Purification Process Design of Vinyl Acetate Based on Aspen Plus

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Abstract. Based on Aspen Plus process simulation, the purification stage of the production of vinyl acetate by 450000 tons of calcium carbide acetylene process was optimized. The main equipment involved in the process are degassing tower, deacetaldehyde tower, crude separation tower, vinyl acetate refining tower, acetic acid distillation column and so on. The unit operation involved mainly includes general distillation, azeotropic distillation, distillation with side line extraction, absorption, extraction and so on. Aspen Plus sensitivity analysis function is used to analyze and optimize tower parameters such as reflux ratio, the number of theoretical plates, distillate feed ratio, feed position, side line extraction position. The results will provide reference for improving the problems of low purity and energy waste of products.

1. Introduction
Catalytic Vinyl acetate is one of the 50 most produced chemical raw materials in the world, mainly used in the production of polyethylene, vinyl alcohol, poly composite resin and aldehyde resin derivatives, in coating synthetic fiber, soil improvement and other applications. Ethylene acetate derivatives are widely used and are very closely related to the needs of our lives.

The purity of the product in the purification section of vinyl acetate directly determines the quality of downstream derivative products, so it is of great significance to optimize the purification section of vinyl acetate reasonably to ensure the quality of subsequent derivative products [1]. In the process of purification of vinyl acetate, distillation is mainly used, including ordinary distillation, azeotropic distillation, distillation with side line extraction, and absorption unit operation.

With the continuous progress of science and technology, computer software simulation and calculation provides a continuous power for the progress and innovation of industrial technology. Aspen Plus is the simulation software derived from the development of thermodynamics [2], which has the ability of accurate and fast simulation. According to the process flow of the vinyl acetate industrial plant and the simulation of the Aspen Plus, the optimal process parameters are obtained.

2. Process Simulation and Optimization
Methods of establishing simulation process for purification process of vinyl acetate:

(1) The process of refining and purification of vinyl acetate is analyzed, summarized and studied in combination with industrial production equipment. At the same time, according to the relevant data,
the operating conditions and component separation index of each equipment in the process of refining and purification of vinyl acetate are determined, which provides a reference for simulation.

(2) According to the system in the refining and purification equipment of vinyl acetate, select the reasonable Aspen Plus module and the corresponding operation parameters and physical property method method, optimize the corresponding equipment.

(3) After the simulation convergence of a single tower is correct, a single equipment is connected to form a complete refining process for simulation.

The equipment parameters are optimized by using the Sensitivity tools under the Model Analysis Tools option in the Aspen Plus after the whole process simulation data convergence is correct.

3. Simulation and Optimization of Process for Purification of Vinyl Acetate

3.1. Summary of Process for Purification of Vinyl Acetate

Materials from the reactor in the reaction section contain not only vinyl acetate products, but also raw materials for unreacted acetic acid and acetylene, byproducts such as acetaldehyde, butyraldehyde and anhydride. The whole purification process involves many unit operations, such as absorption, extraction, conventional distillation, azeotropic distillation, and secondary pipeline distillation.

The reaction liquid produced in the reaction synthesis stage is first passed into the degassing tower, and the unreacted acetylene material and carbon dioxide impurity in the reaction solution are separated and extracted in the column flow unit of the degassing tower. the top flow strands of the degassing tower are then obtained through the pickling of the first washing tower and the washing of the second washing tower and subsequent drying, and the acetylene gas with the purity of the target is obtained for the recovery and utilization of the raw materials [3]. In addition to the acetic acid raw materials and vinyl acetate products, acetaldehyde, butylene aldehyde and polymer inhibitor were extracted from the column top of the column. In the crude separation tower, acetic acid and vinyl acetate products were separated from the top of the crude separation tower. Ethylene acetate was extracted from the top of the crude separation tower and sent to the vinyl acetate refining tower for further refining and purification. The high purity vinyl acetate product was obtained from the side-line flow of the vinyl acetate refining tower.

The refining process of vinyl acetate involves material circulation, reflux in the tower, which makes the simulation of the whole process complicated, so it is decided to simulate the equipment of the unit of ethylene acetate purification unit separately first [4].

3.2. Simulation and optimization of degassing tower

3.2.1. Establishment of simulation process for degassing tower

The raw material liquid was pretreated from the top of the degassing tower into the tower. in order to facilitate the simulation, the light components in the raw material solution were extracted from the top gas phase of the degassing tower. the top logistics mainly contained acetylene and a small amount of acetaldehyde and vinyl acetate, etc [5], into the subsequent washing system for pickling treatment. the degassing tower kettle mainly contained vinyl acetate, acetic acid, acetaldehyde and a small amount of butene. the degassing tower kettle liquid enters the deacetaldehyde tower to separate the acetaldehyde [6]. Aspen Plus model of the degassing tower and the flow-strand connection are shown in figure 1.
3.2.2. Simulation of degassing tower

Table 1 Feed Composition

| Components            | Abbreviations | mass fraction |
|-----------------------|---------------|---------------|
| Ethylene acetate      | VAC           | 0.3954        |
| Acetic acid           | HAC           | 0.5778        |
| Acetaldehyde          | C2H4O         | 0.0105        |
| butadiene             | CRALD         | 0.0002        |
| Water                 | H2O           | 0.002         |
| Acetic acid           | C4H6O3        | 0.0021        |
| Acetone               | ACT           | 0.0002        |
| ethyl acetate         | C6H10O4       | 0.0018        |
| Acetylene             | C2H2          | 0.01          |

Table 2 Operation parameters of degassing tower

| Units   | Tower top | Tower kettle |
|---------|-----------|--------------|
| Temperature °C | 32 | 105 |
| Pressure kPa | 125 | 170 |

3.2.3. Simulation and Analysis

The generally prescribed separation requirement for degassing tower is that the mass fraction of acetylene in the tower reactor logistics should be below 0.01%[7], the simulation process and simulation conditions are determined, and the degassing tower is simulated and calculated. The flow-strand simulation results of the degassing tower are shown in table 3.

Table 3 Simulation results of export flow in degassing tower (mass fraction)

| Components            | Abbreviations | Tower top | Tower kettle |
|-----------------------|---------------|-----------|--------------|
| Ethylene acetate      | VAC           | 0.1822    | 0.3754       |
| Acetic acid           | HAC           | 0.0408    | 0.6078       |
| Acetaldehyde          | C2H4O         | 0.0292    | 0.0100       |
| butadiene             | CRALD         | 0.0000    | 0.0002       |
| Water                 | H2O           | 0.0005    | 0.0019       |
| Acetic acid           | C4H6O3        | 0.0001    | 0.0022       |
Acetone ACT 0.0001 0.0002
ethyl acetate C₆H₁₀O₄ 0.0000 0.0019
Acetylene C₂H₂ 0.7472 0.0000

It can be seen that acetylene is mainly distributed in the top flow strands, and the mass fraction of acetylene in the bottom flow strands of the degassing tower is less than 0.01%, which meets the prescribed separation requirements.

3.2.4 Optimization of degassing tower
The size of the theoretical plate number determines the separation effect of the degassing tower. Sensitivity analysis of acetylene mass fraction of tower by theoretical tray number of degassing tower is established under the condition of feed flow condition and feed ratio of top distillate fixed. The relationship between acetylene content and the number of theoretical plates is shown in Figure 2.

![Fig.2 Relationship between acetylene content and the number of theoretical plates in degassing tower](image)

From Fig.3, we can see that with the increase of the number of theoretical plates, the acetylene content of the tower kettle decreases sharply, and the latter section is basically 0. Because increasing the number of theoretical plates will increase the equipment cost, the number of theoretical plates will be reduced as much as possible to save the investment cost when the separation requirements are met. So the number of theoretical plates is set at 6.

The distillate feed ratio is the mass flow rate of the stream strands extracted from the top of the tower divided by the mass flow rate of the stream strands in the tower. The effect of different distillate feed ratios on acetylene content in the stream strands of the tower is analyzed using the Aspen Plus Sensitivity tool function under the condition of the feed stream strands condition and the number of theoretical plates is fixed, as shown in figure 3.
3.3. Simulation and Optimization of Ethylene Acetate Refining Tower

3.3.1. Establishment of Simulation of Ethylene Acetate Refining Tower

The flow strands distilled from the crude separation tower top are mainly vinyl acetate, but the mass fraction is not up to the standard, so the crude separation tower top flow strands are fed into the vinyl acetate refining tower to further improve the purity of the vinyl acetate product. The flow strands of the gas phase are extracted from the top of the vinyl acetate refining tower and sent to the condenser to condense the flow strands into the stratified tank of the vinyl acetate refining tower. The upper layer is vinyl acetate, which is divided into two flow strands through the shunt, one reflux to the vinyl acetate refining tower and the other stream strands to the subsequent polymerization section [8]. The lower water phase is sent to the acetaldehyde sink. The flow strands from the central gas phase of the vinyl acetate refining tower are qualified vinyl acetate products with a mass fraction of more than 99% [9]. In addition to vinyl acetate, there are also polymerization inhibitors and some high boiling substances in the tower kettle liquid, which can be sent to other tower middle circulation polymerization inhibitors. Aspen Plus model and flow-strand connection of ethylene acetate refining tower are shown in figure 4.

![Figure 4 Flow chart of vinyl acetate refining tower](image-url)

### Table 4 Operation parameters of vinyl acetate refining tower

| Units               | Tower top | Tower kettle |
|---------------------|-----------|--------------|
| Temperature (°C)    | 73        | 91           |
3.3.3. Simulation Results and Analysis of Ethylene Acetate Refining Tower

The simulation of vinyl acetate refining tower is established, the results are shown in Table 5 below.

| Components        | Abbreviations | Tower top | Tower kettle |
|-------------------|---------------|-----------|--------------|
| Ethylene acetate  | VAC           | 0.9926    | 0.9997       |
| Acetic acid       | HAC           | 0.0000    | 0.0000       |
| Acetaldehyde      | C2H4O         | 0.0001    | 0.0000       |
| Butadiene         | CRALD         | 0.0000    | 0.0000       |
| Water             | H2O           | 0.0066    | 0.0002       |
| Acetic acid       | C4H6O3        | 0.0000    | 0.0000       |
| Acetone           | ACT           | 0.0006    | 0.0000       |
| Ethyl acetate     | C6H10O4       | 0.0000    | 0.0000       |
| Acetylene         | C2H2          | 0.0000    | 0.0000       |

It can be seen that the flow strands into the distillation column of vinyl acetate mainly contain vinyl acetate, as well as a small amount of water and acetaldehyde, and the acetaldehyde is mainly concentrated on the top of the tower. Because the tower kettle concentrates a part of the inhibitor, the product of vinyl acetate is selected to be extracted in the middle part of the tower. The quality fraction of vinyl acetate in the streamed strands produced in the side line is more than 99.9%.

3.3.4. Optimization of ethylene acetate refining tower

The influence of the Aspen Plus Sensitivity analysis on the side line extraction position on the side line product purity and tower reactor reboiler load was simulated under the condition of feed condition and the number of theoretical plates fixed, the simulation results are shown in figure 5 and figure 6.
Fig. 5 Relation diagram of extraction position and bottom reboiler

It can be seen from figure 5 that the purity of vinyl acetate increases with the extraction position closer to the tower kettle, but the purity of vinyl acetate decreases after the 32nd plate, because the tower kettle aggregates a certain amount of inhibitor impurities; acetaldehyde decreases rapidly with the downshift of the side line extraction position, and the content is basically 0 after the 14th plate. It can be seen from figure 6 that the heat load of the reboiler in the tower kettle increases with the downshift of the side line extraction position, considering the separation effect and energy saving, the side line extraction position is selected as the 30th plate.

In the case of feed condition, theoretical plate number and side line extraction position fixed, the extraction amount of side line extraction flow strands of vinyl acetate refining tower is simulated and analyzed on the purity of product flow strands. The simulation results are shown in Fig. 7.

Fig. 6 Relation diagram of extraction position and bottom reboiler

Fig. 7 Relationship between the yield of the side line and the purity of the product stream

It can be seen from Fig. 12 that with the gradual increase of the yield, the side line guesses that the mass fraction of the product in the flow strand first rises slowly, and after the yield reaches, the purity of vinyl acetate begins to decrease. If the output of the side line is too low, the output will be too low, and the purity of the product will be reduced if the output too large, so 59000 kg/h is the best choice.

4. Conclusions

By using Aspen Plus simulation software and selecting suitable model and physical property method, the main separation equipment in the purification process of vinyl acetate is simulated and optimized, and the simulation separation results are good and the product purity is high.
Based on the establishment of correct full-process simulation, the simulation optimization of Sensitivity analysis is carried out, and the optimal equipment parameters are finally determined as shown in Table 6.

| Table 6 Simulation and Optimization of Refining System Equipment |
|---------------------------------------------------------------|
| The number of theoretical plates (degassing tower) | Ethylene acetate refining tower |
| Reflux ratio | 6 | 39 |
| Feed board | 1 | 4 |
| Feed ratio of distillate (degassing tower) | 0.014 | 0.417 |
| The side line extraction position (degassing tower) | 30 |
| Side line extraction (degassing tower) | 59000 kg/h |

The product and recycled raw material quality fraction is shown in Table 7.

| Table 7 Quality fractions of products and recycled materials |
|-------------------------------------------------------------|
| recycled materials | Ethylene acetate | Acetic acid |
| Mass fraction (%) | 99.97 | 95.58 | 98.64 |

Through the simulation and optimization of the equipment in the refining and purification process of vinyl acetate, the optimal equipment parameters are determined, which meet the actual production requirements.

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