
**PARAMETRIC STUDIES ON SYNTHESIS OF DI-BENZYL
SULPHIDE USING H₂S AND ALIQUAT-336**

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PARAMETRIC STUDIES ON SYNTHESIS OF DI-BENZYL SULPHIDE USING H₂S AND ALIQUAT-336

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Certificate

This is to certify that the thesis entitled “Parametric studies on synthesis of Di-benzyl sulfide (DBS) using hydrogen sulfide (H_2S) and Aliquat-336” submitted by ALISHER KHAN (109CH0581) to the National Institute of Technology Rourkela, Rourkela, in partial fulfillment of the requirements for the prescribed curriculum of Bachelor of Technology in Chemical Engineering Session 2009-2013. This is an authentic work carried out by him under my supervision and guidance.

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Abstract

The Crude oil contains a little percentage of sulfur in it with some composition. Removal of sulfur from crude is an essential purpose because sulfur can corrode the system and may lead to unwanted side reactions, which is a cause of reactants and energy consumption. Sour crude oil which is h high sulfur contents is being forced to process in oil refineries. In refineries, sulfur is removed by absorption in ammonia solution which is further processed in the “Claus Unit” to get elemental sulfur from H_2S . Claus process of producing elemental sulfur is a highly energy expensive process. And outside supply demand of elemental sulfur is not so high thereby eroding the profit-margins. With a view to making more sophisticated fine chemicals which have higher usability and better market value, this project was undertaken to study parameters on synthesis of Di-benzyl sulfide using hydrogen sulfide and Aliquat-336. The objective of this work is to maximize the Di-benzyl sulfide conversion from hydrogen sulfide (H_2S), which need to maximize the conversion of benzyl chloride. In this work the benzyl chloride has been used along with toluene as a solvent. H_2S rich MEA is used as a reactant in this project. The MEA and benzyl chloride are two different phases and normally their reaction is very difficult. So to carry out this reaction a phase transfer catalyst Aliquat-336 is used so that these two immiscible reactants can react. Phase transfer catalyst is useful primarily for performing reaction between anions and neutral compound from the aqueous or solid phase into the organic reaction phase where the anion or neutral compound can freely react with the organic reactant already located in the organic phase. Phase transfer catalyst is not likely to be involved in the manufacture of large tonnage heavy organic chemicals but is an unusual an elegant catalytic technique that is energy sparing and gives high yields at low residence times under mild conditions.

Keywords: Hydrogen sulfide, Benzyl Chloride, Di-benzyl Sulfide, Phase Transfer Catalyst, Conversion, Mono-ethanol-amine, Aliquat-336

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Nomenclature

- **DBS- Di-benzyl Sulfide**
- **H₂S- Hydrogen Sulfide**
- **BM- Benzyl Mercaptan**
- **MEA- Mono-ethanol-amine**
- **BC- Benzyl Chloride**
- **PTC- Phase Transfer Catalyst**

Chapter 1

Introduction

1.1 Introduction

In refineries, crude oil is refined on the basis of boiling point separation by distillation process. There are different types of distillation units present in refineries. Mainly, crude oil contains products like hydrocarbons, liquefied petroleum gas (LPG), kerosene, diesel, petrol, bitumen, light naphtha and heavy naphtha etc. which are recovered by distillation in a distillation column. Some impurities like sulfur, nitrogen and some amount of phosphorous also present in crude oil along with above products. By the processing of crude in refinery, removal of sulfur is in the form of hydrogen sulfide. Now hydrogen sulfide is further process in different units to utilize hydrogen sulfide. Refineries are hydro-treating such a heavy crude and bringing down levels of sulfur content and nitrogen content up-to environmental acceptable conditions. Process of hydro-treating of heavy crude oil gives large amount of hydrogen sulfide and ammonia. Removal of ammonia is done by scrubbing stream of hydrogen sulfide and ammonia, with water and hydrogen sulfide is recovered in amine treating unit. Hydrogen sulfide is further processed by Claus process to get elemental sulfur. Elemental sulfur is used in rubber industry and as well as in production of sulfuric acid. Due to low market value of elemental sulfur compare to cost of producing elemental sulfur from hydrogen sulfide, Claus process is not so efficient so, any process of treating hydrogen sulfide to get some value added product will be very useful in refineries. The present work was done to synthesize di-benzyl sulfide and benzyl mercaptan by using hydrogen sulfide gas. Nearly 42% hydrogen sulfide is present in natural gas. Elemental sulfur or sulfur containing compound comes in contact with some organic materials to give hydrogen sulfide at high temperature. Production of hydrogen sulfide is in sulfur extraction process, in waste water treatment plants, in coke ovens, in wood pulp production and mostly in oil refineries.

1.2 Hydrogen Sulfide

Hydrogen sulfide gas (H_2S) is a colorless gas with rotten egg smell. H_2S is heavier than air. H_2S is flammable and corrosive in nature. H_2S is corrosive and very poisonous gas. Various petroleum and coal industries lead to produce gaseous by-product, H_2S is also present a by-product in these industries. In absence of air, bacterial breakdown of organic matter results in production of hydrogen sulfide gas and this process of producing H_2S is named as anaerobic digestion. A small amount of H_2S is also produced by human body which is used as in signaling

molecule. H_2S is also produced from animal wastes and sewage. H_2S also present in natural gases, in some long time storage water and also in volcanic gases. H_2S is also named as gas which includes sewer gas. Liquid form of H_2S also exists, which is liquid compressed gas. Marine aquariums, is also surprising to be a source of H_2S , particularly those, who build up with fine sand like aragonite. There, absence of air is created due to presence of tightly packed layer of sand at higher depth, which allows anaerobic bacteria for production of H_2S . This phenomenon is also confined in industries like the food industry, the pulp and paper industry and in digestion. There are some other sources of hydrogen sulfide include natural gas and petroleum extraction and refining, rayon textile production, waste disposal and chemical manufacturing. Industrially, largely accepted process, to produce sulfur free natural gas is hydro desulfurization. All the refineries have only one option of processing heavy crude with soaring contents of nitrogen and sulfur in it. Environmental conditions of presence of sulfur contents and nitrogen contents in atmosphere is to be maintained up to set level by processing heavy crude oil. In coal processing industries, there are some process which is responsible for emission of ammonia and hydrogen sulfide. Hydrogen sulfide is often found in some mineral rock and in oil and natural gas deposits. Hydrogen sulfide is found in following:

- The petroleum industry, especially refineries where hydrogen sulfide is removed from oil and natural gas and in pipelines where unrefined petroleum is transported.
- Hydrogen sulfide is a by-product in the pulp and paper industry where wood breaks down in pulp.
- Hydrogen sulfide is released in the construction industry, at the time of excavation work in landfills or swamps.
- Hydrogen is also released during treatment in sewers or sewage plants, manure tanks and also from organic material breakdown in absence of oxygen/air.
- Hydrogen sulfide may also present in some mines and tunnels mineral rock.
- Hydrogen sulfide also found in coke ovens and some iron smelters.

Crude petroleum contains small amount of hydrogen sulfide whereas natural gas may contain up to 90%. Hydrogen sulfide can be resulted from action of sulfide reducing bacteria which is

generally found in well water. The coal gas has about 0.3 to 3% hydrogen sulfide content. Around the globe 10-12% of the total emissions of hydrogen sulfide are due to human activity.

1.3 Need for treating hydrogen sulfide gas

Hydrogen sulfide (H_2S) is highly toxic and hazardous gas because of its flammable nature (flammable range: 4.3-4.6%). H_2S gives blue flame when it burns with oxygen/air and formation of sulfur-di-oxide along with some amount of water. H_2S can corrode process equipment in refineries. H_2S deactivates the catalyst in the reactor which may be a big problem. Required process pressure is increased from undesired side reactions which results in increase in the capacity of gas compressor. H_2S is heavier than air so that it tends to accumulate at the lower level of less ventilated spaces. H_2S quickly deadens the sense of smell, although it is very pungent at first, so victim may be too late to identify the presence of H_2S . It is considered to be a broad-spectrum poison so that it is harmful to several systems in the body and mostly affected to nervous system. Exposure to lower concentration of hydrogen sulfide may be resulted to eye irritation, shortness of breath, nausea, fluid in the lungs and a sore throat and cough. It is believed that these effects are due to reaction of hydrogen sulfide with alkali present on moist surface which results in the formation of caustic, sodium sulfate. A time of few weeks is spent in process of going these symptoms away.

1.4 Industrial process for recovery of hydrogen sulfide

There are many industrial processes have been developed for removal of hydrogen sulfide which brings its concentrations up to acceptable limits for confirmation of strictly environmental conditions. Hydrogen sulfide can be used in alkaline solution so removal of hydrogen sulfide can be effected due to weakly acidic nature. Solution which weakly alkaline in nature, can be used to remove and recover hydrogen sulfide. Strongly alkaline solution like potassium hydroxide and sodium hydroxide cannot be used to remove hydrogen sulfide from gas stream where hydrogen sulfide and carbon dioxide are present. This is because irreversible reaction takes place in between weakly acidic hydrogen sulfide and strongly alkaline sodium hydroxide. Some industrial processes for recovery of hydrogen sulfide are discussed as follows:

1.5 Sulfur recovery from hydrogen sulfide

Sulfur is a very hazardous to environment so it must not exceed from a certain limit of safe environmental conditions. We cannot expose it to environment directly so removal and recovery of sulfur before exposing it to environment is necessary. Recovery of sulfur includes mainly following process:

1.5.1 Amine absorption based process

In view of presence of high percentage of ammonia in the acid gas, it is done to take special care in amine absorption and amine regeneration of sulfur recovery process. Amine absorption process is generally situated in the battery area of vis-breaking section inside the refinery. Amine absorption sweetens the gas by scrubbing fuel gas containing hydrogen sulfide as well as reformer gas with mono-ethanol-amine and di-ethanol-amine. Lean amine is recycled back here. The rich amine containing hydrogen sulfide is sent to amine regeneration section where it is regenerated. It had been well practiced by Harvey and Makrides, 1980 and Hamblin, 1973, that the removal hydrogen sulfide from gas streams using aqueous ammonia. Although removal of carbon dioxide and hydrogen sulfide from gas streams, by the use of ammonia, has been declined in recent years, still this process is being used in coke oven gas for the purpose of desulfurizing coke oven gas. There are some reactions occurred in this process which is given as:



There are some advantages of ammine based process over ammonia based process over the (kohl and Nielsen, 1997).

For gas streams containing both ammonia as well as hydrogen sulfide, it is best suited to use ammonia based process. The removal of hydrogen sulfide and ammonia is done in two steps in alkanol amine based process whereas it is done in single step in ammonia process.

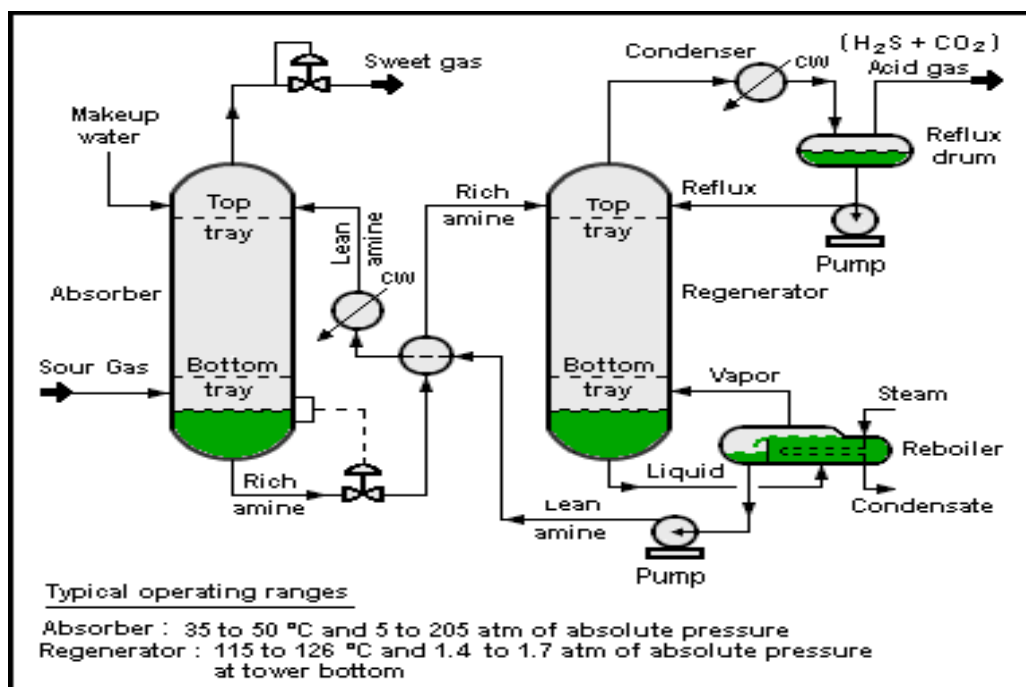


Figure 1: Schematic of amine gas treating process flow diagram

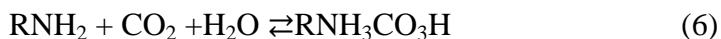
When both carbon dioxide (CO_2) and hydrogen sulfide (H_2S) present in gases then aqueous ammonia solution are contacted with gases containing both H_2S and CO_2 , a rapid absorption of H_2S takes place. It is possible to select absorption of H_2S and CO_2 in liquid ammonia by varying liquid ammonia concentration. Selectivity of absorption of H_2S can lead by giving short time and using spray column. In this amine regeneration section, stripping is done for the removal of H_2S regenerates the rich amine which contains H_2S from amine absorption section. Approximately, up to 99% of H_2S removal is achieved during regeneration. Lean amine is recycled back to amine scrubbing section for reuse. The sour gases released in amine absorption process are sent to sulfur recovery process. A sour water stripper is used to remove H_2S and ammonia which is present in the sour water. In view of large amount of ammonia present in that sour water, stripping is done in multi-stage stripper so that residual ammonia present in the stripped water should be below 50 ppm. It is restricted to use this process because there are some operational difficulties which are associated with ammonia scrubbing. Some operational difficulties which are associated with this process (Hamblin, 1973) are such as:

-
- The process is conducted at higher temperatures so the use of dilute scrubbing solutions results in increasing regeneration cost.
 - Use of soluble catalysts in the scrubbing step result in contamination of sulfur product with the catalyst with regeneration of rich absorbent solution
 - It is found that alkanol amine based process is commercially accepted in a wide range for gas treating or removal of H₂S and carbon dioxide. It is because of low vapor pressure of alkanol amine which results in getting flexibility in terms of concentration, temperature and in operating pressure and it is a very good advantage of this process.

1.5.1.1 Chemical reaction with hydrogen sulfide



1.5.1.2 Chemical reaction with carbon dioxide



The absorption reaction takes place in absorber and then stripping of absorbed gases takes place in stripping column.

1.5.2 Sulfur recovery from hydrogen sulfide by Claus process

Claus process is also a good process which is widely accepted in industries now a day. In recent time, Claus process is mostly used in refineries for recovery of elemental sulfur from H₂S gas

and it is also mostly significant as gas desulfurizing process. Claus process is first patented by Carl Friedrich Claus in 1883. Claus process reduces emissions of sulfur dioxide to atmosphere today, Claus process is considered to be potentially problematic for air pollution.

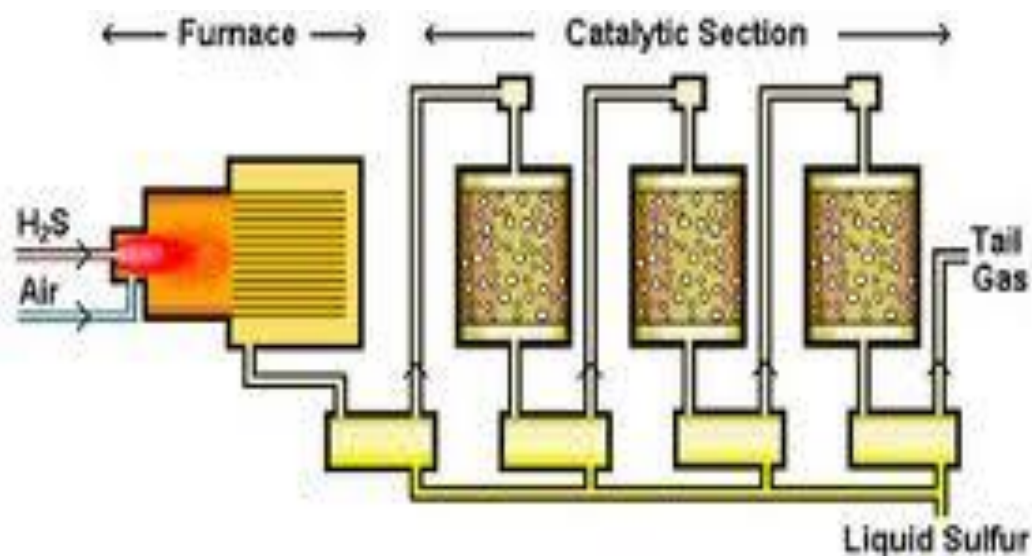
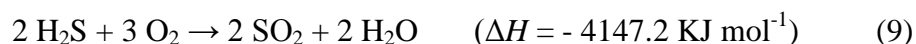


Figure 2: Schematic flow diagram of Claus sulfur recovery plant

Gases with a content of over 25% of H_2S are suited to recover sulfur straight-through using Claus process otherwise Claus process is not suitable. There are two different steps in Claus process which are thermal step and catalytic step, both are given simultaneously.

In thermal step, conversion of H_2S into elemental sulfur takes place at high temperature ($>1800^\circ F$) without the aid of catalyst. H_2S bearing gas of acidic in nature feed stream flows to the reaction furnace burner after passing it through an inlet knockout drum. A sufficient amount of air is added to burn (oxidize) the H_2S in the acid gas to sulfur dioxide (SO_2) and it also burns all hydrocarbons (if present) and ammonia to CO_2 , nitrogen and water. Claus gases (acid gas) with no further combustible contents apart from hydrogen sulfide are burned in lances surrounding a central muffle by the following chemical reaction (9) and around two-third of hydrogen sulfide is converted into elemental sulfur.

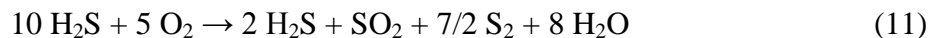


This is a strongly exothermic free-flame total oxidation of hydrogen sulfide generating sulfur-dioxide that reacts away in subsequent reactions. The most important one is the Claus reaction (10) which is given below



In a catalytic step, a certain amount of hydrogen sulfide residue remains in the tail gas which along with other trace sulfur compounds is dealt in the tail gas unit. The unconverted tail gas in thermal step is further processed to recover elemental sulfur in catalytic step. This can provide an appreciable sulfur recovery of about 99.8% which can further be put forth to several other uses like manufacturing medicines, cosmetics, fertilizers etc.

The overall chemical reaction (11) is given below.



This equation shows that in the thermal step alone two-thirds of the hydrogen sulfide is converted to sulfur. Hydrogen sulfide produced, for example, in the hydro-desulfurization of refinery naphtha and other petroleum oils, is converted to sulfur in Claus plants. The overall main reaction (12) is given below.



1.6 Present work

The present work was better utilization of hydrogen sulfide present in various gas streams so that it can be the development of alternative process of Claus sulfur recovery process and other sulfur recovery process also. This work deals to produce some value-added chemicals which utilize the hydrogen sulfide present in various gas streams resulted as byproduct from various chemical industries. The removal of hydrogen sulfide was also assumed to be done with the help of conventional process. It has been synthesized to get value-added fine chemicals like benzyl mercaptan, di-benzyl sulfide and aryl amines under liquid-liquid phase condition using the H_2S

rich MEA in presence of a phase transfer catalyst, Aliquat-336. It has been studied to influence by the variation in process variables like concentration of reactant, stirring speed, temperature, catalyst loading and amount of catalyst used with the selectivity of various products and conversions of organic reactants. Establish a suitable stoichiometry or mechanism to utilize the effects of various parameters. Parametric study has been done to synthesize value-added chemicals.

Chapter 2

Literature Review

2.1 Preparation of Di-benzyl sulfide using phase transfer catalyst

Di-benzyl sulfide (DBS) has many applications such as stabilization of photographic emulsions, additives for external pressure lubricants, in refinery, recovery of precious metals, anti-wear additives for motor oils and in different anti-corrosive formulations (**Pradhan and Sharma**, 1990). DBS can also be oxidized to prepare some useful synthetic intermediates like di-benzyl sulfone and benzyl sulfide (Verma et al, 1997, Mohammadpurbultork et al, 2005).

Synthesis of DBS and bis (P-chloro-benzyl) sulfide is done by **Pradhan and Sharma** (1990) by the reaction with its respective chlorides with sodium sulfide by the use of different phase transfer catalysts under solid-liquid and liquid-liquid mode. It was found that Tetra-butyl ammonium bromide (TBAB) is the most effective phase transfer catalyst for this conversion. Using this catalyst a detailed study was performed. **Pradhan and Sharma** (1992) have also performed the kinetic study of preparation of DBS and bis(4-chlorobenzyl) sulfide under liquid-solid mode with sodium sulfide by the use of easily separable un-impregnated solid catalyst which is inorganic like basic ammonia and Amberlite A27(chloroform) anion exchange resins. DBS was synthesized by the reaction of aqueous ammonium sulfide and benzyl chloride (BC) using tetra-butyl-ammonium-bromide (TBAB) as phase transfer catalyst. The parametric study was done on the selectivity of DBS. It was found that di-benzyl sulfide can be selectively prepared by keeping high concentration of BC, Low H_2S/NH_3 ratio. This work was done by **SujitSen, Patwardhan, N C Pradhan, S K Maity, 2007**.

2.2 Synthesis of sulfide sulfoxides

In this paper, sulfide sulfoxide has been synthesized by the action of thionyl chloride on mixed organo-magnesium compounds. The present work was done by **G. D Gelpert, N. P. Volynskii** and **V.V. Smolyaninov** (1962). They study the action of thionyl chloride on organomagnesium compounds, the reaction conditions have been regined, and the applicability of this reaction to be a production of a number of difficulty available sulfide, by omitting the stage of formation of mercaptans, has been shown.

- 1) It has been shown that the sulfoxides first produced are reduced to sulfides by the thionyl chloride and not by the organomagnesium compounds.

-
- 2) The preparation of dodecyl, dicyclohexyl, decyl, sulfides by the action of thionyl chloride on organomagnesium compounds has been carried out for the first time.

2.3 Synthesis of 2, 4-dichlorophenoxyacetic acid

The present work was done by **G. D. Yadav** and **Y. D. Yadav** (17 June, 2002). The work deals with the inverse (L-L) Phase transfer catalyzed synthesis of 2,4-dichlorophenoxyacetic acid (2,4-D) by using 2,4-dichlorophenol (2,4-DCP) and chloro acetic acid (CAA), wherein the location of the reaction is the aqueous phase. By varying the amount of sodium hydroxide (NaOH) used, the product can either be obtained in an organic phase or in the aqueous phase as sodium salt. 2, 4-dichlorophenoxyacetic acid has been synthesized using stoichiometrically deficient quantity of sodium hydroxide and a low molecular weight quaternary salt, such as tetra ethyl ammonium bromide (TEAB). The paper brings out the novelties vis-à-vis the mechanism and kinetics of inverse phase transfer catalyzed. Synthesis of 2,4-D has been done.

2.4 Reaction of nitro-chloro-benzenes with sodium sulfide

The present work was done by **Narayan C Pradhan** and **Man Mohan Sharma (1992)**. The work was done for the reaction of nitrochlorobenzenes with sodium sulfide. In this reaction, reduction of o-Nitro and p-Nitrochlorobenzene to the corresponding chloroanilines was studied with the solutions of sodium sulfide both in the presence and absence of phase transfer catalyst (PTC). It was found to change the course of the reaction completely to dinitrodiphenyl sulfide was done by using phase transfer catalysts with sodium sulfide. The mass transfer role in the system was assessed with m-Nitrochlorobenzene as the organic substrate.

2.5 Process for removing H₂S and ammonia from gaseous streams

The present work was done by **Walter W. Harvey** and **Alkis C. Makrides (March 11, 1980)**. The present work was done on the process for simultaneously removing ammonia and hydrogen sulfide from gaseous streams which contain other acid and basic gases. The comparison of the process was done in closed loop with scrubbing of the gaseous stream along with an ammonium sulfate-copper sulfate solution. This gives the yield of copper sulfide precipitate and concurrent

acidity neutralization which was generated in the scrubbing step by the scrubbing or addition of ammonia and other basic gases which are hydrothermally leaching the precipitate by separating the precipitate. Leaching was done with oxygen or air under controlled pressure and temperature condition to re-oxidize the sulfide to copper sulfate. Recycling of copper sulfate was done to scrub and to reject sulfur from the system in the form of $(\text{NH}_4)_2\text{SO}_4$.

Chapter 3

Project Work

3.1 Project work

This work has been done to substitute Claus process, the main aim of this project is to optimize utility of hydrogen sulfide found in various gas streams. The present work accounts to deal with the process of getting value added chemicals which utilize the hydrogen sulfide produced in industries. The value added chemicals that we found here, are DBS and BM by using hydrogen sulfide rich MEA. The entire process occurs in the presence of Aliquat-336 which is an effective phase transfer catalyst (PTC). The process can vary with the variables like concentration of reactants and stirring speed of stirrer in batch reactor.

3.2 Phase transfer catalyst

This is a catalyst which is used to enhance the rate of the reaction between an organic phase reactant and an aqueous phase reactant. PTC used in this work is Aliquat-336. This is a slow heterogeneous reaction carried out in between two phases, organic phase (toluene and BC) as well as aqueous phase (H_2S rich MEA). Now, the use of PTC is to speed up and enhance the strength of slow heterogeneous reactions either in liquid-liquid phase or in liquid-solid phase. PTC has its certain merits such as reduced consumption of raw materials, its simplicity, increased rate of reaction and mild operating conditions. Because of these special attributes, PTC has its prior use in organic synthesis. Need of phase transfer catalyst is because many anions in their salt form and neutral compound from the solid or aqueous phase in to the organic reaction phase (or interfacial region) where neutral compound and anion can freely react with the organic reactant which is already located in the organic phase.

Generally, both mechanism (interfacial and extraction) are used to explain the phenomena of liquid-liquid phase transfer catalysis on the basis of lipophilicity of the quaternary cat-ion. The catalysts which are highly lipophilic are suitable for extraction mechanism (Figure 3) because that have tendency to distribute themselves between the aqueous and the organic phase. Some highly lipophilic catalysts are dodecyltrimethylammonium, benzyltriethylammonium and tetrabutylammonium salts ^{[2] [3]}. At the interface model, catalysts like trioctylmethylammonium and tetrahexylammonium salts entirely remains in the organic phase because they have high lipophilicity. Anions are exchanged across the liquid-liquid interface ^[5].

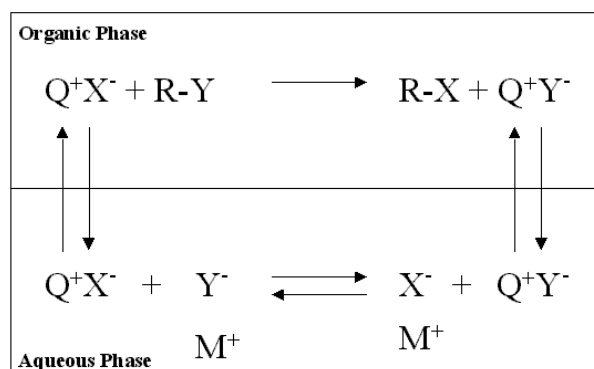


Figure 3: Schematic of extraction mechanism

Sometimes reactivity is further enhanced by orders of magnitude, because neutral compound (anion) has very little hydration or solvation, once it is in the organic phase, thereby it is greatly reducing the activation energy. In this work, Aliquat-336 was used as PTC.

3.3 Aliquat-336

Aliquat-336 is a colorless viscous liquid and used as PTC for good conversion. It is a quaternary ammonium salt and also metal extraction reagent. It includes the catalytic oxidation of cyclohexane to 1,6-hexanedioic acid. Aliquat-336 contains a mixture of octyl (C₈) and decyl (C₁₀) chains with predominating of octyl (C₈) chain. It is compared with the traditional method, in which hazardous wastes are produced by oxidizing cyclohexanone or cyclohexanol with potassium permanganate or nitric acid. Molecular formula of Aliquat-336 is C₂₅H₅₄ClN with molar mass of 404.16 g mol⁻¹. Aliquat-336 is primarily irritant and also harmful. It may cause skin burn, eye burn and also cause irritation with the respiratory track of burning pain in the throat and nose, shortness of breath, coughing, wheezing and pulmonary edema by inhalation. It causes chemical burns to the respiratory track. Vapors generated by heating of Aliquat-336, may form explosive mixture with air which cause explosion hazardous.

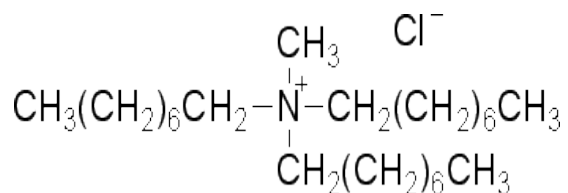


Figure 4: Structure of Aliquat-336

Aliquat-336 is a viscous colorless to pale orange liquid. Some synonyms of Aliquat-336 are 1-octanaminium, N-methyl-N,N-dioctyl, chloride capriquat, Methyltricaprylammonium chloride, Trioctylmonomethylammonium chloride and Tricaprylmethylammonium chloride.

3.4 Experimental work

3.4.1 Preparation H₂S rich MEA

The experiment was carried out in the Kipp's apparatus by using chemicals such as: fill the FeS fillets in the middle part of the apparatus then set the apparatus with two bottles in ice (Reaction is exothermic) so that recovery of H₂S rich MEA be possible and then Sulfuric acid is filled from top of the apparatus then put it for further reaction.

There are three basic steps in preparation of required H₂S rich MEA which are like.

- 1) Preparation of MEA
- 2) Absorption of H₂S in MEA
- 3) Estimation of sulfide content in MEA

Chemicals required in preparation of H₂S rich MEA are given below.

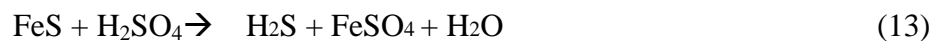
- 1) Fe S fused stick for producing H₂S
- 2) Sulfuric acid
- 3) Silicon high vacuum grease
- 4) MEA

There are three major parts in Kipp's apparatus as shown in the given diagram.

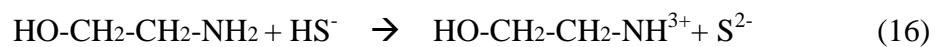
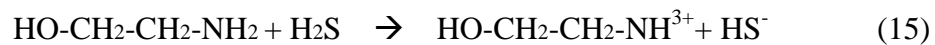


Figure 5: Setup of Kipp's apparatus

Absorption of hydrogen sulfide in MEA has been done in Kipp's apparatus. Here we are producing hydrogen sulfide gas in addition with ferrous sulfate and water using ferrous fillets along with sulfuric acid in Kipp's apparatus which is shown in reaction (13) given below.

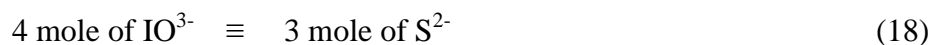
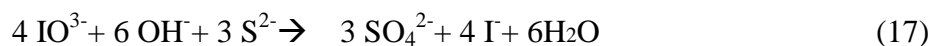


Prepared hydrogen sulfide has been absorbed in MEA using direct connection of MEA containing beaker to condensing (middling) zone of Kipp's apparatus.



3.4.2 Estimation of sulfide concentration

H₂S can be determined by oxidation with potassium iodate in an alkaline medium. 15cm³ of standard (0.025M) potassium iodate solution was taken in a conical flask. 10cm³ of sulfide solution which contains about 2.5 mg of sulfide which was then added to solution followed by the addition of 10cm³, 10M sodium hydroxide solution. The boiling of mixture was done gently for about 10 minutes then cooled and then 5cm³ of KI solution and 20cm³ of 4M sulfuric acid solution were added to solution. Then iodine liberated from it was titrated, liberated iodine was equivalent to the unused potassium iodate, with the standard 0.1M sodium thiosulfate. In the alkaline medium, the potassium iodate oxidizes the sulfide to sulfate which is given in following (17) reaction. Sulfide concentration must be high in sulfide solution. Before the estimation of sulfide, suitable dilution was made by above mentioned procedure.



$$\text{H}_2\text{S concentration} = [15 * \text{S}_{\text{iodate}} - (\text{V}_{\text{thiosulfate}} * \text{S}_{\text{thiosulfate}}) / 6] * 3/4 * \text{Nd} / 10$$

Where S_{iodate} = Strength of KIO₃

V_{thiosulfate} = Volume of thiosulfate

S_{thiosulfate} = Strength of thiosulfate

N_d = Number of times of dilution

3.4.3 Equipment

The reaction was carried out in a mechanically agitated glass reactor. In this reactor a 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 it is flexibility of maintaining a fixed certain reaction temperature.

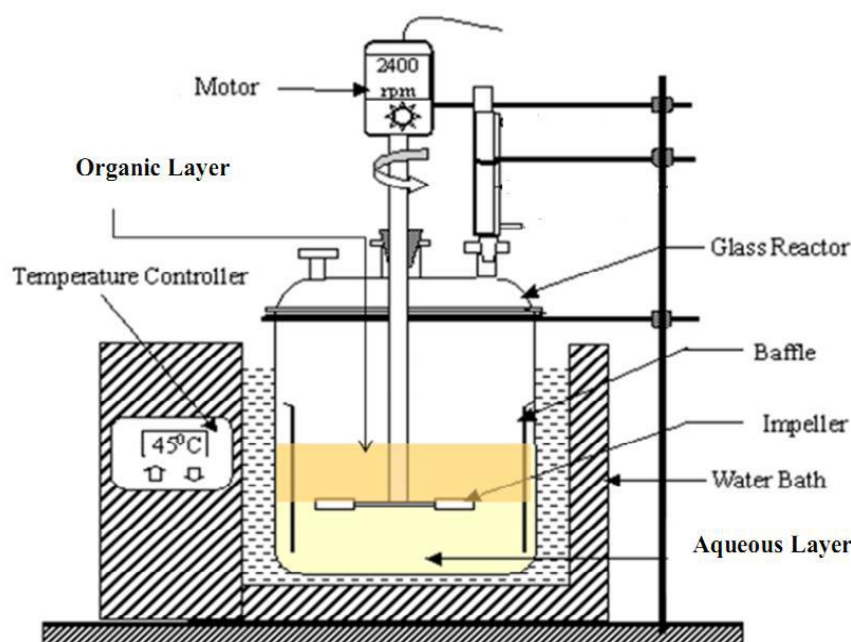


Figure6: Setup of Batch reactor

This batch reactor is carrying the main reaction of present work. A complete setup of batch reactor consists of a mechanical agitator, a cylindrical vessel type glass reactor and a water bath around the reactor which is having flexibility of maintaining different-different temperatures. The main reaction is occurring with BC and H₂S rich MEA in presence of a certain PTC to give some valuable product like DBS and BM. PTC which is used in this work is Aliquat-336. Aliquat-336 is a liquid catalyst which appears colorless to pale orange with very high density and high lipophilicity.

3.4.4 Chromatograph

The analysis part of the present work was done by chromatography which gives us chromatograph containing different peaks for individual compounds on the basis of their boiling point. The chromatograph is shown in figure 7.

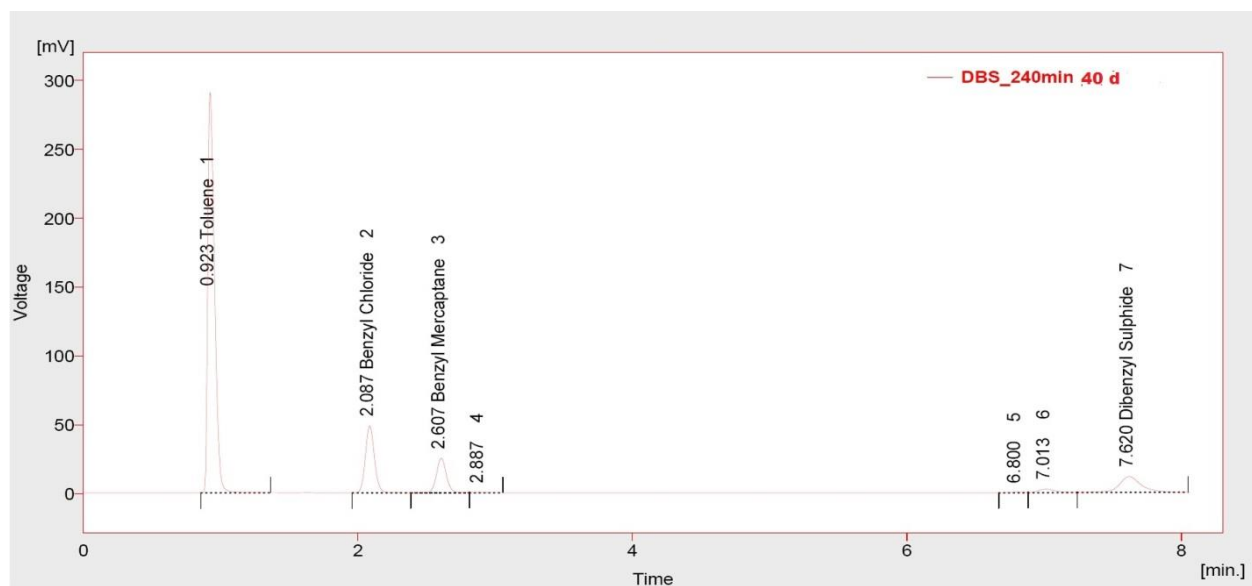


Figure 7: A typical Chromatograph for synthesis of DBS after 240min and at 40⁰ C

Chapter 4

Results and Discussion

4.1 Introduction

Hydrogen sulfide is usually removed from various gas streams by absorption in aqueous alkanolamine in all refineries and petrochemical industries. Releasing of H_2S from stripper where amines are also regenerated then elemental sulfur is further being released in Claus unit. Stripping and various other steps involved in Claus process consume lot of energy. So it would be a great value in refineries, if some other value-added chemicals can be produced by using H_2S rich amine as a large scale production of hydrogen sulfide takes place here in refineries.

MEA is highly alkaline so that it can be used to absorb H_2S . The reaction between H_2S rich MEA with BC gives DBS and BM. DBS has applications as stabilizing of photographic emulsion, additives for extreme pressure lubricants, recovery of precious metal in refinery, anti-wear additives for motor oil and in different anti corrosive formulation. BM is having valued in medical field which is used for formation of herbicides. The MEA and BM are having different densities and they are of two different phase. Hence, use of catalyst is required here for better reaction and desired product formation.

Parametric studies was performed to see the variation in various parameters like aqueous sulfide concentration, stirring speed, BC conversion, BC concentration, MEA concentration and amount of catalyst used in the reaction. A detailed studied has been done on variation of various parameters of the reaction.

4.2 Parametric studies of products

4.2.1 Variation of stirring speed on conversion of BC

The stirring speed has been varied and graph is plotted by observing the corresponding with the reaction rates to evaluate the role of mass transfer resistance. As seen from the figure 8 it has been observed that the conversion of benzyl chloride is slightly varying as the stirring speed goes on increasing. Thus it can be concluded that up to some extent mass transfer factors does not affect the conversion rate in the present system which can be controlled by kinetics. All experiments were performed at different stirring speed starting from 500rpm to 1500rpm.

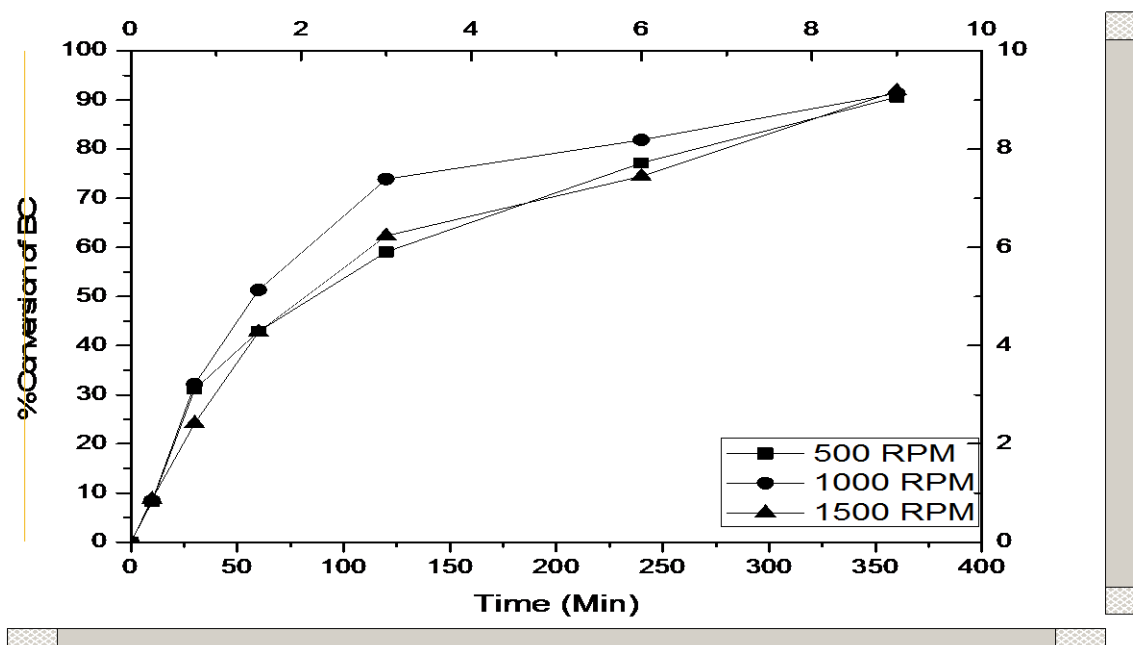


Figure 8: Percentage conversion of BC with stirring speed at 40°C and Sulfide Conc. 2.35

4.2.2 Variation of benzyl chloride concentration on conversion of BC

It has been studied that the effect of BC concentration on conversion benzyl chloride. As seen from the figure 9 it can be observed that as decreasing the concentration of benzyl chloride, the benzyl chloride conversion going on increasing. It happens because increasing benzyl chloride concentration but sulfide content is same that reduces the conversion. It happens because at low concentration of benzyl chloride there is not sufficient amount of benzyl chloride to produce DBS. The data are shown in the figure 9 which represents the percentage conversion of benzyl chloride with the concentration of benzyl chloride.

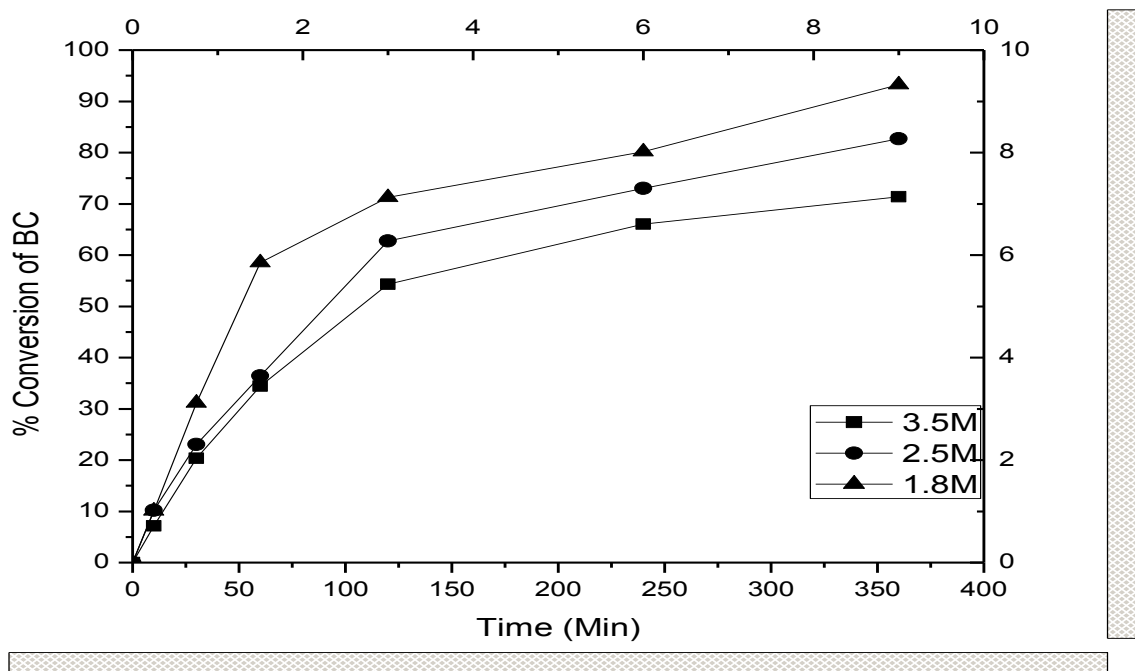


Figure 9: Percentage conversion of BC with BC concentration at 40°C, Sulfide Conc. 2.35 and 1000 RPM

4.2.3 Variation of initial sulfide concentration on conversion of BC

Keeping MEA concentration fixed, it has been studied that variation in initial sulfide content is effected and effect is shown in figure 10. When initial sulfide content is increased, because of presence of more amounts of sulfide ions conversion is being increased. In case that fixed amount of MEA, the increase in the initial sulfide concentration results in decrease in the MEA/sulfide mole ratio in aqueous phase which is having a responsibility of determining the concentration of hydrosulfide ions and sulfide ions in MEA. In presence of more amount of MEA/sulfide molal ratio, the equilibrium dissociation shifts towards more ionization so that more sulfide ions (H^-) are formed compared to hydrosulfide ions (HS^-), in the aqueous phase.

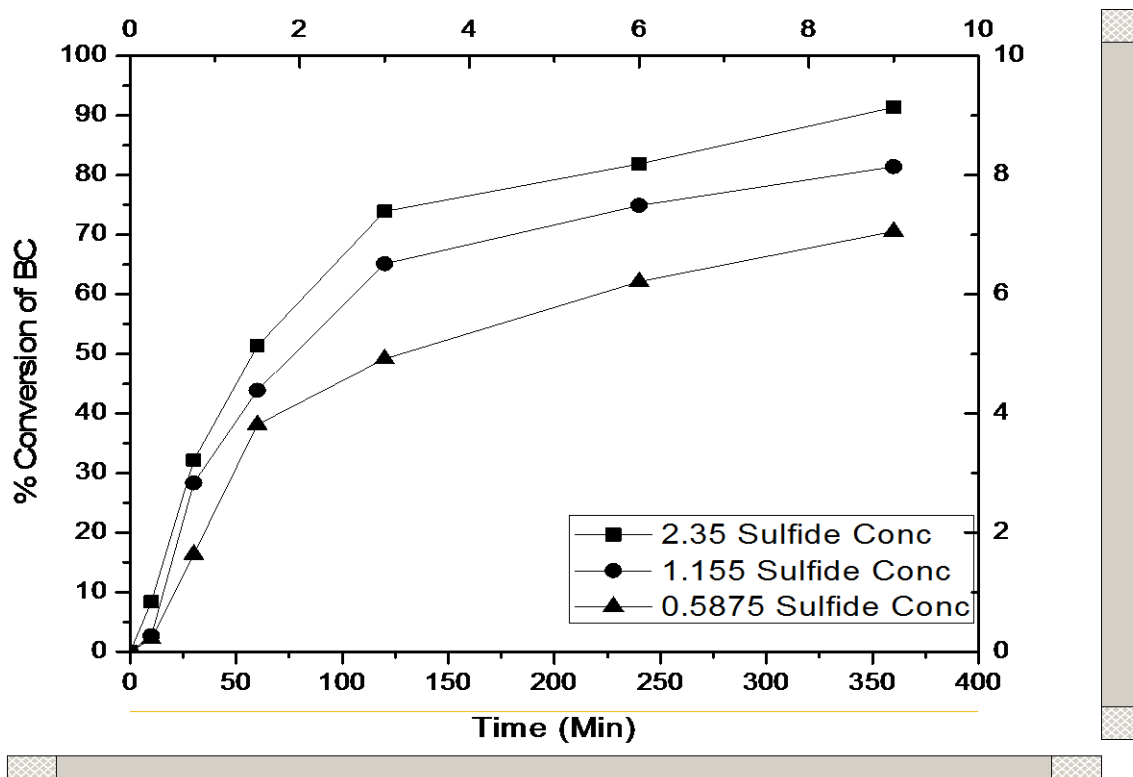


Figure10: Percentage conversion of BC with initial sulfide concentration at 40°C and 1000 RPM

Chapter 5

Conclusion

5.1 Conclusion

The reaction of benzyl chloride (BC) and H₂S rich MEA present with toluene as a solvent in presence of phase transfer catalyst, Aliquat-336 produces valuable products like benzyl mercaptan (BM) and Di-benzyl sulfide (DBS). Keeping the initial sulfide content high, high reaction time and low concentration of Benzyl Chloride will lead to give us high conversion of Benzyl Chloride. It has been found that the maximum conversion of Benzyl Chloride which was achieved in this work by using Aliquat-336 as a Phase Transfer Catalyst was nearly 92%. On the basis of parameters which were examined, it has been observed that increasing the initial sulfide and decreasing the benzyl chloride concentration preferentially increase the percentage conversion of Benzyl Chloride.

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