

Production technology of adiponitrile

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Abstract: This paper introduces the technical routes and characteristics of four traditional adiponitrile production processes, including acrylonitrile dimerization method, butadiene method, adipic acid catalytic ammonification method and caprolactam method, were introduced and compared in terms of reaction principle, process, production cost and environmental protection. The production process with low cost, low energy consumption and good environmental benefits was found to provide reference for the production and development of adiponitrile in China.

1. Introduction

Adiponitrile (ADN), also known as 1,4-dicyanobutane, has the molecular formula of $\text{NC}(\text{CH}_2)_4\text{CN}$. It is a colorless transparent oily liquid with a slight bitter taste at normal temperature and pressure. The substance is flammable and toxic, and it is mostly stored in a cool and ventilated warehouse^[1].

Adiponitrile undergoes addition reaction with H_2 under the action of a related catalyst to generate hexamethylene diamine(HMD)^[2], and then hexamethylene adipate (nylon 66 salt) can be generated by adipic acid and hexamethylene diamine through strict material ratio, which is the most important industrial use since its development^[3]. Due to the gradual enhancement of people's awareness of environmental protection, hexamethylene diisocyanate (HDI), a light industrial product with the characteristics of non-yellowing, color preservation, light preservation and sun exposure resistance, is increasingly favored by people. It is found that HDI can be synthesized from hexamethylene diamine by phosgene method, which is another very important use in the downstream products of adiponitrile at present^{[4]-[5]}. In addition, adiponitrile is also widely used in electronic batteries, organic synthesis and other fields, and is also used to make rocket fuel, washing additives, pesticides and so on^[6].

At present, the main production processes of adiponitrile include electrolytic dimerization of acrylonitrile (AN), catalytic ammonification of adipic acid (ADA), butadiene (BD) and caprolactam degradation^[7]. Adiponitrile production technology is currently in the hands of a few large foreign companies, foreign companies monopolize the supply of raw materials in China, seriously restricting the development of nylon 66 and related industries in China, this paper introduces four traditional adiponitrile production technology routes and puts forward the future research

direction of adiponitrile production technology according to the current situation of the domestic adiponitrile market.

2. Acrylonitrile dimerization

2.1 Electrolytic dimerization of acrylonitrile

The electrolytic dimerization of acrylonitrile is that propylene is oxidized in the presence of ammonia to produce acrylonitrile, and acrylonitrile is polymerized and dimerized at the cathode to produce adiponitrile. Its production process is mainly divided into diaphragm electrolysis method and diaphragm-free electrolysis method, while diaphragm electrolysis is divided into solution method and emulsion method.

As early as 1961, Monsanto Company of the United States for the first time used the solution method in the diaphragm electrolysis method to prepare adiponitrile by electrolysis of the cathode liquid consisting of 20-40% of the mass fraction of acrylonitrile and electrolyte salts. In the later period, Asahi Kasei Company of Japan used emulsion method to electrolyze low-concentration acrylonitrile solution with cathode solution composed of high-conductivity salt (tetraethylamide phosphate) and emulsifier (polyvinyl alcohol) to produce adiponitrile and realize industrialization. Later, the Belgian Chemical Joint Research Company found that the main reaction to generate adiponitrile occurred at the cathode, and the anode reaction did not interfere with each other, so it took the lead in canceling the diaphragm and developing the direct electrolytic dimerization method (diaphragm-free method). Germany's BASF modified the electrolytic bath and adopted a new capillary electrolytic bath with PbO_2 -plated graphite as the anode and graphite as the cathode, eliminating the ion exchange membrane^[8]. Because the diaphragm-free electrolysis method further amplifies the advantages of electrolytic preparation of adiponitrile in terms of cost and three

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wastes treatment, it has the concept of green chemical industry [9]. At this point, the diaphragm-free electrolysis method began to develop [10]. Later generations continued to study and devote on this basis, and committed to improving the yield of adiponitrile and the current efficiency of the electrolytic cell. Luo Zhonglin [11] used lead as cathode and carbon steel as anode to electrolytic

dimerization of acrylonitrile into adiponitrile in a diaphragm-free electrolytic cell, and discussed the basic conditions such as the optimum acrylonitrile content, tetraethylammonium hydroxide content, temperature and PH. The process flow of electrolytic dimerization of acrylonitrile is shown in Figure 1.

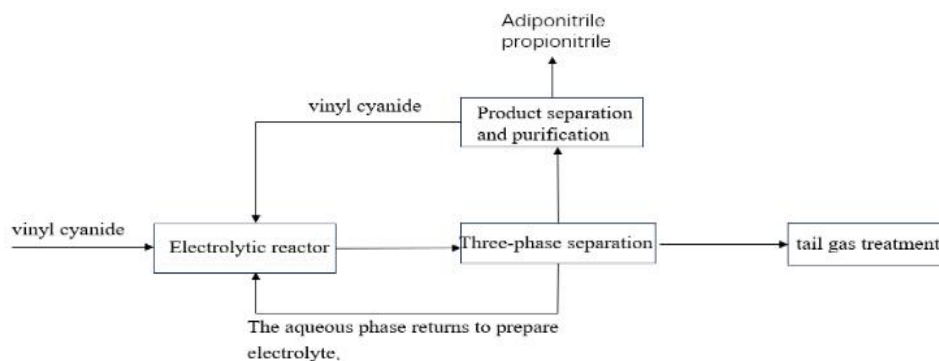


Fig. 1 Process flow of electrolytic dimerization of acrylonitrile

2.2 Acrylonitrile catalytic dimerization

Acrylonitrile catalytic dimerization is a commonly used organic synthesis method, the principle is by adding the catalyst to the acrylonitrile reaction solution, the dimerization between acrylonitrile molecules to form high polymers. This method is widely used in organic synthesis and can be used to prepare various organic compounds, such as polymers, drugs, fuels, etc.

Acrylonitrile catalytic dimerization has become an important part in the field of modern industrial chemical reaction because of its advantages of simple reaction, high yield and controllable molecular weight distribution. By optimizing for different influencing factors, the reaction efficiency and product quality can be improved to the greatest extent, which provides strong support for the development of related industries.

3. Butadiene method

3.1 Cyanidation of butadiene

Butadiene cyanide chlorination is also known as the "two-step method" [12]-[14]. In the first step, 1, 3-butadiene and chlorine gas undergo conjugate addition reaction to

produce 1,4-dichloro-2-butene. In the second step, 1,4-dichloro-2-butene and metal cyanide (preferably sodium cyanide) undergo SN2 nucleophilic substitution reaction to produce 1,4-dichloro-2-butene. Finally, with RandyNi as catalyst, 1,4-dichloro-2-butene was added to hydrogen to produce adiponitrile.

3.2 Butadiene direct cyanide method [15]

In the 1970s, DuPont Company of the United States developed the butadiene direct hydrocyanide process based on the butadiene cyaniding process, and established the first production plant in Texas and realized industrialization [16]. In this method, 1, 3-butadiene and hydrocyanic acid are reacted in liquid phase at 100 °C in the presence of catalyst [17] composed of zero-valent nickel and phosphate-containing ligands to produce an isomer mixture of pentenenitrile. After separation and isomerization of the isomer into linear pentenenitrile, the isomer is then added to hydrocyanic acid to produce adiponitrile. The actual reaction process is divided into three steps: primary hydrocyanation, isomerization and secondary hydrocyanation [18]-[20].

The process flow of this method is shown in the figure 2:

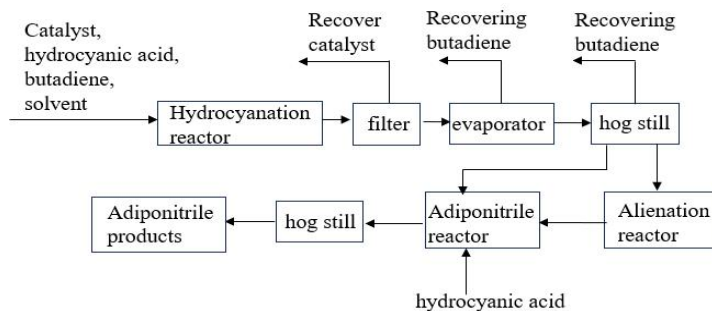


Fig. 2 Process flow of butadiene direct cyanidation

Butadiene, hydrocyanic acid, solvent and catalyst (complex composed of phosphorus-containing ligand and zero-valent Ni) are added into a reactor with a stirrer for hydrocyanation reaction, the temperature is about 100 °C, and the reactant is kept in the liquid phase with sufficient pressure, which is about 6.8atm^[21]. Pure 3- pentenenitrile (3-PN) obtained by rectification is sent to secondary hydrocyanation, and 2- methyl -3- butenenitrile (2M3BN) distilled from the top of distillation tower is sent to isomerization reaction section.

The isomerization reaction section is also homogeneous reaction, the reaction temperature is 80-120 °C, the isomerization reactor and the catalyst and intermediate products obtained in the filter and evaporator reaction to obtain 4-PN and 3-PN, and the single-pass conversion rate of 4-PN and 3-PN is 26.4% and the selectivity is 79.8%.

The raw materials for the second-stage hydrocyanation reaction are HCN and 3-PN generated by the first-stage hydrocyanation and isomerization reaction. The 3-PN, 4-PN, hydrocyanic acid and aromatic solvent are put into the adiponitrile reactor for hydrocyanation reaction to generate adiponitrile, and then the final product adiponitrile is obtained through the refining system^[22].

3.3 Butadiene carbonylation method

Butadiene first reacts with carbon monoxide and methanol under the action of catalyst to produce 1,6-methyl adipate, and then through ammonolysis and dehydration under the action of catalyst to synthesize adiponitrile, in which the by-product methanol can be recycled as raw material.

4. Adipic acid catalytic ammonification method

The production process of adipic acid (ADA) catalytic ammonification was first developed and successfully by Rhone-Planck in France in the late 1960s, and then industrialized production was formed by BASF, Lattice Chemical Plant and Liaohua in China^[23]. The process is divided into liquid phase method and gas phase method. The reaction principle of the two methods is basically the same, both are based on phosphoric acid or its salts or cheese as the catalyst, adipic acid and ammonia react to produce diammonium adipate, and then heat and dehydrate to obtain crude adiponitrile, after refining to get the finished product. The reaction formula is as follows:

The production process flow of adipic acid is shown in Figure 3:

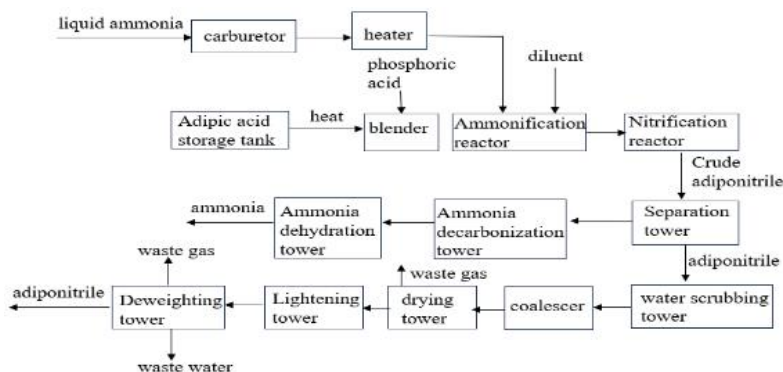


Fig. 3 Process flow of catalytic ammonification of adipic acid

4.1 Adipic acid liquid phase method

The liquid phase method is about 200 ~ 300 °C molten adipic acid, ammonia gas, catalyst (phosphoric acid or acid salt) and diluent (semi-nitrile compound) mixed into the reactor for ammonification reaction. After washing, settling and filtering, the organic layer is mainly composed of crude adiponitrile and water. The bottom product of the tower is a semi-nitrile compound containing adipic dinitrile. Part of the liquid phase from the rectification column enters the scraper film evaporator for ammonification and dehydration. All the products at the top of the evaporator are used as diluents, and the residue is discharged from the bottom^[24]. The crude adiponitrile enters the refining system to obtain the product adiponitrile. The liquid phase method has a long history but the product quality is poor. The yield of adiponitrile is 84% ~ 93% when diluent is used. The yield of adiponitrile was 65%-73.5% without diluent.

4.2 Adipic acid gas phase method

The reaction temperature of adipic acid gas phase method is 350 ~ 420 °C, the powder adipic acid is vaporized, the ammonia gasification dehydration reaction is carried out, and the yield of adipic acid is 92% ~ 96%. After further treatment. The recovered ammonia goes into the reactor for recycling, and the final product is obtained by the refining section of adiponitrile. The gas phase method is divided into BASF method and Monsanto method, the main difference is that the reactor type is different.

5. Caprolactam method

Caprolactam method^[25] was developed by Toray Company in Japan to produce adiponitrile from waste lactam as raw material by first degrading lactam and then hydrolyzing it. The scale of the law is small, and the products are only used by the downstream products of his

company. The process focuses on the recycling of waste raw materials, which is a good development idea, and the production cost has been reduced, but it cannot be large-scale production due to the lack of raw materials.

6. Comparison of adiponitrile production process

In summary, the four production process pairs of adiponitrile are shown in Table 1 below:

Table 1 Comparison table of adiponitrile production process

Project	Acrylonitrile method		Butadiene method		Adipic acid process	
	diaphragm valve	Diaphragm-free method	Chlorination cyanidation method	Direct cyanidation method	liquid phase method	Gas phase method
source of feed	extensive	extensive	extensive	extensive	extensive	extensive
Raw material cost	tall	tall	tall	low	tall	tall
Technological process	common	common	complex	common	complex	complex
Energy consumption	tall	lower	tall	lower	common	common
production capacity	small scale	small scale	large scale	large scale	moderate scale	moderate scale
product quality	common	tall	common	tall	common	common
yield coefficient	lower	tall	higher	tall	lower	lower
environmental protection	heavy pollution	heavy pollution	serious pollution	Pollution is average	pollution is average	pollution is average
investment	higher	higher	tall	lower	lower	lower

Through the comparative analysis of the production process route of adiponitrile, it can be seen that the acrylonitrile method has a wide range of raw materials, and the diaphragm-free electrolysis method has the characteristics of low energy consumption, high product quality and high yield, which is a very promising process route, but due to the current market price of raw material acrylonitrile and the difficulty of catalyst research and development, there is no fundamental breakthrough, and it is urgent to develop efficient and low-cost catalysts^[26]; In the process route of butadiene process, the cyanidation process of cyanidation is complex, the corrosion is serious, the investment is large, and a large amount of chlorine and hydrocyanic acid need to be consumed, which is basically eliminated. Direct cyanidation is the most advanced production technology in the industrial adiponitrile plant, suitable for large-scale industrial production, and is also a good way to treat hydrocyanic acid by-product of acrylonitrile plant, but its technology is monopolized by DuPont; Butadiene carbonylation method has the advantages of simple process, low production cost and clean process, and is a very promising production route for adiponitrile, but it has not yet achieved industrial equipment, and this technology deserves the attention of domestic enterprises^[27]; The adipic acid catalytic ammonification method has a long process route, and the market price of adipic acid before 2012 was high, which was not an ideal process route at that time, but with the overcapacity of adipic acid, the price has fallen sharply, and the adipic acid catalytic ammonification method is also an important production process^[28].

7. Conclusion

With the development of China's economy, the demand for adiponitrile will increase, although INVISTA may expand production globally, but it will leave about 70% of its own use, and the international market will remain tight in supply for a long time. In order to ensure the healthy and stable development of China's nylon 66 industry and its downstream related fields, it is urgent for China to develop and build its own adiponitrile production equipment^[29].

Before 2019, there was no enterprise in China that could produce adiponitrile on a large scale, and all the required adiponitrile relied on imports. In 2020, domestic Huafeng Group took the lead in breaking through the industrial production technology of adiponitrile and put into production of 50,000 tons^[30].

According to statistics, the raw material cost accounts for 80%~85% of the production cost of adiponitrile, which has a decisive role in the economy of the process technology route. With the change of supply and demand in the market, the price of adipic acid was high before 2012, resulting in the lack of competitiveness of the adipic acid process^[31]. On the whole, the domestic should combine the raw material supply and demand market situation, coordinate the layout, on the basis of accelerating the existing butadiene cyanide route and acrylonitrile electrolysis technology research, under the condition that the domestic adipic acid price remains low, it is feasible to re-enable the adipic acid process route to produce adiponitrile in China, and realize the industrial production and technological autonomy of adiponitrile in China as soon as possible.

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