KINETICS STUDIES IN SYNTHESIS OF DIBENZYL SULPHIDE IN LIQUID-LIQUID-SOLID MODE

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109CH0582

KINETICS STUDIES ON SYNTHESIS OF DIBENZYL SULPHIDE IN

LIQUID-LIQUID-SOLID MODE

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IN

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by

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CERTIFICATE

This is to certify that the thesis report titled "**KINETICS STUDIES ON SYNTHESIS OF DIBENZYL SULPHIDE IN LIQUID-LIQUID-SOLID MODE**" submitted by AKASH KUMAR having roll no. 109CH0582 is final report of the project work regarding assessment for the prescribed curriculum of Bachelor of Technology in Chemical Engineering Session 2009-2013 in the Department of Chemical Engineering, National Institute of Technology, Rourkela is an authentic work to the best of my knowledge and belief.

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ABSTRACT

As high quality of crude reserves are depleting and what we are left with high sulphur crude there is a strong need for some process which can effectively and economically remove sulphur from the process otherwise it may lead to unwanted side reactions which would entail consumption of reactants and energy. Usually the sulphur is removed by absorption in ammonia solution which is further processed in a Claus Unit to produce elemental sulphur which requires a high amount of energy. With a view to making more sophisticated fine chemicals which have higher usability and better market value, this project was undertaken to study the kinetics of the synthesis of dibenzyl sulphide was carried out using hydrogen sulphide rich monoethanolamine under tri phase transfer catalysis with a phase transfer catalyst (PTC). The Amberlite IR400 has been chosen the phase transfer catalyst as it is solid and can be reused. Parametric studies of the reaction between benzyl chloride in presence of organic solvent and H_2S rich MEA were done in this work and it is tried to determine what type of conditions favor the more conversion of benzyl chloride and more synthesis of dibenzyl sulphide.

CONTENTS

LIST OF FIGURES:

ABBREVIATIONS LIST

BC	benzyl chloride
BM	benzyl mercaptan
DBS	dibenzyl sulphide
MEA	monoethanolamine
GC	gas chromatography
PTC	phase transfer catalyst
TPC	tri phase catalyst
TBAB	Tetra Butyl Ammonium Bromide

CHAPTER 1

INTRODUCTION

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1.1 HYDROGEN SULPHIDE

Hydrogen sulphide is a heavier-than-air, flammable gas with a characteristic rotten egg odour. Individuals can detect this odor when hydrogen sulfide gas is present at very low levels. It is soluble in water and organic solvents and will corrode metals.

Molecular formula: H_2S

Melting Point: -85.4°C

Boiling Point: -60.3°C

Vapour Density: 1.189

Flashpoint: -82.4°C

1.2 SOURCES OF HYDROGEN SULPHIDE

A continuous increase in present economy demands exponential rise in industrial industries. But price of increased economy and industrial development is paid by the unwanted production of unwanted chemicals (many a times waste materials) and worries comes with their disposal. One such compound is hydrogen sulfide. Its properties make it a dangerous gas to be just left in open air thus it is needed that either it treated within environmental terms and then left in atmosphere or converted to an altogether different product.

When it comes to its occurrence it is a common fact that light and easy in processing crude are declining day by day and hence refineries are forced to process high sulfur crude which in return produces high quantity of hydrogen sulfide and this is a major source of hydrogen sulfide due to the hydro treatment process they use to remove sulfur from crude oil. Hydrogen sulfide is in atmosphere due to both natural and industrial process. Natural sources which account for almost 90% of the total hydrogen sulfide in atmosphere comes from crude oil, natural gas, salt marshes, sulfur springs, and swamps. Whereas man made processes which accounts for approx. 10% comes from manure handling operations, oil refineries, pulp and paper mills, tanneries, wastewater treatment plants, and solid waste landfills. 1% hydrogen sulfide comes from landfill gas emissions where it is formed under conditions like moisture content, temperature, pH level,

anaerobic conditions and sulfate source. There is large variation in hydrogen sulfide content of natural gas (from 0.1 ppm to 150,000 ppm) whereas in case of coal gas it is 0.3-3% hydrogen sulfide content.

1.3 NEED TO REMOVE HYDROGEN SULPHIDE

Hydrogen sulfide in crude oil is a bag full of problems as it will corrode the metals in the processing of the oil and will cause air pollution resulting from the burning of the fuels having high sulfur content obtained from fractionation of high sulfur containing crude oil. When dissolved in water it will dissociate into bisulfide ion and sulphide ion. It form insoluble sulphide salt with varios metals like copper, zinc, nickel, iron. Threshold for odour of hydrogen sulphide is variable in humans which range from 0.0005 to 0.3ppm. At high conc. people may not be able to detect it by smelling because it sheds of its unique pungent smell. It has an explosion limit of 4.3% - 46%. Its presence in refineries gas stream causes problems like deterioration and deactivation of catalysts, some undesirable side reactions, and increase in pressure requirements of process and increment in requirement of gas compressor capacity. So in order to ensure safety standards a Hydrogen Sulphide Material Datasheet (MSDS) should be consulted.

1.4 PROCESS USED IN INDUSTRIES TO TREAT HYDROGEN SULPHIDE (REMOVAL AND RECOVERY)

For the treatment of hydrogen sulphide different process are being developed by different scientist depending on various conditions. Mostly weak acidic nature of hydrogen sulphide is used for its removal using alkaline solution. Sodium hydroxide which is a strong alkaline solution when used for removal of hydrogen sulphide from gas streams forms irreversible chemical reaction product (carbon dioxide is also present in the reaction and gas stream), thus it is not suitable for streams containing carbon dioxide concentration more than 4% (Robin, 1999). Solution of this problem is use of weak alkaline like Ammonium hydroxide and alkanolamines. Two process of hydrogen sulphide removal is discussed below:

1.4.1 AMMONIA BASED PROCESS

A detailed description on the use of ammonia to remove hydrogen sulphide from gas stream was given by two patents Hamblin (1973) and Harvey and Makrides (1980). Though its use is being declined but still used for desulphurising coke ovens.

Rich gas is passed through series of ammonia and hydrogen sulphide scrubbers. In the top of ammonia scrubber stripped water is fed where water absorbs ammonia from gas. The solution obtained from bottom is used in hydrogen sulphide scrubber as absorbent. The solution from series of scrubbers is taken to deacidifier where ammonium sulphide is decomposed to produce hydrogen sulphide rich vapour and ammonia liquor.

$$NH_3 + H_2O \longrightarrow NH_4OH$$

$$NH_3 + H_2S \longrightarrow NH_4HS$$

$$2NH_3 + H_2S \longrightarrow (NH_4)_2S$$

Various advantages of the process:

-: This process is best suited for rich gas streams which usually contain both hydrogen sulphide and ammonia because both the compounds are removed in one single step.

-: in case of carbon dioxide presence hydrogen sulphide can be absorbed more quickly by varying the concentration of liquid ammonia. Use of spray and short contact time helps in selective absorption of hydrogen sulphide.

Along with these advantages there are some disadvantages also due to the high partial pressure of ammonia dilute ammonia is used or instead high pressure can be used otherwise separate water wash step is to be introduced.

1.4.2 ALKANOLAMINE BASED PROCESS

Mostly used for the removal of constituents like hydrogen sulphide and carbon dioxide. It has an advantage of low vapour pressure which makes this process popular and also makes it flexible in terms of pressure, temperature and concentration.

Alkanolamine like monoehthanolamine and diethanolamine are favoured for removal of acid (kirk and Othmer, 1983). While in case of hydrogen sulphide methyldiethanolamine gives the best result (kohl and Nielsen, 1997).

Reaction with H_2S:

$$2RNH_2 + H_2S \longrightarrow (RNH_3)_2S$$

$$RNH_2 + H_2S \longrightarrow RNH_3SH$$

Reaction with CO_2:

$$2RNH_2 + CO_2 + H_2O \longrightarrow (RNH_3)_2CO_3$$

$$RNH_2 + CO_2 + H_2O \longrightarrow RNH_3CO_3H$$

$$2RNH_2 + CO_2 \longrightarrow RNH\text{-}CO\text{-}ONH_3R$$
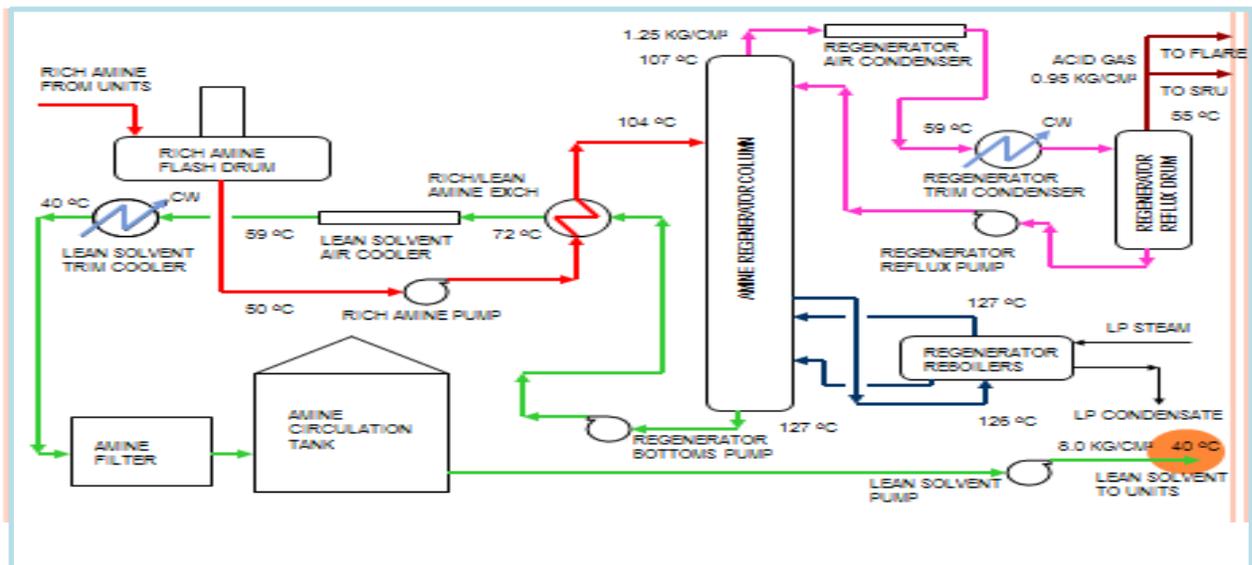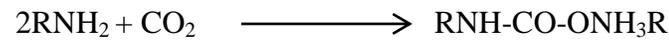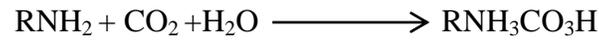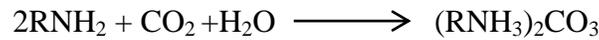

Fig1.1 Flow Diagram of Amine Treating Process

1.5 TREATMENT OF HYDROGEN SULPHIDE RECOVERED

1.5.1 CLAUS PROCESS

After the hydrogen sulphide is being removed from gas stream for the sake of environmental laws it is then converted into non-poisonous substance sulphur. In most of the plants, process used for this conversion is Claus process developed by C. F. Claus in 1883. In Claus unit conversion takes place in two steps :

1. Thermal step : flame free partial oxidation of hydrogen sulphide with air at a high temp. of 1000-1400oC. While one third of hydrogen sulphide is converted some sulphur dioxide and sulphur is formed.

$$2H_2S + 2O_2 \longrightarrow SO_2 + 2H_2O + S$$
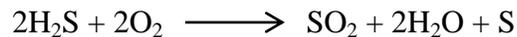
2. Catalytic step : remaining (two third) hydrogen sulphide is converted in presence of catalyst at a lower temperature of around 200-350oC when reacted with sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

Process has some disadvantages like high operating pressure, ratio of oxygen to hydrogen sulphide should be controlled accurately, and loss of hydrogen energy, due to the high sulphur content of tail gas a separate tail gas treatment plant is needed.
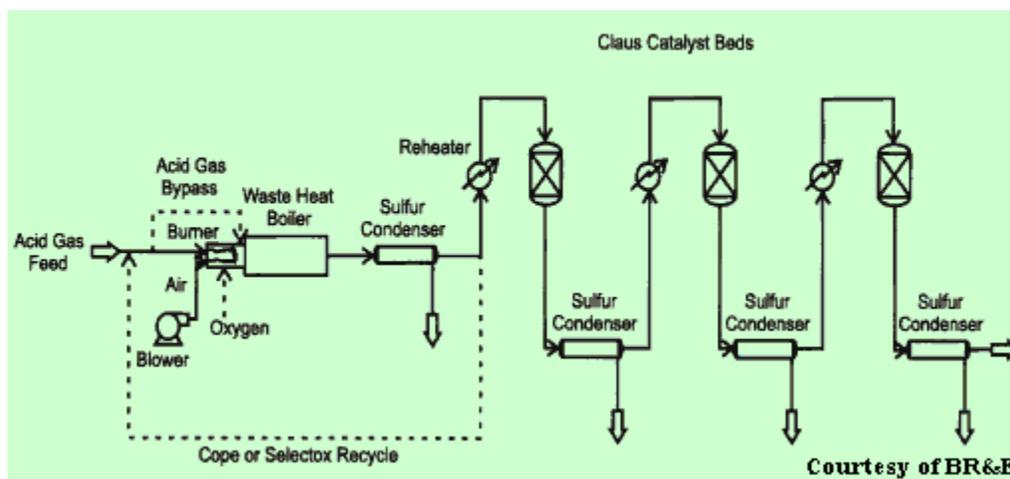
Fig. 1.2 Sulphur Production by the Claus Process

PROCESS IMPROVEMNETS

Various improvements are made to the Claus process

- SUPERCLAUS: special catalyst for the selective conversion of hydrogen sulphide to sulphur, less formation of sulphur dioxide, more conversion.
- OXYGEN CLAUS: oxygen is mixed to air thus increasing the rate of combustion.
- BETTER CATALYSTS: catalyst having high surface area and better porosity is choosen.
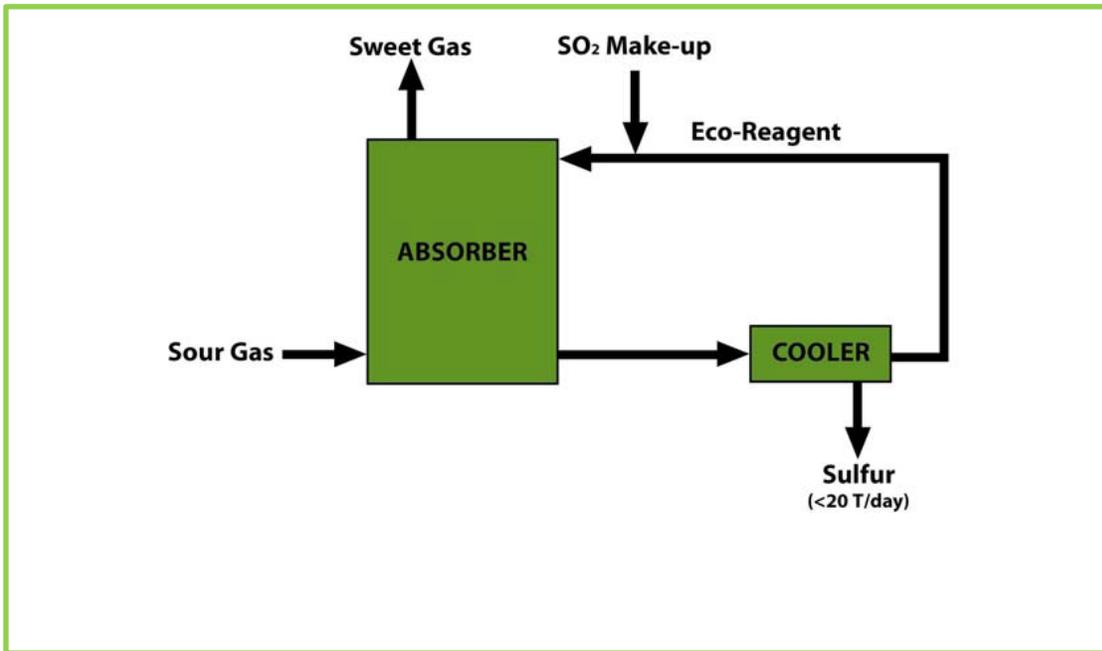
Fig. 1.3 Improved Clause process

1.5.2 CRYSTA SULF

Heavy liquid hydrocarbon is passed through absorber where it contacts with hydrogen sulphide rich gas. In second step after the absorption of hydrogen sulphide it reacts with sulphur dioxide and form sulphur

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

1.5.3 WET OXIDATION LO-CAT PROCESS

Environmentally safe catalyst is used for the conversion of hydrogen sulphide to sulphur. Hydrogen sulphide absorbed in solution gives sulphur when oxidised while iron ions are reduced.

1.6 PRESENT WORK

The work being done in this project is a replacement of Claus and other process which produces elemental sulphur but instead here a different approach is being taken to produce a value added product from the by products of the plant (hydrogen sulphide) which will help refineries economically. Basis of this work is:

- Synthesis of chemicals like dibenzyl thioether (high value product) in liquid-liquid-solid mode with hydrogen sulphide rich MEA in presence of Amberlite IR 400.
- Parametric study of above reaction
- Kinetic study of above reaction

1.7 PHASE TRANSFER CATALYST

Phase transfer catalyst are gaining popularity over the years as they can accelerate many of the slow heterogeneous reactions which generally involves organic and ionic reactant (mode may be liquid-liquid or solid-liquid). Simplicity, easy operating conditions, high rate of reactions and less consumption of raw materials are the added benefits of PTC. Quaternary ammonium salts are most used PTC. Liquid-liquid PTC depends on the property of lipophilicity of quaternary ion. Starks (1971) suggested extraction mechanism for less lipophilic catalyst which is easily present in both aqueous and organic phase. In interfacial mode catalyst mainly remains in organic phase. Liquid-liquid-solid PTC solves the problem of purification of the final products.

AMBERLITE IR400

Catalyst is ion exchange resin. It has a complex polymer matrix structure. It is in form of solid beads yellow in colour. The anionic part is Cl⁻ while the cationic part is –N+R3.
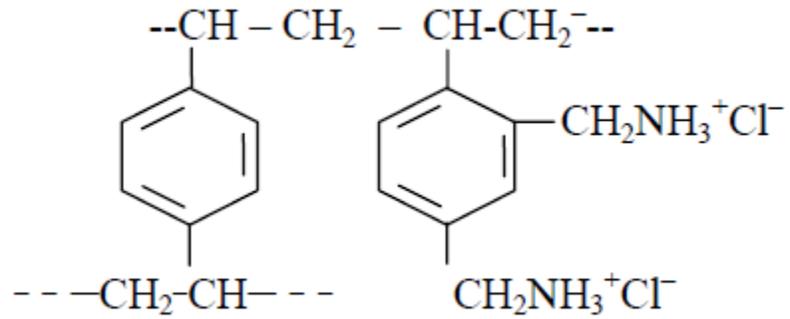
Fig. 1.4 Amberlite IR 400

CHAPTER 2

LITERATURE SURVEY

CHAPTER 2

LITERATURE SURVEY

ABSTRACT:

Before the start of the experiment various study is done understand the standing of the following work in the world. Various literatures are being read for the topics related like removal of hydrogen sulphide, production of dibezyl thioether and benzyl mercaptan and working of phase transfer catalyst.

2.1 TREATMENT OF HYDROGEN SULPHIDE

Hamblin, 1973   developed the process for removal of hydrogen sulphide from streams with NH_4OH to give ammonium hydrosulphide which was oxidised to get elemental sulphur.

Kohl and Neilsen, 1997 updated the abouve process which was discussed in 1.4.2.

Asai (1989) : at a time absorption rate of hydrogen sulphide and NH_3 in water along a flat interface

Lawson (1976), Isaacs (1980), Austgen (1989), Sidi-Boumedine (2004) all these studied the process of alkanolamine use for the treatment of hydrogen sulphide and most of the work was to attain equilibrium solubility of hydrogen sulphide along with the development of mathematical model.

2.2 DIBENZYL SULPHIDE AND BENZYL MERCAPTAN

Dibenzyl sulphide as value added compound has many applications like additive in pressure lubricants, photographic emulsions stabilisers, motor oils additives (anti-wear), precious metals recovery and refining and anticorrosive formulations. Also sometimes used for preparation of dibenzyl sulfoxide.

One important use of bezyl mercaptan is production of thiocarbonate family herbicides.

Heather (1988) benzyl chloride was reacted with sodium sulphide within hydrogen sulphide atmospherein two phase condition(50°C temp.)

Labet (1989) reaction of benzyl chloride and $(NH_4)SH$ (ratio 1). First at 80°C benzyl chloride is added to hydrosulphide then the reaction mixture was taken to 100°C.

Pradhan and Sharma (1990) different chlorides were reacted with sodium sulphide in presence of PTC to produce dibenzyl sulphide. Different types of catalyst were tried while tetrabutylammonium gave the best result.

Pradhan and Sharma (1992) this time they did the kinetic study of dibenzyl sulphide preparation in solid-liquid mode.

Bandgar (2000) and lakouraj (2002) various permutations and combination was applied to preparation of dibenzyl sulphide one of them was in presence of aluminium chloride reduction of sulphides with the help of zinc powders.

Pradhan, Patwardhan and Maity (2006) nitrotoleunes reduction by ammonium sulphide under liquid-liquid PTC was kinetically studied. Benzyl chloride with $(NH_4)_2S$ was also studied.

Sujit Sen, Pradhan, Maity, Patwardhan (2007) for determining the better selectivity of dibenzyl sulphide different parametric study was done. High benzyl chloride conc. gives high selectivity.

Sujit Sen, Pradhan, Patwardhan (2010) hydrogen sulphide rich MEA was reacted with benzyl chloride and different parametric study was done with liquid-liquid PTA

2.3 PHASE TRANSFER CATALYST

The most important feature of a solid tri phase transfer catalyst is its reusability which is achieved by its extraction and distillation.

Pradhan and Sharma (1990) were the first to study the process of a phase transfer catalyst. Their catalyst was alumina and Amberlyst A27. Its effect was studied on the reaction of BC and $(NH_4)_2S$.

Yadav and Kirthivasan (1997) effect of a novel catalyst with the help of clay supported heteropolyacid

Yadav and Josi (2001) solid catalyst (acidic) to produce tertiary amyl methyl ether by reacting alcohol and methanol. After proper analysis and comparison solid catalyst were found to be most suitable.

<u>Yadav and Badure (2007)</u> they found encouraging results from the introduction of third phase in initially used two phases reaction. They introduced third phase (liquid) and found increment in conversion and selectivity.

<u>Pradhan, Patwardhan and Maity (2008)</u> reduction of p-nitrotoluene by aq. Ammonium sulphide anion exchange resin as triphasic catalyst (serelite SRA 400).

2.4 CONCLUSION

Literature survey indicates that most of the initial work was done on two phase catalyst. But in recent times better activity of catalyst was found with the introduction of third phase. The third phase can be liquid or solid (L-L-L or L-S-L PTC). There are some works on L-L-L PTC catalyst which show better conversion and selectivity but very poor in reusability. Therefore in case of reusability solid catalyst is excellent. While the production of dibezyl sulphide and bezyl mercaptan from benzyl chloride and hydrogen sulphide with the help of solid tri phase catalyst is not being done. Therefore this work is new in the field. Moreover there is not much work done for Amberlite IR 400. It's an easy available catalyst and is used in food industry and is less costly. It's a resin with ammonium functional group and chloride ion.

CHAPTER 3

EXPERIMENTS

CHAPTER 3

EXPERIMENTS

ABSTRACT:

The present section deals with the experimental work being carried out in the work. The experimental work can be divided in four section. The manner in which they will be carries out will be:

    1. H_2S rich MEA preparation

    2. Estimation of sulphide content

    3. Batch reaction experiments

    4. Analysis of organic phase

3.1 CHEMICALS

Toluene ($\geq$99.5%) was brought from RFCL Limited, New Delhi. Amberlite IR 400 was brought from Merck Pvt. Ltd., Mumbai. MEA ($\geq$98%) was acquired from LOBA CHEMIE Pvt. Ltd., Mumbai. BC ($\geq$99%) was brought from Merck (India) Ltd., Mumbai.

3.2 PREPARATION OF HYDROGEN SULPHIDE RICH MEA

First 30-35 wt% of MEA solution was initially prepared by mixing appropriate amount of monoehtanolamine and distilled water. Then the H_2S gas generated in the Kipp's apparatus was bubbled in the monoehtanolamine solution in a gas bubbler. H_2S gas was prepared by reacting FeS with sulphuric acid .The concentration of sulphuric acid was taken as 1molar.

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

Since the reaction between H_2S and MEA solution is exothermic (Kohl and Nielsen, 1997), the gas bubbler containing MEA solution was kept immersed in ice bath in order to prevent the oxidation of sulphide and to increase the absorbance in MEA solution as absorbance increases with decrease in temperature. The unabsorbed H_2S gas from the first bubbler was sent to second

gas bubbler containing MEA solution so that the H_2S gas is vented out under prescribed environmental norms. When the gas bubbling stops, the H_2S rich MEA solution sample is withdrawn time to time and its sulphide content was analysed (Scott,1966). The gas bubbling was continued unless the desired concentration of H_2S was obtained in MEA solution.

Fig 3.1 Kipp's apparatus set up in lab

3.3 DETERMINATION OF SULPHIDE CONTENT

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

3.3.1 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 wt. of $Na_2S_2O_4.5H_2O$ is 248 gm.2-3 drops of chloroform were added to keep the solution for 1-2 days.

3.3.2 Standardization of $Na_2SO_4.5H_2O$ 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.

$$KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3H_2O + 3K_2SO_4$$
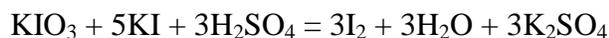
The iodine liberated was titrated with thiosulphate solution. When the colour of solution changed to pale yellow, it was diluted to 200ml by adding distilled water .Then about 2-3 drops of 2% by weight of starch solution was added to the diluted solution. The colour of solution changed from pale yellow to blue. Then titration was continued till the colour of the solution changed from blue to colourless.

$$2 Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$
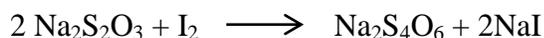
Therefore, from the above reaction it can be seen that for every 1mole of KIO_3, 6 moles of $Na_2S_2O_3$.

So, Strength of $Na_2S_2O_3$ solution = (6*strength of KIO_3*volume of KIO_3)/volume of $Na_2S_2O_3$

3.3.3 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.

3.3.4 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. Then it was boiled for about 10min till the colour of mixture changed from white to 23 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:

$$4IO_3^- + 6OH^- + 3S2^- = 3SO_4^{2-} + 4I^- + 6H_2O$$
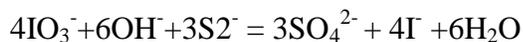
From the above balanced reaction we can see that 4mole of iodate ion is equivalent to 3 moles of sulphide ion.

So, H_2S concentration= $[15 * S_{iodate} - (V_{thiosulphate} * S_{thiosulphate})/6] * (3/4) * (100/10)$

S_{iodate} = Strength of KIO_3

$V_{thiosulphate}$ = Volume of thiosulphate

$S_{thiosulphate}$ = Strength of thiosulphate

3.4 BATCH REACTION

In a typical experimental run, $50cm^3$ of aqueous phase containing a known concentration of sulphide is charged into the three neck batch reactor. The amount of catalyst required is weighed and fed into the. Then 50 ml of organic phase of known concentration of benzyl chloride was added to the reactor. The reaction mixture was then agitated at constant stirring rate. On regular time interval of 10min, 30min, 60min, 120min, 240min, 360min, 0.5ml of organic phase was taken for analysis after allowing the reaction to stop and allowing the phase separation to occur.
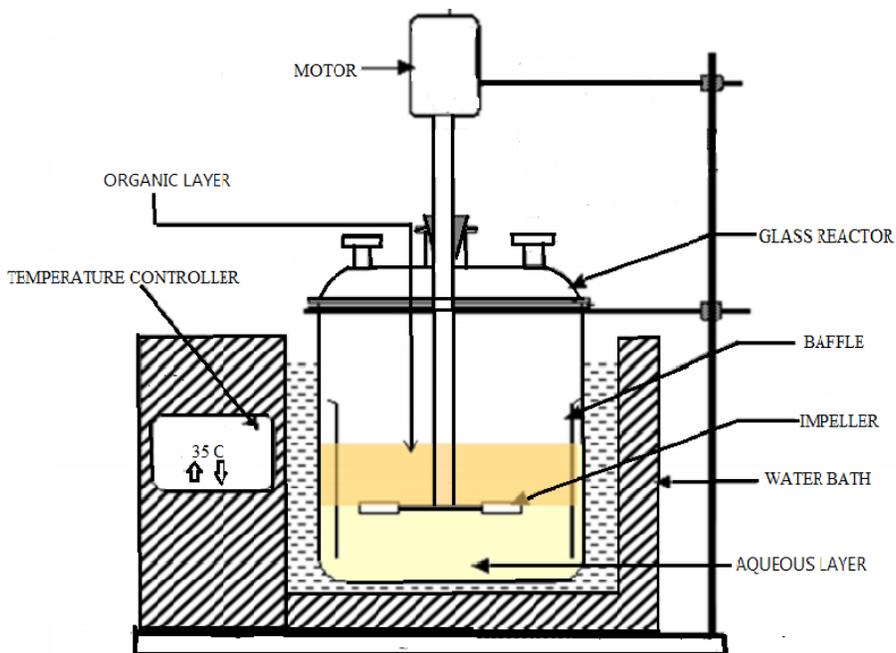
Fig 3.2 Batch reactor

3.5 ANALYSIS OF ORGANIC PHASE

All organic samples were analysed by the help of gas liquid chromatography (GLC) using a 2m long and 3mm in diameter stainless steel column packed with 5%SE 30. A Flame Ionisation Detector (FID) was used with nitrogen as the carrier gas. Nitrogen gas flow rate is kept at 0.8bar, injection temperature was kept at $250^{o}C$ and detector temperature was $300^{o}C$.Oven program is set in a way that oven is maintained at $150^{o}C$ for 2min and then it is heated up to $300^{o}C$ at the rate of $20^{o}C/min$ and $300^{o}C$ is maintained for 4 min.

$\%Conversion = ((Ca^{o} - Ca)/Ca^{o}) * 100\%$.

Ca_{o} = Initial concentration

Ca = Final concentration

$\%Selectivity\ of\ DBS =$

(Moles of BC from which DBS is formed/ moles of BC converted)*100%.

# CHAPTER 4

REACTION, RESULTS AND DISCUSSION

CHAPTER 4

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4.1 REACTION

In refineries, H_2S in gas streams removal is done by dissolving alkanol amine solution in it. The alkanolamine is regenerated in stripper and by using Claus process the H_2S gas so obtained is used for producing elemental sulphur. This is a lot of energy consuming process mainly in stripping and various other steps. So instead of producing sulphur if this H_2S rich amine can be used for producing different valuable chemicals, then it would of great value in refineries as H_2S is produced in large scale here.

High alkalinity of mono ethanol amine can be used for absorbing hydrogen sulphide gas. The reaction between benzyl chloride and H_2S rich mono ethanol amine gives benzyl mercaptan and dibenzyl sulphide which is of great industrial value and is a more valuable product than elemental sulphur. Dibenzyl sulphide is used as an additive for extreme pressure lubricants , anti-wear additive for motor oil, stabilizer for photographic emulsion, in refinery and recovery of precious metal and in different anti corrosive formulation. Benzyl mercaptan is having medicinal value and is used for the formation of herbicides.

The benzyl chloride and monoethanolamine are having different densities and hence, are of two different phase. Hence, for formation of desired product and for better reaction 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 H_2S rich monoethanolamine solution such as Tetra Butyl Ammonium Bromide, Poly ethylene glycol, etc. The problem with these liquid catalysts 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. Amberlite is used as it is not much costly and is easily available. The overall reaction can be represented by:

$$PhCH_2Cl + H_2S(\text{rich MEA}) \xrightarrow{\text{Amberlite IR 400}} PhCH_2SCH_2Ph + PhCH_2SH$$
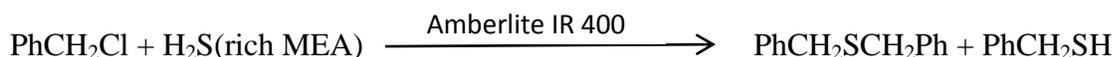
Various parametric studies were done for the reaction. In the studies various parameters like initial sulphide concentration, concentration of benzyl chloride, stirring speed were changed to study its effect on conversion of benzyl chloride with the proceeding of reaction (in min.).

4.2 RESULTS AND DISCUSSION

4.2.1 PARAMETRIC STUDY

4.2.1.1 EFFECT OF INITIAL SULPHIDE CONCENTRATION

For a fixed MEA concentration of 3.5M, the effect of variation of initial sulphide content was studied. With the increase of initial sulphide content, the conversion increases because of the presence of more amounts of sulphide ions. For fixed amount of MEA, the increase in the sulphide concentration decreases the MEA/sulphide mole ratio in the aqueous phase. This is responsible for determining the concentration of sulphide ion and hydrosulphide ion in MEA. Maximum conversion obtained here is around 76% which is quite a good value regarding solid catalyst.
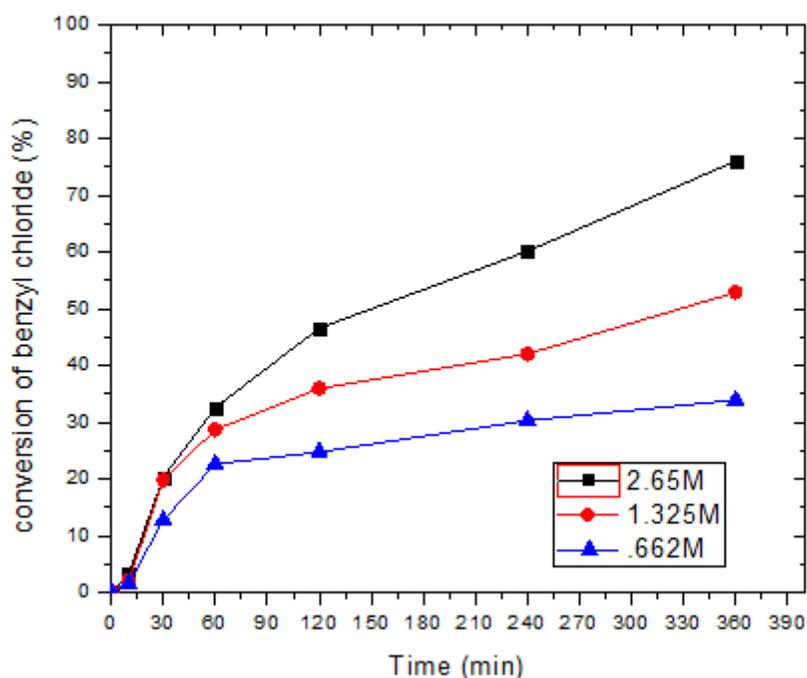

Fig 4.1 Initial sulphide concentration effect on Benzyl chloride conversion

Operating conditions:

Organic phase 50ml, aqueous phase 50 ml, benzyl chloride concentration 3.5M, stirring speed 1000rpm, temp 50°C.

4.2.1.2 EFFECT OF STIRRING SPEED

Elimination of mass transfer resistance is very important in order to do kinetic study. The effect of stirring speed was studied under the range of 500-1500 rpm, other conditions were kept identical in the presence of Amberlite IR 400 catalyst. From the graphs it is clear that for this range effect of stirring speed does not much effect on conversion of benzyl chloride. Therefore for any further reaction all the reactions can done with speed 1000 rpm.
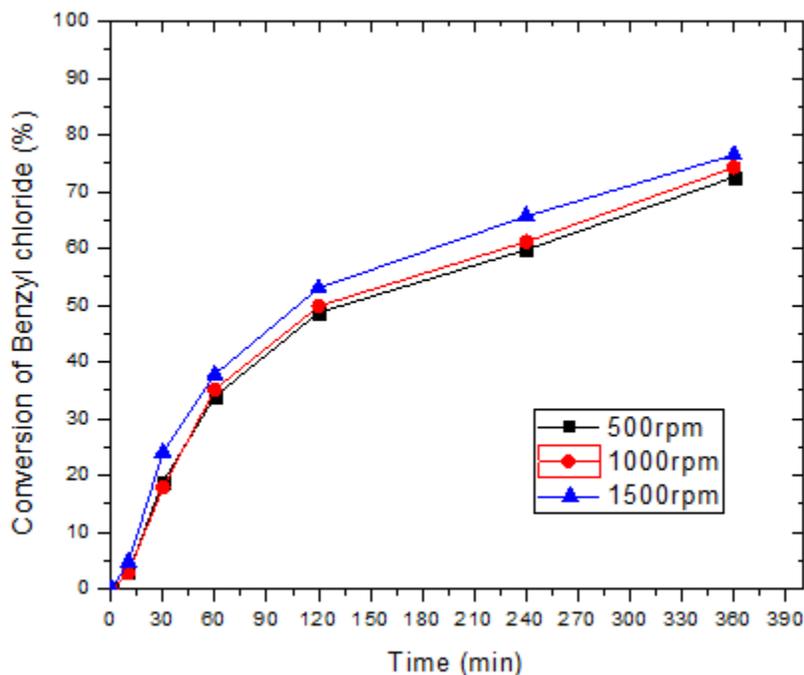

Fig 4.2 Stirring speed effect on Benzyl chloride conversion

Operating conditions:

Organic phase 50ml, aqueous phase 50 ml, benzyl chloride concentration 3.5M, initial sulphide concentration 2.65, temp 50°C.

4.2.1.3 EFFECT OF BENZYL CHLORIDE CONCENTRATION

The benzyl chloride concentration effect was studied on benzyl chloride conversion. We find that with the increase of benzyl chloride concentration the conversion of benzyl chloride decreases. This is because sulphide content is same for all cases but the benzyl chloride concentration increases that reduce the conversion. Maximum conversion obtained here is approximately 90% thus for low value of benzyl chloride concentration and high value of sulphide concentration this conversion is a good result.
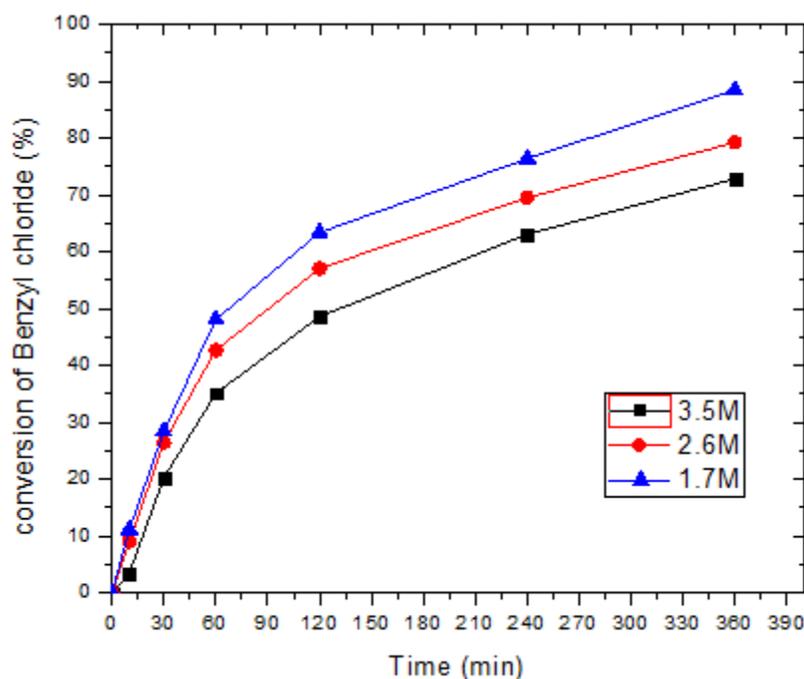

Fig 4.3 Benzyl chloride effect on Benzyl chloride conversion

Operating conditions:

Organic phase 50ml, aqueous phase 50 ml, initial sulphide concentration 2.65, temp 26°C, stirring speed 1000rpm.

4.2.1.4 RECYCLE AND REUSE OF AMBERLITE IR400

Being a solid catalyst in tri phase catalysis, catalyst is easy to recycle for the use or that purpose it is necessary to wash off and the procedure is as follows:

After the use the catalyst microsphere was filtered from the solution by the use of filter paper. It was washed with acetone and water and was dried to remove the adsorbed substance. Due to the absence of statistics its extent of use cannot be commented here.

4.3 CONCLUSION

In the present work reaction between benzyl chloride and H_2S rich MEA was performed in presence of Amberlite IR 400 which gives a liquid-liquid-solid catalysis. It has a promising industrial use due to its reusability. The effect of various parameters was studied on %conversion. Thus by taking proper combination of parameters, production of dibenzyl sulphide or benzyl mercaptan can be maximised. Low sulphide concentration or higher value of MEA/H_2S ratio, high benzyl chloride concentration and long reaction time favours the formation of DBS. Results obtained from analysis and graph are as anticipated from various previous work studies. Conversion of benzyl chloride is not poor against various parameters study in comparison to already done related work by various scholars. And this work has a very positive point of reusability of catalyst which is not present in many of the previously done works.

CHAPTER 5

CONCLUSION

CHAPTER 5

CONCLUSION

5.1 INTRODUCTION

The work done in this project can be easily adopted in industrial process for generation of dibenzyl sulphide and benzyl mercaptan from the hydrogen sulphide present in by product gas streams. According to the present process, H_2S present in the gas stream can be used for the production of DBS and BM in two steps:

1) Removal of H_2S gas from the gas stream by absorbing it in monoethanolamine solution.

2) Second step involves the production of DBS and BM using the H_2S rich MEA obtained from the first step

5.2 SUMMARY AND CONCLUSION

The reaction of H_2S rich monoethanolamine and benzyl chloride present with toluene as solvent produced DBS and BM which is very much valuable. One can selectively prepare DBS by keeping the initial sulphide content high, long reaction time and high benzyl chloride conversion. The reaction can be carried out for more than 360 mins as reaction was not complete even after this time. The Amberlite IR400 has great reusability property and can be reused again.

CHAPTER 6

FUTURE WORK

CHAPTER 6

FUTURE WORK

ABSTRACT

This chapter focuses on scope of further work based on results and conclusion of present study. This chapter is dedicated to finding the area where improvement can be done to get better conversion and selectivity.

6.1 INTRODUCTION

The work described in this thesis deals with the preparation of DBS and BM by using H_2S rich monoethanolamine and benzyl chloride by using tri phase catalyst with solvent. There are number of things where we could have and should have tried but we could not do because of lack of facility, finance and delay in the supply of materials.

6.2 INVESTIGATION OF MECHANISM AND ITS PATHWAY

With more extensive data and studies mechanism of the reaction can be determined. Aq. phase ions can be analysed to know the mechanics involved which will give rise to its pathway.

6.3 OTHER PARAMETERS EFFECT

There are many other parameters whose study can be done to better the production of dibenzyl sulphide. One such parameter is variation of temperature which can give rise to kinetic study of the reaction. Then there is effect of catalyst loading which change in conc. of catalyst in the reaction mixture and its effect on conversion of benzyl chloride.

Toluene is used as organic solvent which plays an important role as it effect the transport properties of PTC but it does not take part in chemical reaction hence organic solvent free reaction mechanism can be designed to see its effect on conversion because it will reduce the cost of reaction.

More over results obtained from chromatography, selectivity of Dibenzyl sulphide and benzyl mercaptan can also be studied.

6.4 OTHER AQUEOUS PHASE

The aq. phase used here is monoethanol amine instead of this Diethanol amine can be used or for even better results methyldiethanol amine can be used. These compounds being very expensive with respect to MEA are not used here but if circumstances arise they can give better hydrogen sulphide absorption.

CHAPTER 7

REFERENCES

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REFERENCES

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