figure 19 shows the maximum PHDBT conversion percentage for the three catalysts at 450 °C at three different pressures that are 1, 1.8 and 3 bar. It follows the same trend as in Figure 15. It can be seen that with the increasing pressure the conversion percentage decreases comparatively. It means that with increasing pressure the catalyst activity become less and conversion percentage is less because the conversion is directly related to the catalyst stability and activity. At higher pressure the coke formation on the surface of the catalyst occurs due to which additional H<sub>2</sub> stream is added to the reactor with the feed stream to avoid coke formation and increase the catalyst stability and activity.

### 4.3 Pentinithiophene (PTH)

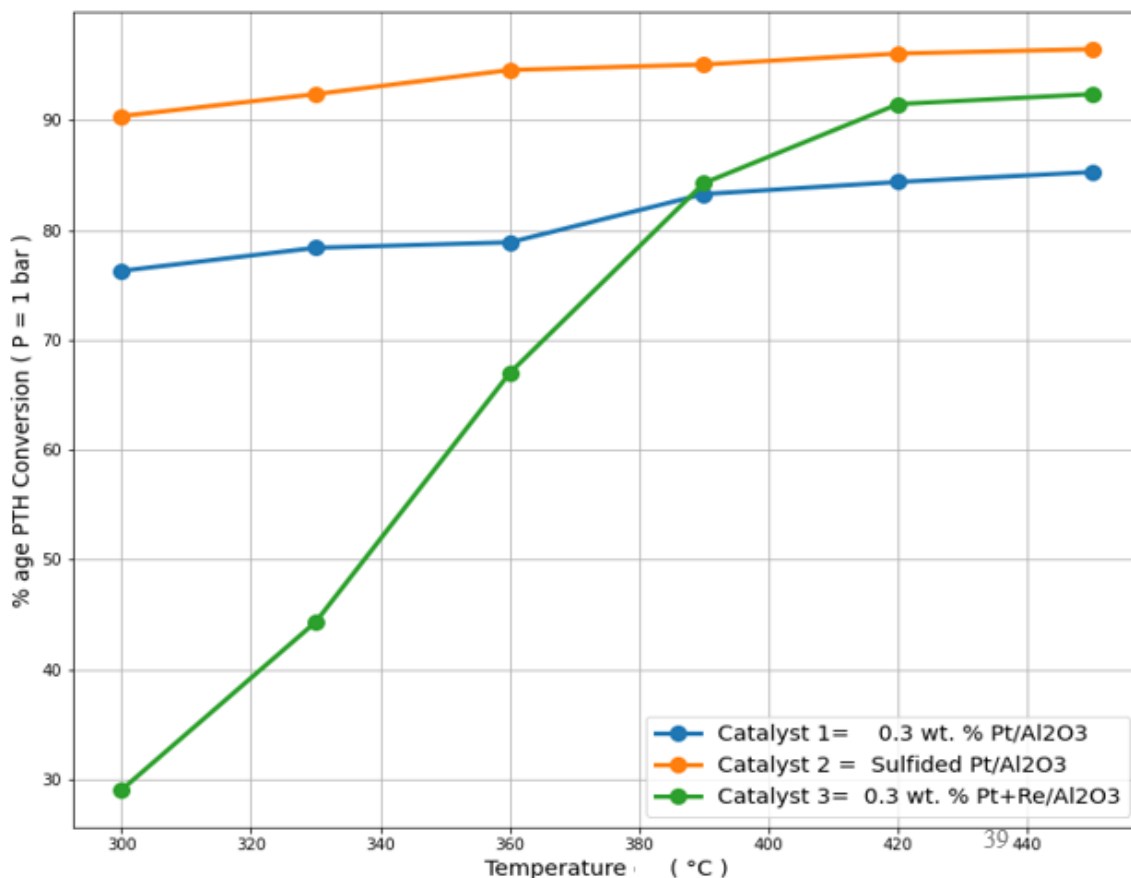
For PTH conversion the graphs are

#### 4.3.1 Pressure (1 bar):

In Figure 20 the trends are a little different than the previous two LOHCs. The catalyst 2 shows more conversion than catalyst 1 and 3. The conversion rate is more in catalyst 3

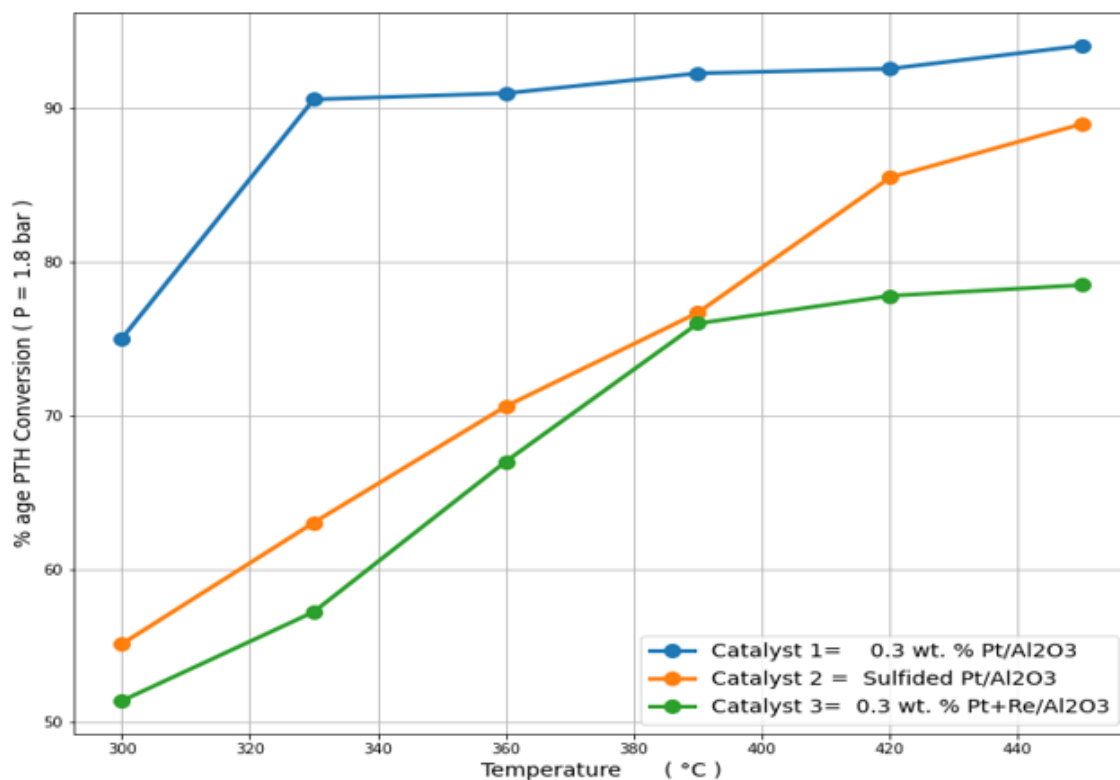


over the varying temperatures as compared to catalyst 1 but overall conversion is more in catalyst 2. The trend for catalyst 2 is almost linear that means the conversion is less over varied temperatures while for catalyst 3 the conversion at 300 °C temperature is 29% while at 450 °C its 92.4 % which means that with increasing the temperature the conversion has a drastic increase. At 390 °C the catalyst 1 and catalyst 3 has almost same conversion that is 83% and 84%.



**Figure 20.** Catalysts effect on PTH conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 1$  bar.

### 4.3.2 Pressure (1.8 bar):

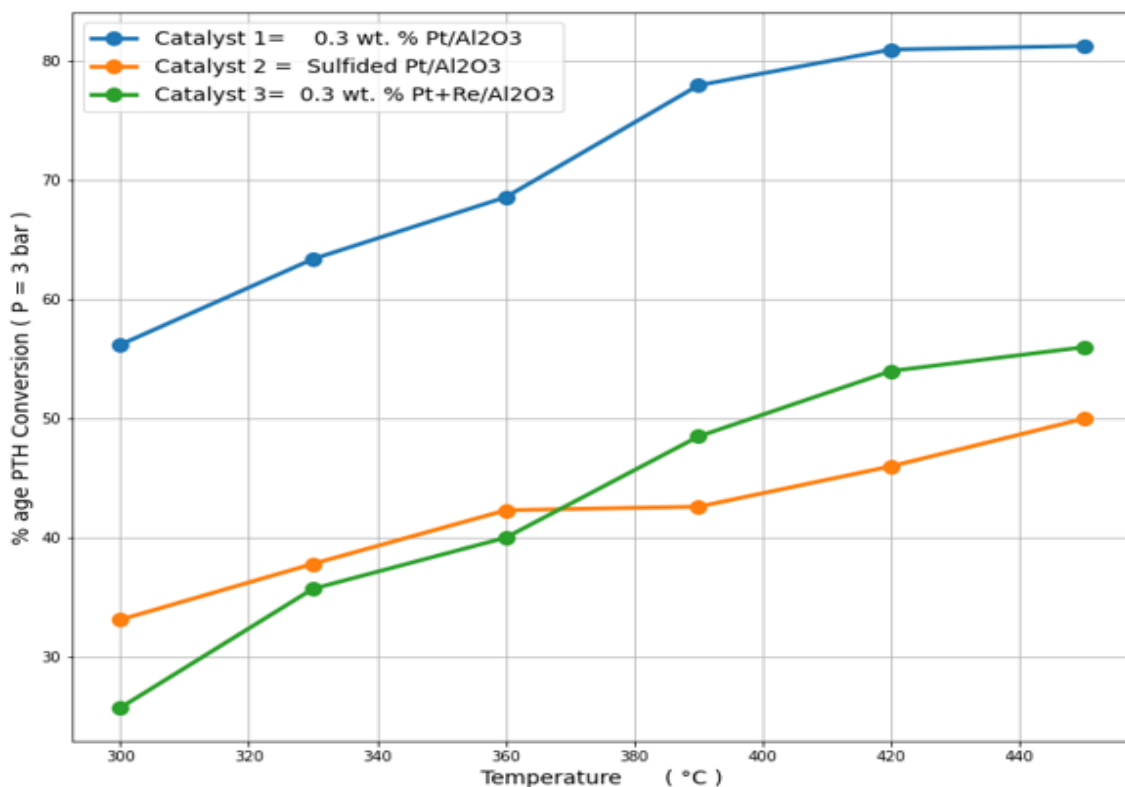


**Figure 21.** Catalysts effect on PTH conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 1.8$  bar.

In Figure 21 catalyst 1 has more conversion value at 450 °C as compared to the other catalysts, i.e., 94.1% while catalyst 2 is 89% and catalyst 3 is 78.5% at same temperature, while at 390 °C the catalyst 2 and 3 shows almost the same conversion that is 76.7% and 76%. After 390 °C the catalyst 2 shows the same conversion trend till 450 °C while catalyst 3 has almost a linear trend which means that less conversion takes place. The catalyst 1 shows a large difference in conversion from 300 to 330 °C that is from 75% at 300 to 90.6% at 330 °C and a very less conversion from 330 °C to 450 °C. The conversion of catalyst 1 at 390 °C is 92.3% and 420 °C is 92.6% which is nearly the same, this means that catalyst 1 has a very less effect of increasing temperature after it reaches its optimum temperature.

### 4.3.3 Pressure (3 bar):

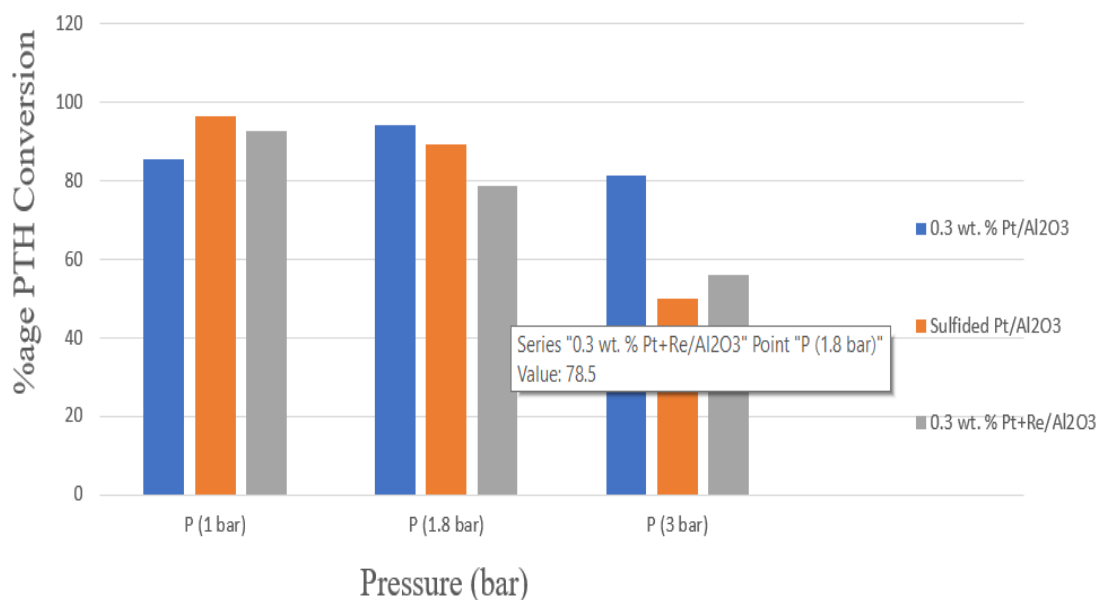
In Figure 22 the pressure is 3 bar so the conversion is less as the catalyst shows less efficiency at higher pressure value, also the catalyst 2 conversion has decreased tremendously at this pressure that is from 33.1% at 300 °C to 50% at 450 °C. The overall conversion is more in catalyst 1 that is 56.2% at 300 °C to 81.3% at 450 °C. The trend suggests that catalyst 3 has less conversion at 300 °C than catalyst 2 that is 25.7% and 33.1% but surpasses it and has more conversion at 390 °C, 420 and 450 °C i.e., 48.5%, 54% and 56% whereas catalyst 2 conversion at the same temperatures are 42.6%, 46% and 50%. These trends suggest that three catalysts react differently at varying temperatures and pressures for the three LOHC's. The trends in the above figures are different than this because the results are different, as the conditions change the results change automatically. Secondly results depend upon the stability and activity of the catalyst which also changes with change in the conditions.



**Figure 22.** Catalysts effect on PTH conversion percentage at  $H_2/MCH = 0.5$ ,  $P = 3$  bar.

#### 4.3.4 Effect of pressure on PTH conversion percentage:

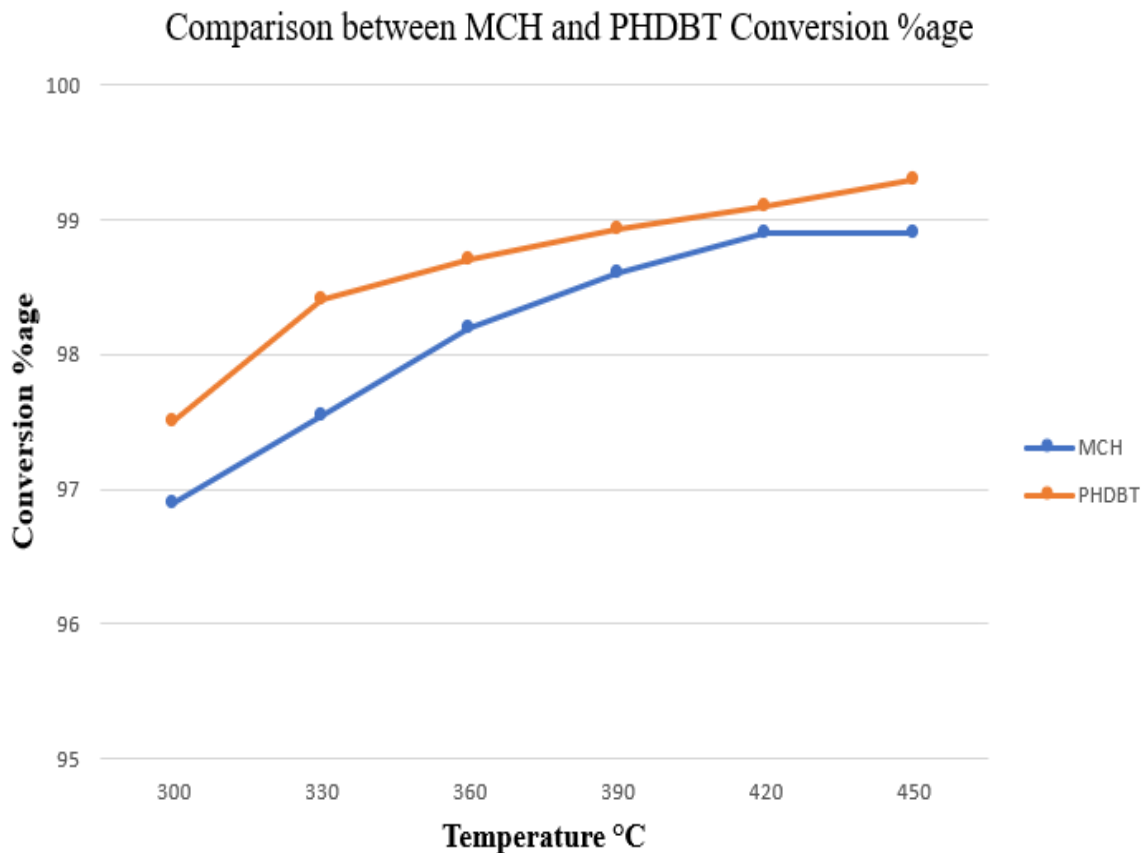
The Figure 23 shows the maximum PTH conversion percentage for the three catalysts at 450 °C at three pressures that are 1, 1.8 and 3 bar. It can be seen that with the increasing pressure the conversion percentage decreases comparatively. It means that by increasing pressure the catalyst activity become less and less conversion percentage takes place because the conversion is directly related to the catalyst stability and activity. At higher pressure the coke formation on the surface of the catalyst which affects the catalyst activity, due to which additional H<sub>2</sub> stream is added to the reactor with the feed stream to avoid coke formation and increase the catalyst stability and activity.



**Figure 23:** Effect of pressure on %age PTH conversion

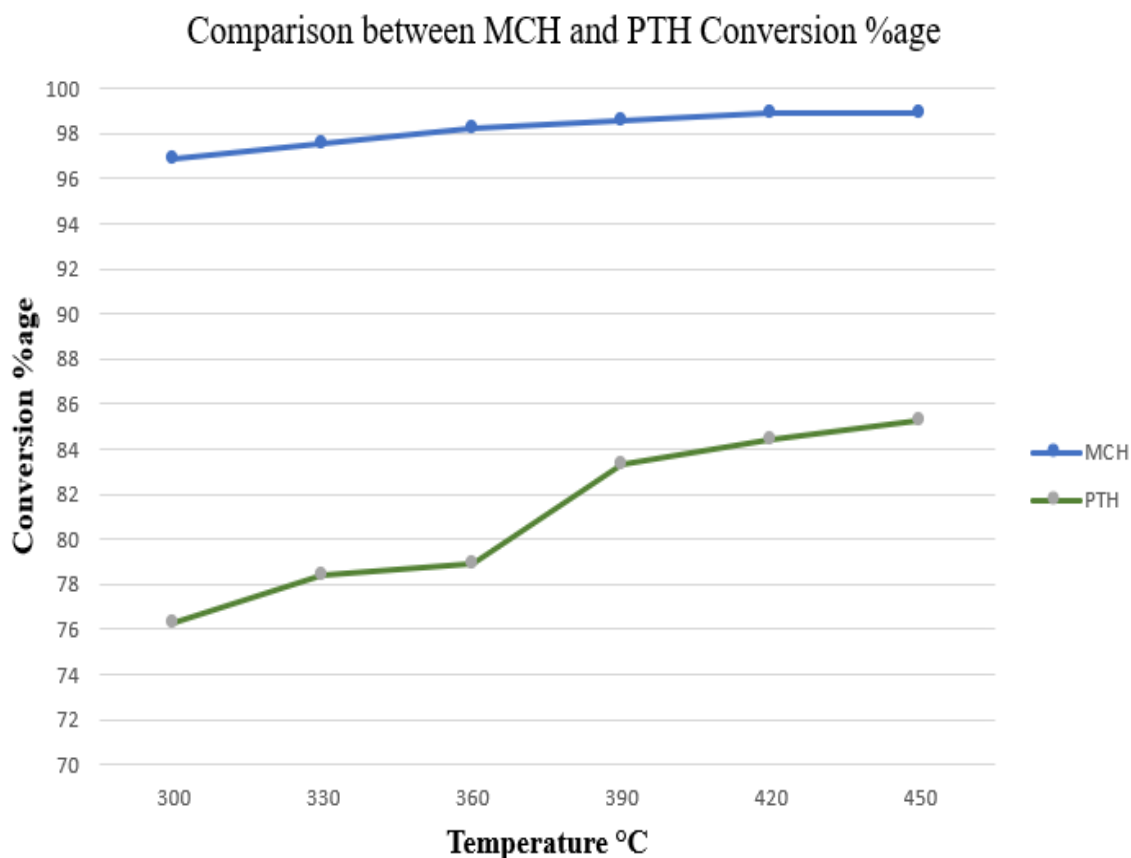
#### 4.4 Comparison between MCH, PHDBT and PTH conversion %age at P (1 bar):

In figure 24 comparison between MCH and PHDBT conversion percentage is shown. Conversion is more at pressure 1 bar and at 450 °C as from the results. PHDBT conversion i.e., 99.3 % at 450 °C is more than MCH i.e., 98.8 %.



**Figure 24:** Comparison between PHDBT and MCH %age conversion

In figure 25 comparison between MCH and PTH conversion is shown and PTH has relatively very low conversion. The difference in conversion percentage is due to the difference of reaction kinetics and activation energies and also due to the difference in structure of molecules of each LOHC.



**Figure 25:** Comparison between MCH and PTH conversion %age

#### 4.5 Discussion:

Many researchers have worked on green fuel to avoid different sorts of pollution which can result in global warming and climate changes that can affect human lives and can cause diseases, hydrogen fuel was the best for the cause. The main hurdle was the transportation and storage of hydrogen, as the techniques used and available had multiple drawbacks like high energy consumption, hydrogen lost as a result of dehydrogenation etc. The Liquid Organic Hydrogen Carrier hydrogenation and dehydrogenation technique was more efficient and cheaper. The researchers had worked experimentally on MCH but some other LOHC's were also there that had the potential to give us more efficient results through simulation. As from the results PHDBT at 450 °C and pressure 1 bar gives us 99.3% conversion which is more than the MCH.

In this study different trends of the graphs were observed, which showed that catalysts react differently to LOHC's at different conditions of temperature and pressure, it was noticed that with the increase in temperature, the stability and activity duration or life of the catalyst decreases but the conversion of the feed increases and secondly with the increase in pressure the conversion decreases which means conversion and pressure are indirectly proportional whereas temperature and conversion are directly proportional.

In this study the focus was to select the best catalyst and Liquid Organic Hydrogen Carrier among the three catalysts and three LOHC's mentioned above by comparing their results and to select the most efficient conditions for dehydrogenation in which minimum hydrogen was lost but there are still many other LOHC's and catalysts available that can be used for this purpose and most probably their efficiency could be more. Similarly, the model can also be modified accordingly for more efficient results like more heat exchangers can be added to carry out the simulations at a higher temperature in the presence of catalysts whose stability and activity could be more than the present catalysts studied in this study.

## Conclusions

Firstly, the model was developed using Aspen Plus simulation software for the parametric simulation study of dehydrogenation process of the Liquid Organic Hydrogen Carriers. Afterwards simulations were carried out on the same Aspen PLUS model and data was generated and were put on the graphs, as a result trends were determined for the conversion percentage of the feed. Results were accumulated and drawn on the graphs for conversion percentage at temperature ranges from 300-450 °C and pressure at 1, 1.8 and 3 bar for three catalysts. It was observed from the results that a decrease in pressure and rise in temperature resulted in high percentage conversion of LOHCs dehydrogenation and vice versa. This was the case with all the three Liquid Organic Hydrogen Carriers studied in this thesis. The maximum conversion took place in PerhydroDibenzylToluene (PHDBT) at 450 °C when pressure was kept at 1 bar. The conversion was 99.3 % which is the highest achieved in the three LOHCs. The main objective was to determine the Optimum Operating Conditions for the process, that were pressure 1.8 bars and temperature at 390 °C. At these conditions the catalyst activity is maximum and the reaction operation time also increases that helps in cost effectiveness. The H<sub>2</sub>/MCH ratio in the feed was controlled at 0.5 for the dehydrogenation process, the presence of hydrogen brought about a slightly reduced dehydrogenation rate, whereas, it enhanced the catalyst activation by avoiding coke formation on the surface of the catalyst, as a result less catalyst is used and more conversion takes place with a specified amount of catalyst.



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