Experiment and optimization of a large scale xenon/krypton cryogenic distillation system

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Abstract. A highly efficient cryogenic distillation system has been designed, developed and assessed to remove radioactive krypton-85 ($^{85}$Kr) from xenon (Xe), which is commonly used as a valuable medium for dark matter detectors. By using the self-designed distillation system, the concentration of krypton (Kr) in a commercial xenon product can be reduced from $10^{-9}$ to $10^{-12}$ mol/mol with 99% xenon collection efficiency at maximum flow rate of 5 kg/h. Over 1000 kg of xenon has been purified and employed as the detection medium in project Panda X, the first dark matter detector developed in China. In this present paper, detailed process simulation was conducted to refine the working parameters and to define the optimum operating conditions for the cryogenic distillation system. The predicted results were compared with those of experimental data obtained from the distillation system. The influence of comprehensive factors was investigated. Simultaneously, a dynamic model for the cryogenic distillation system was established to provide an in depth analysis of the dynamic characteristics of the system.

1. Introduction

Liquid xenon is known to be one of the most attractive mediums for use in dark matter detectors in the field of astroparticle and particle physics [1]-[4]. The advantages of xenon include a large light yield comparable to that of NaI (TI), low energy threshold, high energy resolution and a low $\gamma$ and $\beta$-ray background from uranium and thorium due to self-shielding. Moreover, xenon has no long-lived radioactive isotopes.

The concentrations of xenon and krypton in air are in the range of $\sim 10^{-7}$ mol/mol and $\sim 10^{-6}$ mol/mol, respectively. Commercially available xenon is distillated from air, but is contaminated with $^{85}$Kr. The isotope $^{85}$Kr is a radioactive nucleus which decays into rubidium-85 with a half-life of 10.76 years and emits $\beta$-rays with a maximum energy of 687 keV with a 99.57% branching ratio. The concentration of $^{85}$Kr in air is about 1Bq/m\textsuperscript{3} [5],[6], corresponding to a $^{85}$Kr / Xe $\sim 10^{-11}$ mol/mol ratio. Ideally in dark matter detectors, the concentration of krypton in liquid xenon should be less than $10^{-12}$ mol/mol. In other words, the concentration of $^{85}$Kr should be less than $10^{-23}$ mol/mol. Only in this way can the liquid xenon meet the accuracy requirement of dark matter detection experiments [7].
The Panda X detector is a gas-liquid two-phase xenon Time Projection Chamber (TPC) operated at cryogenic temperatures for direct searches of the dark matter WIMPs (Weakly Interacting Massive Particle). This dark matter detector is located at the China JinPing Deep Underground Laboratory in Sichuan province, P.R. China [8],[9]. To ensure a high sensitivity to WIMPs, large mass detectors are required. The amount of liquid xenon planned for use in the Panda X project is at least one ton. Therefore, a highly productive purification system is required for removing $^{85}$Kr.

Distillation and adsorption are widely used in the gas industry to remove krypton from xenon. The development of adsorption-based chromatography to decrease the concentration of Kr has been reported [10]. However, the capacity for Kr removal is limited using this technique and thus not suitable for the current Panda X situation. The distillation tower developed by Abe K, et. al [1] is the first device that can remove Kr from Xe to the level of $10^{-12}$ mol/mol. Unfortunately, the processing speed of this system (Xe 0.6kg/h) is not sufficient to provide the tons of clean Xe needed for the Panda X detector.

A highly efficient cryogenic distillation system has been designed and developed to remove Kr from commercially available Xe ($\text{Kr}/\text{Xe} \sim 10^{-6}$mol/mol). The purpose of the system is to decrease the concentration of Kr by three orders of magnitude, with 99% Xe collection efficiency (i.e., the amount of rejected Xe is only 1%) at a flow rate of 5kg/h. Considering the complicity of the experimental device and the ultrahigh purity requirements of the purified xenon, it is important to simulate and optimize the cryogenic distillation system including the operation parameters and technological process. Using the ultrahigh purity xenon cryogenic distillation system, this reported study compared experimental results with those simulated results using the HYSYS database to optimize the system. Comprehensive system factors were studied including column pressure, feeding velocity, reflux ratio and boiling power to determine their impact on the product and system efficiency. Simultaneously, a dynamic model of this cryogenic distillation system was also established to study the dynamic characteristics of the system. The simulation is significant for optimizing the design and operation of the distillation system. The combination of these two approaches ensured improvement of that the efficiency of the distillation system and the purity of the purified xenon.

2. The developed cryogenic distillation system

The distillation tower was designed using the M-T (McCabe-Thiele) method [11]. There were six theoretical plates in the distillation tower. According to the geometric design, the height of the distillation tower was 2.1 m [12]. The purity of purified xenon is related to the height of the distillation tower, generally speaking, the higher the distillation tower, the purer the purified xenon. Therefore, the total height of the distillation tower was set at 4 m corresponding to twelve theoretical plates to guarantee the purity of the distilled xenon. The lengths of the rectifying section and stripping section of the distillation column were 1.9m and 2.1m, respectively. As a result, the feeding point of the distillation column was at the centre. The inner diameter of the distillation column was 0.08m. The flow diagram of the distillation column is shown in figure 1. The cryogenic distillation column was thermally insulated using high vacuum multilayer insulation and a vacuum was maintained at about 0.006Pa using a vacuum pump. The total heat leakage of the column was less than 6W. Stainless steel alloy 304 was used as the material of the distillation tower.

3. The developed cryogenic distillation system

3.1. Comparison of experimental and simulated results

The geometrical and operating parameters of the distillation column can be reasonably simulated by using HYSYS through twelve ideal stages [16]. With the simulated boundary conditions set to be equivalent to the experimental conditions, a comparison of experimental data [17] and simulated results are listed in Table 1.

As can be seen from Table 1, the simulated results are in reasonable agreement with the experimental data, which demonstrate that the simulated model corresponds well with the experimental method.
Table 1. Comparison of experimental data and simulated results

| Column parameter                                      | Experimental results | Simulated results |
|-------------------------------------------------------|----------------------|-------------------|
| Height of distillation column, m                       | 4                    | 4                 |
| Kr concentration in purified xenon, mol/mol           | $1 \times 10^{-12}$  | $3 \times 10^{-13}$ |
| Kr concentration in off xenon gas, mol/mol            | $3 \times 10^{-6}$   | $3 \times 10^{-6}$  |
| Heating power of re-boiler, W                         | 23                   | 25                |
| Cooling power of condenser, W                         | 120                  | 180               |
| Temperature of re-boiler, K                           | 179.8                | 180               |
| Pressure of re-boiler, kPa                            | 221                  | 221               |
| Feed flow, kg/h                                       | 2.5                  | 2.5               |
| Flow of off xenon gas, kg/h                           | 0.025                | 0.035             |
| Flow of purified xenon, kg/h                          | 2.475                | 2.465             |

1-Raw Xenon; 2-Getter; 3-Heat exchanger; 4-Cryocooler #1; 5-Off Gas; 6-Cryocooler #2; 7-Condenser; 8-Distillation column; 9-Liquid meter; 10-Re-boiler; 11-Heater; 12-Vacuum chamber; 13- Purified Xenon; 14-Pump port.

“Raw Xenon” indicates the inlet where natural Xenon is introduced; “Off Gas” indicates the outlet where the Xenon enriched with Krypton is collected; “Purified Xenon” indicates the outlet where the purified Xenon is collected.

Figure 1. Flow diagram of the distillation system.

3.2. Effect of different parameters of distillation system

3.2.1 Effect of feed flow

To study the relationship between the feed flow rate and Kr concentration in the purified xenon (heating power of re-boiler was 25W), the results from the HYSYS simulation are shown in figure 2. The Kr concentration of purified xenon is seen to be significantly influenced by the feed flow. The variation of Kr concentration is consistent with the rate of the feed flow, which means a higher Xe feed produces more Kr in the Xe product. When the value of feed flow is below 1.5kg/h, the ascending velocity of Xe gas is too low to get to the condenser, thus the distillation process is terminated.
3.2.2 Effect of feed temperature and feed pressure
The effect of feed temperature and feed pressure on the Kr concentration of the xenon product are shown in figures 3 (a) and 3 (b), respectively. The conditions for these results are a heating power in the reboiler of 25W and feed rate of 2.5kg/h. One can see from figure 3 that the higher the feed temperature and feed pressure, the higher the Kr concentration of purified xenon. However, these influences are relatively weak.

3.2.3 Effect of heating power of the reboiler
The Kr concentration of the purified xenon decreases with the increase of the input power to the reboiler when the Xe feed rate is set as 2.5kg/h, as shown in figure 4. This influence is pronounced even when the heating power of the re-boiler is low. Considering both the input energy and Kr concentration of purified xenon, it is found that the optimum input heating power of the re-boiler should be between 10W to 40W. Outside this range there is quite small effect of the heating power on the Kr concentration of the purified xenon.

3.2.4 Effect of pressure of the distillation tower
The effect of the pressure of the distillation tower on the Kr concentration of the purified xenon is also simulated when the heating power of re-boiler is set at 25W and the feed flow at 2.5kg/h. The results of the simulation are shown in figure 5. It can be seen that the Kr concentration of the purified xenon increases slowly when the pressure of the distillation tower increases. Consequently, it appears that the influence of the pressure of the distillation tower on the product quality is not obvious.
4. Uniform experimental design for optimization

A uniform experimental design method is developed to investigate the simultaneous effects of system operating parameters, such as the tower pressure, reflux ratio and feed flow [18],[19]. The ranges for the tower pressure, reflux ratio and feed flow are set at 210~240 kPa, 161~221, and 1~5kg/h, respectively. To get the optimized operating parameters, the stepwise regression method is used to analyze the simulation results. Considering there are interactions between the operating parameters, and the relation of them is non-linear, the form of the regression equation is multinomial:

\[
y = b_0 + \sum_{i=1}^{m} b_i x_i + \sum_{i=1}^{m} \sum_{j=1}^{m} b_{ij} x_i x_j + \sum_{i=1}^{m} b_{ii} x_i^2 \quad (T = C_m^2) \tag{1}
\]

\[
L_{ij} = \sum_{k=1}^{N} (x_{ik} - \bar{x}_i)(x_{jk} - \bar{x}_j) \quad i,j = 1,2,\cdots, m \tag{2}
\]

\[
L_{iy} = \sum_{k=1}^{N} (x_{ik} - \bar{x}_i)(y_k - \bar{y}) \quad i = 1,2,\cdots, m \tag{3}
\]

\[
L_{yy} = \sum_{k=1}^{N} (y_k - \bar{y})^2 \tag{4}
\]

\[
\bar{x}_i = \frac{1}{N} \sum_{k=1}^{N} x_{ik} \quad i = 1,2,\cdots, m \tag{5}
\]

\[
\bar{y} = \frac{1}{N} \sum_{k=1}^{N} y_k \tag{6}
\]

In which \(x_{ik}\) expresses the value of factor \(x_i\) at experiment \(k\), \(y_k\) expresses the corresponding value of \(y\) at experiment \(k\).

The coefficients of the regression equations can be determined by equation set (7):

\[
\begin{align*}
L_{11} b_1 + \cdots + L_{1m} b_m &= L_{1y} \\
L_{21} b_1 + \cdots + L_{2m} b_m &= L_{2y} \\
&\cdots \\
L_{m1} b_1 + \cdots + L_{mm} b_m &= L_{my} \\
b_0 &= \bar{y} - \sum_{k=1}^{N} b_i \bar{y}_i 
\end{align*} \tag{7}
\]
Calculation software SPSS and Matlab are used to analyse the simulation results (the product flow, Kr concentration of purified xenon and extraction efficiency), and the processes of optimizing calculation are shown as below:

1. Build a regression equation. The model of the regression equation chosen is based on Eq. (1).
2. Select variables preliminarily. Enter the values of pressure, reflux ratio, feed flow and the simulation results in the computer, then analyze the regression equation and select variables using backward elimination method [20], and eliminate the variables whose sigF > 0.10.
3. Optimized analysis. Optimize the regression equation using strong constraint programming: write a program by Matlab, and optimize the regression equation using BFGS quasi-Newton algorithms and least square method in the program.

Using the uniform experimental design based on the HYSYS simulation, the optimized operational conditions for the cryogenic distillation system are found to be: Feed flow rate: 2.5kg/h; Tower Pressure: 215kPa; Reflux ratio: 191.

5. Dynamic simulation of the distillation system
The total reflux is an important process in the distillation system. The Kr concentration of the purified xenon during distillation is directly related to the final Kr concentration in the re-boiler during the reflux process. Therefore, the Kr concentration during dynamic variations in the distillation tower at total reflux should be studied.

To accomplish this, the simulation model of the ultra-purity xenon cryogenic distillation system was built using Aspen Plus and inserted the calculation formula of the liquid retained in the packing into the model using a subroutine, then translated it into the Aspen Dynamic document.

In our laboratory and simulated experiments, the temperature of raw xenon was pre-cooled to 190K, the pressure of raw xenon was set at 215kPa, the value of the liquid level in the re-boiler was 10cm and the applied heating power in the re-boiler was set at 23W. Based on these operating conditions, the simulated and experimental results concerning the temperature and pressure at the top, middle and bottom of the distillation tower during the total reflux process are compared in figure 6a and 6b. In figure 6, the laboratory experimental data indicate that the distillation system attains an equilibrium state in 13 hours for the total reflux process. The final stabilized temperature and pressure of the condenser are 178.8K and 215kPa, respectively. The final stabilized temperature and pressure of re-boiler are 179.8K and 221kPa, respectively. In comparison, the simulated results show that the distillation system is stable in 10 hours for the total reflux process. In this case, the final stabilized temperature and pressure of condenser are 179K and 215kPa, respectively. The final stabilized temperature and pressure of re-boiler are 180K and 221kPa, respectively. The temperature and pressure in the laboratory experiment fluctuate in comparison to those in the simulation. However, the final stabilized results are basically the same between the two. This demonstrates that the simulated model accurately reflects the experimental apparatus.

![Figure 6](image)

**Figure 6.** Comparison of experimental and dynamic simulated temperature (a) and pressure (b) variations during the total reflux process
Figure 7. Variations of krypton concentration during the total reflux process.

The dynamic variation of Kr concentration of the distillation system at total reflux process is shown in figure 7. It can be seen that the off xenon gas in the condenser is stable within 10 hours and the final Kr concentration in the condenser is $3 \times 10^{-6}$ mol/mol. The purified xenon in the re-boiler is stable in 25 hours and the final Kr concentration in the re-boiler reaches $3 \times 10^{-13}$ mol/mol. The Kr concentration at the feed point stabilizes at $3 \times 10^{-9}$ mol/mol basically.

At steady state, the variables of the distillation process are constant. However, as the process unfolds, the operational parameters and process variables can change which will push the system out of equilibrium. Fluctuations of the process feed and xenon yield can affect the Kr concentration in the purified xenon. The dynamic response curves corresponding to the changes in process feed and product yield are shown in figure 8(a) and 8(b). The step-shaped lines termed Line 1 in figure 8 show the fluctuations of process feed and xenon yield. The amplitude of fluctuation is 12.5% of the designed value and the period of fluctuation is 4 hours. The effect of the fluctuations of the feed and yield on the Kr concentration of the product is weak with a Kr concentration in the purified xenon of between $3 \times 10^{-13}$ mol/mol and $7 \times 10^{-13}$ mol/mol. This result demonstrates that the robustness of the system.

Figure 8. Influence of the disturbances of input (a) and output (b).
6. Conclusion
A high efficiency cryogenic distillation system was designed and fabricated that can remove Kr from Xe to a concentration of $\sim 10^{-12}$ Kr/Xe [mol/mol]. The collection efficiency of the distillation system was 99% (indicating that the amount of rejected Xe was only 1%), and the process speed was 5 kg/h. The system yielded 1000 kg of purified xenon. Detailed simulations were conducted to obtain the optimum operating conditions for the distillation system. The effects of the operating parameters, such as column pressure, feed rate, reflux ratio and boiling thermal power on the product were studied. An optimized design for an experimental apparatus was achieved by combining the computer simulations with the uniform experimental testing. The simulation results are in good agreement with the experimental data. In addition, a dynamic model of the cryogenic distillation system was established to study the dynamic characteristics of the system. The results showed that the optimum operational conditions in the distillation column were given as followings: the boiling power is 25W; the column pressure is 215kPa and the reflux ratio is 191, respectively.

7. References
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