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RAPID COMMUNICATION

Purification of R-12 for refrigerant reclamation using existing industrial-scale batch distillation: design, optimization, simulation, and experimental studies

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Abstract−Many design variables and constraints, such as operating temperature and pressure of existing batch distillation or operating temperature of existing cooling and heating media, must be verified and satisfied during design and optimization when an existing batch distillation column is utilized for new mixture. The convergence of batch distillation simulation is sensitive with the initial values of these variables. Thus, a new systematic methodology was proposed to design and optimize separation of a new mixture using an existing batch column. The systematic methodology was based on an industrial case study of dichlorodifluoromethane (R-12) reclamation from a waste refrigerant mixture. Based on a comparison of the Pxy diagram with experimental data, "REFerence fluid PROPerties" was selected as the thermodynamic model. After design and optimization using shortcut and rigorous methodologies, the existing batch distillation unit was operated to validate the proposed methodology. The experimented performance match well with the simulated results. Under the optimized operating condition, complete purification of R-12 (purity=99.5%) was achieved experimentally after 28.3 h. The advantages and disadvantages of the proposed methodology were then discussed.

Keywords: Batch Distillation, Design, Experiment, Refrigerant Reclamation, R-12, Separation

INTRODUCTION

Hydrochlorofluorocarbons (HCFCs) are chemicals that are mainly used as refrigerants. $CHClF_2$ (R-22), an HCFC refrigerant, is often used in air-conditioning equipment. In addition, chlorofluorocarbons (CFCs) containing only carbon (C), chlorine (Cl), and fluorine (F) with dichlorodifluoromethane CCl_2F_2 (R-12) are also employed as refrigerants. Because HCFCs and CFCs contribute to the ozone depletion in the upper atmosphere, they are replaced with other products such as hydrofluorocarbons (HFCs) (e.g., $C_2H_2F_4$ or R-134a) [1-5]. However, these refrigerants are still widely used in the industry, and an imbalance wherein demand is higher than supply still exists. This issue can be overcome by collecting waste refrigerants, purifying them, and supplying them to the industry.

Refrigerant reclamation is carried out to process used refrigerant gas, which has previously been used in cooling loops, to meet purity specifications and achieve new refrigerant gas before re-entering the market. Reclamation allows the re-use of existing refrigerants, thereby minimizing the environmental impact of used refrigerants and avoiding the need to manufacture new refrigerants [5,6]. This process contributes to the prevention of ozone depletion and global warming. One of the main challenges in refrigerant reclamation is to separate and purify refrigerant mixtures because CFCs often form azeotropic mixtures with fluorocarbons [5,7].

Various techniques have been developed to facilitate the separation of azeotropic mixtures, including the use of various zeolites and molecular sieves [7-11]. However, these techniques have not been entirely satisfactory because the components of these azeotropic mixtures often have similar boiling points, thereby making it difficult to separate highly pure components. In addition, prior art zeolite/molecular sieve processes need frequent changing and/or regeneration of the zeolite material or molecular sieves, thus requiring that the separation process be stopped for a period of time.

Batch distillation, which is preferable to continuous distillation when small quantities need to be separated, can be considered [12-15]. The most outstanding feature of batch distillation is its flexibility, which allows overcoming the uncertainties of feedstock or product specification [16]. The design and optimization of batch distillation columns have received significant research attention [12,13,17-19].

PROBLEM STATEMENT

There are uncertainties of feedstock or product specification in real operation. Furthermore, many new feed mixtures appear which need to be separated and purified in an existing plant during operation. One of main concerns when utilizing an existing batch distillation column for separating and purifying new mixtures is the design and optimization of the operating conditions. There are many design variables, such as operating pressure, overhead tem-

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perature and collector level or generator level, that are needed for designing. The convergence of batch distillation simulation is sensitive to the initial values of these variables. A convergence failure often occurs in batch distillation simulation when unsuitable initial value of overhead temperature and collector level or reboiler level are input to Aspen Batch Modeler. Moreover, many constraints, such as operating temperature and pressure of existing batch distillation or operating temperature of existing cooling and heating media, must be verified and satisfied during design and optimization. Furthermore, hydraulics or flooding is required to be verified during design and optimization. Therefore, there is clearly an urgent need for an easy, convenient and efficient rigorous approach for designing and optimizing the separation in an existing batch distillation.

In this work, an existing batch distillation unit was proposed for reclaiming R-12 from a waste refrigerant. As mentioned above, there are many design variables and constraints to be considered and satisfied when using an existing batch distillation unit for separating new mixtures. In addition, the operation mode used in this study is under neither variable reflux nor constant reflux condition. Thus, a new systematic methodology was proposed for the design and optimization of an existing batch distillation unit. A real batch distillation operation was conducted to validate the proposed systematic methodology and separation feasibility. The advantages and disadvantages of the proposed methodology were then discussed.

PROPOSED SYSTEMATIC METHODOLOGY

As mentioned above, an unsuitable initial value of overhead temperature and collector level or reboiler level can cause convergence failure when simulating the batch column. The new methodology should supply good initial values of operating pressure, overhead temperature and collector level or reboiler level, which can overcome convergence failure during batch distillation simulation. Meanwhile, in many cases, simulation of a continuous column is much easier and convenient while taking shorter time as compared to that of batch distillation. The above information is required for the preliminary design and simulation of batch distillation under the operating mode in OunR2tech.

Fig. 1 shows the systematic methodology of the design and optimization of separation carried out using an existing batch distillation unit. As the first step, a literature survey on the availability of components in Hysys, boiling point temperatures, Pxy, Txy, azeotropes, and existing separation methodologies was carried out for target separation. If the results indicate that distillation can be used, shortcut simulation and rigorous methodologies are then conducted to check the feasibility of separation using an existing batch column because the minimum number of stages of the batch column, which is identical to the rectifying section of a continuous column, can be estimated. Aspen Hysys V10 was employed to find a suitable property package for simulating the refrigerant mixture as well as simulate a shortcut column and a rigorous column. Furthermore, operating conditions as well as good initial values including overhead temperature, density of liquid in collector or reboiler, collector level or reboiler level can be predicted for simulating the batch column in Aspen Batch Modeler. The liquid level or the amount in the collector or reboiler can be optimized in the step of continuous distillation simulation. In the next step, the batch column with existing number of trays, optimized operating reflux, and vapor loading policies was simulated before the experiment through industrial batch distillation. The simulation and experimental data must be compared to validate the systematic methodology proposed for target separation using the existing batch distillation.

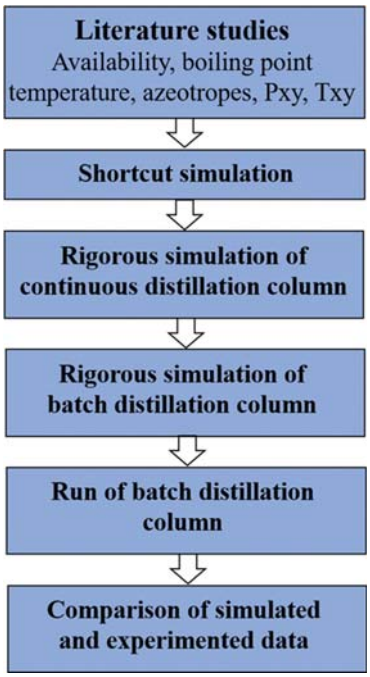

Fig. 1. Systematic procedure of batch distillation design.

RESULTS AND DISCUSSION

1. Thermodynamic Model

The literature data [20] for the Pxy equilibrium phase diagram were compared with the simulation result using REFerence fluid PROPerties (REFPROP). As shown in Fig. 2, the Pxy curves closely match the experimental data. Thus, REFPROP was selected as the property package for the prediction of the vapor-liquid equilibrium and for all simulations in this study.

A mixture of R-12 (boiling point −29.8 °C) and R-134a (boiling point −26.3 °C) is an azeotrope with composition of around 60 mass% R-12 and azeotropic temperature of approximately −34.5 °C. Although it is easier to separate at 1 atm (1.013 bar), the temperature is too low to use a cheap cooling medium, as shown in Fig. 3. Thus, the column should be operated at a higher operating pressure. The column pressure was selected such that the existing heating and cooling media in the company can work. Thus, a pressure of 8 bar was chosen in this study. The minimum-boiling azeotrope at 8 bar contains 52 wt% R-12 at 24.2 °C.

2. Shortcut Simulation of Continuous Distillation

After removing contaminants such as oil and water, the feed (91.31 wt% R-12 and 8.69 wt% R-134a) was pumped into the gen-

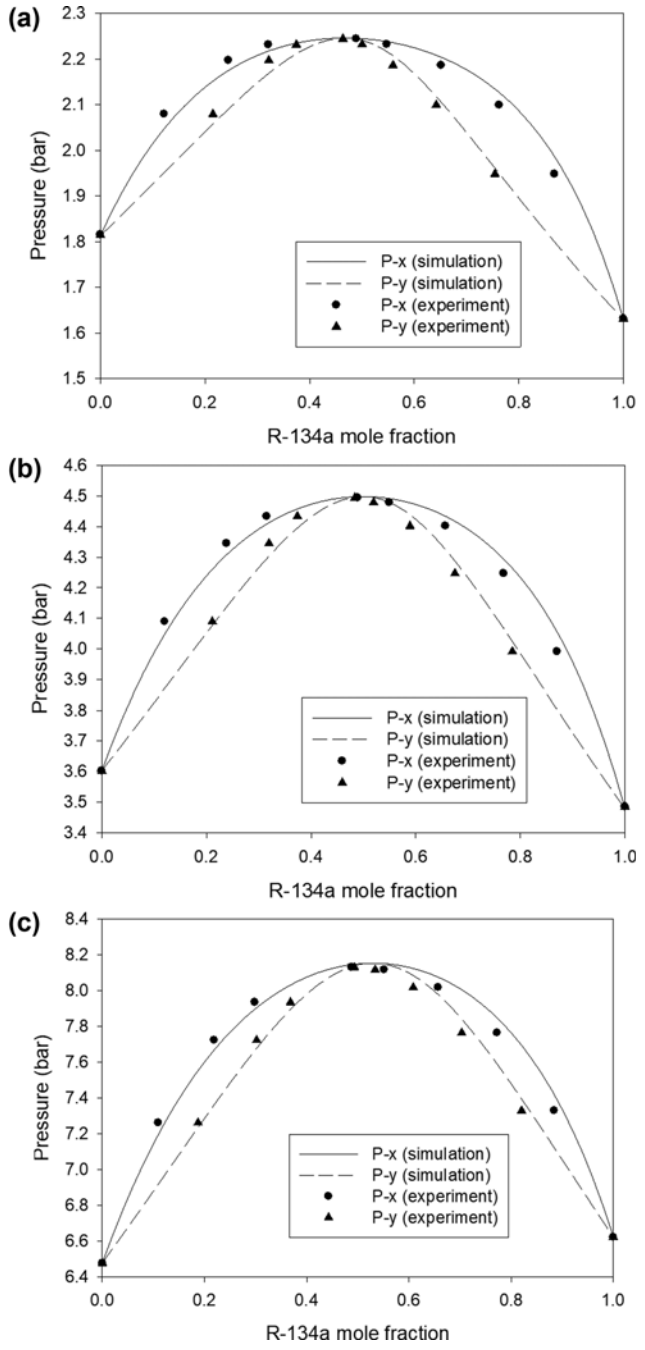

Fig. 2. R-134a+R-12 vapor-liquid equilibrium phase diagrams compared with literature values at (a) −15 °C; (b) 5 °C; and (c) 25 °C.

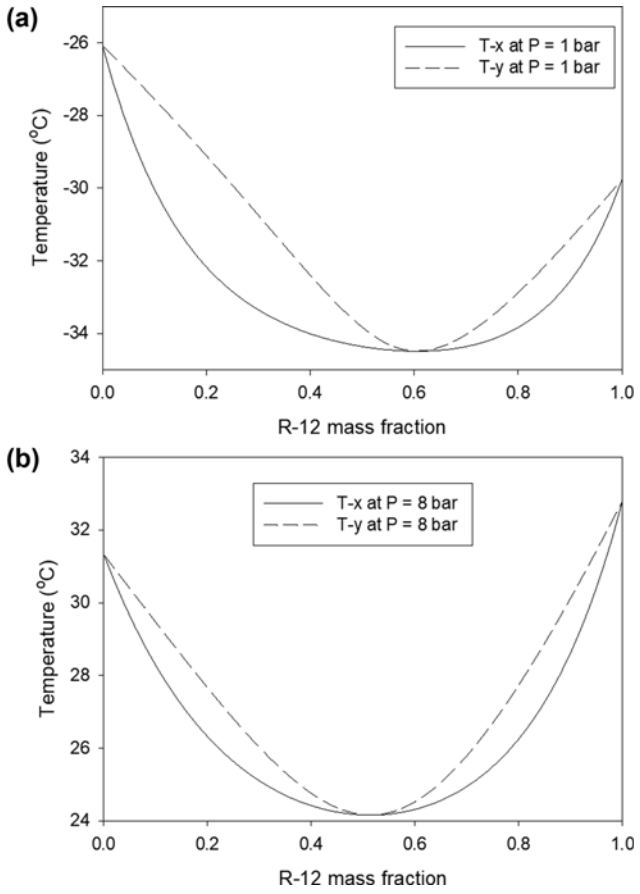

Fig. 3. Temperature vs. composition plot at (a) 1 bar and (b) 8 bar.

erator (or the reboiler) of batch distillation (as shown in Fig. 4). The required product purity was 99.5 wt% R-12 in the generator, while the collector contained the mass amount of substances approaching azeotropic composition of R-12 and R-134a that had to be removed. For the design and optimization of batch distillation, a shortcut simulation of a continuous column was first carried out. Through this simulation, initial operating conditions of continuous distillation could be determined, which were then used to design the batch distillation. Because a suitable flow rate is required in the shortcut and rigorous simulation of a continuous distillation, instead of mass amount as in batch distillation, a flow rate of 1,280 kg/h was used for the simulation. Light key in bottom of 0.0059 satisfied the mass fraction of R-12 (0.995) in bottom. The reflux flow ratio (R) was expressed as $R=1.2\ R_{min}$.

3. Rigorous Simulation of Continuous Distillation

Continuous distillation was then rigorously simulated using the initial operating conditions from the results of the shortcut simulation. From the rigorous simulation of the continuous distillation, information needed to simulate batch distillation could be obtained. This operating information included top and bottom temperatures, mass amount of substances that must be removed to obtain the target purity of the main product, and density of removed substances. Based on the information of mass amount and density, the collector level could be determined.

In particular, the temperatures in the top and bottom sections (from rigorous simulation) were 24.7 °C and 33.5 °C. The temperature in the top section was used to simulate the batch distillation. Furthermore, the distillate flowrate, which was equivalent to the mass amount of substances that must be removed, was then optimized. Fig. 5 shows the effect of distillate flowrate on reboiler duty and R-12 recovery. R-12 purity of 99.5% was kept constant in all cases for fair comparison. The values 320 kg/h in distillate or 320 kg in collector, which could balance the reboiler duty and recovery of R-12 (larger than 80%), were selected. The density of

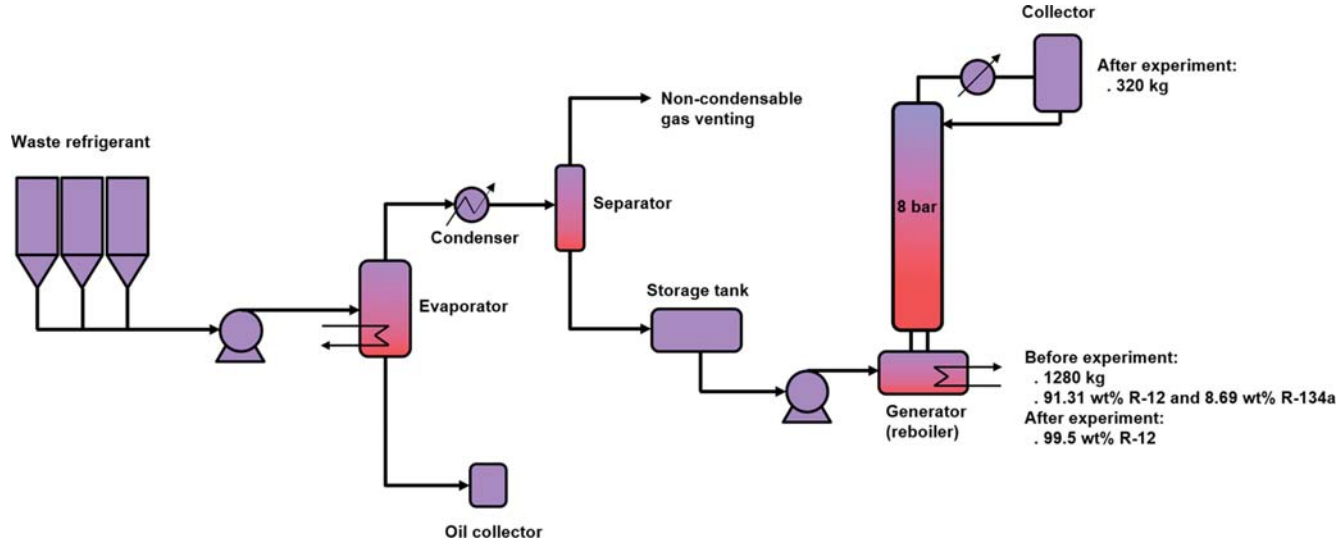

Fig. 4. R-12 reclamation process.

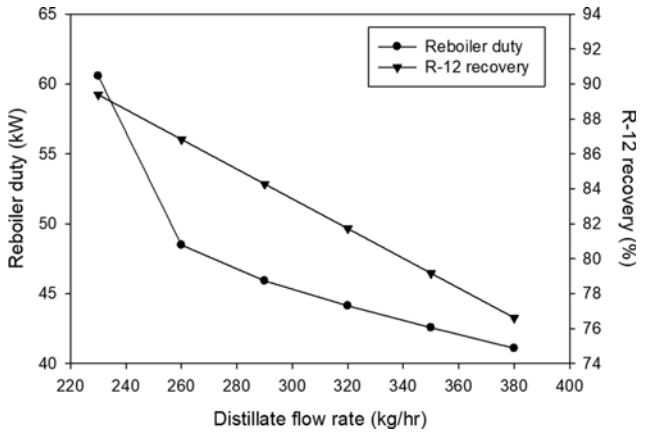

Fig. 5. Effect of distillate flow rate on reboiler duty and R-12 recovery.

this amount was 1,242 kg/m^3. Thus, the volume of liquid in collector was 0.2576 m^3, which was equivalent to the height of liquid in collector, 0.407 m. This value was used to set the collector level controller.

Note that the minimum number of stages of the batch column, which was identical to the rectifying section of a continuous column, was 7. This means that the batch distillation could be used in this specific separation since the number of trays of this batch column was 8.

4. Rigorous Simulation of Batch Distillation

The batch distillation was then simulated using Aspen Batch Modeler. The existing batch distillation included the following reflux operating and vapor loading policies.

a. Reflux operating policy

- No reflux is noted in the first period (approximately 4-5 h). In this period, no distillate product is observed. All vapor is contained in the collector after being condensed.
- When the collector height is 0.407 m, which depends on an individual case as estimated above, the reflux pump starts to run. The main degrees of freedom in this protocol include the collector level or collector holdup. This is determined in rigorous simulation of continuous distillation step.
- The collector level is controlled; therefore, the vapor flow rate in the top is equal to the reflux flow rate.

b. Vapor loading policy

- Notably, another variable in batch distillation is the vapor loading in the reboiler.
- The reboiler heat input is typically set at or near its highest capacity without flooding the column and is held constant throughout the batch processing time [12]. Thus, the maximum value of reboiler duty (5 kW) is used and kept constant during operation (shown in Table 1).
- With increase in time, the more volatile components in the distillation material are reduced and its flowrate decreases because the reboiler duty is kept constant. This process is continued until the desired specifications for the residue in the reboiler are satisfied.

Table 1. Hydraulics, energy performance, and product specifications of existing industrial-scale batch distillation columns

Tray type	Packing
Packing type	Wire gauze structure packing
Bed height (mm)	2,668
Column diameter (mm)	102
Energy requirement of reboiler (kW)	5
	Purity (mass%)
R-12	99.5

5. Batch Distillation Run

The industrial-scale batch distillation unit with wire gauze structure packing from Hanbal Masstech company (shown in Fig. 6) constructed at the OunR2tech Company was used to purify R-12 from waste refrigerant mixture. Before starting batch distillation, the column and collector were prepared under vacuum and the

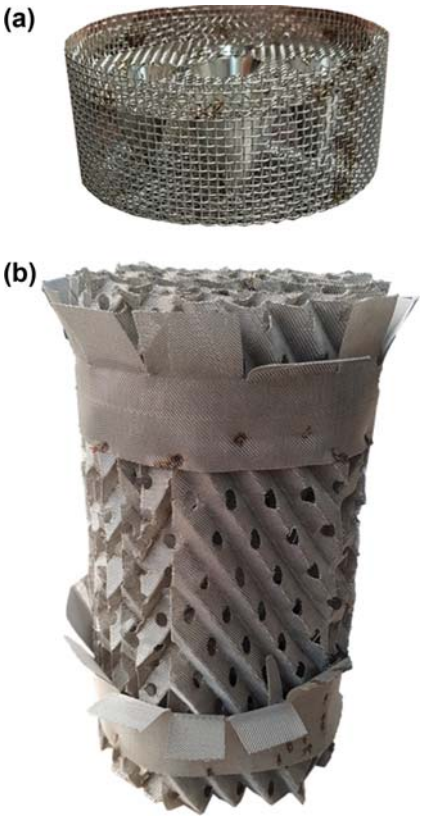

Fig. 6. (a) Liquid distributor and (b) Hanbal's structured packing.

generator was charged (1,280 kg liquid at ambient temperature (18 °C), 4 bar). Thereafter, the system was started by opening the valve in the vapor line on the regenerator and switching on the pumps for cold and hot water. In the beginning, the heat transfer rate was high because the temperature difference between generator liquid and hot water was high and the liquid started to boil. The concentration of the more volatile components and volume of liquid decreased. The column was filled with the liquid hold-up.

During the run, the generator temperature increased as the concentration of the more volatile components decreased. Notably, the cold and hot water available in company were at 13 °C and 48 °C The purity of R-12 of all samples of the generator was analyzed by gas chromatography. After the target purity of R-12 in the generator was achieved, the batch distillation was stopped and all remaining components inside the column and collector were removed. Thereafter, the column and collector were regenerated under vacuum before a subsequent batch was started.

6. Comparison between Simulation and Experimental Results

Experimental variation in the generator composition and the temperatures in the reboiler with the operation time were compared with simulation results afforded by Aspen Batch Modeler software. Fig. 7 displays the variation in the composition of R-12 and Fig. 8 shows the temperature variation in the reboiler. Excellent agreement is observed between the two data sets. Herein, 28.3 h was required in real operation to achieve to achieve 99.5% R-12, which closely matches with simulated operation time (28.7 h). Under these operating conditions (from Aspen Batch Modeler), the flooding was 84.7%.

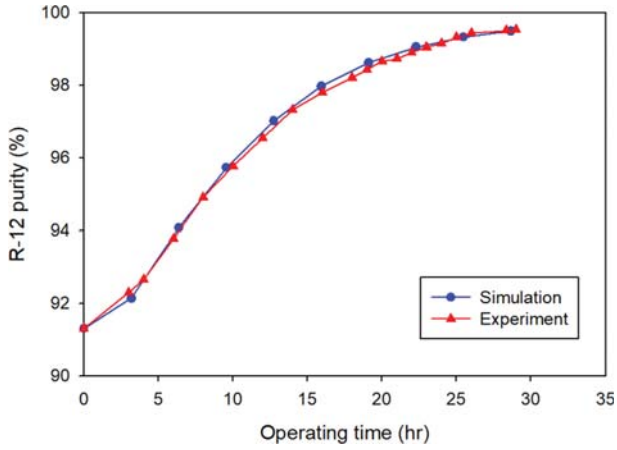

Fig. 7. R-12 composition purity history.

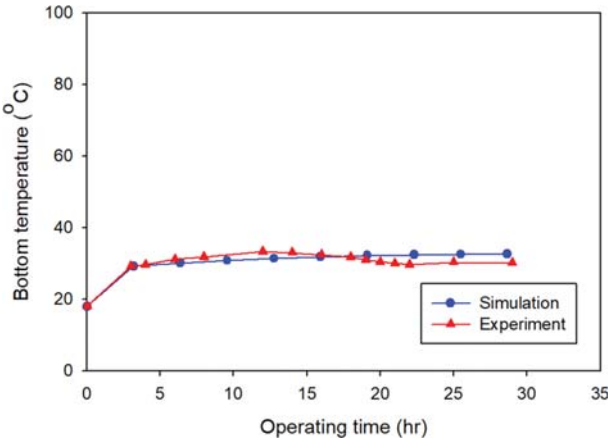

Fig. 8. Bottom temperature history.

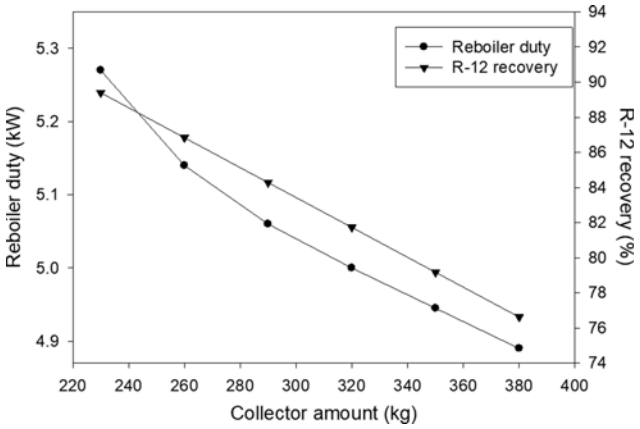

Fig. 9. Effect of collector amount on reboiler duty and R-12 recovery.

The collector amount, which was equivalent to the mass amount of substances that must be removed or the loss of main product R-12, was then considered in sensitive study. Fig. 9 shows the effect of collector amount on reboiler duty and R-12 recovery. Note that all cases have the same simulated operation time (28.7 h). The

result in Fig. 9 is not used for batch distillation operation. It is only used for comparing the trend of distillate rate's effect on reboiler duty and R-12 recovery in continuous distillation shown in Fig. 5. As can be seen clearly, this effect is quite similar to the effect of distillation rate on reboiler duty and R-12 recovery in continuous distillation case. Because the capacity of continuous distillation and batch distillation are different, the reboiler duty between continuous distillation and batch distillation is different. In particular, the capacity of batch distillation is 1,280 kg/batch, while that of continuous is 1,280 kg/hr. Because simulation of a continuous column is easier and more convenient while taking shorter time as compared to that of batch distillation in many cases and especially in this case, it is recommended that the results from continuous column simulation can be used for the design and optimization of separation in an existing batch distillation. The simplicity and effectiveness during designing and optimizing the operating conditions of existing batch distillation to separate new mixtures can be achieved by using the proposed methodology.

However, compared to other methodologies this one has more steps. Furthermore, simulation of a continuous column can only predict good initial values of operating pressure, overhead temperature and collector level or reboiler level, while it cannot predict the reboiler duty or operation time of batch operation. Thus, rigorous simulation of a batch distillation column is still needed.

CONCLUSIONS

A simple and effective batch distillation method was proposed for refrigerant reclamation in this work. The proposed design and optimization methodology, tested through the study of a current industrial case including difficult separation of R-12 and R-134a, showed its simplicity and effectiveness. The new methodology supplies good initial values of operating pressure, overhead temperature and collector level or reboiler level, which can overcome the unconvergence problem during simulation. Simulation and experimental results demonstrated that it was possible to obtain high-purity R-12 in the generator by using an existing batch distillation unit. Experimental results in a commercial batch distillation column were in good agreement with the simulation results. Under the optimized operating conditions, complete purification of R-12 (purity=99.5%) was achieved experimentally after 28.3 h.

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