SYNTHESIS OF DIBENZYL SULPHIDE BY USING PEG-6000 AS A GREEN CATALYST

THE THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUREMENTS
FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY IN CHEMICAL ENGINEERING

By

KUMUDA RANJAN MAHALING

109CH0509

Under the guidance of

DR. SUJIT SEN

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

May 2013

National Institute of Technology, Rourkela

CERTIFICATE

This is certified that Kumuda Ranjan Mahaling having roll no. 109CH0509 submitted his final thesis report on "Synthesis of Dibenzyl Sulphide by using PEG-6000 as Green Catalyst" in the fulfilment of requirements 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.

Date : 08.05.2013

Dr. Sujit Sen
Department of Chemical Engineering
National Institute of Technology
Rourkela
Rourkrla- 769008

ACKNOWLEDGEMENT

I would like to express my heartiest appreciation to my guide **Dr. Sujit Sen** as he continually and convincingly guide throughout the year for the completion of my project successfully. Also he helped me lot to provide proper knowledge about the experiment and many other sources.

I also wish to thank **Prof. R. K. Singh**, Head of Department and **Prof. H. M. Jena** for providing me an opportunity to carry out the work and express my indebtedness towards the Department of Chemical Engineering, NIT Rourkela, for supporting me in successfully completing the project. I also thanks **Mr. Dhruba Sakha,** technical assistant in the department of Chemical engineering, IIT Kharagpur to help us in analysis of samples.

Date- 08-05-2013

Kumuda Ranjan Mahaling
109CH0509
Dept. Of Chemical Engineering
NIT, Rourkela

ABSTRACT

Now a days Hydrogen Sulphide become a major pollutant for degradation of environment. So it is essential to remove this problem efficiently and effectively. The present project provides an alternative method to utilise the Hydrogen Sulphide to produce more economic, sophisticated product like Dibenzyl Sulphide and Benzyl Mercaptan. The whole process followed by the proper absorption of Hydrogen Sulphide in Monoethanolamine & then reacting the entire mixture with Benzyl Chloride to produce Dibenzyl Sulphide and Benzyl Mercaptan using Polyethylene Glycol 6000 as a phase transfer catalyst as the reaction involve two different phase. The main objective of this work is to maximize the conversion of Benzyl Chloride. It is also involve the analytical study of effect of different parameters like stirring speed, benzyl chloride concentration, sulphide concentration.

CONTENT

Content

List of Figures

List of Tables

List of Abbreviations

H_2S-Hydrogen Sulphide

MEA-Mono Ethanol Amine

PTC-Phase Transfer Catalyst

DBS-Dibenzyl Sulphide

PEG-Polyethylene Glycol

BM-Benzyl Mercaptan

BC-Benzyl Chloride

CHAPTER 1

INTRODUCTION

INTRODUCTION

1.1 Sources of Hydrogen Sulphide

Hydrogen Sulphide is a prime source of air pollution. It can produce both from natural sources and from men made process.

1.1.1 Natural Sources

There are a plenty of natural sources for the production of H_2S. A little amount of H_2S also present in crude petroleum. Natural gas is the main sources of H_2S as it contain up to 90% also. Volcanoes and some hot springs also emit some H_2S. It can be present in well water due to the action of sulphate reducing bacteria.

1.1.2 Men Made Sources

For the rapid growth in industrialisation, human activity contribute 10% total global emission of H_2S. Beside these the largest H_2S producer is petroleum refineries. Sulphur is liberated from the petroleum by the process of hydrodesulfurization by the action of hydrogen. The final H_2S converts to elemental sulphur via Claus process due to partial combustion. There are a lot of anthropogenic sources like coke ovens, paper mills, and tanneries. H_2S can be rise from rise anywhere when the elemental sulphur comes in vicinity of organic material subjected at high temperature.

1.2 Necessity for treatment of H_2S laden gas

The occurrence of the H_2S effects both the human body and also the plant equipments. Some of the immense reason for the removal of H_2S as follows:

- H_2S is odiferous in nature. Also corrosive in the presence of water and poisonous in very little concentration also. Therefore it is necessary to remove completely from gases stream before use and conveniently before transport.
- The occurrence of H_2S in refinery gas stream lead numerous damaging in subsequent process steps like deactivation of catalyst, corrosion of process equipment, undesired side reaction, increase in the process pressure requirement, and increase in the gas compressor capacity.

- Due to the toxic, inflammable and heavier than air, it is usually accumulate at the bottom of poor ventilated space. So it can have potential effect on human health as given in table given in table 1 by epa 1985:

Concentration(ppm)	**Physiological Effect**
0.1-3	Odour Threshold
3-10	Offensive Odour
10-50	Headache Nausea Throat and eye irritation
50-100	Eye Injury
100-300	Conjunctivitis Respiratory tract irritation, Olfactory Paralysis
300-500	Pulmonary Edema Imminent Threat to Life
500-1000	Strong Nervous System Stimulation
1000-2000	Immediate Collapse with Respiratory Paralysis Risk of Death

Table 1: Physiological Effect of H_2S on Human

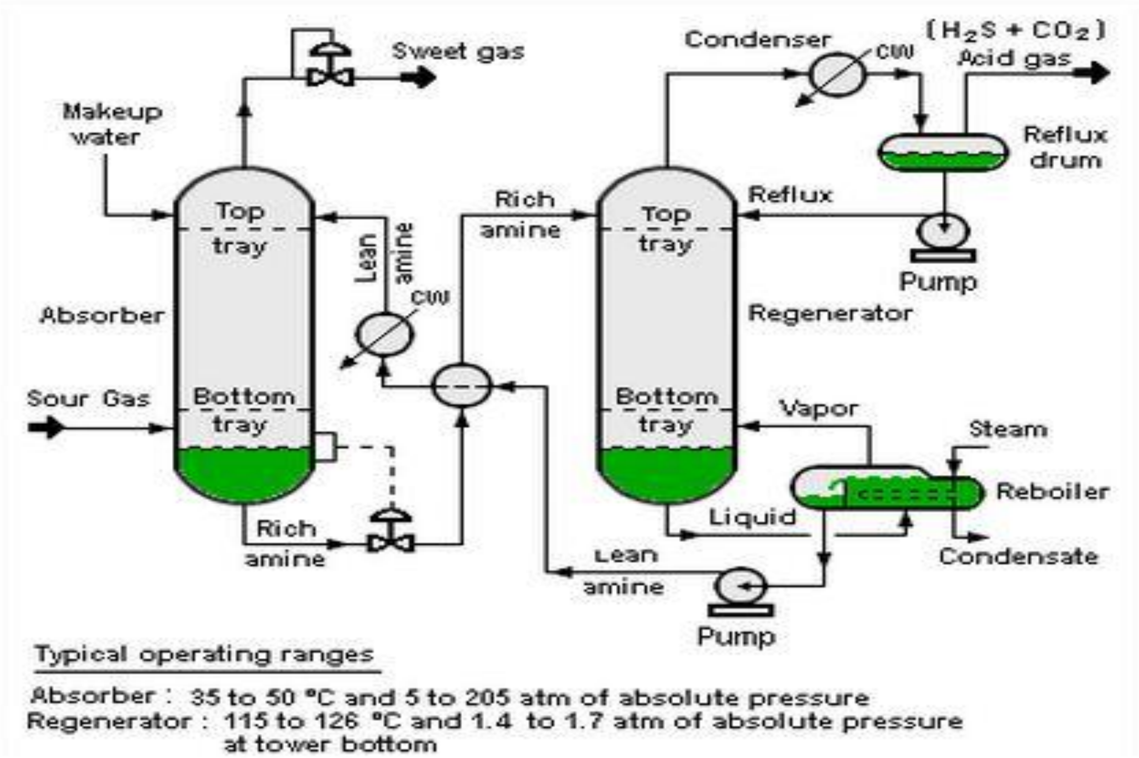
1.3 Industrial Process for Removal & Recovery of H_2S

For the safety of environment and health of human body industries have to control their H_2S emission up to a safe limit. There are number of industrial processes available for removal and recovery H_2S up to a safe limit. Due to weak acidic nature of H_2S, the removal of H_2S can possible by using alkaline solution. Irreversible chemical reaction products are likely formed by reaction between strong alkaline solutions like sodium hydroxide hence strong alkaline solution cannot be used for the removal of H_2S from the gas stream.

1.3.1 Alkanolamine based process

From the lot of H_2S removal industrial processes alkanolamine based process is accepted as commercial process. The greater advantage of this process is possible due to use of low vapour pressure and ease of reclamation. The low vapour pressure of alkanoamines leads the process operation to more flexible in the terms of temperature, operating pressure & concentration of alkanolamine in addition to the negligible vaporisation losses.

The process involves the treatment in circulating gas stream upward through a absorber and counter current to the stream of aqueous alkanolamine solution. The rich solution from the bottom of absorber is heated by the exchange of heat with lean solution from bottom of the stripping column and then it is fed to stripping column where the absorbed gases are used to stripped off from the alkanolamine solution. The alkanolamine is generated in the process is then recycled to the absorber. The rich H_2S gas is obtained from the top section of the stripping column then it is subjected to recovery or disposal of sulphur. The flow diagram of alkanolamine based process is shown in the Figure 1.



Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure at tower bottom

Figure 1. Schematic flow diagram of Amine base process

The alkanolamine have a hydroxyl group and one anime group so the hydroxyl group serve to reduce the vapour pressure and increase the water solubility while the amino group helps to maintain the alkalinity in water so the acidic gases gets absorbed. The reaction in the above process is as follow

Reaction with H_2S

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

$$RNH_2 + H_2S \rightleftharpoons RNH_3SH$$

Reaction with CO_2

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

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3CO_3H$$

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

1.3.2 Ammonia Based Process

The use of ammonia is also a method for the removal of hydrogen sulphide and also for the carbon dioxide from the gas stream. This process is mainly used in desulphurisation of coke oven gas. The basic principle in the removal of this process is:

Gas stream containing both H_2S and NH_3 is passed through a series of H_2S and a NH_3 scrubber. H_2S scrubber is fed with the stripped water from the top where ammonia is absorbed from the gas. The ammoniacal solution from the scrubber is used as absorbent in H_2S scrubber. The solution comes out from the unit contain ammonium sulphide which is used to decompose in the deacidifier to produce ammoniacal sulphide and H_2S. The reactions occurring in the above process is shown below:

$NH_3+H_2O \rightarrow NH_4OH$

$NH_3+H_2S \rightarrow NH_4HS$

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

The important advantages if ammonia based process over amine based process are:

- The gas containing both NH_3 and H_2S are passed with aqueous ammonia solution, the H_2S is get absorbed more easily and rapidly. Bye varying the concentration of liquid ammonia it is possible for the selective absorption of H_2S & NH_3 in liquid ammonia.
- The process is best for the gas stream containing both H_2S and NH_3. The removal of H_2S & NH_3 is possible done in single step in ammonia based process unlike amine process.

Beside these advantages the ammonia based process is also associated with some major difficulties so this process is no widely accepted. The difficulties are as follow:

- The high partial pressure of ammonia forces the scrubbing step to conducted with the relatively more dilute NH_3 solution or a relatively high pressure or a separate water wash step after the NH_3 scrubbing step in order to remove the NH_3 from the treated gas stream. The formation cost is increased with the use of dilute scrubbing solutions though it is conducted at higher operating temperature.
- The generation of rich absorbent solution is withdrawn from the scrubbing step involves the use of soluble catalysts, so there is possibility of contamination of contaminated product with the catalyst.

1.4 Recovery of Sulphur from Hydrogen Sulphide

1.4.1 Claus Process

Hydrogen sulphide is transformed into non- poisonous and better utility sulphur at most of the locations because of its objectionable nature. Patented after the name of the scientist Carl Friedrich Claus in 1883,this process has become an industrial benchmark. In this process, sulphur is retrieved from the gaseous hydrogen sulphide found in natural gases and other by- product gases containing hydrogen sulphide. These by-product gases originate from physical and chemical gas treatment units.

Process Description:

Hydrogen Sulphide gas is put forth in the Claus unit(Fig 2) after being separated from the host gas using amine extraction. In this unit, the gas undergoes 2 steps:

1. Thermal Step: The gas embedded with hydrogen sulphide reacts in a substoichiometric combustion with air in a reaction furnace at a high temperature (1000-1400^{0}C). Now the claus gases with the only combustible content “H_2S” is burnt in burner by the given chemical reaction-

$$2H_2S + 2\,O_2 \rightarrow SO_2 + 2H_2O + S$$

This includes a total flame free oxidation of H_2S generating Sulphur Di Oxide. one third of all H_2S is converted to sulphur di oxide in proper air to acid gas ratio.

2. Catalytic Step:- In this step, the reaction gases leaving the Sulphur condenser are heated again to 200-350 degree celcius and are put into a series of catalytic converter and sulphur condenser where a reaction takes place between H_2S and SO_2 to produce elemental sulphur:

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

A certain amount of H_2S residue remains in the tail gas which along with other trace sulphur compounds is dealt in the tail gas unit. This can provide an appreciable sulphur recovery of about 99.8% which can further be put forth to several other uses like manufacturing medicines, cosmetics, fertilizers.

Besides that it is accepted as the industrial process, it is associated with many drawback. Few of them are:

- High operation temperature
- Need of exact process control over oxygen and H_2S
- High sulphur content in tail gas, unacceptable to environmental regulation and safety

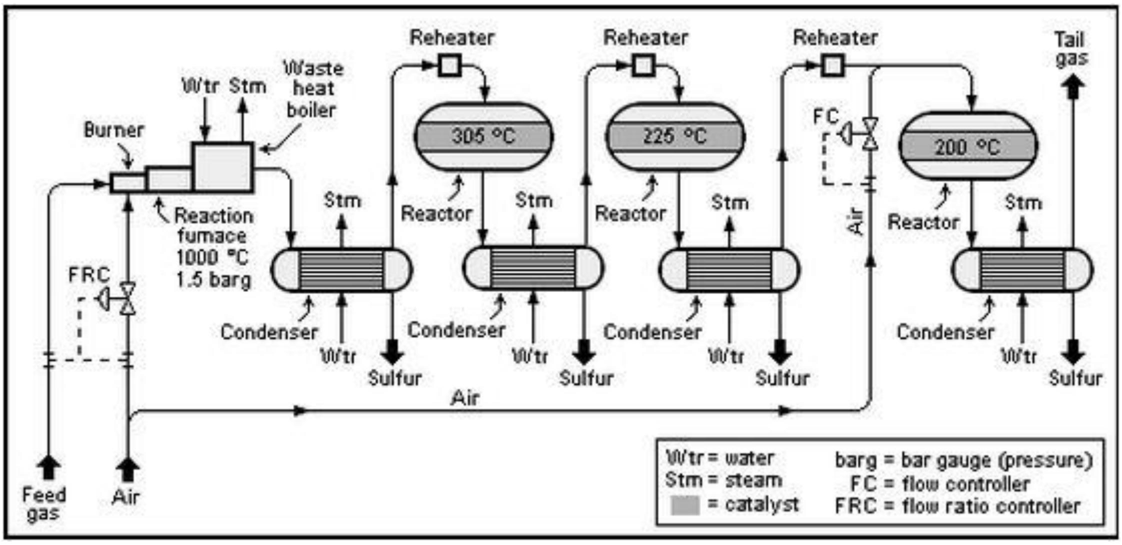


Figure 2.Schematic flow diagram of Claus Process

1.4.2 Wet Oxidation LO-CAT Process

This process mainly involves the conversion of H_2S into elemental sulphur with the help of an iron catalyst taking into consideration of environmental issues like the proper maintenance of environment. The iron catalyst wrapped by organic chelated agents in a clawed pattern is introduced in a solution. The claw like fashion is aimed at not allowing the precipitation of either iron sulphide or iron hydroxide. In this process, H_2S absorbed in aqueous LO-CAT solution is oxidized to produce elemental sulphur with the reduction of iron ions from ferric to ferrous state. The reduced iron ions are transferred from the absorber to the oxidizer which is the re-oxidation location of ferrous iron to ferric iron with the help of atmospheric oxygen absorbed into the LO-CAT solution thereby, regenerating the catalyst.

1.4.3 Crysta Sulf

This is a chemical process used in refineries to separate H_2S from natural gas and gas streams (Deptt. of Energy Report). In this process H_2S is converted into elemental sulphur with the help of a liquid phase claus reaction and the sulphur thus obtained is then removed by filtration. This can be a supplant to the Amine-Claus process.

Crysta Sulf process involves the spurting of heavy liquid hydrocarbon through an absorber where the liquid comes in contact with H_2S rich gas streams. In the subsequent step, H_2S gets absorbed from the gas stream and the resultant clean gas stream then leaves absorber. The H_2S prevailing in the liquid reacts with SO_2 to form elemental sulphur and water.

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

1.5 Present Work

The Claus or LO-CAT processes are the expansive process for the removal of the elemental sulphur from H_2S. So our current work is to produce alternative method to use H_2S to produce more valuable market product instead for going to recovery of elemental suphur.

It can be directly used the H_2S rich amine. The present work con be reduced to:

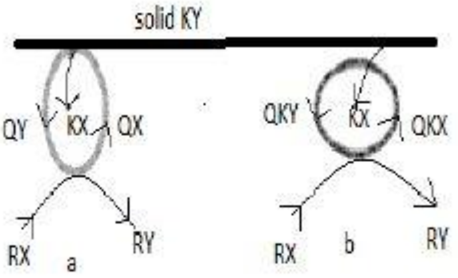
- More value added sophisticated products like dibenzyl sulphide, benzyl mercaptan can be produce from H_2S rich monoethanol amine. The entire reaction involve two phase, so a Phase Transfer Catalyst (PTC), Poly ethylene glycol-6000(PEG-6000) is in the reaction.
- Variation in conversion is studied by using the parameter like stirring speed, temperature, benzyl chloride concentration, sulphide concentration. Reusability of catalyst is also checked. This is prime advantages of using a solid catalyst over a liquid catalyst.
- Formulation of an apt and an operational mechanism which can easily utilise the impacts of various parameters on the rate of reaction and conversion so that the objective of reaction can be put forth in an explanatory fashion.

1.6 Phase Transfer Catalysis

Now a day’s Phase Transfer Catalysts have versatile use in many industries, because it enhance the reaction involving aqueous phase and organic phase. The PTC has many advantages given below:

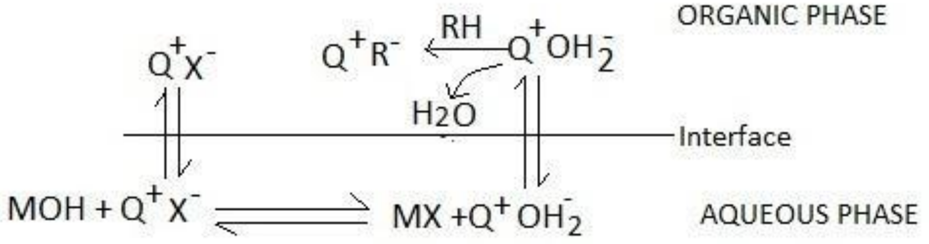
- Increase productivity
- Improve environmental performance
- Increase quality
- Reduce the solvent used
- Improve the selectivity
- Reduce the side reaction

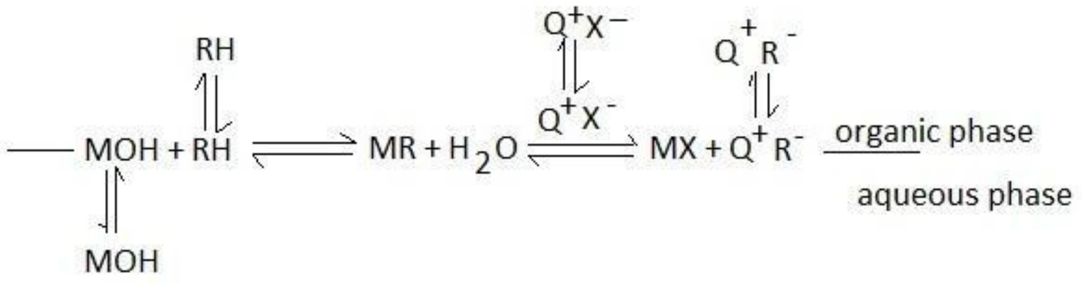
For the purpose of carrying out solid-liquid phase transfer catalysis, two mechanisms have been proposed. One among the two is suitable for conditions where the inorganic salt is substantially soluble in the given solvent and the catalyst is not able to contact the solid surface. The second mechanism is functional in situations where the inorganic salt is either insoluble or soluble in negligible proportions in the organic solvent and the catalyst can approach and react with the solid surface directly. This entire mechanism is coined as homogeneous and heterogeneous solubilisation. Increase in rate of reactions in solid-liquid phase due to small quantity of aqueous phase is termed as omega phase. Scheme 1.1 is a pictoral depiction of the 2 mechanisms:



a) Heterogeneous b) homogeneous solubilisation

Interfacial and extraction mechanisms are basically used to detail the liquid-liquid phase transfer catalysis based on the lipophilicity of the quaternary cation. The extraction mechanism (scheme 1.2) propounded by starks is applied to low lipophilic catalysts such as benzyltriethylammonium and tetrabutylammoniun salts. The interfacial mechanism(scheme 1.3) allows the catalysts such as tetrahexylammonium and trioctylmethylammonium to remain in the organic phase only owing to their high lipophilicity. In this phase anions are also exchanged across the liquid-liquid interface.





Solid phase transfer catalyst is well known as Tri Phase Catalysts (TPC), it have advantages associated with heterogeneous catalysts such as it can easily recover and reuse the catalyst and the reaction can be easily carried out in continuous reactor with continuously separating the catalyst.

1.7 Polyethylene Glycol-6000 (PEG) as Green Catalyst

PEG is widely used in many industrial processes because of its eco-friendly nature. These days the objective has shifted to not only increase the productivity but also doing it in such a way so as to have minimum adverse impact on the environment. Organic reactions without the use of harmful organic solvents are now of great interest inorganic synthesis. Attempts have been made to develop solvent-free chemistry, which to some extent have been successful in a few transformations. PTCs like TBAB and cryptands are very harmful to environment and also they are very difficult to recover and reuse. But the PEG is far away from these disadvantages. PEG and its monoethyle ethers are thermally stable, inexpansive, recoverable, and also non toxic media for phase transfer catalysis. The figure of PEG depicted below

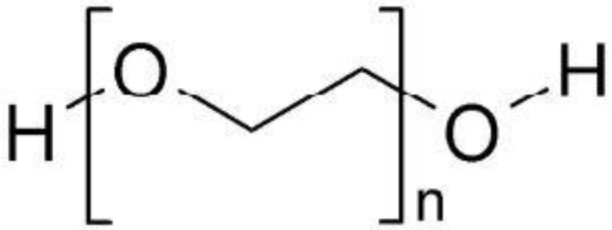


Figure 3. Structural formula of PEG

CHAPTER 2

LITERATURE SURVEY

LITERATURE SURVEY

Kohl and Neilson, 1997, had used the ammonium hydroxide for the removal and recovery of hydrogen sulphide. This process was developed by Hamblin, 1973, which was focus on sulphur recovery.

Various alkanolamine are now a days in use for the removal of hydrogen sulphide from the gas stream. Lot of research work has been done to study the solubility of hydrogen sulphide and carbon dioxide. The experimental data of solubility has been mathematically represented by Austgen et al., 1989, Lee et al.

Pradhan and Sharma, 1992, had studied the effect of catalyst on basic alumina and Amberlyst, on the reaction benzyl chloride and para chlorobenzyl chloride with solid sodium sulphide. The catalyst used in this case is Tri Phase catalyst.

G.D Yadav and S.S Naik(2000) , prepared a clay supported phase transfer catalyst and used it for the preparation of benzoic anhydride from benzoyl chloride and sodium benzoate using clay-supported quaternary ammonium salts at 30 °C They found that clay supported catalyst were more active than polymer supported catalyst.They found the selectivity to be 100%.

Pradhan and Sharma, 1990, had produced DBS and para chlorobenzyl sulphide by reacting respective chlorides with sodium sulphide using different types of catalysts under L-L and L-S mode. Out of the six catalyst they tried, TBAB(Tetra Butyl ammonium bromide) was found to be the best.

Sujit Sen, Patwardhan, S K Maity, N C Pradhan, 2007, DBS was synthesized by reacting benzyl chloride and aqueous ammonium sulphide using TBAB as phase transfer catalyst. The parametric study was done on the selectivity of DBS. It was found that DBS can be selectively prepared by keeping high benzyl chloride concentration, High NH_3/H_2S ratio.

S.K.Maity,Narayan C Pradhan ,Patwardhan, 2008, had reduced p-nitrotoluene by using SR400 as a triphase catalyst with aqueous ammonium sulphide. 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.

B Gao, Z Wang, L Wang, 2010, studied the effect of different type of quaternary salt type tri phase catalyst on the esterification reaction of benzyl chloride with sodium acetate. They found that 1) Among quaternary phosphonium and quaternary ammoninum type TPC,ammonium type have the higher activity than quaternary ammonium-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 groupand hence influences the catalytic activity.

CHAPTER 3

EXPERIMENTAL SETUP

EXPERIMENTAL SETUP

3.1. Chemicals

1. Monoethanolamine (>99%) from Loba Chemie (India) Pvt. Ltd. Mumbai
2. Toluene from RFCL Limited, New Delhi, India
3. Benzyl chloride (>99%) from Merck (India) Ltd., Mumbai
4. PEG-6000 from Thermo Fisher Scientific India Ltd., Mumbai
5. H_2SO_4 (98%) and NaOH pellets (97%) from Merck (India) Ltd., Mumbai
6. Na_2SO_4 (>99%) from Merck (India) Ltd., Mumbai
7. KI (>99.2%) from Merck (India) Ltd., Mumbai
8. KIO_3 (>99.5%) from Merck (India) Ltd., Mumbai

3.2 Equipment

All the reactions was carried out in a mechanically agitated glass reactor of capacity 250cm^3.A 2cm diameter ,4 bladed turbine impeller was used for stirring the reaction mixture. The stirrer was kept at a height of 1.5cm (approx.) from the base of reactor and it was having the provision for speed control. The reactor was kept in a water bath so that a fixed temperature can be maintained. The schematic diagram is as shown in the figure 4

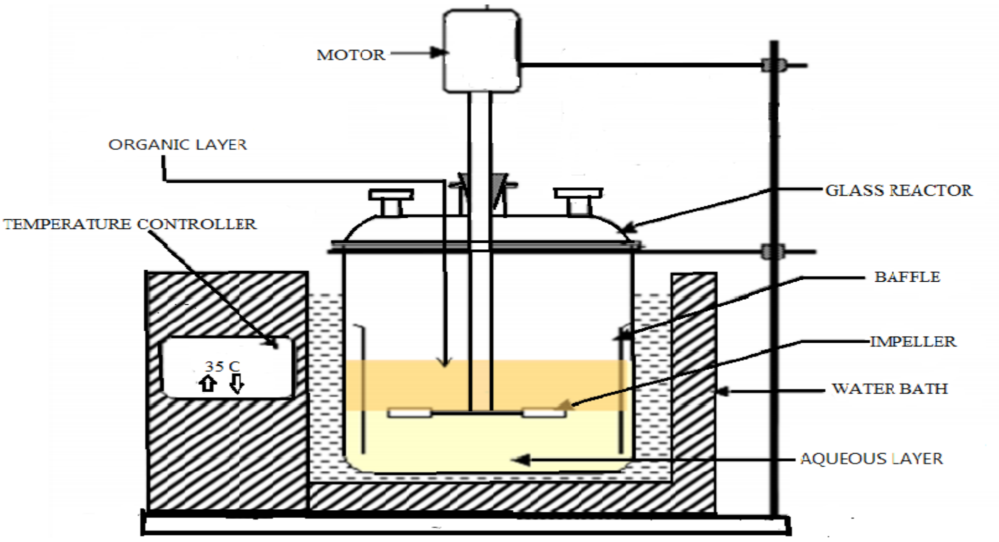


Figure 4. Schematic diagram of Batch Reactor

3.3 Preparation of H_2S-rich Monoethanolamine

To prepare the 30-40% of MEA solution, appropriate amount of MEA was mixed with distilled water. Then the mixture was kept in two bubblers. Iron sulphide pellet was poured into the kipps apparatus, the dilute sulphuric acid was allowed to pass through the top. The reaction was taken place and H_2S was liberated. The reaction is as follow:

Then the H_2S gas was allowed to pass through series of MEA bubbler. According to Kohl and Nielsen, 1997, the reaction between H_2S and MEA is exothermic, the gas bubblers containing MEA solution were kept immersed in ice bath to prevent the oxidation of sulphide and also to increase the absorption of H_2S in MEA solution as absorption increases with decrease in temperature. The unabsorbed H_2S gas from the first bubbler was used to send the second gas bubbler containing MEA solution so that the H_2S gas is vented out under prescribed environmental norms and condition. When the bubbling of H_2S was stop, the H_2S rich MEA solution was withdrawn and its sulphide concentration was analysed, Scott, 1966. Unless the desired concentration of H_2S was not obtained in MEA solution, the gas bubbling was continued. The schematic diagram is shown in fig 5

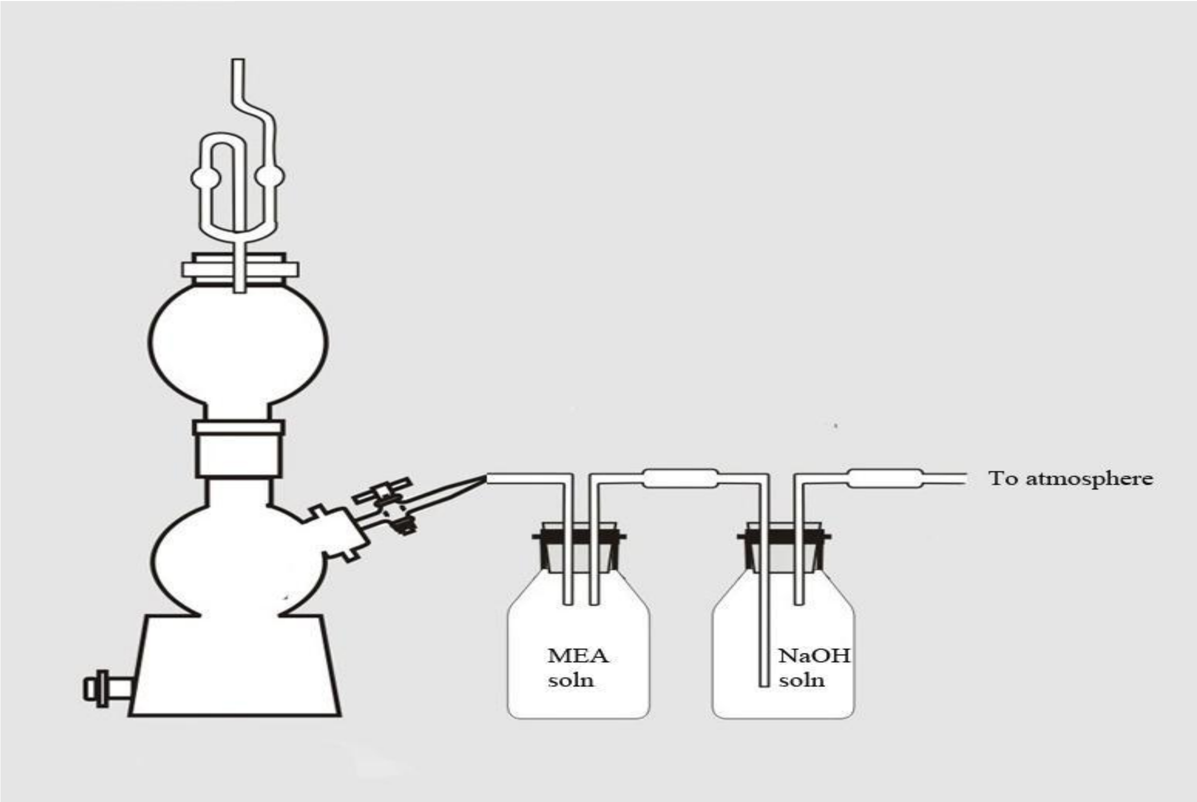


Figure 5.Schematic diagram of Kipp’s apparatus

3.4 Experimental Procedure

In a typical experimental run, 50cm^3 of aqueous phase containing a known concentration of sulphide was charged into the three neck batch reactor. The amount of catalyst required was weighed and fed into the reactor by the help of funnel. Then 20 ml of benzyl chloride was added as reactant and then 30 ml of toluene was added as organic solvent. The reaction mixture was then agitated at constant stirring rate. On regular time interval of 10 min, 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 for 10 minute.

3.5 Analysis

3.5.1 Analysis of Organic Phase

All samples from the organic phase were analyzed by gas liquid chromatography (GLC) using a 2 m × 3 mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A Chemito Model 8610 GC was used for the analysis. An FID detector was used with nitrogen as the carrier gas during the analysis.

3.5.2 Determination of Sulphide concentration

The Initial sulphide concentrations were determined by standard iodometric titration method (Scott, 1966) as given below.

<u>Preparation of Standard (0.1 M) sodium thiosulphate solution:</u>

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

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.

$$2\, Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

Therefore, from the above reaction it can be seen that for every 1mole of KIO_3, 6 mole of $Na_2S_2O_3$.

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

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 was 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. Then 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:

$$4IO^{3-}+6OH^{-}+3S^{2-} = 3SO_4^{2-} + 4I^{-} +6H_2O$$

From the above balanced reaction we can see that 4mole of iodate ion is equivalent to3moles 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

CHAPTER 4

RESULT AND DISCUSSION

RESULT AND DISCUSSION

4.1 Introduction

For the environmental norms, the refineries are subjected to H_2S removal. The H_2S removal from the gas stream is mainly carried out by absorption of H_2S in alkanol amine solution. After the absorption of H_2S, alkanol amine is recovered from the stripping unit. The H_2S is sent for removal of elemental sulphur in Claus process.

Now the whole study provide a alternative for the Claus Process as it directly used the H_2S rich alkanol amine solution instead sending for stripping unit then the elemental sulphur recovery unit. In the present work the H_2S rich MEA solution is allowed to react with the BC to produce DBS and BM, which have better market value which are discussed in the conclusion. The overall reaction can be depicted as below in fig-6

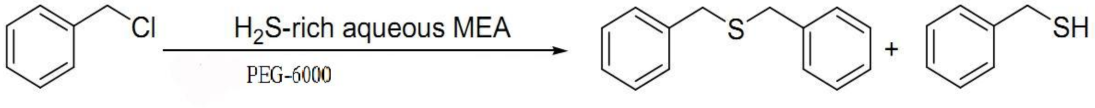


Figure 6.Representation of Overall Reaction

The reaction involves between the H_2S rich MEA and BC occur in different phase, the H_2S rich MEA in aqueous phase and BC in organic phase. Hence for the better reaction between them it is required to use a phase transfer catalyst. PEG-6000 solid is used as PTC as it is cheaper and also non toxic in nature. Also it is more easily recovered and reused.

The parametric study is done with the variation of stirring speed, temperature, benzyl chloride concentration, sulphide concentration.

4.2 Result and Discussion

4.2.1 Effect of Stirring Speed

To determine the role of mass transfer in the system as increasing the speed the mass transfer coefficient increase. So the stirring speed is increase from 500 rpm to 2000 rpm and the corresponding conversion rate is observed and plotted in on the graph. From the graph (Fig 7) we observe that there is less increase in the conversion of BC although the speed varied so much. So we conclude that the conversion of BC is independent of stirring speed and mass transfer factor do not effect as much to the conversion. So the process is not controlled by mass transfer but only by reaction kinetics. So it is preferable to use medium speed for the process.

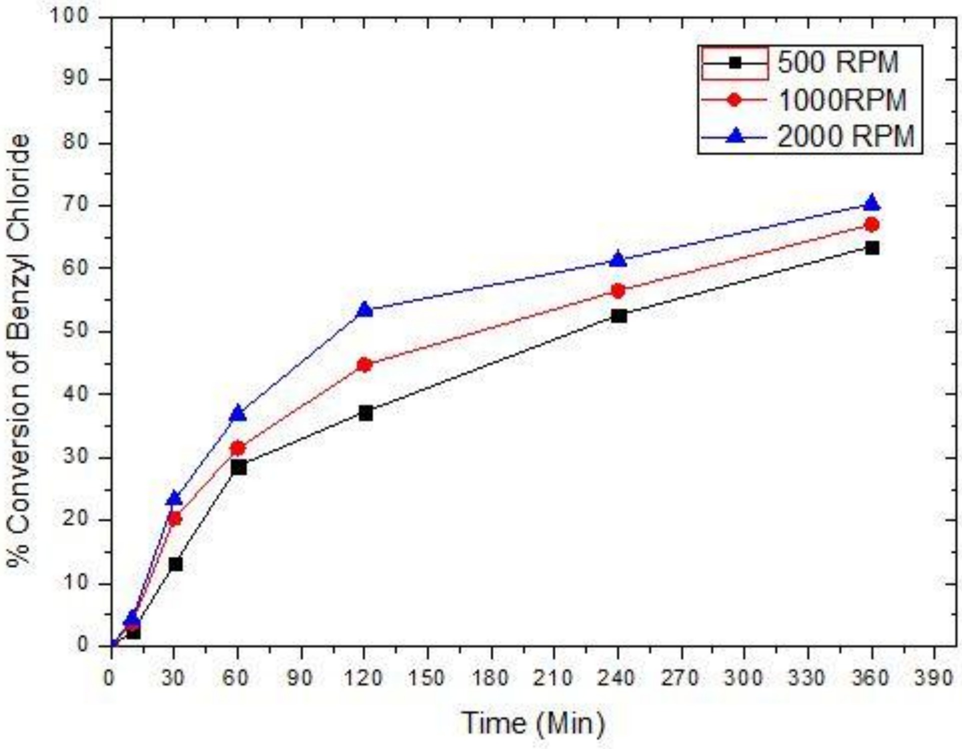


Figure 7: Effect of Stirring Speed on BC conversion

Operating Condition: Volume of Organic Phase-50ml, Volume of Aqueous Phase-50ml BC concentration-3.5M, Initial Sulphide concentration-2.35M, Catalyst Loading-5% (W/V), Temperature-25^0 C

4.2.2 Effect of Sulphide Concentration

From the graph (Fig 8), it was concluded that the conversion rate increased as the sulphide concentration increase. This can be explained by considering the fact that although MEA as such does not participate in the reaction with BC, it does affect the equilibrium among MEA, H_2S, and water, which results in two active anions, sulfide (S^{2-}) and hydrosulfide (HS^-), in the aqueous phase. These two active anions participate in two different reactions. In the presence of a base (MEA), the dissociation equilibrium shifts toward more ionization and the concentration of sulfide ions, relative to hydrosulfide ions in the aqueous phase, increases as the MEA concentration increases. Therefore, only by changing the MEA concentration with constant sulphide concentration in the aqueous phase, it would be easy to prove the existence of two different reactions.

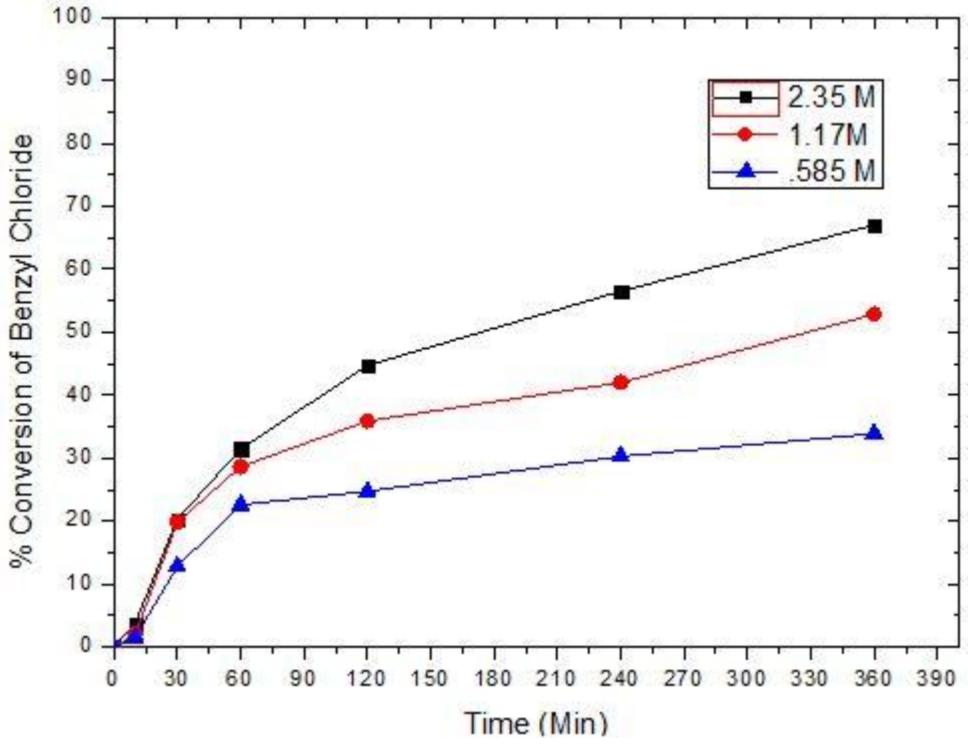


Figure 8: Effect on Initial Sulphide concentration on BC Conversion

Operating Condition: Volume of Organic Phase-50ml, Volume of Aqueous Phase-50ml BC concentration-3.5M, Stirring Speed-1000 RPM, Catalyst Loading-5% (W/V), Temperature-25^0 C

4.2.3 Effect of Benzyl Chloride Concentration

The effect of BC concentration in conversion was shown in fig 9. From the graph it was observed that with increase in the concentration of BC the conversion rate get reduced. This is happened because there is limited amount of sulphide present in the aqueous phase as simple there same amount of sulphide concentration in all the case but as BC concentration increase the availability reduce.

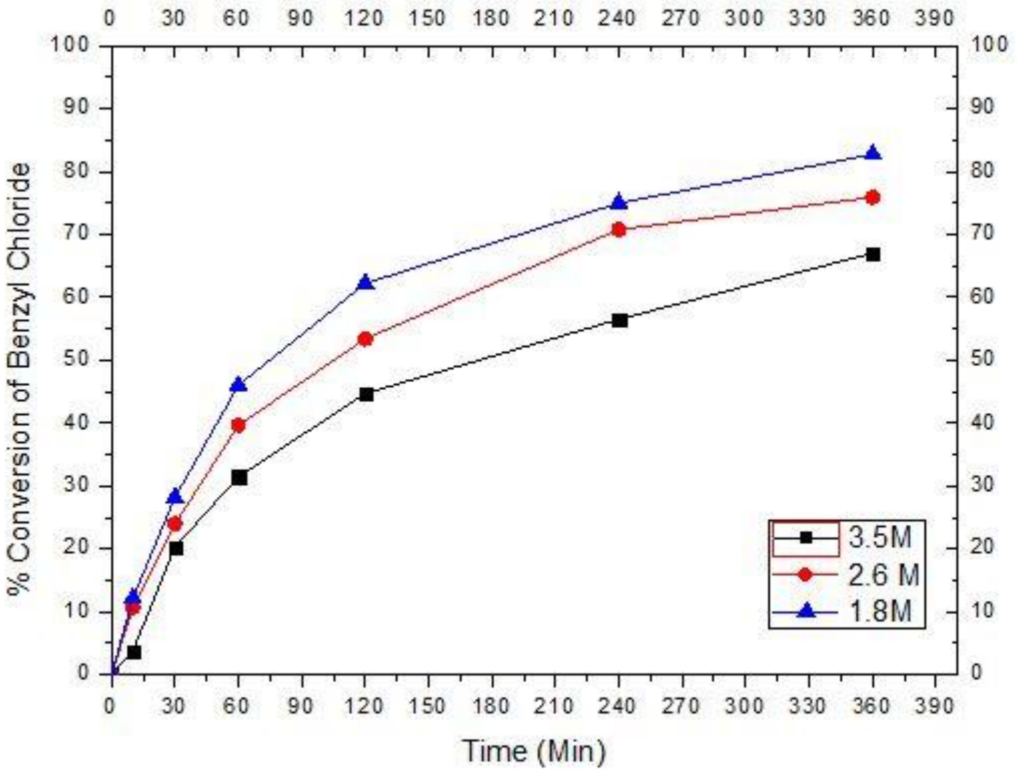


Figure 9: Effect on BC concentration on BC Conversion

Operating Condition: Volume of Organic Phase-50ml, Volume of Aqueous Phase-50ml, Initial Sulphide concentration-2.35M, Catalyst Loading-5% (W/V), Temperature-25^0 C, Stirring Speed-1000 RPM

CHAPTER 5

CONCLUSION

CONCLUSION

The entire process provides an alternative path for production of DBS and BM as a product which have greater market value from the non valuable H_2S present in different gas streams. The DBS or BM can be selectively produces by use of PTC.

The study doesn’t involve all the parameters for the reaction due to technical problem. From the experimental observation it was found that by increasing the initial sulphide concentration and decreasing the BC concentration the production of DBS was optimum. So if we study further more parameters like temperature, we would get enough data to optimize the entire process with suitable reaction mechanism and kinetic model.

Some application of the DBS

- Anti wear additive for motor oils
- Additive for extreme pressure lubricant
- Stabilising agent for the photographic emulsion
- Anticorrosive formulation
- In refining and recovery of precious metals

BM have also wide application as raw material for the synthesis of herbicides in thiocarbamate family such as esprocarb, prosulfocarb, tibocarbazil.

CHAPTER 6

SCOPE FOR FUTURE WORK

SCOPE FOR FUTURE WORK

6.1 Introduction

The present work describes the preparation of DBS and MC by H_2S rich MEA and BC in the presence of PEG-600 as a triphase catalyst. Further study can be done to understand the reaction.

6.2 Finding out Effect of Other Parameter

To find out the proper mechanism of the reaction effect of temperature has to study which also necessary for modelling also. This can be also help to increase the conversion and decreasing the use of catalyst.

Catalyst loading is also another parameter which has an important role in the reaction. on increasing the catalyst loading conversion would increase.

6.3 Use of Other Aqueous Phase

The aqueous phase used in the present work is MEA which can absorb both CO_2 and H_2S. Our present work is applicable for the stream containing H_2S and CO_2, only if the aqueous phase is H_2S selective. So other aqueous phase can be used having more H_2S selectivity.

REFERENCE

Maity S.K., Pradhan N.C. , Patwardhan A.V., Kinetics of the reduction of nitrotoluenes by aq. ammonium sulfide under liquid-liquid phase transfer catalysis, Applied Catalysis A: General 301 (2000), pp. 251-258

Maity S.K., Pradhan N.C. , Patwardhan A.V., Reaction of benzyl chloride with ammonium sulfide under liquid-liquid phase transfer catalysis: Reaction mechanism and kinetics, Journal of Molecular Catalysis A: Chemical 250 (2006), pp. 114-121

Maity S.K., Pradhan N.C. , Patwardhan A.V., Kinetics of reduction of nitrotoluenes by H2S rich aqueous ethanolamine, Industrial and Engineering Research, 45 (2006), pp 7767- 7774

Maity S.K., Pradhan N.C. , Patwardhan A.V., Reduction of o-nitroanisole to o-anisidine by H2S rich aqueous diethanolamine: A novel method for utilization of H2S laden gas streams, Chemical Engineering Science, 62 (2007), pp. 805-813

Maity S.K., Pradhan N.C. , Patwardhan A.V., Kinetics of phase transfer catalyzed reduction of nitrochlorobenzenes by aqueous ammonium sulfide: Utilization of hydrotreater off-gas for the production of value-added chemicals, Applied Catalysis B: Environmental 77 (2008), pp. 418-426

Maity S.K., Pradhan N.C. , Patwardhan A.V., Reduction of p-nitrotoluene by aqueous ammonium sulfide: Anion exchange resin as a triphasic catalyst, Chemical Engineering Journal 141 (2008), pp. 187-193

Maity S.K., Sen S., Pradhan N.C. , A new mechanistic model for liquid-liquid phase transfer catalysis: Reaction of benzyl chloride with aqueous ammonium sulfide, Chemical Engineering Science 64 (2009), pp. 4365-4374

Sen S., Maity S.K., Pradhan N.C., Utilization of hydrogen sulfide for the synthesis of dibenzyl sulfide: Effects of process parameters on conversion and selectivity, International Journal of Chemical Science: 5 (4), 2007, pp. 1569-1578

Pradhan N.C., Sharma M.M., Solid-Liquid reactions catalyzed by alumina and ion exchange resin: Reactions of Benzyl Chloride/ p-Chlorobenzyl Chloride with solid sodium sulfide, Industrial and Engineering Chemistry Research, 31 (1992), pp. 1610-1614

Yadav G.D., Badure O.V., Role of third phase in intensification of reaction rates and selectivity: Phase transfer catalyzed synthesis of benzyl phenyl ether, Industrial and Engineering Chemistry Research, 46 (2007), pp. 8448-8458

Kamal A., Reddy D.R., Rajendar, A simple and green procedure for the conjugate addition of thiols to conjugated alkenes employing polyethylene glycol (PEG) as an efficient recyclable medium, Tetrahedron Letters, 46 (2005), pp. 7951–7953

Naik S.D., Doraiswamy L. K., Phase Transfer Catalysis:Chemistry and Engineering, Reactors, Kinetics and Catalysis, 44 (1998), pp. 612-646

Hamblin, R. Removal and Recovery of Sulfur from a Gas Stream Containing Hydrogen Sulfide. Patent No. US3728441, 1973.

Harvey, W. W.; Makrides, A.C. Process for Removing Hydrogen Sulfide and Ammonia from Gaseous Streams. Patent No. US4192854, 1980.

Kohl, A.L.; Nielsen, R.B. Gas purification, Gulf Publishing Company Houston, Texas, 1997.

Plummer, M.A. Process for Recovering Sulfur and Hydrogen from Hydrogen Sulfide. Patent No. WO9412431, 1994.

Plummer, M.A.; Beazley, P.M. Conversion of Hydrogen Sulfide to Sulfur and Hydrogen. Patent Number US4592905, 1986.