

**SYNTHESIS OF BIS-(P-CHLORO) BENZYL
SULFIDE USING HYDROGEN SULPHIDE AND
TBMAC POLYMER BOUND AS PHASE
TRANSFER CATALYST**

ANIMESH

**Synthesis of Bis-(p-Chlorobenzyl) Sulphide using H₂S and
TBMAC Polymer bound as Phase Transfer Catalyst**

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CERTIFICATE

This is to certify that the thesis entitled “**Synthesis of Bis-(p-Chlorobenzyl) Sulfide using H₂S and TBMAC Polymer bound as Phase Transfer Catalyst**” submitted by **Animesh (111CH0501)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology Degree in Chemical Engineering Session 2011-2015 at National Institute of Technology, Rourkela. This is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the report is his bona fide work.

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ANIMESH

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Effect of Chloro Benzyl Chloride concentration
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List of Abbreviations

CBC	Chloro Benzyl Chloride
CBM	Chloro Benzyl Mercaptan
DCBS	Dichlorobenzyl Sulphide
DEA	Diethanolamine
GLC	Gas Liquid Chromatography
MDEA	Methyl Diethanolamine
MEA	Mono Ethanolamine
PTC	Phase Transfer Catalyst
TBAB	Tetra Butyl Ammonium Bromide
PTC	Phase Transfer Catalyst

Abstract

The aim of this project is the utilization of Hydrogen Sulphide (H_2S) in the synthesis of Dichlorobenzylsulfide (DCBS) and Chloro Benzyl Mercaptan (CBM). This is done by the absorption of H_2S in methyl Diethanolamine first and then reaction of this H_2S rich methyl Diethanolamine with ChloroBenzyl Chloride for the formation of DBCS and CBM. The reaction of methyl Diethanolamine and Chloro Benzyl Chloride is very difficult as they are two different phases, So the phase transfer catalyst has been used to carry out this reaction. The TBMAC Polymer bound has been chosen as the PTC as it is solid and reusable. The overall objective of this project is to maximize the conversion of Chloro Benzyl Chloride and maximize the selectivity of DBCS. In this project Chloro Benzyl Chloride has been used along with Toluene as a solvent. It also includes study about sources of hydrogen sulfide, need for removal, recovery and PTC study. Parameters chosen for maximizing conversion and selectivity are Reaction time, catalyst loading, stirring speed, temperature and Chloro Benzyl Chloride concentration

Keywords: Hydrogen sulphide; Dichloro benzyl Sulphide; Phase Transfer Catalyst ;TB MAC polymer bound; conversion; selectivity

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CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

ABSTRACT

This project describes an expansive overview of the present research and its essentialness. It describes the sources of hydrogen sulphide, need to clean it off and recovery. It likewise describes the usual techniques utilized as a part of the industrial operations, the aim of this study and gives a record of the association and structure of this thesis.

1.1 SOURCES OF HYDROGEN SULPHIDE

A part of Hydrogen Sulfide outflow is due to human activities. Various processes being carried on by the petroleum and coal industries result to the creation of vaporous byproducts with H₂S inside it. Hydro desulfurization is a useful process used in commercial ventures to make regular gas free from sulfur. Other major contributor for Hydrogen Sulfide is petroleum refinery. Environmentalists have put pressure on the refineries to check the sulfur level and put it under the safe levels. Other major business which emits a large amount of hydrogen sulfide and ammonia is coal treatment plant. Coal preparation emanates a large amount of undesired gas. Hydro treatment of some important crude further produces colossal segment of these undesired gases. During hydro treatment of heavy and sour crude, large quantities of H₂S and ammonia are produced. Other major sources of hydrogen sulfide are paper mills, coke ovens and tanneries.

1.4 NEED FOR TREATMENT OF HYDROGEN SULPHIDE LADEN GASES

With the growing number of problems cause by the hazardous gas on the environment, pressure has been put on the chemical industries to dump the poisonous product in a safe and green method. Hydrogen sulfide causes a great amount of harm to both environment and social health and must be treated before releasing to the outer world The major need for the treatment of Hydrogen

sulfide laden gases and removal of hydrogen sulfide from any given fluid Streams is because of the reasons stated below:

- H_2S is a very poisonous and explosive gas (4.3%-4.6% explosive limits). It is heavier than air, so it accumulates at the base of any space which does not have a proper ventilation. Its odor is hard to smell, so if out in open, the person cannot sense it despite of being harmed by this extremely pungent gas.
- Hydrogen sulfide is a very toxic, destructive and odiferous gas. Its presence in gas stream must be minimized before transportation. H_2S is corrosive in the presence of water, therefore it must be completely removed before transport.
- If refinery gas with hydrogen sulfide is used in the operation, it can spoil many processing steps, for example, corrosion of equipment, catalyst deactivation, unwanted side reactions and so forth..

1.2 INDUSTRIAL METHOD FOR THE TREATMENT OF HYDROGEN SULFIDE

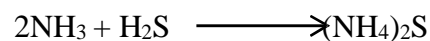
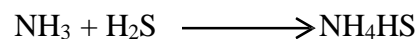
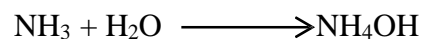
There is an urgent requirement for the chemical industries need to bring down the hydrogen sulfide discharge beneath the safety level with a specific end goal to guarantee environmental wellbeing and sound health of their workers . Many industrial methods have been devised for the removal and recovery of hydrogen sulfide. Industries remove H_2S by the virtue of its acidic nature and recovery by using alkaline solution. A Strong alkaline solution like sodium hydroxide, however, forms irreversible chemical reactions products and henceforth could not be used for the removal of H_2S

from the gas streams most notably if both H₂S and CO₂ is present in the gas stream where the CO₂ concentration exceeds 4% (Robin, 1999). In this way, weak alkaline solutions are used in the treatment of hydrogen sulfide.

1.2.1 AMMONIA BASED PROCESS

Using aqueous ammonia for the removal of H₂S had been very much used (Hamblin, 1973 and Harvey and Makrides,1980) .The major process used in this operation is :

A scrubber of hydrogen sulfide and ammonia is put in series through which the gas stream is passed. This gas stream contains both the gas which is H₂S and NH₃. Stripped water is injected in ammonia scrubber from top where ammonia which is present in the gas is absorbed from it. The following NH₃ solution is used as absorbent for scrubbing hydrogen sulfide. The rich solution which we get through the unit is ammonium sulfide. Then deacidifier decomposes this solution to create H₂S and ammonia rich liquor. Reaction occurring during the process is shown by:



Major benefits with ammonia based processes over the ammine processes (kohl & Nielsen,1997):

- Process using ammonia is ideally suitable for the gas stream containing both hydrogen sulfide and ammonia. Moreover, the elimination of NH₃ and H₂S is done in single step while in two stage in the other process.

- Absorption rate of hydrogen sulfide into aqueous ammonia solution is rapid and depend on the concentration of ammonia. Hence, on sufficient interface NH_3 concentration, it is thus possible that the gas film resistance decides rate of absorption of hydrogen sulfide.

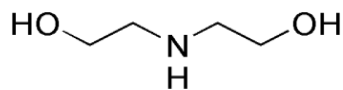
The operational challenges associated with the ammonia based processes has limited its uses as system for removing H_2S . A portion of the major disadvantages of this method (Hamblin, 1973) are:

- NH_3 has high partial pressure. So a dilute ammonia solutions is to be used for the scrubbing step. High temperature is required for the use of dilute solution. This increases the expense and makes the process costly.
- Another difficulty includes the catalyst used in the scrubbing step is soluble. So it reacts with the sulfur and makes it poisonous.
- Other problems are the recovery of the elemental sulfur from the regeneration step.

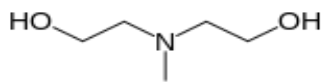
1.2.2 ALKANOLAMINE BASED PROCESS

Procedure of alkanolamine based process has got wide commercial acceptance because of its preference of low vapour pressure. It makes the operation more flexible in terms of operating temperature, pressure, and concentration.

Triethanolamine (TEA), was the firstly used in gas treatment plants (Bottoms, 1930). It was hugely successful. Amines that have been used for the gas purification are mono ethanol amine (MDEA), di ethanol amine (DEA) and methyldiethanol amine (MDEA). MDEA and DEA are not specific for H_2S in their response.



Diethanol amine(DEA)

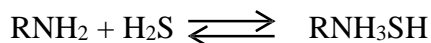
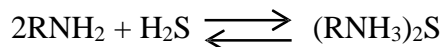


Methyldiethanol amine(MDEA)

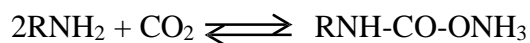
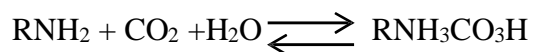
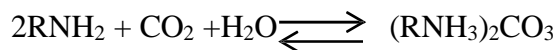
Fig 1.1: Structural formulas of alkanolamine

The alkanolamine has one hydroxyl group and one amine group. The hydroxyl group reduces the vapor-pressure and increase the water solubility. The amine group provides necessary alkalinity in water to absorb the acidic gases.

Reaction with H₂S:



Reaction with CO₂



SULPHUR RECOVERY FROM HYDROGEN SULPHIDE

1.4 CLAUS PROCESS

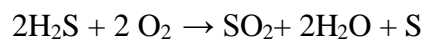
Hydrogen sulphide is obnoxious in nature. So it is first converted to nonpoisonous and useful elemental sulfur at its various origins. Scientist Carl Friedrich Claus first patented it in 1883 and since then this process has become an industrial standard. In this process, sulphur is recovered from the gaseous hydrogen sulphide found in raw natural gases and other by-product gases containing hydrogen sulphide. These by-product gases mainly originate from

physical and chemical gas treatment units.

DESCRIPTION OF CLAUS PROCESS

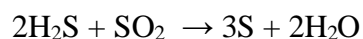
Hydrogen sulfide is isolated from the host gas utilizing amine extraction and then put forth in the Claus unit(Fig 1.3) followed by 2 steps:

1. Thermal Step:- H₂S laden gas reacts in a substoichiometric combustion with air..The temperature of around 1000-1400⁰C is attained in the reaction furnace where the reaction is done. Hydrogen sulfide is oxidized by the following reaction:



The reaction involves zero flame generating Sulphur Di Oxide.

2. Catalytic Step:- The reaction gases leaving the Sulphur condenser are heated again to 200-350 degree celcius .Then this is fed to a series of catalytic converter and sulphur condenser. Here hydrogen sulfide goes on to react with sulfur dioxide and elemental Sulphur is produce.The reaction goes on as follows:



Claus process has some drawbacks (Plummer, 1994 and Plummer and Beazley, 1986).Examples are:

- Operation temperature is very high.

- The important hydrogen energy is vanished in this procedure
- The Sulphur content of the tail gas released in the Claus process is very high.

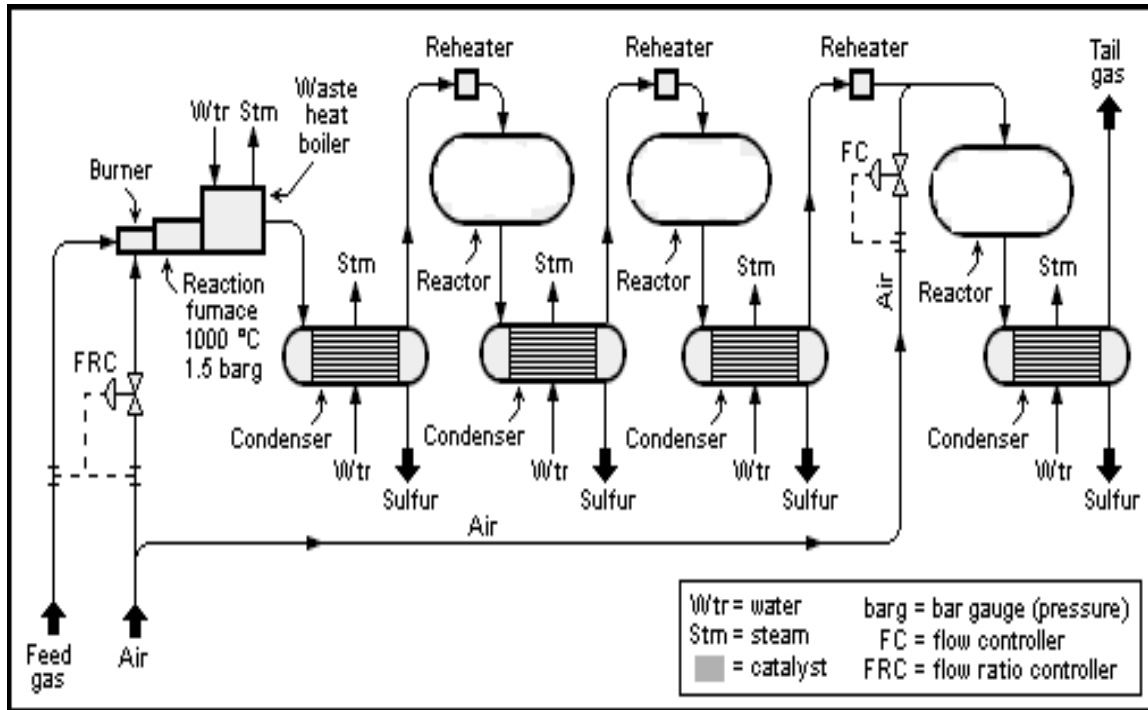


Fig 1.3: Process Flow diagram of Sulphur Recovery Unit

OTHER WAYS TO PROCESS SOUR GAS:

Amine extraction is not suitable for the treatment of some H₂S laden gas due to high CO₂ levels. Some of the techniques like CrystaSulf or ARI-LO-CAT is used there. A liquid solution containing oxidized iron is utilized as a part of lieu of air in such sort of techniques.

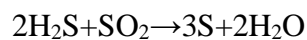
As an insignia of curiosity, H₂S Splitting Process is likewise being produced to make hydrogen and also sulfur from H₂S.

1.4.1 CRYSTA SULF

Cryta Sulf is a chemical process used to separate H₂S from natural gas, synthesis gas and gas

streams (Deptt. of Energy Report). H₂S is changed over into elemental sulfur through a fluid stage claus response and the sulfur accordingly got is then removed by filtration. This is used as an alternative to the Amine-Claus process.

In Crysta Sulf process includes the pumping of heavy liquid hydrocarbon through an absorber where the liquid interacts with H₂S rich gas streams. Next H₂S gets absorbed from the gas stream and the resultant clean gas stream then exits absorber. The H₂S stays in the liquid reacts with SO₂ to form elemental sulfur and water according to the following reactions:



1.4.2 WET OXIDATION LO-CAT PROCESS

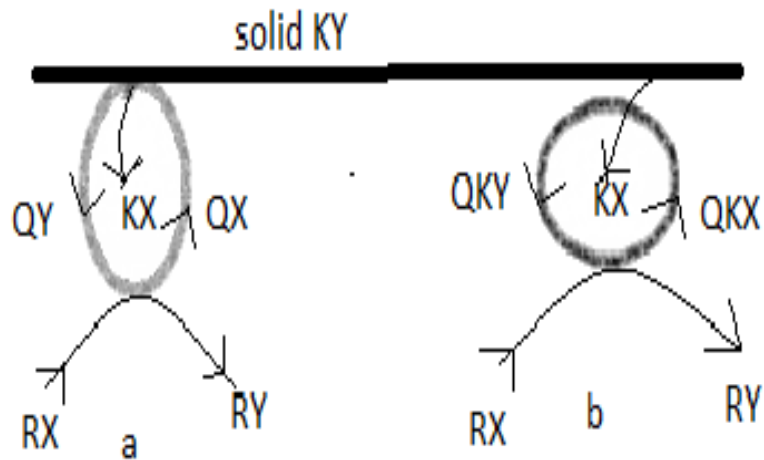
In the LO-CAT process, it involves the conversion of H₂S into elemental sulphur with the help of an iron catalyst taking into consideration the environmental issues. The iron catalyst wrapped by natural chelated agents in a mauled example is presented in an answer. The paw like style is gone for not permitting the precipitation of either iron sulfide or iron hydroxide. In this methodology, H₂S ingested in fluid LO-CAT arrangement is oxidized to create basic sulfur with the diminishment of iron particles from ferric to ferrous state. The diminished iron particles are exchanged from the absorber to the oxidizer which is the reoxidation area of ferrous iron to ferric iron with the assistance of climatic oxygen ingested into the LO-CAT arrangement subsequently, recovering the impetus.

1.5 PHASE TRANSFER CATALYSIS

PTC is widely used to speed up and enhance the strength of otherwise slow heterogeneous

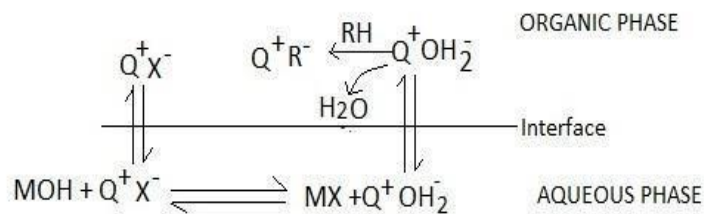
reactions with the help of an organic layer and an ionic reactant either in liquid- liquid phase or in solid state. PTC has certain merits such as simplicity, reduced consumption of raw materials, mild operating conditions and increased rate of reaction. These special attributes provide PTC a cutting edge and priority for the purpose of organic synthesis. Quaternary Ammonium salts are the most “to be opted” class of PTC owing to their quality of action and easy availability.

For the purpose of carrying out solid-liquid phase transfer catalysis, two mechanisms have been proposed. One among the two is suitable for conditions where the inorganic salt is considerably dissolvable in the given dissolvable and the impetus is not ready to contact the strong surface. The second system is utilitarian in circumstances where the inorganic salt is either insoluble or soluble in irrelevant extents in the natural dissolvable and the impetus can approach and respond with the strong surface specifically. This whole system is begat as homogeneous and heterogeneous solubilisation (Melville and Goddard). Increase in rate of responses in strong fluid stage because of little amount of watery stage is termed as omega stage. Scheme 1.1 is a pictorial delineation of the 2 mechanisms:

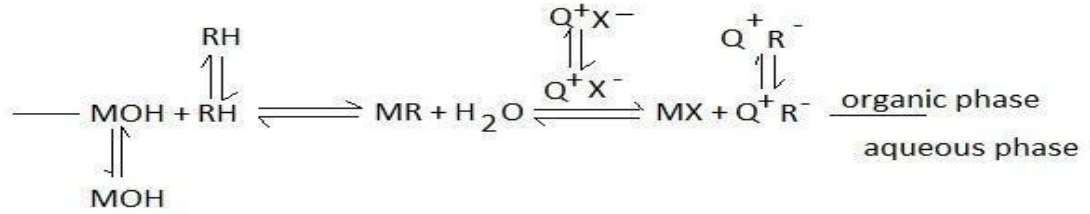


Scheme 1.1: Two distinct mechanisms for Solid-Liquid Phase Transfer catalysis

- a) Heterogeneous b) Homogeneous solubilization



Scheme 1.2: Schematic representation of Extraction mechanism.



Scheme 1.3: Schematic representation of Interfacial mechanism.

Solid phase transfer catalyst otherwise called Tri Phase Catalysts(TPC),offer Numerous favorable circumstances connected with heterogeneous impetuses, for example, effectively recouping and reusing of the impetus and the response can be done in nonstop reactor with consistently differentiating the impetus.

The strong impetus utilized as a part of this work is TBMAC polymer bound. It is a particle trade sap. The polymer lattice is polystyrene DVB(polystyrene crosslinked with di vinyl benzene).The practical gathering is $-\text{N}^+\text{R}_3$.The ionic structure is Cl^- .It seems yellow to brilliant yellow globules.

The absorbent utilized is methyldiethanol amine. It has got a plenty of advantages.

Some of them are listed below:

- MDEA is useful in absorbing H_2S from stream having both CO_2 and H_2S .
- MEA and DEA are more corrosive than MDEA.
- It saves more energy than MEA and DEA due to low desorption temperature and low heat of reaction.
- Low vapour pressure thus less volume of loss due to evaporation.

CHAPTER 2

LITERATURE REVIEW

CHAPTER-2

LITERATURE REVIEW

Abstract

This section describes the literature survey of the alkanolamine as H₂S gas absorbent. It shows various methods through which chlorobenzylchloride and dichlorobenzyl sulfide can be prepared.

2.1 USES OF AQUEOUS ALKANOLAMINES FOR REMOVAL OF H₂S

Kohl and Neilson,1997,showed the removal and recovery of hydrogen sulphide by the use of ammonium hydroxide. Process was also developed by Hamblin,1973 which was focused on sulphur recovery. Now a days various alkanolamine are in use for the removal of hydrogen sulphide from the gas stream.Lot of research work has been in operation to study the solubility of hydrogen sulphide and carbon dioxide. The experimental data of solubility has been mathematically represented (Austgen et al., 1989, Lee et al., 1976, Lawson and Garst, 1976, Vallée et al., 1999, Isaacs et al., 1980, Kaewsichan et al., 2001, Al-Baghli et al., 2001, Sidi-Boumedine et al., 2004, Weiland et al., 1993).

2.2 SYNTHESIS OF CHLORO BENZYL MERCAPTAN

Labat(1989) used BM in the synthesis of various herbicides.IT is used in the synthesis of long polypeptide benzylthio esters,odour in certain alcohols,tiocarbazil and others.

J.E.Bittell et al.(1978)developed an economically viable route for the synthesis of benzyl mercaptan.He reacted benzyl chloride with an alkaline sulfahydrate .The medium was alcoholic and nucleophilic substitution of chlorine takes place. W.S.Hoffman et al.(1923) synthesized Benzyl Mercaptan by saturating crystalline sodium sulfide with hydrogen sulfide. Then the

solution was reacted with ethyl alcohol and then hydrogen sulfide was used to resaturate this solution. Then benzyl chloride was added and the system was stored in cold for four days.

Anthony Loverde (1945) produced organic mercaptans by the reaction of corresponding chlorides with an alkali metal hydrosulfides. John L. Speiver (1975) synthesized Benzyl Mercaptan by forming a mixture of hydrogen sulfide and amine. Then this mixture was reacted with aliphatic chloride at a temperature range of 0-175 degree celcius. Polar solvent like methanol was used and reaction was carried out under autogenous pressure. Reaction time was around eighteen hours.

Labat (1989) reacted benzyl chloride and ammonium sulfahydrate to produce benzyl mercaptan. Reaction proceeded in two steps in a closed reactor under autogenously pressure. First, benzyl chloride was added to aqueous ammonium sulfahydrate solution. The temperature was maintained below 80 degree celcius. After this, mixture was heated in the range of 80-100 degree celcius.

2.3 SYNTHESIS OF DICHLOROBENZYL SULFIDE

Dichlorobenzyl Sulfide (DCBS) has a number of applications such as anti-corrosive agent for metals, additive lubricant, extraction of precious metals, reduce friction in motor oils (Pradhan and Sharma, 1990). DBS was prepared by Shriner et al (1930) by reacting aqueous solution of sodium sulfide with benzyl chloride. The reaction was performed in a steam bath and completed in around 3 days with a continuous stirring of the system.

Vronkov et al. (1969) reacted benzyl chloride by pouring it drop by drop to aqueous sodium sulfide solution. Temperature of the system was 60 degree celcius first and then 90 degree after the whole mixing. It took 4 hours to complete the reaction. DBS was synthesized by Tozzi et al. (1975) along with various other disulphides by using PTC like dilauryldimethylammoniumchloride.

Anionic surfactant was used by Kutil et al. (1982) to prepare DBS. He reacted BC with sodium

sulfide solution and the reaction temperature was 75 degree celcius.

Raju et al.(2005) reduced sulfoxides into various sulfides using Al-NiCl₂.6H₂O. Time taken was short and yields was high.

2.4 USE OF PHASE TRANSFER CATALYST

In the L-L PTC the catalyst was discovered to be solvent in both the phases and it poses a significant issue that we don't get it in immaculate structure. For evacuating the broke up catalyst it obliges a few water washes of the fluid phase and treatment of the high volume of the emanating. The detachment of catalyst from the response mixture can be accomplished by extraction, refining and adsorption and all these are energy concentrated.

Pradhan and Sharma(1992), studied the synergist impact of fundamental alumina and Amberlyst A27(Cl⁻) structure), on the response of benzyl chloride and para chlorobenzyl chloride with strong sodium sulfide. The catalyst utilized as a part of this case is Tri Phase catalyst.

G.D Yadav and N Kirthivasan(1997) , concentrated on the utilization of a novel catalyst in view of heteropolyacid upheld on mud, particularly dodecatungstophosphoric corrosive (DTP) bolstered on K- 10 dirt and they contrasted it and some other strong catalyst. DTP/K-10 catalyst was discovered to be reusable and proficient at high temperatures.

G.D Yadav and S.S Naik(2000) , arranged an earth upheld phase exchange catalyst and utilized it for the readiness of benzoic anhydride from benzoyl chloride and sodium benzoate utilizing mud bolstered quaternary ammonium salts at 30 °C They found that dirt bolstered catalyst were more dynamic than polymer upheld catalyst. They discovered the selectivity to be 100%.

G.D Yadav and A.V Joshi(2001) , utilized strong corrosive catalyst to blend tert amyl methyl ether (TAME) by responding tert amyl alcohol and methanol. A correlation was made among diverse strong catalyst and Amberlyst-36 was discovered to be extremely successful.

Quici et al.(1979) used free neutral alumina as PTC for the reaction of 1-bromooctane. The system temperature maintained for this reaction was 90 degree celcius and completed in one day. Stirring was done and conversion rate was 95%.

Schneider et al.(1982) successfully oxidized various alcohol to form different sulfides with periodate ion. Phase transfer catalyst used was Polystyrene bound phosphonium ions.

Polymer bound quaternary ammonium catalysts was used as PTC by Arrad and Sasson(1989) in the oxidation of secondary alcohol. This nucleophilic substitution reaction was done in a non polar solvent. Reagent used was inorganic solid type and the reaction was alkylation reaction.

Sujit Sen(2010) found a noble way to form DBS by reacting CBC with hydrogen sulfide rich MDEA. L-L PTC was used and various parameters were studied that effected the conversion of CBC and selectivity of DBS. Conversion increased with increase in catalyst loading with a similar increase in the selectivity of the formation of DBS.

S.K.Maity et al.(2008) used sterlite SRA400 as PTC to reduce p-nitrotoulene by using aqueous ammonium sulfide. The rate of reduction of PNT was established to be proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. Enhancement of the rate was also observed with the once used catalyst due to the presence of elemental sulphur on the surface of the catalyst.

Gao et al.(2010) reacted benzyl chloride with sodium acetate by using different quaternary salt as PTC. Concluding points were: 1) Among quaternary phosphonium and quaternary ammonium type PTC, quaternary ammonium type catalyst has lesser activity than ammonia type catalyst, 2) TPC which is highly lipophilic, substitution takes place at N atom and they have higher catalytic activity, 3) TPC having longer spacer arm that links the quaternary onium salt group to the matrix microsphere, shows higher catalytic activity, 4) The hydrophilic and hydrophobic

property of the TPC is affected by the bonding density of quaternary onium salt group and hence influences the catalytic activity.

2.1 CONCLUSION

There is no detailed work on the kinetic study of preparation of CBM. From literature it was found that there are two types of triphase catalyst that can be used for the synthesis of Benzyl mercaptan and Dichlorobenzyl Sulfide by reacting H₂S rich alkanolamine with benzyl chloride. They are L-L-L PTC and L-S-L PTC. The L-L-L PTC does not show very good reusability property but they show a good conversion and selectivity. The Polymer matrix supported catalyst can have very good reusability and selectivity is also good. The use of solid catalyst is very useful for industrial production as the cost of catalyst is minimized by reusing it. There is no published work on the use of TBMAC Polymer bound catalyst as phase transfer catalyst used for reaction between H₂S rich methyl diethanol amine and chloro benzyl chloride. TBMAC polymer bound is easily available in the market as it finds use in the food industries and is not much costly.

CHAPTER 3

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL

ABSTRACT

This section shows experimental process followed to complete the study, chemicals taken and equipment used for the project.

3.1 CHEMICALS

Toluene($\geq 99.5\%$) were procured from RFCL Limited, New Delhi. TBMAC Polymer bound was obtained from Merck specialities Pvt. Ltd., Mumbai. Methyl diethanol amine ($\geq 98\%$) was obtained from LOBA CHEMIE Pvt. Ltd., Mumbai. Chloro benzyl chloride ($\geq 99\%$) was obtained from Merck(India) Ltd., Mumbai.

3.2 EQUIPMENT

The process was carried out in a mechanically agitated glass reactor of capacity 250cm^3 . A 2cm diameter, 4 bladed turbine impeller was used to stir the system containing mixture. A stirrer was used to control the speed and is maintained at an optimum height for the proper mixing of the mixture. To carry the reaction at a constant temperature, the baffle is kept in water.

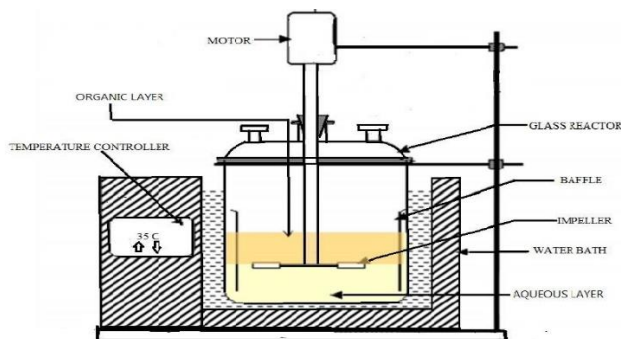
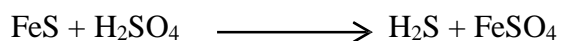


Fig 3.1: Schematic diagram of the batch reactor

3.3 PREPARATION OF H₂S RICH METHYL DI ETHANOL AMINE

First of all 30%, of MDEA solution by weight is made by dissolving MDEA in distilled water. H₂S gas is formed with the help of Kipps apparatus and this gas is absorbed in the absorbent which is MDEA. In Kipps apparatus, FeS stick is put which is made to react with 1M sulfuric acid. The reaction happening is shown by the following equation:



MDEA solution is dipped in ice to prevent sulfide oxidation as the above reaction is exothermic. It also increases the tendency of MDEA to absorb hydrogen sulfide as rate of absorption is inversely proportional to temperature. After 4-5 hours the green turned MDEA solution is taken out and stored in a cool temperature. After this the sample is made to go through the Iodometric test to check the amount of hydrogen sulfide absorbed in the MDEA solution. MDEA is added according to the need of the H₂S concentration.

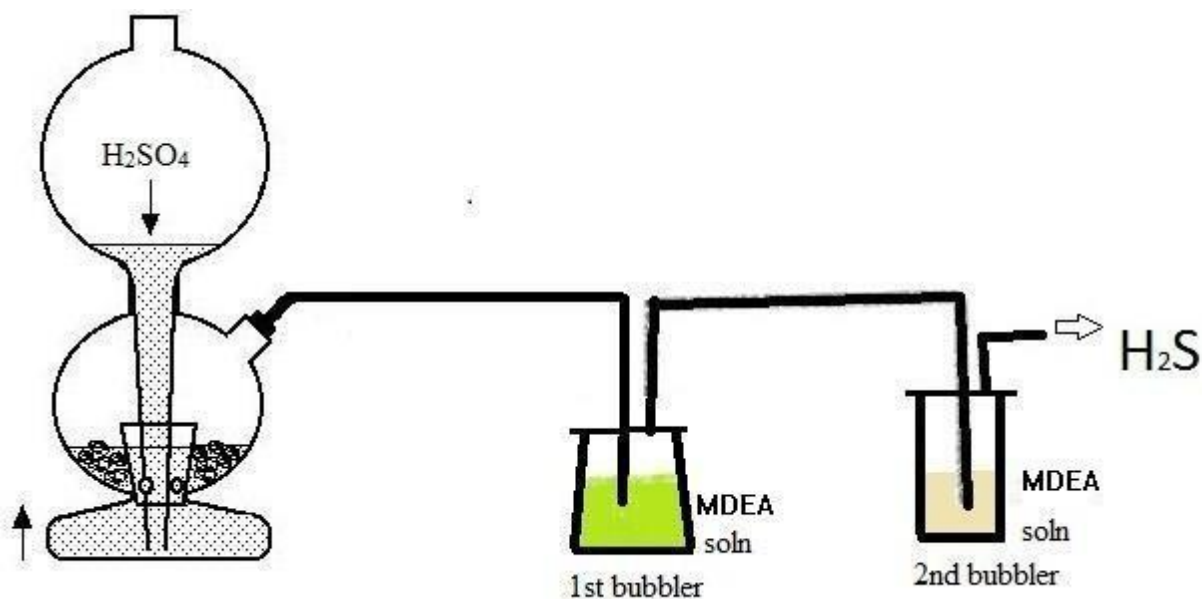


Fig 3.2: Schematic diagram for the absorption of H₂S in MDEA solution

3.3 PREPARATION OF ORGANIC PHASE

Chloro benzyl chloride is dissolved in the solvent (toluene is used here as a solvent) which makes the organic phase of the system. The amount of CBC used depends upon the need of the reactant and is taken 7.5 ml where the reactant is constant. A total of 25ml of organic phase was prepared with CBC and toluene present in it.

3.4 EXPERIMENTAL PROCEDURE

In the experiment a total of 50ml of mixture was prepared with both aqueous and organic phase having a volume of 25 ml each. The required amount of PTC is fed in the baffle. Then the stirrer is made to rotate and 0.5 ml of organic phase is taken out through pipette at a known interval from beginning-5,10 15,30,60,120,240,360,480 min. After stopping the reactor after the above intervals 2-3 min of time is given for the mixture to settle down. After the separation of phases, the above mentioned amount of organic phase is taken out and put in the gas chromatographer. GC analyses the sample and shows the concentration of each product in the organic phase as the product is formed in the organic phase.

3.5 ANALYSIS

3.5.1 ANALYSIS OF ORGANIC PHASE

Organic samples which are collected at every interval were analysed by the help of gas liquid chromatography (GLC). GC vaporizes the component without decomposition and a carrier gas (which is nitrogen here) carries the formed gases to pass through column. The time taken for each component to cross the column is known as retention time which is unique for every compound. Thus GC recognizes the compound and shows the concentration of every component through a graph.

$$\% \text{Conversion} = ((C_{a0} - C_a) / C_{a0}) * 100\%$$

C_{a0} = Initial concentration C_a

= Final concentration

%Selectivity of DBCS =
(moles of DBCS formed/ moles of CBC converted)*100%.

3.5.2 DETERMINATION OF SULPHIDE CONTENT

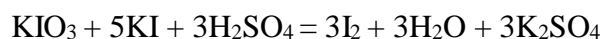
Initial sulphide concentration was determined by standard iodometric titration method (Scott,1966) as given below:

Preparation of standard (0.1M) sodium thiosulphate solution:

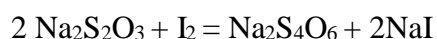
25 gm of sodium thiosulphate pentahydrate was added in distilled water and the volume of the solution was made upto 1litre. The molecular mass of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ is 248 gm.2-3 drops of chloroform was added to keep the solution for 1-2 days.

Standardization of $\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ by standard KIO_3 solution:

25ml of 0.025 molar KIO_3 was taken and 1 gram excess of KI was added to it followed by adding 3ml of 1M sulphuric acid.



The iodine liberated was titrated with thiosulphate solution. When the colour of solution changed to pale yellow, it was diluted to 200ml by adding distilled water .Then about 2-3 drops of 2% by weight of starch solution was added to the diluted solution.The colour of solution changed from pale yellow to blue. Then titration was continued till the colour of the solution changed from blue to colourless.



Therefore, from the above reaction it can be seen that for every 1mole of KIO_3 , 6 moles of $\text{Na}_2\text{S}_2\text{O}_3$.

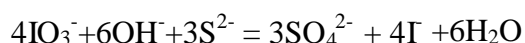
So,Strength of $\text{Na}_2\text{S}_2\text{O}_3$ solution = (6*strength of KIO_3 *volume of KIO_3)/volume of $\text{Na}_2\text{S}_2\text{O}_3$

Preparation of 0.025M KIO_3 Solution

4.28gm of KIO_3 was weighed and added to distilled water and the volume of solution was made upto 1litre.

Estimation of sulphide concentration:

First 1ml of the concentrated sulphide solution is taken and diluted to 100 ml. 15ml of standard (0.025M) KIO_3 solution is taken in a conical flask. 10 ml of diluted sulphide solution was taken and added to the conical flask. 10 ml of 10M NaOH solution was added to the conical flask. The mixture was gently boiled for about 10min till the colour of mixture changed from white to colourless. Now 5ml of 5% (by wt) of KI solution and 20ml of 4M sulphuric acid solution was added to the mixture. The liberated iodine was titrated with standard sodium thiosulphate solution, which was equivalent to the unused KIO_3 solution. The potassium iodate in the alkaline medium oxidizes the sulphide to sulphate as given by the reaction:



From the above balanced reaction we can see that 4mole of iodate ion is equivalent to 3moles of sulphide ion.

$$\text{So, H}_2\text{S concentration} = [15 * S_{\text{iodate}} - (V_{\text{thiosulphate}} * S_{\text{thiosulphate}}) / 6] * (3/4) * (100/10)$$

$$S_{\text{iodate}} = \text{Strength of KIO}_3$$

$$V_{\text{thiosulphate}} = \text{Volume of thiosulphate}$$

$$S_{\text{thiosulphate}} = \text{Strength of thiosulphate}$$



Fig 3.3: Kipp's apparatus set up in lab

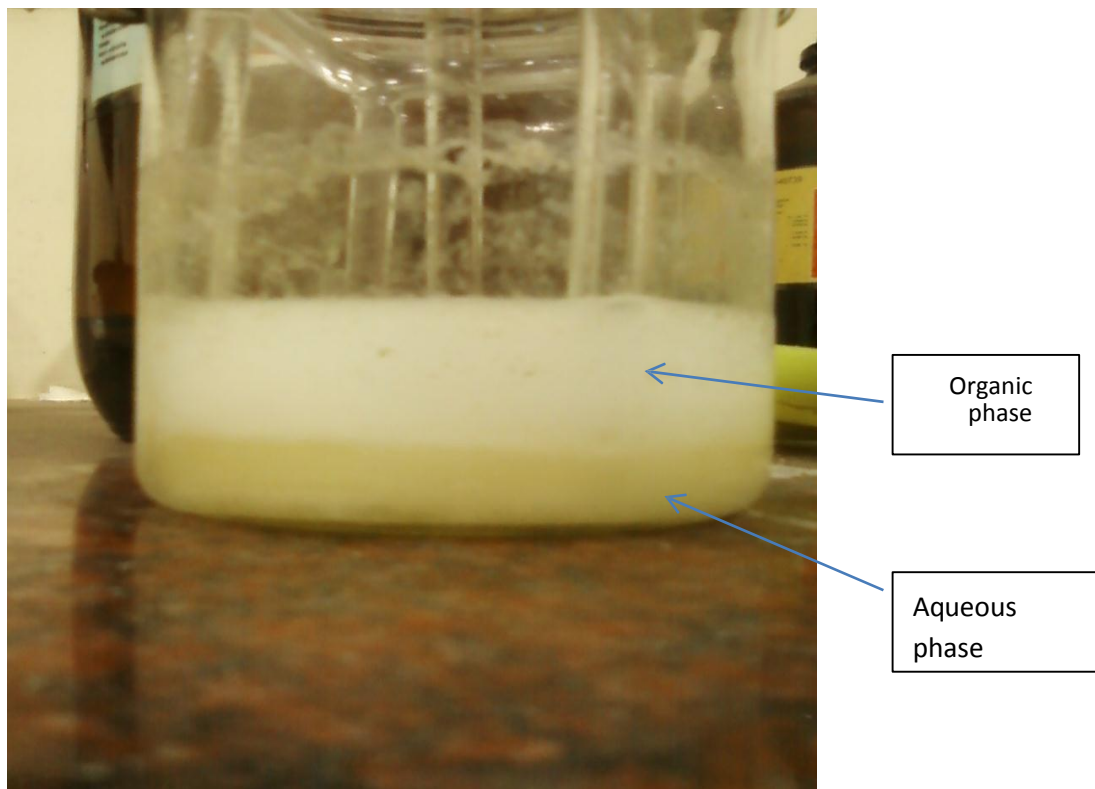


Fig 3.4: Phase separation between organic and aqueous phase

CHAPTER 4

**REACTION OF CHLORO BENZYL
CHLORIDE WITH H₂S RICH
METHYL DIETHANOL AMINE
SOLUTION UNDER PHASE
TRANSFER CATALYST**

CHAPTER 4

REACTION OF BENZYL CHLORIDE WITH H₂S RICH METHYL DIETHANOL AMINE SOLUTION UNDER PHASE TRANSFER CATALYST

ABSTRACT

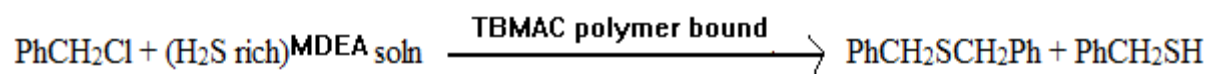
This chapter discusses about the effect of different parameters on the preparation of di benzyl chlorosulphide and benzyl mercaptan on reacting H₂S rich methyl diethanol amine with chloro benzyl chloride with the presence of TBMAC Polymer bound as phase transfer catalyst. The parameters studied are stirring speed, concentration of reactant, catalyst variation and temperature variation is checked.

4.1 INTRODUCTION

To remove H₂S gas from various gas stream, it is dissolved in alkanol amine solution in refineries. High alkalinity of methyl diethanol amine can be used for absorbing hydrogen sulphide gas. The reaction between chlorobenzyl chloride and H₂S rich methyl diethanol amine gives benzyl mercaptan and Dichlorobenzyl Sulfide which is of great industrial value and is a more valuable product than elemental sulphur. Dichlorobenzyl sulphide is used as an additive as high pressure lubricants, photographic emulsion stabilizer, recovery of costly metal in refineries and in different anti corrosive formulation. Chloro Benzyl mercaptan is having medicinal value and is used for the formation of herbicides.

The benzyl chloride and MDEA are having different densities and hence, are of two different phase. Hence, for better reaction and for formation of desired product it required the use of a catalyst. From literature it has been found that a lot of liquid catalyst have been used for the reaction of benzyl chloride and H₂S rich MDEA solution such as TBAB (Tetra Butyl Ammonium Bromide), PEG (Poly ethaline glycol), etc. The problem with these liquid catalyst is that they can't be separated easily from the solution after adding and hence purity of the

product is not so good. This also creates a problem as quaternary ammonium compounds are harmful in liquid effluents. Liquid catalyst is lost after its use so cost of catalyst increases the cost of production. So considering the cost and purity of product solid catalyst has to be used. TBMAC Polymer bound is used as it is not much costly and is easily available. The overall reaction can be represented by scheme 4.1:



Scheme: 4.1

Parametric studies have been performed following one variable at a time approach to see the effect of various parameters such as stirring speed, catalyst loading on benzyl chloride conversion and DBCS selectivity.

4.2 RESULTS AND DISCUSSION

4.2.1 PARAMETRIC STUDY

4.2.1.1 EFFECT OF STIRRING SPEED

Mass transfer resistance should be eliminated in order to do kinetic study. Stirring speed was varied under from 1000rpm to 2000 rpm in order to study its effect on the reaction, other parameters were kept constant with the presence of TBMAC polymer bound catalyst. The data obtained is shown in figure 4.1. From the figure it was observed that when stirring speed is varied under the above range, the benzyl chloride conversion variation was very little. This indicates that the factor of mass transfer is very small and hence stirring speed of 1500 rpm is kept constant for other variations.

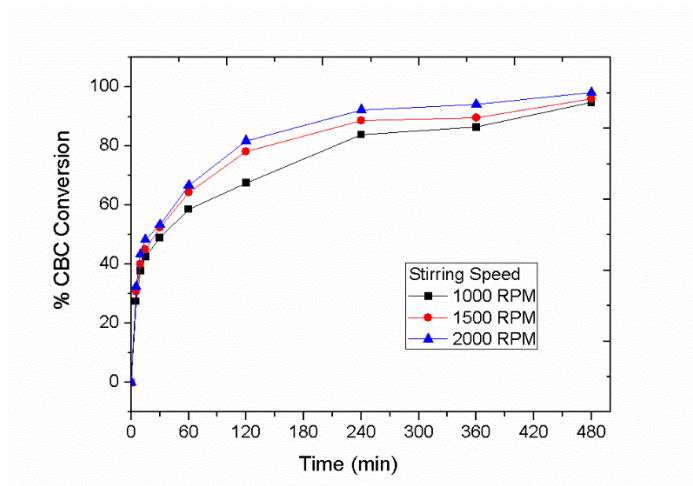


Fig 4.1: Effect of Stirring Speed on CBC conversion

Operating Conditions:

Aqueous and Organic Phase Volume = $25 \times 10^{-5} \text{m}^3$ each, Sulphide Conc. 2 kmol/m^3 Aqu.Phase, p-Chlorobenzyl chloride concentration = 2.4 kmol/m^3 , TBMAC polymer bound = $6 \times 10^{-6} \text{ kmol/m}^3$ org. phase, Temperature = 323K , MDEA Conc. = 3.05 kmol/m^3 , speed of agitation (1000 rpm, 1500 rpm, 2000 rpm) sing

4.2.1.2 EFFECT OF CATALYST VARIATION

The effect of catalyst TBMAC Polymer bound was studied in the range of 0 (kmol/m^3) to 2.4×10^{-6} (kmol/m^3). The data obtained is shown in figure 4.2(a). With the increase of catalyst loading the chloro benzyl chloride conversion increases. On increasing the catalyst concentration from 0 to $2.4 \times 10^{-6} \text{ kmol/m}^3$ the conversion increases from 40% to 99% . Therefore, the selectivity of DBCS increases with the increase in catalyst loading

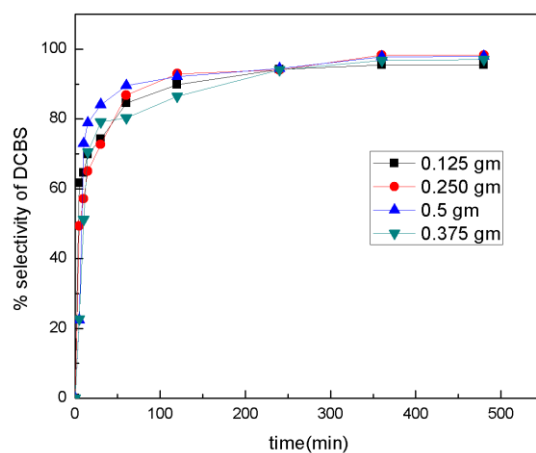


Fig 4.2(a): Effect of catalyst loading on the DCBS selectivity.

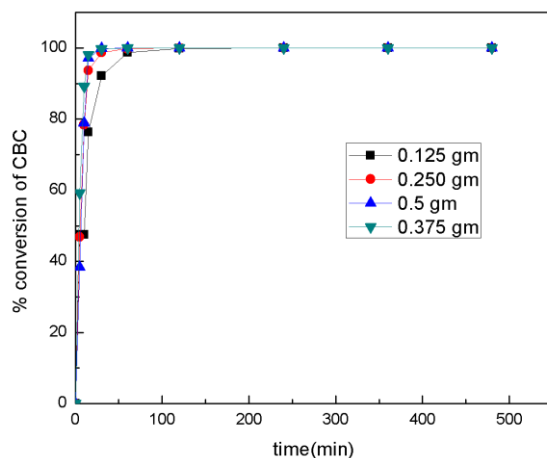


Fig 4.2(b): Effect of catalyst loading on the conversion of CBC.

Operating Condition :

Aqueous and Organic Phase Volume = $25 \times 10^{-5} \text{m}^3$ each,

Sulphide Conc. = 2.0 kmol/m^3 Aqu.Phase, p-chlorobenzyl chloride concentration = 2.4 kmol/m^3 ,

Temperature = 323K, Agitation speed= 1500 rpm, MDEA Conc. = 3.05 kmol/m^3

4.2.1.2 EFFECT OF TEMPERATURE

For a fixed CBC concentration of 2.4 kmol/m^3 , the effect of variation of temperature on initial sulphide content was studied. With the increase in temperature, the conversion increases because of the increase in thermal energy. The data obtained is shown in figure 4.3(a). But for the case of selectivity, The selectivity of DCBS increases with an increase in the temperature. The data is shown in figure 4.3(b).

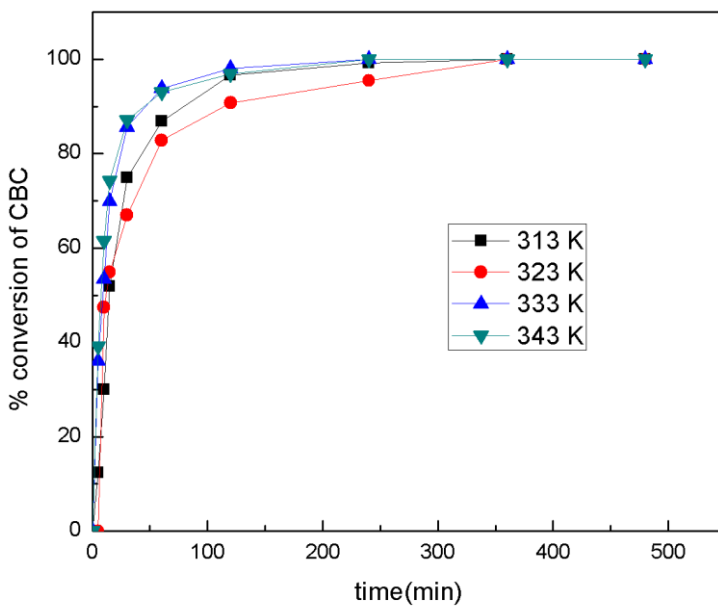


Fig 4.3(a): Effect of temperature on the conversion of CBC

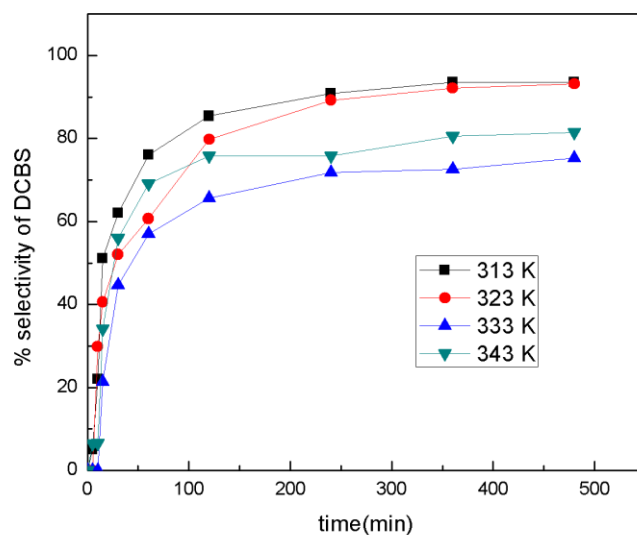


Fig 4.3(b):Effect of initial temperature on DCBS selectivity.

Operating Condition :

Aqueous and Organic Phase Volume = $25 \times 10^{-5} \text{ m}^3$ each,

Sulphide Conc. = 2 kmol/m^3 Aqu.Phase, TBMAC polymer bound = $6 \times 10^{-6} \text{ kmol/m}^3$

org phase, p-chlorobenzyl chloride concentration = 2.4 kmol/m^3 , Agitation speed=

1500 rpm, Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3 .

4.2.1.4 EFFECT OF CHLORO BENZYL CHLORIDE CONCENTRATION

The concentration of chloro benzyl chloride was varied to observe the conversion of CBC and selectivity of DBCS. As shown in the figure 4.4(a), the conversion of CBC decreases with the increase in the concentration of CCBC. This is because sulphide content is same for all cases but the benzyl chloride concentration increases that reduces the conversion. But on increasing

the concentration of chloro benzyl chloride, the selectivity of DCBS increases. This is because at low benzyl chloride concentration there is insufficient amount of benzyl chloride to produce DBCS which result in low selectivity. The data is represented in fig 4.4(b).

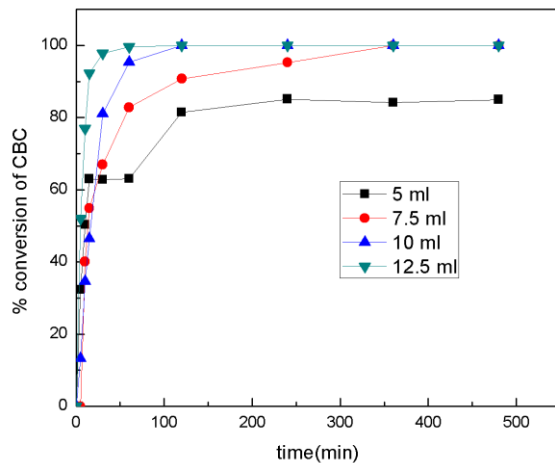


Fig 4.4(a): Effect of CBC concentration on the conversion of CBC

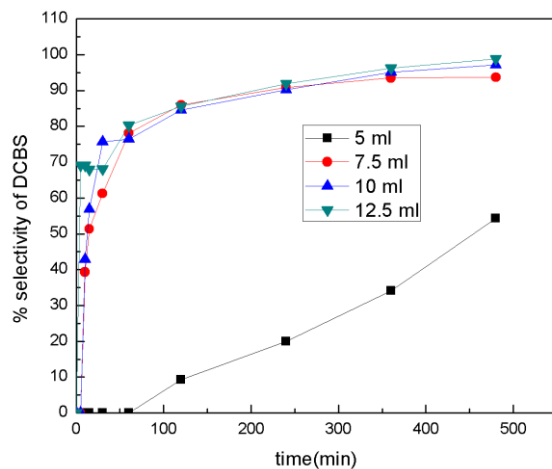


Fig 4.4(b): DCBS selectivity on reactant variation

Operating Condition :

Aqueous and Organic Phase Volume = $25 \times 10^{-5} \text{ m}^3$ each, Sulphide Conc. = 2

kmol/m^3 Aqu.Phase, TBMAC polymer bound = $6 \times 10^{-6} \text{ kmol/m}^3$ org phase,

Agitation speed= 1500 rpm,

Temperature = 323K, MDEA Conc. = 3.05 kmol/m^3

4.3 CONCLUSION

H_2S reacts with chloro benzyl chloride to form DCBS and CBM in the presence of TBMAC polymer bound (PTC). The reaction has a great industrial significance . Different parameters was taken to increase %conversion and the selectivity of DCBS .Low sulfide concentration or higher estimation of MDEA/ H_2S proportion, high chloro benzyl chloride concentration and long reaction time supports the selectivity of DCBS. The opposite is for the formation of benzyl mercaptan. For higher conversion of chloro benzyl chloride, the concentration of chloro benzyl chloride is kept low, MDEA/ H_2S proportion is additionally kept low. On increasing the amount of catalyst, the conversion of chloro benzyl chloride increases.

CHAPTER 5
SUMMARY AND CONCLUSION

CHAPTER 5

SUMMARY AND CONCLUSION

Abstract

The remarks of the previous chapter has been summarized in this chapter

5.1 INTRODUCTION

This work has generated the method for the industrial procedure for producing of DCBS by the utilization of hydrogen sulfide generated alongside the various biproducts. DCBS and CBM can be produced using the H₂S gas present in the gas stream in the following ways.

- 1) Absorption of H₂S gas from gas stream in MDEA solution.
- 2) Utilization of H₂S rich MDEA in the preparation of DCBS and CBM.

5.2 SUMMARY AND CONCLUSION

H₂S rich MDEA reacts with chloro benzyl chloride to form Dichloro Benzyl Sulfide and Chloro Benzyl Mercaptan in the presence of TBMAC polymer bound (PTC)The conversion of CBC is increased by increasing catalyst loading, greater reaction time and increasing chloro benzyl concentration. The two active ions pairs QSQ and QSH are transferred from the aqueous phase to the organic phase where it forms DCBS and CBM.The reaction time was 8 hours and some amount of H₂S remains unreacted in MDEA solution in some cases even after the completion of the reaction. The TBMAC Polymer bound catalyst has incredible reusability property and can be reused once more. So this catalyst can be modernly extremely significant for this procedure.

CHAPETR 6

SCOPE FOR FUTURE WORK

CHAPTER 6

SCOPE FOR FUTURE WORK

ABSTRACT

This chapter deals with the extent of further work taking into account results and analysis of the present study. Areas are highlighted where improvement can be done to improve the selectivity of DCBS and conversion of CBC.

6.1 INTRODUCTION

This project deals with the formation of DCBS and CBM by reacting H_2S with CBC. Various parameters are studied but there is a scope for studying many other parameters which should be studied.

6.1 FINDING OUT EFFECT OF OTHER PARAMETERS

Effect of sulfide concentration on the conversion rate can be studied out as it is very important in the modeling of the process. Reaction kinetics can be known effect of pH can be observed as it is an ion exchange reaction and formation of both the reactants depend on the pH of the solution (Yang et al). Solvent used here is toluene. We can use other solvent like chloro benzene, n-heptane to observe the kinetics of the reaction. As PTC is used so solvent plays an important role in the conversion of CBC.

6.2 USE OF OTHER AQUEOUS PHASE

We are using MDEA as an absorbant for the absorption of H_2S . We can study the project taking some other absorbant like MEA and make that the aqueous phase.

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