



## Carbon-13 Isotope Enrichment Process by CF<sub>4</sub> Distillation

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### 1. Introduction

The carbon stable isotope <sup>13</sup>C, which exists in nature at around 1%, is used as a raw material as a diagnostic agent in the urea breath test, a non-invasive test for *Helicobacter pylori*, which causes stomach cancer and other diseases<sup>1)</sup>. Demand for this test is growing in Asia, and it is estimated that the market is valued at several billions of yen.

We have developed the world's first separation technology for oxygen stable isotopes using oxygen distillation by applying the cryogenic air separation technology that we have cultivated for years, and have three separation units<sup>2,3,4)</sup>. We are the largest supplier of stable isotopes in Japan, and in order to increase self-manufactured isotope species, we have studied production units that apply this technology to <sup>13</sup>C separation.

One of the <sup>13</sup>C separation methods already in practical use is carbon monoxide distillation (hereinafter referred to as "CO distillation"). However, CO is flammable and toxic, which increases the cost of equipment for safety measures and legal compliance. Therefore, we examined carbon tetrafluoride distillation (hereinafter referred to as CF<sub>4</sub> distillation), which is a method of separating <sup>13</sup>C using inert gas.

This paper reports on a CF<sub>4</sub> distillation test we conducted to evaluate the <sup>13</sup>C separation performance, and a enrichment process we designed.

### 2. Carbon isotope <sup>13</sup>C distillation separation technology

Apart from the CO distillation method, methane distillation (hereinafter referred to as CH<sub>4</sub> distillation) is another <sup>13</sup>C separation method that has been put to practical use in the past (Table 1).

The CO distillation method has the advantage of having a higher separation factor than other distillation methods, but has disadvantages such as flammability and toxicity. The CH<sub>4</sub> distillation method is not toxic, but requires

similar safety measures because CH<sub>4</sub> is a flammable gas. On the other hand, we consider that by using the CF<sub>4</sub> distillation method, it is possible to build a very safe production unit at low cost compared to other methods because CF<sub>4</sub> is an inert gas. However, data on separation factors are scarce, and experimental data were available only for CF<sub>4</sub> at 90 K. Therefore, we conducted a distillation test under actual operating pressure to obtain separation factors.

Table 1 Comparison of <sup>13</sup>C separation method by isotope distillation

Material	CO	CH <sub>4</sub>	CF <sub>4</sub>
Standard boiling point	82 K	112 K	145 K
Separation factor	1.0068 at 82 K <sup>5)</sup> ( <sup>12</sup> C <sup>16</sup> O- <sup>13</sup> C <sup>16</sup> O)	1.0028 at 118 K <sup>6)</sup> ( <sup>12</sup> CH <sub>4</sub> - <sup>13</sup> CH <sub>4</sub> )	1.0045 at 90 K <sup>7)</sup> ( <sup>13</sup> CF <sub>4</sub> - <sup>12</sup> CF <sub>4</sub> )
Handling	Flammable Toxic	Flammable	Inert
*GWP	-	25	7,390

\*GWP: Global Warming Potential

### 3. Distillation test

We conducted the distillation test in our own distillation test equipment. The equipment consists of a distillation column, a reboiler, and a condenser in a vacuum-insulated vessel. Figure 1 shows a flow diagram of the equipment. The test fluid was high-purity CF<sub>4</sub> gas produced by Taiyo Nippon Sanso JFP, which was liquefied by the condenser, stored in the reboiler, and operated at a total reflux condition with the top pressure set at 20 kPaG. An electric heater was used as the heat source for the reboiler, and liquefied nitrogen was used as the condenser cold source. We measured isotopic composition using a mass

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spectrometer by sampling gas from the top and bottom of the column at intervals of 6 to 12 hours after the start of the experiment until the  $^{13}\text{C}$  concentrations at the top and bottom of the column became constant.

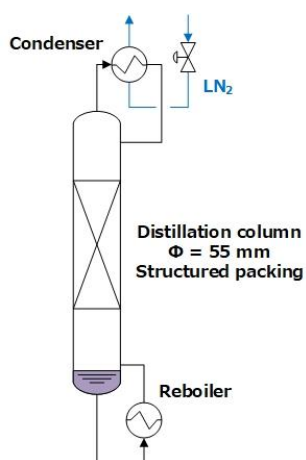


Figure 1 Flowsheet of  $\text{CF}_4$  distillation test

Figure 2 shows the transition of  $^{13}\text{CF}_4$  enrichment at the bottom and at the top of the column obtained in the experiment. The plotted value at time 0 h was obtained from the isotopic composition of high-purity  $\text{CF}_4$  gas measured in advance using a mass spectrometer. The concentration distribution in the column reached a steady state at about 24 h with the concentration of  $^{13}\text{CF}_4$  at the top of the column of 1.0 to 1.1%. Based on the actual performance of height equivalent of one theoretical plate in the air system of the regular packing used, the calculated separation factor was  $\alpha(^{13}\text{CF}_4/^{12}\text{CF}_4) = 1.0047$ . Although this is smaller than the separation factor of  $\text{CO}$ , it was determined to be sufficiently separable, and a two-component distillation calculation program of  $\text{CF}_4$  isotopologue was constructed based on the above results.

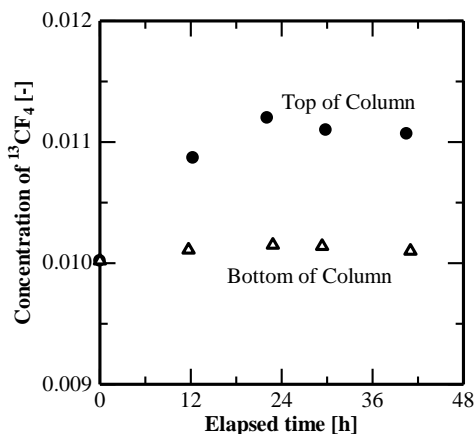


Figure 2 Transition of  $^{13}\text{CF}_4$  enrichment

## 4. Basic design of the process

### 4.1 Process calculation

We studied a  $^{13}\text{C}$  enrichment process using a two-component distillation calculation program. The flow rate of  $\text{CF}_4$  gas as the raw material was set to  $4 \text{ Nm}^3/\text{h}$ , the product specification was set to an isotopic concentration of  $>99 \text{ atom}\% \text{-}^{13}\text{C}$ , and the volume of the product was set to  $200 \text{ kg/y-}^{13}\text{C}$ . The product isotopic concentration is the same as that of commonly distributed  $^{13}\text{C}$  products. The height of each distillation column was determined based on experiences of oxygen stable isotope separation units.

In isotope distillation separation units, when the isotope natural abundance to be enriched is small, a quantity of waste gas almost equal to the amount of feed gas is generated. As shown in Table 1,  $\text{CF}_4$  has a large GWP value and its release is unfavorable. Therefore, in order to reduce the amount of raw material feed, we provided recovery sections to establish a process with a  $^{13}\text{C}$  yield of 90%. If a process with a  $^{13}\text{C}$  yield of 30% was used without recovery sections, the amount of both feed and waste  $\text{CF}_4$  gas would be approximately three times higher.

As a result of process calculation, the enrichment process consists of 17 distillation columns in total for the recovery and enrichment sections. Figure 3 shows the isotopic composition distribution in the distillation columns.

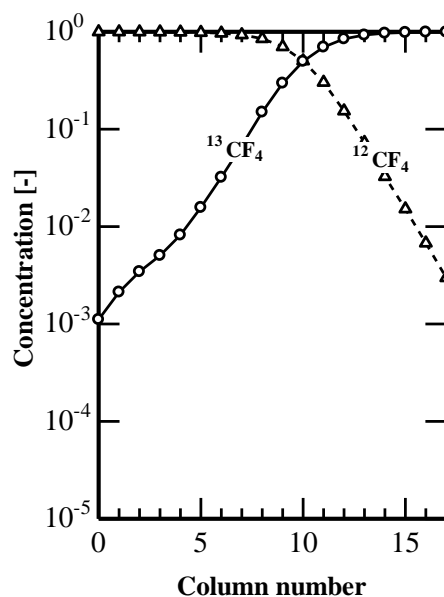
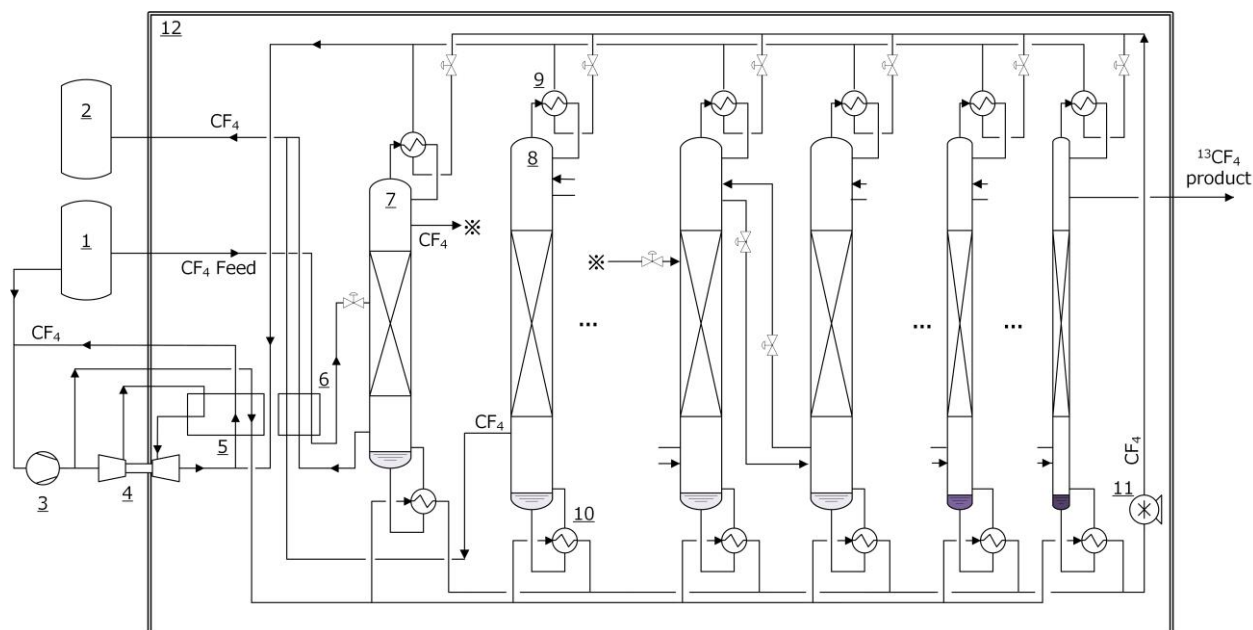


Figure 3 Concentration profile of isotopic carbon tetrafluoride



- |   |   |                                       |
|---|---|---------------------------------------|
| 1: CF <sub>4</sub> feed tank                      | 2: CF <sub>4</sub> reserver tank                | 3: CF <sub>4</sub> recycle compressor |
| 4: Expansion turbine                              | 5: Heat exchanger 1                             | 6: Heat exchanger 2                   |
| 7: Ultra pure CF <sub>4</sub> distillation column | 8: CF <sub>4</sub> isotope distillation columns | 9: Condensers                         |
| 10: Reboilers                                     | 11: Liquid CF <sub>4</sub> pump                 | 12: Cold box                          |

Figure 4 Flowsheet of the CF<sub>4</sub> isotope distillation unit

The concentration of <sup>12</sup>CF<sub>4</sub> in the first column is about 99.9% because of the high yield process. If necessary, <sup>12</sup>C products (<sup>12</sup>C > 99.998%) can be produced by adding small diameter distillation columns.

#### 4.2 Process specifications

Figure 4 shows an flow example of a <sup>13</sup>C production unit with CF<sub>4</sub> distillation examined based on the basic design described above. The basic configuration is the same as that of the oxygen stable isotope separation unit<sup>3)</sup>. The difference is that the fluid used in the circulation system is CF<sub>4</sub> instead of N<sub>2</sub> because the boiling points of N<sub>2</sub> and CF<sub>4</sub> differ significantly. For this circulation system, a leak-tight compressor needs to be selected. In addition, the ultra-pure CF<sub>4</sub> distillation column is required to be designed according to the purity of the feed gas. The product is formed as <sup>13</sup>CF<sub>4</sub> gas, but this unit can also supply <sup>13</sup>CO gas, for example, which is the main supply form of <sup>13</sup>C at present, by introducing equipment to convert the gas type.

#### 4.3 Important point of the process

For the realization of this process, it is necessary not to release waste CF<sub>4</sub> gas emitted from the isotope production

unit into the atmosphere. This is because of the large GWP value of CF<sub>4</sub> as mentioned above. Although the isotopic composition of this waste CF<sub>4</sub> gas is different from that of natural CF<sub>4</sub>, it is an ultra-high purity CF<sub>4</sub> gas and can be used in the semiconductor industry. For example, this plant can be installed adjacent to an existing CF<sub>4</sub> production facility (Figure 4 shows both the CF<sub>4</sub> gas supply source and collection point as tanks as an example). In this case, it is possible to purify and isotopically enrich the CF<sub>4</sub> gas supplied from the existing facility as raw material, and return the waste gas to the production facility in a state of enhanced purity. Another method to avoid emission of CF<sub>4</sub> gas is to recycle the CF<sub>4</sub> gas, although it increases the operating cost. Since the waste gas has a reduced <sup>13</sup>C concentration, it cannot be fed again as a raw material. However, by restoring the <sup>13</sup>C concentration in CF<sub>4</sub> gas to the same level as the natural abundance, through isotope exchange reaction with another carbon source, it can be used as a raw material again. We have already developed the above method and its patent is pending<sup>8)</sup>.

## 5. Conclusion

We devised and examined a carbon stable isotope  $^{13}\text{C}$  enrichment process by  $\text{CF}_4$  distillation<sup>9)</sup>. We conducted a  $\text{CF}_4$  distillation test, and calculated the separation factor of the  $\text{CF}_4$  isotope based on data acquired from a test. Using this result, we performed the distillation process calculation and completed the basic design of a very safe  $^{13}\text{C}$  enrichment process on the scale of a commercial plant.

We are the largest supplier of stable isotopes in Japan, and we are working to increase the variety of isotopes that we treat, and to provide stable isotopes at a lower cost. We will continue to develop new isotope separation processes such as the one presented in this paper.

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