

**SYNTHESIS OF DIBENZYL DISULFIDE USING HYDROGEN SULFIDE
AND SOLID TRI-PHASE CATALYST**

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by

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CERTIFICATE

This is to certify that the thesis entitled “**Synthesis of Dibenzyl Disulfide using Hydrogen Sulfide and Solid Tri-Phase Catalyst**”, submitted by **Ms. Shreya Sah, Roll No: 110CH0016**, to National Institute of Technology Rourkela is a bonafide report of the research work carried out by her, in the Department of Chemical Engineering, National Institute of Technology, Rourkela under my supervision and guidance.

The thesis submitted by Ms. Sah, is worthy of consideration for the partial fulfillment of award of the degree of “Bachelor of Technology” in accordance with the regulations of this Institute. The results incarnated in the report are authentic to the best of my knowledge.

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ABSTRACT

Hydrogen sulfide is a colorless gas with an obnoxious rotten egg odour. H₂S is highly flammable, noxious, and vitriolic in nature. Many petroleum and natural gas processing industries produces H₂S as a by-product gaseous stream. Most H₂S in the air comes from natural sulfur cycle. Exposure to H₂S can lead to various health issues like burning/tearing of eyes, cough, and shortness of breath. Moderate concentration can lead to respiratory issues. So it is advisable to make use of this gas in other industrial operations. In industries, normally H₂S present in gas streams is absorbed in amines and is converted to sulfur through conventional Claus process. From economical point of view, sulfur is not so good product, so the idea is to find out a substitute for the Claus process where H₂S rich amine instead of going to the scrubber is fed to some reactor for production of compounds like thioether, disulfides which are more valuable than sulfur. Also the need of additional scrubber and other Claus units is ruled out in the new alternative process which makes the overall process economical. The present work includes the study of synthesis of Dibenzyl Disulfide using H₂S rich aq. Alkanolamine, sulfur and Benzyl chloride in presence of triphase catalyst. Also kinetic study by variation of temperature, speed, catalyst loading etc is done to examine their effect on conversion.

Keywords: Hydrogen sulfide; Dibenzyl disulfide; Phase transfer catalyst; Conversion; Alkanolamine

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NOMENCLATURE

H ₂ S	Hydrogen sulfide
DBDS	Dibenzyl Disulfide
BC	Benzyl Chloride
CO ₂	Carbon Dioxide
SO ₂	Sulfur dioxide
NH ₃	Ammonia
MEA	Monoethanolamine
DEA	Diethanolamine
MDEA	Methyldiethanolamine
DIPA	Diisopropanolamine
GLC	Gas Liquid Chromatography
aq.	Aqueous
org.	Organic
PTC	Phase Transfer Catalysis
TEA	Triethanolamine
H ₂ SO ₄	Sulfuric acid
KIO ₃	Potassium iodate
KI	Potassium iodide
FID	Flame ionization detector
AMP	2-amino-2-methyl-1-propanol
OSHA	Occupational Health and Safety Administration
PEL	Permissible Exposure limit
PEG	Polyethylene Glycol
TBAB	Tetra butyl ammonium Bromide
T	Temperature
r	Regression coefficient

CHAPTER 1

INTRODUCTION

1.1 HYDROGEN SULFIDE - OVERVIEW

Hydrogen sulfide (H_2S) is a colorless gas with an obnoxious rotten egg odour. H_2S is highly flammable, noxious, and vitriolic in nature. Its presence can be felt by smell at very low levels in air. Many petroleum and natural gas processing industries produce H_2S as a by-product in gaseous stream. Most H_2S in the air comes from the natural sulfur cycle. It is produced when bacteria decompose plant and animal material, often in stagnant waters where oxygen content is low such as bogs and swamps. Volcanic eruptions, sulfur springs, salt marshes, undersea vents, swamps, and stagnant bodies of water are also sources of gaseous H_2S .

Petroleum refineries, natural gas extraction plants, coke oven plants, chemical manufacturing and waste disposal, pulp and paper manufacturing, food processing plants, textile production, water treatment plants and leather tanneries form industrial sources of H_2S emission. Calcium sulfate, which is one of the major components of wallboard, can be easily transformed into H_2S by bacteria. Hence, if wallboard is present in large amounts in construction and demolition debris, H_2S can be produced on a large scale.

1.2 TREATMENT OF H_2S -RICH GAS

H_2S is a highly virulent and is corrosive in nature with an obnoxious smell. Few reasons which support the requirement of removing H_2S from gas and fluid streams are underlined below.

1. H_2S is a highly toxic and combustible gas with explosion limits ranging from 4.3 - 46 %. Toxic vapors and gases, such as sulfur dioxide, are produced on ignition.
2. Owing to high density as compared to air, H_2S tends to travel in low-lying areas.
3. H_2S gas is rapidly absorbed by the lungs and contact with liquid H_2S causes frostbite.
4. H_2S has a very pestering effect and protracted exposures may cause redness in eyes, headache, fatigue, inability to sleep, irritability, digestive disorders and reduction in weight.
5. The presence of H_2S in the refinery gas streams can cause damage, corrosion issues, degradation of catalyst activity, undesired side reactions, and products. For industries, OSHA has given PEL value for H_2S : 10 ppm.
6. If exposed to a concentration greater than 100 ppm for a long duration of time, respiratory maladies, paralysis, and ultimately death can occur.

1.3 INDUSTRIAL PROCESSES FOR THE REMOVAL OF H₂S

Multiple processes have been built in industries for the riddance and retrieval of H₂S from gas streams. Its acidic (weak acid) nature, lays down a basis for its removal by using an alkaline solution. Sodium hydroxide being a strong alkaline solution forms an irreversible chemical reaction product with H₂S and hence can't be utilized for H₂S removal. This becomes more important particularly in case if the gas contains both H₂S and CO₂ where the concentration of CO₂ is more than 4% (Robin, 1999).

1.3.1 AMINE GAS TREATMENT

It is the most conventional and commercially accepted way of eliminating H₂S from sour gases or industrial effluents. Alkanolamines possess low vapor pressure, which therefore increases the flexibility of operating conditions like pressure, temperature, alkanolamines concentration etc. In addition, insignificant vaporization losses occur.

The amine gas treatment plant (Figure 1.1) consists of absorption column in which an upcoming sour gas (containing H₂S) is allowed to meet a down flowing amine solution. Amine absorbs H₂S from gas stream (Scheme 1.1) and produces a sweetened gas stream (Free from H₂S). Then H₂S rich amine stream is fed to a regenerator. Regenerator unit is a stripper with boiler. Here in regenerator, concentrated H₂S is obtained as stripped overhead gas. H₂S retrieved can be now converted into elemental sulfur using Claus process. In addition to this, amount of H₂S recovered can be found out.

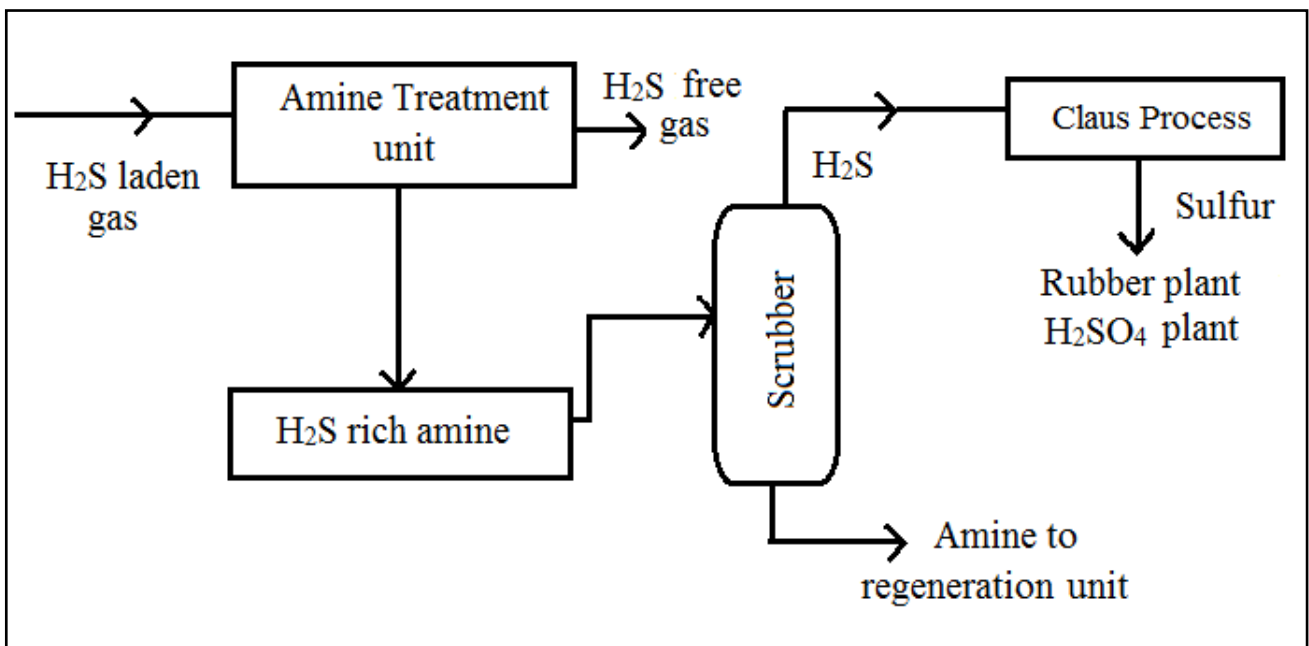
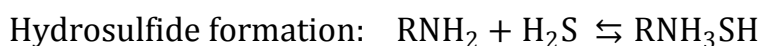
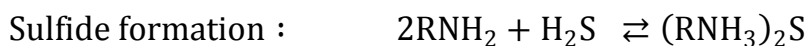


Figure 1.1: Schematic Diagram – Amine treating process used in industrial plant

Reaction with H₂S:**Reaction with CO₂:****Scheme 1.1**

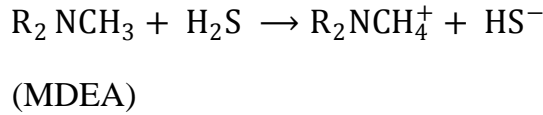
First commercially available alkanolamines was Triethanolamine (TEA); and it was used in the gas treatment plants (R. R. Bottoms, 1930). However, being a tertiary amine, it possesses less reactivity and has relatively poor stability. Aq. solution of alkanolamines like Diethanolamine (DEA), Monoethanolamine (MEA), and (Methyldiethanolamine) MDEA etc are used generally. MEA and DEA are not selective to H₂S in their reaction when gas stream contains both H₂S and CO₂. Generally 30-35 % of MDEA (expressed as wt% of pure amine in aq. solution) is used for extraction of H₂S. Although MDEA was described by Kohl et al. (1951) as a selective absorbent for extraction of H₂S from stream containing CO₂ in early 1950s, its industrial application become important in recent years.

DIPA (Bally, 1961; Klein, 1970) has been put to use in the Adip process, Sulfinol process and SCOT process. Blohm and Riesenfeld (1955) proposed the use of DGA – a different type of alkanolamine, 2-(2-aminoethoxy) ethanol. Companies like Dow Chemical Company, Union Carbide Corp., Huntsman Corporation, and BASF used formulated solvents, which were mixture of the amines and various additives. However, the most substantial growth in formulated solvents is the onset of tailored amine blends. Primarily based on MDEA, they contain other amines, corrosion inhibitors, foam depressants, buffers, etc. They offer advantages like selective H₂S removal, partial or complete CO₂ removal, high acid gas loading, COS removal etc. (Manning and Thompson, 1991; Thomas, 1988; Pearce and Wolcott, 1986; Meissner and Wagner, 1983; Meissner, 1983; Niswander et al., 1992).

MDEA- Methyldiethanol amine is clear, colorless pale yellow with ammonia odour, miscible with water, alcohol, benzene with chemical composition CH₃N(C₂H₄OH)₂. It is a sweetening agent.

Advantages of using MDEA over MEA or DEA:

1. The fact that MDEA is a tertiary amine makes it less basic. In addition, there is no hydrogen attached to nitrogen. So in case if any CO₂ is present in gas, it can react only after CO₂ in gas dissolves to form bicarbonate, which then undergoes acid-base reaction with amines. However, both MEA and DEA react with all the CO₂ present in the gas stream.



2. MDEA is more selective than MEA and DEA. Both MEA and DEA form degradation corrosion products when reacted with CO₂ whereas MDEA does not.
3. Using MDEA increases capacity for existing unit, decrease capital cost for new units and it also lowers the energy costs.

MEA - Owing to its low weight, MEA increases solution capacity and also its high alkalinity and low cost as compared to MDEA, makes its use more economical. So MEA has been used throughout the reaction because the H₂S rich amine is produced in lab and contains no other gases like CO₂.

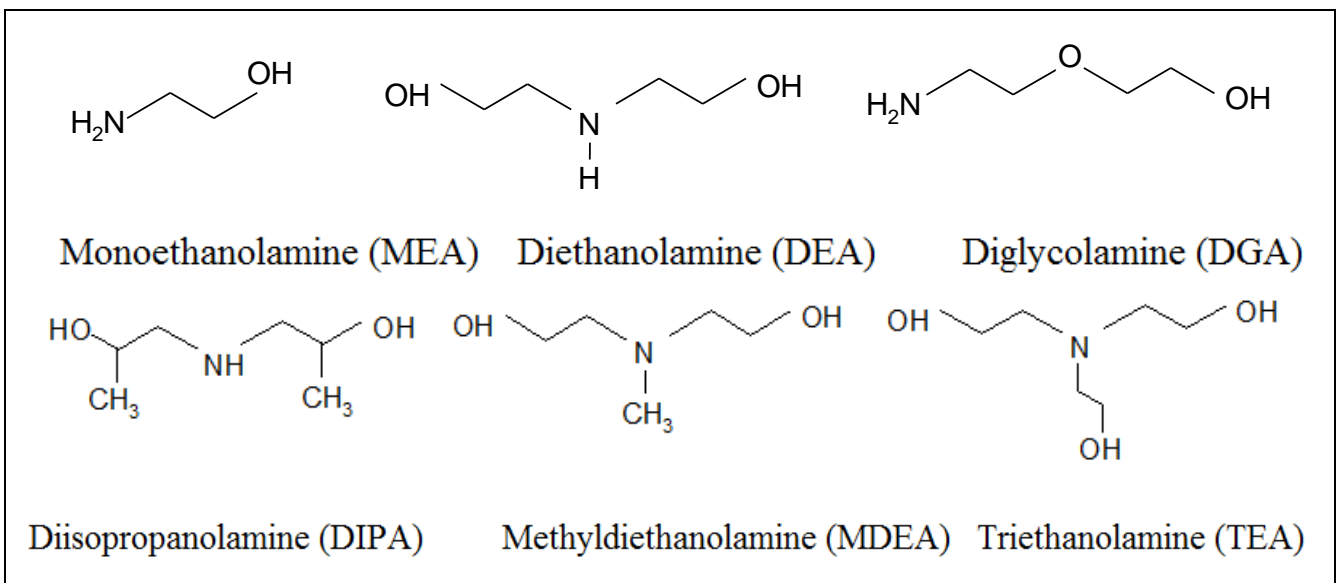
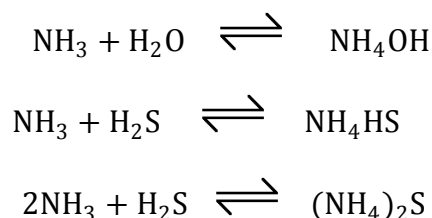


Figure 1.2: Structural formulas of different alkanolamines ^[1]

1.3.2 AMMONIA-BASED PROCESSES

H₂S riddance from gaseous streams using aq. ammonia had been well-practiced (Hamblin, 1973 and Harvey and Makrides, 1980). Gaseous streams containing H₂S and NH₃ passes through H₂S and NH₃ scrubbers sequentially as shown in Fig.1.1.

Stripped water is feeded to the NH₃ scrubber from the top. Here NH₃ is absorbed from the gas. The ensuing NH₃ stream is then used as receptive for H₂S in the H₂S scrubber. The ensuing rich stream containing ammonium sulfide, is then fed to a deacidifier. Here ammonium sulfide breaks down to yield H₂S rich vapor and NH₃ rich liquor. This ammonia based process was proposed by the Krupp Wilputte Corporation, 1988; Davy-still Otto, 1992; and Mitsubishi Kakoki Kaisha Ltd., 1986; (Kohl and Nielsen, 1997). The following equation represents the reactions happening (Scheme 1.2)



Scheme 1.2

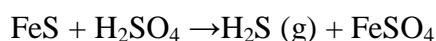
Advantages of NH₃-based process over amine-based process (Kohl and Nielsen, 1997):

1. The ammonia-based process is benefit for gas streams carrying both H₂S and NH₃, as simultaneous removal of NH₃ is obvious in this process.
2. By using aqueous NH₃, the selective absorption of H₂S over CO₂ is possible from the gases containing both H₂S and CO₂.
3. Gases like carbonyl sulfide, hydrogen cyanide, carbon disulfide (CS₂) and (HCN) does not affect NH₃ process.

Ammonical scrubbing has not been globally accepted in the gas treating because of a number of operational problems associated with its implementation (Hamblin, 1973), like high partial pressure of NH₃, because of which dilute NH₃ solution is used which increase regeneration cost and temperature in regeneration.

1.4 LABORATORY PREPARATION OF H₂S

On laboratory scale, H₂S can be prepared in Kipps apparatus. FeS sticks are made to react with H₂SO₄. H₂SO₄ of 1 molar concentration is taken as and the reaction occurs as follows:



Kipps apparatus is a combination of three vertically stacked cylinders. A tube connects top and bottom cylinder. Stopcock is attached in middle cylinder to draw off evolved gases. When reaction needs to be stopped, stopcock is closed, which decrease pressure in middle cylinder and expels all acid back to top cylinder. Solid used should be insoluble in acid and usually apparatus is made of glass. Sulfide content in gas is estimated by iodometric titration method. Chemicals used for titration are sodium thiosulfate, potassium iodide, potassium iodide; starch powder 98% pure H₂SO₄ and sodium chloride pellets.

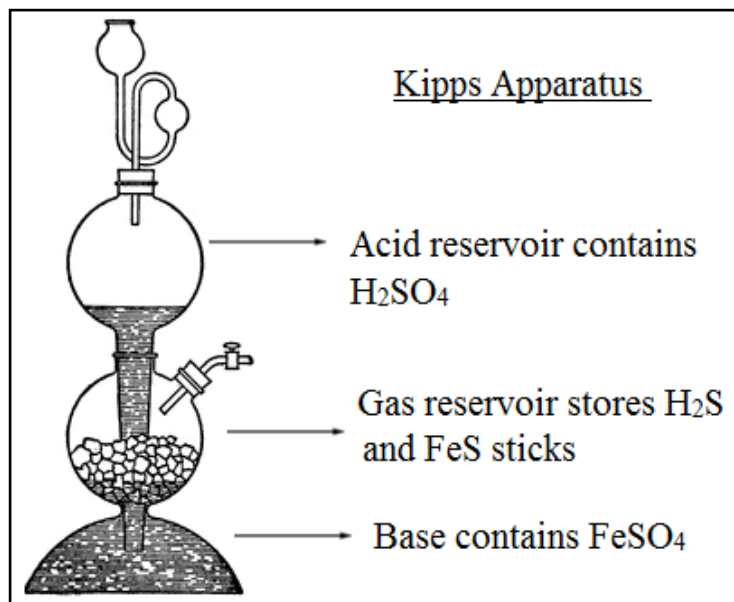


Figure: 1.3: Schematic - Kipps Apparatus ^[2]

1.5 PHASE TRANSFER CATALYST

PTC is heterogeneous catalyst that facilitates migration of reactant ions from one phase to other which otherwise is not possible. For anionic reactants, generally quaternary ammonium and phosphonium salts are used as PTC. CM Starks introduced concept of PTC in 1971.

Depending upon the different physical states involved, PTC systems generally include liquid-liquid (L-L), liquid-solid (L-S), liquid-liquid-liquid (L-L-L), and gas-liquid (G-L). In presence of PTC systems, anions from reactant side (aq. phase) migrates to organic phase. An L-L-S system also known as 'triphasic catalyst' offers easy recovery and reusability owing to the presence of solid cation. The present work uses Amberlite IR 400 as an L-L-S PTC. It is a resin bound PTC and is insoluble in both the phases.

Table 1.1: Commonly used PTCs ^[3]

<u>Catalyst</u>	<u>Cost</u>	<u>Stability & Activity</u>	<u>Use & Recovery</u>
Ammonium salts	Cheap	Moderately stable up to $100^{\circ}C$. Moderately active.	Widely used. Relatively difficult recovery.
Phosphonium salts	Costly	More stable thermally than ammonium salts, although less stable under normal conditions.	Widely used. Relatively difficult recovery.
Crown ethers	Expensive	Stable and highly active both under normal conditions and up to even $150-200^{\circ}C$.	Often used. Recovery is difficult and possesses environmental issues due to their toxicity.

Cryptands	Expensive	Stable and highly reactive, in absence of strong acids.	Higher reactivity increases usage in spite of high costs and toxicity.
PEG	Very cheap	More stable than quaternary ammonium salts, but lower activity.	Often used. Relatively easy to recover.

1.5.1 ADVANTAGES OF USING PTC:

1. High yield and purity of products
2. Low energy consumption and investment cost.
3. Ionic solutions are soluble in aq. phase and generally insoluble in organic phase when there is no PTC. Addition of PTC reduces/eliminates need of organic solvents.
4. Phase transfer catalysis reaction is highly scalable.

1.5.2 RESIN BOUND PTC

A Resin bound PTC is a kind of polymer supported catalysts which includes polymer/resin linked to NR_3^+ , -PPh_3^+ , -SR_2^+ , -crown ether, -cryptands, -azacrown, -PEG, etc. Also popular as triphase catalyst, this system consists of an aq. salt solution that acts as a dispersion medium in which solid resin particles and small droplets of solution of an organic reagent in water immiscible solvent are dispersed.

1.5.3 MECHANISM OF TRIPHASE PTC

Lipophilicity of the catalyst decides the reaction mechanism for triphase catalysis reaction. A highly lipophilic catalyst implies that it remains entirely dissolved in org. phases and hence it will follow interfacial mechanism (Dehmlow, 1983), i.e. anion exchanges will occur near liquid - liquid interface. But if the catalyst is not so highly lipophilic, then it will not dissolve in any phases and hence they will follow extraction mechanism which was proposed by Starks, 1971. Amberlite IR 400 is a solid resin bound catalyst and is not soluble in any of the two phases, so it will follow Starks extraction mechanism (Figure 1.4)

Reaction between catalyst (QX) and alkali metal salt (MY) generates in aq. phase, ion pair QY. This is how anion Y^- is pulled through phase boundary into organic phase. Here it reacts with alkyl halide. Displacement takes place and displaced anion X^- is transferred into aq. phase as QX and cycle is completed.

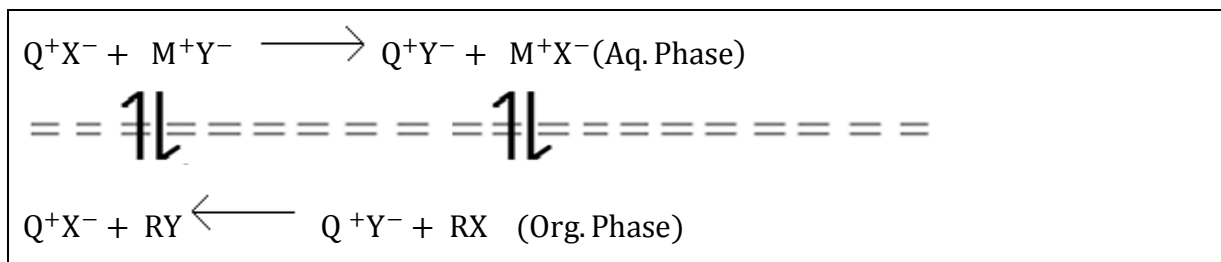
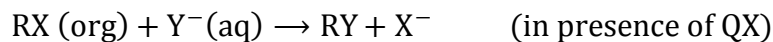


Figure 1.4: Starks Extraction Mechanism of PTC ^[4]

A resin bound PTC offers advantage over normal soluble PTC as they can be easily separated from reactor mixture by normal filtration and can be used in continuous flow reactor. When soluble catalyst is used, migration of ion pairs between phases is free but in case of resin based PTC, cation is part of resin which is solid and this subsequently makes its recovery easy.

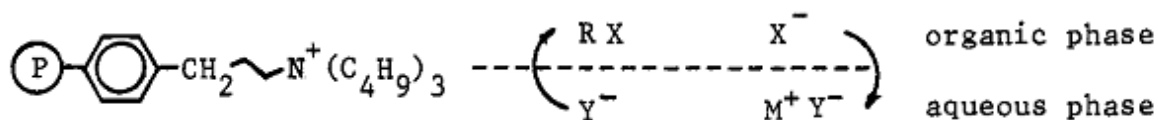


Figure 1.5: Mechanism of Resin bound PTC ^[4]

The resin-bound form has also disadvantages: physical attrition of particles, low chemical and thermal stability of resin quaternary onium groups, lower activity, higher cost in comparison with soluble analogs, etc.

Sieve outlined various advantages of resin bound PTC:

1. Improved reaction rates and lower reaction temperature.
2. Modified product ratio and selectivity.
3. Increase yield due to suppression of side reactions.
4. Expensive anhydrous/aprotic solvents not required.
5. Aq. alkali metal employed instead of alkoxides, amides, hydrides, or metals.
6. Commercial available, inexpensive catalysts are used.

1.5.4 FACTORS THAT AFFECT MECHANISM OF PTC

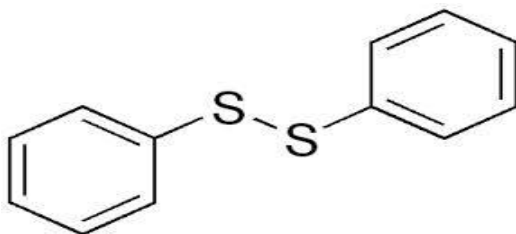
1. As interfacial area increases, reaction becomes faster.
2. Rate of transfer becomes slower as alkyl group in RN^+ becomes larger.
3. Large weakly hydrated or organic liquids (like iodine per chlorate) are easily transferred while small hydrated anions (fluorides, hydroxides) are poorly transferred.

1.5.5 AMBERLITE IR 400 CHLORIDE FORM

Amberlite is anion exchange resin bound catalyst made up of styrene and divinyl benzene. Its particle size is 16-50 mesh and contains active quaternary ammonium functional group. Amberlite being a solid catalyst offers edge over other liquid catalyst like PEG, TBAB. Its separation is easy and it can be used repeatedly. In addition, it is easily available at low price. Amberlite offers more activity than PEG, TBAB

1.6 DIBENZYL DISULFIDE

Dibenzyl Disulfide (DBDS) also called Benzyl disulfide is an aromatic disulfide with molecular formula $C_{14}H_{14}S_2$. It has a structural unit, which consists of a linked pair of sulfur atoms. It is insoluble in water whereas soluble in hot methanol, benzene, ether and hot ethanol. Large disulfides-linked agglomerates are rife found in proteins and many other biologically active molecules.



Formula: $C_{14}H_{14}S_2$

Molar mass: 246.38 gm/mole

Boiling point: 210-216 °C

Melting point: 72 °C

Density: 1.5 gm/cm³

1.7 USES OF DIBENZYL DISULFIDE

1. DBDS is widely used as building blocks in production of organosulfur compound.
2. Used in compounding of rubber and elastomers for increasing their tensile strength.
3. Increases tensile strength of rubber
4. As an additive to silicone oils.
5. Used as stabilizers for petro fractions.

CHAPTER 2
LITERATURE
SURVEY

2.1 REMOVAL OF H₂S

Kohl and Riesenfeld (1979) used conventional process of absorption to remove H₂S from sour gases. However, need of a selective absorption was felt when sour gases contained other acidic gases (CO₂) also. Hamblin (1973) used ammonium hydroxide to treat sour gas by converting it into ammonium hydrosulfide. Blauwhoff and Swaaij (1985) showed that mass transfer resistance in gas and liquid phase influence selectivity. Versteeg and Swaaij (1988) ^[6] designed centrifugal reactor and Schrauwen and Thoenes (1988) designed cyclone reactor to improve K_G/K_L and selectivity. Kraulen et al. (1992) ^[6] used micro porous membrane and pure alkanolamines to see its effect on the production and selectivity. Membrane absorption method offered several advantages like large interfacial area/volume, separate control of liquid-gas flow rates, which eliminates flooding, foaming, and entrainment.

K. Li et al. (1998) ^[7] used aq. solution containing 10% NaOH and analyzed H₂S removal by varying operating pressure, gas velocities in fibre lumen membrane area and resistance. They concluded that membrane resistance solely controlled H₂S removal rate. Hedayat et al. (2011) ^[8] used MDEA, MDEA/DEA and MDEA/MEA to separate H₂S from gas using PSF (Polysulfone) and PVDF (Polyvinylidene fluoride) hollow fibre membranes. A.B. Jensen and C. Web (1995) ^[9] used microbiological alternatives to treat sour gases. Ghawas et al. (1991) used MDEA for simultaneous absorption of CO₂, H₂S, and COS. Shiflett and Yokozeki (2010) ^[10] used ionic liquid [bmim][PF₆] for separation of CO₂ and H₂S. Mandal et al. (2004) ^[11] used aqueous solutions of MDEA and AMP for selective removal of H₂S from N₂ streams containing H₂S and CO₂. Boumedine et al. (2004) ^[12] determined solubility of H₂S in aq. alkanolamine solutions. Xia et al. (2003) ^[13] studied solubility of H₂S in (H₂O + piperazine) and in (H₂O + MDEA + piperazine).

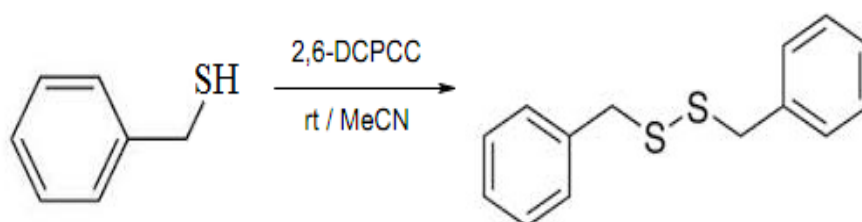
2.2 PHASE TRANSFER CATALYST AND ITS APPLICATIONS

Broad study and investigation of resin bound catalyst has been done by Cinouini et al. (1976) ^[14] where they bounded some typical PTC to resin matrix (resin). Their results showed that reaction with resin bound PTC are relatively slower than similar non-immobilized PTC but at the same time resin bound catalyst can be recovered by simple filtration at the end of reaction and can be reused. Pradhan and Sharma (1992), studied the effect of basic alumina and Amberlyst A27 (Cl) as catalyst, on the reaction of BC and Parachlorobenzyl chloride with solid sodium sulfide. The catalyst used in this case is triphase catalyst. S K Maity et al. (2008) examined the reduction of Para-nitrotoluene by aq. ammonium sulfide using Serelite SRA400 in a triphase catalysis reaction. Para-nitro toluene's reduction rate was found to be proportional to the square of sulfide's concentration and it was proportional to the cube of PNT's concentration.

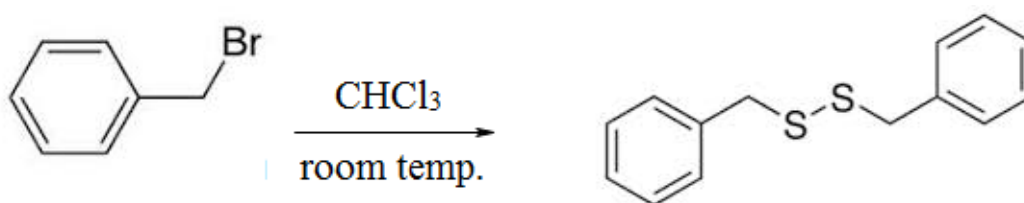
B Gao, Z Wang, L Wang (2010), studied the effect of different type of quaternary salt type triphase PTC on the esterification reaction of BC with sodium acetate. They found that ammonium type have the higher activity than quaternary phosphonium-type catalyst. S K Maity et al. (2006) analyzed the kinetics of reaction of BC with ammonium sulfide under L-L phase transfer catalyst. G.D Yadav and O.V Badure (2007) studied the benefits of formation of a third phase in dual phase reaction. They found that use of L-L-L PTC enhances the conversion and increase the selectivity also. He confirmed it by reacting phenol with BC under L-L PTC and L-L-L PTC separately and comparing the data obtained.

2.3 DIBENZYL DISULFIDE SYNTHESIS

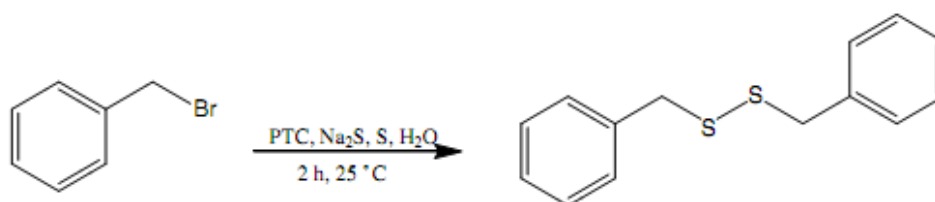
1. Md. Tajbakhsh et al. (2004) ^[15] synthesized disulfide from thiols by oxidation with 2,6-DCPCC in acetonitrile at room temperature. For synthesis of DBDS, they used benzyl mercaptan. In 8 min, 96% yield was obtained.



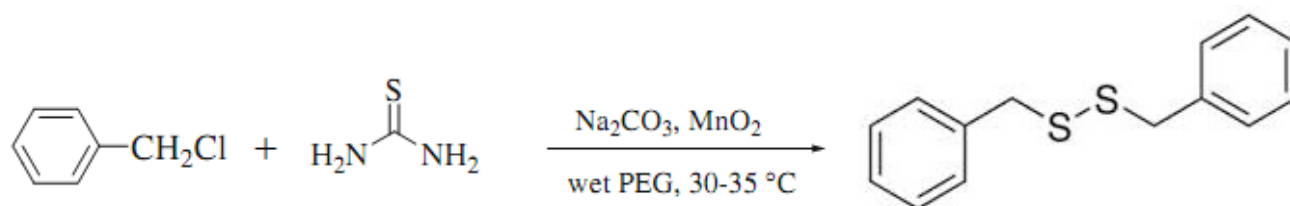
2. Vivek Polshettiwar et al. (2003) ^[16] obtained disulfide from reaction of alkyl halide with reagent (C₆H₅CH₂N(Et)₃)₆Mo₇S₂₄ in presence of CHCl₃ at room temperature. Pure disulfide was obtained by purification by column chromatography method on silica gel. 89% yield was obtained.



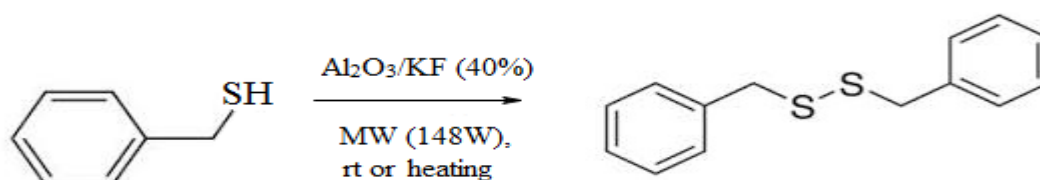
3. Sachin U. Sonavane et al. (2007) ^[17] used different PTC to prepare disulfide in presence of Na₂S, sulfur at room temperature. With TBAB 95% conversion and 88% yield was obtained. With TBMBB 91% conversion and 80% yield, with DDAB 100% conversion, 96% yield and with PEG-300, 83% conversion and 68% yield was obtained. Chloroform-water solvent system was found to be the best among the various systems tested.



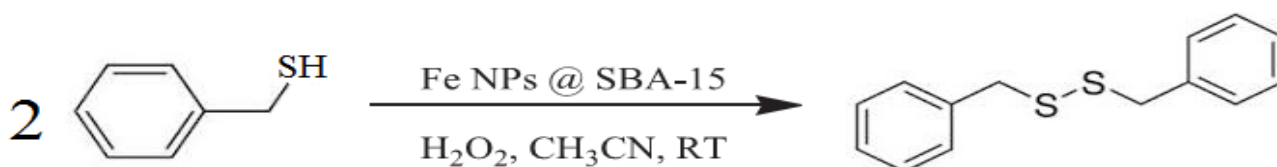
4. Habib Firouzabadi et al. (2010) ^[18] prepared disulfide using wet PEG-200, thiourea, MnO₂ and Na₂CO₃. The overall process was free from foul smell of thiols. After 4 hrs, 80-84% yield of DBDS was obtained.



5. E. J. Lenardao et al. (2007) ^[19] analyzed the oxidation reaction where thiols get converted to disulfides in the presence of Al₂O₃/KF in solvent free condition by heating at room temperature (A) or by irradiating in MW at 148W (B). For method (A) time taken was 5 hrs 30 min and yield was 73% and for method (B) time taken was 4 min and yield was 86%. This effect of MW irradiation was confirmed by work of S. Thurow et al. (2011). They used 1-n-butyl-3-methylimidazolium methyl selenite to oxidize thiols to corresponding disulfides.



6. Fathemeh Rajabi et al. (2013) ^[20] used bound iron oxide nano particles as catalyst for oxidation of thiols to disulfides. H₂O₂ was used as oxidant and CH₃CN as solvent gave maximum yield. Time taken was 90 min and yield was 95% with benzyl mercaptan.



2.4 CONCLUSION

The absorption of H₂S and NH₃ into water and the use of NH₄OH and aqueous alkanolamine for the extraction of H₂S from gas streams are well documented. Few works have been done on conversion of H₂S rich amine into products like Benzyl sulfide. However, there is no promulgated information anywhere in the literature on the utilization of H₂S-rich aqueous alkanolamines to produce disulfides. Disulfides have always been synthesized from thiols, alkyl halides in presence of other reagents. No attempt has been made in the past to prepare DBDS by reacting Benzyl Chloride (BC), H₂S-rich aqueous alkanolamine, and sulfur in presence of PTC.

2.5 OBJECTIVE

1. To study the synthesis of DBDS using H_2S rich aq. alkanolamine, sulfur in presence of phase transfer catalyst. In industries, normally H_2S present in gas streams is absorbed in amines and is converted to sulfur through conventional Claus process. From economical point of view, sulfur is not so good product, so the idea is to find out a substitute for the Claus process where H_2S rich amine instead of going to the scrubber is fed to some reactor for production of compounds like thioether, disulfides which are more valuable than sulfur. Also the need of additional scrubber and other Claus units is ruled out in the new alternative process which makes the overall process economical.
2. The present work includes preparation of DBDS by using BC, H_2S , and sulfur in presence of Amberlite IR 400. No attempt has been made in past to prepare DBDS using H_2S and Phase Transfer Catalyst.
3. Kinetic study by variation of temperature, speed, catalyst loading etc and their effect on conversion.

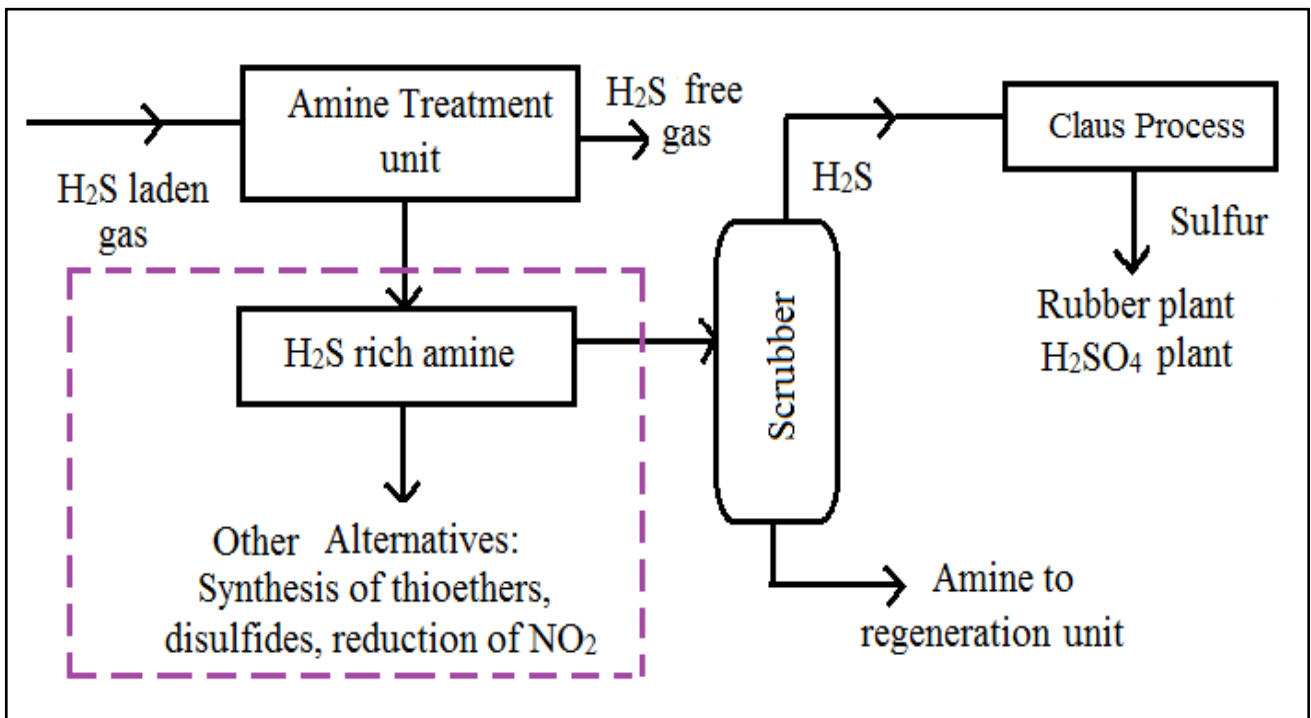


Figure 2.1: General Layout of Objective

CHAPTER 3

EXPERIMENTAL

SETUP

3.1 CHEMICALS AND CATALYST

H₂S will be prepared in the laboratory using Kipp's apparatus. Sulfide content is estimated by iodometric titration method, details of which are given in 3.3. Distilled water is used here and is purified by deionization.

- Chemicals brought from Merck (India) Ltd., Mumbai

Toluene ($\geq 99.5\%$) of analytical grade; Amberlite IR 400; MEA ($\geq 98\%$) synthesis grade; the chemicals used for iodometric titration for the estimation of sulfide content i.e., sodium thiosulfate, potassium iodate, potassium iodide, starch powder, sulfuric acid (98% pure) and sodium hydroxide pellets of analytical grade.

- Chemicals procured from Sigma Aldrich, Mumbai, India

Sulfur, Iron (II) sulfide (FeS) sticks.

3.2 PREPARATION OF H₂S-RICH AQUEOUS ALKANOLAMINES

30-35% of MEA solution is prepared by diluting a suitable amount of MEA in distilled water. Kipp's apparatus was used to prepare H₂S gas in laboratory scale by reacting FeS sticks with H₂SO₄. The concentration of H₂SO₄ is taken as 1 molar. Then H₂S gas produced (as shown in below Fig. 3.1) is bubbled through this MEA solution in a 250 mL std. gas bubbler.

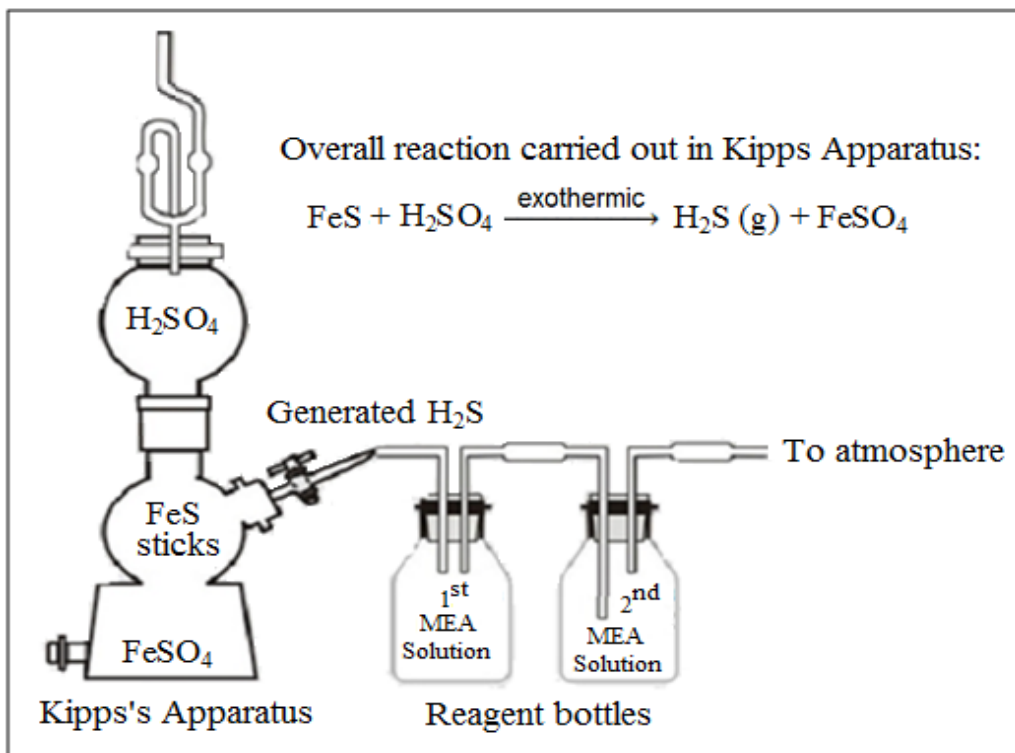


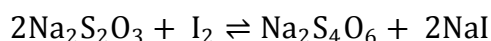
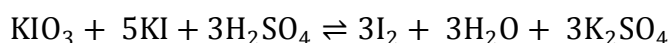
Figure 3.1: Schematic diagram- H₂S absorption in MEA solution ^[5]

The reaction between H₂S and alkanolamines is exothermic (Kohl and Nielsen, 1997), and hence the gas bubbler containing aqueous alkanolamine is immersed in water bath full of ice to preclude disulfide formation via oxidation of sulfide. Unabsorbed H₂S gas from the 1st bubbler is then sent to 2nd bubbler containing ~ 1M MEA solution. Its outlet is kept open to the atmosphere. Liquid samples will be drawn off time to time after the gas bubbling is ceased and the sample is tested for sulfide concentration (Scott, 1966). The gas bubbling was continued till we get coveted concentration of sulfide in the aq. alkanolamines.

3.3 DETERMINATION OF SULFIDE CONCENTRATION

Standard iodometric titration test were performed to find initial sulfide concentrations (Scott, 1966) as given below:

- **Preparation of standard (0.025 M) KIO₃ solution:** Weigh 4.28 gm of KIO₃ accurately and dissolve it in distilled water and make up to 1 L in a graduated volumetric flask.
- **Preparation of standard (0.1 M) sodium thiosulfate solution:** Weigh 25 gm of Na₂S₂O₃·5H₂O crystals and make up to 1 L by dissolving it in distilled water in a graduated volumetric flask. Add about 0.1 g of sodium carbonate or three drops of chloroform to this solution to keep the solution for more than a few days.
- **Standardization of sodium thiosulfate solution by standard KIO₃ solution:** Take 25 mL of 0.025M KIO₃ solution and add 1 gm (excess) of KI to it followed by 3 mL of 1 M H₂SO₄. Titrate the liberated iodine (I₂) with thiosulfate. When the color of the solution turns pale yellow, add distilled water to dilute it to 200 mL. Add 2 mL of starch solution and the titration is continued until the color changes from blue to colorless. The chemical reaction involved in this titration is given below

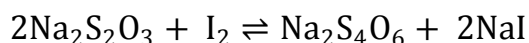
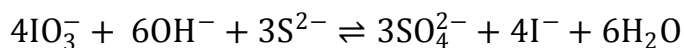


Therefore, 1mole of KIO₃ = 3 * 2 mole of Na₂S₂O₃

$$\text{Strength of thiosulfate solution} = \left(\frac{6 * \text{Strength of KIO}_3 * \text{Volume of KIO}_3}{\text{Volume of thiosulfate consumed}} \right)$$

Take 15 mL of standard (0.025M) KIO₃ solution in a conical flask. Add 10 mL of sulfide solution followed by the addition 10 mL of 10M NaOH solution. The mixtures are boiled gently for about 10 minutes, cooled, and add 5 mL of KI solution and 20 mL of 4M H₂SO₄ solution to it. The liberated iodine is titrated, which is equivalent to the unused KIO₃, with a standard 0.1M sodium thiosulfate in the usual manner. The KIO₃ in the alkaline medium oxidizes the sulfide to sulfate as given by the following reaction.

For sulfide solution having sufficiently high sulfide concentration, suitable dilution is made before the estimation of sulfide by above mentioned procedure.



Therefore, 4 mole of $\text{IO}_3^- = 3$ mole of S^{2-}

$$\text{H}_2\text{S concentration} = \left\{ \left[(15 * S_{\text{iodate}}) - \frac{(V_{\text{thiosulfate}} * S_{\text{thiosulfate}})}{6} \right] * \frac{3}{4} * \frac{N_d}{10} \right\}$$

Where S_{iodate} = Strength of KIO_3

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

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

N_d = Number of times of dilution

3.4 APPARATUS AND EQUIPMENT SETUP

All the reactions will be carried out into a thermo stated (± 0.5 °C) three-necked 250-mL (2.56 inch id) glass reactor. Borosilicate glass beaker was used as the contactor. A 0.79 inch-diameter 6-bladed glass disk turbine stirrer with the facility of speed regulation was used for agitating the reaction mixture for obtaining excellent solid-liquid mixing which as a result increased the mass transfer rate. To maintain isothermal conditions, whole assembly is placed in a water bath with controlled temperature within ± 0.5 °C and is mechanically agitated at a known speed with an electric motor.

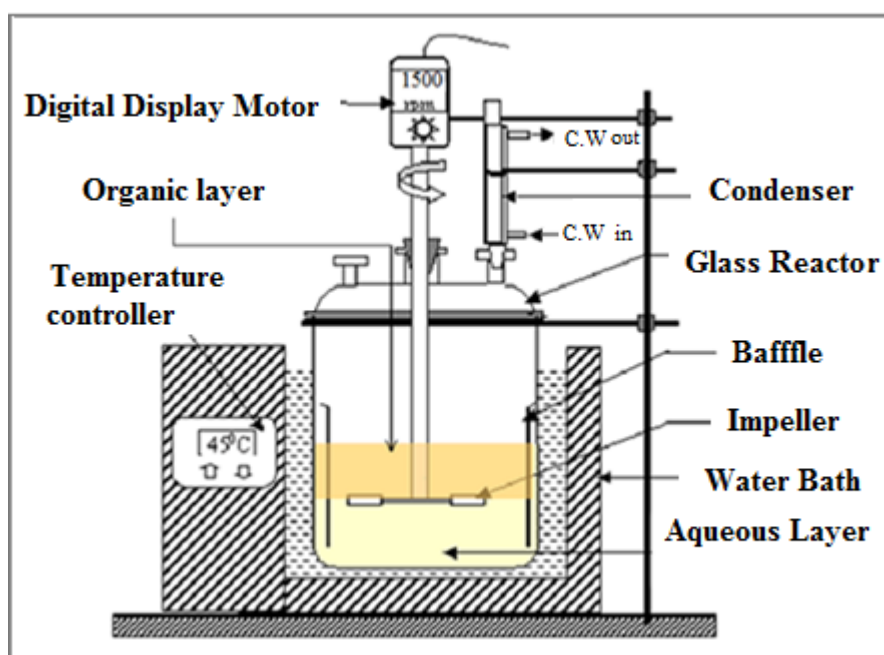


Figure 3.2: Schematic - Experimental setup^[1]

3.5 PROCEDURE

- a) 30-35 wt % of MEA solution was prepared by blending necessary amount of MEA and distilled water.
- b) H₂S gas obtained from Kipps Apparatus was absorbed in MEA (Fig: 3.1) and iodometric titration were performed to find the concentration.
- c) For preparation of org. phase, 35 ml of toluene and 15 ml of BC were mixed.
- d) For preparation of aq. phase, 3 gm of sulfur was dissolved in 50 ml of H₂S-MEA solution.
- e) 3 gm of Amberlite IR 400 was taken.
- f) 50 ml of each phase was fed in the reactor (Fig: 3.2). First aq. phase was fed followed by organic phase.
- g) Temperature was set at 323K and stirrer speed was set at 1500 rpm and system was switched ON.
- h) Then whole reactor along with mixture is immersed in an isothermal water bath. The mixture was stirred constantly.
- i) Around 0.1 ml of sample was collected after 5, 10, 15, 30, 60, 120, 240, 360, 480 min. Each time the sample was collected, the stirrer was switched OFF, and the agitation was stopped.
- j) Later on the product obtained was analyzed in Gas Chromatograph.
- k) Temperature, Stirrer speed, Catalyst conc., Reactant conc. were varied and all the above steps from (a) to (i) were repeated for each parameter.

3.6 ANALYSIS OF PRODUCT

0.2 mL of organic layer from the product was taken carefully from the reactor and 0.1 μ L was injected in gas chromatography (GC) for separation. Flame Ionization Detector (FID) was used to quantify the products in GC. Nitrogen gas (25 mL/min) was used as carrier gas during the analysis. The working principle of FID includes detection of ions which are produced during combustion of organic compounds in presence of a hydrogen flame (30mL/min). Air flow rate was 400 mL/min. Oven temperature was 300 °C. Ions generated are proportional to the concentration of organic species present in the sample gas stream.

CHAPTER 4

RESULTS AND

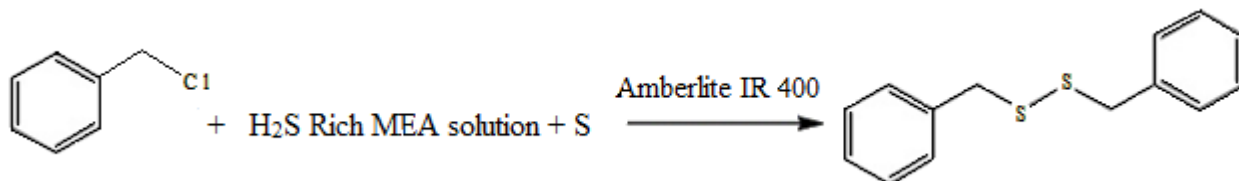
DISCUSSION

4.1 ABSTRACT

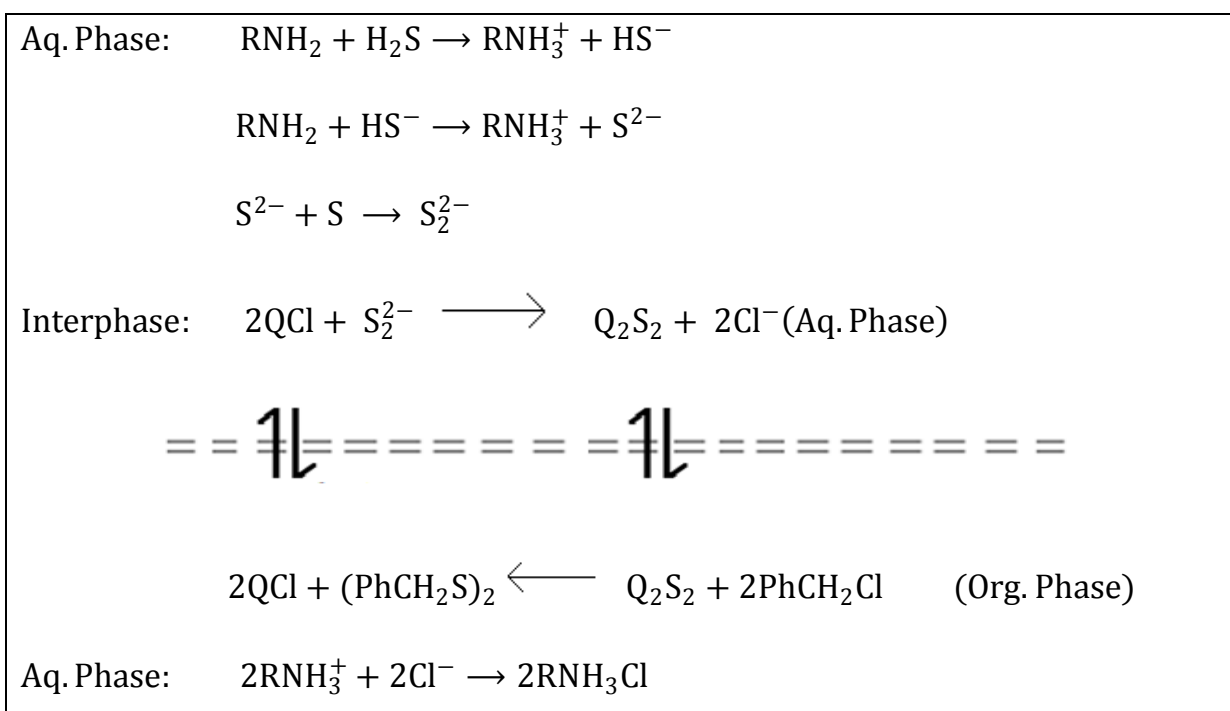
This chapter discusses the reaction mechanism between BC, Sulfur, and H₂S rich MEA solution in presence of triphase catalyst Amberlite IR 400. Various parameters have been varied like catalyst loading, stirrer speed and reactant concentration, and temperature and simultaneously their effect on conversion and selectivity has been studied.

4.2 REACTION and MECHANISM

Reaction can be represented as:



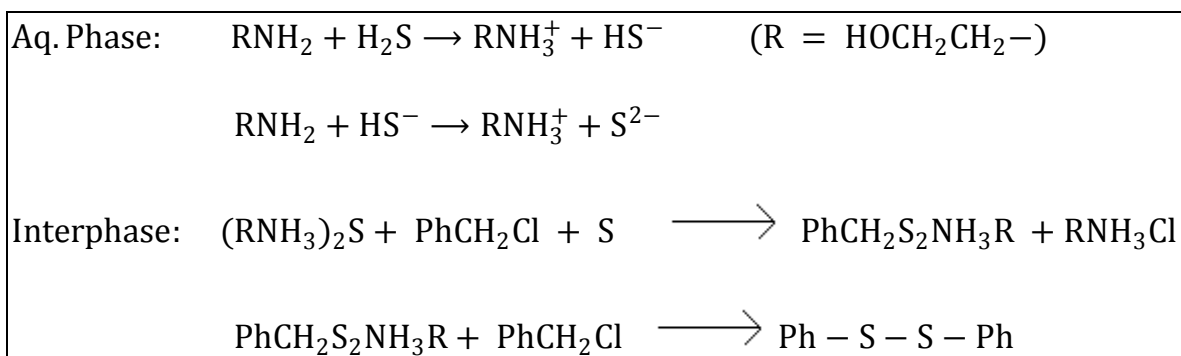
Lipophilicity of the catalyst decides the reaction mechanism for triphase catalysis reaction. A highly lipophilic catalyst implies that it remains entirely dissolved in org. phases and hence it will follow interfacial mechanism (Dehmlow, 1983), i.e. anion exchanges will occur near liquid - liquid interface. But if the catalyst is not so highly lipophilic, then it will not dissolve in any phases and hence they will follow extraction mechanism which was suggested by Starks (1971). Amberlite IR 400 is a solid resin bound catalyst and is not soluble in any of the two phases, so it will follow extraction mechanism. However, it was observed that the gel beads of Amberlite IR 400 swells and that the beads remained in organic phase and ammonium ion remains in aqueous phase. Since the nucleophilicity of sulfide ion and hydrosulfide ion is more than that of the chloride ion present in the catalyst, it replaces chloride ion on the catalyst. The following reaction takes place (Scheme 4.1)



Scheme 4.1

Reaction between catalyst (QCl) and S_2 generates ion pair Q_2S_2 in aq. phase. This is how anion S_2^{2-} is pulled through phase boundary in org. phase. Here it comes in contact of BC. Displacement reaction takes place and displaced anion Cl^- is transferred to aq. phase as QCl and thus the cycle gets completed. Being resin and solid in nature, catalyst can be recovered and reused again and again.

If we consider the non catalyzed pathway in presence of catalyst, from aq. phase reactions, we get ethanolanmonium sulfide RNH_3HS and hydrosulfide $(RNH_3)S$ which will react with BC directly at the interface of the aq. - org. phase as they are insoluble in org. phase. (Scheme 4.2)



Scheme 4.2

Four parameters like stirrer speed, catalyst concentration, initial BC concentration, and temperature were varied. Every time one parameter was varied keeping the other operating conditions same. Samples were collected after 5, 10, 15, 30, 60, 120, 240, 360, and 480 min for each individual experiment.

4.3 EFFECT OF STIRRER SPEED

For reaction's kinetic study, riddance of mass transfer resistance is very crucial. The effect of stirring speed was examined in range of 1000-2000 rpm; keeping other conditions identical in the presence of Amberlite IR 400 catalyst. The data obtained has been plotted as graph between percent BC Conversion vs. time (min) for different stirring speed. It is shown in Figure 4.1. From the graph it can be clearly seen that under this range of agitation speed, the variation in BC conversion is very small. This suggests that the mass transfer factor is very trifling. In the light of same, other reactions were conducted at 1500 rpm stirring speed to guarantee the absence of mass transfer resistance.

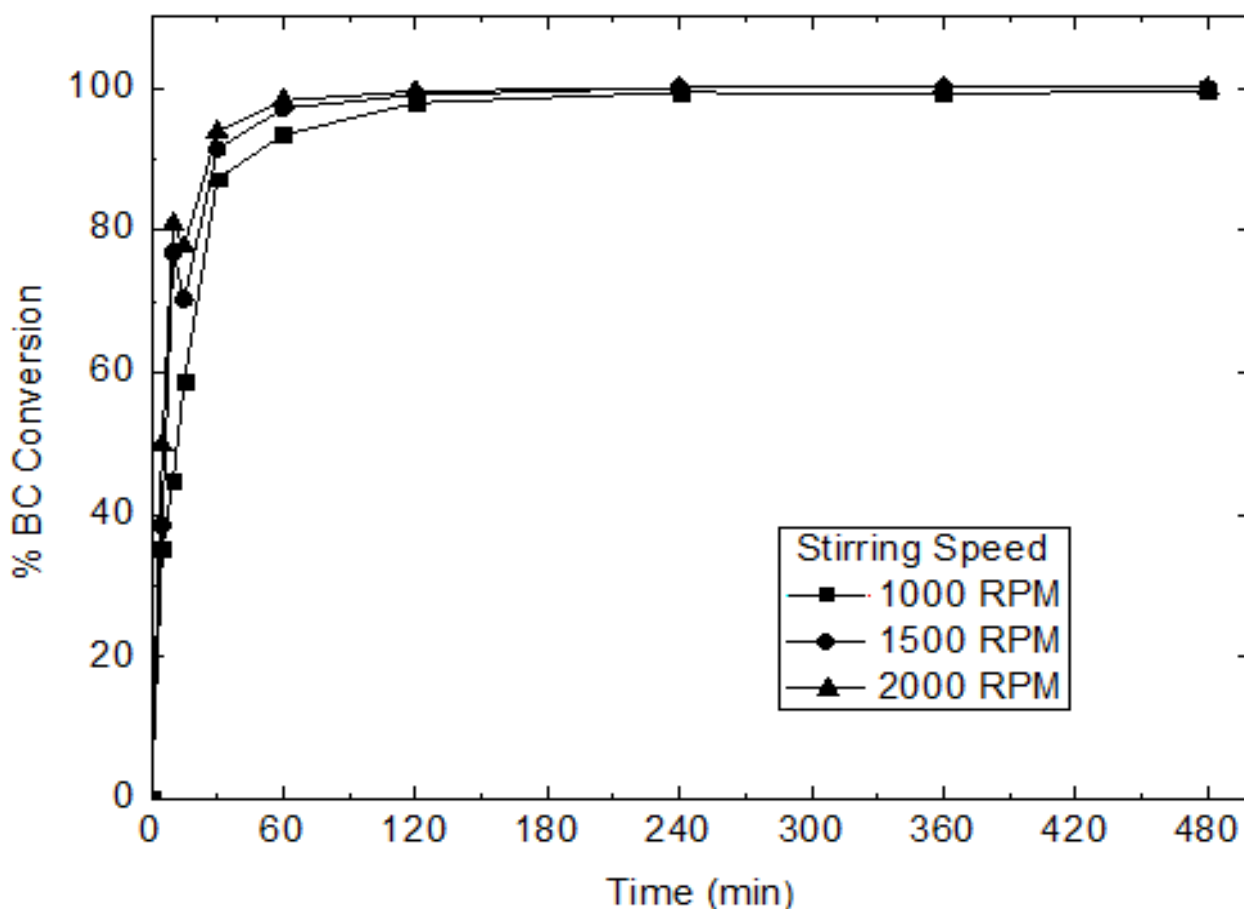


Figure 4.1: Effect of Stirrer Speed

% BC Conversion vs. Time for varying stirrer speeds

Operating Conditions: Organic phase Volume = 50 mL; Aqueous phase Volume = 50 mL; Sulfur = 3gm; BC concentration = 2.6 kmol/m^3 org. phase; Toluene concentration = 6.6 kmol/m^3 org. phase; Moles of catalyst = 0.29; Sulfide concentration of = 2.53 kmol/m^3 ; MEA/H₂S mole ratio = 2.28; Temperature = 323 K.

4.4 EFFECT OF CATALYST LOADING

For Amberlite IR 400, the outcome of varying catalyst concentration was examined in the range of 0 gm -10 gm (Figure 4.2). In general a catalyst provides an alternate path with lower energy of activation for reaction to take place. This is quite clear from the graph. It can be seen that with the increment in catalyst concentration, the BC conversion increased from 58% without catalyst to 100 % with catalyst after 6 hours of operation. It can be also observed from the graph that after 5gm catalyst loading, the conversion is almost same. This evidences that the mass transfer of the active species attains a maximum value after 5gm catalyst loading. DBDS is formed due to the migration of Q_2S_2 to the organic phase. Q_2S_2 is obtained as product in reaction of Q^+ ion obtained from the catalyst with the S_2^{2-} present in the aqueous phase. This Q_2S_2 then reacts with the BC and nucleophilic substitution takes place and DBDS is formed. So as the catalyst concentration increases, more Q^+ ion will be available and as a result more Q_2S_2 will be produced, which will increase the yield of DBDS.

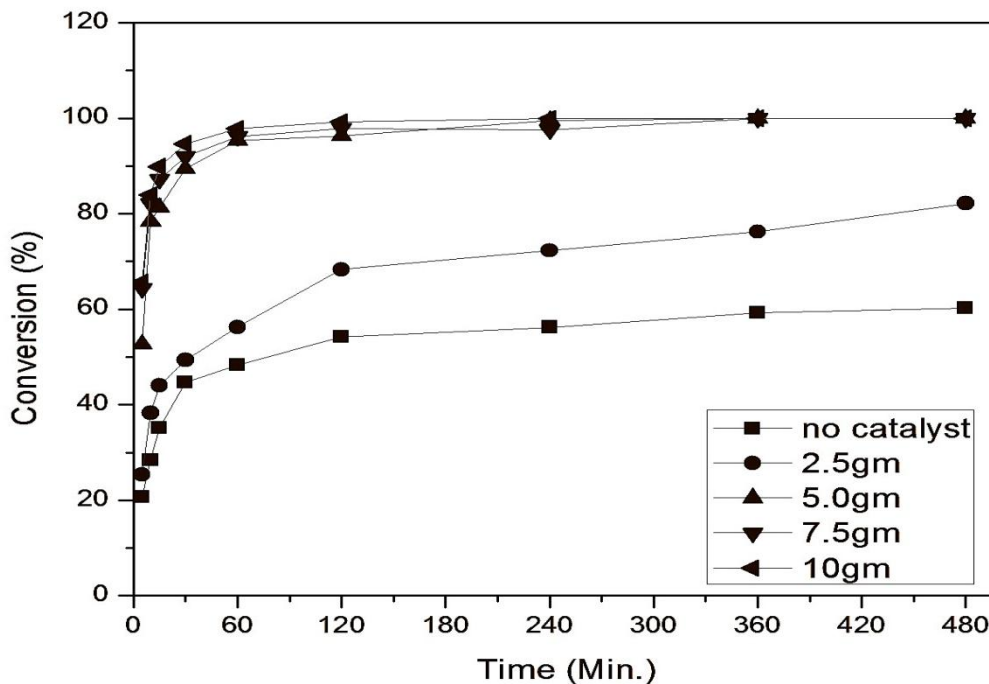


Figure 4.2: Effect of Catalyst variation

% BC Conversion vs. Time for varying Catalyst Concentration

Operating Conditions: Organic phase volume = 50 mL; Aqueous phase volume = 50 mL; Sulfur = 3gm; BC concentration = 2.6 kmol/m³ org. phase; Toluene concentration = 6.6; kmol/m³ org. phase; Sulfide concentration = 2.53 kmol/ m³; MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Stirrer speed = 1500 rpm.

4.5 EFFECT OF INITIAL BENZYL CHLORIDE CONCENTRATION

The result of varying BC concentration was examined by varying BC/sulfide mole ratio, by keeping H₂S concentration constant and subsequently a graph was plotted between percent BC Conversion vs. time (min) for different BC/sulfide mole ratio (Figure 4.3). From the plot, we find that as the concentration of BC rises, its % conversion reduces. This reduction in conversion can be explained by the fact that initial sulfide content remains same for all cases where the BC concentration has been varied and increased. So 1.04 has been chosen as optimum BC/sulfide ratio as it gave almost same conversion after 4 hrs as the ratio 0.70 gave. Though 0.70 gives slightly more conversion in all time intervals, still it is not chosen because it will give less yield as compared to ratio 1.04 which otherwise gives almost same conversion.

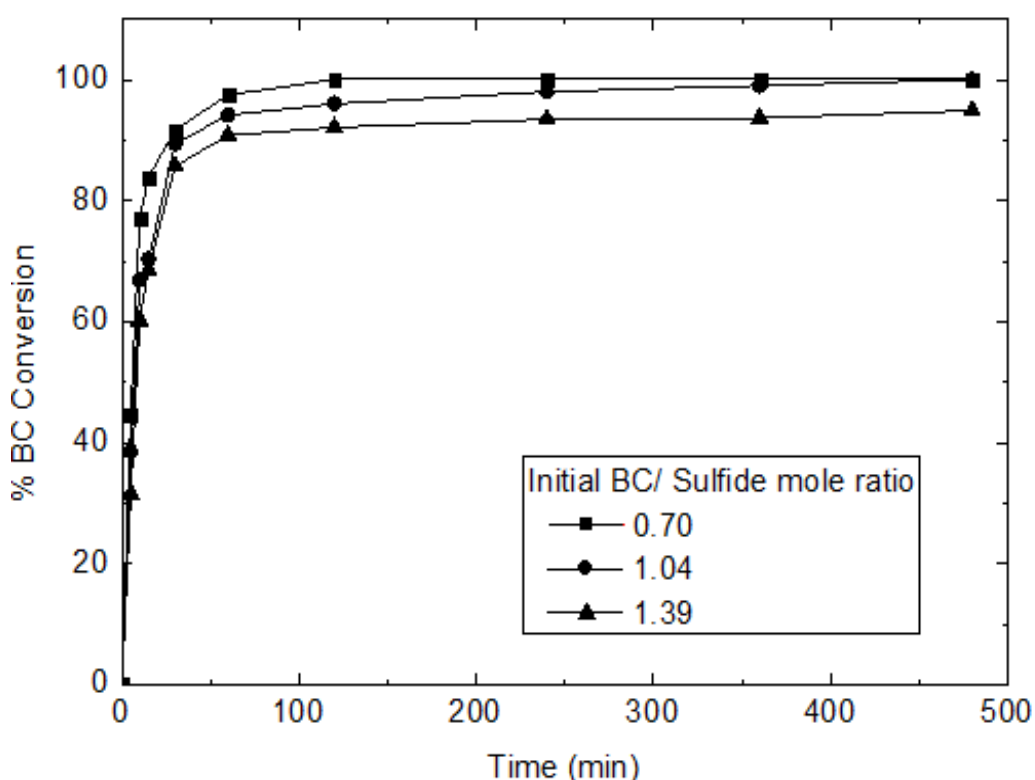


Figure 4.3: Effect of Reactant (BC) Variation
% BC Conversion vs. Time for varying Reactant Concentration

Operating Conditions: Organic phase volume of = 50 mL; Aqueous phase volume = $5.0 \times 10^{-5} \text{ m}^3$; Sulfur = 3gm; Moles of catalyst = 0.29; Sulfide concentration = 2.53 kmol/m^3 ; MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Stirrer speed = 1500 rpm.

4.6 EFFECT OF TEMPERATURE

The present work investigates the reaction of BC (in Toluene) with sulfur and H₂S-rich aqueous MEA catalyzed by Amberlite IR 400. Keeping the other operating conditions same, temperature was varied in the range 303 – 333K. A graph was plotted between percent BC Conversion vs. time (min) for different temperatures (Fig. 4.4). According to the transition-state theory, as temperature increases, the collision frequency increases. Also the number of particles (having a minimum activation energy required for participating in reaction) increases. As a result reaction rate increases. Simultaneously reactivity (conversion) of BC increases. 323K was selected as optimum temperature because after this temperature variation gave almost same conversions after 2 hrs.

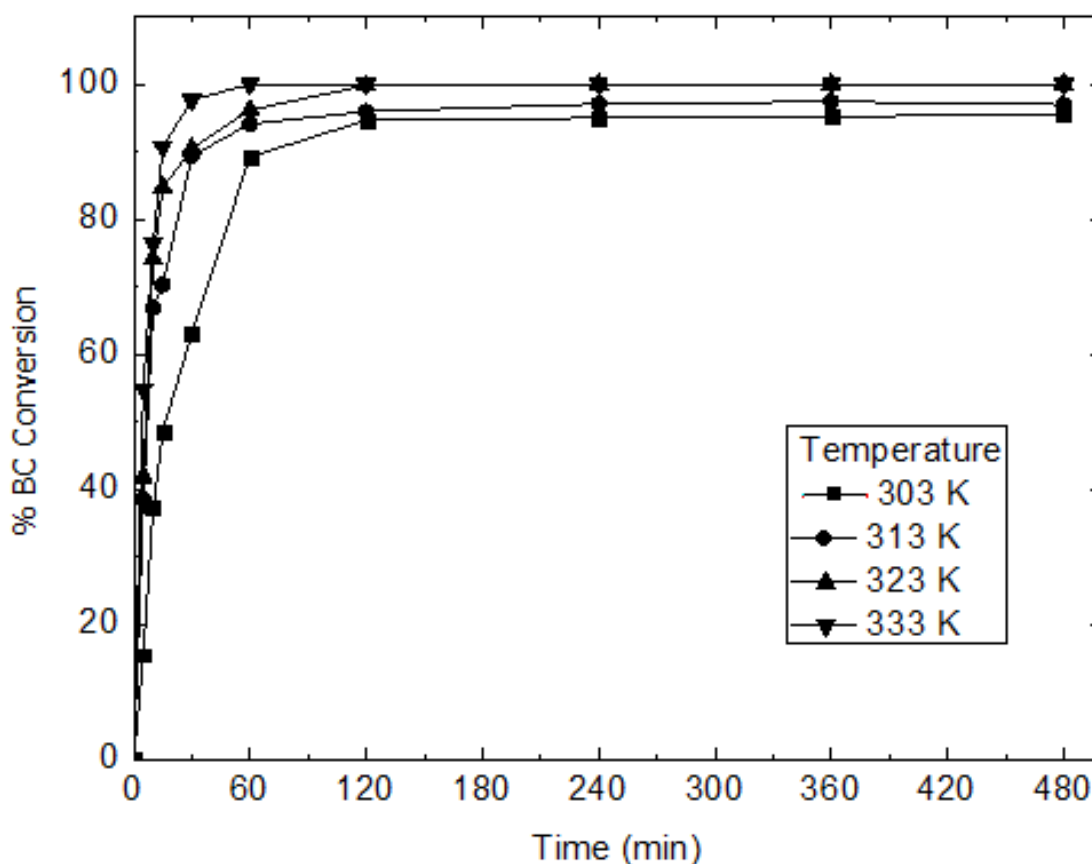


Figure 4.4: Effect of Temperature
% BC Conversion vs. Time for varying Temperature

Operating Conditions: Organic phase volume = 50 mL; Aqueous phase volume = 50 mL; Sulfur = 3gm; BC concentration = 2.6 kmol/m³ org. phase; Toluene concentration = 6.6 kmol/m³ org. phase; Moles of catalyst = 0.29; Sulfide concentration = 2.53 kmol/ m³; MEA/H₂S mole ratio = 2.28; Stirrer speed = 1500 rpm.

Initial reaction rate was ciphered at different temperatures values and subsequently an Arrhenius equation was drawn between the natural logarithm of initial rate and inverse of temperature (Fig. 4.5). The apparent energy of activation for the reaction of BC was ciphered from the slope of the straight line as 22.4kJ mol^{-1} . The ascertained high apparent activation energy confirmed the fact that the reaction is kinetically controlled.

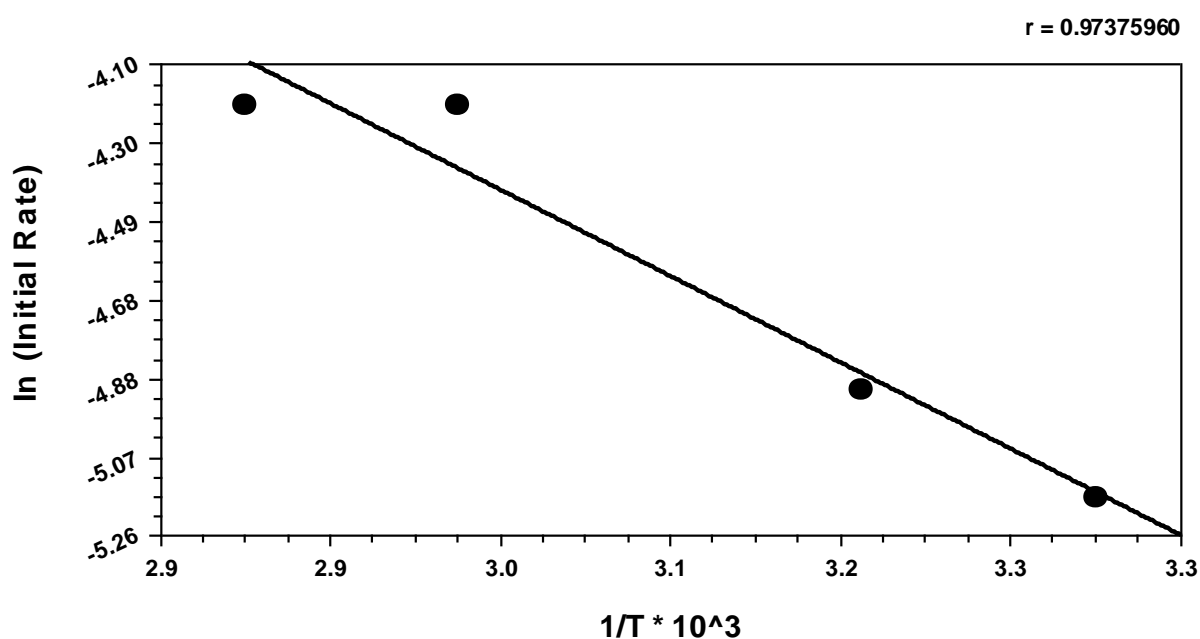


Fig. 4.5: Arrhenius plot for activation energy

Operating Conditions: Organic phase volume = 50 mL; Aqueous phase volume = 50 mL; Sulfur = 3gm; BC concentration = 2.6 kmol/m^3 org. phase; Toluene concentration = 6.6 kmol/m^3 org. phase; Moles of catalyst = 0.29; Sulfide concentration = 2.53 kmol/m^3 ; MEA/H₂S mole ratio = 2.28; Stirrer speed = 1500 rpm.

4.7 CONCLUSION

The present work includes reaction of H₂S rich MEA, sulfur, and BC (in toluene) in presence of Amberlite IR 400. DBDS was obtained as product which has better commercial value as compared to the sulfur obtained from Claus process. In this whole process of triphase catalysis, the one active ion pair Q₂S₂ was produced in aq. phase and it then migrated to the organic phase where it produced DBDS on reaction with BC. The maximum conversion of 100% and selectivity of 100% has been obtained under the operating conditions:

Operating Conditions: Organic phase volume = 50 mL; Aqueous phase volume = 50 mL; Sulfur = 3gm; BC Concentration = 2.6 kmol/m³ org. phase; Toluene Concentration = 6.6 kmol/m³ org. phase; Moles of catalyst = 0.29; Sulfide concentration of = 2.53 kmol/ m³; MEA/H₂S mole ratio = 2.28; Temperature = 323 K; Stirrer speed = 1500 rpm.

It was found that high catalyst concentration and low initial BC concentration favored the production of DBDS. The reaction was found to be first order with respect to BC. The effect of stirring speed was found to be negligible which confirms that mass transfer does not controls the reaction and that the reaction is kinetically controlled.

SCOPE OF FURTHER WORK

- The work in this thesis delineated the preparation of DBDS by using H₂S rich MEA and BC (in toluene) by using Amberlite IR 400 as triphase catalyst. Parameters like Stirring speed, temperature, Initial BC concentration were studied and corresponding graphs were plotted. But many other parameters could have been varied and studied like effect of initial sulfide concentration, effect of MEA concentration. We could not try them because of lack of facility, late installation of GC-MS, and delay in the supply of materials.
- Toluene has been used as solvent for organic phase. In present study, toluene has been used as a solvent and swelling was observed in the catalyst. In any triphase catalysis reaction, solvent affects the transport properties of PTC and active ions formed (Q₂S₂). The whole reaction procedure can be repeated with chlorobenzene or n-heptane can solvents.
- Other aq. Phase can be used like MDEA, DEA depending on the type of gas stream. If stream contains CO₂, then for selective removal of H₂S, absorption in MDEA will be appropriate.
- This whole work is aimed at preparation of DBDS. But if we vary the reactant and use some substituted halide, we will be able to produce substituted sulfides.
- Selective preparation of tri sulfides and poly sulfides can be done by controlling the amount of sulfur in the reactant.

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