Natubhai V. Patel College of Pure & Applied Sciences

T. Y. B.Sc. (Industrial chemistry)

IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals

UNIT – 1B

Syllabus

Amination: Introduction of amination by reduction and by ammonolysis. Different types of reduction reactions and manufacturing of Aniline by Bechamp reduction, m-nitro aniline and Aniline by ammonolysis.

AMINATION BY REDUCTON

1.20 INTRODUCTION

Amination by reduction involve the synthesis of amines by reductive methods. **Amines** can be **produced by reducing** nitro, nitroso, hydroxylamino, azoxy, azo and hydrazo compounds as well as oximes, amides, nitriles and azides. In each case, a carbon to nitrogen bond already exists. Amines may also be formed by **reacting compounds** containing certain **labile groups** (e.g. halogens, hydroxyl and sulfonic) with ammonia.

1.21 METHODS FOR THE PREPARATION OF PRIMARY AMINES

  - The **reduction of** nitro, nitroso, hydroxylamino, azoxy, azo and hydrazo compounds.
  - The **reduction of** nitrites, amides, oximes and azides.
  - The **replacement of labile groups**, such as nitro, halogen, hydroxyl and sulfonic acid by reaction with ammonia or ammonia progenitors such as urea.
  - **Intramolecular replacement** of (a) hydrazobenzenes and hydroxylamines (b) amides and (c) secondary and tertiary amines.
  - The **hydrolysis** of N-substituted amides.
  - **Direct amination** by means of hydroxylamine and sulfuric acid.
    First four are the most important methods from chemical engineering point of view.

1.22 USES OF AMINES

Amines are of very great importance **as intermediates** in the chemical process industries. They are used in **production of** dyes, rubber chemicals, nylon, pharmaceuticals, gasoline additives, surfactants, textile auxiliaries, photographic chemicals, chelating agents, sweetening agents, agricultural chemicals, polyurethanes, inks, plastics etc.

In recent years, the production of diamines by reductive methods has become increasingly important. **Hexamethylenediamine** is a prime intermediates, together with adipic acid, in the production of nylon 66. **m-phenylenediamine** is used as a crosslinking agent in epoxy resin. **Toludenediamines** are intermediates in the production of toluene disocyanates, from which are made polyurethane foam, rubbers, coatings and adhesives.

1.23 METHODS OF REDUCTION

A great variety of reduction methods have been used for the preparation of amines. Among these are:
  1. **Metal and acid:** Iron and acid (Bechamp method) is the major example in this category, but other metals (tin, zinc) have also been employed. Generally, hydrochloric acid is preferred, but sulphuric acid, acetic acid and formic acid have also been used.

2. **Metal and alkali:** This method is used mainly for the production of azoxy, azo and hydrazo compounds. The latter are important in the manufacture of the benzidine series.
3. **Metal hydrides**
4. **Catalytic:** This method involves the use of hydrogen (or hydrogen - containing gases) and a catalyst such as nickel, copper, platinum, palladium or molybdenum sulfide.
5. **Sulfide:** This is used mainly for the partial reduction of polynitro aromatic compounds to nitro-amines and for reduction of nitro-anthraquinones to amino- anthraquinones.
6. **Sulfite (Piria method):** The reaction of sodium sulfite and bisulfite on an aromatic nitro compound leads to a mixture of amine and aminoaryl sulfonic acid.
7. **Sodium hydrosulfite** (hyposulfite).
8. **Electrolytic**
9. **Sodium and sodium alcoholate**.
10. **Strong caustic oxidation-reduction**.
11. **Hydrogenated quinolines and naphthalene**.

By a **proper selection** of reducing agent and careful **regulation of** the **process**, reduction may often be stopped at intermediates states and **valuable products** other than amines **obtained**. **Metal and acid** reduction is most vigorous and usually yields amines as end products. When nitrobenzene is treated with zinc and a mineral acid, the resultant product is aniline. When an **alkaline solution** is employed, hydrazobenzene is generally obtained, but very vigorous conditions sometimes result in the formation of aniline. When **zinc dust** and **water** are used, reaction product is phenyl hydroxylamine as shown below.
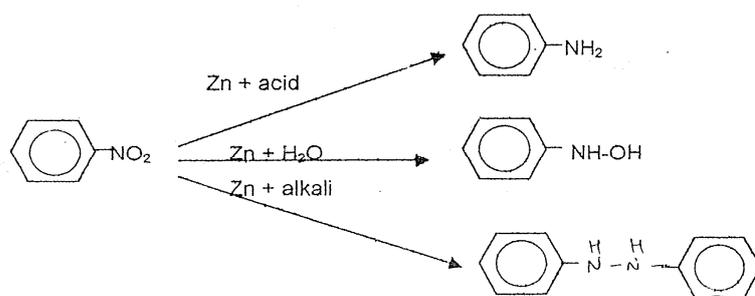
When the compound to be treated contains **more than one nitro group**, the product of **reduction depends** upon the agents used. Thus, m-phenylenediamine is obtained by the iron and acid reduction of m-dinitrobenzene, while the alkaline sulfide reduction yields m-nitro aniline.
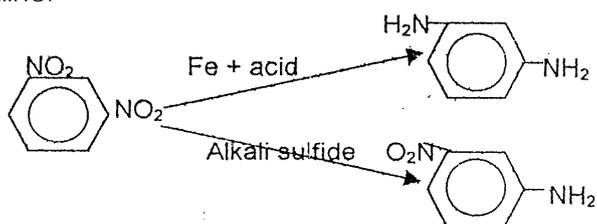
With certain compounds containing acid or alkali sensitive groups (e.g. ester or amides), it is necessary to adjust the pH carefully to avoid decomposition and side reactions. In such reductions on the acid side, it is generally advisable to replace the normally used mineral acids with organic acid like acetic acid. An example of the latter is the reduction of nitroanilides, for here the presence of mineral acids would tend to hydrolyze the anilide to an amine.

The **method** to be **used** will therefore, **depend upon** the degree of reduction desired, the sensitivity to the process of both starting material and final product, the need for avoiding contaminants and the overall economics.

The reduction of nitro compounds involves the progressive removal and replacement by hydrogen of the oxygen in the -NO_2 group. The **intermediate products** in the reduction of

nitrobenzene, whose **interrelationships** are shown in the following figure are obtained by control of the reduction potential of the system.
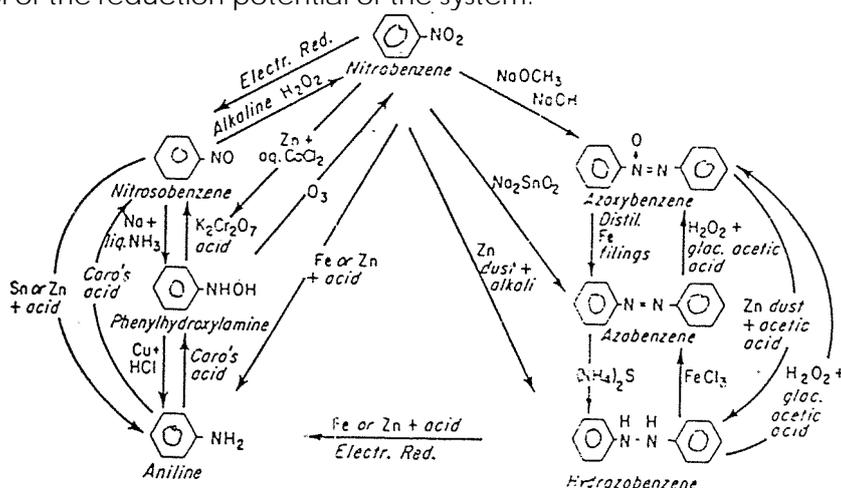

Figure: Reduction products of Nitrobenzene

1.24 <u>IRON AND ACID (BECHAMP) REDUCTION</u>

Bechamp's discovered in 1854 that nitro compounds could be reduced in the presence of iron and acetic acid. **Parkin** applied the reaction in the commercial production of aniline. Technical progress in the application of this reaction was first made by substituting hydrochloric acid for the acetic acid, originally employed. Subsequently, it was discovered that the ferrous functions in such a way that reduction could be carried out with far less than the theoretical quantity of acid.

Reaction: $C_6H_5NO_2 + 2Fe + 6HCl \longrightarrow C_6H_5NH_2 + 2H_2O + 2FeCl_3$
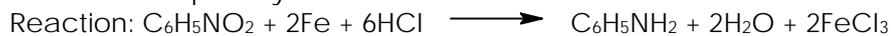
Formula wt.:123 2(55.84) 6(36.45)

In industrial practice, less than 2 % of the amount indicated above is actually used. Operating experience has shown that 3.0 lb of hydrochloric acid (10 lb of 30 % solution) is sufficient to bring about a satisfactory reduction of 100 lb of nitrobenzene to aniline.

The presence of free acid has been shown to be unnecessary. It is demonstrated that nitrobenzene could be reduced with iron powder in alcoholic or aqueous solution, in the presence of magnesium or calcium chloride. The absence of free acid is advantageous. It has been demonstrated that aniline hydrochloride, aluminium chloride, sodium bisulfate or other salts derived from strong acids can be successfully employed. All that is required is a salt that acts like an acid in water solution, liberating hydrogen ion.

1.24.1 Chemical and physical factors

1.24.1.1 Amount of iron

In plant practice, it is customary to use slightly over **2 moles Fe** per mole nitro compound to carry out the reduction process. Under such circumstances, not all the iron is converted to the ferrosoferric oxide, some reducto - active ferrous hydroxide also being present. In plant, practice, it has been found that when **insufficient iron** is present the addition of heat or acid is not effective in carrying the reduction to completion and poorly filtering iron oxide sludge is obtained. The introduction of some finely divided iron under such circumstances brings about a vigorous reaction, which results in the complete reduction of the nitro compound. The range of iron generally used is about **2.5 - 5.0 moles** per mole of nitro compound. This has been found satisfactory for a wide variety of aromatic amines. Some operation prefers to use very **finely divided iron** to finish a reduction and this practice is particularly advisable when the bulk of the iron turnings is not of good quality.

1.24.1.2 Physical condition of iron

The iron fed into the reducer not only supplies the metal absorption surface but also enters into the reactions by providing the iron for the regeneration of the ferrous chloride upon the hydrolysis of the phenyl ammonium chloride (aniline hydrochlorides) and also acts

as an oxygen carrier. A clean, finely divided, soft, gray cast iron yields the best results. The **rate of reduction** depends on the **fineness** and **porosity** of the iron particles, the homogeneity of the charge in the reducer, and the degree of etching imparted to the iron by the preliminary acid treatment. To ensure thoroughly **etched iron** it is customary to boil the iron and acid suspension before adding any nitro compound. When this precaution is observed, the reaction proceeds very readily, with no danger of a violent deferred reaction. Iron borings, turnings or shavings are generally used. With coarse particles, the oxidation of the iron is retarded and an excess of it must be provided. It is clear that the use of **finely divided iron shortens** the **time** of reaction.

1.24.1.3 Amount of water

Theoretical considerations indicate the desirability of using 4-5 moles of water per mole of nitro compound treated.

$$4RNO_2 + 9Fe + 16H_2O \longrightarrow 4RNH_2 + 3Fe(OH)_2 + 6Fe(OH)_3 \longrightarrow 4RNH_2 + 3Fe_3O_4 + 12H_2O$$

Owing to the fact that part of the iron hydroxides formed losses water to form the ferrosoferric oxide during the course of the reaction, it is entirely possible that the reduction may be made with less than 4moles of water. **Practical problems** relating to (1) the agitation of the reaction mass (2) the promotion or a smooth active reaction and (3) the conservation of the heat of reduction make it advisable to use a slight excess. Where the nitro compound contains a solubilizing group, such as sulfonic or carboxylic residue, and the resulting amine is filtered from alkalinized iron oxide sludge, **much more water** is generally **used (50-100moles)**

1.24.1.4 Amount of acid

This reaction required the presence of small amounts of ferrous ion to act as a catalyst. Generally about **0.05 - 0.22** of an equivalent of **acid** is **used**. The acids usually employed in the reduction process are hydrochloric and sulfuric acid.

1.24.1.5 Effects of agitation

A sturdy **sleeve and propeller** or **double impeller type** of stirrer will be superior to the slow moving plow type, speeding up the reaction considerably.

Most aromatic nitro compounds (not containing basic groups) are practically insoluble in faintly acid solution, and through mixing is a factor of major importance. A method involving **use of rotary mills** having freely moving ponderous agitators, such as iron balls for the reduction of nitro, nitroso and azo compounds to amines with iron in aqueous emulsion in order to effect grinding action during the reduction. Such mills are also useful in the distillation of aromatic amines from the iron oxide sludge in vacuum.

1.24.1.6 Reaction temperature

The use of a high catalyst concentration (3 % or more compared to nitrobenzene taken) during reduction results in a finely divided iron sludge which although it is generally a poor filtering sludge, is of possible a commercial value (for removing sulphur compound from illuminating gas). This result can obtain by limiting the quantity of water introduced into the jacketed reducer and utilizing the heat of reaction to carry on the reaction. An obvious advantage arising from operating with such **concentrated solution** is the fact that the charge is easily maintained at the **boiling temperature**. The vigorous reflux that characterizes such as a reduction ensures against the formation of intermediate product of reaction. The reaction is not only rapid but is economical on account of the lower consumption of steam.

1.24.1.7 Additions of solvents

Where a very insoluble and **difficulty reducible** nitro compound is to be reduced, the addition of a **solvent miscible** with **water**, such as ethyl alcohol, methanol or pyridine is often considerable help. This makes for a smoother and more rapid reduction. In carrying out the reduction, the alkalinized iron oxide sludge is filtered off hot and washed with hot solvent. The resulting amine is then isolated from the filtrate. This method is used where reduction in water alone is extremely slow or where the final amine can be isolated only by solvent extraction.

1.24.1.8 Testing for completion

Reduction will **not take place** in the **absence of ferrous ions**, which can be demonstrated by the lack of a black precipitates on spot testing with sodium sulfide solution. The reaction is considered complete when an aliquot no longer increases its take up sodium

nitrite on further reduction with a stronger reducing agent, such as zinc and hydrochloric acid.

1.24.1.9 Work up of reaction mixture

Soluble iron is generally precipitated with alkali, using caustic soda, soda ash, lime or magnesia. Where the amine is volatile, it may be isolated by steam distillation or by vacuum distillation from the iron oxide cake after distilling off the water. Where the **final amine** is **soluble in alkaline solution** the iron oxide cake is filtered off and the amine isolated from the filtrate. When the final amine is **volatile** but **sensitive to alkali**, as is the case with some polychloroamine the amine may be steam distilled from the slightly acid mixture.

1.24.1.10 Continuous processing

Although the Bechamp reduction is generally carried out on a batch basis, it has been run continuously. This involves passing an acidified solution or emulsion of the nitro compound through a suitable tower packed with iron shavings or scraps iron and kept at the required temperature.

1.24.1.11 Recovery of by- products

In the technical preparation of amines by catalytic reduction with iron and a soluble salt, it is not customary to **recover and utilize** the dissolved **catalyst**.

1.24.1.12 Yield of amine

In plant, yields in the range of **85-98% of theory** are obtained with the Bechamp reduction.

1.24.2 Equipment

1.24.2.1 Material of construction

Bechamp reduction is usually carried out in **cast - iron vessels** and **alkali reduction** in **carbon steel vessels** of desired sizes. The larger ones (1,600 gal capacity) are favoured by plant engineers because of the possibilities of more economical operation.

The **reducers** for iron and acid reductions are sometimes equipped with side and bottom **cast - iron lining plates**, which may be reversed or replaced, in order to protect the vessel against the continuous, erosive action of the iron borings. Alternatively the reducers may be **lined partially** or **entirely** with acid resisting brick or tile. **Wooden equipment** is also used, particularly for the reduction of solid nitro compounds such as p-nitro aniline.
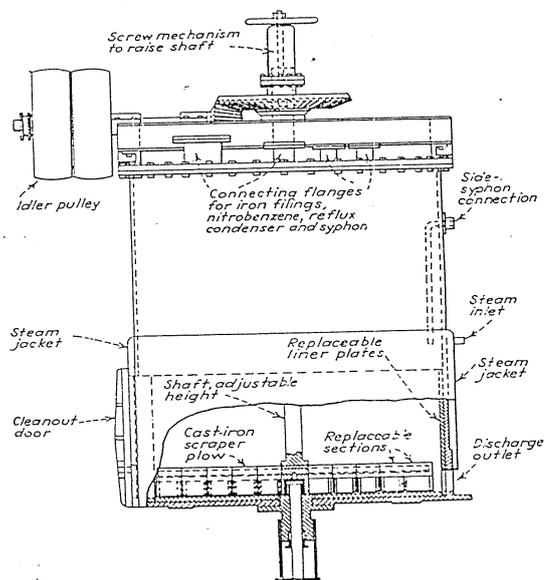

Figure: Jacketed reducer

1.24.2.2 Agitation

In some reducers, a vertical shaft carries a set of **cast iron plows**, which can be removed through the side door to the reactor. These plows travel at the rate of **30-50rpm** and serve to keep the iron particle in suspension in the lower part of the vessel. It will be recalled that the **iron and acid** reduction process is a **four component system** e.g. reducible

organic compound, water, acid or metal salts and metal. Obviously, the best results in such a catalytic process can be obtained only when all of the components are in intimate contact.

1.24.2.3 Jacketing of reducers

Practically all the iron reducers employed for the Bechamp reduction of liquid nitro compounds are **equipped** with **jackets**. Although the reduction process is distinctly **exothermic**, the reaction precedes best at slightly elevated temperatures. It is customary, therefore, to warm the reactants at the start.

When jacketed reducers are employed, the heat is applied indirectly and no dilution of the charge occurs. Under such circumstances, the **optimum** quantity of **water** can be delivered during the **"feeding" stage** and the reaction is kept active by regulating the introduction of the reactants.

When the reaction **vessels** are **not jacketed**, as is the case with brick or tile-lined kettles, live steam is introduced to start and maintain the reaction. Care must be taken that the charge does not become unduly diluted. Otherwise, the concentration of acid is lowered and the reaction rate decreased. Yields may also suffer.

1.25 <u>MANUFACTURE OF ANILINE FROM NITROBENZENE BY BECHAMP REDUCTION</u>

1.25.1 Raw materials

Basis: 1 metric ton aniline
Nitrobenzene: 1390 kg
Iron borings: 1600 kg
Hydrochloric acid: 125 kg

1.25.2 Reaction

$$4C_6H5NO_2 + 9Fe + 4H_2O \xrightarrow{\text{HCl}} 4C_6H_5NH_3 + 3FeO_4 \quad 90 – 95\% \text{ Yield}$$
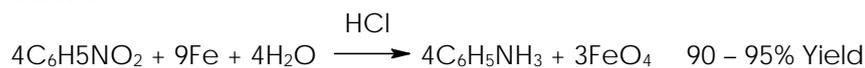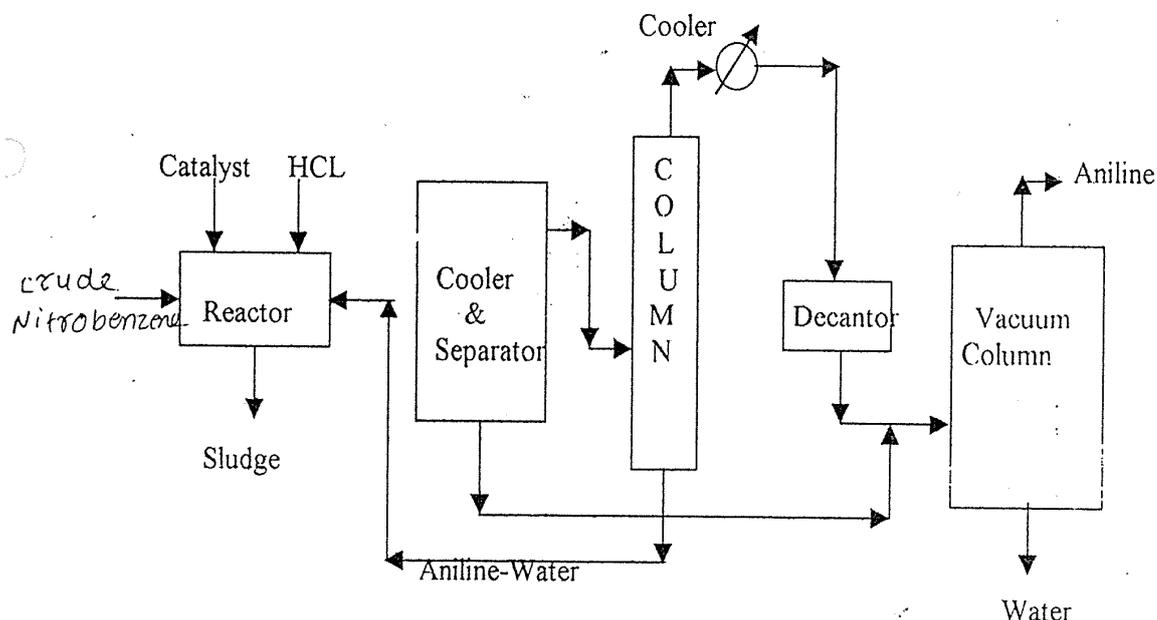
1.25.3 Manufacture

Figure: Manufacture of aniline from nitrobenzene by Bechamp reduction

Crude **nitrobenzene** is charge into a **reducer** (reactor) fitted with an efficient reflux condenser. The reducer is a **steam jacketed cast iron** enclosed cylindrical vessel containing an agitator. **Cast iron** borings (turnings) or powder (free from oil and non - ferrous metals), **water** and **catalyst** are added gradually, in small quantities, to the nitrobenzene. Generally **10 to 20%** of the total iron is added at the beginning and the mixture is heated by steam to **reflux temperature** (200°C). The remaining iron is added over a period of time at a rate

determined by the proper pressure temperature balance. The **addition rate** is fast enough to maintain lively reflux by the heat generated from the exothermic reaction, yet slow enough to prevent excessive hydrogen, pressure build up.

The **water** required for the reaction is generally in the form of aniline water recovered from the **separator** or column and is added to the reducer in bulk at the start or in small quantities along with the iron additions. Dilute **(30%) HCl** acid is added along with the water **as catalyst**. The acid reacts with the iron borings. Forming catalytically active iron salts. Subsequent runs may utilize aniline hydrochloric acid mother liquor as the source of the catalyst and some of the reaction water; the **weight ratio of reactants** is approximately 115 parts of **iron borings**, 0.27 parts of 100% **hydrochloric acid** and 60 parts of **water** per 100 parts of **nitrobenzene**. After the last addition, the reaction is heated with steam to maintain lively reflux.

At the **end of the reduction** (about 10 hrs. for 2250kg charge), the **aniline** is **separated** from the reducer charge by one or more of several methods, The liquid **water aniline mixture** may be separated from the solid iron oxide iron hydroxide sludge by steam distillation, vacuum distillation, filtration, centrifugation or siphoning. For example the finished reduction product may be neutralized with a small amount of sodium carbonate (about equal to the amount of hydrochloric acid in the charge) and allowed to settle. Most of aniline and some water siphoned off and the residual aniline is separated from the sludge by steam distillation. The **sludge** consisting of ferric oxide, water and small amount of ferric oxide is dumped and may be marketed after drying.

The water aniline mixture from the reducer is run to a separator where the lighter aniline separates and is withdrawn from the upper. The top layer, which contains 3 to 5% aniline, is partially distilled until the aniline content in the water is low. The residual aniline water is returned to the reducer for subsequent runs. The aniline in the distillate is separated by decantation and the water layer is redistilled to obtain the remaining aniline. An **alternate procedure** is to extract aniline from the aniline water with nitrobenzene.

The aniline streams from the separator and decanter are united and vacuum distilled to yield purified aniline. The **yield** based on nitrobenzene is approximately **95%** by weight.

1.26 MANUFACTURE OF ANILINE FROM CHLOROBENZENE BY AMMONOLYSIS

1.26.1 Raw materials
Basis:1 ton aniline

Chlorobenzene	= 2,500 lb
Ammonia solution(28%)	= 7,450 lb
Cuprous oxide	= 350 lb

1.26.2 Reaction

$$C_6H_5Cl + 2NH_{3(aq)} \longrightarrow C_6H_5NH_2 + NH_4Cl \text{ (soln)}$$
$$96\% \text{ yield}$$
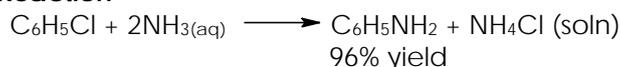
1.26.3 Manufacture

Chlorobenzene is charged into a series of horizontal, rotating high - pressure rolled steel **autoclave**. Approximately 0.1 mole of **cuprous oxide** and 4 to 5moles of 28 to 30% aqueous **ammonia** per mole of **chlorobenzene** are added. The reaction is initiated at a temperature of **180°C** and is later maintained at **210 to 220°C** under constant agitation. The pressure rises to **750 to 850 psi**. The **active catalyst** is **cuprous chlorine** produced from cuprous oxide by the product ammonium chlorine as follows:

$$Cu_2O + 2NH_4Cl \longrightarrow Cu_2Cl_2 + 2NH_3 + H_2O$$

A **large excess** of **ammonia** solution is used to **suppress** the phenol producing **side reaction** ($C_6H_5Cl + NH_3 + H_2O \longrightarrow C_6H_5OH + NH_4Cl$). If the indicated ratio of reactants is used, the rate of aniline formation is about 20 times greater than the rate of phenol formation.
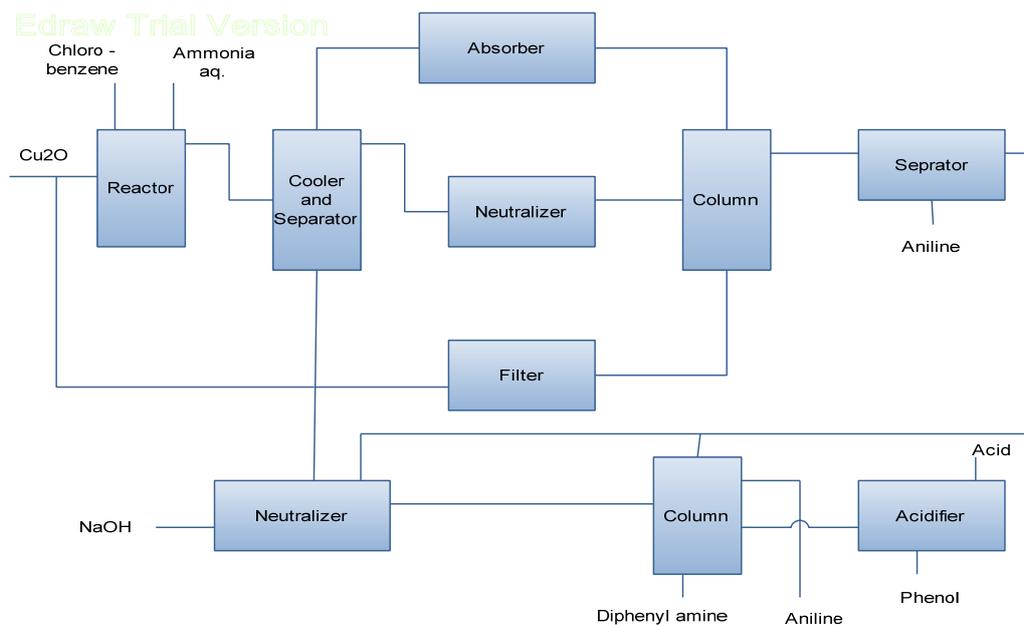
Figure: Flowchart for production of Aniline from chlorobenzene by Ammonolysis

The reaction **products** are **cooled** below 100°C and run to a **separator**. The free ammonia continues to absorption and condensing system for recovery. The settled **reaction mass** separates into **two layers**: **aniline rich** lower and an **aqueous** upper layer. The approximate distribution of reaction products not including unreacted chlorobenzene in the two layers is as follows: **aniline layer** 82% aniline, 5% phenol, and 1% diphenylamine; **water layer** 5 % aniline, 0.5% phenol, 9% chlorine ion (NH_4Cl), 3% cuprous oxide and 14% ammonia.

The **aqueous layer** is drawn from the top of the separator and is run to a **neutralizer**, where it is treated with **sodium hydroxide** or **lime**. A sufficient amount of alkali is used to react with the ammonium chloride and phenol. The solution is **fractionally distilled**, and the liberated ammonia expelled first is recovered in an **absorption system**. The **second fraction** consists of aniline and water, which are separated by decantation. The **residual solution** of sodium phenate and sodium chloride is filtered to remove the precipitated copper oxides, which are reused in subsequent runs.

The **aniline layer** is withdrawn from the bottom of the separator and treated with 50% **sodium hydroxide** solution. Approximately 0.2 percent of the volume of the aniline layer is used. The solution is fractionally distilled, yielding first aniline -water mixture, which is further treated as described previously. The **second fraction** is technically pure (97 to 90%) **aniline**, the residue is steam distilled, yielding diphenylamine. The phenol is recovered by acidifying the residue mostly sodium phenate and distilling. The **yield** of aniline is 96% based on chlorobenzene.

1.27 m-NITROANILINE

100 parts of **dinitrobenzene** is added to 1000 parts of **water** at **90⁰C** contained in a reducer fitted with reflux condenser and a propeller type stirrer. **Upon emulsification**, 245 parts of **sodium sulfide** ($9H_2O$), dissolved in a minimum of water, is gradually run in. The **dinitro** compound is gradually **reduced** to **m-nitro aniline**, the **end point** being determined by the formation of a definite black streak when ferrous sulfate solution is added to filter paper spotted with some of the reducer liquor.

A **modification** in the preceding process involves the **use** of an **organic solvent**, which is immiscible with water, for the m-dinitrobenzene. Accordingly, 100 parts of technical **dinitrobenzene**, 90% purity and 160 parts of either solvent **naphtha** or **toluene** are put into reducer, and the mixture is warmed to **60⁰C** to effect solution. Then, 4000 parts of **hot water** is added, and the m-dinitrobenzene solution is stirred and heated to **95⁰C**. A hot **polysulfide** (Na_2S_3) solution – made by heating 720 parts of 7% Na_2S with 40 parts of flowers of sulfur – is

then added rather rapidly. The reaction of polysulfide is distinctly exothermic, and the charge boils vigorously, but overheating is avoided because of vaporization of solvent. Reduction of the dinitrobenzene to m-nitro aniline is found to take place quickly under such conditions.

To hot **reduction mass** is first **filtered** to remove any free sulfur, and the solvent naphtha in the filtrate is distilled with steam. The dissolved **m-nitro aniline crystallizes out** in the form of bright **yellow crystals** when the residual liquor is cooled. After washing, the product has a **melting point** of about **113^{0}C** and can be **used** directly in the manufacture of **azo dyes**. A **yield** of approximately **90–92%** of theory is attainable, and the process is applicable to other m-dinitro compounds, e.g., m- dinitro derivatives of toluene and xylene.