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Part 1

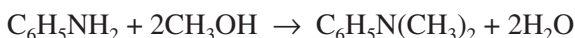
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# REACTION TYPES

# ALKYLATION

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Alkylation is usually used to increase performance of a product and involves the conversion of, for example, an amine to its alkylated homologs as in the reaction of aniline with methyl alcohol in the presence of sulfuric acid catalyst:



Thus, aniline, with a considerable excess of methyl alcohol and a catalytic amount of sulfuric acid, is heated in an autoclave at about 200°C for 5 or 6 hours at a high reaction pressure of 540 psi (3.7 MPa). Vacuum distillation is used for purification.

In the alkylation of aniline to diethylaniline by heating aniline and ethyl alcohol, sulfuric acid cannot be used because it will form ether; consequently, hydrochloric acid is employed, but these conditions are so corrosive that the steel used to resist the pressure must be fitted with replaceable enameled liners.

Alkylation reactions employing alkyl halides are carried out in an acidic medium. For example, hydrobromic acid is formed when methyl bromide is used in the alkylation leading, and for such reactions an autoclave with a replaceable enameled liner and a lead-coated cover is suitable.

In the petroleum refining industry, alkylation is the union of an olefin with an aromatic or paraffinic hydrocarbon:



Alkylation processes are exothermic and are fundamentally similar to refining industry polymerization processes but they differ in that only part of the charging stock need be unsaturated. As a result, the *alkylate* product contains no olefins and has a higher octane rating. These methods are based on the reactivity of the tertiary carbon of the *iso*-butane with olefins, such as propylene, butylenes, and amylenes. The product *alkylate* is a mixture of saturated, stable isoparaffins distilling in the gasoline range, which becomes a most desirable component of many high-octane gasolines.

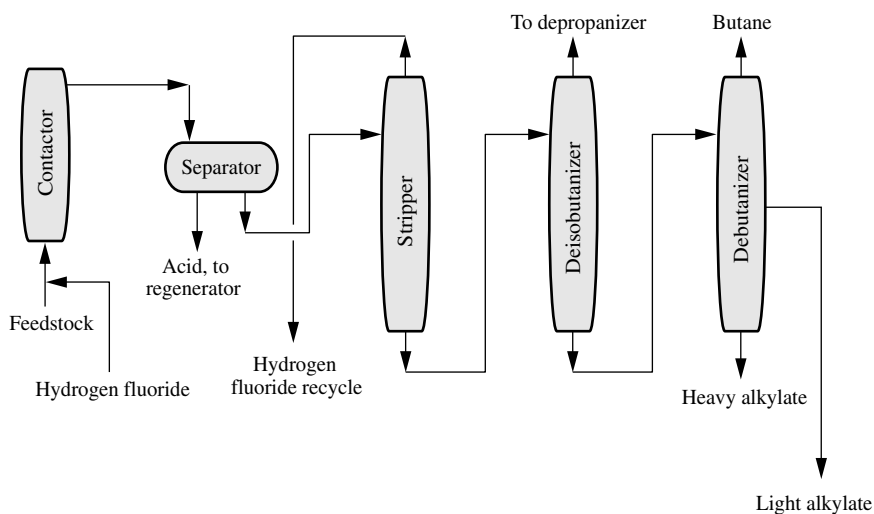


FIGURE 1 Alkylation using hydrogen fluoride.

Alkylation is accomplished by using either of two catalysts: (1) hydrogen fluoride and (2) sulfuric acid. In the alkylation process using liquid hydrogen fluoride (Fig. 1), the acid can be used repeatedly, and there is virtually no acid-disposal problem. The acid/hydrocarbon ratio in the contactor is 2:1 and temperature ranges from 15 to 35°C can be maintained since no refrigeration is necessary. The anhydrous hydrofluoric acid is regenerated by distillation with sufficient pressure to maintain the reactants in the liquid phase.

In many cases, steel is suitable for the construction of alkylating equipment, even in the presence of the strong acid catalysts, as their corrosive effect is greatly lessened by the formation of esters as catalytic intermediate products.

In the petroleum industry, the sulfuric acid and hydrogen fluoride employed as alkylation catalysts must be substantially anhydrous to be effective, and steel equipment is satisfactory. Where conditions are not anhydrous, lead-lined, monel-lined, or enamel-lined equipment is satisfactory. In a few cases, copper or tinned copper is still used, for example, in the manufacture of pharmaceutical and photographic products to lessen contamination with metals.

Distillation is usually the most convenient procedure for product recovery, even in those instances in which the boiling points are rather close together. Frequently such a distillation will furnish a finished material of

quality sufficient to meet the demands of the market. If not, other means of purification may be necessary, such as crystallization or separation by means of solvents. The choice of a proper solvent will, in many instances, lead to the crystallization of the alkylated product and to its convenient recovery.

The converse reactions *dealkylation* and *hydrodealkylation* are practiced extensively to convert available feedstocks into other more desirable (marketable), products. Two such processes are: (1) the conversion of toluene or xylene, or the higher-molecular-weight alkyl aromatic compounds, to benzene in the presence of hydrogen and a suitable presence of a dealkylation catalyst and (2) the conversion of toluene in the presence of hydrogen and a fixed bed catalyst to benzene plus mixed xylenes.

# AMINATION

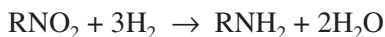
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Amination is the process of introducing the amino group ( $-\text{NH}_2$ ) into an organic compound as, for example, the production of aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) by the reduction of nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) in the liquid phase (Fig. 1) or in the vapor phase in a fluidized bed reactor (Fig. 2). For many decades, the only method of putting an amino group on an aryl nucleus involved adding a nitro ( $-\text{NO}_2$ ) group, then *reduction* to the amino ( $-\text{NH}_2$ ) group.

Without high-pressure vessels and catalysts, reduction had to be done by reagents that would function under atmospheric pressure. The common reducing agents available under these restrictions are:

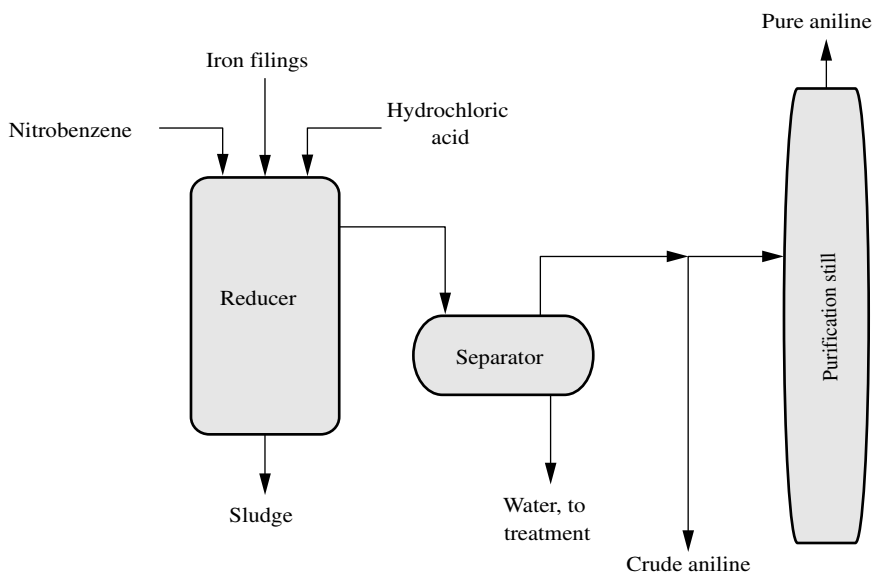
1. Iron and acid
2. Zinc and alkali
3. Sodium sulfide or polysulfide
4. Sodium hydrosulfite
5. Electrolytic hydrogen
6. Metal hydrides

Now liquid- and gas-phase hydrogenations can be performed on a variety of materials.

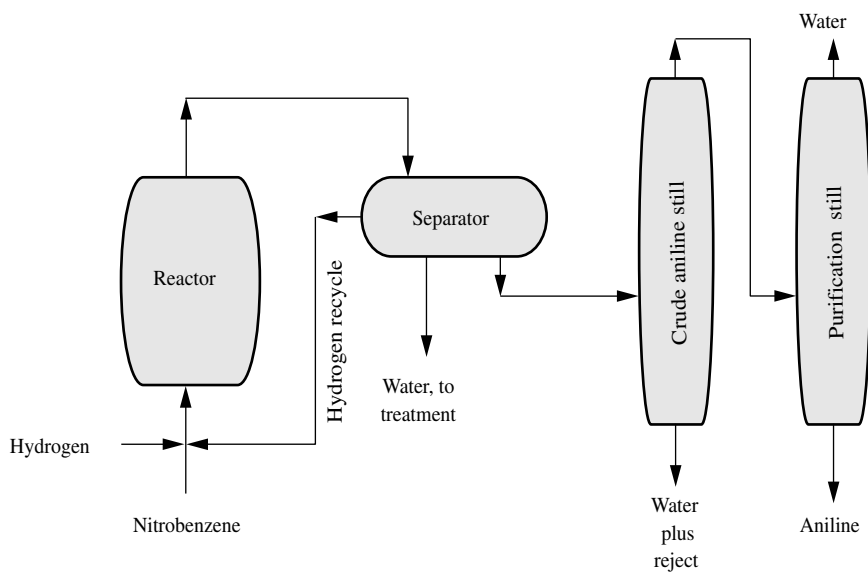


Where metals are used to produce the reducing hydrogen, several difficult processing problems are created. The expense is so great that it is necessary to find some use for the reacted material. Spent iron can sometimes be used for pigment preparations or to absorb hydrogen sulfide. Stirring a vessel containing much metal is quite difficult.

On a small scale, cracking ammonia can produce hydrogen for reduction. Transport and storage of hydrogen as ammonia is compact, and the cracking procedure involves only a hot pipe packed with catalyst and



**FIGURE 1** Aniline production by the reduction of nitrobenzene.

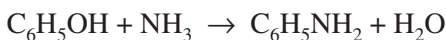


**FIGURE 2** Vapor phase reduction of nitrobenzene to aniline.

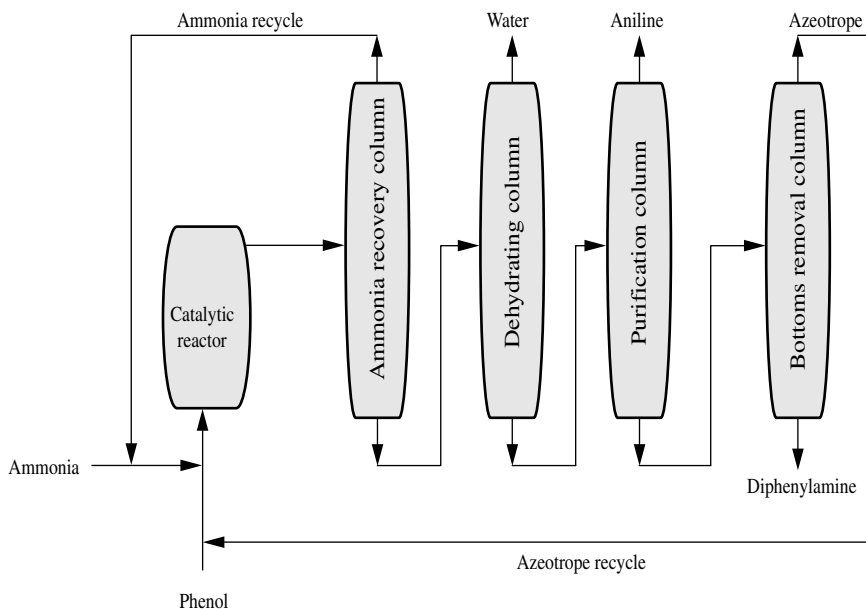
immersed in a molten salt bath. The nitrogen that accompanies the generated hydrogen is inert.

Amination is also achieved by the use of ammonia ( $\text{NH}_3$ ), in a process referred to as *ammonolysis*. An example is the production of aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) from chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ) with ammonia ( $\text{NH}_3$ ). The reaction proceeds only under high pressure.

The replacement of a nuclear substituent such as hydroxyl ( $-\text{OH}$ ), chloro, ( $-\text{Cl}$ ), or sulfonic acid ( $-\text{SO}_3\text{H}$ ) with amino ( $-\text{NH}_2$ ) by the use of ammonia (*ammonolysis*) has been practiced for some time with feedstocks that have reaction-inducing groups present thereby making replacement easier. For example, 1,4-dichloro-2-nitrobenzene can be changed readily to 4-chloro-2-nitroaniline by treatment with aqueous ammonia. Other molecules offer more processing difficulty, and pressure vessels are required for the production of aniline from chlorobenzene or from phenol (Fig. 3).



Ammonia is a comparatively low cost reagent, and the process can be balanced to produce the desired amine. The other routes to amines



**FIGURE 3** Aniline and diphenylamine production from phenol.

through reduction use expensive reagents (iron, Fe, zinc, Zn, or hydrogen,  $H_2$ , gas) that make ammonolysis costs quite attractive. Substituted amines can be produced by using substituted ammonia (amines) in place of simple ammonia. The equipment is an agitated iron pressure vessel; stainless steel is also used for vessel construction.

Amination by reduction is usually carried out in cast-iron vessels (1600 gallons capacity, or higher) and alkali reductions in carbon steel vessels of desired sizes. The vessel is usually equipped with a nozzle at the base so that the iron oxide sludge or entire charge may be run out upon completion of the reaction.

In some reducers, a vertical shaft carries a set of cast-iron stirrers to keep the iron particles in suspension in the lower part of the vessel and to maintain all the components of the reaction in intimate contact. In addition, the stirrer assists in the diffusion of the amino compound away from the surface of the metal and thereby makes possible a more extensive contact between nitro body and catalytic surface.

Thus, amination, or reaction with ammonia, is used to form both aliphatic and aromatic amines. Reduction of nitro compounds is the traditional process for producing amines, but ammonia or substituted ammonias (amines) react directly to form amines. The production of aniline by amination now exceeds that produced by reduction (of nitrobenzene).

Oxygen-function compounds also may be subjected to ammonolysis, for example:

1. Methanol plus aluminum phosphate catalyst yields monomethylamine ( $CH_3NH_2$ ), dimethylamine [ $(CH_3)_2NH$ ], and trimethylamine [ $(CH_3)_3N$ ]
2. 2-naphthol plus sodium ammonium sulfite ( $NaNH_3SO_3$ ) catalyst (Bucherer reaction) yields 2-naphthylamine
3. Ethylene oxide yields monoethanolamine ( $HOCH_2CH_2NH_2$ ), diethanolamine [ $(HOCH_2CH_2)_2NH$ ], and triethanolamine [ $(HOCH_2CH_2)_3N$ ]
4. Glucose plus nickel catalyst yields glucamine
5. Cyclohexanone plus nickel catalyst yields cyclohexylamine

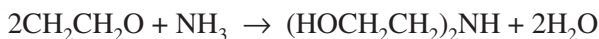
Methylamines are produced by reacting gaseous methanol with a catalyst at 350 to 400°C and 290 psi (2.0 MPa), then distilling the reaction mixture. Any ratio of mono-, di-, or trimethylamines is possible by recycling the unwanted products.



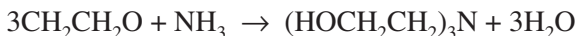
An equilibrium mixture of the three ethanolamines is produced when ethylene oxide is bubbled through 28% aqueous ammonia at 30 to 40°C. By recirculating the products of the reaction, altering the temperatures, pressures, and the ratio of ammonia to ethylene oxide, but always having an excess of ammonia, it is possible to make the desired amine predominate. Diluent gas also alters the product ratio.



monoethanolamine



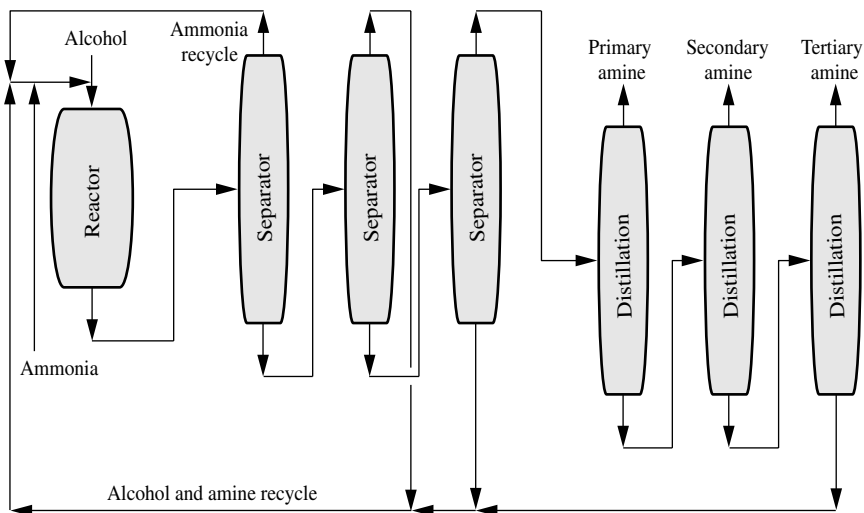
diethanolamine



triethanolamine

After the strongly exothermic reaction, the reaction products are recovered and separated by flashing off and recycling the ammonia, and then fractionating the amine products.

Monomethylamine is used in explosives, insecticides, and surfactants. Dimethylamine is used for the manufacture of dimethylformamide and acetamide, pesticides, and water treatment. Trimethylamine is used to form choline chloride and to make biocides and slimicides.



**FIGURE 4** Amination process for amine production.

Other alkylamines can be made in similar fashion from the alcohol and ammonia (Fig. 4). Methyl, ethyl, isopropyl, cyclohexyl, and combination amines have comparatively small markets and are usually made by reacting the correct alcohol with anhydrous ammonia in the vapor phase.