

An Optimum Process Design for Acetic Acid Recovery with Energy Integration

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<Abstract>

Process designs for acetic acid recovery with energy integration have been carried out with respects to solvent flow rate, tower pressure and reflux ratio.

Energy 중합을 고려한 초산화수공정의 최적설계

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<요 약>

Energy중합을 고려하여 용매유량, 탑압 및 환류비에 대한, 초산화수공정의 최적설계를 행하였다.

I. Introduction

Recently short supply of acetic acid and jumped price of petroleum on which acetic acid price based on have made the present market price of acetic acid to about double the price of a few years ago. Even from the water quality standard, it is being recognized as a considerable expense to treat waste water containing significant amount of acetic acid to meet the standard.

The above combined factors of value, demand and water quality standard plus the cost associated with separation make recovery and removal highly desirable.

Typical processes developed and in use presently for the acetic acid recovery from water are distillation, extraction and the combination of the two. Extraction followed by distillation is widely employed because it is

applicable for wide range of acetic acid concentrations. And orthodox solvents used were selected from the standpoint of only high distribution of solute. High distribution of solute is, regardless to say, favored for less amount of solvent is consumed for given amount of solute. But so far as the ultimate purpose of the separation is not usually restricted to the removal, and expanded to get pure product, further separation device should be considered together. And in the case that the latter device be distillation, much attentions might well be paid on solvent having high selectivity.

Solvents with high distribution and with high selectivity will be the best but they are hardly to be found yet.

In the present work, solvent having good selectivity with relatively poor solute distribution was selected for the alternative design purpose. Solvent with high selectivity and poor

solute distribution will permit very low migration of solvent to diluent in nature. In other words, further treatment for raffinate is not required.

To compensate excess heat duty on the extract caused by the low distribution, energy integration on the distillate subsystem was successfully carried out.

II. Selections of Solvent and Separation Process

Heuristics available for the recovery of acetic acid from water have devoted to classify the processes into simple distillation, extraction and the coupling of the two.¹⁻³⁾ At high concentration above 50%, simple distillation can at least be considered although a large number of equilibrium stages and a very high reflux ratio are necessary.

As a device to reduce energy consumption, azeotropic dehydration distillation can be employed.

In that case an entrainer relatively immiscible to water is involved to decrease the effective boiling point relative to that of acetic acid by forming the mixture a constant boiling point mixture. For intermediate concentration, from 5 to 50%, solvent extraction is usually employed typically followed by distillation to recover the solvent and for the further purification³⁾. For the extraction, solvents having good distributions for acetic acid at aimed concentrations have been widely used with respect to the less consumption of solvents.⁴⁻⁹⁾ Those solvents having good distribution coefficients involve low molecular weight esters, ethers and ketons which are common to entrainer for azeotropic dehydration distillation.

In the above mentioned orthodox solvents, there is one important facet unnoticed. The important fact almost neglected is, in general term, separation factor.

Since the object of a separation device is to

produce products to differing compositions, it is logical to define the separation factor in terms of product composition¹⁰⁾:

$$\alpha_{ij}^s = \frac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}} \dots \dots \dots (1)$$

which is the ratio of mole fraction of two components, *i* and *j*, in product 1 divided by the ratio in product 2. For the liquid extraction the separation factor is clearly the ratio of distribution coefficients of solute and diluent, i. e., selectivity:

$$\beta = \frac{m_A}{m_B} = \frac{y_A/x_A}{y_B/x_B} \dots \dots \dots (2)$$

Solvents having high distribution coefficient of solute, and low mutual solubility are most favourable not only because they reduce the amount of solvent but also because they enhance selectivity. But usually employed solvents for the solvent extraction of acetic acid from water have good distribution but poor selectivity because of the high mutual solubilities. More attentions have been paid on distribution coefficient. Difference in densities, appropriate interfacial tension, no chemical reaction, high recoverability and low cost are also required for solvent selection. In all extraction, it is necessary to remove the extraction solvent from the products not only to prevent contamination of products but also to permit reuse of solvent.

If distillation is the method to be used for solvent recovery, solvent properties such as large difference in volatility and less latent heat of vaporization become important. Armed with the above described solvent screening standards with lengthy calculation, the author noticed benzene as one of the most eligible solvent which satisfied nearly all of the constraints except a little poverty in distribution coefficient but very high selectivity with very low mutual solubility.

By parallel advancing of process system decision and solvent selection with characteristics restricted to the material system, the process system can be modified by eliminating raffinate

recovery subsystem from the system to which heuristics have reached.^{1,8)}

Additionally, to reduce excess heat duty entrained by the poor distribution coefficient

of benzene, distillation is being thermally integrated.

The process system thus arrived is shown in Fig. 1.

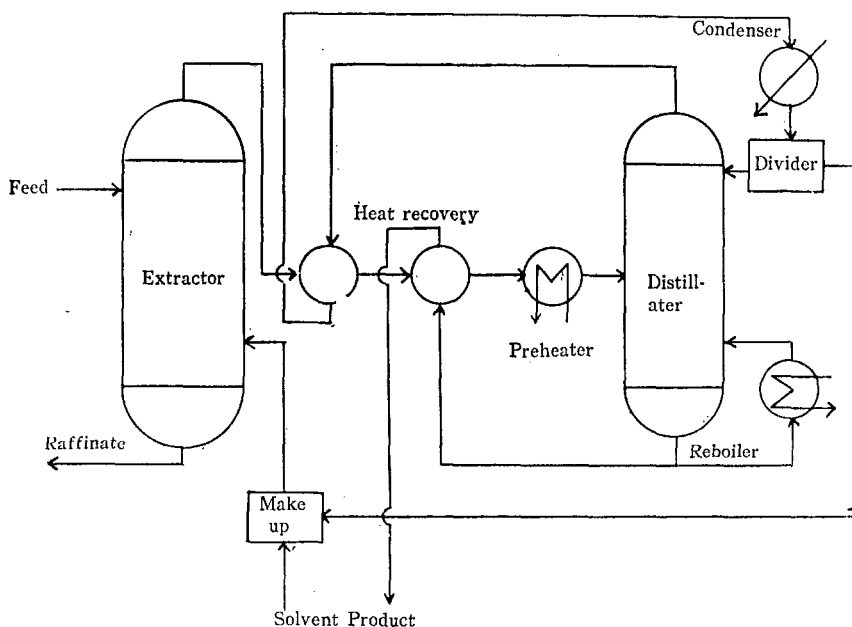


Fig. 1. The flow sheet of present process.

III. Process Analysis

Design variable selection algorithms have been developed to remove the computational troubles which are not inherent to the system but introduced by careless selection of distinguished design variables. Namely, they are established for the systems wherein no persistent recycle exists.¹¹⁻¹⁴⁾

But in reality almost all of the chemical processes involve many recycle streams connecting in the form of loops. The direct sequential solution of the mathematical model of the units

in the recycle process is not possible. The units in the process must all be solved simultaneously, but this is not feasible for the process involving nonlinear units thus an iterative solution procedure must be used. The most often used approach to recycle streams is that of decomposition. In that case, there will remain two important questions associated with iterative procedure: which stream should be torn and how should estimates be corrected?

Work done by Sargent¹⁵⁾, and followed by Upadhye and Grens¹⁶⁾ has been proposed method which can always obtain an optimal torn set using dynamic programming. But because of

the inherent dimensionality difficulty, the method can not be used generally to solve large recycle problems.

A more efficient procedure is the direct graph simplification method proposed by Sargent and later expanded by Christensen and Rudd.¹⁷⁾ The simplification techniques seek to reduce a process flow sheet graph to a null graph by eliminating streams and merging nodes in such a way that the solution is not changed. The simplification involves two way edge reduction which cuts recycle loop formed by two streams and the elimination of streams which are ineligible to be a member of the optimal torn set. If the simplification technique results in a residual graph, Sargent used dynamic programming, and Christensen and Rudd suggested examining all the possible combinations of the index mode. When both approaches are not efficient and involve severe combinatorial difficulty, interval stream reduction¹⁸⁾ and branch and bound method¹⁹⁾ are available.

The other question that of correction of the estimates is convergence procedure.

Since the appropriate streams have been cut to introduce the convergence algorithm, the procedure is equal to the solution of the system

$$g(x) = x \dots\dots\dots(3)$$

where x is the vector of cut streams.

$$g(x) = g(x_n) + J(x_{n+1} - x_n) \dots\dots\dots(4)$$

where the subscripts refer to the iteration index and

$$J = \frac{\partial g}{\partial x} \dots\dots\dots(5)$$

the Jacobian of the decomposed net work.

In the case that the system be decomposed with the objective of

$$M_{in}\{J\} \text{ or } M_{in}\{J_{wi}\} \dots\dots\dots(6)$$

where $\{J\}$ denotes cut set of streams of all the set of streams, $\{I\}$, and $\{J_{wi}\}$ denotes cut set of stream variables,

equation(3) reduces to direct substitution

algorithm

$$x_{n+1} = g(x_n) \dots\dots\dots(7)$$

becomes

$$g(x_{n+1}) = J^{n+1}(g(x_0) - x_0) + g(x_n) \dots\dots\dots(8)$$

Obviously equation(8) achieves stationarily, $g(x_{n+1}) = g(x_n)$, if $\lim_{n \rightarrow \infty} J^{n+1} = 0 \dots\dots\dots(9)$

and the solution is nontrivial if $g(x_0) \neq 0$

More sophisticated methods, independent acceleration of variables toward convergence and simultaneous Newton-Raphson iterations are also frequently used.

For the present work, ineligible stream elimination, with two way edge reduction algorithm is being used to decompos the whole system. For the torn stream convergence, direct substitution method is adopted for its simplicity and natural stability.

As the result of the direct application of tearing algorithm, distillate stream was to be the optimum torn stream with

$$M_{in}\{J_{wi}\} = 3 \dots\dots\dots(10)$$

But according to the design experience¹⁴⁾, it was recognized that to make convergence three variables at the same time is about three times difficult than to make by one and by two stepwisely.

Accordingly, for the rapid convergence, solvent balance was previously achieved among raffinate, product and fresh solvent stream.

IV. Design Equations and Optimizations

Sieve plate extractor

Liquid-liquid equilibrium data are available from resources.²⁰⁻²²⁾ Data for extractor performance are also available from previous publications.^{32,33)} Both of them were corrected for the purpose of practical design.

Choice of hole size

$$\left(\frac{1}{2}\right) \left(\frac{\nu}{\Delta \rho g}\right)^{1/2} < d_N < \pi \left(\frac{\nu}{\Delta \rho g}\right)^{1/2} \quad (11)$$

Estimation of jet diameter.

$$\frac{d_N}{d_f} = 1.0 + 0.485 \left(\frac{d_N}{(\nu/\Delta\rho g)^{1/2}} \right)^2$$

for $d_N \left(\frac{1}{\nu/\Delta\rho g} \right)^{1/2} < 0.7$ (12-a)

$$\frac{d_N}{d_f} = 0.12 + 1.51 \frac{d_N}{(\nu/\Delta\rho g)^{1/2}}$$

for $d_N \left(\frac{1}{\nu/\Delta\rho g} \right)^{1/2} > 0.7$ (12-b)

Velocity at the nozzle of hole

$$U_N = 2.69 \left(\frac{d_f}{d_N} \right)^2 \left(\frac{\nu/d_f}{0.5137\rho_d + 0.4719\rho_c} \right)^{1/2} \quad (13)$$

Total minimum head

$$h_t = h_N + h_v + h_c \quad \dots\dots\dots(14)$$

where $h_N = \frac{U_N^2(1 - S_0/S_t)^2 \rho_d}{2g_c c_N^2 \Delta\rho} \quad \dots\dots\dots(15)$

$$h_v = \frac{6\nu}{(d_p)_{0.1} \Delta\rho g} \quad \dots\dots\dots(16)$$

$$h_c = 4.5 \left(\frac{U_c^2}{2g_c} - \frac{\rho_c}{\Delta\rho} \right) \quad \dots\dots\dots(17)$$

Plate spacing

$$z_c = 10h_t \quad \dots\dots\dots(18)$$

Dispersed phase hold up

$$x(1-x) = (u_d/\bar{u}_0) \quad \dots\dots\dots(19)$$

where $\frac{\bar{u}_0}{(\nu\Delta\rho g/\rho_c^2)^{1/4}} = 1.088 \left(\frac{U_N^2}{2gd_N} \right)^{-0.0818} \quad \dots\dots\dots(20)$

Interfacial area of contact during free rise

$$a = \frac{6x}{d_{vs}} \quad \dots\dots\dots(21)$$

Interfacial area during formation

$$A_f = \pi d_p^2 \quad \dots\dots\dots(22)$$

Mass transfer coefficients

$$k_c = 0.023 U_s \left(\frac{\mu_c}{\rho_c D_c} \right)^{-1/2} \quad \dots\dots\dots(23)$$

$$k_d = 0.023 U_s \left(\frac{\mu_d}{\rho_d D_d} \right)^{-1/2} \quad \dots\dots\dots(24)$$

Overall volumetric coefficient for drop rise

$$\frac{1}{(K_{od}a)_r} = \frac{m}{k_c a} + \frac{1}{k_d a} \quad \dots\dots\dots(25)$$

Overall volumetric coefficient during drop formation and coalescence

$$(K_{od})_f = \frac{0.805}{m} \left(\frac{D_c}{\theta_f} \right)^{0.5} \quad \dots\dots\dots(26)$$

$$(K_{od}a)_f = 2(K_{od})_f \frac{A_f N_N}{S(Z_c - h_t)} \quad \dots\dots\dots(27)$$

where $\theta_f = \frac{\pi d_p^3/6}{\pi d_N^2 U_N/4} \quad \dots\dots\dots(28)$

The total effective mass transfer coefficient

$$K_{od}a = (K_{od}a)_r + (K_{od}a)_f \quad \dots\dots\dots(29)$$

Stage efficiency(Murphree)

$$\eta_{Md} = \frac{\exp\left(\frac{mU_d}{U_c}(\eta_{Md})_i - 1\right)}{m \frac{U_d}{U_c}} \quad \dots\dots\dots(30)$$

where local efficiency

$$(\eta_{Md})_i = 1 - \exp(K_{od}a)(z_c - h_t)/U_d \quad \dots\dots\dots(31)$$

The number of stages, n ,

$$\eta_n = \eta_0(1 + (1 - \eta_0) + (1 - \eta_0)^2 + \dots\dots\dots + (1 - \eta_0)^{n-1}) \quad \dots\dots\dots(32)$$

Material balances

$$(\beta - \alpha)(n_R^B)^2 + \eta \cdot n_F^A - W \cdot m \cdot n_S^A - \alpha(m \cdot n_S^A - \eta \cdot n_F^A - n_S^B + (1 + \alpha)mn_S^B W \chi_R^B) = 0 \quad \dots\dots\dots(33)$$

where

$$\alpha = \frac{\chi_E^W}{1 - \chi_E^W} \quad \dots\dots\dots(34)$$

$$\beta = \frac{1 - \chi_R^B}{\chi_R^B} \quad \dots\dots\dots(35)$$

$$W = n_F^A + n_F^W + n_S^A + n_S^B + n_S^W \quad \dots\dots\dots(36)$$

$$n_E^B = n_S^B - n_R^B \quad \dots\dots\dots(37)$$

$$n_R^A = n_F^A + n_S^A - \eta \cdot n_F^A - m \cdot n_S^A \left(\frac{W \cdot \chi_R^B}{n_R^B} - 1 \right) \quad \dots\dots\dots(38)$$

$$n_E^A = n_F^A + n_S^A - n_R^A \quad \dots\dots\dots(39)$$

$$n_R^W = \frac{1}{\alpha} n_R^B - n_R^A \quad \dots\dots\dots(40)$$

$$n_E^W = n_F^W + n_S^W - n_R^W \quad \dots\dots\dots(41)$$

Distillation

Liquid-vapor equilibrium data for two binary system^{23,24} and azeotropic data for benzene-water system are available from publication^{24,25}.

The activity coefficients of three components in ternary system were obtained from Wilson's equation:^{26,27}

$$l_n \gamma_i = 1 - l_n \left(\sum_{j=1}^v \chi_j A_{ij} \right) - \sum_{k=1}^v \frac{\chi_k A_{ki}}{\sum_{j=1}^v \chi_j A_{kj}} \quad \dots\dots\dots(42)$$

For the calculation of Wilson's parameter in ternary system, those of binary systems were calculated with the objective function of activity coefficients of binary systems.

The vapor pressures of pure components at arbitrary temperature were estimated by Antoine equation:

$$\log P_i^0 = A_i - \frac{B_i}{t + C_i} \quad \dots\dots\dots(43)$$

And $y_i = \frac{r_i P_i x_i}{\pi} \dots\dots\dots(44)$

The temperature approximation in Newton's method was carried by

$$t = t_0 + \Delta t = t_0 - \frac{\sum \frac{r_i x_i}{\pi} (e^{Ai - \frac{B_i}{t+C_i}})}{\sum \frac{r_i x_i B_i}{\pi (t+C_i)^2} (e^{Ai - \frac{B_i}{t+C_i}})} \dots\dots\dots(45)$$

Latent heats were predicted by the following equation on the assumption of ideal gas²⁸⁾:

$$\frac{L_b}{T} = 23.61 \left(\frac{P}{T} \right)^{-0.119} \dots\dots\dots(46)$$

where P pressure(atm), T temperature($^{\circ}$ K), and L_b is the latent heat[kcal/kgmole]

Minimum reflux ratio was obtained by Acrivos' equation³⁰⁾.

$$Dx_0(i) = \frac{B(i)}{P(i)} \left\{ R_m D - \frac{P(h) Dx_0(h)}{B(h)(P(i) - P(h))} - \sum_{j=i+1}^m \frac{P(j) x_F(j)}{B(j)(P(i) - P(j))} \right\} \dots\dots\dots(47)$$

, where $h < i \leq l$

$$\sum_{i=1}^m Dx_0(i) = D \dots\dots\dots(48)$$

Minimum theoretical number of plater was obtained by employing Fenske method.

The location of feed plate was decided by applying Fenske's equation to the key components of feed flashed.

Number of plates by Rathore's suggestion²⁹⁾ as follows:

for $\left[\frac{R - R_m}{R + 1} \right] < 0.125$

$$\left[\frac{S - S_m}{S + 1} \right] = 0.5039 - 0.5963 \left[\frac{R - R_m}{R + 1} \right] - \log 0.0908 \log \left[\frac{R - R_m}{R + 1} \right] \dots\dots\dots(49-a)$$

for $\left[\frac{R - R_m}{R + 1} \right] > 0.125$

$$\left[\frac{S - S_m}{S + 1} \right] = 0.6257 - 0.9868 \left[\frac{R - R_m}{R + 1} \right] + 0.5160 \left[\frac{R - R_m}{R + 1} \right]^2 - 0.1738 \left[\frac{R - R_m}{R + 1} \right] \dots\dots\dots(49-b)$$

Diameter of the column

$$D_c = \left[\left(\frac{4}{\pi v} \right) (D)(r+1)(22.2) \left(\frac{T_{Dv}}{273} \left(\frac{1}{P} \right) \right) \left(\frac{1}{3600} \right) \right]^{1/2} \dots\dots\dots(50)$$

where $V = 7.61 \left(\frac{1}{P} \right)^{1/2} \dots\dots\dots(51)$

Height of column

$$H_c = 0.61 \left(\frac{S}{\eta} \right) + 4.27 \dots\dots\dots(52)$$

Temperature correction factor and minimum allowable temperature difference for heat transfer were assumed to be unity and 10° C respectively³¹⁾.

Cost basis of optimization^{29,30)}

$$\text{Total annual cost} = \text{annual operating cost} + \frac{\text{total installed cost}}{\text{project life}} \dots\dots\dots(53)$$

Installed cost of column = $4.34 \left[762 D_c \right.$

$$\left. \left(\frac{H_c}{12.2} \right)^{0.68} \right] \dots\dots\dots(54)$$

If the column pressure is more than 3.4 atms, a correction factor of

$$1 + 0.0147(P - 3.4)$$

is applied.

$$\text{Installation cost of trays} = 70 \left(\frac{S}{\eta} \right) \left(\frac{D_c}{1.22} \right)^{1.19} \dots\dots\dots(55)$$

Instrumentation = 4,000.00

Maintenance cost of the column = 2% of the total installed cost.

utility costs

steam: \$ 3.24/10⁶kcal

ammonia: \$ 20/10⁶kcal

Benzene: 0.13\$/kg, Acetic acid; 0.23\$/kg

Material of construction: carbon steel. When stainless steel is employed, the installation cost becomes five times of CS.

Assumed values

$\eta = 80\%$ in all the column for distillation

degrec of extraction = more than 60%

acetic acid recovery = above 95%

operating hours = 8500hrs/yr

project life = 10 years.

The design procedures are represented in Fig. 2.

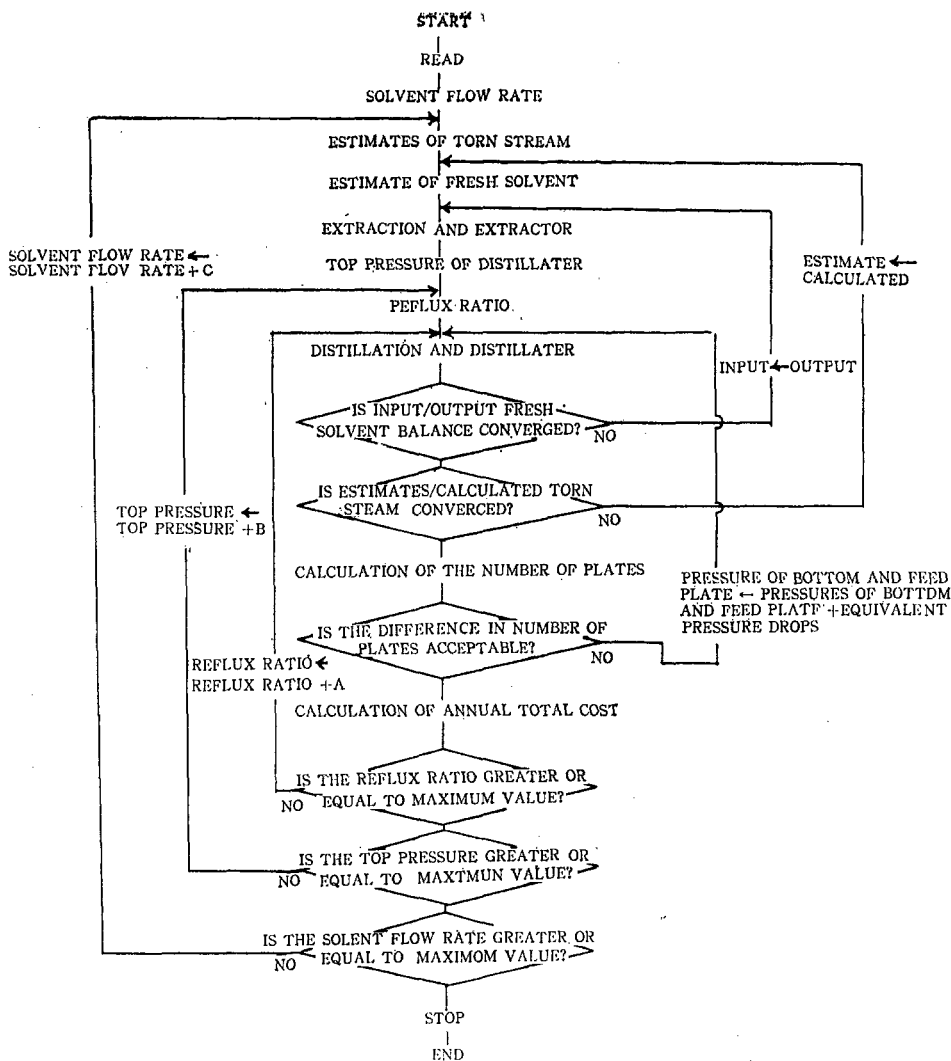


Fig. 2. Computational procedure.

V. Results and Discussions

Through the present work, more than 1,500 designs were carried. The results represented here are rough-out results. Data are arranged to show the effects of energy integration, solvent flow rate, tower pressure and reflux ratio on total cost.

The availability of energy integration is shown in Fig.3. From the figure, it is recognized

that energy integration is at least available with minimum benefits of 5% of total cost. The availability is rapidly increased with increasing solvent flow rate to the extent of some ten percents.

Fig.4 shows the effect of solvent flow rate on total cost. As was shown in Fig.3, energy integration was at least available, accordingly following discussions are on energy integrated system. Increase in solvent flow rate may cause

direct increase in heat duty which in turn cause direct increase in utility cost. But Fig.4 reveals the increase in flow rate affects the separation cost not so much as expected. That unexpected appearance is due to energy integration. The availability of energy integration was considerable at high solvent flow rate. Accordingly, at high solvent flow rates, the costs were not strongly influenced by solvent flow rate.

Next to be examined is the effect of pressure as shown in Fig.5. The pressures of distillation tower were changed from one up to five atms. Within that range of pressures, no oligomers are formed.

As one atm was increased, about two percents

of cost increase were found. It is based on the increased boiling temperature followed by increased heat duty and finally followed by higher utility cost of heat exchanger operation.

The effect of reflux ratio on annual total cost is shown in Fig. 6.

Reflux ratio was varied wide ranges of times of that of minimum. Increasing reflux ratio induces heavy heat duty deducing the height of tower of which installation cost decrease can not follow the increase of cost associated with increased heat duty.

Optimum reflux ratio was found at 1.03 times of minimum reflux ratio. But this is not considered to be physically operable.

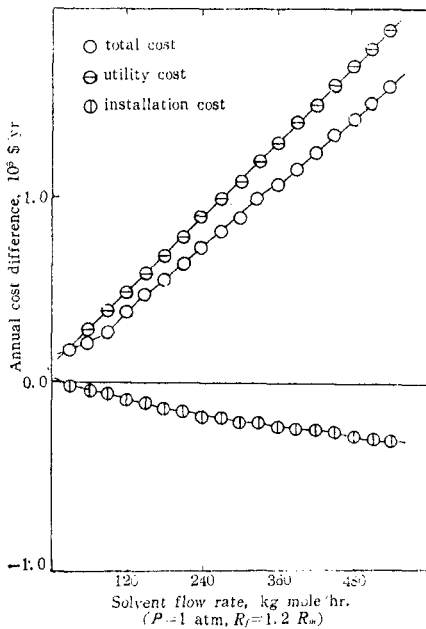


Fig. 3. Financial benefits by energy integration.

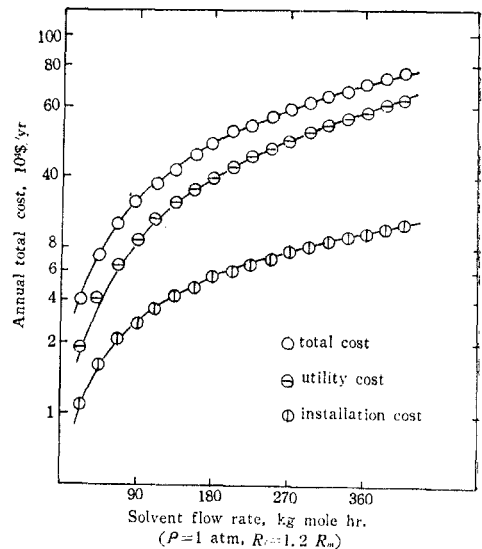


Fig. 4. The effect of solvent flow rate on annual total cost.

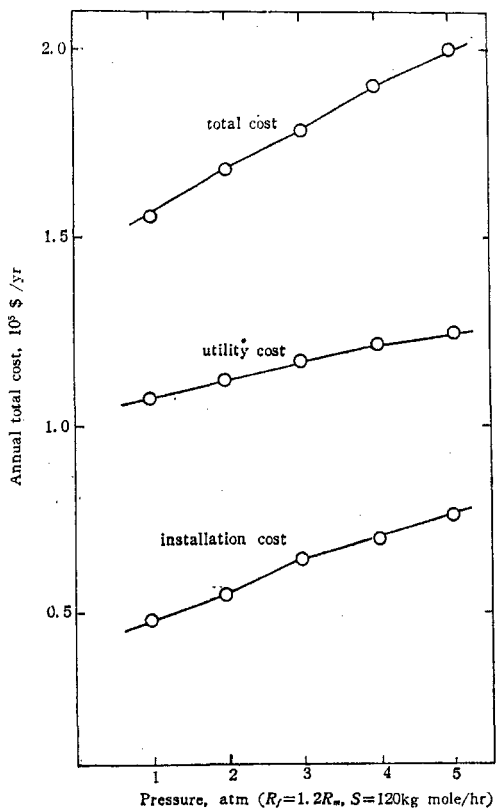


Fig. 5. The effect of pressure on annual total cost.

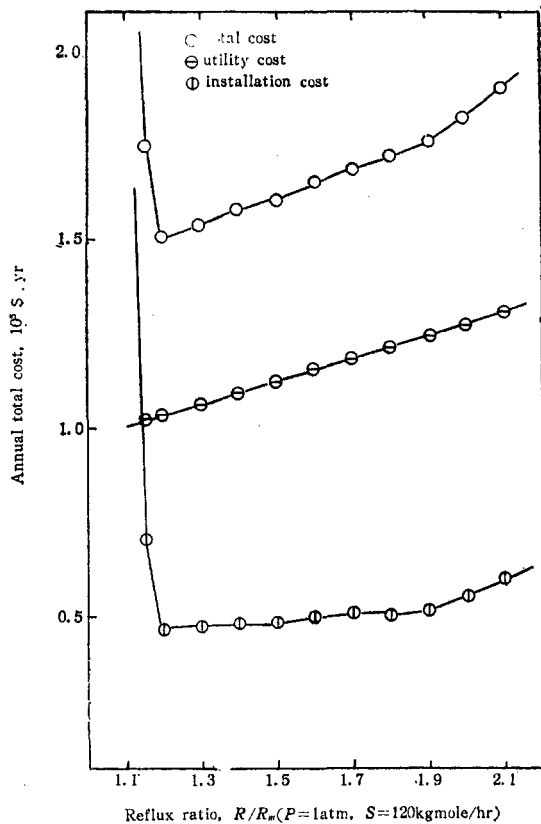


Fig. 6. The effect of reflux ratio on annual total cost.

VI. Conclusions

From the obtained results, it can be concluded as follows.

1. As possible as we can operate the extractor, the least amount of solvent flow rate is desirable.
2. The operation of distillation tower is required to be performed at atmospheric pressure with the closest reflux ratio to minimum as long as the distillation tower can be operated physically.
3. Energy integration is at least available with rapid increasing availability with increasing solvent flow rate.

Nomenclature

- D_c =column diameter [m]
- d_N =nozzle diameter [inch] or [ft]
- d_j =jet diameter [inch] or [ft]
- h_c =head required to overcome the continuous phase flow effect [ft]
- h_N = head required to overcome friction through perforation [ft]
- h_v =head required to overcome interfacial effect [ft]
- m = equilibrium distribution coeff. [-]
- N_N =number of perforations [-]
- U_N =velocity at nozzle [ft/hr]
- U_c =superficial velocity of continuous phase [ft³/hr-ft²]
- U_d = superficial velocity of dispersed phase

k_a =individual volumetric mass transfer coeff.	[ft ³ /hr-bt ²]	14. D. F. Rudd, C. C. Wastson, Strategy of Process Engineering J. Wiley & Sons Inc., New York(1968)
	[hr ⁻¹]	15. R. W. H Sargent, A. W. Westerberg, Trans. Inst. Chem. Engrs., 42 , 7190(1964).
K_a =overall volumetric mass transferer coeff.	[hr ⁻¹]	16. R. S. Upadhye, E. A. Grens, AIChE EJ., 18 , 465(1972).
n_F^A =molal flow rate of acetic acid in extractor feed	[kgmole]	17. J. H. Christensen, D. F. Rudd, AIChE J., 15 , 94(1969)
R_m =minimum reflux ratio	[-]	18. R. W. Barkley, R. L. Motard, Chem. Eng. J., 3 , 265(1972)
S_m =minimum number of theoretical step.	[-]	19. T. K. Pho, L. Lapidus, AIChE J., 19 , 1170 (1973)
T_{DV} =dew point at the column top	[°K]	20. Hand, J. Phys. Chem., 34 , 1961(1930).
μ =viscosity	[cP]	21. International Critical Table, Vol. 3, McGraw Hill, New York (1929)
ν =interfacial tension	[dyne/cm]	22. Soc. of Chem. Engrs., Japan, Bussei Jyosu, Maruzen, Tokyo(1966).

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