

Studies on Fractional Fusion Method II

Scale up and Gas Permeating Fractional Fusion

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For a purification of organic compound there are various methods, that is, distillation, sublimation, extraction, recrystallization, chromatography, etc. These techniques have been used effectively as the unit operations in the field of chemical industries.

Zone melting method, which was developed by W. G. Pfann⁽¹⁾, is a powerful method for the preparation of extremely pure substance. Pfann's first application has been tried to the purification of materials employed as semiconductors in transistor diodes, etc. Since 1952 many papers have been reported on the applications of this technique to the purification of metals and inorganic compounds⁽²⁾. Zone melting method has been also used in purification of organic compounds⁽³⁾.

This method is fundamentally a family of fractional separation processes. The application to organic compound was named as fractional fusion method by C.H.L. Goodman⁽⁴⁾.

From a standpoint of chemical engineering, a scale up of fractional fusion as a new unit operation for the purification of organic compound has been studied here experimentally. A design of new apparatus for fractional fusion has been studied in this laboratory.

For the purification of organic compound by fractional fusion, especially in a large scale, the properties of substances, e.g. thermal conductivities of the solid and liquid, the latent heat of fusion, the constitutional supercooling, etc. perform important functions. The smaller heat conductivity compared with metal is the cause of difficulty in the purification of organic compound by fractional fusion method. The high volatility of molten compound is also one of the problems. Because of these characteristic properties, it was reported that a 40 mm. i. d. tube will be the maximum scale of container for fractional fusion of organic compound⁽⁵⁾.

In the previous report⁽⁵⁾, a 10 mm. i. d. glass tube as a container was used for the purification of anthracene. In the present paper, a stainless steel column of 120 mm. i. d. was used as the container, and the scale up of fractional fusion method was investigated experimentally. The sample used here was the same one used in the previous work⁽⁵⁾, and it was regard as a bi-components system of anthracene and phenanthrene. Phenanthrene as an impure component was

removed from anthracene by fractional fusion.

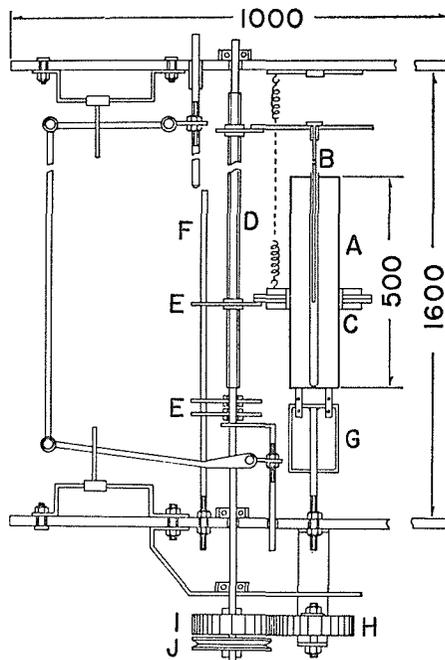
Experiment and Result

1. Determination of Purity

There are a lot of methods for the analysis of phenanthrene coexisted in anthracene. From the result of the experimental investigation, spectrophotometry was selected as the analytical method⁽⁶⁾. Procedure: 30.0mg. of anthracene sample is dissolved into 250 ml. of benzene. An absorbance of the solution prepared is measured at 293m μ . An absorbance due to anthracene (0.3233) is deducted from the measured value. A relationship between absorbance and concentration of phenanthrene showed linearity.

II. Experimental Apparatus

A new apparatus used for fractional fusion method, which was designed in this laboratory, is shown in Fig.1. It can also be used for continuous treatments. The apparatus was set in a frame of 1.8 \times 2.0 \times 1.2 meter. The container was a 120 mm.i.d. stainless steel column(SUS 27), and 5 Kg. of sample to be purified was packed in a batch operation. A nichrome wire of 1 KW. was used as a heating source. The heater was set on supporters connected to two feed screws with 10 pitches a inch and was moved upwards or downwards. The moving rate of the heater could be changed extensively by five reducers. An on-off thermo-regulator (Shimazu, ERC-122) was used to control the temperature of molten zone. An iron-constantan thermocouple was used as temperature detector and it was devised to travel with the heater along the column. The temperatures at six points in the column were measured and recorded.



- | | |
|--------------------------|--------------------------|
| A : Column | F : Guide Rod |
| B : Thermocouple | G : Supporter for Column |
| C : Heater | H : Idle Gear |
| D : Feed Screw | I : Feed Gear |
| E : Supporter for Heater | J : Pulley |

Fig. 1 Experimental Apparatus

III. Purification of Anthracene by Fractional Fusion Method under Various Conditions

(1) Ordinary Fractional Fusion

The purification of anthracene was performed in a large scale under an ordinary procedure of fractional fusion. The sample of 940 g. was charged in the column. The purity of anthracene used was 92.04% by weight. The heater was moved at a rate of 9.96 mm. per hour and it was moved downwards from a top of column. A single molten zone was passed once. The concentration profiles resulted from ordinary fractional fusion are shown in Fig. 2. The graph shows the relationship between specific concentration and the distance from a surface of charged sample.

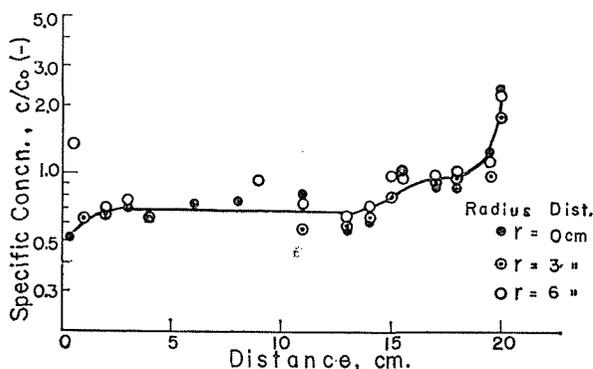


Fig. 2 Ordinary Fractional Fusion

From the results of the experiment, it was recognized that a little purification was developed. The horizontal distribution of phenanthrene in the sample treated was not so clear. An upper part of the sample treated did not show so high purity as expected. It was presumed that this poor purification was due to the volatility of phenanthrene i.e. the impure component. The recording chart of temperature change in the column showed that about 90 min. was required to melt the sample at the center of column since melting the one at the interior wall. It seems that, therefore, some of phenanthrene will be sublimated before forming the complete molten zone in a start of the operation.

An influence of sublimation is not so large in an experiment of smaller scale but remarkable in larger scale. The purification by means of sublimation is due to mass transfer between gas and solid phase. It will not be expected the higher purification. On the other hand, fractional fusion based on a phenomenon of segregation between liquid and solid phase performs the much higher purification of substance.

(2) Fractional Fusion with Internal and External Heaters

There happened a contamination by sublimation in forming the first molten zone. For a rapid formation of first molten zone, the internal heater was used together with the external one. The internal heater was consisted of a 200 W. nichrome wire, and was formed into cylinder of 30 mm. i. d. and 30 mm. length. It was guided through an inner pipe which was set in a center of the column. The both heaters were moved upwards from a bottom of the column. The moving rate of molten zone was 10.86 mm. per hour.

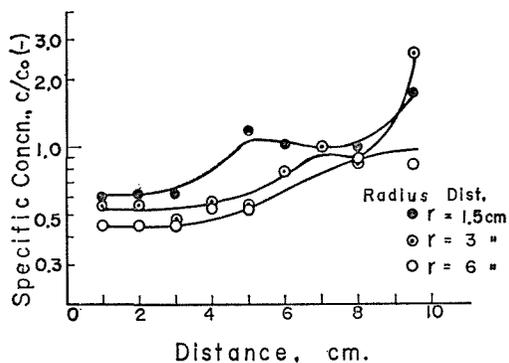


Fig. 3 Fractional Fusion with Internal and External Heaters

The result of this experiment is shown in Fig. 3. The purification expected was recognized. The distribution of the impurity in radius direction was clear. It will be due to the same phenomenon called "coring" (2) in the growth of single crystal from a melt. A cause of coring is thought that a heat from the internal heater affected a freezing rate so that the freezing interface became concave

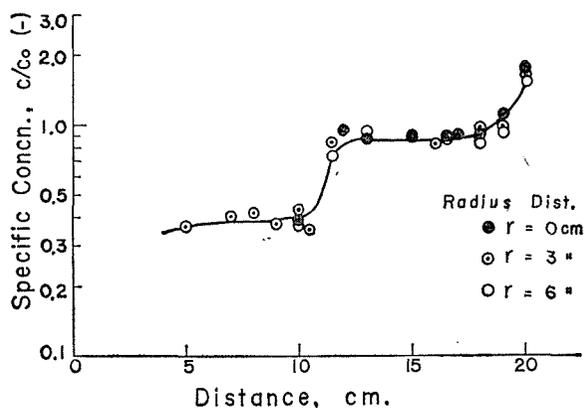


Fig. 4 Fractional Fusion with the Covering of Pure Anthracene

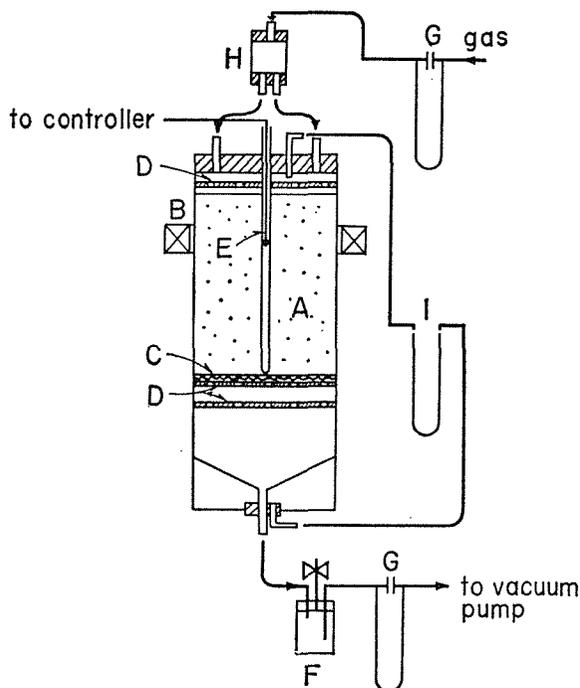
into downside, and the coring phenomenon occurred by the concave interface.

(3) Fractional Fusion with the Covering of Pure Anthracene

To prevent the sample from contaminating by sublimation in forming of first molten zone, a 200 g. of the purified anthracene was charged on the sample to be purified in the column. A single molten zone was passed downwards at the rate of 8.10 mm. per hour. The concentration profiles of the sample treated is shown in Fig. 4. The result of the experiment shows that the considerable purification was developed. After fractional fusion, some of phenanthrene was recognized in the pure anthracene charged on the top of the column. This means that phenanthrene shows an inclination to sublimate more than anthracene.

(4) Gas Permeating Fractional Fusion

A scale up of fractional fusion for the purification of organic compound, that is, a separation of phenanthrene from anthracene in this case, has been tried under various conditions. A satisfactory result, however, was not obtained. It will be due to the phenomena of the coring and the volatility of phenanthrene



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|---------------------|---------------------|
| A : Sample Charged | F : Trap |
| B : Heater | G : Gas Flow Meter |
| C : Brass Net | H : Gas Distributor |
| D : Perforated Tray | I : Manometer |
| E : Thermocouple | |

Fig. 5 Column for Gas Permeating Fractional Fusion

i.e. the impure component. To prevent coring and contaminating, and to succeed in the scale up of fractional fusion, a new technique is proposed here. The new technique will be named as a gas permeating fractional fusion method.

The essential feature of the apparatus is given in Fig. 5. The sample is charged on a brass net of 32 mesh in the column. The gas which does not react naturally with the sample e.g. nitrogen, carbon dioxide, air, etc. is passed through the charged sample.

For a preliminary investigation of the gas permeating fractional fusion, air was passed from the top of column with a vacuum pump which was connected to a bottom of the column. The rate of air passed was 1 litre per minute. The first molten zone was formed at the top of packed sample by the external heater.

Table 1 Results of Gas Permeating Fractional Fusion

Sample No.	Distance (cm)	Radius Dist., r(cm)	Absorbance at 293 m μ	Purity of Anthracene. wt. %	Specific Concn. of Phenanthrene
4101	0.5	0	0.0514	99.49	0.211
4102	2.0	0	0.0524	99.48	0.215
4103	4.0	0	0.0535	99.46	0.223
4104	6.0	0	0.0555	99.44	0.231
4105	7.0	0	0.0746	99.25	0.310
4106	7.5	0	0.1688	98.31	0.698
4107	8.2	0	0.2234	97.77	0.921
4108	9.0	0	0.2600	97.40	1.074
4109	10.0	0	0.3150	96.85	1.302
4110	11.0	0	0.3565	96.43	1.475
4111	12.0	0	0.4672	95.33	1.930
4112	13.0	0	0.3504	96.50	1.446
4113	14.0	0	0.2453	97.55	1.012
4201	0.5	3	0.0639	99.36	0.264
4202	2.0	3	0.0649	99.35	0.269
4203	4.0	3	0.0703	99.30	0.289
4204	6.0	3	0.0757	99.24	0.314
4205	7.0	3	0.0746	99.25	0.310
4206	7.5	3	0.1452	98.55	0.599
4207	8.2	3	0.1910	98.09	0.789
4208	9.0	3	0.2405	97.59	1.000
4209	10.0	3	0.2437	97.56	1.008
4210	11.0	3	0.3545	96.45	1.467
4211	12.0	3	0.4362	95.64	1.802
4212	13.0	3	0.2983	97.02	1.231
4213	14.0	3	0.2358	97.64	0.975
4301	0.5	6	0.0535	99.46	0.223
4302	2.0	6	0.0535	99.46	0.223
4303	4.0	6	0.0639	99.36	0.264
4304	6.0	6	0.0639	99.36	0.264
4305	7.0	6	0.0535	99.46	0.223
4306	7.5	6	0.0867	99.13	0.360
4307	8.2	6	0.1504	98.50	0.620
4308	9.0	6	0.1517	98.48	0.628
4309	10.0	6	0.1996	98.00	0.826
4310	11.0	6	0.3486	96.51	1.442
4311	12.0	6	0.4808	95.19	1.988
4312	13.0	6	0.2840	97.16	1.174
4313	14.0	6	0.2421	97.58	1.000

The heater was moved downwards till 10 mm. above the net. The moving rate of the heater was 8.16 mm. per hour. The stainless steel column was used of 120 mm. i. d. and 1.00 Kg. of 97.58% by weight anthracene was packed in the column. The air was passed continuously before forming the molten zone. When the zone was formed, the inside of column showed lower pressure in this case.

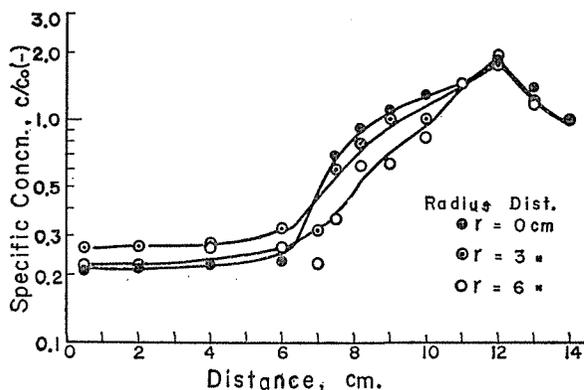


Fig. 6 Gas Permeating Fractional Fusion

The results of the experiment are shown in Table 1 and Fig. 6. The purification of anthracene was more progressed than the other procedures above mentioned. After one pass of a single molten zone, 40% of the sample treated showed higher purity, that is, about 0.2 of specific concentration. Any changes in the characteristics of the treated anthracene was not recognized in the results of ultra-violet and infra-red spectrophotometries. It will be, however, recommended the use of nitrogen gas instead of air for the gas permeating fractional fusion of organic compounds.

Discussion and Conclusion

There are a lot of studies on the purifications of organic compounds by fractional fusion method. These investigations are performed in a small scale, and it is stated that a 40 mm. i. d. tube is probably the maximum that can be used. This is due to the smaller heat conductivities or volatilities, etc. of organic compounds. In a scale up of fractional fusion, an influence of sublimation or volatilization becomes important factor. Little attention has been paid to volatility of organic compound in the published papers.

The gas permeating fractional fusion is considered to prevent the contaminating by volatilization, and it has developed the purification of anthracene. The method presented here will be most effective procedure for fractional fusion of

organic compound, especially in a large scale. For an organic compound easily oxidized at so high temperature as the melting point, some proper inactive gas should be used in the procedure. The gas flow during the operation will be also effective to preheat the sample to be purified, and to form the homogeneous molten zone. A mechanism of the gas permeating fractional fusion is not clear yet, but it is to be investigated in succeeding work.

The freezing interface has various directed facets, and the rate of movement of facets differs at the each part of the concave interface. The phenomenon of the coring happens in such concave interface so that the temperature control of molten zone becomes important. At present time, a proportional integral derivative controller is using in the experiment.

From the results of the presented experiments, it was found that the purification of organic compound by the gas permeating fractional fusion is possible in a large scale container as a column of 120 mm. i. d. It is presumed to be possible to use much larger column in this method. The operation presented here will be developed to be a new unit operation in chemical engineering in the future.

Acknowledgment

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References

- (1) W.G.Pfann : Trans. A.I.M.E., **194** 747 (1952)
- (2) W.R. Wilcox, R. Friedenber, N.Back : Chem. Review, **64** 187 (1964)
- (3) E.F.G. Herington : Zone Melting of Organic Compounds, John Wiley and Sons. Inc., New York, (1963)
- (4) C.H.L. Goodman : Research (London), **7** 168, 465 (1954)
- (5) T. Osawa, T. Yokota : Bull. of the Yamagata Univ. (Engineering), **9** 169 (1966)

分別熔融法に関する研究Ⅱ スケールアップと通気分別熔融

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W.G. Pfann により開発された帯域熔融法は, 初め金属および無機化合物の超高純度なものをつくるのに用いられ, その後, 有機化合物の精製にも応用された。この方法は, 基本的には分別操作の一種である。

C.H.L. Goodman はこの操作を分別熔融法と呼ぶことを提案しており, 筆者らもこれを採用し, 化学工学の新しい単位操作としての開発を試みた。

分別熔融法による有機化合物の精製は, 試料の物理的諸性質のためスケールアップは困難といわれ, いままでに報告された実験装置は, 直径 40 mm のパイレックス硝子管が最大である。

本報においては直径 120 mm. ステンレス製円筒を用いアントラセン-フェナンスレン 2 成分系につき, スケールアップについての種々の検討を行なった。

その結果, 新しい方法として通気分別熔融法 (Gas Permeating Fractional Fusion) を提案した。本法によると, 不純成分が揮発や昇華により上方に移動して精製効果を低下させるのを防ぎ, 熱的経済性をも向上させる等, 分別熔融法のスケールアップにおいて, きわめて良好な結果が得られた。また, 新しい大型分別熔融実験装置も設計製作したのでこれらにつき報告した。

山形大学紀要（工学）第9巻第2号 正誤表

頁	行	誤	正
22	下から6行目	$F = \frac{\pi}{4} GR^4 \theta^3$	$F = \frac{\pi}{4} GR^4 \theta^3$
" 31~41	見出し	(Ⅲ)	式の次に(1)と入れる (Ⅱ)
72	下から7行目	$\nabla^2 \cdot B$	$\nabla^2 B$
73	上から5行目	函 数	関 数
76	上から11行目	$\left(\frac{1}{2} ir_+ - 1\right)$	$\left(\frac{1}{2} ir_+\right)$
"	上から13行目	$r_{\pm} = \text{Tan}^{-1}$	$r_{\pm} = \text{Tan}^{-1}$
77	上から12行目	(4・21)	(4・2・1)
"	下から7行目	$e^{-i\theta} j_z$	$e^{-i\theta} j_z$
"	下から5行目	$e^{-i\theta} \theta_{EZ}$	$e^{-i\theta} E_z$
"	下から2行目	θ_{j_z} 及び θ_{Ez}	θ_{j_z} 及び θ_{Ez}
"	"	の位相か	の位相か
82	下から1行目	の位相と x との	の位相と χ との
94	上から9行目	$\xi > \xi$	$\xi > \xi$
101	第20図	R_2	R_{a2}
"	下から17行目	$\sqrt{R_a^2 - R_g^2}$	$\sqrt{R_a^2 - R_g^2}$
"	下から16行目	$\sqrt{(R_g + \delta)^2 - R_g^2}$	$\sqrt{(R_g + \delta)^2 - R_g^2}$
"	下から15行目	R_g	R_g
105	下から12行目	低	位
"	下から5行目	$l \sin x$	$l \sin \alpha$
106	上から5行目	D_g	D_g
118	第3図 第4図		タテシク Rolling Force Pkg/mm 横シク H _R B
130	上から13行目	不鮮明	[B] C ₁ の
"	上から14行目	"	磁心 C ₁ が点
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131 153~161	下から13行目 見出し	" 近野:	V' _{D1} , r' _{D1} 近野・富川・高野:
153	下から13行目	$\sqrt{\left\{ \left(\frac{1}{w_1^2} - \frac{1}{w_2^2} + \right. \right.$	$\sqrt{\left\{ \left(\frac{1}{w_1^2} - \frac{1}{w_2^2} + \right. \right.$
155	下から1行目 (注)	$\left. \frac{1}{L_2} \left(\frac{w_1}{w_2} \right) \right\}$	$\frac{1}{L_2} \left(\frac{w_1}{w_2} \right) \right\}^2$
157	上から2行目	らの側定を	らの測定を
167	下から11行目	Sc= の式	(13)
"	下から10行目	Sc= の式	(14)
169	下から1行目	$\frac{w^2 - w_j^2}{w^2 - w_{j\infty}^2}$	$\frac{w - w_j^2}{w^2 - w_{j\infty}^2}$
190	下から5行目	Ou	OV
199	上から2行目	Frectional	Fractional
207	下から8行目	explicitely	explicitly
"	下から1行目	(i, j=0, 1, 2, 3)	(i, j=0, 1, 2, 3)
208	上から10行目	$-\overset{\ast}{C}^{i\nu\sigma} \overset{\ast}{g}^{i\mu}$	$-\overset{\ast}{C}^{j\nu\sigma} \overset{\ast}{g}^{i\mu}$
"	上から17行目	$\overset{\ast}{G}^{i\nu\sigma} = 0$	$\overset{\ast}{G}^{i\nu\sigma} = 0$
"	上から21行目	Discusson	Discussion
211	下から17行目	electrode	electrode
"	下から7行目	Inor der	In order
213~217	見出し	SUGANVMA	SUGANUMA
215	下から1行目	craked	cracked
216	下から14行目	NO ₃ -	NO ₃ -