

**Upscaling of Longifolene Isomerization  
In  
Continuous Flow Reactor  
Over Solid Acid Catalyst**

By

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**DEPARTMENT OF CHEMICAL ENGINEERING**

**AHMEDABAD**

**382481**

**Upscaling Longifolene Isomerization  
In  
Continuous Flow Reactor  
Over Solid Acid Catalyst**

**Major Project**

Submitted in partial fulfillment of the requirements

For the Degree of  
Master of Technology in Chemical Engineering

By  
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# Undertaking for the originality of the work

I Chirag B. Mehta , 11MCHC18, give undertaking that the major project entitled “**Upscaling Of Longifolene Isomerization In Continuous Flow Reactor Over Solid Acid Catalyst**” submitted by me,towards the partial fulfillment of the requirements for the degree of master of technology in Chemical Process and Plant Design of Nirma University, Ahmedabad is the original work carried out by me and i give assurance that no attpemt of plagiarism had been made.

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# Certificate

This is to certify that the Major Project entitled "**Upscaling of Longifolene Isomerization In Continuous Flow Reactor Over Solid Acid Catalyst**" submitted by **Mr.Chirag B. Mehta (11MCHC18)**, towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering of Nirma University, Ahmedabad is the record of work carried out by him under my supervision and guidance. In my opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

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## Abstract

Isomerization, is the chemical process by which a compound is transformed into any of its isomeric forms & Longifolene is the common (or trivial) chemical name of a naturally occurring, oily liquid hydrocarbon found primarily in the high-boiling fraction of certain pine resins. Isomerization of longifolene with solid acid catalyst such as sulfated zirconia gives Isolongifolene.

Isolongifolene and its derivatives, which extensively used in perfumery industry due to their woody and floral odor. The acid catalysed and hydroformylated products of this isomerized isolongifolene have also woody amber odor and are used as a flavor in many pharmaceutical industries.

Isomerisation of longifolene with nano-crystalline sulphated zirconia (SZ) solid acid catalyst and obtained 95-97% conversion of longifolene and 100% selectivity of isolongifolene at 180°C within 15-30 minutes under stirred batch reactor. It is noteworthy that SZ exhibited similar catalytic activity over a wide range of longifolene to SZ weight ratio, i.e.,10:1 to 100:1.

The acid catalysed and hydroformylated products of this isomerized isolongifolene have also woody amber odor and are used as a flavor in many pharmaceutical industries. isomerisation of longifolene with nano-crystalline sulphated zirconia (SZ) solid acid catalyst and obtained 95-97% conversion of longifolene and 100% selectivity of isolongifolene at 180°C within 15-30 minutes under stirred batch reactor.

It is noteworthy that SZ exhibited similar catalytic activity over a wide range of longifolene to SZ weight ratio, i.e., 10:1 to 100:1.

so now for industrial production of isologifolene we need to upscaling this process by using the continuous flow fixed bed reactor.so we transfer this isomerization process lab scale to industrial scale. The up scaling of the process for the said reaction will be carried out in continuous flow reactor: so in this upscaling we Design and modification of existing continuous flow reactor.

we also study Different forms of the catalyst such as beads, granules and powder studied using different binders and their effect on the activity and life of the catalyst and we also study the Various reaction parameters such as temperature, time and substrate to catalyst weight ratio. so and optimized this parameters we can get the achieve maximum conversion and selective formation of the product from lab scale to large scale.

# List of Tables

4.1	Stirred Batch Reactor Reaction Condition & Results . . . . .	16
4.2	Fixed Bed Reactor Reaction Condition & Results . . . . .	17
4.3	Fixed Bed Reactor Reaction Condition & Results . . . . .	18
4.4	Fixed Bed Reactor Reaction Condition & Results . . . . .	19
4.5	Fixed Bed Reactor Reaction Condition & Results . . . . .	20
4.6	Fixed Bed Reactor Reaction Condition & Results . . . . .	21
4.7	Fixed Bed Reactor Reaction Condition & Results . . . . .	22
4.8	Fixed Bed Reactor Reaction Condition & Results . . . . .	23
4.9	Temperature Variation Effect . . . . .	26
4.10	Catalyst Shape & Loading Effect . . . . .	27

# List of Figures

1.1	Appearance of Longifolene . . . . .	2
3.1	Distillation Arrangement Of Longifolene . . . . .	9
3.2	Batch Rector (RBF) Reaction Arrangement . . . . .	11
3.3	Fixed Bed Reactor Arrangement . . . . .	13
3.4	Glass Fixed Bed Reactor . . . . .	14
3.5	Extrudate & Tablet/Pellet Shape . . . . .	15
3.6	Pellet & Flakes Shape . . . . .	15
5.1	GC Analysis of Longifolene Before Distillation . . . . .	31
5.2	GC Analysis of Longifolene after Distillation . . . . .	31
5.3	GC Analysis of Experiment -5(Fixed Bed Reactor) . . . . .	32
5.4	GC Analysis of Experiment -1 (Batch Reactor) . . . . .	32



# Contents

<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
1.1	Isomerization . . . . .	1
1.2	Longifolene . . . . .	2
<b>2</b>	<b>LITERATURE SURVEY</b>	<b>3</b>
2.1	ISOMERIZATION OF LONGIFOLENE . . . . .	3
2.2	SOLID ACID CATALYST . . . . .	5
2.3	VARIOUS KINDS OF SOLID ACID CATALYSTS . . . . .	6
2.4	AIMS OF THE PROPOSAL . . . . .	7
<b>3</b>	<b>EXPERIMENTAL STUDY</b>	<b>8</b>
3.1	DISTILLATION OF THE LONGIFOLENE: . . . . .	8
3.2	CATALYST PREPARATION . . . . .	10
3.2.1	Catalyst Preparation Method.[10] . . . . .	10
3.3	CATALYTIC ISOMERISATION OF LONGIFOLENE . . . . .	11
3.3.1	Stirred Batch Reactor Reaction . . . . .	11
3.3.2	Fixed Bed Reactor Reaction . . . . .	13
<b>4</b>	<b>RESULT AND DISCUSSION</b>	<b>16</b>
4.1	Stirred Batch & Fixed Bed Reactor Reactions Conditions And Results . . . . .	16
<b>5</b>	<b>CONCLUSION</b>	<b>28</b>
	<b>bibliography</b>	<b>29</b>
	<b>Appendix I</b>	<b>31</b>

# Chapter 1

## INTRODUCTION

### 1.1 Isomerization

Isomerization, is the chemical process by which a compound is transformed into any of its isomeric forms, i.e., forms with the same chemical composition but with different structure or configuration and, hence, generally with different physical and chemical properties.

An example is the conversion of butane, a hydrocarbon with four carbon atoms joined in a straight chain, to its branched-chain isomer, isobutane, by heating the butane to 100°C or higher in the presence of a catalyst. Butane and isobutane have widely different properties. Butane boils at -0.5°C and freezes at -138.3°C, whereas isobutane boils at -11.7°C and freezes at -159.6°C.

The isomerization of straight-chain hydrocarbons to their corresponding branched-chain isomers is an important step (called reforming) in gasoline manufacture.

There are numerous other examples of isomerization reactions of great industrial importance.[1][2]

In chemistry, Isomerisation is the process by which one molecule is transformed into another molecule which has exactly the same atoms, but the atoms are rearranged e.g. A-B-C → B-A-C (these related molecules are known as isomers). In some molecules and under some conditions, isomerisation occurs spontaneously. Many isomers are equal or roughly equal in bond energy, and so exist in roughly equal amounts, provided that they can interconvert relatively freely, that is the energy barrier between the two isomers is not too high.

When the isomerisation occurs intramolecularly it is considered a rearrangement reaction. An example of an organometallic isomerisation is the production of decaphenylferrocene.[17][18]

#### Instances of Isomerisation

Isomerisations in hydrocarbon cracking. This is usually employed in organic chemistry, where fuels, such as pentane, a straight-chain isomer, are heated in the presence of a platinum catalyst. The resulting mixture of straight- and branched-chain isomers then have to be separated. An industrial process is also the isomerisation of n-butane into isobutane.[18]

**Trans-cis isomerism or Entgegen-Zusamen Isomerism:** In certain compounds an interconversion of cis and trans isomers can be observed, for instance, with maleic acid and with azobenzene often by photoisomerization.

**Valence isomerisation:** The isomerisation of molecules which involve structural changes resulting only from a relocation of single and double bonds. If a dynamic equilibrium is established between the two isomers it is also referred to as valence tautomerism. The energy difference between two isomers is called isomerisation energy.[18]

## 1.2 Longifolene

Longifolene<sup>[2][3]</sup> is the common (or trivial) chemical name of a naturally occurring, oily liquid hydrocarbon found primarily in the high-boiling fraction of certain pine resins.

The name is derived from that of a pine species from which the compound was isolated. Chemically, longifolene is a tricyclic sesquiterpene hydrocarbon.

Longifolene is present in the indian turpentine oil obtained from chirpine to the extent of 5-7 % .<sup>[1][2]</sup>



Figure 1.1: Appearance of Longifolene

### Longifolene Properties

- Molecular Formula :-  $C_{15}H_{24}$
- Molecular weight :- 204.35 gm/mol
- Boiling Point :- 254 °C
- Density :- 0.925 to 0.935 gm/cm<sup>3</sup>
- Solubility :- Soluble in benzene, cyclohexane, Petroleum ether, Partly soluble in alcohol, Insoluble in water
- Appearance :- Colorless to Light pale yellow, Slightly viscous liquid.

### • Iso-Longifolene Properties

- sesquiterpene terpene, is new kind of flavor.
- It can be used to produce iso-longitolanone, Isolongifone, Isolongifolol, Isolongifolene ethyl ester, hydroxymethyl Isolongifolene.
- Uses: material of essence and flavor

# Chapter 2

## LITERATURE SURVEY

### 2.1 ISOMERIZATION OF LONGIFOLENE

The economical utilization of this terpene hydrocarbon involves its transformation into isomeric product isolongifolene and its derivatives, which extensively used in perfumery industry due to their woody and floral odor.

The acid catalysed and hydroformylated products of this isomerized isolongifolene have also woody amber odor and are used as a flavor in many pharmaceutical industries.

Existing procedures involve either reacting longifolene with protic acids like dilute sulfuric acid or with Lewis acids such as  $\text{BF}_3$ . These methods have serious drawbacks.[9]

Such drawbacks are:

- This multistep process which results large quantity of unwanted waste chemicals as a by products and that requires further treatment before disposal.
- Sulfuric acid also hazardous, corrosive, irritant material and not safe from the handling point of view.
- The isomerized product obtained which possesses some color due to the impurities generated and this requires further purification.

Other acid catalysts have also been used by several workers, which are briefly mentioned below:

1. Breyler, R.E and Ourisson et al., In this synthesis they used boron trifluoride etherate.

This typical reaction involves multi step synthesis of isolongifolene using hazardous chemicals like  $\text{KOH}$ ,  $\text{BF}_3$  and sodium metal. Separation of the product from the reaction mixture involves several chemical treatment and more time consuming before product can be obtained.[4]

2. Prabhad, J.R. et al., Who used acid treated silica gel for the synthesis of isolongifolene from the longifolene. But major drawback in the stability of the catalyst used as leaching of acid occurs from silica gel with prolonged use.[5]

3. Bisarya S.C et al., In this synthesis they obtain isolongifolene from longifolene using Amberlyst-15 at 95 °C for 36 hours. they get 95% yield of isolongifolene.

The drawback is that amberlyst, which is ion exchange resin having poor thermal stability and also swell with prolonged use[6]

4. Ramesha A.R. et al, In this synthesis they obtain isolongifolene from longifolene using montmorillonite clay K10 at 120°C. they get 100% selectivity and 90% conversion.

But draw back is that natural clay have lot of impurities and difficult to reproduce with the requisite surface acidity, and thermal stability of clay is low and deactivated with use[7]

5. Wang, Hui, et al., Wherein the isolation and identification of isolongifolene along with other products from the volatile oil in the stems and leaves of pawns ginseng have been reported but this process is time consuming and it cannot meet the demand of the large production.[8]

6. Beena Tyagi et al., have studied the solvent free isomerisation of longifolene with nano-crystalline sulphated zirconia (SZ) solid acid catalyst and obtained 95-97% conversion of longifolene and 100% selectivity of isolongifolene at 180°C within 15-30 minutes under stirred batch reactor.

It is noteworthy that SZ exhibited similar catalytic activity over a wide range of Longifolene to SZ weight ratio, i.e., 10:1 to 100:1.[9]

## 2.2 SOLID ACID CATALYST

Solid-acid catalysts are generally categorized by their Brønsted and/or Lewis acidity, the strength and number of these sites, and the morphology of the support (e.g., surface area, pore size).

The synthesis of pure Brønsted and pure Lewis acid catalysts attracts a great degree of academic interest, although the latter is harder to achieve because Brønsted acidity often arises from Lewis acid-base complexation. Acid catalysts are widely used in chemical industry.

They are either 'Bronsted acids' or 'Lewis acids'. Bronsted acids owe their acidic character to protons. Lewis acids are usually metal salts like aluminium chloride, ferric chloride, antimony fluoride, titanium chloride and tin chloride.

The isomerization process right now is using Pt-promoted Al<sub>2</sub>O<sub>3</sub> catalyst and the process requires continuous addition of chlorine, which is toxic and corrosive, therefore new catalysts are required to be developed in order to have environmentally safe and highly activity catalysts such as (SZ)sulfated Zirconia, (WZ) Tungsted Zirconia.[24]

Heterogeneous catalysts offer several intrinsic advantages over their homogeneous counterparts: ease of product separation and catalyst reuse; and process advantages through reactor operation in continuous flow versus batch configuration.

However, to maintain economic viability, a suitable heterogeneous system must not only minimize the production of waste, but should also exhibit activities and selectivities comparable or superior to the existing homogeneous route.[12][13]

## 2.3 VARIOUS KINDS OF SOLID ACID CATALYSTS

- **Clay Minerals**

Clays were the first solid acid catalysts used in organic synthesis. However, due to their wide variety they lack perfect reproducibility in yields with different samples. Otherwise, they have considerable potential as environmental friendly solid acid catalysts. Some of the types of clays frequently used are Bentonite, Montmorillonite K10 and Montmorillonite-KSF.[12][13]

- **Zeolites**

Zeolites are also known as molecular sieves. They have a tetrahedral structure with each atom of silicon and aluminium surrounded by oxygen atoms.

In natural samples, they have three-dimensional crystalline microporous channels in which molecules of appropriate size can diffuse and react. The pore size in zeolites can be controlled using synthetic methods.[12][13]

- **Synthetic Resins**

Resins are supports made of synthetic polymers like polystyrene or co-polymers of polystyrene and divinylbenzene. They are used very often in the form of beads of various sizes. The beads may be micro-porous (pore size  $< 20 \text{ \AA}$ ), meso-porous (pore size  $20\text{--}100 \text{ \AA}$ ) or macro-porous (pore size  $> 100 \text{ \AA}$ ) or non-porous.

The diameters of the spherical beads decide the surface area. If the bead is also porous then this contributes to enhancement of surface area.[12][13]

- **Amorphous Silicas and Aluminas**

Silica and alumina constitute a group of polymeric oxides of silicon and aluminium respectively. They can also be obtained in mixed polymeric forms.[12,13]

- **Metal Oxides**

Oxides like zirconia, titania, magnesia as well as mixed oxides are also used. The physical structures of all these oxides consist of pores in which adsorption and catalysis takes place.

The extent of their usefulness is dependent on particle size, surface area, pore structure and acidity.[13]

## 2.4 AIMS OF THE PROPOSAL

The present study includes the upscaling of the isomerisation of longifolene in continuous flow reactor over SZ (Sulfated Zirconia)catalyst with following aims.

The up scaling of the process for the said reaction will be carried out in continuous flow reactor:

- Design and modification of existing continuous flow reactor will be carried out.
- Different forms of the catalyst such as beads, granules and powder will be studied using different binders and their effect on the activity and life of the catalyst.
- Various reaction parameters such as temperature, time and substrate to catalyst weight ratio will be optimized to achieve maximum conversion and selective formation of the product from lab scale to large scale.



# Chapter 3

## EXPERIMENTAL STUDY

### 3.1 DISTILLATION OF THE LONGIFOLENE:

Distillation Of Longifolene done under applying the vacuum, in which the substance boils lower than the its boiling point, Alpha-Pinene was found as main impurity in crude longifolene which was removed due to its lower boiling point (155 °C ).

Distillation of longifolene carried out in simple lab vacuum distillation equipment arrangement,for this vacuum distillation apparatus needed are,

R.B Flask(Round Bottom)Flask,  
Condenser,  
Magnetic Stirrer,  
Oil Bath, Ice,  
and Vacuum Pump.

first, ensure the perfect arrangement of the distillation unit for this distillation and then take 25 ml. of longifolene in R.B Flask and then put it into the oil bath. Distillation done under the vacuum, so increase the temperature gradually,

so first set the temperature at 80 °C with magnetic stirring at 400 rpm. then apply the complete vacuum wait for 20 - 25 minutes and and carefully observe the condition of distillation.

During the first 20 min. no distillate(impurity alpha pinene) come out from the condenser. so now increase the oil bath temp upto 120°C, and observe carefully the condition of the distillation.

so after the 15 min at 120 °C ,first drop from the condenser seen and after this the distillate (alpha pinene) comes continuously for 20 min.from this way, distillation of the longifolene done and alpha pinene separated from the longifolene.



Figure 3.1: Distillation Arrangement Of Longifolene

Purity of the longifolene from the GC-MS result(area%),

- 1.Before distillation (crude longifolene) = 84.94 %
- 2.After the distillation = 92.49 %

## 3.2 CATALYST PREPARATION

### 3.2.1 Catalyst Preparation Method.[10]

Catalyst prepared by two step precipitation method.

#### Step:1

- Zirconium Oxychloride used as precursor.
- Diluted it with distilled water
- add liquor Ammonia drop wise till get PH around 9-10, then continuous stirring for 3 hr.
- Precipitate separated, washing,drying for 12 hr.
- After drying,crush it and convert into the powdered from.

#### Step:2

- After converting into powdered form diluted it with sulfating agent such as sulfuric acid.
- stirring for 30 min.
- washing, drying, crushing into fine powder.
- Calcinations for 4 hr at 600°C.

### 3.3 CATALYTIC ISOMERISATION OF LONGIFOLENE

The Catalytic Isomerisation Of Longifolene was Carried Out In stirred Batch Reactor & fixed bed reactor.

#### 3.3.1 Stirred Batch Reactor Reaction

Typically in the Experiments ionic liquid and dry 1-octene and a magnetic stirring bar were placed in a 100 ml round bottom flask. 1-octene and catalyst (Ionic Liquid) are mixed in to the glove box in absence of oxygen.

Initially, the catalytic isomerisation of longifolene was carried out in stirred batch reactor to check the re-productibility of the previous report.[10]

Typically, a 50 ml Round Bottom Flask (RBF) equipped with a water condenser is kept in a constant temperature oil bath in which temperature was maintained within  $\pm 1$  °C.

Longifolene along with the catalyst (preactivated at 450 °C for 2 h) were added to the flask. The reaction was carried out at atmosphere pressure under stirring at around 500 rpm using a magnetic stirrer.



Figure 3.2: Batch Reactor (RBF) Reaction Arrangement

The product samples were drawn at regular intervals and analyzed with a GC-MS.[10][11] The conversion and selectivity were calculated as follows:

$$\text{Conversion (wt\%)} = 100 * [\text{Initial wt\%} - \text{Final wt\%}] / [\text{Initial wt\%}]$$

**Selectivity of iso-longifolene** =  $100 * [\text{GC peak area\% of iso-longifolene}] / [\text{Total peak area for all the products}]$

### 3.3.2 Fixed Bed Reactor Reaction

Liquid phase longifolene isomerization to iso-longifolene was studied in a fixed bed reactor.

The catalyst sample was packed in a glass reactor with desire catalyst bed arrangement and in situ activated at 450 °C for 2 h under air.

Catalyst bed temperature was brought down to reaction temperature and longifolene was delivered by syringe pump injector with a desire flow rate under air.

Product samples were collected and analyzed with GS-MS.[3,11,14,15,16][3][11][14][15][16][19][20][21][22]



Figure 3.3: Fixed Bed Reactor Arrangement

#### Reaction:-

Longifolene  $\rightarrow$  180 °C (catalyst- sulphated zirconia)  $\rightarrow$  Iso- longifolene (isomerization)

Experiments carried out in fixed bed reactor with different operating condition such as,

- Change in the shape (pellet, extrudate) of the catalyst in which the catalyst bind with the different binders,
- Flowrate variation,
- Different types of bed arrangements.
- Amount of catalyst loading

**Fixed Bed Glass Reactor :**

- Height - 28 cm
- Inner Diameter - 1.5 cm.
- Outer Diameter - 1.7 cm



Figure 3.4: Glass Fixed Bed Reactor

Various Catalyst Shape Used In Fixed Bed Reactor Reaction :-

Figure 3.5: Extrudate & Tablet/Pellet Shape



Figure 3.6: Pellet & Flakes Shape



# Chapter 4

## RESULT AND DISCUSSION

### 4.1 Stirred Batch & Fixed Bed Reactor Reactions Conditions And Results

#### Stirred Batch Reactor Reaction Condition & Results

Table 4.1: Stirred Batch Reactor Reaction Condition & Results

Exp. No	Long. (gm)	Cat. (gm)	Temp (°C)	Time (min)	Long. Peak	Long. Area	Iso-Long. Peak	Iso-Long. Area	Conv. (%)	Selec. (%)
	Distl. Longi				12.740	92.49				
1.	3	0.04	180	60	12.593	1.24	12.421	84.04	98.66	85.09
2.	6	0.06	180	15	12.559	3.91	12.349	86.67	95.77	90.02
				30	12.596	1.92	12.415	84.25	97.92	85.90
				50	12.557	2.29	12.435	70.99	97.52	72.65
3.	4	0.4	180	30	12.386	9.20	12.255	64.89	90.05	71.46
				60	12.385	9.30	12.249	58.46	89.94	64.45

**Fixed Bed Reactor Reaction Condition & Results:-**

Table 4.2: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi. (ml)	Catalyst	Flow Rate (ml/hr) & Temp (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-Longi.	Iso-Long.	Conv (%)	Selec (%)
				Distill. Longi.	12.719	92.49				
4.	4 Longi	0.3 gm (pwd.)	3 & 180	With Catalyst only	12.721	87.49	12.334	3.74	5.41	29.90
5.	3 Longi	0.3 gm (pwd.)	3 & 180	Cat. + Helical Rings	12.734	59.65	12.416	27.91	35.51	69.17
10.	3 Longi	SZ-0.04 gm + KBr-0.4 gm	3 & 180	Pellet + Glass Bead	12.610	80.26	12.262	3.77	5.5	19.09
11.	3 Longi	SZ-0.3 gm + KBr-0.2 gm	30 & 180	Pellet + Glass Bead	12.663	79.78	12.272	4.32	6.07	21.36
12.	6 Longi	SZ 2.75gm, Bent. Clay 0.275 gm, 1.51gm Extru	60 & 180	Extru Cat.	12.671	71.70	12.272	8.22	15.59	29.04
13.	6 Longi	1 gm. Extru (Bent. Clay)	60 & 100	Extru. Cat. (13.1)	12.588	61.27	12.373	16.48	27.86	42.55
				(13.2)	12.583	63.40	12.266	13.77	25.35	37.62
15.	5 Longi	0.51 gm Extu. (Bent. Clay)	30 & 100	Cat. + Glass Bead	12.664	73.76	12.252	4.27	13.16	15.97

Table 4.3: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	Conv. (%)	Selec. (%)
16.	3ml Long. + 3ml Tol.	0.53 gm Extu. (kaolin clay)	21 & 100	Cat. + Glass Bead	12.654	68.96	12.202	4.87	18.81	15.67
17.	3ml Long. + 3ml Tol.	0.52 gm Extru. (kaolin clay)	21 & 100	Cat. + Glass Bead	12.531	80.71	12.186	4.67	4.97	24.21
18.	3ml Long. + 3ml Tol.	0.51 gm Extu. (kaolin clay)	21 & 100	Cat. + Glass Bead	12.771	62.18	12.231	8.61	26.79	22.76
19.	3ml Long. + 3ml Tol.	0.52 gm Extu. (kaolin clay)	15 & 100	Cat. + Glass Bead	12.752	58.21	12.270	12.19	31.45	29.17
20.	3ml Long. + 3ml Tol.	1 gm Extru. (kaolin clay)	21 & 100	Cat. + Glass Bead	12.813	57.91	12.242	10.08	31.82	23.95
22.	3ml Long. + 3ml Tol.	1 gm Extru. (kaolin clay)	21 & 100	Cat. + Glass Bead	12.704	61.32	12.212	9.74	27.81	25.18
23	3ml Long. + 3ml Tol	1 gm Extru (kaolin clay)	6 & 100	Cat. + Glass Bead	12.713	18.54	12.217	3.27	78.17	4.01

Table 4.4: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi. Peak	Iso-longi. Area	Conv. (%)	Selec. (%)
26	3ml Long. + 3ml Tol	1 gm Extru (kaolin clay)	3 & 100	Cat. + Glass Bead	12.696	57.44	12.226	13.39	32.38	31.46
27	3ml Long. + 3ml Tol	1 gm Extru (kaolin clay)	3 & 100	Cat. + Glass Bead	12.813	50.25	12.265	18.25	40.84	36.68
28	6ml long.	1 gm Extru (kaolin clay)	3 & 100	Cat. + Glass Bead	12.927	35.16	12.266	8.58	58.61	13.23
29	6ml Long.	1 gm Extru (kaolin clay)	2.5 & 180	Cat. + Glass Bead	12.696	57.48	12.297	20.07	32.33	47.20
30	6ml Long.	0.56 gm (kaolin clay) Cat.pellet flakes.	2.5 & 180	Cat. + Glass Bead	12.597	55.49	12.243	21.16	34.67	47.54
31	6ml long.	2 gm Extru. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	12.621	58.79	12.239	18.05	30.1	43.8
32	3ml Long. + 3ml Tol	1 gm Extru. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	12.619	67.68	12.206	10.22	20.32	31.62

Table 4.5: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi.	Catalyst	flow Rate (ml/hr) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	conv. (%)	Selec. (%)
31	6ml long.	2 gm Extr. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	12.621	58.79	12.239	18.05	30.1	43.8
32	3ml Long. + 3ml Tol	1 gm Extr. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	12.619	67.68	12.206	10.22	20.32	31.62
33	3ml long. + 3ml Tol	2 gm Extr. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.994	39.30	17.625	13.37	46.48	22.00
34	6ml long	2 gm Extr. (kaolin clay)	2.5 & 190	Cat. + Glass Bead	17.948	55.39	17.620	30.55	24.56	68.48
35	6ml Long	1 gm Extr. (kaolin clay)	3 & 140	Cat. + Glass Bead	18.032	53.87	17.702	25.01	26.6	54.21
36	6ml Long	1 gm Extr. (kaolin clay)	3 & 130	Cat. + Glass Bead	18.062	12.50	17.725	7.64	82.97	8.73
37	6ml Long.	1 gm Extr. (kaolin clay)	3 & 150	Cat. + Glass Bead	18.069	41.58	17.734	24.91	43.37	42.63
38	6ml Long.	1 gm Extr. (kaolin clay)	3 & 160	Cat. + Glass Bead	18.111	44.94	17.772	27.98	38.79	50.82
39	6ml Long.	1 gm Extr. (kaolin clay)	3 & 170	Cat. + Glass Bead	18.097	47.76	17.765	24.84	34.96	47.05
40	6ml Long.	1 gm Extr. (kaolin clay)	3 & 200	Cat. + Glass Bead	18.103	44.96	17.769	28.02	38.77	50.9

Table 4.6: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	Conv. (%)	Selec. (%)
33	3ml long. + 3ml Tol	2 gm Extru. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.994	39.30	17.625	13.37	46.48	22.00
34	6ml long	2 gm Extru. (kaolin clay)	2.5 & 190	Cat. + Glass Bead	17.948	55.39	17.620	30.55	24.56	68.48
35	6ml Long	1 gm Extru. (kaolin clay)	3 & 140	Cat. + Glass Bead	18.032	53.87	17.702	25.01	26.6	54.21
36	6ml Long	1 gm Extru. (kaolin clay)	3 & 130	Cat. + Glass Bead	18.062	12.50	17.725	7.64	82.97	8.73
37	6ml Long.	1 gm Extru. (kaolin clay)	3 & 150	Cat. + Glass Bead	18.069	41.58	17.734	24.91	43.37	42.63
38	6ml Long.	1 gm Extru. (kaolin clay)	3 & 160	Cat. + Glass Bead	18.111	44.94	17.772	27.98	38.79	50.82
39	6ml Long.	1 gm Extru. (kaolin clay)	3 & 170	Cat. + Glass Bead	18.097	47.76	17.765	24.84	34.96	47.05

Table 4.7: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	Conv. (%)	Selec. (%)
40	6ml Long.	1 gm Extruded (kaolin clay)	3 & 200	Cat. + Glass Bead	18.103	44.96	17.769	28.02	38.77	50.9
41	6ml Long.	1 gm Extruded (kaolin clay)	3 & 220	Cat. + Glass Bead	18.108	29.96	17.766	28.08	59.19	40.1
42	6ml Long.	1 gm Sphere Shape Cat (kaolin clay).	2.5 & 170	Cat. + Glass Bead	17.802	44.26	17.489	21.24	39.72	38.10
43	6ml Long.	1 gm Sphere Shape Cat. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.815	61.14	17.485	9.57	16.74	24.63
44	6ml Long.	0.5 gm Sphere Shape Cat (kaolin clay).	2.5 & 180	Cat. + Glass Bead	18.055	79.89	17.616	6.23	8.79	30.97
45	6ml Long.	2 gm Sphere (kaolin clay)	2.5 & 180	Cat.+ Glass Bead	18.018	64.03	17.679	24.89	12.8	69.19
46	6ml Long.	1.5 gm Sphere (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.930	59.18	17.574	9.74	19.4	23.86

Table 4.8: Fixed Bed Reactor Reaction Condition &amp; Results

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	Conv. (%)	Selec. (%)
47	6ml Long.	0.75 gm. Sphere (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.942	65.87	17.573	7.74	10.3	22.68
48	6ml Long.	0.44 gm. Sphere (kaolin clay)	2.5 & 220	Cat. + Glass Bead	17.812	61.46	17.482	9.53	16.3	24.73
49	6ml Long.	1 gm. Sphere (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.880	5.11	17.617	31.28	93.04	32.96
50	6ml Long.	1 gm. Pellet (kaolin clay) flakes	2.5 & 180	Cat. + Glass Bead	17.814	51.02	17.497	17.32	30.52	35.36



**From the GC-MS (Gas Chromatography and Mass Spectroscopy) results,****1. In Batch Reactor**

Experiment 1 to 3 done with, pure longifolene, different amount of catalyst loading (catalyst to longifolene ratio varying from 1:10 to 1:100), at same temperature 180°C and sample collected at different time intervals, in stirred batch reactor.

The GC-MS result shows, almost 99% conversion of longifolene and upto 90 % selectivity of iso-longifolene achieved within very short time 15 - 20 minutes and with very less catalyst loading (catalyst to longifolene ratio 1:100)

**2. In Fixed Bed Reactor**

Conclusion based on, changing the the parameters such as binder effect, reaction done with solvent or without solvent, flow rate variation and bed arrangement.

By changing the various experiment conditions such as Amount of catalyst loading, catalyst shape (pellet and extrudate), catalyst bed arrangements, flow rates variation, reaction done with solvent or without solvent, various types of binders (to make various shape of catalyst such as pellet and extrudate).

we get the different conversion and selectivity. main task is that to optimize the proper condition at which we can get maximum conversion and selectivity.

so by changing various experiment condition we got the different results. when reaction done with powder catalyst (sulfated zirconia) only (without any binder or packing such as glass beads or helical glass ring )

shows the only 5% conversion and 30 % selectivity at 180 °C, but main problem in this reaction is that catalyst clog in the glass reactor and difficult to remove from it, and catalyst color also becomes change from white to brownish black.

**Effect of various parameters:-****Binder & Solvent Effect:**

So due to this we have to bind catalyst with different binders, such as potassium bromide and different types of clays. when reaction done by making catalyst pellet (KBr + catalyst ) with varying composition of

KBr to catalyst , results show very low conversion and selectivity.( experiment-10,11)

Reaction done with extrudate shape catalyst, making by using Bentonite clay as a binder (binder to catalyst ratio 1:10),result shows very less conversion 15 % and selectivity 29 %,but in this reaction shows

that after the reaction the catalyst burns out totally and its becomes black. (experiment-12,13,15)

When reaction done with the solvent for the proper distribution of longifolene over the catalyst, using the extrudate catalyst making with the bentonite clay, result shows the conversion(28%)

and selectivity(42%) increase slightly then the without solvent.(experiment-12,13,15)

**Catalyst Bed Arrangement, Flow Rate And Catalyst Loading Effect:**

When the reaction done with the extrudate shape catalyst made with kaolin clay used as binder, but varying the catalyst bed size, flow rate and amount of catalyst loading.

First comparison with the experiments in which the catalyst loading , flow rate, feed amount(longifolene + toluene) and reaction temperature (100° C)are same .

Such as 0.5 gm catalyst, 21 ml/hr flow rate,3 ml longi + 3 ml toluene. but varying in the height of the bed (glass beds + catalyst) from 6 cm,7cm,8 cm.,

The result not perfectly shows the increase or decrease in conversion and selectivity when we increase the height of the bed.(experiment 16,17,18).

Now comparison with the experiments(experiment 20,22) in which the only amount catalyst loading varying from 0.5 gm to 1.0 gm, and all other condition are same as mention earlier,

Such as 21 ml/hr flow rate,3 ml longi. + 3 ml toluene ,reaction temperature (100°C). the result shows that the conversion and selectivity very slightly increase as compare with the experiment 16,17,18.

When varying in the flow rate such as 3 ml/hr instead of 21 ml/hr with the all condition are same shows that the by decreasing the flow rate , the conversion and selectivity are increase,

This because of contact time is more with the catalyst.(experiment 24,25,26,27 compare with experiment 16,17,18.)

**Temperature Variation Effect:**

Table 4.9: Temperature Variation Effect

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	Conv. (%)	Selec. (%)
35	6ml Long	1 gm Extru. (kaolin clay)	3 & 140	Cat. + Glass Bead	18.032	53.87	17.702	25.01	26.6	54.21
36	6ml Long	1 gm Extru. (kaolin clay)	3 & 130	Cat. + Glass Bead	18.062	12.50	17.725	7.64	82.97	8.73
37	6ml Long.	1 gm Extru. (kaolin clay)	3 & 150	Cat. + Glass Bead	18.069	41.58	17.734	24.91	43.37	42.63
38	6ml Long.	1 gm Extru. (kaolin clay)	3 & 160	Cat. + Glass Bead	18.111	44.94	17.772	27.98	38.79	50.82
39	6ml Long.	1 gm Extru. (kaolin clay)	3 & 170	Cat. + Glass Bead	18.097	47.76	17.765	24.84	34.96	47.05
40	6ml Long.	1 gm Extru. (kaolin clay)	3 & 200	Cat. + Glass Bead	18.103	44.96	17.769	28.02	38.77	50.9
41	6ml Long.	1 gm Extru. (kaolin clay)	3 & 220	Cat. + Glass Bead	18.108	29.96	17.766	28.08	59.19	40.1

Experiment no.36,35,37,38,39,40,41 done with different temperature variation from 130°C to 140,150,160,170,200,220 °C.

The other parameters are same such as,  
catalyst amount :- 1 gm (extudate) ,  
flow rate :- 2.5 ml/hr ,

Bed Arrangement :- catalyst filled in-between the two layers of glass beads.

from the GC-MS results ,

shows that by increasing the temperature, at 130°C we get the maximum conversion 82.97%, but the selectivity very less only 8.73%.

**Catalyst shape and loading effect:**

catalyst shape :- sphere(bind with the kaolin clay)

experiment no.44,47,43,46,45, done with the different amount of catalyst loading (0.5gm,0.75gm,1gm,1.5 gm,2 gm)

in sphere shape catalyst bind with the kaolin clay.

In these experiments all other parameters are same such as,

flow rate :- 2.5 ml/hr

temp:- 180 °C

Bed Arrangement :- catalyst filled in-between the layer of glass beads.

**Table 4.10: Catalyst Shape & Loading Effect**

Ex. No	Longi.	Catalyst	Flow Rate (ml) & Temp. (°C)	Bed Arrang.	Longi. Peak	Longi. Area	Iso-longi Peak	Iso-longi Area	Conv. (%)	Selec. (%)
43	6ml Long.	1 gm Sphere Shape Cat. (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.815	61.14	17.485	9.57	16.74	24.63
44	6ml Long.	0.5 gm Sphere Shape Cat(kaolin clay).	2.5 & 180	Cat. + Glass Bead	18.055	79.89	17.616	6.23	8.79	30.97
45	6ml Long.	2 gm Sphere(kaolin& clay)	2.5 & 180	Cat.+ Glass Bead	18.018	64.03	17.679	24.89	12.8	69.19
46	6ml Long.	1.5 gm Sphere (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.930	59.18	17.574	9.74	19.4	23.86
47	6ml Long.	0.75 gm. Sphere (kaolin clay)	2.5 & 180	Cat. + Glass Bead	17.942	65.87	17.573	7.74	10.3	22.68

from the GC-MS results , shows that by increasing the catalyst loading from 0.5,0.75,1,1.5 to 2 gm, the conversion and selectivity increases.

# Chapter 5

## CONCLUSION

We conclude that the by variation of parameter such as, solvent effect, flow rate variation effect, temperature and bed arrangement effect, results are varying and results are not reproducible .

so,in future work we have to optimize the all parameter such as temperature, solvent ,bed arrangement, Amount of catalyst loading, flow rate to get the maximum conversion and selectivity.

so finally, we conclude that the increase the catalyst amount, the conversion and selectivity both increases, and the variation in the temperature shows, the variation in the results of conversion and selectivity.

so further work is to find the best combination of parameters such as temperature, flow rates, catalyst loading ,bed arrangements which gives us maximum conversion and selectivity.

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# Appendix I

## RESULT OF GC ANALYSIS:-

Figure 5.1: GC Analysis of Longifolene Before Distillation

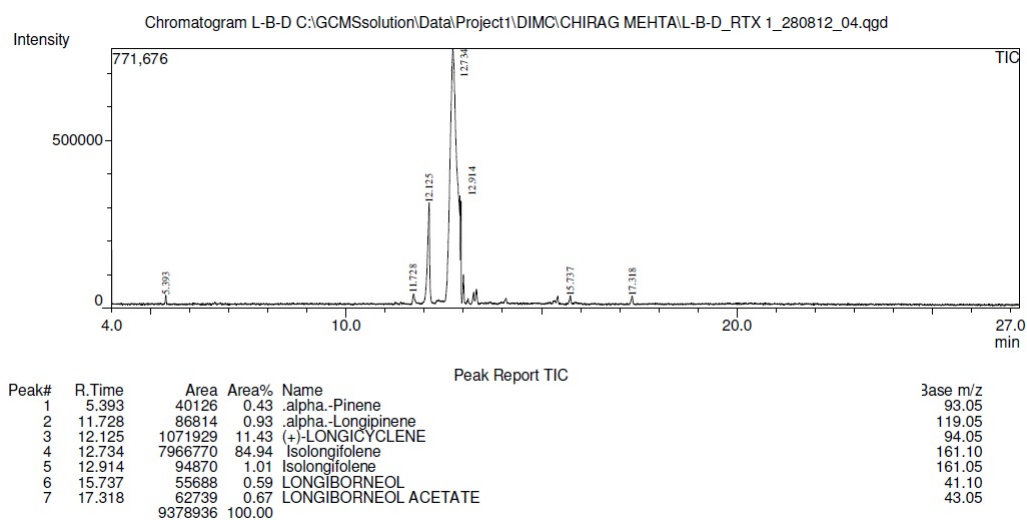


Figure 5.2: GC Analysis of Longifolene after Distillation

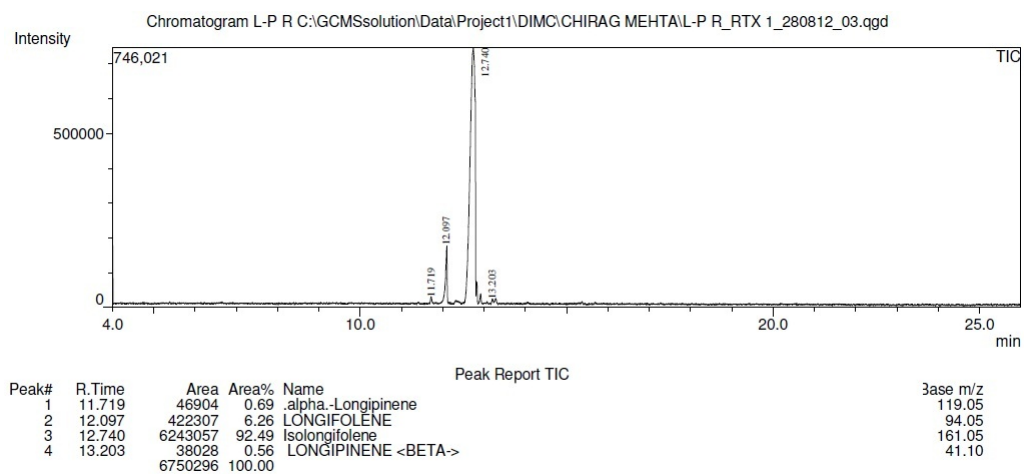




Figure 5.3: GC Analysis of Experiment -5(Fixed Bed Reactor)

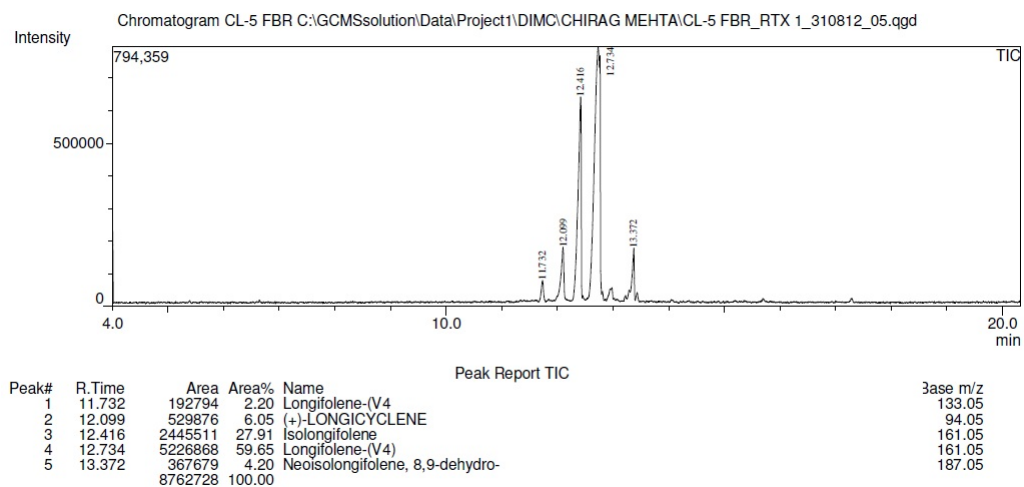


Figure 5.4: GC Analysis of Experiment -1 (Batch Reactor)

