Lecture 5
Cylohexane, Caprolactam, Nylon 6, Adipic Acid and Hexamethylenediamine, Nylon 66
LECTURE 5

CYLOHEXANE, CAPROLACTAM, NYLON 6
ADIPIC ACID AND HEXAMETRHYLENE DIAMINE, NYLON 66

Nylon 6 and Nylon 66 are two important polyamides and find application in woven and non-woven industries. Caprolactam is monomer for Nylon-6 while monomer for Nylon 66 is nylon 66 which is made from adipic acid and hexamethylene diamine. Nylons are exceptional strong, elastic, abrasion resistant, lustrous, easy to wash, resistant to damage from oil and many chemicals, low in moisture absorbency [http://www.fibersource.com/f-tutor/nylon.htm]. Characteristics of nylon 6 and nylon 66 is given in Table M-VIII 5.1. Nylon fibre find application in apparel, home furnishings, tire cord, hose, conveyor and seat belts, parachutes, racket strings, ropes, tents, thread, mono filament fishing line, dental floss. Nylon 66 is preferred for tire cord because of high melting point. Melt spinning process is used for producing fibre stable and yarn.

Nylon 6 is the first synthetic fibre introduced in India starting with a modest volume of 175 tonnes in 1962. Installed capacity and production of nylon filament yarn and nylon industrial yarn is 36000 and 70000 tonnes and 33000, 86000 tonnes in 2010-11 respectively in India.

Table M-VIII 5.1: Major Synthetic Fibers and Their Characteristics

<table>
<thead>
<tr>
<th>Name of the synthetic fiber</th>
<th>Monomer</th>
<th>Basic chemicals</th>
<th>Properties of the synthetic fiber</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Densit y</td>
<td>Moisture regain</td>
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<tr>
<td>Nylon 6</td>
<td>Phenol, cyclohexane, toluene</td>
<td>1.14</td>
<td>4.5</td>
<td>213-221 °C</td>
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</tr>
<tr>
<td>Nylon 66</td>
<td>Adipic Acid</td>
<td>Phenol, cyclohex-</td>
<td>1.14</td>
<td>Resistant to weak acid, decomposed by strong mineral acid. Chemically it is extremely stable. Good biological resistance. Tenacity 8.0 gm/denier, elongations at break 16-20%.</td>
</tr>
<tr>
<td></td>
<td>HOOC-(CH₂)₄-</td>
<td>ane, butadiene,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>COOH,</td>
<td>furfural</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexamethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diamine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂N-(CH₂)₆–</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NH₂</td>
<td></td>
<td></td>
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</tbody>
</table>

**CYCLOHEXANE**

Cyclohexane is an important chemical intermediate derived from benzene. It is used for the manufacture of adipic acid and hexamethylene diamine used for manufacture of Nylon 66 and caprolactam used for the manufacture of Nylon 6. Major portion of 90% of the cyclohexane is used in the manufacture of nylon fiber and nylon molding resin and remaining 10% of cyclohexane ends up as solvents or in plasticizers. Cyclohexane is made by catalytic hydrogenation of benzene in liquid phase or vapor phase. Process flow diagram of manufacturing process is shown in Figure M-VIII 5.1.

UOP hydrogenation process uses liquid phase hydrogenation of benzene at 200-300 °C in presence of platinum based catalyst promoted by lithium salt at 3 MPa pressure. In the IFP process cyclohexane is produced by liquid phase hydrogenation of benzene at 160-200 °C and 4 MPa using Raney nickel catalyst.
CAPROLACTAM

- Caprolactam is the principal raw material for Nylon 6, a versatile material used as fibers, industrial yarns and floor covering as well as for engineering plastics/films.
- Nylon 6 was first made in 1899 by heating 6-aminohexanoic acid but commercially feasible synthesis from caprolactam was first discovered in 1935 by Paul Shalack.
- Global caprolactam production and demand scenario is given in Table M-VIII 5.2.

Table M-VIII 5.2: Global Caprolactam Production and Demand Scenario

<table>
<thead>
<tr>
<th>Year</th>
<th>Caprolactam Production ('000 Tonnes)</th>
<th>Caprolactam Demand ('000 Tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibers</td>
<td>Resins</td>
</tr>
<tr>
<td>1990</td>
<td>2,463</td>
<td>499</td>
</tr>
<tr>
<td>2010</td>
<td>2,559</td>
<td>1,845</td>
</tr>
</tbody>
</table>

Source:

Process of manufacturing caprolactam involves three basic steps.
- Manufacture of Cyclohexanone
- Manufacture of Hydroxylamine Sulphate
- Manufacture of Caprolactam
MANUFACTURE OF CYLOHEXANONE

In subsequent stages cyclohexane is oxidised in multi compartment reactor at a temperature of 158-160 °C and 10 atm pressure where the liquid flows in series from one chamber to another using cobalt salt as catalyst. The product stream is treated with sodium hydroxide to neutralise acids, saponify esters and to decompose peroxides. Sodium salts which are immiscible with the main product stream are separated in a gravity settler.

Organic phase containing cyclohexane, cyclohexanol, cyclohexanone are fed to series of three distillation columns where these are separated. Cyclohexane is separated as top product from the last column. Cyclohexanol separated in the last column as bottom product is dehydrogenated to cyclohexanone in presence of zinc carbonate and calcium carbonate catalyst at 400 °C. The unconverted cyclohexanol and cyclohexanone after removal of light ends recycled to third distillation column for recovery of cyclohexanone.

HYDROXYLAMINE SULPHATE

Production of hydroxylamine sulphate involves. Production of ammonium carbonate by absorption of CO₂ in 24% aqueous ammonium solution. Production of nitrous oxide from mixture of NO and NO₂, which is produced by combustion of ammonia in presence of platinum catalyst at 85 °C. Absorption of nitrous gases from the ammonia combustion in ammonium carbonate to yield ammonium nitrite

CAPROLACTAM

Manufacture of caprolactam involves Production of cyclohexanone oxime by reacting cyclohexanone with hydroxylamine sulphate in a multi compartment reactor. During this process ammonium sulphate is formed as byproduct. Caprolactam & aqueous ammonium sulphate are sent to a series of extractors where toluene is used as a solvent. Various routes of caprolactam is shown in Figure M-VIII 5.2 [Nair & Lal, 1969; Taverna & Chiti, 1970; Vaidya & Gupta, 1986; Chavel & Lefebvre, 1989, Mall, 2007]. Ammonium sulphate collected from the extractor bottom is purified, crystallised, centrifuged and dried. Caprolactam solution is concentrated in multiple effect evaporators and finally purified. Flow diagram for the manufacture of caprolactam is given in Figure M-VIII 5.3 [Mall,2007].
1. **Original Process:**
   
   Phenol $\rightarrow$ Cyclohexanol $\rightarrow$ Cyclohexanone $\rightarrow$ Cyclohexanone Oxime $\rightarrow$ Caprolactam

2. **Allied Chemical Phenol Process:**
   
   Phenol $\rightarrow$ Cyclohexanone $\rightarrow$ Cyclohexanone Oxime $\rightarrow$ Caprolactam

3. **Cyclohexane Process, Via Cyclohexanone:**

   Cyclohexane $\rightarrow$ Cyclohexanol $\rightarrow$ Cyclohexanone $\rightarrow$ Cyclohexanone Oxime $\rightarrow$ Caprolactam

4. **Toyo Rayon Photonitrosation:**

   Cyclohexane $\rightarrow$ Cyclohexanone Oxime $\rightarrow$ Caprolactam

5. **SNIA Viscosa Toluene Process:**

   Toluene $\rightarrow$ Benzoic Acid $\rightarrow$ Cyclohexane Carboxylic Acid $\rightarrow$ Caprolactam

6. **Union Carbide Process via Caprolactam:**

   Cyclohexane $\rightarrow$ Cyclohexanol $\rightarrow$ Cyclohexanone $\rightarrow$ Caprolactone $\rightarrow$ Caprolactam

7. **Du Pont Process, via Nitrocyclohexane:**

   Cyclohexane $\rightarrow$ Nitrocyclohexane $\rightarrow$ Cyclohexanone Oxime $\rightarrow$ Caprolactam

8. **Techni-Chem Process:**

   Cyclohexane $\rightarrow$ Cyclohexanol $\rightarrow$ Cyclohexanone $\rightarrow$ Nitrocyclohexanone $\rightarrow$ Nitrocaproic Acid $\rightarrow$ Aminocaproic Acid $\rightarrow$ Caprolactam

**Figure M-VIII 5.2: Various Routes for Caprolactam**
Figure M-VIII 5.3: Manufacture of caprolactam
NYLON 6

Nylon 6 is produced from polymerisation of caprolactam. Process steps involved in production of Nylon 6 involve the following steps:

- Caprolactam melting and addition of additives
- Polymerisation: Batch/continuous and chips production
- Chips washing and drying
- Spinning of nylon
- Recovery section

Caprolactam is polymerised to Nylon 6 polymer by ring opening polymerisation at 240-270 °C in presence of water, which opens the ring structure of the caprolactam to give amino caproic acid. Reacting SO₂ with ammonium nitrite & ammonium carbonate which results in production of hydroxylamine disulphonate finally hydrolysis of hydroxylamine disulphonate at 95 °C to yield hydroxylamine sulphate & ammonium sulphate as by-product. Process flow diagram for nylon 6 manufacturing is shown in Figure M-VIII 5.4.

![Figure M-VIII 5.4: Manufacture of Nylon 6](image)

NYLON 66

Nylon 66 is produced by polymerisation of adipic acid & hexamethylene diamine. Manufacturing process flow diagram for nylon 66 is shown in Figure M-VIII 5.5. Process step involved in manufacture of Nylon 66
• Production of nylon salt (hexamethylene diammonium adipate) by reaction of adipic acid & hexamethylene diamine

• Concentration of nylon salt

• Polymerisation of nylon salt into a jacketed vessel equipped with internal coils and heated by dowtherm

• Cooling and chips production

• Spinning of nylon 66 chips

• Recovery section

• Nylon salt (hexamethylene diammonium adipate) is prepared by mixing adipic acid and hexamethylene diamine in 1:1 molar ratio.

\[ \text{Adipic acid} \xrightarrow{\text{Hexamethylene diamine}} \text{Nylon salt} \xrightarrow{\text{Evaporator}} \text{Casting wheel} \xrightarrow{\text{Chip cutter}} \text{Chip storage} \]

\[ \xrightarrow{\text{Bobbin}} \text{Cold drawing} \xrightarrow{\text{Spinning}} \text{Nylon yarn} \]

**Figure M-VIII 5.5: Process of Nylon 66 manufacture**

• Adipic acid is the basic raw material for the manufacture of Nylon 66

• World overall demand for adipic acid is growing by 3.6% during 2000-2010.

• Adipic acid is manufactured from number of starting raw materials like phenol, cyclohexane, tetrahydrofuran, etc. Various routes for adipic acid manufacture

**Adipic Acid**

Various routes of adipic acid manufacturing is shown in Figure M-VIII 5.6 [Vaidya & Gupta, 1986; Chavel & Lefebvre, 1989; Saxena, 2000, Mall2007].

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Figure M-VIII 5.6: Various Routes for Manufacture of Adipic Acid

Process

Cyclohexane is oxidised by air to form cyclohexanol & cyclohexanone in presence of cobalt naphthenate catalyst at temperature of 145-150 °C. The cyclohexanol and cyclohexanone mixture is oxidised to adipic acid in presence of nitric acid using ammonium metavanadate and copper scrap at 60-80 °C. The adipic acid formed is crystallised, centrifuged and finally dried with hot air.
Hexamethylene diamine is another intermediate for the manufacture of Nylon 66. Hexamethylene diamine is manufactured by the catalytic hydrogenation of adiponitrile. Hexamethylene diamine is manufactured by catalytic hydrogenation of adiponitrile in presence of catalyst either by high pressure process (60-65 MPa) or low pressure process (3 MPa). Catalyst in low pressure is nickel whereas in case of high pressure process it is cobalt and copper. Process flow diagram for the manufacture of Hexamethylene diamine is given in Figure M-VIII 5.7

\[ \text{NC(CH}_2\text{)}_4\text{CN} + 2 \text{H}_2 \rightarrow \text{HN}=(\text{CH}_2\text{)}_4\text{CH}=\text{NH} \]

**Figure M-VIII 5.7: Process flow diagram for Hexamethylene diamine**

**REFERENCES:**

3. Nair, S.R., Lal, I.B., “Technology and applications of polyamides fibers”, Seminar or synthetic chemical fibers in India in the coming decade, organised on IIChe North Regional Centre, New Delhi, 28 December, 1969, p. 17
4. Saxena, M.P., “Monomers for Synthetic Fibre”, AICTE Staff Development Programme,’