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Caprolactam is in high demand in the new materials industry as a monomer for nylon and polyamides. Although the schemes of traditional processes such as hydroxylamine production (hydroxylamine sulphate oxime process, hydroxylamine phosphate oxime process, nitric oxide reduction process) and cyclohexanone production were still involved in the caprolactam production industry, the modern technical adaptations achieved higher atomic utilisation and higher selectivity. In this review, the basic traditional schemes for the production of caprolactam are for the first time presented. The modern technical adaptation, the rectification dehydrogenation of the by-product cyclohexane in cyclohexanone production, was highlighted to achieve an increase in atomic utilisation from 78 % to 98 %. The higher selectivity achieved with membrane separation resulted in a conversion of cyclohexanone of > 99.6 % and a selectivity of cyclohexanone oxime of > 99.5 %. In addition, the progress of the catalysts used in the modern technical adaptation was briefly discussed. This review highlights the modern process with atom economy and high selectivity.

Keywords: caprolactam, rectification dehydrogenation, membrane separation, atomic economy reactions.

1. INTRODUCTION

Caprolactam, as a monomer of polyamide, is an important petrochemical product and chemical fibre raw material, which is widely used in the production of nylon-6 fibre and polyamide engineering plastics [1]. The main products of Nylon-6 fibre were filament, staple fibre and cord. The gloss, semi- extintion and full-extinction nylon developed by Eversun Technology Co., Ltd. were mainly used in conventional spinning, microfibre leather, carpet and staple micro-industries [2 – 7].

The history of the caprolactam industry (shown in Table 1) began in 1899 when Gabriel and Meas first synthesised caprolactam by heating ε-aminocaproic acid [8, 9]. The industrial production of caprolactam in China started in the late 1950s, when caprolactam production technology was mainly introduced by DSM (Netherlands) [10]. In 2014, Eversun Technology Co., Ltd. introduced German continuous caprolactam technology to achieve 300,000 tonnes of caprolactam production capacity. Now, with an additional 600,000 tonnes of caprolactam II production capacity coming on stream, Eversuns becomes the largest producer of polyamide monomer caprolactam in Fujian and among the top ten in China.

The review started with the traditional process for caprolactam, as many traditional manufacturing methods for the production of caprolactam were still the dominant processes at this stage. Traditional methods of producing caprolactam had many shortcomings, such as excessive yields of cyclohexane by-products, heavy pollution and difficulties in post-treatment. So the recent technical adaptations by Eversun were also presented through the transformation of the production process to increase the atomic economy and reduce carbon emission while enhancing the output and quality.

Table 1. The history of caprolactam production

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1899</td>
<td>Gabriel and Meas first synthesised caprolactam</td>
</tr>
<tr>
<td>1938</td>
<td>Schrock polymerized nylon 6 from caprolactam</td>
</tr>
<tr>
<td>1943</td>
<td>I.G. Farben used hydroxylamine sulphate oxime process to produce hydroxylamine</td>
</tr>
<tr>
<td>After World War II</td>
<td>DSM, SNIA, Evi Chemicals and Toyor Rayon (now Toray) used the technologies of I.G. Farben to produce caprolactam</td>
</tr>
<tr>
<td>1950</td>
<td>BASF expanded caprolactam production to 5kt</td>
</tr>
<tr>
<td>1956</td>
<td>BASF switched to nitric oxide reduction for hydroxylamine</td>
</tr>
<tr>
<td>1960</td>
<td>BASF prepared cyclohexanone by oxidation of ethylene oxide</td>
</tr>
<tr>
<td>1961</td>
<td>DuPont industrialised nitrocyclohexane method</td>
</tr>
<tr>
<td>1962</td>
<td>Dow produced caprolactam by cyclohexane oxidation</td>
</tr>
<tr>
<td>1971</td>
<td>DSM and UBE industrialized with hydroxylamine phosphate oxime method</td>
</tr>
</tbody>
</table>

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2. TRADITIONAL PROCESS

Hydroxylamine and cyclohexanone are two essential intermediates in caprolactam production. Today about 95 %...
of the world's caprolactam is still produced by the cyclohexane-hydroxylamine route, derived from the Lassie process [11]. Cyclohexanone reacts with hydroxylamine to form cyclohexanone oxime, which then undergoes the Beckman rearrangement reaction under the action of fuming sulphuric acid to form caprolactam. Hydroxylamine sulphate, hydroxylamine phosphate and nitric oxide reduction methods are available for hydroxylamine production, while the cyclohexene hydration method and cyclohexene oxidation method can be considered for the cyclohexanone production [11 – 17].

2.1. Hydroxylamine production

2.1.1. Hydroxylamine sulphate oxime process

The hydroxylamine sulphate oxime process, also known as the Raschig process, was first developed by LG Farben in Germany for the industrial production of hydroxylamine using phenol as a feedstock. The production process was as follows: NH3 is catalytically oxidised with air/O2 to produce NO2 and (NH4)2CO3 is used to absorb NO2 to produce NH4NO3. Then, NH4NO3 reacts with NH3 and SO2 to produce hydroxylamine disulfonate, which is hydrolysed to produce hydroxylamine sulphate (NH4OH)2SO4. The flow of the hydroxylamine sulphate oxime process to produce hydroxylamine is shown in Fig. 1 [18].

![Flow diagram of hydroxylamine sulphate oxime process](image1)

Fig. 1. Flow diagram of hydroxylamine sulphate oxime process production process.

2.1.2. Hydroxylamine phosphate oxime process

The hydroxylamine phosphate process, first proposed by Spencer Chemical Company, was a method for the synthesis of hydroxylamine by hydrogen reduction with nitric acid using a Pd/C catalyst, and its process flow diagram was shown in Fig. 2. This technology in the early time was not industrialised because of the high loss of solubility of palladium in nitric acid and the easy decomposition of hydroxylamine to nitrogen gas or nitrogen oxides (nitric oxide and nitrogen dioxide) in strong acids. In the 1960s, Fibrant (formerly DSM) started to study the new process of synthesising hydroxylamine by catalytic hydrogenation reduction of nitrate in weak acid medium followed by oxime reaction in organic solvent and to build the corresponding caprolactam plant [19 – 21].

2.1.3. Nitric oxide reduction process

The nitric oxide reduction process was first developed by BASF. In this process, NH3 reacts with O2 to produce NO, and then the resulting NO is mixed with a certain proportion of H2 into H2SO4 suspended with Pt/C catalyst, and the three react at 0 °C and 1.5 × 10⁵Pa to produce hydroxylamine sulphate (NH4OH)2SO4. The nitric oxide reduction process flow is shown in Fig. 3 [18, 22 – 24].

![Flow diagram of nitric oxide reduction process](image2)

Fig. 2. Flow diagram of hydroxylamine phosphate oxime process production process.

Fig. 3. Flow diagram of nitric oxide reduction process

2.2. Cyclohexanone production

2.2.1. Aqueous cyclohexene process

The aqueous cyclohexene process was first proposed by Phillips Petroleum in the 1940s, using sulphuric acid as a catalyst to achieve cyclohexene hydration. However, due to the low selectivity of the reaction, the low yield and the corrosiveness of sulphuric acid, the raw material cyclohexene could not be obtained from a stable source and there was no major development [25, 26].

2.2.2. Cyclohexane oxidation process

Cyclohexane oxidation was the main method used to produce cyclohexanone worldwide, accounting for approximately 90 % of total production. This process was available both as a catalyst-free oxidation process and a catalytic oxidation process. The chemical reactions for the production of cyclohexanone by cyclohexane oxidation are as follows [27 – 30]:

\[
\text{[O] catalyst} \quad \text{C}_6\text{H}_{12} + \text{O} \rightarrow \text{C}_6\text{H}_{10} + \text{H}_2\text{O} \quad (1)
\]

3. MODERN PROCESS WITH ATOM ECONOMY AND HIGH SELECTIVITY

The limited production scale, large investment and high production cost of the traditional caprolactam preparation plant have led to the low efficiency of many
caprolactam enterprises, which cannot meet the demand for chemical fibre monomers in the global market, and the original caprolactam technology route was not based on green chemistry, and most of the environmental pollution was serious. Based on the original caprolactam production process, Eversun has developed a green, efficient and safe caprolactam production process to realize the production of caprolactam with large output and high quality, mainly including the three-step cyclohexanone production process with hydration reaction [31–33], two-step aminoxime method [34–37], which has contributed Eversun company to become the largest producer of caprolactam in Fujian Province.

3.1. Cyclohexanone: three-stage atomic economy reactions

Cyclohexanone was the main chemical raw material for the production of caprolactam. With the development of the petrochemical industry, large quantities of cheap benzene became available and benzene became the dominant feedstock for the production process. The chemical reaction for the production of cyclohexanone by oxidation of cyclohexane in the project based on the aqueous method was as follows [31]:

\[
\text{Cyclohexane} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{Cyclohexane} + \text{H}_2 \quad (2)
\]

\[
\text{Cyclohexane} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{Cyclohexanol} \quad (3)
\]

\[
\text{Cyclohexanol} \xrightarrow{\text{catalyst}} \text{Cyclohexanone} + \text{H}_2 \quad (4)
\]

First, benzene was partially hydrogenated in the presence of a catalyst to produce cyclohexene and partially cyclohexane, then cyclohexene was hydrated with water in the presence of a catalyst to produce cyclohexanol, and finally cyclohexanol was dehydrogenated with the catalyst to produce cyclohexanone and hydrogen [32]. The process is shown in Fig. 4.

In modern chemical engineering, green chemistry should be considered and the concept of "atom economy" of chemical reactions is one of the core elements of green chemistry. Atomic utilisation determines the extent to which reactants are used in chemical production and can be calculated from the mass of atoms utilised compared to the mass of the total atoms, using the formula:

\[
\text{Atomic utilisation} = \frac{M_{\text{expected product}}}{M_{\text{total product}}} \times 100\% \quad (5)
\]

where \(M_{\text{expected product}}\) means the total relative molecular mass of expected products and \(M_{\text{total product}}\) means the total relative molecular mass of products produced.

The overall three-step hydrolytic cyclohexanone production is the reaction of benzene with \(\text{H}_2\) and \(\text{H}_2\text{O}\) to give the cyclohexanone product and cyclohexane by-product, which has an atomic utilisation rate of 78 %. The by-product cyclohexane was of low value and recognised as a hazardous chemical in storage and transport. In collaboration with three universities (Putian University, Fujian Normal University and Fuzhou University), Eversun developed the cyclohexane rectification dehydrogenation process, which converts the by-product cyclohexane into the high-value raw material benzene and \(\text{H}_2\) (reaction 5) [33]. The process of rectification dehydrogenation is also shown in Fig. 4 highlighted in red, which increases the benzene efficiency from 78 % to 98 %. The process not only consumes less hydrogen and the by-product cyclohexane can be reused, but also has a simpler process than the traditional production process.

![Fig. 4. Process sketch of three-step hydrolytic cyclohexanone production (pale blue) and the atomic economy technical adaptations of cyclohexane rectification dehydrogenation (red)](image)

3.2. Cyclohexanone aminoxime: high selectivity with membrane separation

The new ammoxidation process included an ammoxidation unit, a membrane separation unit, a catalyst discharge unit, a solvent recovery unit, a toluene extraction unit, a toluene/oxime fractionation unit, a toluene separation unit, and an effluent treatment unit, etc. The reaction process was as follows [34]:

\[
\text{NH}_3 + \text{H}_2\text{O}_2 \xrightarrow{\text{catalyst}} \text{NH}_2\text{OH} + \text{H}_2\text{O} \quad (7)
\]

\[
\text{NH}_2\text{OH} \xrightarrow{\text{catalyst}} \text{Cyclohexanone} + \text{H}_2\text{O} \quad (8)
\]

The ammonia oxime reaction was mainly divided into two steps, the first step was the oxidation of ammonia to hydroxylamine by hydrogen peroxide under the action of catalyst, and the second step was the uncatalysed reaction of hydroxylamine with cyclohexanone to produce cyclohexanone oxime [35].

After membrane separation, the cyclohexanone oxime produced was transferred to the solvent recovery unit with the aqueous solution of tert-butanol, which was separated by distillation and returned to the reactor; toluene was used as an extractant to transfer the cyclohexanone oxime from the aqueous phase to the organic phase, and the remaining aqueous phase was separated from the dissolved toluene by a vapour extraction tower and then entered the waste water.
treatment system, while the toluene from the vapour extraction continued to be used for extraction and separation [36]. The toluene and cyclohexanone oxide in the organic phase were separated by distillation to obtain the final cyclohexanone oxide product, while any impurities such as alcohols and ketones that may be present are separated from the toluene by redistillation. Here the conversion of cyclohexanone and the selectivity of cyclohexanone oxide were defined as:

\[
Conversion = \frac{n_{\text{added}}-n_{\text{react}}}{n_{\text{added}}} \times 100\% \\
Selectivity = \frac{n_{\text{product}}}{n_{\text{added}}-n_{\text{react}}} \times 100\%.
\]

For the conversion of cyclohexanone, \( n_{\text{added}} \) and \( n_{\text{react}} \) were the amount of substance of initially added and unreacted cyclohexanone respectively. For the selectivity of cyclohexanone oxide, \( n_{\text{product}} \) means the amount of substance of produced cyclohexanone oxide. Under optimised conditions, the conversion of cyclohexanone was >99.6\% and the selectivity of cyclohexanone oxide was >99.5\% by the third-party certification organisations, which effectively improved the reaction conversion and yield, and significantly reduced the consumption of raw materials such as catalyst, hydrogen peroxide and ammonia, etc [37]. It also reduced the load of refining and dehydrogenation, which played a role in energy saving and consumption reduction and made a positive contribution to improving the quality and reducing the production cost of caprolactam.

3.3. Catalysts: soul of modern caprolactam production

The catalysts were the soul in the atom economy reactions of cyclohexanone production and the high selectivity of cyclohexanone aminoxime. In cyclohexanone production, Pt series catalysts were investigated as efficient catalytic cyclohexane dehydrogenation for benzene and hydrogen production. The dehydrogenation of methycyclohexane over Pt catalysts supported on different supports was studied and the results showed that the electron interaction between Pt and supports determines the order of catalytic activity: Pt/La\(_2\)O\(_3\) > Pt/ThO\(_2\) > Pt/Al\(_2\)O\(_3\) > Pt/MnO\(_2\) > Pt/Fe\(_2\)O\(_3\) > Pt/ZrO\(_2\) > Pt/CeO\(_2\). The electron donating effect of La on Pt facilitated the reduction of Pt, while more reduced Pt was more conducive to the hydrogen overflow effect, thus increasing the catalytic activity [38–40]. Pt/Al\(_2\)O\(_3\) has been widely used in the chemical industry considering the source and cost of supports. Ni co-catalyst was used to form Pt-Ni/γ-Al\(_2\)O\(_3\), which increased the activity and stability of the catalyst, which was used in the real industrial in the China Petroleum & Chemical Corporation and Eversun [41–44]. The supported Pt catalysts had a high metal atom utilization efficiency, but a high reaction temperature of more than 533 K was required. Therefore, in a recent laboratory research, a series of Pt ensembles were designed to enable efficient catalytic cyclohexane dehydrogenation for benzene and hydrogen production at 473 K [45–47]. In addition, some Pt/black TiO\(_2\) photocatalysts have shown high performance for alkane dehydrogenation in visible to near-infrared light at room temperature. For cyclohexane dehydrogenation, the turnover number for benzene and H\(_2\) production were reported to be more than 100,000 without any deactivation over 80 reaction cycles, far beyond thermal reactions [48]. The Pt ensembles and Pt/black TiO\(_2\) photocatalysts were at the stage of laboratory research and have not been applied in industry.

In the ammonoxidation process, the high selectivity was strongly related to the catalysts, in addition to the use of membrane separation. The traditional catalyst was the titanosilicate TS-1, first developed by EniChem [49]. In modern industry, Au-Pd-Pt/TS-1 has been used to bridge the wide gap in conditions that existed between the two different reaction pathways: H\(_2\)O\(_2\) direct synthesis and cyclohexanone ammonoximation, overcoming the significant economic and environmental concerns associated with the production of a key reagent, H\(_2\)O\(_2\) [50].

4. CONCLUSIONS

Caprolactam is an important organic chemical raw material, mainly used to produce nylon 6 fibres or engineering plastics, which is highly profitable in the chemical industry and has been a hot spot for chemical investment and technological innovation. Although the schemes of traditional processes involving hydroxylamine production and cyclohexanone production were still involved in the caprolactam production industry, the modern technical adaptations achieved higher atomic utilisation in cyclohexanone production by rectification dehydrogenation of by-product cyclohexane and higher selectivity with membrane separation in cyclohexanone aminoxime production. In cyclohexanone production, the addition of rectification dehydrogenation increased benzene efficiency from 78 % to 98 %. In cyclohexanone aminoxime production, the conversion of cyclohexanone was >99.6 % and the selectivity of cyclohexanone oxide was >99.5 % with membrane separation.

Acknowledgments

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