EFFECT OF FLOW PATHS ON SEPARATION OF BINARY COMPONENTS BY GAS-LIQUID CHROMATOGRAPHY

Kyung Ho ROW and Won Kook LEE*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 131 Dongdaemun, Seoul, Korea

(Received 31 March 1986 • accepted 5 October 1986)

Abstract—A scaled-up chromatographic system was used to separate two close-boiling components, diethylether and dichloromethane, by gas-liquid chromatography. The system was composed of 12 segmented columns and sixty solenoid valves controlled by a programmable controller.

Effects of various flow paths on outlet concentration profiles were investigated to find optimum conditions. Compared to conventional preparative chromatography, moving feed-injection and product-withdrawal made it possible to separate the feed mixtures continuously in two sections, partition section and desorption section.

From the results of experiments, the operating principle of the desirable method was that within a certain time (switching time), less-absorbed component was obtained purely in the partition section, and in the desorption section the remained components were separated by increase in column length. Therefore, continuous separation can be achieved if the operations in the sections are performed within a switching time.

INTRODUCTION

Many separation methods have emerged and found practical applications. However, one of the most powerful and versatile separation processes that has been developed is chromatography [1]. From the start, it was recognized that this method could be used for quantitative separation [2]. Until now, much attempts to scale up analytical gas chromatographic units have been made to treat larger quantity of feed mixtures.

Advantages of the analytical gas chromatography are fast time of analysis, convenient quantitative and qualitative treatment, sensitivity of detection, and simplicity of the apparatus [3]. But it is known that the conventional chromatography is inherently difficult to scale up on an industrial size for the reasons that the method is batch operation for handling the feed mixture as a pulse, and it presents a problem of stabilizing the symtem against mixing or natural convection [4].

Different view points of the way the chromatographic system can best be scaled up have been taken and these fall into two main categories, batch [5] and continuous [6]. In the batch system, a direct scale up of the analytical process is attempted by using larger diameter and length of packed beds. In the continuous system, the chromatographic bed is connected with segmented columns, in which moving feed-injection and product-withdrawal are simultaneously achieved.

In a gas-liquid chromatography, the feed mixtures are distributed preferentially by a stationary phase supported on a relatively inert surface of porous solid particle. That is, the separation is mainly affected by the different solubilities of the feed with the stationary phase [7,8]. The main advantages of the partition system in comparison to adsorption are as follows [9]:

(1) easier desorption of the partitioned products
(2) wider field of application (for heat-sensitive or high boiling liquid mixtures)
(3) more versatile separation systems (more stationary liquid phases than adsorbents)

It is almost impossible to separate continuously feed mixtures using single columns. Therefore, in this system, 12 segmented columns were classified into partition and desorption sections. Each section formed a closed loop, through which carrier gas and desorbent passed respectively. In this paper, the purpose of this work is to investigate the effect of the two flow paths on separation of binary close-boiling components by the gas-liquid chromatography.

EXPERIMENTAL

Materials used in this experiment

The column was packed with Chromosorb A obtain-

* To whom all correspondence should be addressed.

ed from Alltech Associate (U.S.A.). The particle has good capacity to contain stationary liquid and does not easily break down with handling, so it is mainly used for large scale chromatographic separation [10]. The Chromosorb A of 45/60 mesh sizes commercially available were used.

Feed materials used in the experiments were diethylether (DEE) and dichloromethane (DCM), which have the close-boiling points, 34.7°C, and 39.0°C, respectively. Dinonylphthalate was used as a stationary liquid on the solid support and coated by 20% weight fraction with a rotary evaporator (Brinkmann Co.).

Experimental apparatus

Schematic diagram of the overall experimental apparatus is shown in Fig. 1 [11]. Nitrogen was used as the carrier gas and the desorbent. The flow rates of these were controlled by the microneedle valves (A_4, A_5). The two streams were put into the main chromatographic system (I).

Feed reservoir (C) was made of stainless steel, 6cm I.D., 50 cm height, and filled with 1/8″ and 1/2″ ceramic Raschig rings to enlarge the interfacial area between the carrier gas and the liquid feed mixtures.

Twelve columns were arranged in a circular form. The column was made of stainless steel, 1cm I.D., 30cm height, and the packed height was 25cm. In both ends of the column, glass wool was used to retain the solid particles in place. Each column had four openings, two for entering streams and two for withdrawing streams, and it was covered with ceramics to keep the column temperature constant.

All the lines were made of 1/8″ copper tube to reduce the dead volume in the system and transparent tube was used in the connection part to prevent any gas leakage.

Five solenoid valves (CKD, AB 31-01-4) were used per column. Schematic diagram of the main chromatographic system (I) is shown in Fig. 2. A supporter was made to fix the twelve columns, sixty solenoid valves, and four distributors, and was enclosed with the covers

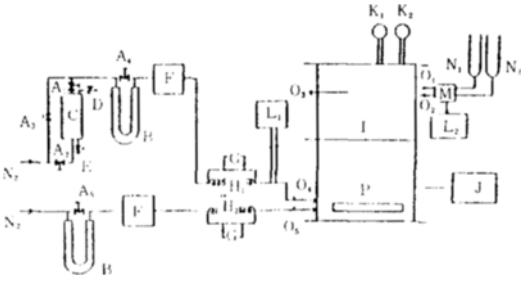

Fig. 1. Schematic diagram of the experimental apparatus.

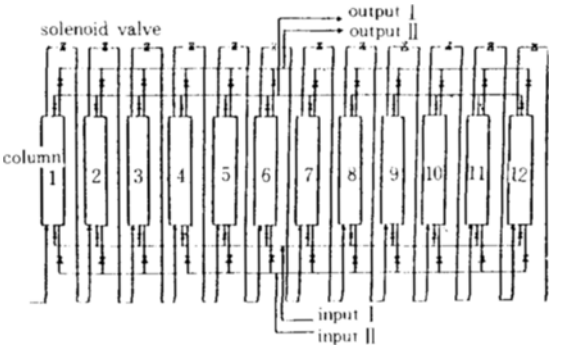

Fig. 2. Schematic diagram of the main chromatographic system.

to maintain room temperature in the system. The four distributors, two for entering streams and two for withdrawing streams, were set up.

Two outlet streams and inlet feed mixtures were analyzed by conventional gas chromatographs (Gow Mac 550P thermal conductivity detector, L_1 and L_2) with syringe (Hamilton Co.) and ten-port multi-functional sampling valves (Valco Instruments Co., M), in which desired amount of sample was taken and transferred to the chromatograph. The sampling valve provides a wide variety of analytical benefits in both gas and liquid chromatography. Table 1 shows the operating conditions of the gas chromatographs (L_1 and L_2). Programmable controller (PC, J) was used to control the solenoid valves.

Before the start of each experimental run, all columns were cleaned by fresh nitrogen. The feed mixture

Table 1. Operating conditions of gas chromatograph.

Sample	DEE, DCM
Detector	thermal conductivity (TCD)
Packing material	Chromosorb A (45/60 mesh)
Column length	1.2 m
Type	coiled copper tube
Diameter	1/8 inch
Oven temperature	140 ℃
Injection temperature	150 ℃
Detector temperature	250 ℃
Current	200 mA
Carrier gas	He, 30 psi
Flow rate	50 cm^3/min

was put into the reservoir (C) through the inlet valve (D) and drained through the outlet valve (E). With the solenoid valve, A_2 and A_3, on, the part of nitrogen was passed into the feed reservoir (C), and the concentration of the inlet feed mixture was controlled by adjusting the microneedle valve (A_1). Outlet flow rates were measured by the bubble flow meters, N_1 and N_2.

Lines of 1/8" copper tube to the main system (I) were wrapped with the heating wire (H_1) to prevent condensation of the feed materials in carrier gas.

By use of the programmable controller (J), the flow paths of partition section and desorption section were programmed respectively, and the paths automatically turned to the next stage after every switching time. The temperatures of several positions were read by the temperature indicator connected to the thermocouples (O_1-C_5). Pressure gauges (K) were installed at inlet and outlet of the main system (I), respectively, so the pressure drops of the two sections were observed.

Dead volume was determined from the measurement of the retention time of a helium sample. The results showed that the dead volume per column was about 31 cm^3 and that of inlet and outlet lines was 10cm^3. Elution profile from the data points in each experimental run was corrected for the total dead volume.

RESULTS AND DISCUSSION

One of the advantages of chromatographic system over simple distillation is that separations can be done even in the cases of small differences in boiling points [12]. When the feed mixture of less-absorbed component, DEE, and more-absorbed component, DCM, was injected into the column of 150 cm, outlet concentration profiles of the components are shown in Fig. 3, in which c_0 denotes the inlet concentration. That is, DEE is eluted initially from the column, and after a while, DCM comes out together with the DEE. Resolution between both components was partially achieved due to the solubility difference of the feed mixture with stationary liquid phase. Using the single column, it is more difficult to separate the feed efficiently as time of feed-injection becomes longer. Therefore different locations for feed-injections and product-withdrawals are needed to operate continuously the system. If the system is equipped with segmented columns and solenoid valves and the feed mixture is injected systematically at a regular intervals, the section of the unseparated components can be reduced. The interval is called by the switching time.

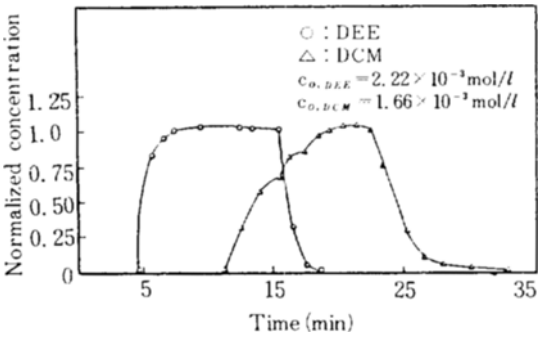

Fig. 3. Concentration profiles in case of pulse input.

150cm, 10min of feed-injection time, outlet carrier velocity = 19.0 cm/sec.

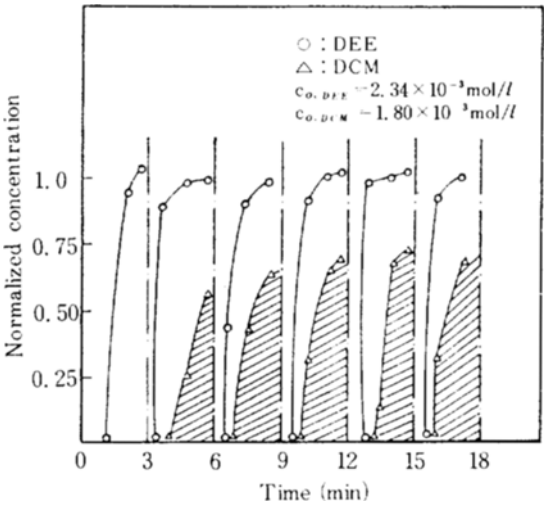

Fig. 4. Concentration profiles in partition section with continuous feed-injection.

SW = 3min, outlet carrier velocity = 19.0 cm/sec, Type = I.

Figures 4 and 5 show the concentration profiles in the partition section. The types of flow paths in the partition section of Figures 4 through 7 are illustrated in Table 2. The overlapped column length in the table means the length of overlapped column section after sequent switching times. At the same carrier flow rates, as the flow paths were changed, different quantities of DCM (areas of the inclined lines in the figures) were obtained. In other words, after a switching time, decrease in number of the overlapped columns lessened the quantity of the more-absorbed component in the partition section.

Generally, the stationary liquid should be chosen to give as high a selectivity with feed materials as possible. Once the system was determined, the switching time could be experimentally measured as the elapsed time from the start to just before the elution of the more-absorbed component, DCM. The column temperature had mainly effect on the switching time, because the

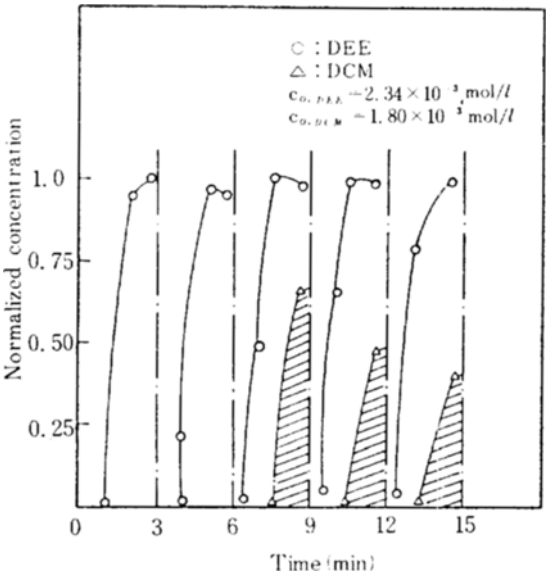

Fig. 5. Concentration profiles in partition section with continuous feed-injection.

SW=3 min, outlet carrier velocity=19.0 cm/sec, Type=Ⅱ.

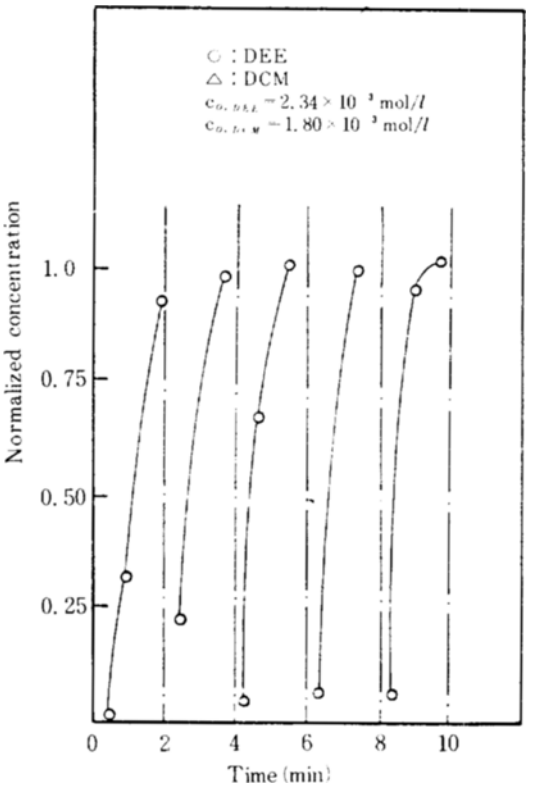

Fig. 6. Concentration profiles in partition section with continuous feed-injection.

SW=2 min, outlet carrier velocity=19.0 cm/sec, Type=Ⅱ.

elution of components from the column depended on the temperature. As the switching time takes a smaller value, as seen in Fig. 6, the less-absorbed component can be obtained purely in the partition section. Moreover, the switching time was also affected by the column length (Fig. 7).

Although DEE is eluted in pure state in the partition section as in Fig. 6, different methods were considered for the effect of flow paths on the resolution of the binary components in desorption section in order to separate continuously the remained components in the section.

Three types of the paths in the partition section and desorption section are listed in Table 2. In Figures 8 through 11, the concentration profile in the partition section was expressed by solid lines, and that in the desorption section by dotted lines. Method of type Ⅳ was that the location of feed-injection and product-withdrawal was shifted to the right side of 3 columns from the inlets of the two sections after every switching time. Figures 8

Table 2. Types of flow paths in partition and desorption sections.

Type	column length (cm)		overlapped column length (cm)		SW (min)	Figures
	partition	section	partition	section		
Ⅰ	75		50		3	4
Ⅱ	75		25		2, 3	5, 6
Ⅲ	150		75		7	7
Type	partition	desorption	partition	desorption		
Ⅳ	150	150	75	75	5, 7	8, 9
Ⅴ	150	150	75	0	7	10
Ⅵ	100	200	0	0	7	11

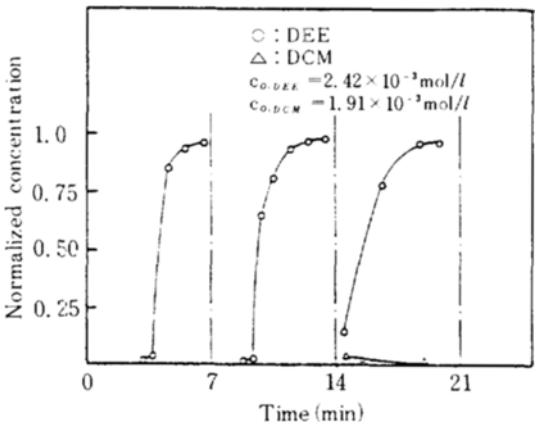

Fig. 7. Concentration profiles in partition section with continuous feed-injection.

SW=7min, outlet carrier velocity=19.0 cm/sec, Type=Ⅲ.

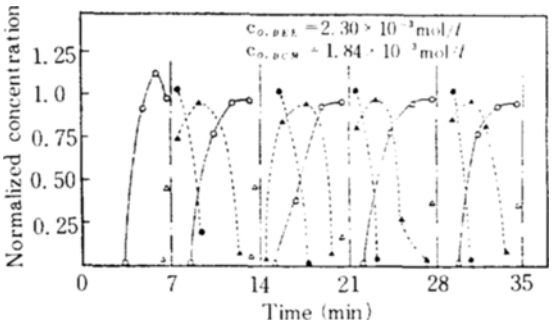

Fig. 9. Concentration profiles in partition section and desorption section.

SW=7min, outlet carrier velocity=19.0 cm/sec, outlet desorbent velocity=18.3cm /sec, Type=Ⅳ.

and 9 show the case for the switching time of 5 min and 7 min, respectively. Under the conditions of the constant velocities of the carrier gas and the desorbent, as the switching time of 5 min was increased to 7 min, the less-absorbed component, DEE, was obtained more, but the more-absorbed component, DCM, also came out from the column within the switching time. Moreover, for both cases, initially the two components were not separated in the desorpation section. Type Ⅳ is similar to the conventional preparative chromatography, and the method has only advantage of obtaining the pure product of the less-absorbed component in an easy and automatic manner.

To improve the resolution in the desorption section of the type Ⅳ, in the method of type Ⅴ (Fig. 10) the direction of carrier gas was made countercurrent to that of desorbent and three columns were added at the end of the desorption section even though the flow path in the partition section was similar to that of the previous type Ⅳ. The experimental results of the type Ⅴ showed that the two components were separately obtained in the

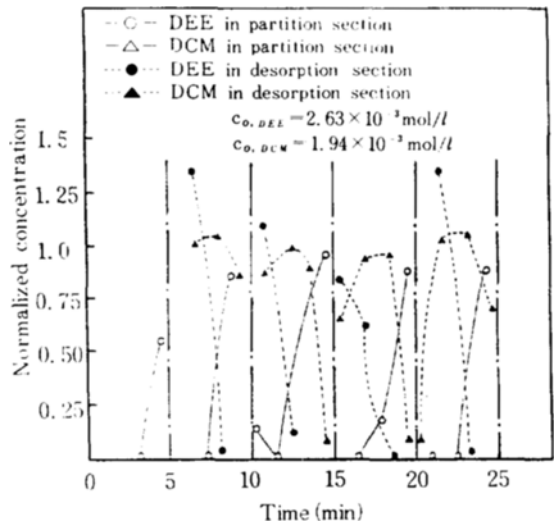

Fig. 8. Concentration profiles in partition section and desorption section.

SW=5min, outlet carrier velocity=19.0 cm/sec, outlet desorben velocity=18.3cm /sec, Type=Ⅳ.

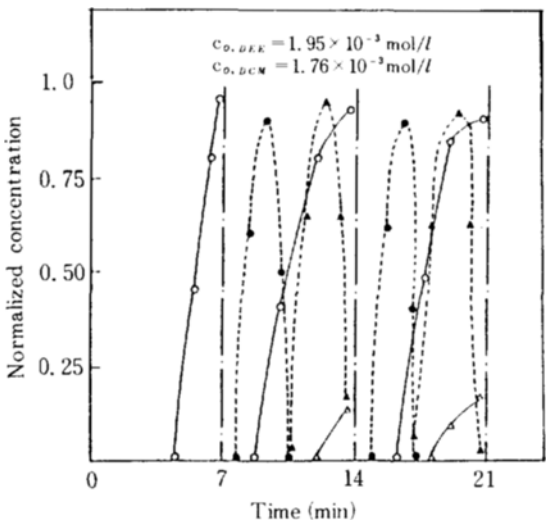

Fig. 10. Concentration profiles in partition section and desorption section.

SW=7min, outlet carrier velocity=19.0 cm/sec, outlet desorbent velocity=18.3cm /sec, Type=Ⅴ.

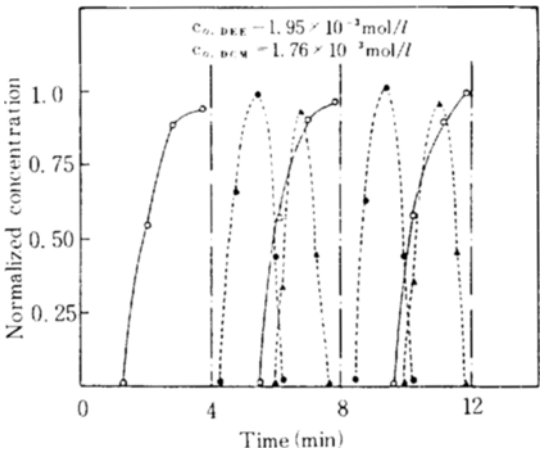

Fig. 11. Concentration profiles in partition section and desorption section.

SW=7 min, outlet carrier velocity = 19.0 cm/sec, outlet desorbent velocity=18.3cm /sec, Type = VI.

desorption section.

In contrast with the types IV and V, characteristics of type VI was that the same column were not used in the partition section, while carrier gas and desorbent flow in the same direction. The type VI prevents the possibility that the more-absorbed component is eluted in the partition section and increases the resolution of the two components in the desorption section by virtue of the longer additional column length (see Fig. 11).

CONCLUSIONS

Twelve segmented columns with solenoid valves were used for separating two close-boiling components, diethylether (DEE) and dichloromethane (DCM), by gas-liquid chromatography.

Various flow paths were considered to find optimum condition, and from the results of experiments, it could be concluded that

1. Compared to conventional preparative chromatography, moving feed-injection and product-withdrawal made it possible to separate the feed continuously.
2. Switching time was determined as the elapsed time from the start to just before the elution of more-absorbed component, and affected by the column temperature and the column length if the feed mixture and the stationary liquid were fixed.
3. Within a switching time, less-absorbed component could be obtained purely in the partition section, and in the desorption section, the remained components could separated by increase in column length.

NOMENCLATURE

A_{11}, A_4, A_5	:	microneedle valves
A_4, A_5	:	solenoid valves
B	:	manometers for adjustment of flow rates
C	:	feed reservoir
D	:	inlet of feed
E	:	outlet of feed
F	:	preheaters for carrier gas and desorbent
G	:	temperature controllers
H_1, H_2	:	heating wires
I	:	main chromatographic system
J	:	programmable controller
K	:	pressure gages
L_1, L_2	:	gas chromatographs
M	:	multi-functional sampling valve
N_1, N_2	:	bubble flow meters for carrier gas and desorbent
O_1-O_5	:	thermocouples
P	:	electric heater

REFERENCES

1. Littlewood, A.B.: "Gas Chromatography: Principles, Techniques and Applications", 2nd Ed., Academic Press, New York, (1966).
2. James, D.H. and Phillips, C.S.G.: *J. Chem. Soc.*, 1600 (1953).
3. McNair, H.M. and Bonelli, E.J.: "Basic Gas Chromatography", 5th Ed., varian instrument, Berkeley (1968).
4. King, C.J.: "Separation Processes", 2nd Ed., McGraw Hill, N.Y. (1980).
5. Verzele, M.: *J. Gas. Chrom.*, **3,** 186 (1965).
6. Sussman, M.V.: *CHEMTECH*, 260 (1976).
7. Row, K.H. and Lee, W.K.: *Korean J. Chem. Eng.*, **3**(1), 7 (1986).
8. Row, K.H. and Lee, W.K.: *J. Chem. Eng. Japan*, **19,** 173 (1986).
9. Husband, W.H., Barker, P.E. and Kini, K.D.: Trans. Instn. Chem. Engrs., **42,** T387 (1964).
10. Chromosorb Diatomite Supports for Gas-Liquid Chromatography, Johns-Manville (1984).
11. Row, K.H. and Lee, W.K.: *J. Chromatogr.*, in revision (1986).
12. Moon, I., Row, K.H. and Lee, W.K.: *Korean J. Chem. Eng.*, **2**(2), 155 (1985).