

Separation of triethoxysilane from tetraethoxysilane by batch distillation in a packed column

Yun Jae Lee, Hyeyun Jeong, Hoey Kyung Park, Kyun Young Park[†], Tae Won Kang, Jungho Cho, and Dong-Sun Kim

Department Chemical Engineering, Kongju National University, 275 Budae-dong, Cheonan, Chungnam 31080, Korea

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Abstract—A batch distillation of a crude tetraethoxysilane containing 8 mol% triethoxysilane was performed in a glass packed column, 2.54 cm in diameter and 1 m in height. Two distillate rates, 3.0 mL/min and 6.0 mL/min, were used and the reflux ratio was varied up to 3.0. Experimental data were compared with predicted values by Pro/II, a process simulator widely used in the chemical industry. The differential condensation of the vapor in the packed column due to heat losses from the vapor to the column internals and to the surroundings affected the separation efficiency seriously so that a considerable discrepancy was observed between experimental data and prediction by Pro/II in which such heat-loss effects are unaccountable. A model was developed to explain the effect of the differential condensation. For a larger distillation unit scaled up by 100 times where the heat-loss effect is regarded to be minimal, Pro/II simulations were performed to produce 99.9% TEOS with varying reflux ratio, number of stage, and feed composition.

Keywords: Tetraethoxysilane, Triethoxysilane, Batch Distillation, Packed Column

INTRODUCTION

Tetraethoxysilane (TEOS) is used as a precursor for SiO₂ thin films [1], as a cross-linking agent in silicene polymers [2] and as a source for zeolites and aerogels [3,4]. TEOS is produced by reaction of either silicon tetrachloride (SiCl₄) or metal silicon with ethanol [5,6]. The SiCl₄-based process is mature in technology and has been the principal route to TEOS, but produces HCl gas as a by-product that is poisonous and corrosive. By comparison, the silicon-based process is relatively new and environmentally benign, but is known to produce a considerable amount of triethoxysilane (TES) as a side-product [7] that must be removed afterward to obtain pure TEOS. To our knowledge, data on the separation of TES from TEOS are not available in the open literature, although the silicon-based production of TEOS is already in commercial stage.

The boiling points of TES and TEOS are 134 °C and 168 °C, respectively. Such a difference of more than 30 °C in boiling point may be large enough to effect the separation of TES from TEOS by distillation. Batch distillation is known to be advantageous over continuous distillation where relatively small quantities of material are to be processed as for fine and specialty chemicals to which TEOS belongs [8]. The system is simpler by batch distillation: the reboiler works as feed and product tanks as well and no separate heat exchanger to preheat the feed is necessary, unlike in continuous distillation. TES and TEOS are sensitive to moisture and should be kept under moisture-free atmosphere. With continuous distillation, not only the reboiler but also the feed tank, the feed preheater, the product tank, and the associated pipelines must be under moisture control to make the system more costly and vulnerable to oper-

ational problems.

The purpose of the present study was to explore the feasibility of applying a batch distillation to the separation of TES from TEOS through experiments in a laboratory-scale unit with varying operating variables and to investigate the effects of the variables on the separation efficiency as a first step toward future optimal design of the separation. A batch distillation of a mixture of TES (8 mol%) and TEOS was carried out in a laboratory-scale packed column with varying distillate rate and reflux ratio. TES mole fractions of the distillate tank, the still pot, and the reflux drum were compared between experimental data and calculated values by Batch Distillation module in Pro/II, a steady-state simulator for equilibrium-stage based distillation. The condensation of the vapor in the column due to the heat losses from the vapor to the column internals initially at room temperature and to the surroundings through the column wall was calculated with a differential-condensation model to interpret experimental observations in the early stage of the distillation. For scale-up of the distillation unit by 100 times, the effects of the number of stage, the reflux ratio, and the initial composition of the feed on the yield of 99.9% TEOS were investigated by Pro/II simulation.

EXPERIMENTAL

Fig. 1 shows the experimental apparatus, which consisted of a glass column 2.54 cm in diameter packed with glass rings (Wilson Helics) to the height of 1.0 m, a 1 L flask (or still pot) in a heating mantle, a water-cooled condenser, a reflux drum, a distillate tank, and a NaOH scrubber. The distillation pressure was maintained at 1 atm by the scrubber that is open to the atmosphere. The packed column was wrapped for insulation with a 1.5 cm thick glass wool. A thermocouple installed at the top of the column was used to measure the temperature of the vapor that enters the condenser. Before a run, the distillation system was purged with nitrogen for

[†]To whom correspondence should be addressed.

E-mail: kypark@kongju.ac.kr

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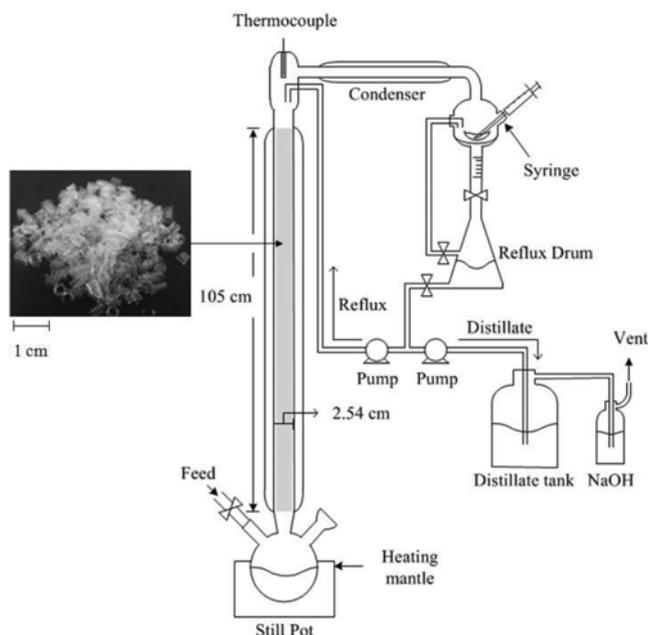


Fig. 1. Schematic drawing of experimental setup for batch distillation of TES-TEOS mixture.

1 h at a rate of 600 mL/min to remove any water vapor present in the system. After the purge, the still pot at the bottom of the distillation column was charged with 550 mL of the TES (reagent grade, Aldrich)-TEOS (reagent grade, Aldrich) mixture using a feeder operated under moisture-free atmosphere. The still pot was then heated with a predetermined power input. The rate of the condensation was measured intermittently by measuring the volume of the condensate accumulated for a given time in a mess cylinder located between the condenser and the reflux drum. The condensate exiting the mess cylinder was passed by gravity to the reflux drum. Immediately after the volume in the reflux drum reached 150 mL, a total reflux was started and continued until the rate of reflux and the rate of condensation were balanced to maintain a constant condensate level in the reflux drum. Then, the distillate withdrawal from the reflux drum to the distillate tank followed, while the reflux rate was reduced by the amount of the distillate rate.

Samples, 50 μ L each were collected in situ during a run at the condenser outlet sequentially using a syringe that was inserted through a septum into a 1 mL pool under the condenser outlet. At the end of a run, three samples were collected from the still pot, the reflux drum, and the distillate tank, respectively. The collected samples were analyzed by gas-chromatography (Model YL6500, Young In Scientific Co., Ltd.) with a capillary column (HP-5), a flame ionization detector, and helium gas as carrier. The injector and the detector temperatures were set at 200 $^{\circ}$ C and 250 $^{\circ}$ C, respectively. The oven temperature was programmed to increase from 100 $^{\circ}$ C to 150 $^{\circ}$ C at rate of 10 $^{\circ}$ C/min and maintained at 150 $^{\circ}$ C for 3 min.

RESULTS AND DISCUSSION

1. Early-stage Distillation without Reflux

A distillation run was carried out in the absence of reflux, which

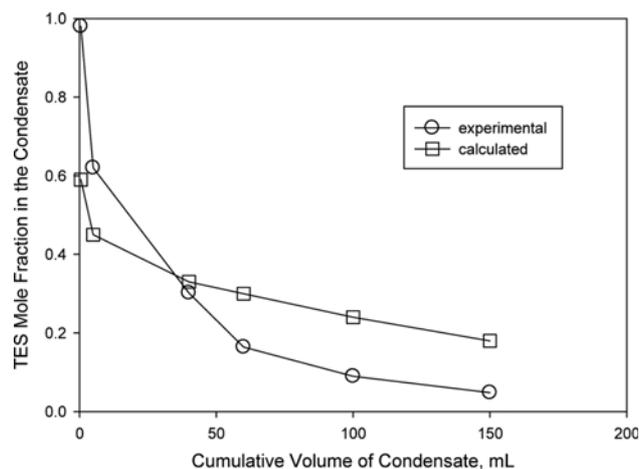


Fig. 2. Instantaneous mole fractions of TES at the condenser outlet at different cumulative volumes of condensate in the reflux drum.

is similar to simple distillation, with the power input to the still pot set at 243.2 J/s. During the distillation, six condensate samples were collected in situ sequentially at the outlet of the condenser until the volume of the condensate in the reflux drum reached 150 mL that is necessary to establish a liquid level for the reflux pump to be run without cavitation. Fig. 2 shows the instantaneous mole fractions of TES at the condenser outlet at different cumulative volumes of condensate in the reflux drum. The TES mole fraction in the initial condensate was measured to be as high as 0.98. The initial condensate is meant by about 1 mL of the condensate that appeared for the first time. The TES mole fraction in the condensate decreased gradually as the volume of condensate increased: 0.62 at 5 mL, 0.16 at 60 mL, and finally 0.048 at 150 mL. The gradual decrease in TES mole fraction in the condensate was expected because TES is more volatile than TEOS, and consequently the mole fraction of TES in the still pot should decrease continuously with increasing extent of distillation.

Initially, the packed column was at room temperature and the vapor generated in the still pot condensed on the packings on the way before the vapor exited the column to enter the condenser. The condensation front moved upward as the internals of the column were heated by the vapor. Eventually, the condensation front reached the top and the vapor that was not condensed in the column was carried over to the condenser downstream to form a condensate enriched in TES. The enrichment was calculated by a model in the appendix, which is based on the differential condensation [9]. The differential condensation is like a condensation in a chain of compartments in series. Even after the column internals were heated up sufficiently to the temperature of the vapor, a fraction of the vapor was still condensed in the column, which was verified by observation of a liquid flowing down the column into the still pot, due to a heat loss from the vapor to the surroundings through the column wall of probably incomplete insulation.

In a model of batch distillation [10], the Rayleigh equation was used to calculate the composition of the condensate until the reflux drum was filled to a pre-determined level. The mole fraction of TES in the initial condensate calculated by the Rayleigh equation was 0.17, far below that measured. In contrast, the initial mole frac-

tion of TES by the present model was calculated to be 0.59, closer to that experimentally observed but still underestimated. By model calculation, 72-75% of the vapor generated in the still pot was condensed in the column due to the heat loss to the surroundings through the column wall. The condensate that was formed inside the packed column flowed down the column and probably acted like a reflux from the reflux drum to further enrich the vapor in TES, which was not considered in the present model. Numerical problems were encountered when the mass transfer by diffusion between the vapor and the condensate was included to take into account the reflux-like effect. Such numerical problems were reported to be attributed to interactions between fast and slow dynamics generating stiff differential-algebraic equations [11]. In an application of Radfrac, a rate-based stage model [12,13], in Aspen-Plus to a packed distillation, there were difficulties in convergence [14]. It is regarded as quite challenging to calculate the early-stage batch distillation rigorously, in particular for packed columns.

The TES mole fraction by model prediction decreased gradually with increasing the volume of the condensate (0.45 at 5 mL; 0.33 at 40 mL; 0.30 at 60 mL; 0.24 at 100 mL; 0.18 at 150 mL), which is similar in trend to that observed experimentally. Measured TES mole fraction turned lower than the calculated one when the condensate volume increased past 40 mL, probably because the amount of TES that had actually escaped from the still pot must be greater and consequently the TES mole fraction in the still pot was caused to be lower than with the model.

2. Normal Distillation with Reflux

Distillations in the presence of reflux were carried out for two distillate rates, 3 ml/min and 6 ml/min. Table 1 shows the operating conditions and the resulting TES mole fractions in the distillate tank, the reflux drum, and the still pot. The reflux ratio was varied up to 3 for the distillate rate of 3 mL/min. A further increase in the reflux ratio brought flooding in the column. At the distillate rate of 6 mL/min, the reflux ratio was limited to 1.0 for the reflux rate not to exceed 12 mL/min that was determined to be the limit for flooding-free operation through the preceding variation of the reflux ratio at the distillate of 3 mL/min. Each distillation continued until 150 mL of distillate was obtained.

With varying reflux ratio, the TES mole fractions in the distillate tank and in the reflux drum are shown in Fig. 3. The TES mole fractions ranged from 0.140 to 0.159 in the distillate tank and from 0.080 to 0.104 in the reflux drum, respectively. At the distillate rate of 3 mL/min, with increasing reflux ratio the TES mole fraction increased in the distillate tank and decreased in the reflux drum. As the distillate rate was increased from 3 ml/min to 6 mL/min

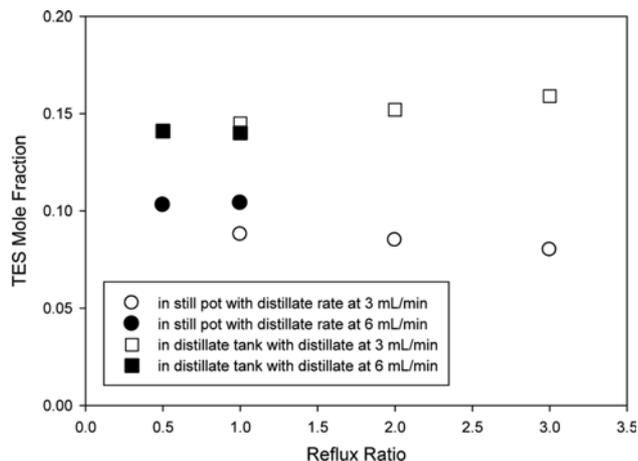


Fig. 3. TES mole fractions in the distillate tank and in the reflux drum with varying reflux ratio for two different distillate rates.

holding the reflux ratio at 1.0, the TES mole fraction in the distillate tank decreased from 0.145 to 0.140, while the TES mole fraction in the reflux drum increased from 0.088 to 0.104. The decrease of TES mole fraction in the distillate tank with increasing the distillate rate, although the decrement is small, indicates that the separation efficiency in the column was probably reduced by an increase in vapor flow rate to meet the increase of distillate rate. At the distillate rate of 6 mL/min, the variation of reflux ratio from 0.5 to 1.0 had little effect on the TES mole fractions. The increasing effect in separation efficiency by the increase of reflux ratio was probably offset by the decreasing effect due to the increased vapor load in the column. In all runs, an increase of TES mole fraction in the distillate tank was accompanied by a decrease of TES mole fraction in the reflux drum, and vice versa. In every case, the TES mole fraction in the still pot was smaller than 0.001 set as the minimum limit of the mole fraction that could be measured with confidence through a preliminary test. The TES mole fraction smaller than 0.001 in the still pot means that TEOS higher than 99.9% was produced from the crude TEOS containing 8% TES. The loss of TEOS as contained in the reflux drum and the distillate tank is too high, as shown in Table 1. A reason for so much TEOS in the reflux drum and the distillate tank is that the hold-up of the reflux drum is as much as 150 mL, 27% of the feed volume. In larger-scale distillations, the ratio of the hold-up to the feed volume could be reduced, and the fraction of TEOS lost as waste would be reduced. Another reason is that the reflux ratio and the column height may be insufficient.

Table 1. Operating conditions and resulting TES mole fractions in distillate tank, reflux drum, and still pot after 150 mL of distillate was obtained (Feed volume: 550 mL; TES mole fraction in the feed: 0.08; reflux drum hold up: 150 mL)

Run no.	1	2	3	4	5
Distillate rate, mL/min	3.0	3.0	3.0	6.0	6.0
Reflux ratio	1.0	2.0	3.0	0.5	1.0
TES mole fraction					
Distillate tank	0.145	0.152	0.159	0.141	0.140
Reflux drum	0.088	0.085	0.080	0.103	0.104
Still pot	<0.001	<0.001	<0.001	<0.001	<0.001

For run 3 in Table 1, the theoretical number of stage equivalent to the height of the distillation column was determined to be five by comparing the TES mole fractions in the distillate tank and reflux drum between experimental data and predictions by Pro/II with varying number of theoretical stages, as shown in Fig. 4. With the theoretical number of stages thus determined, a Pro/II simulation was performed to predict the TES mole fractions in the condensates sampled at the condenser outlet at three different distillate volumes: 0 mL, 75 mL and 150 mL. The volume of 0 mL means that the distillate withdrawal has just been started. The predictions are compared with experimental data in Fig. 5. Both in experimental data and in prediction by Pro/II, the TES mole fraction at the condenser outlet, which is assumed to be the TES mole fraction in the vapor leaving the distillation column, decreased as the volume of the distillate increased. This behavior is attributable to the gradual

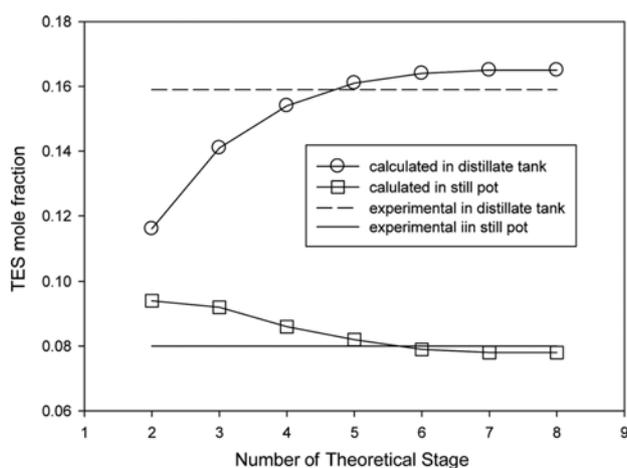


Fig. 4. Comparison in TES mole fractions in distillate tank and still pot for run 3 between experimental data and calculated values by Pro/II with varying number of theoretical stages. The number of stage equivalent to the packed column was determined by reading the stage at which calculated values best fit experimental data.

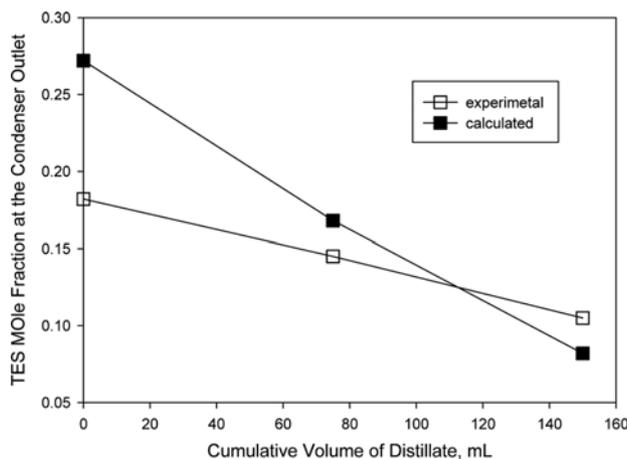


Fig. 5. Comparison in instantaneous TES mole fractions in the condensate at the condenser outlet for run 3 between experimental data and prediction by Pro/II at different cumulative volumes of distillate.

decrease of TES mole fraction in the still pot with distillation time. Measured TES mole fractions are lower than those by Pro/II until the distillate volume of 75 mL, supporting that TES escaped from the still pot faster than prediction due to the differential condensation in the start-up stage, and resultantly the TES concentration in the still pot was actually lower than with the model during the period of the distillate withdrawal in discussion.

3. Pro/II Simulation for Scale Up

The heat loss in the column, which is usually unavoidable in small

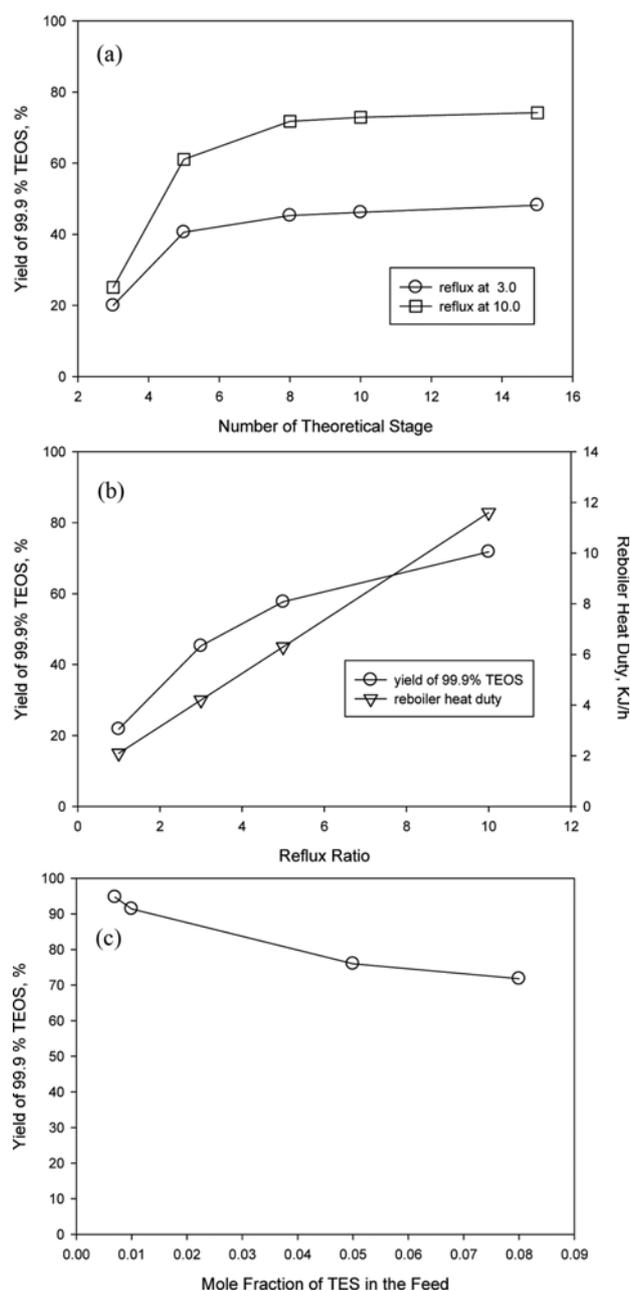


Fig. 6. Pro/II prediction of effects of operating variables on yield of 99.9% TEOS for a scale-up by 100 times: (a) Number of theoretical stages was varied at two reflux ratios, 3 and 10, (b) reflux ratio was varied with number stage fixed at 8, and (c) TES mole fraction in the feed was varied holding the number of stages at 8 and the reflux ratio at 10.

scale units as in the present study, affected the separation efficiency to result in a serious deviation of predicted values from experimental data. The deviation should decrease as the distillation unit is scaled up because the surface area-to-volume ratio decreases, and consequently the fraction of the heat loss out of the heat supplied to the distillation unit would decrease. In large-scale units where the heat-loss effect is regarded to be minimal, Pro/II simulation could be better predictive. In an attempt to build a step toward commercial design of the separation of TES from TEOS by batch distillation, Pro/II simulations were performed for a larger batch distillation unit scaled up by 100 times with distillation conditions extended to those outside the present experimental limitations that the TES mole fraction in the feed was fixed at 0.08, the packing height or the equivalent number of stage was fixed, and the reflux ratio was limited up to 3 due to the structural characteristics of the packings and the diameter of the distillation column. The goal is to produce TEOS having a purity of 99.9% that was implemented in the present experimental study, with a yield as high as possible.

The effects of the number of stage on the yield of 99.9% TEOS are shown in Fig. 6(a) for two reflux ratios, 3 and 10. In both reflux ratios, the yield increased steadily up to the stage of 8, beyond which the increments were minimal. Holding the theoretical stage at 8 and the TES mole fraction in the feed at 0.08, the reflux ratio was varied from 1 to 10, the result of which is shown in Fig. 6(b). The yield of 99.9% TEOS increased from 21.8% at the reflux ratio of 1 to 71.8% at 10, the slope exhibiting a gradual decrease. While, the reboiler duty increased almost linearly with reflux ratio, implying that there should be a trade-off between reflux ratio and yield. The yield was insensitive to a variation of the distillate rate at the same reflux ratio and number of theoretical stage. An increase in the distillate rate, however, may require an increase in the column height to compensate for possible loss in separation efficiency due to the increased vapor load in the column unless the column diameter is increased sufficiently. The TES mole fraction in the feed was reduced from 0.08 down to 0.007 with the reflux ratio at 10 and the theoretical stage at 8. The yield increased from 71.8% at the TES mole fraction of 0.08 to 92.8% at 0.01 and to 96.3% at 0.007, as shown in Fig. 6(c). A further reduction of the TES mole fraction to 0.005 brought a failure in convergence of the Pro/II program. The feed composition is thus as important as the reflux ratio and the number of stages in determining the yield of 99.9% TEOS that is produced from silicon and ethanol.

CONCLUSION

In a laboratory-scale batch distillation, it was verified that TEOS higher than 99.9% in purity was producible from a crude TEOS containing 8 mol% TES by batch distillation. The loss of TEOS as contained in the reflux drum and the distillate tank was unexceptionally high because the hold-up of the reflux drum was as high as 27% of the feed volume due to the inherent nature of the small-scale distillation unit. By scaling up the unit, the ratio of the hold-up to the feed volume could be decreased to reduce the TEOS loss. The loss could be even further reduced by increasing the height of the distillation column and the reflux ratio. The differential condensation of the vapor in the column due to the losses of heat from the

vapor to the column internals and to the surroundings affected the separation efficiency seriously, so that a considerable discrepancy was observed between experimental data and prediction by Pro/II in which such heat-loss effects are unaccountable. The differential condensation model that was proposed to explain the TES enrichment in the condensate during the start-up period was qualitatively predictive, but was not able to adequately predict the TES mole fraction in the first condensate. The reflux-like effect of the condensate flowing down the column must be included to improve the model. For a larger unit scaled up by 100 times where the heat-loss effect is regarded to be minimal and under broader ranges of reflux ratio, equivalent number of stage, and TES mole fraction in the feed, Pro II simulations were performed to produce 99.9% TEOS. The yield of 99.9% TEOS increased steadily up to a stage of 8, beyond which the increments were minimal. Holding the stage at 8 and the TES mole fraction in the feed at 0.08, the yield increased from 21.8% at the reflux ratio of 1 to 71.8% at 10. The increasing slope exhibited a gradual decrease, while the reboiler duty increased almost linearly with reflux ratio. This implies that there should be a trade-off between the reflux ratio and the yield. With the reflux ratio at 10 and the theoretical stage at 8, the yield increased from 71.8% to 96.3% as the TES mole fraction in the feed was reduced from 0.08 to 0.007.

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NOMENCLATURE

A	: surface area of column wall per unit volume of column [m ⁻¹]
a _p	: vapor-packing interfacial area per unit volume of column [m ⁻¹]
C _p ^V	: molar heat capacity of vapor [J mol ⁻¹ K ⁻¹]
C _{p,i} ^L	: molar heat capacity of liquid component i [J mol ⁻¹ K ⁻¹]
C _p ^S	: heat capacity of packing [J kg ⁻¹ K ⁻¹]
d _p	: diameter of packing equivalent to a sphere of same volume [m]
H _{L,i}	: liquid hold up of component i per unit volume of column [mol m ⁻³]
h _v	: heat transfer coefficient between vapor and packing [J m ⁻² s ⁻¹ K ⁻¹]
k	: thermal conductivity of vapor [J s ⁻¹ m ⁻¹ K ⁻¹]
L _{i,k}	: molar flow rate of liquid component i leaving the k th section [mol s ⁻¹]
I _i ^C	: rate of condensation of component i from the vapor [mol s ⁻¹ m ⁻³]
m _s	: mass of the packing per unit volume of column [kg m ⁻³]
N _{i,B}	: instantaneous number of moles of component i in the still pot [mol]
nsec	: number of sections in the packed column
P	: pressure in still pot [Pa]
P _i [*]	: vapor pressure of component i [Pa]
Q _R	: energy input to the still pot from the heating mantle [J s ⁻¹]
T	: instantaneous temperature of wetted packing [K]

T_a	: ambient temperature [K]
T_R	: reference temperature [K]
T_V	: vapor temperature [K]
t	: time [s]
U	: overall heat transfer coefficient of heat loss through column wall [$J m^{-2} s^{-1} K^{-1}$]
u	: linear velocity of vapor [$m s^{-1}$]
V_B	: molar evaporation rate in still pot [$mol s^{-1}$]
$V_{i,k}$: molar flow rate of component i in the vapor entering the k^{th} section [$mol s^{-1}$]
$V_{M,i}$: liquid molar volume of component i [$m^3 mol^{-1}$]
$X_{i,B}$: mole fraction of component i in still pot
Y_i	: vapor mole fraction of component i in the column
$Y_{i,B}$: mole fraction of component i in the vapor leaving the still pot

Greek Letter

α	: fraction of energy that is lost to the surroundings from the still pot
γ_i	: latent heat of vaporization of component i [$J mol^{-1}$]
μ	: viscosity of vapor [$N s m^{-2}$]
ρ	: density of vapor [$kg m^{-3}$]

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APPENDIX

The mass and energy balances in the still pot and the packed distillation column were set up to calculate the differential conden-

sation in the early stage of distillation. The pressure drop in the column was neglected. Initially, the column was assumed to be at room temperature and the still pot was assumed to be at the boiling point. The vapor generated in the still pot flows upward and is condensed on the way before it reaches the top of the column until the internals of the column have been heated sufficiently. A partial condensation of the vapor inside the column is unavoidable even after the internals and the vapor have reached thermal equilibrium, due to a heat loss from the column to the surroundings through the wall. The heat transfer coefficient of the heat loss through the wall of the packed column and the fraction of the energy that was lost to the surroundings from the still pot were treated as adjustable parameter.

Mass and Energy Balances:

1. Still Pot

1-1. Mass Balance

$$\frac{dN_{i,B}}{dt} = -V_B Y_{i,B} + L_{i,1} \quad (A1)$$

where $N_{i,B}$ is the instantaneous number of moles of component i in the still pot, V_B is the molar evaporation rate in the still pot, $Y_{i,B}$ is the mole fraction of component i in the vapor leaving the still pot, $L_{i,1}$ is the molar rate of component i in the liquid flowing down to the still pot at the bottom of the packed column, and t is the time elapsed since the start of evaporation in the still pot. The subscript i refers to species throughout the equations to follow: 1 for TES and 2 for TEOS.

1-2. Equilibrium Relationship

$$Y_{i,B} = X_{i,B} P_i^* / P \quad (A2)$$

$$X_{i,B} = \frac{N_{i,B}}{\sum N_{i,B}} \quad (A3)$$

where $X_{i,B}$ is the mole fraction of component i in the still pot, P_i^* is the vapor pressure of component i , and P is the pressure in the still pot. The binary mixture of TES and TEOS was assumed to follow Raoult's law because the two components are similar in molecular structure; in TEOS silicon is connected to four ethoxy (-O-CH₂-CH₃) groups, while in TES one ethoxy group is replaced by hydrogen. A calculation of vapor-liquid equilibrium by Pro/II with NRTL model supported the assumption.

1-3. Bubble Point Relationship

$$\frac{\sum X_i P_i^*}{P} = 1.0 \quad (A4)$$

1-4. Energy Balance

$$V_B = \frac{Q_R(1-\alpha)}{\sum \gamma_i Y_{i,B}} \quad (A5)$$

where Q_R is the amount of energy that is supplied to the still pot from the heating mantle, and α is the fraction of the energy that is lost to the surroundings, and γ_i is the latent heat of vaporization of component i .

2. Packed Column

The packed column was divided into a number of sections. In each section, time-dependent mass and energy balances were set

up where uniform temperature, liquid hold up, and concentrations were assumed.

2-1. Mass Balance

2-1-1. Liquid Phase

2-1-1-1. During Build-up of Liquid Hold Up

$$\frac{dH_{L,i}}{dt} = L_i^c \quad (A6)$$

where $H_{L,i}$ is the liquid hold up of component i on the packing per unit volume of column, L_i^c is the rate of condensation of component i from the vapor per unit volume of column. L_i^c is related to the transfer of heat from the vapor to the liquid on the packing and to the loss of heat to the surroundings through the column wall, as follows:

$$\sum \gamma_i L_i^c = UA(T_V - T_a) + h_v a_p (T_V - T) \quad (A7)$$

$$\frac{L_i^c}{\sum L_i^c} = \frac{Y_i P}{P_1} \quad (A8)$$

where U is the overall heat transfer coefficient of the heat loss from the vapor through the wall of the column, A is the surface area of the wall per unit volume of the column, T_V is the temperature of the vapor, T_a is the ambient temperature, h_v is the heat transfer coefficient between the vapor and the wetted packing, a_p is the vapor-packing interfacial area per unit volume of the column, and T is the instantaneous temperature of the wetted packing. The overall heat transfer coefficient, U was treated as an adjustable parameter. The heat transfer coefficient between the vapor and the wetted packing, h_v was estimated by the following equation:

$$\frac{h_v d_p}{k} = 2 + 0.6 \left(\frac{d_p u \rho}{\mu} \right)^{0.5} \left(\frac{C_p^V \mu}{k} \right)^{0.33} \quad (A9)$$

where d_p is the diameter of the packing, k is the thermal conductivity of the vapor, u is the linear velocity of the vapor, ρ is the density of the vapor, μ is the viscosity of the vapor, and C_p^V is the molar heat capacity of the vapor. k , μ and C_p^V were calculated using the methods in the book by Reid et al. [15]. In Eq. (A6), the liquid hold-up was allowed to build up to a value, which was obtained from the measured static hold-up of 11 mL and the volume of the packed column, beyond which the derivative was set to zero to have any further condensates immediately flow downward.

2-1-1-2. After Completion of Build-up of Liquid Hold Up

After the completion of the build-up of liquid hold-up, further condensates formed from the vapor flow down the column by gravity.

$$L_{i,k} = L_{i,k+1} + V_{i,k} - V_{i,k+1} \quad (A10)$$

where $L_{i,k}$ is the molar flow rate of component i in the condensate leaving the k^{th} section, $L_{i,k+1}$ is the flow rate of component i in the condensate entering the k^{th} section from the upper $(k+1)^{\text{th}}$ section, $V_{i,k}$ is the molar flow rate of component i in the vapor entering the k^{th} section, and $V_{i,k+1}$ is the flow rate of component i in the vapor leaving the k^{th} section to enter the $(k+1)^{\text{th}}$ section. $L_{i,k+1}$ at the top of the column is set at zero because there is no reflux, and $V_{i,k}$ at the bottom of the column is set to be equal to the vapor rate from the still pot, $Y_{i,B}$ in Eq. (A2) times V_B in Eq. (A5).

2-1-2. Vapor Phase

$$V_{i,k+1} = V_{i,k} - L_i^c \quad (A11)$$

$$Y_i = \frac{V_i}{\sum V_i} \quad (A12)$$

where Y_i is the mole fraction of component i in the vapor phase.

2-2. Dew Point Relationship

$$\sum \frac{Y_i P}{P_i^*} = 1.0 \quad (A13)$$

2-3. Energy Balance

2-3-1. Vapor

The vapor was assumed to be at the dew point (T_V) throughout the condensation. The dew point temperature, which is dependent upon the vapor composition, was determined from the dew point Eq. (A13) in which the temperature is not shown explicitly, but is hidden in the vapor pressure.

2-3-2. Wetted Packing

The temperature gradients within the liquid on a packing and inside that packing were neglected to assume that the temperature is uniform within the wetted packing. The energy balance for a section k can be represented by

$$\frac{dT}{dt} = \frac{h_v a_p (T_V - T) + \sum (L_{i,k+1} - L_{i,k}) C_{p,i}^L (T - T_R) + \sum L_i^c C_{p,i}^L (T_V - T_R)}{\left(\sum \frac{H_{L,i} C_{p,i}^L}{V_{M,i}} + m_s C_p^S \right)} \quad (A14)$$

where $C_{p,i}^L$ is the molar heat capacity of the liquid component i , T_R is the reference temperature, $V_{M,i}$ is the molar volume of the liquid component i , m_s is the mass of the packing per unit volume (or bulk density of packing), and C_p^S is the heat capacity of the packing. The first, second, and third terms in the numerator represent, respectively, the convective heat transfer from the vapor to the packing, the rate of energy input to the k^{th} section due to any difference in flow rate between the liquid entering from above and the liquid leaving the k^{th} section, and the rate of energy carried by the condensates to the wetted packing.

Calculation Procedure:

The number of unknowns are $(12 \times n_{\text{sec}} + 8)$: 8 in the still pot ($N_{1,B}$, $N_{2,B}$, $Y_{1,B}$, $Y_{2,B}$, V_B , $X_{1,B}$, $X_{2,B}$ and T_B) and 12 ($H_{L,1}$, $H_{L,2}$, L_1^c , L_2^c , Y_1 , Y_2 , T_V , L_1 , L_2 , V_1 , V_2 , and T) times n_{sec} in the packed column, where n_{sec} is the number of sections in the packed column. The number of equations from A(1) to (A14) end up with the same as the number of unknowns. The system of $(12 \times n_{\text{sec}} + 8)$ equations was solved by Fortran using the IMSL library for the differential Eqs. (A1), (A6), and (A14) and the nonlinear Eqs. (A4) and (A13). The physical properties and constants that appear in those equations are listed in Table A1.

Determination of Adjustable Parameters:

The number of sections in the packed column was varied from 5 to 50 to see the effect of the number on the movement of the condensation front in the column. 50 sections were found to be enough for arbitrarily chosen sets of α in Eq. (A5) and U in Eq. (A7). With the number of sections at 50, the two adjustable parameters, α and U were determined at 0.4 and $556.4 \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-1}$,

Table A1. Physical properties and constants in Eqs. (A1) to (A14)

Physical properties and constants	Values
Vapor pressure (P_i^*), mmHg	Triethoxysilane [16]: $\ln P = 18.394 - 4791.8/T$ Tetraethoxysilane [17]: $\ln P = 19.365 - 5594.3/T$
^a Latent heat (γ_i), J mol ⁻¹	Triethoxysilane: 39,839 Tetraethoxysilane: 46,510
Heat capacity of liquid ($C_{p,i}^L$), J mol ⁻¹ K ⁻¹	^b Triethoxysilane: (heat capacity of TEOS-91.5) Tetraethoxysilane [17]: $aT^{-2} + bT + c$ $a = 20.7540 \times 10^5$; $b = 589.116 \times 10^{-3}$; $c = 165.4624$
Liquid molar volume ($V_{M,i}$), m ³ mol ⁻¹	Triethoxysilane: 184.57×10^{-6} Tetraethoxysilane: 223.29×10^{-6}
Heat capacity of packing (C_p^S), J Kg ⁻¹ K	840.0
Packing diameter (d_p), m	0.00323
Interfacial area (a_p), m ² m ⁻³	615.4
Bulk density of packing (m_s), kg m ⁻³	243.0
Column pressure (P), atm	1.0
Power input to still pot (Q_R), J s ⁻¹	Varied from 202.7 to 243.2

^aThe latent heat of vaporization was estimated from the slope of a plot, logarithm of vapor pressure vs. reciprocal of temperature

^bThe heat capacity of triethoxysilane is not available in the literature. It was estimated by subtracting 91.5 J mol⁻¹ K⁻¹ from the heat capacity of tetraethoxysilane by taking into account the difference in molecular structure using Missenard method, a group contribution method [15]

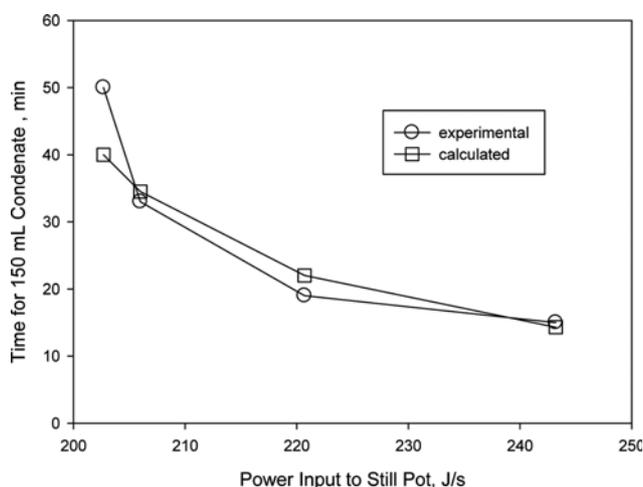


Fig. A1. Comparison of times taken from first appearance of condensate drop to accumulation of 150 mL condensate in the reflux drum for different power inputs to still pot between experimental data and prediction with the adjusted parameters, α at 0.4 in Eq. (A5) and U at $556.4 \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-1}$ in Eq. (A7).

respectively, to best fit measured times taken from the first appearance of a condensate drop to 150 mL accumulation of the condensate in the reflux drum, with the power input to the still pot varied from 202.7 J/s to 243.2 J/s. Fig. A1 shows a comparison between experimental data and those calculated using the adjusted param-

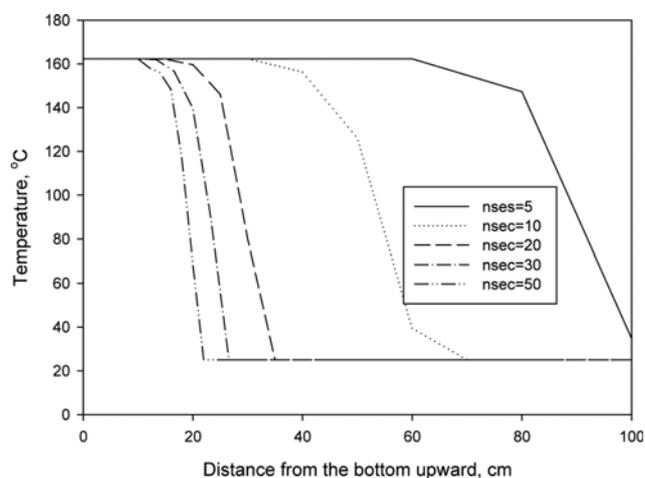


Fig. A2. Convergence of longitudinal temperature profile of packings at 6 s after the start of boiling in the still pot with increasing number of sections in the column.

eter values. Fig. A2 shows the calculated temperature profiles of the wetted packing at 6 seconds after the start of evaporation in the still pot for a power input of 202.7 J/s with the number of sections varied from 5 to 50. As the number of sections was increased, the temperature profile moved towards a convergence. The profile curves with the number of sections higher than 50 overlapped nearly on the curve at 50, and are not indicated in Fig. A2.