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CONTINUOUS ETHANOL STRIPPING PROCESS COUPLED WITH A RECTIFICATION SYSTEM

Chay B. Pham*, Masatoshi Matsumura** and Hiroshi Kataoka**

ABSTRACT

Elimination of ethanol inhibition to improve the productivity and the productivity and the separation of ethanol from the fermentation broth were carried out by the continuous stripping process coupled with the rectification system using coconut shell charcoal (CSC) as packing material. The ethanol stripping ability of inert gas in the stirred tank and bubble column reactors was interacted with the aeration rate, time and temperature. As the aeration rate, time, and temperature increased, the stripping rate increased. With the use of 0.75 mm of CSC particle at 45°C for the rectifier column, the condensate ethanol concentration ranged from 730-670 g/L as gas flow rate was increased from 0.5-6 L/min in the rectifier. These results establish the process of concentrating ethanol from 80 g/L to 730 g/L [to 92% (v/v)] by a two step operation without applying reflux.

Introduction

Process of fermentation production can be performed by batch, fed batch and continuous culture. Generally, continuous culture is said to give the highest productivity among the various culture modes if it can be operated with no touble and the activity of microorganisms does not degenerate. In industry, however, few continuous cultures have been carried out successfully for various reasons. Most fermentations and many chemical reactions are characterized by some degree of product inhibition (Ghose and tyagi, 1979). The production of inhibitory products or by-products during the course of a fermentation causes growth rates and reaction rates to slow and increase cell death rates. If the inhibitory compounds are removed as they are formed, the reaction rates and cell variability can be maintained. Ethanol fermentation, for example, is product inhibited reaction with a maximum final tolerable ethanol concentration ranging from 6-15% (w/v) depending upon the microorganism (Bazua and Wilke, 1977).

Present distillation methods to separate ethanol from fermentation broths are energy intensive and frequently use more energy than the fuel value of re-

*National Institutes of Biotechnology and Applied Microbiology (BIOTECH), University of the Philippines at Los Baños, College, Laguna, Philippines.
**Institute of Applied Biochemistry, University of Tsukuba, Ibaraki, Japan.

covered ethanol. Using traditional distillation methods range from 50 to 80% of the energy required for ethanol production depending on the ethanol concentrations in fermentation broths. This accounts for 4.4 to 9.2 MJ/L of 95% (v/v) ethanol and 2.6 MJ/L of ethanol by additional energy needed to break the azeotrope (Malik, Ghose and Ghose, 1983). During the past 10 years, many separation processes have been developed to overcome these problems such as ethanol separation from the fermentation broth under vacuum (Cysewski and Wilke, 1978), solvent extraction (Minier and Goma, 1982) perstraction (Matsumura and Markl, 1986) and ultrafiltration (Sourirajan, 1987). These innovations have certain limitations of the practical application.

The objective of this study is to develop the stripping process coupled with rectifification system. In this process, the inert gas is used for the stripping of ethanol from the solution in a reactor and the stripped ethanol vapor is concentrated with the rectifying column packed with coconut shell charcoal (CSC).

Theoretical Considerations on Ethanol Stripping

Batch process. The schematic diagram of the stripping process is shown in Fig. 1. Gas is fed into the bottom of the vessel at a constant volumetric flow rate Q. The initial ethanol concentration is C_{Li} and and its concentration leaving the liquid surface to transfer into the gas phase is $C\phi$. Under steady gas flow conditions, the total gas volume being $V\phi$, the liquid volume in the reactor is V_L.

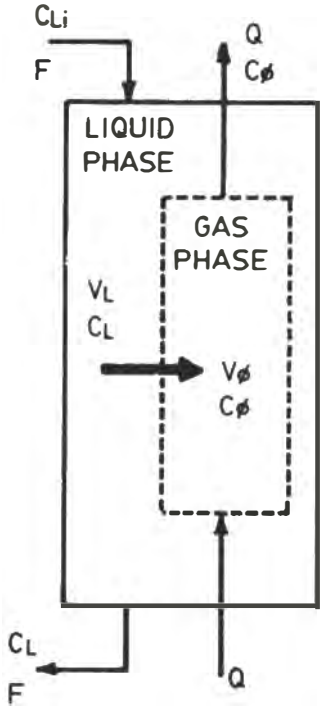


Figure 1. Schematic diagram of stripping process.

The liquid phase is assumed to be well mixed, so that C_L is constant throughout the vessel, and changes with time. The mass transfer for ethanol in the batch liquid phase in an unsteady state is given by equation (1).

$$V_L \frac{dC_L}{dt} = V_L (k_{La}) (C_L - \frac{RT}{P^* \gamma \nu m} C\phi) \tag{1}$$

where it is assumed that Henry's law defined by equation (2) is held between the gas and liquid interfaces.

$$C\phi = \frac{\nu m \gamma P^*}{RT} C_L \tag{2}$$

When the inlet gas concentration is allowed to vary, equilibrium is upset and the vapor ethanol transfers across the phase interface. An unsteady state, mass transfer for ethanol in the continuous gas phase is given by equation (3).

$$V\phi \left(\frac{dC\phi}{dt}\right) = V_L (k_{La}) \quad C_L - \frac{RT}{P^* \gamma \nu m} C\phi - QC\phi \tag{3}$$

By combining equations (1) and (3), one obtains the following equation (4)

$$V\phi \left(\frac{dC\phi}{dt}\right) = -QC\phi - V_L \frac{dC_L}{dt} \tag{4}$$

Differentiating the equation (2) with time t:

$$\frac{dC\phi}{dt} = \frac{\nu_m \gamma P^*}{RT} \cdot \frac{dC_L}{dt} \tag{5}$$

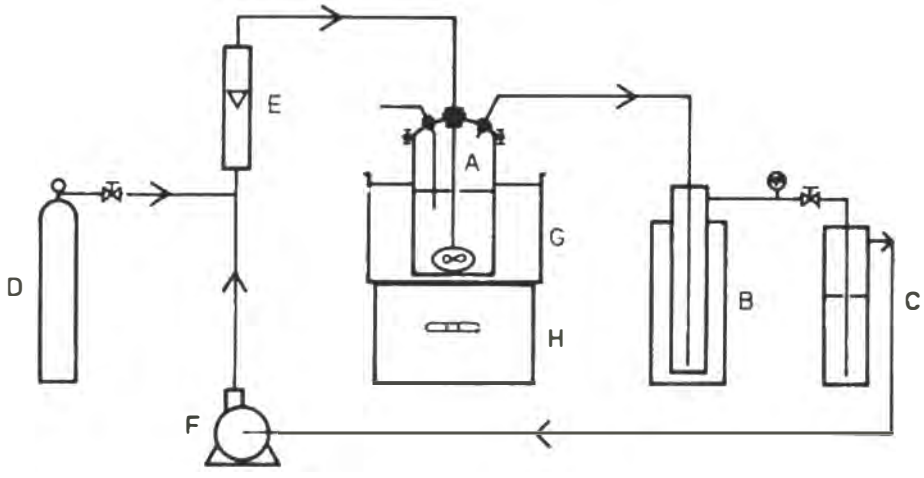
Using equations (2) and (5), equation (4) becomes equation (6).

$$\left(1 + \frac{V\phi}{V_L} \cdot \frac{\nu_m \gamma P^*}{RT}\right) \frac{dC_L}{dt} = - \frac{\phi}{V_L} \cdot \frac{\nu_m \gamma P^*}{RT} C_L \tag{6}$$

When the second term of the left side of equation (6) is very small compared to 1, equation (6) then becomes:

$$\frac{dC_L}{dt} = \frac{Q}{V_L} \cdot \frac{\nu_m \gamma P^*}{RT} C_L \tag{7}$$

Integrating equation (7) with the initial condition that $C_L = C_{Li}$ at t = O, the stripping rate of ethanol can be expressed by equation (8):



A: conventional stirred tank reactor, B: cold trap, C: gas humidifier, D: N_2 gas cylinder, E: flow meter, F: pump, G: water bath, H: magnetic stirrer.

Figure 2. A schematic diagram of stripping ethanol in a conventional stirred tank reactor.

Continuous process. The experimental set up is shown in Figure 3, but without the rectification system. It is composed of a bubble column, cold trap 1 (–25°C), and cold trap 2 (–50°C). The temperature of the cold trap was maintained by a cooler (Taiyo Coolpipe 50 L for cold trap 1 and Taiyo Coolpipe 600 L for cold trap 2) which is controlled by the automatic temperature controller.

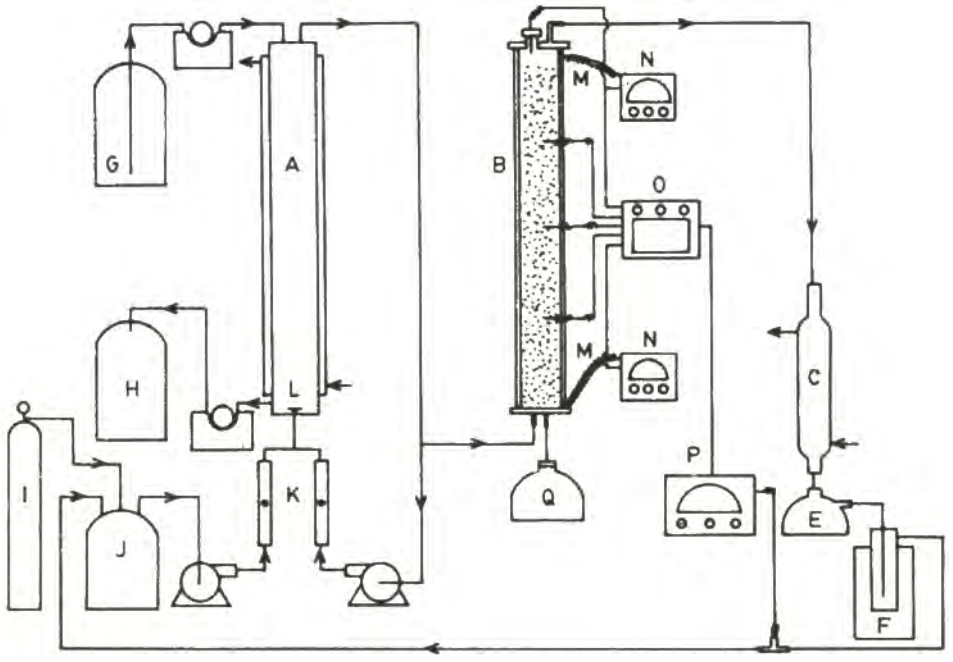
The bubble column had an inner diameter of 5 cm and a total height of 105 cm. A pipe with 16 holes of 0.05 cm. diameter was connected in the bottom of the bubble column and used as a sparger. The column was made of poly-acrylate. The temperature of the aqueous ethanol solution in the bubble column was maintained by a temperature controlled water jacket. The water was supplied from a water batch, the temperature of which was controlled by the automatic tempreature of which was controlled by the automatic temperature controller (Taiyo Thermo Minder DX-80).

The feed was supplied continuously by a peristaltic pump to the top of the bubble column. To keep the volume constant in the bubble column, a portion of the aqueous ethanol solution was continuously pumped out at the bottom of the column. Carbon dioxide (CO_2) gas from a CO_2 cylinder pumped through a sparger and this gas stripped the ethanol from the aqueous solution. The stripped ethanol condensed in the cold traps.

The process variables were feed rates (2, 4, 8 and 12 mL/min), feed concentrations (65, 80 and 100 g/L), temperature (20, 30 and 37°C) and gas flow rates (4, 6, 10 and 15 L/min). A 1 mL aqueous ethanol solution sample was collected. The ethanol concentration was measured at time intervals of 0, 30, 60, . . . and 420 minutes).

Continuous stripping and rectification process

Figure 3 also shows a schematic diagram of the experimental set up fo the stripping ethanol and rectification process. The same bubble column previously used was employed for stripping of ethanol from the aqueous solutions.



A: stripper; B: rectifier; C: water condenser; E: collector; F: cold trap; G: feed tank; H: by-product tank; I: CO_2 cylinder; J: gas reservoir; K: rotameter; L: sparger; M: heating tap; N: temperature controller; O: recorder; P: gas detector.

Figure 3. Experimental set up for continuous stripping and rectification process.

The rectifier column has an inner diameter of 3 cm and a total height of 105 cm. The column, which was made of stainless steel was packed with 300 g of coconut shell charcoal (CSC). The rectifier bed depth was 92 cm with screening sieves (JIS-Mesh Nos.: 64-32, opening: 0.25-0.5mm) placed above and below to retain the CSC. The column was jacketted with heating tapes to maintain the temperature at a selected level of by using an automatic temperature controller (Nippon Electric Company, FCK-122). The outside surface of heating tapes was insulated by asbestos sheet to prevent heat loss. The temperature in the column was verified by thermocouples 1, 2, 3, and 4. The temperature signals from the automatic temperature controller was recorded by the recorder.

Carbon dioxide (CO_2) gas from a CO_2 cylinder was supplied through a sparger and this stripped the ethanol from the aqueous solution. The stripped ethanol was rectified by the CSC particles packed in a rectifier column.

The ethanol vapor coming out of the rectifier column was measured by the gas detectors (Riken Keiki, Model GP-226) connected with the recorders (Rikadenki Kogyo Co., Ltd. Model R-302).

The process conditions applied for the bubble column were: total CO_2 gas flow rate: 10L/min; recycled gas flow rate: 4 to 9.5 L/min; feed concentration: 80 to 400 g/L; temperature: 30°C and feed rate: 12 mL/min.

Studies on concentrating ethanol in the rectification system were carried out without reflux. The process conditions used for the rectification were 300 g CSC size (0.75 mm), temperature (45°C), and gas flow rate (0.5 to 6 L/min). The preliminary studies showed that the highest condensate concentration of ethanol was obtained at 45°C rectifier column.

Analytical methods

Ethanol concentration was measured by gas chromatography using a Shimadzu GC-BA gas chromatograph with FID detector and integrator (Chromatopac C-RIB, Shimadzu-Corp. Japan) and a glass column (3 mm I.D. x 2 m) packed with Chromosorb 105 (60/80) mesh) at 165°C. The injector and detector temperature were 180°C. Calibration for ethanol analysis was made using a known amount of absolute ethanol solutions and n-propanol was used as the internal standard.

Results and Discussion

Stripping studies

The ethanol stripping ability of N_2-gas in the conventional stirred tank reactor (CSTR) was conducted using aqueous ethanol solutions. Results of the experiments indicated a strong dependence of stripping on gas flow rate, process temperature and time.

The effect of gas flow rate on the stripping rate of ethanol was process temperature dependent. At a given process temperature, the stripping rate of ethanol increased with increasing gas flow rate (Figure 4). With the increase in gas flow rate the effect of thermodynamic mass transfer of ethanol in the liquid phase into the vapor phase increased and subsequently stripped ethanol out of the aqueous ethanol solution.

The stripping of ethanol from the aqueous solution by the N_2-gas was also studied at three temperatures commonly used in the fermentation practice. At higher operating temperatures, there was a greater stripping rate from an efficiently aerated system (Figure 5). By the employment of equation (8), the experiment results are plotted in a semilog paper, from which it can be seen that the stripping rate is a linear function of the aeration rate and time. It could be expressed as follows:

$$\ln \frac{C_L}{C_{Li}} = -kqt \qquad (11)$$

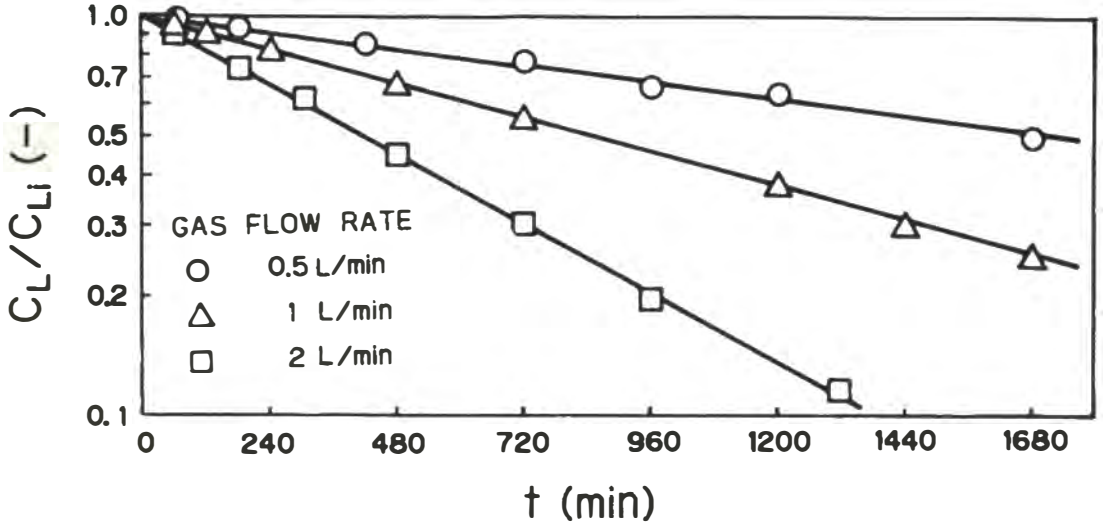


Figure 4. Effect of N_2 gas flow rate on the stripping rate of ethanol in the CSTR using 80 g/L of 400 mL aqueous ethanol solution at 30°C.

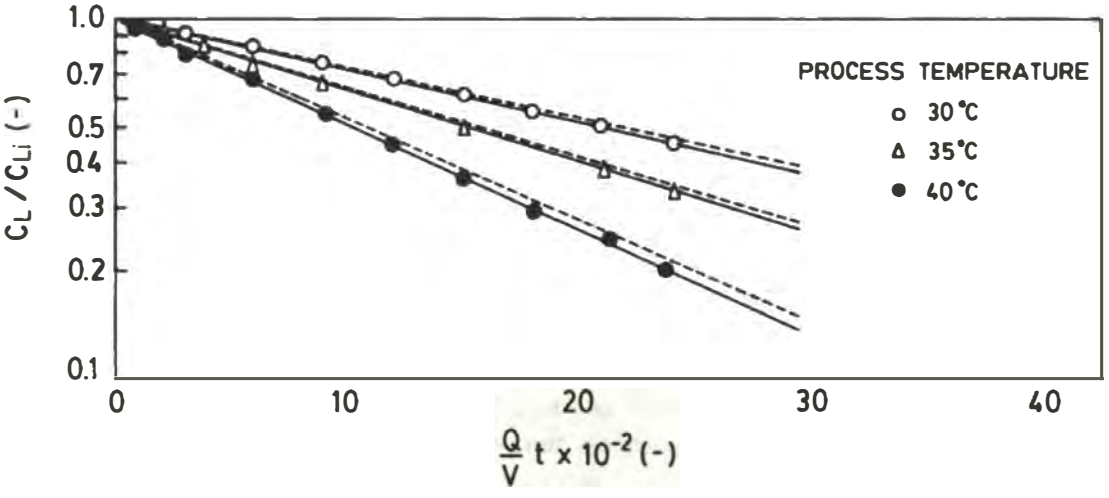


Figure 5. Effect of the process temperature on the stripping rate of ethanol in the CSTR using 80 g/L of 400 mL aqueous ethanol solution and 0.5 L/min N_2 gas flow rate.

– – – – – – theoretical value
———— experimental value

From the slope of the experimental curve in Figure 5, the value of k in Equation (11) was determined.

For the theoretical calculation based on the experimental conditions, the value of k in Equation (8) was also determined. The experimental values of k agree fairly well with the theoretical values (Table 1). It appears to be supported by the assumptions that the gas outlet from a reactor was saturated with ethanol vapor

and that there was an equilibrium relation in the ethanol concentration between the liquid and the gas interfaces.

Table 1. Comparison of k values between the experimental result and theoretical calculation for stirred tank reactor

Temperature (°C)	$k \times 10^{-4}$ (–)	
	Experimental value	*Theoretical value*
30	3.31	3.22
35	4.58	4.41
40	6.74	6.60

Continuous stripping studies

Recently, the continuous operation process has gained much attention in fermentation technology. The operating conditions affecting the stripping system to obtain a steady state were studied. Figure 6 shows the effect of the feed rate and liquid depth in the bubble column on the liquid ethanol concentration at steady state using 80 g/L feed concentration at 30°C and 10 L/min CO_2-gas flow rate. At a liquid depth of 13.5 cm, a steady state of the stripping process could not be obtained at all feed rates.

The variations in the ethanol concentration in the bubble column using different CO_2-gas flow rate was also observed (Figure 7). The operating process to obtain steady state occurred at high flow rates and low liquid depth. This phenomenon could be due to the increase of mass transfer of the gas phase into liquid phase resulting in the increase of the stripping rate of ethanol.

The process operation needed to achieve a satisfactory separation of ethanol also depends on the temperature of the bioreactor. If the fermentation process is assumed to be carried out at a temperature range of 20-37°C, the liquid concentration of ethanol in the bioreactor at steady state could be maintained at 57.4, 63 and 69.5 g/L with operating temperatures at 37°C, 30°C and 20°C, respectively and 54 cm liquid depth (Figure 8).

The product inhibition associated with the liquid ethanol concentration in the bioreactor was eliminated by using the stripping process. This allows the use of high sugar levels to be fermented in the fermentation process. The liquid concentration of ethanol could be maintained at 50-70 g/L at steady state and maximum ethanol supplied for the stripping system would be 65-100 g/L with the liquid depth variation of 27-81 cm (Figure 9).

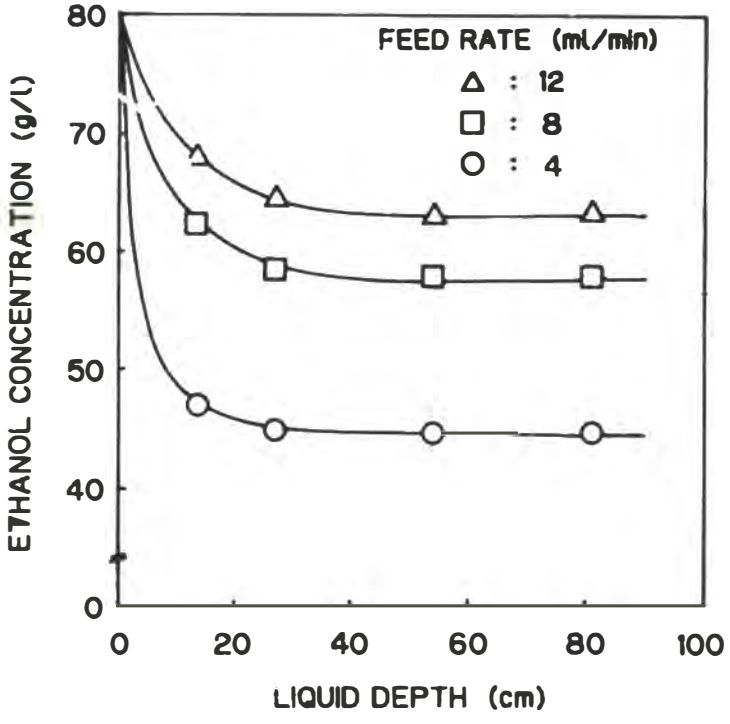


Figure 6. Effect of feed rate and liquid depth in column on residual ethanol concentration at steady state using 80 g/L feed concentration at 30°C cand 10 L/min in CO_2 gas flow rate.

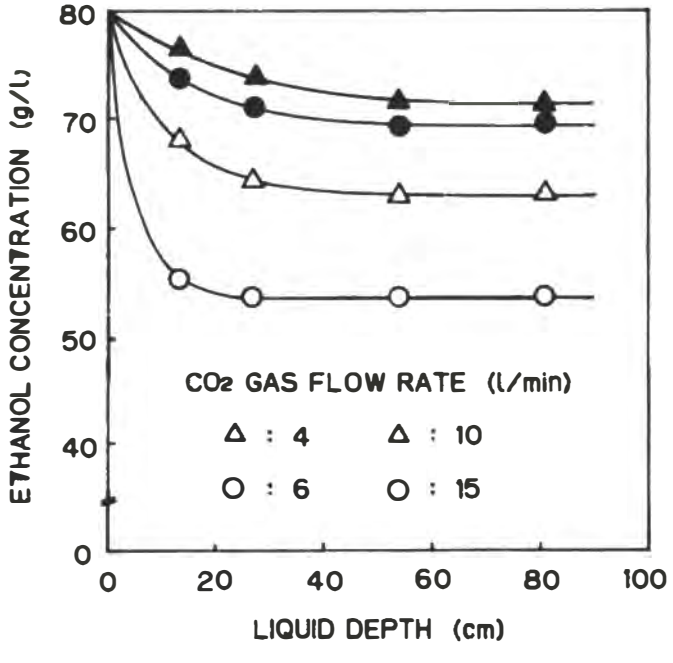


Figure 7. Effect of CO_2 gas flow rate and liquid depth in column on residual ethanol concentration at steady state using 80 g/L feed concentration at 30°C and 12 mL/min feed rate.

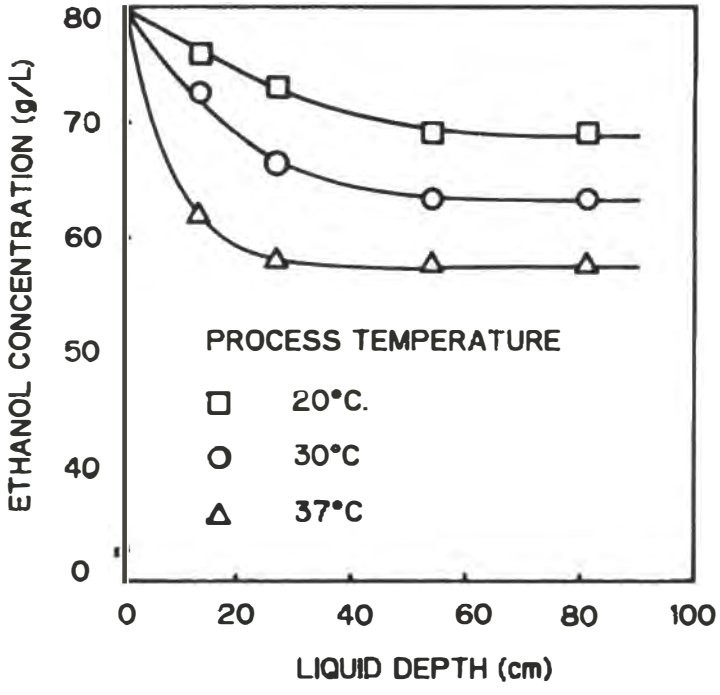


Figure 8. Effect of process temperature and liquid depth in column on residual residual ethanol concentration at steady state using 80 g/L feed concentration, at 12 mL/min feed rate and 10 L/min CO_2 gas flow rate.

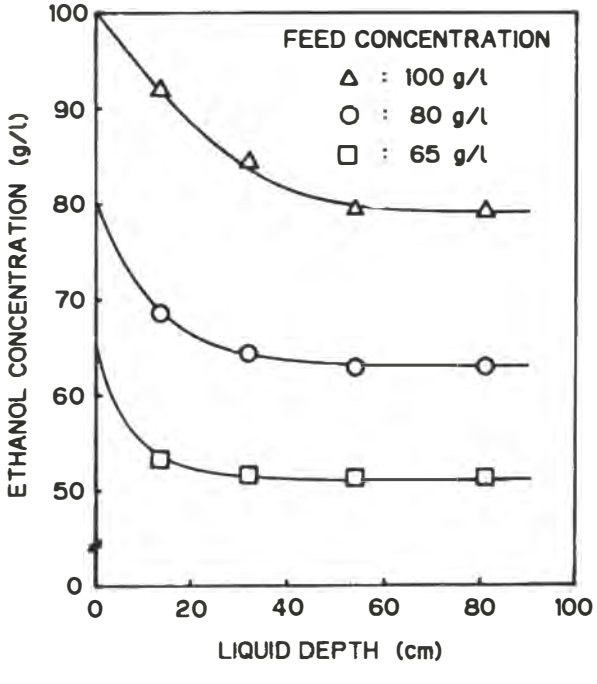


Figure 9. Effect of feed concentrations and liquid depth on residual ethanol concentration at steady state using 12 mL/min feed rate at 30°C and 10 L/min CO_2 gas flow rate.

The ethanol concentration in a bubble column reactor at steady state calculated using equation (10) are shown in Table 2. The experimental values of the ethanol concentration at steady state obtained from Figure 6 to 9 coincide fairly well with those of theoretical ones, showing that the assumption used for derivation of equation (10) are reasonable.

It is interesting to note that this innovation process could be applied for the simultaneous fermentation and stripping process. The yeast-strains used in the fermentation process usually exhibited ethanol inhibition at concentrations ranging from 60-100 g/L. If the ethanol is removed by applying this stripping process during the fermentation, the high reaction rates and good substrate utilization could be obtained.

Table 2. Comparison of the experimental and theoretical values of the ethanol concentration in the reactor at steady state based on process conditions

	Process conditions			*Ethanol concentration (g/L) at steady state*	
Feed rate (mL/min)	*Temperature (°C)*	*Feed concentration (g/L)*	*Gas flow (L/min)*	*Experimental value*	*Theoretical value*
4	30	80	10	44.5	44.3
8	30	80	10	57.5	37
12	30	80	10	63.5	63.1
12	30	80	4	71.5	72.2
12	30	80	6	69.5	68.9
12	30	80	10	63.5	63.1
12	30	80	15	54.5	57
12	20	80	10	69.5	69.2
12	30	80	10	63	63.1
12	37	80	10	57.4	58.8
12	30	65	10	51.2	51.8
12	30	80	10	63	63.1
12	30	100	10	79.5	78.8

Continuous stripping and rectification studies

The pattern of the condensate concentration of ethanol effected by gas flow rate in the continuous stripping and rectification process without reflux is shown in Figure 10. Using 80 to 144 g/L ethanol feed concentrations, the ethanol concentrations of the condensate obtained were 300 to 500 g/L in the water condenser and 600 to 680 g/L in the cold trap. As the feed concentrations of the aqueous ethanol solution were increased, the concentrations of ethanol vapor mixture stripped from the bubble column also increased and consequently increased the ethanol concen-

tration of the condensate in the condenser and in the cold trap. On the other hand, as CO_2 gas flow rate increased, the concentrations of aqueous ethanol solution in the bubble column at steady state decrease and consequently the concentration of ethanol vapor mixture supplied to the rectifier also decreased.

It was similar to the case using 280 to 400 g/L ethanol feed concentration (Figure 11). The condensate ethanol concentrations after rectifier column were 630 to 695 g/L in the water condenser and 705 to 730 g/L in the cold trap.

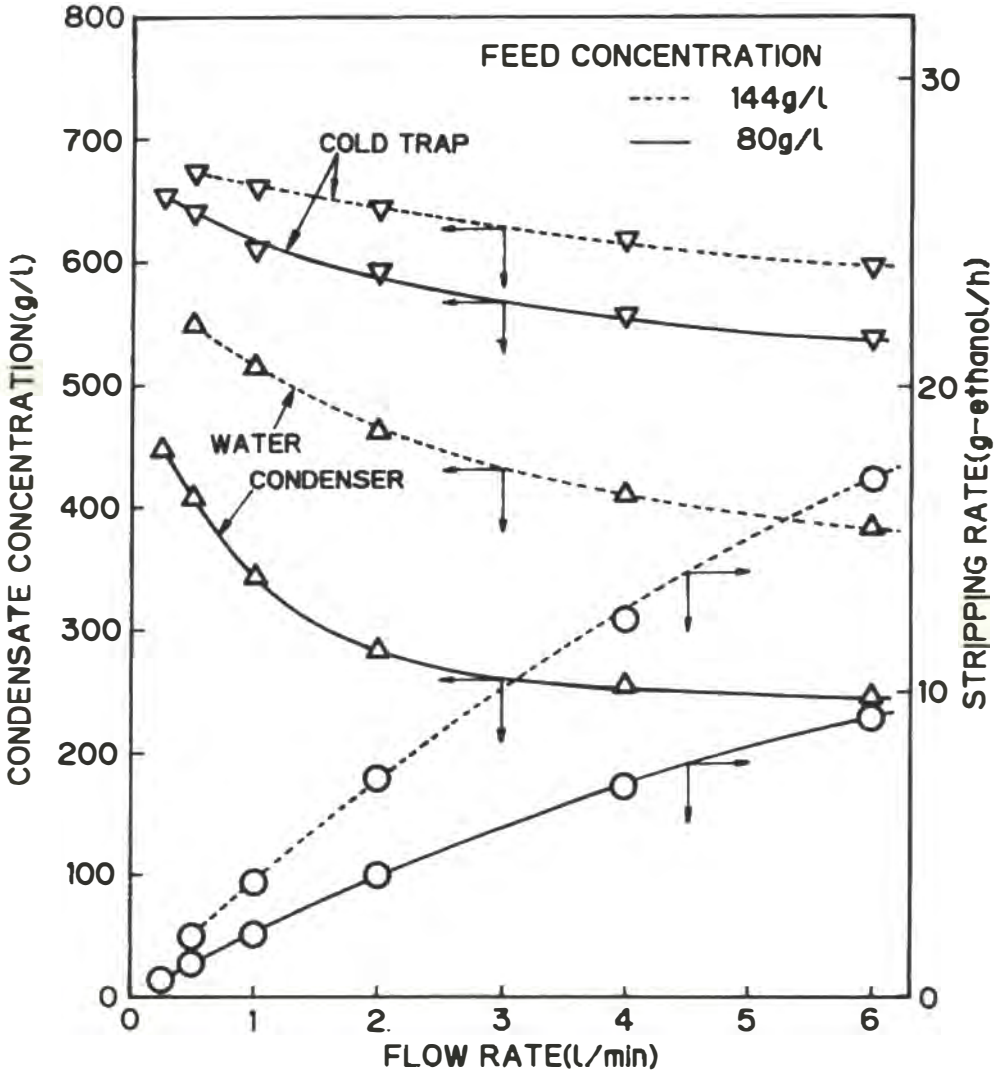


Figure 10. Condensate concentrations of ethanol in the continuous separation process by using a stripper and coconut shell charcoal packed columns.

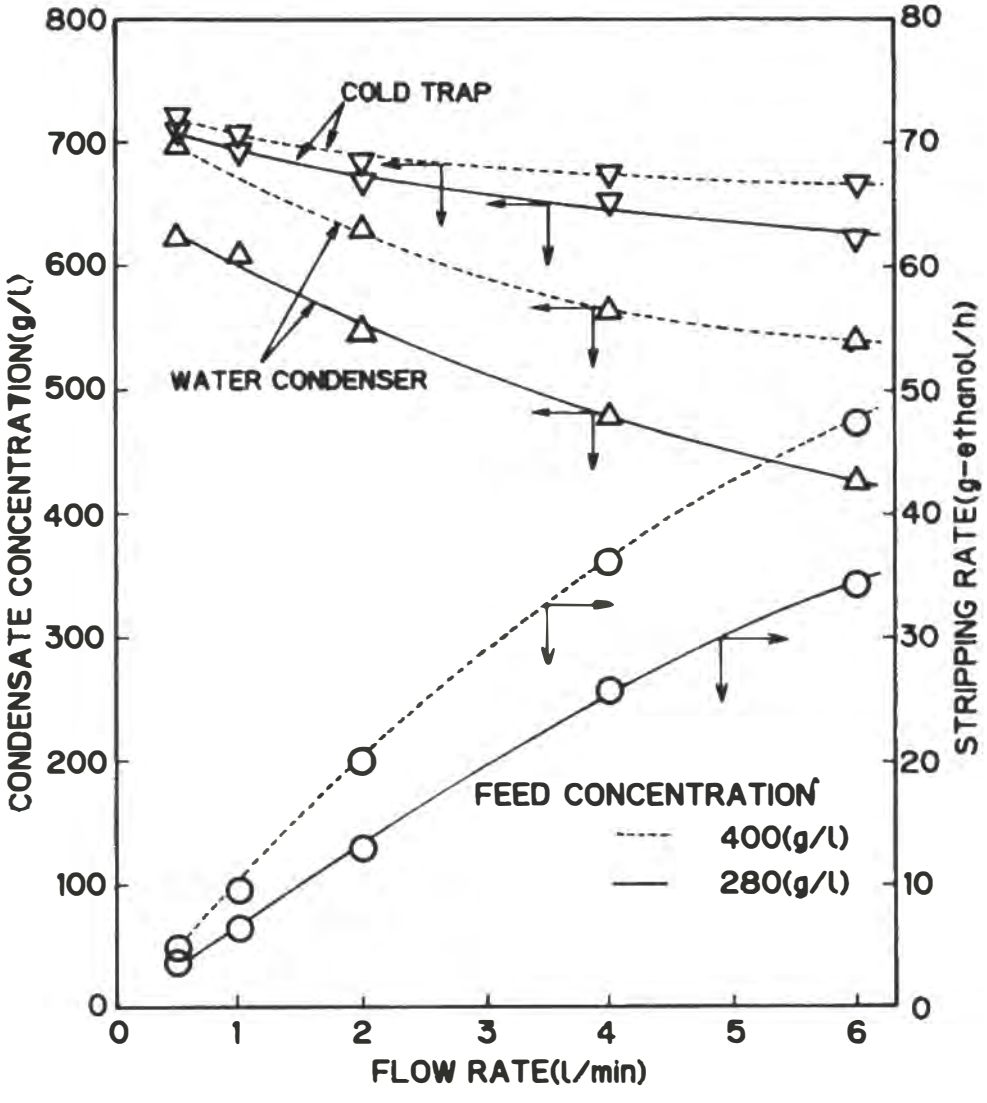


Figure 11. Condensate concentration of ethanol in the continuous separation process by using a stripper and coconut shell charcoal packed columns.

These results establish the possiblity of concentrating ethanol from 80 g/L ethanol feed concentration to to 730 g/L [92% (v/v)] final condensate concentration by a two step process without applying reflux and avoiding the use of very low temperature such as that of the cold trap.

Summary and Conclusion

The stripping process of ethanol used in the fermentation has been developed to eliminate product inhibition and reduce high energy expenditure used for product recovery in the distillation process. The mathematical models for the batch and continuous processes are derived from the assumption that there was no resistance between gas and liquid interfaces. The experimental values are in good agreement with the theoretical values.

The ethanol vapor stripped out from the reactor was continuously rectified on the CSC at 45°C. The condensate ethanol concentration was 730 g/L as gas flow rate of 0.5 L/min was applied. It indicated that the use of the distillation as in the conventional distillation process could be totally eliminated. The new process demonstrates the potential application for the pilot scale.

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Nomenclature

C_L	ethanol concentration in liquid phase	(mole/L)
C_{Li}	initial ethanol concentration in liquid phase	(mole/L)
$C\phi$	ethanol concentration in gas phase	(mole/L)
F	feed rate	(L/min)
K_{La}	volumetric mass transfer coefficient	(min^{-1})
P^*	vapor pressure of pure ethanol	(atm.)
Q	volumetric gas flow rate	(L/min)
R	gas constant	(L. atm/∴K.mole)
T	absolute temperature	(°K)
t	time	(min)
V_L	volume of liquid phase	(L)
v_m	molar volume of liquid solution	(L/mole)
$V\phi$	volume of gas phase	(L)
Greek letter γ	liquid phase activity coefficient	(–)

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