

# Research progress and optimization prospect of constant boiling distillation technology

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**Abstract.** Coboiling distillation is a special distillation method of separating the azeotropic system mixture, which is widely used in petroleum refining and chemical production. This paper reviewed the selection and characteristics of azeolizing agents, and introduced the research progress of home and abroad in detail. The system compares the advantages and disadvantages of the traditional constant boiling distillation and the new heat pump, compare the advantages, and presents the prospect of constant boiling distillation.

## 1 Introduction

Coboiling distillation is the mass transfer and heat transfer to separate the coboiling system mixture, which is commonly used in the actual chemical production, widely used in petroleum refining and chemical product refining. When there are two cozeolite in the components or system with close relative volatility, it is difficult to separate the ordinary distillation method. For such systems, a large return ratio must be set by the conventional distillation method, which increases the equipment cost and operation cost in the actual production process and the economy is reduced.

Cozeolite distillation is to add a third component with a low boiling point, called an azeolizing agent or binding agent, the new added component can form a low boiling point with one or two components of the original system, destroy the original boiling system, so that the dilemma separation component is effectively separated, the method becomes azeotropic (constant boiling) distillation<sup>[1-3]</sup>.

Cozeolite distillation is mainly suitable for the separation process of various organic compounds and hydrocarbon oxides. At present, there is more research on coboiling distillation technology in<sup>[4-6]</sup>, and the new heat pump and next tower technology are relatively reported. This paper summarizes the technical methods of traditional distillation process, new heat pump and heat pump, compares the advantages and disadvantages of the next process of new heat pump, obtains the advanced nature of the distillation, and provides theoretical reference and basis for the improvement of industrial production separation technology.

## 2 Brief introduction of cozeolite distillation

### 2.1 Selection of the azeolite

In the separation process of cozeolite distillation, the selection of azeolite agent plays a decisive role in the separation effect. The currently reported selection principles of coboiling agent<sup>[7-8]</sup> mainly include:

- (1) The selected azeolite should preferably be inhomogeneous to making the separation process simpler.
- (2) Cozeolite can significantly affect the vapor-liquid equilibrium relationship of the key components to be separated.
- (3) The cozeolite forms with at least one or two components in the original system, destroying the cozeolite system in the original component. The newly formed azeolite should be more than 10 °C lower than the coboiling point of the coboiling ite with the original component.
- (4) In the new formation of cozeolite, the lower the cozeolite content, can reduce the dosage and circulation.
- (5) The azeolizer shall have small latent heat for vaporation to save energy consumption, and the azeolizer should have excellent chemical properties, with the characteristics of cheap price, rich raw materials, good thermal stability and small corrosion ability, non-toxic and environmental protection.

### 2.2 Characteristics of azeobolite distillation

If ordinary distillation methods cannot meet the separation requirements, special distillation methods such as coboiling, extraction or variable pressure distillation can be used. Coboiling distillation has the following characteristics<sup>[9]</sup> relative to other separation methods:

- (1) The co-boiling distillation process is highly

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applicable and applicable for both continuous and intermittent operation.

(2) The boiling point of the azeotrope is high and must form a minimum azeotrope with the components in the original component system and the selection range is limited.

(3) entrainer is often steamed from the top of the tower, large energy consumption, only the content of azeotropic agent is small in the new azeotrope is more economical.

(4) The operating temperature of co-boiling distillation at fixed pressure is relatively low and more suitable for separating thermosensitive materials.

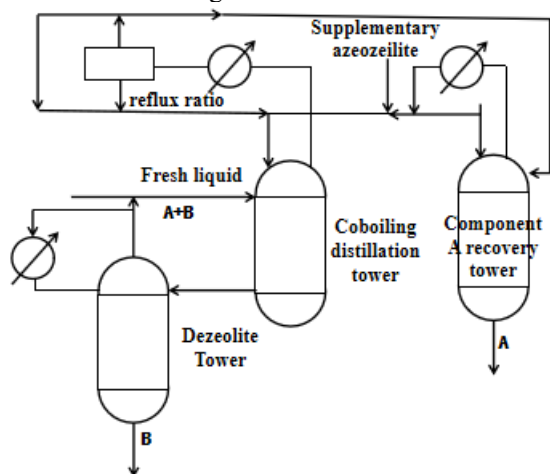
### 3. Progress in cozeolite distillation

#### 3.1 Progress of cozeolite distillation process

##### 3.1.1 process of co-boiling distillation

Yao<sup>[10]</sup> took the separation of A + B mixture as an example and introduced the process of azeolboiling distillation. A is volatile component, low boiling point and light key component; B is non-volatile component, high boiling point and heavy key component.

In the process of co-boiling distillation, the azeotrope is soluble in component A and forms the lowest azeotrope with A. Due to the low new co-boiling point, the top material is heterogeneous mixture, and one phase contains more A and enters the component A recovery tower for further refining; the other is a mixture of azeotrope and A (containing a small amount of A component), whose top backflow flows into the azeolboiling distillation tower. The specific flow chart of the co-boiling distillation process is shown in Figure 1.



**Figure 1** Distillation process with a two-component inhomogeneous azeotrope

From the above process flow chart, the fresh liquid mixture A and B enters the co-boiling distillation tower, the top extracts the co-boiling agent and the mixture of component A as reflux, the other part enters the component A recycling tower, which can finally be recovered at the bottom of the tower component A. The material of the co-boiling distillation tower enters the deazeolizer tower, where the top part of the B, tower returns,

and the other part is mixed with the fresh material liquid and added into the azeolite distillation tower. In order to maintain the concentration of the feed or reflux, the process is the distillation process of heterogeneous cozeolite. In the case of ternary azeolite, the azeolizing agent can be added with fresh material liquid, cycle the ternary component azeolite at the top of the deazeolite agent tower, the pure B component distilled at the bottom of the tower, the upper layer of azeolite reflux at the top of the main tower, and the lower phase rich in component A enters the component A recovery tower for refining.

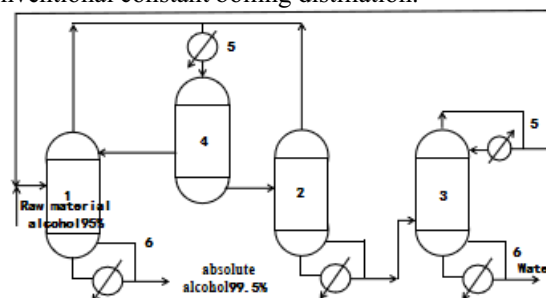
##### 3.1.2 Optimization direction of constant boiling distillation

The biggest defect of the separation process is the large energy consumption. Many new energy-saving processes have been developed to efficiently and fully utilize energy and save<sup>[11]</sup>. It includes thermal integration technology, is a kind of heat logistics heat to heat cold logistics, reduce utility heating as far as possible, achieve heat integration and full utilization; in addition, thermal coupling technology, by improving the internal structure of the distillation tower, form a more complex tower structure, reduce the operation cost and equipment investment cost. Common energy-saving processes mainly include heat pump distillation, multi-effect distillation and adjacent tower distillation. In addition, middle condensation, intermediate reboiling and side extraction are also an energy-saving process through the middle condensate is the middle heat exchange, change the operation line of the distillation section, evenly distribute the heat transfer driving force in the tower, reduce the irreversible degree of heat transfer process, keep the fluid in steady flow state, and improve the separation efficiency.

#### 3.2 Constant boiling distillation process

##### 3.2.1 Traditional constant-boiling distillation process

Zhu Liuliu<sup>[12]</sup> et al. produced 99.5% hydrless alcohol as an example, introduced the process of traditional constant boiling distillation process, Figure 2 is a process flow chart of production purity of 99.5% hydrless alcohol from conventional constant boiling distillation.



**Figure 2** Traditional constant boiling distillation process raw material alcohol

Because it is more difficult to produce anhydrous alcohol under normal pressure conditions, the traditional constant boiling distillation process adds the azeolite that can form the lowest azeolite with ethanol (such as pentane,

benzene), the zeolite can form ternary azeolite with water and ethanol, and the boiling point of the original solution, to produce high purity alcohol through 95% of the raw material alcohol.

The traditional constant boiling distillation method produces anhydrous alcohol after long development and improvement. The process has been mature and is widely used in anhydrous alcohol production enterprises. Its advantages lie in high product quality, large production, relatively stable production and relatively low operating cost, but its energy consumption compared with other advanced processes is the biggest problem, in addition, the azeoiling agent is high and may cause environmental pollution problems in the actual production.

### 3.2.2 New process of Alcohol by constant boiling distillation of heat pump

As a new energy-saving process, heat pump distillation is to pressure the steam on the top of the tower heat up operation, recycle the tower top steam condensation latent heat, this part of the heat as the heat source of the tower kettle reboiler, so as to reduce the tower bottom reboiler, to achieve the effect of energy saving and consumption reduction. Heat pump distillation has achieved good energy saving and consumption reduction effect in the separation of alkane and alcohol components. It has been studied to combine the heat pump technology with constant boiling distillation. This process is not only applicable to the difficult separation system, but also has a good energy saving effect. In the actual production, the system operates in the fully closed system, producing no harmful by-products, which is relatively environmental friendly.

Considering the small temperature difference of the dehydration tower under constant pressure (10-15 °C) Conditions for heat pump distillation. Liu Zongkuan et al. developed a new azeotropic distillation heat pump to produce anhydrous ethanol<sup>[13]</sup>. The ternary azeotrope on the top of the dehydrating tower (64.6 °C) is heated to about 100 °C directly through the heat pump, without the condensation process of the condenser. The energy produced by this process can be used as heat at the bottom of the dehydrating tower, eliminating a reboiler. After the separation of the condensate, the upper benzene-rich phase is used as the top reflux, and the lower water-rich phase flows into the entrainer recovery column. The ethanol and water mixture at the bottom of the recovery column flows into the alcohol recovery column for further refining. The cozeolite distilled at the top of the alcohol recovery tower does not undergo the condensation process at 78 °C, and is pressurized to the heat pump to 120 °C to provide heat to the alcohol recovery tower, once again saving a rezeiler and saving energy consumption. The list of process parameters of anhydrous ethanol developed by Liu Zongkuan et al.<sup>[13]</sup> is as follows:

**Table 1.** Process parameters of anhydrous ethanol produced by constant boiling distillation heat pump

name	numerical value
Temperature difference between tower top and tower kettle	13 °C
Alcohol dehydration tower top steam temperature	64.6 °C
Heat pump compressor heat up 1	100 °C
Alcohol recovery tower top vapor temperature	78 °C
Heat pump compressor heat up 2	120 °C
Alcohol recovery tower and kettle temperature	103 °C

Heat pump constant boiling distillation has many advantages. First of all, to meet the requirements of technical and economic indicators, the product anhydrous ethanol is not vaporized, the distillation tower does not need a large return ratio, reduce operating costs and equipment costs. In addition, through the combination of heat pump technology and constant boiling distillation, the tower top materials are not condensing, and the heat pump compressor can be used as the heat source of the tower kettle reboiler, reducing the use of the reboiler and meeting the requirements of energy saving and consumption reduction. Through this process product high yield and no toxic substances during operation, is a clean production process.

### 3.2.3 Technology of co-boiling distillation of heat pump

Next door tower distillation<sup>[14]</sup> is a higher separation requirements by improving the internal structure of the tower, and can also be combined with a heat pump to further reduce energy consumption. The next tower is divided into four parts, the feed first enters the pre-separation section, the A-B, B-C component mixture is separated in advance, the light component A-B enters the distillation section, the heavier B-C enters the distillation section, the lighter A component of the distillation tower is extracted from the top of the tower, the heavy C component is extracted from the tower kettle, the B component enters is the lateral extraction section, and the material is the more pure B component. Steam in the tower flows upward, the liquid phase flows downward, the gas and liquid of each tower plate are in the phase balance process, the operation is relatively stable, and the quality transfer heat transfer effect is good.

The process of the next tower of the heat pump is the intermediate heat exchange, which can achieve efficient separation of the ternary complex system, and expand the heat pump technology to the wide boiling series separation<sup>[15]</sup>. Constant boiling distillation of the adjacent tower is a typical example of heat-coupled distillation, improving the structure of the two distillation towers into one distillation tower.

Chen Mengqi<sup>[16]</sup> et al. have developed a new process

of co-boiling distillation of the next tower. The steam on the top of the main tower is compressed as the heat pump compressor heat source at the bottom of the tower, and conducts heat exchange with the tower kettle logistics. The feed and organic phase obtained from the phase divider enter the top of the main tower, the tower top pressure is set to 101.35KPa, the partition door top material enters the coboiler recovery tower, and the pressure is also set to 101.35KPa. The heat load of the tower in the coboiler recovery tower is 1208KW, temperature is 102 °C, and the final EDA purity reaches 99.7%. This process has high yield, high purity and energy saving, providing new ideas for the improvement of coboiling distillation process and useful reference for the next tower technology of heat pump and the combination of coboiling distillation process. The process parameters of heat pump co-boiling distillation next tower developed by Chen Mengqi<sup>[16]</sup> et al. are as follows:

**Table 2.** Process parameter value of adjacent tower with coboiling distillation of heat pump

name	numerical value
Number of main tower(MC)	71 boards
Main tower top pressure	1.013bar
Top pressure of the partition door	1.013bar
Heat load of coboiler recovery tower kettle reboiler	1207.6kW
Temperature of cozeolite recovery tower kettle	103 °C
Pressure of azeotropic agent recovery tower kettle	1.063bar
EDA Moore purity	99.7%

## 4 Conclusions

Distillation is an important separation and purification method in the chemical field. For some difficult separation or azeoliling systems, it can be efficiently separated by destroying the lowest azeolite system, and is widely used in chemical product refining. At present, there has been a substantial theoretical foundation in fluid mechanics, process control and gas-liquid heat and mass transfer of distillation tower. Modern chemical industry has put forward higher requirements for separation requirements, and separation technologies such as coboiling distillation are also constantly optimized and improved. Firstly, the research status of constant boiling distillation and tower distillation of the heat pump introduced the three processes in detail. Secondly, the advantages and disadvantages of the three processes are analyzed, highlighting the advantages of constant boiling distillation next to the heat pump, which not only realizes high purity, high yield, greatly reduces energy consumption, makes full use of steam energy, and has good heat transfer quality transfer effect, which is an effective combination of the

heat pump tower technology and constant boiling distillation. Finally, the development prospect of coboiling distillation process is looked forward and provides theoretical reference and design basis for the improvement of industrial production separation technology.

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