Energy-saving Technology in Steady-state Simulation of Ethylene Acetate Production Process Using Aspen Plus

Mei Jin¹, Bao Hu¹, Hongjiao Liu² and Linling Zou¹*

¹ School of Chemical and Environmental Engineering, Jianghan University, Wuhan, Hubei, 430056, China
² Institute of Intelligent Manufacturing, Jianghan University, Jianghan University, Wuhan, Hubei, 430056, China
*Corresponding author’s e-mail: linling.zou@jhun.edu.cn

Abstract. It is necessary to strengthen energy management in chemical and petrochemical industries because of the shortage of energy supply. Aspen Plus was used to simulate and optimize vinyl acetate production process via ethylene gas-phase method. The appropriate thermodynamic equations and unit modules were selected. The simulation and optimization results of vinyl acetate production were in accordance with the industrial production data. Based on steady-state simulation and optimization results, heat exchanger network synthesis and heat pump assisted distillation technology were proposed for energy conservation. For heat exchanger network synthesis technology, energy conservation can be achieved through the energy matching of cold and hot streams based on pinch theory. As a result, cold utilities, hot utilities, heat transfer area and the number of heat exchanger decreased by 25.52%, 59.52%, 70.60% and 30.77%, respectively. For heat pump assisted distillation technology, compared with the conventional distillation technology in the purification of acetic acid from aqueous acetic acid solution, 48.05% of cold energy consumption and 82.40% of heat energy consumption could be saved. Based on the simulation and optimization results, it can be found that heat exchanger network synthesis and optimization as well as heat pump assisted distillation technology can provide good ideas for the rational use of energy.

1. Introduction
Energy conservation is of vital importance to us because our society is facing energy shortage. Hence, it is urgent to adopt measures and methods of rational energy utilization with the technically feasible, economically reasonable, environmentally and socially affordable advantages. In typical chemical and petrochemical industries, energy conservation measures and methods mainly include the following aspects [1,2]. The first is to adopt new energy-saving technology and equipment such as high efficiency fractionation tower, the second is to use high energy efficiency equipment fitted with motor frequency conversion controller, the third is to make comprehensive use of different grades and different types of energy, and the fourth is to strengthen the concept of energy management, and so on. Among the above energy-saving measures and methods, the comprehensive utilization of energy, such as heat exchanger network synthesis and optimization technology or heat pump assisted distillation technology, is a common energy-saving solution for the existing process reconstruction. Heat exchanger network synthesis and optimization technology can effectively combine multiple energy sources in the process system, and heat pump assisted distillation technology provides reasonably use of different grades and types of energy.
Pinch method is a simple heat exchanger network synthesis method, it has been widely used in practical projects and achieved good results. Compared with the traditional heat utilization method, 30-50% energy consumption can be reduced when pinch technology is adopted in the new process design and the existing process reconstruction. Based on system engineering theory and thermodynamic analysis [3], Yao et al. proposed the process system energy integration technology to diagnose the utilization of energy to find out the bottleneck of system energy consumption, and then put forward the energy integration strategy to solve this bottleneck problem. Heat pump assisted distillation is a new type of heat integrated separation technology. The basic principle is to pressurize and heat the stream at the top of the distillation column, so that the stream can be used as the heat source of the reboiler at the bottom of the column, so as to recover the condensation latent heat of the steam at the top of the column, and finally achieve the purpose of reducing the energy consumption of cold and hot utilities [4,5]. These two energy-saving technologies are the important energy-saving technologies of the rational utilization of resources in process industry.

In this paper, the process of vinyl acetate production from ethylene gas phase method was taken as an example, and steady-state simulation and optimization of the process system were carried out by using Aspen Plus V9.0. Furthermore, two energy-saving technologies, the synthesis and optimization of heat exchanger network of the process system and heat pump assisted distillation technology, were proposed. The comparison results of energy consumption before and after the application of the energy-saving technology can provide good ideas for the rational use of energy.

2. Steady-state simulation and optimization of vinyl acetate production process

2.1. Vinyl acetate production process

Vinyl acetate is an important chemical raw material [6,7] which can be used as the raw material such as polyvinyl acetate, polynvinyl alcohol and copolymerization resin, and so on. Among many production processes of vinyl acetate, acetaldehyde acetic anhydride process and carbonylation process are not suitable for the large-scale production due to the high cost. Acetylene gas phase process has the
advantages for low investment and large-scale manufacture, but it is a pity that many by-products generated in the production process so that it is difficult to obtain the required purity for superior quality vinyl acetate product. Due to the advantages of less by-products production, high utilization ratio of raw materials, low environmental pollution, ethylene gas-phase process has a better development prospect [8,9]. The industrial production process of vinyl acetate by ethylene gas phase method comprises three sections, which are vinyl acetate production process (Section 1), vinyl acetate purification and acetic acid recovery process (Section 2) and ethylene gas recovery process (Section 3). According to the industrial production process, the simulation flow chart was drawn in Figure 1 using Aspen Plus V9.0.

2.2. Thermodynamic equations and unit modules selection
In vinyl acetate production process, Section 1 and Section 2 involve non-ideal liquid system, at the same time, acetic acid contained in these Sections which is prone to self-polymerization in the distillation process. Section 3 contains non-polar or less polar gas such as ethylene, oxygen, nitrogen, and so on. Considering the composition and property of the material contained in each Section, different thermodynamic equations were chosen in vinyl acetate production process. It is well known that NRTL activity coefficient equation is suitable for non-ideal liquid system, HOC coefficient equation can predict polymerization system, and PENG-ROB equation is usually used in non-polar or less polar gas system. Hence, NRTL-HOC mixed equation was adopted in the simulation of Section 1 and Section 2, and PENG-ROB equation was used in the simulation of Section 3.

The rationality of the simulation module is the key factor in consistency between the simulation results and the industrial operation data. During the simulation and optimization of vinyl acetate production, RPlug module and RStoic module were selected to simulate the reactor, DSTWU module and RadFrac module were chosen to simulate and optimize the distillation column, RadFrac module was used to simulate the absorption tower, Heater module and HeatX module were adopted to simulate heat exchanger, Flash, Decanter and Sep modules were used for simple separator, Pump and Compr modules were employed for fluid transportation, Mixer and Split modules were put to use for material mixing and splitting.

2.3. Steady-state simulation and optimization of vinyl acetate production process
Based on the industrial data of vinyl acetate production through ethylene gas phase method, steady-state simulation and optimization of the whole process were performed. During reaction simulation, the main reaction and the side reaction were separately simulated with different modules, which meant that RPlug module was adopted for the main reaction and RStoic module was used for the side reaction. The simulation results illustrated that the conversions per pass of ethylene, acetic acid and oxygen were 4.62%, 18.67% and 58.95%, respectively, and the selectivity of ethylene was 93.51%, which were in accordance with the industrial production data. It could be deduced that different reactor modules used to simulate the main reaction and the side reaction in vinyl acetate production were reasonable and feasible. Due to the low conversion per pass, the unreacted acetic acid and ethylene should be recycled in order to make full use of them, therefore Calculator module was used to calculate the amount of the addition of fresh raw materials in the whole process.

The simulation and optimization of the distillation column need to take the following steps. First, DSTWU module is used in the simulation of the simple calculation. Second, RADFRAC module is employed for the strict calculation based on the simple calculation results. Finally, the sensitivity analysis method is adopted to optimized the operation condition of the distillation column, such as total number of trays, location of the feed, recycle ratio R, and so on.

The material balance diagram of vinyl acetate production was drawn in Figure 2 when the production capacity of vinyl acetate was 100000 tons/year. The simulation and optimization results showed that vinyl acetate product contained 99.84 wt.% vinyl acetate, 0.09 wt.% methyl acetate, 0.01 wt.% ethyl acetate and 0.06 wt.% acrolein, which could meet the quality requirements for the superior ethylene acetate product. Meanwhile, the utilization rates of unreacted acetic acid and ethylene were 94.20% and 83.10%, respectively.
3. Application of heat exchange network synthesis and optimization energy-saving technology

In order to reclaim maximum system energy by means of pinch theory, Aspen Energy Analyzer 9.0 software was used to synthesize and optimize heat exchanger network in the production process of vinyl acetate.

According to the results of steady-state simulation and optimization results of vinyl acetate production process, cold streams and hot streams data in the process system were imported in energy analyzer of Aspen Energy Analyzer 9.0 software. Subsequently, the relationship between the total cost and the minimum heat transfer temperature difference ($\Delta T_{\text{min}}$) could be obtained which was shown in Figure 3. From Figure 3, when $\Delta T_{\text{min}}$ was 11 °C, the minimum total investment cost could be obtained. Meanwhile, the combination curve of hot streams and cold streams in the process system could be drawn in Figure 4. It could be seen that there were a lot of platforms in Figure 4, which indicated vaporization heat and condensation heat in the process system which were not effectively utilized.

On the basis of the influences of $\Delta T_{\text{min}}$, heat exchange area and economy of heat exchanger network, the preliminary design scheme of heat exchanger network synthesis shown in Figure 5 could be proposed, which contained 39 heat exchangers. In addition, there were many closed match loops in the preliminary heat exchanger network. In order to make full use of the heat of vaporization and the heat of condensation in the process, as well as to break the closed match loops, the preliminary design scheme of heat exchanger network should be optimized. It is well known that energy relaxation theory is commonly used in heat exchanger network optimization. Meanwhile, it should pay attention to the following aspects during the optimization of heat exchanger network. First, the heat capacity flow rate is not a constant value for materials involving change in phase state or composition during heat transfer. Second, there should be no heat exchanger loop in the optimized heat exchanger network. Third, it is necessary to simplify the streams with frequent heat exchange. According to the energy relaxation theory and the above points for attention, the optimized heat exchanger network could be obtained and was
exhibited in Figure 6. Furthermore, Table 1 showed the comparison results of the preliminary and the optimized heat exchanger network.

![Figure 5. Preliminary design of heat exchanger network.](image)

![Figure 6. Optimized design of heat exchanger network.](image)

### Table 1. Comparison of the preliminary and optimized heat exchanger network.

| Items                  | Preliminary Heat Exchanger Network | Optimized Heat Exchanger Network | Reduction % |
|------------------------|------------------------------------|---------------------------------|-------------|
| Cold utilities /kJ/h   | 2.480×10^8                        | 1.847×10^8                      | 25.52       |
| Hot utilities /kJ/h    | 1.063×10^8                        | 4.303×10^7                      | 59.52       |
| Total heat exchange area /m² | 34660                            | 10190                           | 70.60       |
| Number of heat exchanger | 39                               | 27                              | 30.77       |
| Total cost factor      | 0.2172                            | 0.1487                          | 31.54       |

It could be seen from Table 1 that the optimized heat exchanger network could provide a rational energy utilization of cold streams and hot streams. The cold and hot utilities could decrease by 25.52% and 59.52%, respectively. Meanwhile, the number of heat exchanger could decrease by 12.

#### 4. Application of heat pump assisted distillation energy-saving technology

In the production of vinyl acetate via ethylene gas phase method, the excessive use of acetic acid was involved in the reaction process and the absorption process. While, the excess acetic acid in the process
was ultimately present in the form of acetic acid-water mixed solution. In order to make full use of acetic acid, the conventional distillation method is adopted in industry to separate and purify the acetic acid-water mixed system and then recycled. Take into consideration that temperature difference between the top and the bottom of the distillation column is small, as well as the boiling points of acetic acid and water are close, overhead vapor phase direct compression heat pump assisted distillation technology could be proposed to separate acetic acid-water mixed system.

Figure 7 and Figure 8 illustrated the simulation diagrams of the conventional distillation technology and heat pump assisted distillation technology by using Aspen Plus V9.0 software. In heat pump assisted distillation technology (Figure 8), the stream on top of the column (H1) is heated after the adiabatic compression of the compressor (COMPR), and then used as the heat source of the reboiler (HEATX) for the vaporization of part of the bottom column liquid (C2), while the compressed gas (H2) itself condenses into liquid (H3). After the throttle valve (FSPLIT2), part of the condensate liquid is pumped out as the top distillate (WATER), and the other part used as reflux is returned to the top of the column (R1). In the simulation, besides the common modules of the distillation column, COMPR module was adopted for the compressor, VALVE module was employed for the throttle valve and FSPLIT were put to use for diverter.

Figure 7. Simulation diagram of the conventional distillation technology. Figure 8. Simulation diagram of heat pump assisted distillation technology.

The basic data of acetic acid-water mixed system was from steady-state simulation and optimization results. Feed (FEED) in Figure 6 and Figure 7 was a mixed system containing 3.29 wt.% water and 96.71 wt.% acetic acid. The purity of acetic acid used for recycling should be more than 99.9 wt.% whether adopted the conventional distillation technology or heat pump assisted distillation technology. When the production capacity of vinyl acetate was 100000 tons/year, energy consumption comparison results of the conventional distillation technology and heat pump assisted distillation technology was shown in Table 2.

Table 2. Energy consumption of the conventional distillation and heat pump assisted distillation.

| Items                        | Conventional distillation | Heat pump assisted distillation | Reduction% |
|------------------------------|----------------------------|---------------------------------|------------|
| Energy consumption of overhead cooling tower /MW | 15.42                      | 8.01                            | 48.05      |
| Heat consumption of tower bottom /MW       | 15.17                      | 2.69                            | 82.40      |
| Total energy consumption /MW          | 30.59                      | 10.70                           | 65.02      |

Compared with the conventional distillation technology, it could be seen from Table 3 that the cold energy consumption, the heat energy consumption and the comprehensive energy consumption were reduced by 48.05%, 82.40% and 65.02% in heat pump assisted distillation technology, respectively. It can be concluded that heat pump assisted distillation technology can reduce the heat consumption of the process system, which is one of the important energy-saving technologies.
5. Conclusions

Aspen Plus V9.0 software was used to simulate and optimize the whole process of vinyl acetate production by ethylene gas-phase method. The simulation and optimization results showed that the purity of ethylene acetate was 99.84 wt.% which could meet the quality requirements for the superior ethylene acetate product. Based on steady-state simulation and optimization results, two energy-saving technologies were proposed, which were heat exchanger network synthesis and heat pump assisted distillation technology. In the synthesis and optimization of heat exchanger network technology, the preliminary heat exchanger network could be obtained by using pinch theory and subsequently the optimized heat exchange network could be obtained based on the relaxation theory. Compared with the preliminary heat exchanger network, total cost factor, total heat exchange area and the number of heat exchanger were decreased by 31.54%, 70.60% and 12 in the optimized heat exchange network, respectively. In heat pump assisted distillation technology, due to the closer of the temperature difference between the top and the bottom of the distillation column for acetic acid-water mixed system, overhead vapor phase compression heat pump assisted distillation technology was used for separating acetic acid and water. Compared with the conventional distillation technology, the simulation result exhibited that heat pump assisted distillation technology could save 48.05% of the overhead cold energy consumption and 82.40% of the bottom heat energy consumption. Heat exchanger network synthesis and heat pump assisted distillation technology effectively save the energy consumption of the process system, which can provide a good idea for the rational use of energy.

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