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SHORT COMMUNICATION

Modeling and Simulation of Sulfur Hexafluoride (SF_6) Purification Process

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Abstract–Liquid sulfur hexafluoride (SF_6) contains carbon tetrachloride (CF_4) and air as main impurities. It is very difficult to remove these impurities by using a catalyst column or an adsorption column. In this work a new purification method for SF_6 mixture based on batch distillation is proposed. Experimental study showed good purification performance, where SF_6N50 was obtained from SF_6N30 feed. In the modeling of the batch purification process of SF_6 mixture, the K-value was calculated based on the regular solution theory and a short cut method was employed. Results of simulations showed good agreement with those of experiments.

Key words: Sulfur Hexafluoride, Batch Distillation, Purification, Regular Solution Theory

INTRODUCTION

Sulfur hexafluoride (SF_6) was first prepared by H. Mossian in 1902 and commercial production of SF_6 was initiated by Allied-Signal Inc., U.S.A., in 1948. The basic properties of SF_6 at 25 °C and 1 atm are summarized in Table 1 [Marshall, 1976; Takaiki, 1976; Grant, 1995]. SF_6 is a colorless, odorless and tasteless gas that is neither flammable nor particularly reactive. Its high chemical stability and excellent electrical characteristics have led to widespread uses in various electrical and electronic devices and medical applications.

For the synthesis of SF_6, HF is first electrolyzed to give F_2 that is reacted with melted sulfur or sulfur vapor to give SF_6:

$$2HF \rightarrow H_2 + F_2 \quad (1)$$

$$3F_2 + S \rightarrow SF_6 \quad (2)$$

Sulfur tetrafluoride (SF_4) and disulfur decafluoride (S_2F_{10}) can be produced as byproducts from reaction (2). To inhibit the generation of these byproducts the optimal operating conditions should be identified and applied. In order to prevent the reaction of S_2F_{10} with water and alkali solution, S_2F_{10} should be decomposed into SF_4 and SF_6 by pyrolysis:

$$S_2F_{10} \rightarrow SF_4 + SF_6 \quad (3)$$

The resultant SF_4 can be removed by alkali washing:

$$SF_4 + 6NaOH \rightarrow NaSO_3 + 4NaF + 3H_2O \quad (4)$$

The gas free from acid components is subject to drying followed by dehydration and deodorization. Finally liquified sulfur hexafluoride is obtained through separation from noncondensable gas components. Traces of air, CF_4, H_2O and HF are included in the liquified SF_6 as impurities.

As the estimation model for thermodynamic equilibrium, we used the activity coefficient method which described behavior of highly nonideal liquid mixtures at low pressure very well. The activity coefficient scheme is composed of two methods: molecular method considering attraction among molecular and group contribution method considering attraction among groups. The UNIFAC method, which is one of the group contribution methods [Gmehling et al., 1982, 1993], is reliable and fast in the prediction of liquid phase activity coefficients in nonelectrolyte and nonpolymeric mixtures at low to moderate pressures and temperatures between 300 K and 425 K. However, the method is difficult to use in the low temperature range and we employed Regular solution theory [Prausnitz and Shair, 1961; Prausnitz, 1986; Walas, 1985] which estimated the activity coefficients of each species in a binary liquid mixture from the knowledge of the pure component molar volumes, the mole (or volume) fractions and the solubility parameters (or internal energy changes on vaporization) of each species. To model the batch purification process proposed, we employed a short cut method [Distefano, 1969; Luyben, 1990; Diwekar, 1994]. The primary objective of the present study is to achieve production of SF_6 with N50 (99.999%) from the feed containing air and CF_4 as the main impurities.

Table 1. The basic properties of SF_6 (25 °C, 1 atm)

Property		Value
Molecular weight		146.054
Sublimation point (°C)		−63.9
Triple point (°C)		−50.52
Critical pressure (Mpa)		3.759
Critical temperature (°C)		45.55
Density (g/cm^3)	Solid (−195.2 °C)	2.863
	Liquid	1.336
	Gas	6.0886×10^{-3}
Heat of vaporization (KJ/mole)		9.6419
$\Delta\delta$ (J/cm^3)$^{1/2}$		8.0946

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EXPERIMENTS

Fig. 1 shows a schematic of the batch distillation apparatus

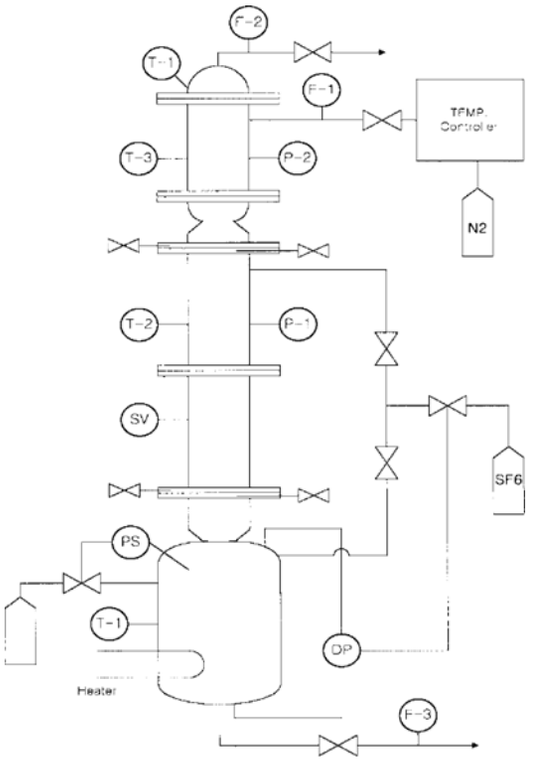

Fig. 1. Schematic diagram of batch distillation unit.

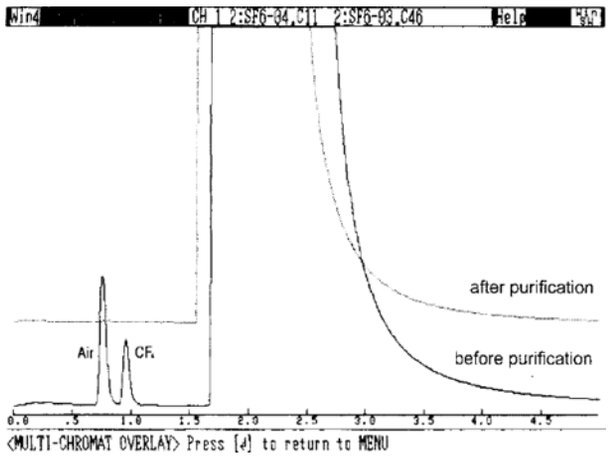

Fig. 2. Changes of concentrations before and after purification.

used in the purification experiment of SF_6 mixture. The distillation column with inside diameter of 108.3 mm was packed with IMPT (Intalox Metal Tower Packing) and consisted of three typical sections with 1,200 mm spacing each. The capacity of the vessel designed was approximately 48 *l*. A differential pressure gauge was installed to identify the amount of SF_6 feed. The maximum liquid head pressure of the vessel was computed to give a full range of differential pressure gauge as 1,000 mmAq. An electric heater was installed at one-fifth of the vessel height so as to vaporize liquid feed mixture. The heater is of the form of a coil for proper distribution of heat and is equipped with sealed gasket to prevent possible leak. To prevent excessive temperature drop due to freezing of SF_6 in tubes, the entrance of the condenser was designed to have the form of a vapor belt. Liquid N_2 was used as a coolant and temperatures of vent gas and the liquid N_2 were detected by thermocouples installed at the upper and lower positions of the condenser. The experiments were performed at −30 °C and 5 bar and helium gas was used to maintain the pressure level. The liquid SF_6 feed was fed into the still pot and vaporized by the heater mentioned before. The SF_6 vapor is liquified at the condenser by liquid N_2 and is recovered at the still pot. The low-boiling point components (air, CF_4) are removed from the top of the column. Samples from the still pot were analyzed by gas chromatography and the heater was off (i.e., distillation operation was stopped) when the target purity of N50 (99.999%) was achieved. Table 2 shows conditions of the gas chromatography used in these work and Fig. 2 shows an example of the analysis. We can see that impurities are almost completely removed.

Table 2. Conditions of gas chromatography

Column:	Porapak-N, 2 M
Column temperature:	80 °C
Detector temperature:	150 °C
Carrier gas:	He, 30 ml/min
Current:	100 mA
Sample flow:	30 ml/min
STD gas:	27.9 ppm N_2, 44.0 ppm O_2, 100 ppm CF_4/SF_6 Bal.

MODELING OF THE PURIFICATION PROCESS

1. Basic Equations

The basic structure of the purification process can be represented as shown in Fig. 3. Equimolal overflow and constant relative volatility is assumed. The basic mathematical model consists essentially of material balances around the main sections of the column shown in Fig. 3, i.e., the still pot, an arbitrary packed section and the reflux drum together with the equilibrium relationships and other equations of state.

For the still pot in the column we have

$$\frac{dM_B}{dt} = -D \tag{5}$$

$$\frac{d(M_B x_{i,B})}{dt} = Rx_{i,1} - Vy_{i,B} \tag{6}$$

which can be rearranged as

$$\frac{dx_{i,B}}{dt} = \frac{(Rx_{i,1} - Vy_{i,B}) - x_{i,B}\frac{dM_B}{dt}}{M_B} \tag{7}$$

where

$$y_{i,B} = \frac{\alpha_i x_{i,B}}{\sum_{k=1}^{m} \alpha_k x_{k,B}} \tag{8}$$

For an arbitrary packed section n ($1 \le n \le N-1$) in the column we have

$$M_n \frac{d(x_{i,n})}{dt} = R(x_{i,n+1} - x_{i,n}) + V(y_{i,n-1} - y_{i,n}) \tag{9}$$

where

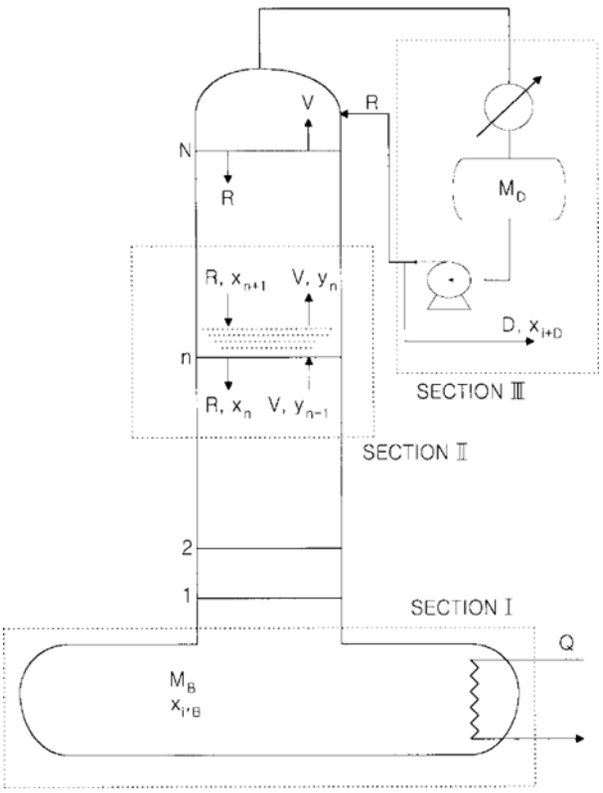

Fig. 3. Schematic of the experimental apparatus.

$$y_{i,n}=\frac{\alpha_i x_{i,n}}{\sum_{k=1}^{m}\alpha_k x_{k,n}} \tag{10}$$

At the top section (n=N) we can write

$$M_N\frac{d(x_{i,N})}{dt}=R(x_{i,D}-x_{i,N})+V(y_{i,N-1}-y_{i,N}) \tag{11}$$

where

$$y_{i,N}=\frac{\alpha_i x_{i,N}}{\sum_{k=1}^{m}\alpha_k x_{k,N}} \tag{12}$$

For the reflux drum in the column we have

$$M_D\frac{d(x_{i,D})}{dt}=Vy_{i,N}-(R+D)x_{i,D} \tag{13}$$

where

$$R=V-D \tag{14}$$

2. Estimation of K-value

We can consider two-step isothermal solution processes when gas is dissolved in a liquid solvent:

$$\Delta G=\Delta G_I+\Delta G_{II} \tag{15}$$

$$\Delta G_I=RT\ln\frac{f^L_{pure2}}{f^G_2} \tag{16}$$

$$\Delta G_{II}=RT\ln\gamma_2 x_2 \tag{17}$$

where f^L_{pure2} is the fugacity of the hypothetical pure liquid solute and γ_2 is the symmetrically normalized activity coefficient of the solute referred to the hypothetical pure liquid ($\gamma_2\rightarrow 1$ as $x_2\rightarrow 1$).

In the first step, the gas isothermally "condenses" to a hypothetical state with the same volume as the liquid. In the second step, the hypothetical liquid-like fluid is dissolved in the liquid solvent. Since the solute in the liquid solution is in equilibrium with the gas at the fugacity f^G_2, we have

$$\Delta G=0 \tag{18}$$

The activity coefficient for the gaseous solute can be obtained from

$$RT\ln\gamma_2=\upsilon^L_2(\delta_1-\delta_2)^2\phi_1^2 \tag{19}$$

Substitution of Eqs. (15), (16), (17) and (19) into Eq. (18) gives

$$\frac{1}{x_2}=\frac{f^L_{pure2}}{f^G_2}\exp\left[\frac{\upsilon^L_2(\delta_1-\delta_2)^2\phi_1^2}{RT}\right] \tag{20}$$

The above equation requires three parameters for the gaseous component: the pure liquid fugacity, the liquid volume and the solubility parameter. These parameters depend on the temperature but, at constant composition, the theory of regular solutions permits

$$\ln\gamma\propto\frac{1}{T} \tag{21}$$

From this fact, we can see that the quantity $\upsilon^L_2(\delta_1-\delta_2)^2\phi_1^2$ is not dependent upon temperature. As a result, any convenient temperature may be used for υ^L_2 and δ_2 provided that the same temperature is also used for υ^L_1 and δ_1 (For convenience, 25 °C is normally used). However, the fugacity of the hypothetical liquid must be treated as a function of temperature. Rearrangement of (20) gives

$$x_2=\frac{f^G_2}{f^L_{pure2}}\exp\left[\frac{\upsilon^L_2(\delta_1-\delta_2)^2\phi_1^2}{RT}\right] \tag{22}$$

where

$f^G_2\doteq y_2P$ (P: total pressure $\doteq$ vapor pressure of SF_6),

$$\log P(atm)=4.3571-\frac{889.85}{T(K)}\quad(-50.8\,^\circ C\text{-}45.6\,^\circ C) \tag{23}$$

Normally x_2 is so small that Φ_1 is estimated as one. f^L_{pure2} is available from the relation given by Prausnitz & Shair as

$$\ln(f^L_{pure2}/P_{C2})=7.81-\frac{8.06}{T_r}-2.94\ln T_r\quad(0.7\le T_r\le 2.5) \tag{24}$$

The K-values (K) is given by the rearrangement of (22) as

$$K=\frac{y_2}{x_2}=\frac{f^L_{pure2}\gamma}{P} \tag{25}$$

where

$$\gamma=\exp\left[\frac{\upsilon^L_2(\delta_1-\delta_2)^2}{RT}\right] \tag{26}$$

Results of application of (25) are summarized in Table 3. All γ's are greater or equal to 1, which means that the solution shows positive deviations from ideal solution behavior as predicted from the regular solution theory.

RESULTS AND DISCUSSION

The difference in the phase equilibrium between the model and

Table 3. Computation of K-values of air, CF_4 and SF_6

	T (K)	f^L_{pure2}	Y	K
N_2(0.7809)	243.15	185.17	1.13	41.60
O_2(0.2094)	243.15	195.18	1.00	38.67
Ar (0.0093)	243.15	198.82	1.25	49.19
CO_2(0.0004)	243.15	14.71	1.62	4.71
Air	-	-	-	41.05
CF_4	243.15	40.12	1.93	15.37
SF_6	243.15	5.30	1.00	1.05

Table 4. Conditions for numerical simulations

Feed:	320 mole
Feed composition:	0.99976 (SF_6)/0.00014 (Air)/0.00010 (CF_4)
Vapor flow rate:	160 mole/hr
Vent flow rate:	25 mole/hr
Hold up (stage):	0.25 mole
Hold up (reflux drum):	2.5 mole

the experiments seems to be caused by the mass transfer due to the difference of compositions. To include the effects of mass transfer, K-values were compensated for by using vaporization efficiency (E) as

$$E=\frac{y_2}{\gamma K^{cal} x_2} \tag{27}$$

$$K^{real}=\frac{y_2}{x_2}=E\gamma K^{cal} \tag{28}$$

Fig. 4 shows changes of the concentration of sulfur hexafluoride in the still pot and reflux drum with respect to time. The experimental batch column is operated at very low temperature (around −30 °C) and strict insulation is required to prevent any heat loss. Even a slight perturbation in flows during operations might cause severe experimental errors. For this reason it was almost impossible to install a sampling hole around the column itself. We took samples at the still pot and at the condenser outlet. It is our opinion that more sampling might deteriorate the experimental results. In the still pot, we can see slow increase in the concentration of SF_6. But, in the reflux drum, air and CF_4 dissolved in the SF_6 mixture

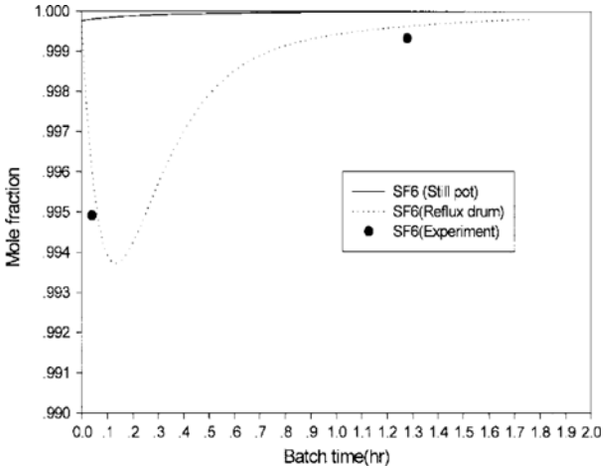

Fig. 4. Change of SF_6 content with time.

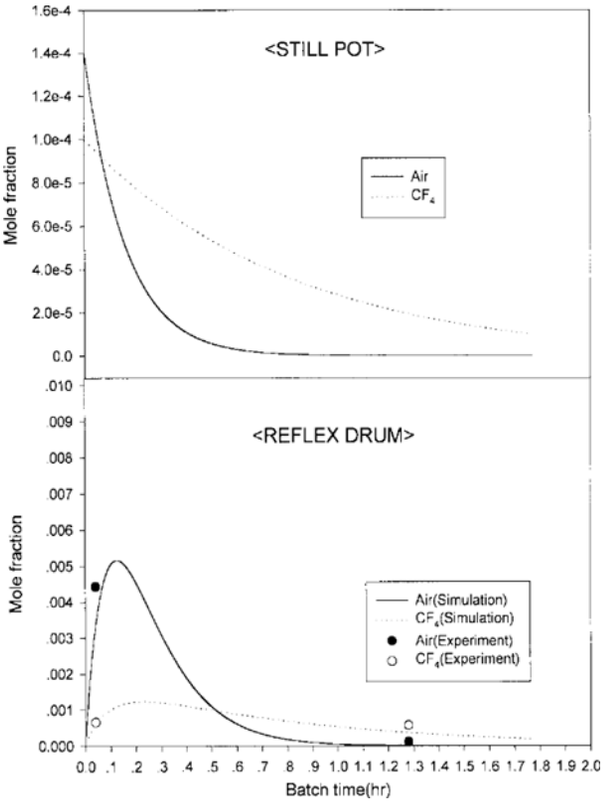

Fig. 5. Changes of concentrations of air and CF_4 with operating time.

are in the unstable state because the temperature is well above critical temperatures of these components. The sharp decrease in SF_6 content (Fig. 4) is due to the vent of SF_6 mixture. After sufficient operation time most of the air and CF_4 are removed as can be seen in Fig. 5 which shows the concentrations of air and CF_4 in the still pot and reflux drum, respectively. In the still pot, due to higher relative volatility, air concentration shows faster decrease than CF_4 concentration. In contrast to the still pot, the concentration of air shows a sharp increase followed by a faster decrease than that of CF_4.

CONCLUSION

A batch distillation technique was employed to design the purification process of SF_6 from N30 to N50. A packed column was used in the batch distillation, and the purification system was investigated both numerically and experimentally. It took approximately 1 hr and 50 minutes to achieve N50 SF_6. Modeling of the purification system was based on the regular solution theory to identify the K-values. Results of numerical simulations showed good agreement with experimental data. Based on these results, a commercial scale pilot plant for the purification of SF_6 mixture is planned.

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NOMENCLATURE

f : fugacity
G : Gibbs free energy
M : liquid molar holdup
R : liquid molar reflux
V : molar vapor flow rate
x : liquid mole fraction
y : vapor mole fraction

Greek Letters

ϕ_i : volume fraction
α : relative volatility
δ_i : solubility parameter
γ_i : activity coefficient

Superscripts

G : gas phase
L : liquid phase

Subscripts

B : still pot
D : reflux drum
i : component
1 : solvent
2 : solute

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