Simulation design of acrylonitrile heat transfer section 100000 tons/year

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Abstract: Acrylonitrile is an important petrochemical material, and the demand for acrylonitrile has increased dramatically as the demand for acrylonitrile has grown rapidly. The production technology of acrylonitrile was introduced. with propane, Choose the ammonia and oxygen as raw material, adopts the direct ammoxidation of propane to acrylonitrile, $MoV_{0.3}\ Te_{0.23}\ Nb_{0.15}\ Ox$ as catalyst, meanwhile oxidative dehydrogenation of propane and propylene ammonia reaction. This design using propane ammonia oxidation to produce acrylonitrile, effectively reducing the energy consumption. The purpose of this design is simulating heat transfer section of acrylonitrile production through the material balance and heat balance, design the heat exchanger capacity of 100000 tons of acrylonitrile, yield no less than 60%. The results are as follows: Select fixed tube heat exchanger, heat exchange area 183.33 m^2, average temperature 250℃, $\Phi 19 \times 2$ thermo-tube (carbon steel), tube diameter: 115 mm, length 6 m, Pipe number n = 264.

Keywords: Acrylonitrile, ammonia, heat exchanger, simulation design.

1. Introduction

Acrylonitrile, also known as cyanoethylene, colorless flammable liquid, toxic, pungent smell, not soluble in water, soluble in organic solvents; In case of fire source and high temperature environment, there is a danger of combustion and explosion. When the steam and air are mixed with each other, they can become an explosive mixture. The upper and lower limits of explosion are 4%~17% (volume fraction). The boiling point is 77.3°C, the melting point is -82.0°C, the spontaneous combustion point is 481°C, and the relative density is 0.8006. Commonly used to produce polyacrylonitrile; Acrylonitrile can be copolymerized to produce acrylic fiber. . Acrylonitrile can also produce acrylate, etc [1].

China's energy supply is still relatively backward, often unable to meet the demand,

and the utilization of energy technology is not very mature, which leads to the slow economic development in China, and the rational utilization of energy is extremely urgent. Reasonable integration and integration of industrial process is an important means of energy saving in current engineering. In the last 30 years, many traditional industries in the world have carried out energy utilization and transformation projects to save resources. But the results these factories have received are not ideal. Therefore, in order to respond to a nation in the process of chemical engineering design, reasonable use of resources, reduce energy consumption, reduce the cost from the viewpoint of green chemistry to contribute to green chemistry, as designers should not only stare at a certain process, but on the whole process of integrated design, reasonable use of resources, realize to the rational use of energy [2].

Typical chemical industry, such as chemical industry, petroleum and chemical fertilizer production, is the key sector of energy consumption. To improve the market competitiveness of products, the first thing is to reduce the production cost. To reduce the production cost, we must first change the energy consumption and reduce the energy consumption by improving the process. For the heat transfer section with a large proportion of energy consumption, the network should be reasonably designed to realize the rational utilization of resources.

2. Design task

As The main task of this design is to design the heat exchange section with an annual output of 100,000 tons of acrylonitrile and simulate the calculation of the heat exchanger, so as to make reasonable use of the excess heat and realize multiple utilization of energy under the condition that the yield of acrylonitrile is not less than 60%.

3. Determination of design scheme

3.1 Production Method of Acrylonitrile

Cellular Before 1960, the main production methods of acrylonitrile were: ethylene oxide method, acetylene method, acetaldehyde method. After 1960, the production technology was improved and the propylene ammoxidation process was developed. The production cost was very low and the product quality was better [3]. The former methods of production are too harmful to the environment and human body and too costly. This method has been replaced by propylene ammoxidation. This method has reached the approval of most enterprises and is the main method for producing acrylonitrile [4].

3.2 BP/Sohio Process

At present, most enterprises use the propylene ammoxidation technology developed by BP company to carry out ammoxidation reaction with propylene. Besides producing acrylonitrile, the reaction products include acetonitrile, hydrocyanic acid, acrolein and other side reaction products [5].

$$CH_2=CHCH_3 + NH_3 + 3/2O_2 \longrightarrow CH_2=CHCN + 3\ H_2O$$
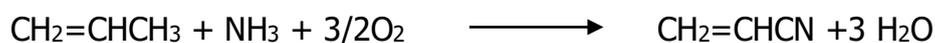
Theoretically, the ratio of propylene, ammonia and air is 1:1:1.5, which can reach a higher yield.

3.3 Propane Ammonia Axidation

Because propane price is cheaper, more suitable for the interests of enterprises. One - step oxidation of propane ammonia has been industrialized. The developed catalyst was supported by sio2-al2o3 and carried the active group into v-sb-mo. The raw material was reacted with propane: ammonia: oxygen: nitrogen: water = 1:2:2:7:3, the temperature was about 450°C, and the pressure was 105 kPa[6].

Propane ammonia oxidation reaction method, there are two commonly used processes, the first propane under the action of industrial catalyst, propane oxidation dehydrogenation reaction and propylene ammonia oxidation reaction, this method is called propane one-step ammonia oxidation process method; The second is the production of acrylonitrile from propane by oxidative dehydrogenation, which is called the propane two-step ammoxidation process [7].

In the early 1990s, BP developed a way to catalyze reactions with oxygen, which was used as an oxidant to speed up the process. The new catalyst was designed and selected to improve the selectivity of acrylonitrile, but few by-products were produced in the final reaction. This method is suitable for the production of oxygen or air as an oxidant. This process greatly reduces the production cost, more is the by-product is also less, can produce more valuable products [8].

3.4 Determination of Final Process

Since propane is relatively cheap, propane is much cheaper than propylene in terms of cost for the long-term benefit of enterprises.

This design USES propane direct ammoxidation reaction to produce acrylonitrile, and the catalyst USES mo-v-nb-te-o. At the same time, propane is used for propylene ammoniation reaction and oxidation dehydrogenation reaction. It has a high selection for acrylonitrile and few reaction by-products.

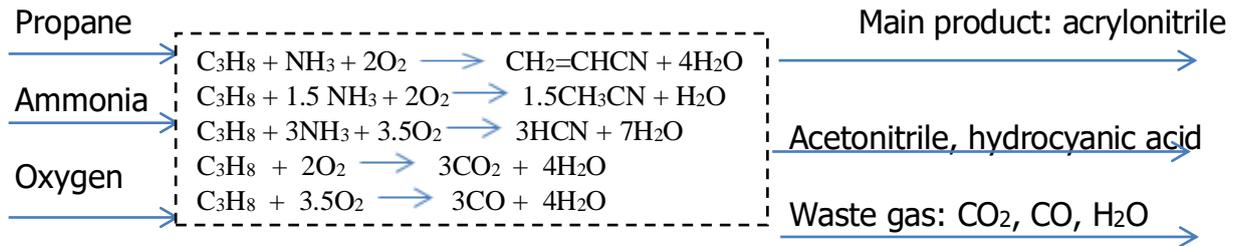Material flow chart and material properties are as follows:

Propane

Ammonia

Oxygen

$$C_3H_8 + NH_3 + 2O_2 \longrightarrow CH_2{=}CHCN + 4H_2O$$
$$C_3H_8 + 1.5\,NH_3 + 2O_2 \longrightarrow 1.5CH_3CN + H_2O$$
$$C_3H_8 + 3NH_3 + 3.5O_2 \longrightarrow 3HCN + 7H_2O$$
$$C_3H_8 + 2O_2 \longrightarrow 3CO_2 + 4H_2O$$
$$C_3H_8 + 3.5O_2 \longrightarrow 3CO + 4H_2O$$

Main product: acrylonitrile

Acetonitrile, hydrocyanic acid

Waste gas: CO_2, CO, H_2O

Fig. 1 Propane material flow chart

3.5 Selection of Quench Process

After the reaction gas leaves the reactor, it goes directly into the quench tower to remove ammonia gas, so as to avoid the loss caused by the reaction of unreacted ammonia gas and acrylonitrile to form impurities. The specific process is in the process of propane ammoxidation, when the reaction reaches the equilibrium, the yield is low. In order to make changes, bp-amoco has designed a process method for the reuse of ammonia to achieve the multi-stage utilization of raw materials, that is, ammonium dihydrogen phosphate generates diammonium hydrogen phosphate from the ammonia in the reaction gas to absorb it. After heating, diammonium hydrogen phosphate can be decomposed again into ammonium dihydrogen phosphate, ammonia gas. After drying and dehydrating the ammonia gas, it can be added to the reaction system again for recycling use.

4. The process flow

4.1 Simulation Process and Optimization

This design USES Aspen Plus software to simulate the entire reaction process. Simulation results ensure that the yield of the reaction product acrylonitrile should reach 261.60kmol/h, and the product quality should have 98% purity.
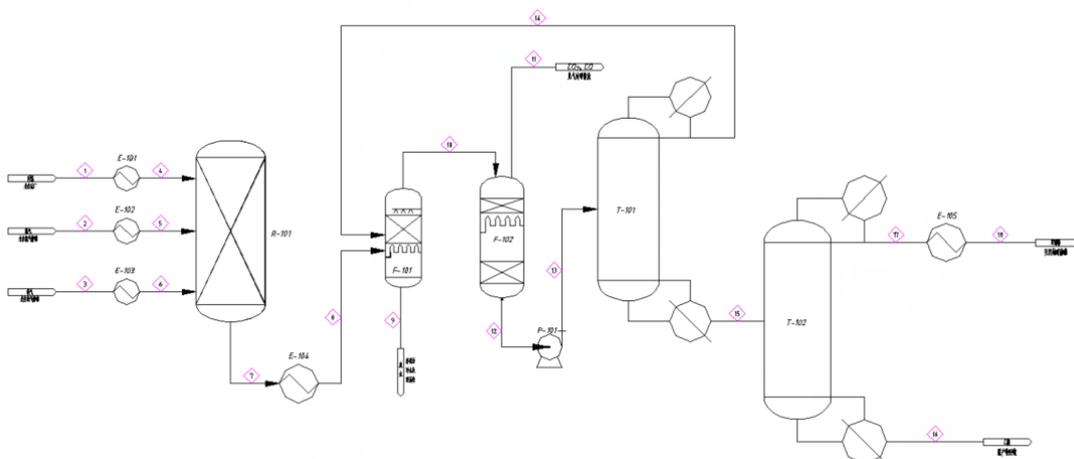

Fig. 2 Aspen Plus software simulates the flow

4.2 Overview of The Process Flow

The process is divided into three sections: reaction section, cooling section and distillation section.

Reaction section: After heating, the temperature of liquid propane, liquid ammonia and oxygen was raised to 70°C, and then these reactants were added into the reactor. The reaction temperature was determined to be around 410°C and the pressure was 120kPa. Then the catalyst was added into the reaction system. After the end of the reaction, the reaction products are then exchanged through the cooler for heat, and the cooling process is carried out until the temperature stops at about 200°C, and finally enters the next process, which is the cooling stage.

Cooling process:The reaction product enters the condensing tower as a gas in contact with the coolant and cools rapidly, cooling the unreacted reactants and, at the same time, washing away the impurities in the reactants. The excess ammonia in the cooling tower reacts with ammonium dihydrogen phosphate to produce diammonium hydrogen phosphate, which is reused in the subsequent reaction. After the condensation reaction decomposition and precipitation, diammonium hydrogen phosphate is reheated and decomposed to produce the required ammonia and ammonium dihydrogen phosphate. Therefore, diammonium hydrogen phosphate is heated to 150-300°C. The ammonia can be dried and recycled again in the reaction synthesis section, and in the case of ammonium dihydrogen phosphate, it can be reused as a coolant component. The reactants come out of this cooling tower and then go into the next cooling tower to cool down and continue to separate the gas and the liquid. After the condensation and separation, the gas that no longer reacts will enter the tail gas treatment stage to reduce air pollution, and the remaining liquid substance at the bottom of the column will enter the distillation column for rectification.

Rectifying section: The residual liquid phase at the bottom of the tower in the previous section enters the distillation column for rectification, and the components such as HCN come out from the top of the tower, and the circulation process needs to be carried out to the condensing tower. The liquid phase at the bottom of the tower continues to be rectified and enters the next distillation column for rectification. The purity of the product is 99%.

5. Design of process conditions

From the perspective of process design, chemical equipment can be divided into two categories: the first category is standard equipment, which is mass-produced in batches, and its specifications and models can be checked from the manufacturer's product catalog or manual, which can be directly purchased from the equipment manufacturer; The second category is called non-standard equipment, according to

the requirements of the process, through the process calculation and equipment professional designer design, is the need for special design of special equipment, and then by qualified manufacturers manufacturing.

5.1 Heat Exchanger

Basic parameters of heat exchanger equipment: For the acrylonitrile production with an annual capacity of 100,000 tons, start work for 320 days, propane conversion rate is 90%, and the required propane is 112,000 tons/year.

Heat exchanger: fixed shell and tube heat exchanger.

Table 1 Feeding situation

Fuid	Name	Inlet temperature	Outlet temperature
Material	Propane	25 °C	70 °C
Heating medium	LP steam	120 °C	105 °C

The basic basis for heat transfer calculation of heat exchanger is the heat balance equation and the total heat transfer rate equation, as follows:

$$Q_T = q_{m,\,c}c_{p,\,c}(t_2 - t_1) = q_{m,\,h}c_{p,\,h}(T_1 - T_2)$$

$$Q_T = KS\Delta t_m$$

Eliminating QT from the above equation will result in two independent equations, such as:

$$q_{m,\,h}c_{p,\,h}(T_1 - T_2) = q_{m,\,c}c_{p,\,c}(t_2 - t_1)$$

$$q_{m,\,h}c_{p,\,h}(T_1 - T_2) = KS\Delta t_m$$

Total heat transfer coefficient: In actual production, dirt will be stained on the heat transfer surface and additional heating resistance will be generated. This heat resistance is called dirt heat resistance. If the heat transfer surface is cylindrical wall, the heat resistance on the inner and outer surface of the pipe wall is Rsi and Rso, respectively. After consulting, it can be seen that the total heat transfer resistance between fluid on both sides of the partition is equal to heat transfer resistance + fouling heat transfer resistance + heat conduction resistance of the pipe wall, and the total heat transfer coefficient can be calculated, that is

$$\frac{1}{K} = \frac{d_o}{a_i d_i} + \frac{b d_o}{\lambda d_m} + R_{so} + \frac{1}{a_o}$$

Heat transfer calculation method: In the design and calculation of heat exchanger, the heat transfer unit number method is obviously convenient and fast.

The heat transfer efficiency of heat exchanger is defined as:

$$\varepsilon = \frac{Q_T}{Q_{max}}$$

If the heat loss of the heat exchanger is ignored, the actual heat transfer QT is equal to the heat absorbed by the cold fluid or released by the hot fluid. If the two fluids have no phase transition, then:

$$Q_T = q_{m,c} c_{p,c} (t_2 - t_1) = q_{m,h} c_{p,h} (T_1 - T_2)$$

Physical property data:

The inlet temperature of propane is $T_1 = 25$ °C

The outlet temperature of propane in the pipeline is $T_2 = 70$ °C

The propane inlet and outlet pressures of the pipe are all equal 1 MPa

The inlet temperature of shell side saturated steam is $t_1 = 410$ °C

The outlet temperature of shell side saturated steam is $t_2 = 200$ °C

The inlet pressure of shell side saturated steam is 1.2 MPa

The outlet pressure of shell side saturated steam is 1 MPa

Qualitative temperature: the average fluid inlet and outlet temperature.

The qualitative temperature of propane in the pipeline is 47.5 °C.

According to the qualitative temperature, the physical property data of propane when the qualitative temperature is 47.5 °C can be obtained from the physical property table as follows:

Table 2 Propane properties at 47.5°C

Physical quantities	Data
ρ_0 （kg/m^3）	996.46
c_{p0}[kJ/(kg•°C)]	3.804
λ_0[W/(m•°C)]	0.6027
μ_0 （Pa•s）	0.000965

Shell side air temperature is 305°C.

According to the qualitative temperature, the physical property data of low-pressure saturated steam at the temperature of 305 °C can be obtained from the physical

① property table as follows:

Table 3 Physical properties of saturated steam at 305°C

Physical quantities	Data
ρ_1 （kg/m^3）	735.37
c_{p1}[kJ/(kg•°C)]	5.952
λ_1 [W/(m•°C)]	0.6201
μ_1 （Pa•s）	0.000108

② Mean temperature difference

The annual working time is 320 days, and the annual working time is 7680 h

$$\Delta t_{m}{}' = \frac{\Delta t_1 - \Delta t_2}{\ln \dfrac{\Delta t_1}{\Delta t_2}} = \frac{(175-25)-(410-70)}{\ln \dfrac{175-25}{410-70}} = 250°C$$

③ Heat transfer area

K value is 240 W/(m•°C)

S=Q/(K Δt_m)= 1.1×10^7 kJ/h÷(240×250) m^2 = 183.33 m^2

④ The number of heat pipes

$$n = \frac{S}{\pi d l} = \frac{183.33}{3.14 \times 0.015 \times 6} \approx 649$$

⑤ Heat pipe arrangement

The arrangement of the heat transfer tube is arranged in the form of equal-triangle. The center distance of the tube is selected as a=1.25d=1.25×19=23.75mm. After rounding, the core distance of the adopted tube is 25 mm.

The area occupied by a single pipe is:

$$A = \frac{\sqrt{3}}{2} a^2 = \frac{\sqrt{3}}{2} \times 0.025^2 = 5.4125^{-4} m^2$$

⑥ Shell inner diameter

$$D = 1.05 a \sqrt{N/\eta} = 1.05 \times 25\sqrt{162/0.8} = 373.54 mm$$

Take the whole: D=400 mm

Material balance and heat balance of heat exchanger:

1) Calculation basis

Inlet gas 410°C, outlet gas 200°C operating pressure 100 kPa

The vapor condensation was 1597.38kmol/h

Table 4 Flow of each material

	Inlet gas	The export gas
Component	kmol/h	kmol/h
Ammonia	55.5808	55.5808
Oxygen	98.0035	98.0035
Acrylonitrile	325.6	325.6
Acetonitrile	8.5536	8.5536
Hydrocyanic acid	50.2656	50.2656
H_2O	1597.38	1597.38
CO_2	90.3936	90.3936

CO	25.7664	25.7664
Propane	53.2224	53.2224
kmol/h	2304.8	2304.8
kg/h	58895	58895
Kg/m^3	0.5407	0.5407
Average molecular weight	25.553	25.553

2) Heat balance

a. Cooler inlet heat Q_1

$Q_1 = 6.58 \times 10^7 kJ/h$

b. Steam condensation and exothermic Q_2

$Q_2 = 1597.38 \times 3280 kJ/h = 5.24 \times 10^6 kJ/h$

c. The condensate takes out heat Q_3:

$Q_3 = 1597.38 \times 4.104 \times （200-0） = 1.31 \times 10^6 kJ/h$

d. The outlet gas takes out heat Q_4:

$Q_4 = (4.355314 \times 55.5808 + 98.0035 \times 32 \times 0.218 + 90.3936 \times 44 \times 0.200 + 25.7664 \times 28 \times 0.250 + 53.2224 \times 44 \times 0.45 + 29 \times 50.265 \times 1.443 + 325.6 \times 53.1 \times 0.210 + 8.5536 \times 41 \times 0.224) \times (200-0) kJ/h$

$= 2.38 \times 10^6 kJ/h$

e. Heat balance calculation to find the heat exchanger load Q_5

Heat balance equation: $Q_1 + Q_2 = Q_3 + Q_4 + Q_5$

$Q_5 = 6.735 \times 10^7 kJ/h$

f. Heat load of ammonia superheater：

$Q = 55.5808 \times 17 \times 1276 \times 1.1 = 1.326 \times 10^6 kJ/h$

g. Propane superheater heat load：

$Q = 53.2224 \times 44 \times 2138 \times 1.715 kJ/h = 8.587 kJ/h$

h. Oxygen superheater heat load：

$Q = 98.0035 \times 32 \times 1.84 \times 2066 = 1.1 \times 10^7 kJ/h$

6. Treatment of waste gas, liquid and residue in acrylonitrile production

6.1 Waste Gas Treatment

After cooling and cooling, the gas generated by the acrylonitrile reactor passes into the absorption tower, where water is used for counter-current absorption, in which the main products such as acrylonitrile, by-product acetonitrile and hydrocyanic acid will be absorbed, and the remaining CO, CO2 and hydrocarbons will be discharged into the atmosphere through the top of the absorption tower. When these gases are discharged, they also contain small amounts of harmful substances such as acrylonitrile, acetonitrile and hydrocyanic acid. Exhaust gas is fed into the incinerator for

incineration, and the high-temperature gas after incineration is heat recovered, and the steam generated is comprehensively utilized. This can not only protect the environment, but also improve the utilization of energy.

6.2 Liquid Waste Processing

The main treatment method of wastewater produced in the acrylonitrile production process is biological treatment.

The solution containing residual acrylonitrile after absorption by the absorber is pumped to the recovery tower. Because the recovery tower will adopt the extractive distillation process, acetonitrile will be extracted from the side; Tower top materials contain high concentration of acrylonitrile, hydrocyanic acid, etc. When the tower kettle is normal, the waste water containing a small amount of toxic substances is sent to the stripper to remove a very small amount of ammonia and light organic matter. The steam from the top of the absorber is recycled for use. Part of the residual liquid in the tower is used as a supplement to the sealed pump, and the rest is uniformly sent to sewage treatment for biochemical treatment.

6.3 Waste Disposal

The waste residue generated by this design is mainly a failed catalyst, which can be divided into molybdenum, vanadium, etc. When the production unit is stopped for maintenance, the catalyst and other impurities will be dug out. When processing, the useful rare metals are recycled and the remaining bags are sealed for deep pit burial.

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