

BEHAVIOR OF A MINUTE AMOUNT OF DIETHYL SULFIDE AND *n*-PROPYL MERCAPTAN IN RECTIFICATION OF KEROSENE

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(Received on May 31, 1980)

The behavior of a minor component in the rectification of a complex mixture was investigated.

Experiments in the continuous distillation of purified kerosene containing a minute amount of diethyl sulfide or *n*-propyl mercaptan were carried out with an Oldershaw-type column.

A computational procedure based on the matrix method was developed and used to obtain the distribution of each fraction of kerosene and the concentration of the minor component in the distillate and bottoms.

From comparisons of the calculated concentrations of the minor component in the bottoms with the experimental ones, the Murphree vapor efficiencies of the minor component were estimated based on certain assumptions. The mean values obtained were 0.278 for diethyl sulfide and 0.107 for *n*-propyl mercaptan.

Introduction

Recently, a number of studies have been carried out on the behavior of a minor component in distillation²⁻⁶. However, the systems dealt with in those studies were binary solutions containing minor components. The behavior of a minor component in the distillation of a so-called complex mixture such as petroleum has not yet been studied.

In this study, the application of methods which have been used for a minor component in binary solutions was tried with regard to a complex mixture, with some necessary modifications. As a complex mixture kerosene was used for convenience. Either diethyl sulfide or *n*-propyl mercaptan was added to the purified kerosene as a minor component.

Experiments in continuous distillation were carried out and the concentrations of the minor component in the distillate and bottoms were obtained under various conditions. The distributions of each fraction in the feed, distillate and bottoms were also measured.

An approximate mathematical model was constructed by assuming a complex mixture as an ideal solution of its fractions. The concentrations of the minor component and the distributions of each fraction in the distillate and bottoms were obtained by a numerical method. The calculated values were then compared with the corresponding experimental ones.

1. Equations for Data Reduction

For distillation calculations, it is preferable to express data on a mole fraction basis.

The relation between the average molecular weight and boiling point was obtained previously by the authors⁷ and is expressed as follows :

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$$MW = 53.237 + 0.44007t_0 + 1.6098 \times 10^{-4}t_0^2 + 1.8639 \times 10^{-6}t_0^3 \quad (1)$$

By using the average molecular weight of each fraction of the kerosene, the concentrations can be converted to mole fractions.

The equilibrium ratios (based on mole fraction) of a minute amount of the sulfur compounds were obtained in the prior paper⁷⁾ and are expressed as the following equations: for diethyl sulfide

$$K = -4.2301 + 6.5367 \times 10^{-2}t_0 - 1.2760 \times 10^{-4}t_0^2 \quad (2)$$

and for *n*-propyl mercaptan

$$K = -12.427 + 1.6929 \times 10^{-1}t_0 - 2.9507 \times 10^{-4}t_0^2 \quad (3)$$

The equilibrium ratio of a major component is also essential for the calculation of the behavior of a minor component in distillation. The formulation of a simple expression for this has been attempted on the assumption that kerosene consists of an ideal mixture of its fractions.

In an ideal solution, the equilibrium ratio ($K \equiv y/x = P/\pi$) at 1 atm becomes equal to its vapor pressure. The equilibrium ratio of a kerosene fraction can be obtained from the following equation, which was formed from the hydrocarbon vapor pressure chart presented by Maxwell and Bonnell⁸⁾.

$$\begin{aligned} \log K &= \log P \\ &= (7.15t_0 + 1055)(t - t_0) / (t + 273.15)(t_0 + 273.15) \end{aligned} \quad (4)$$

2. Experiment

2.1 Apparatus and procedure

A glass distillation apparatus, shown in Fig. 1 was used. The column and the still were the

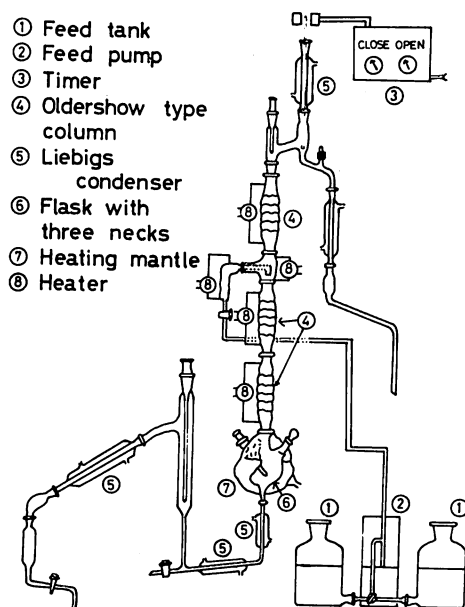


Fig. 1 Schematic diagram of experimental apparatus

same as those used in connection with the previous paper⁶).

Kerosene purified by the extraction method detailed in the prior paper⁷, was distilled and used as the feed liquid. Three types of feed liquid were tested. Type No. 1 consisted of a total range of fractions the boiling points of which ranged from 120 to 250°C, in the same proportions as in raw kerosene. Type No. 2 did not contain fractions the boiling points of which were higher than 220°C. Conversely, type No. 3 did not contain fractions the boiling points of which were lower than 185°C.

The apparatus was operated with feed containing about 0.1 wt% sulfur compound. The temperatures at each point of the column and the concentrations of the sulfur compounds in the distillate and bottoms were measured periodically. After these values became substantially constant, samples of distillate and bottoms were taken. The concentrations of the sulfur compounds were determined by the same method as described in the prior paper⁷.

The samples of feed, distillate and bottoms were fractionated for each 5°C rise in boiling point by fractional distillation with the laboratory packed column. The distributions of each fraction in these samples were obtained on a weight basis.

2.2 Experimental results

The experimental conditions and a part of the results are presented in Table 1.

Table 1 Experimental conditions and results

Exp. No.	Sulfur compound	Feed Type No.	Feed Temp. [°C]	Flow rate [g min ⁻¹]			Concentration of sulfur compound [wt %]		
				Feed	Distillate	Bottoms	Feed	Distillate	Bottoms
1	Diethyl sulfide	1	170	5.596	1.843	3.682	0.0944	0.2827	0.001703
2	"	1	170	3.691	1.171	2.500	0.0942	0.2884	0.003783
3	"	1	170	4.564	1.567	2.952	0.0955	0.2702	0.003602
4	"	1	180	4.570	1.639	2.907	0.0948	0.2598	0.002008
5	"	2	170	3.274	1.488	1.779	0.1030	0.2238	0.002067
6	"	3	180	3.922	1.177	2.733	0.0907	0.2936	0.003284
7	<i>n</i> -propyl mercaptan	1	170	4.664	1.289	3.317	0.0448	0.1576	0.000517
8	"	1	170	4.562	1.429	3.188	0.0948	0.2967	0.000515
9	"	1	170	4.562	1.142	3.513	0.1315	0.5078	0.000367
10	"	2	170	4.451	1.699	2.692	0.0718	0.1846	0.000406
11	"	3	180	4.567	1.589	2.931	0.0740	0.2086	0.000337

By using the distribution of each fraction in a sample and the molecular weight of each fraction obtained from Eq. (1), the units of flow rates and concentrations were converted respectively from g/min to mol/h and from wt % to mol %.

The feed temperature was used to obtain the *q*-value (the heat required to convert the feed to a saturated vapor, divided by the latent heat).

3. Calculation Method

3.1 Model and assumptions

The model is the same as that shown in Fig. 8 of the previous paper⁶⁾. Almost the same assumptions are introduced as in the previous papers^{4, 6)}. In this paper, however, the major component is not a water-ethanol system but an ideal mixture of kerosene fractions, and the minor component is the sulfur compound.

As a method for estimating the equilibrium ratio in a mixture had not been established, it was assumed that the equilibrium ratio of the minor component in a mixture is the same as that in the fraction, which has the same boiling point as that of the mixture. According to this assumption, the aforementioned equilibrium ratio can be obtained from Eq. (2) or (3) when the temperature of a stage is specified.

It was also assumed that the Murphree vapor efficiency of each fraction of kerosene can be assigned a constant value and that the Murphree vapor efficiency of the minor component is not necessarily the same as that of the kerosene fractions.

3.2 Computational procedure

From the definitions of the equilibrium ratio ($K_j = y_j^*/x_j$) and the Murphree vapor efficiency ($EMV = (y_j - y_{j+1}) / (y_j^* - y_{j+1})$) at stage j , the following equation was derived,

$$K_j' = EMV \cdot K_j + (1 - EMV) K_{j+1}' \cdot x_{j+1} / x_j \quad (5)$$

in which K_j' was defined by

$$K_j' = y_j / x_j \quad (6)$$

As the efficiency at the still can be assumed as unity, $K_w' = K_w$ ($w = N + 1$)

When the temperatures and the concentrations at all stages are assigned, K_j 's can be obtained in turn from the still by Eq. (5).

Material balance equations, which contained K_j' in place of K_j , were formulated and solved according to the matrix method given by Amundson et al¹⁾.

At the beginning, the temperatures of all stages were suitably given. The matrix equations of kerosene fractions were solved and the temperatures of all stages were modified by Newton's method. After some iterations, the temperatures and the concentrations of each fraction of all stages were determined. Then, the matrix equation for a minor component was solved. The concentrations obtained on the basis of mole fractions were converted to wt% for comparison with the experimental ones.

3.3 Input data

As the flow rate of the feed did not always coincide with the sum of those of the distillate and bottoms, the latter two flow rates were modified so that the sum of these became equal to that of the feed but their ratios were not varied.

The distribution of fractions and the concentration of the minor component in the feed, q -value and the flow rates were used in the calculation.

The time ratio for opening and closing by a timer was set at unity for all runs. However, since there was a slight accumulation and leakage occurred at the ground-glass portion at the tip of the stopper rod, the reflux ratio was taken not as unity but at one-third, which was estimated from a simple supplementary test and some preliminary calculations.

4. Calculated Results and Discussion

As the reflux ratio was fixed at one-third, the remaining parameters were the Murphree vapor efficiency of fractions (EMVP) and that of the minor component (EMVM).

4.1 Effect of EMVP

Calculations were carried out for Exp. Nos. 1 to 6, in each of which EMVM was fixed at 0.3 and EMVP at 0.6 and 0.8. The concentrations of the minor component in the bottoms became only 0.67% (maximum 1.1%) lower when EMVP was changed from 0.6 to 0.8. The temperatures at the top and bottom of the column was affected only 0.37K (maximum 0.7K) by this change of EMVP.

As the effect of EMVP was not very large, EMVP was fixed at 0.6 in the following calculations.

4.2 Estimation of EMVM

Since the concentration of the minor component in the bottoms is very sensitive to EMVM, the calculated concentrations were plotted against EMVM and compared with the experimental ones. The values of EMVM obtained from this graph are shown in Table 2, with the concentrations calculated by using these values.

Table 2 Estimation of Murphree vapor efficiency of minor component (EMVM)

Exp. No.	Sulfur compound	EMVM	Calculated concentration of sulfur compound in bottoms [wt %]
1	Diethyl sulfide	0.346	0.001697
2	"	0.257	0.003732
3	"	0.235	0.003642
4	"	0.314	0.002033
5	"	0.262	0.002074
6	"	0.255	0.003283
7	<i>n</i> -Propyl mercaptan	0.085	0.000538
8	"	0.103	0.000504
9	"	0.164	0.000344
10	"	0.092	0.000427
11	"	0.091	0.000352

The mean value of EMVM is 0.278 for diethyl sulfide and 0.107 for *n*-propyl mercaptan.

4.3 Distribution of fractions

The distributions of fractions in the distillate and bottoms were also calculated and plotted with the experimental ones. As an example, the graphs of Exp. No. 1 are represented in Fig. 2.

It can be seen in Fig. 2 that the shapes of the calculated distributions do not coincide with those of the observed ones, but deviate slightly in the direction of bad separation, *i.e.*, heigher boiling point in the distillate and lower in the bottoms.

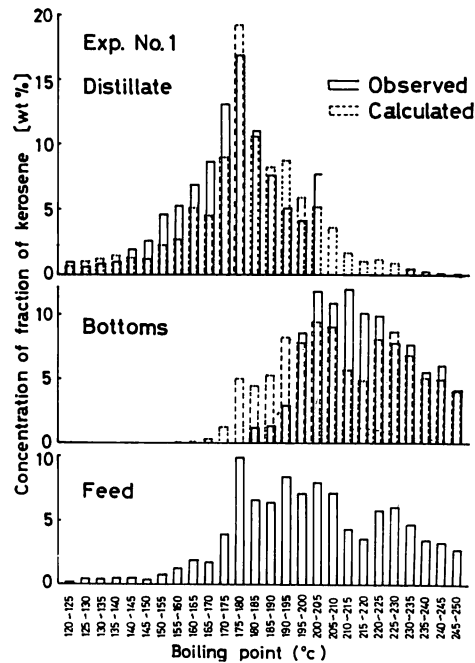


Fig. 2 Distribution of fractions in feed, distillate and bottoms

These disagreements seem to be attributable to many causes, for example experimental errors, the assumptions in derivation of the equations and the inadequately estimated parameters. Further accurate and detailed studies will be required to reduce these deviations.

5. Conclusions

To clarify the behavior of a minor component in the distillation of a complex mixture, purified kerosene containing a minute amount of diethyl sulfide or *n*-propyl mercaptan was studied as an example.

Experiments on continuous distillation of the purified kerosene containing a minor component were carried out with an Oldershaw-type column.

By adopting certain assumptions, a mathematical model was developed and solved according to the matrix method. The computational program has three parameters, in which the reflux ratio was estimated as one third and EMVP was assumed to be 0.6.

From a comparison of the calculated concentrations of the minor component in the bottoms with the experimental ones, the values of EMVM were determined; 0.278 for diethyl sulfide and 0.107 for *n*-propyl mercaptan.

Although these mean values contain considerable uncertainties attributable to the various assumptions adopted and experimental errors, it can be stated at least that EMVM is different for

each component and also from EMVP. To predict the behavior of minor components in rectification, a characteristic value must be given to the Murphree vapor efficiency of each component.

The calculated distributions of each fraction of kerosene were also compared with the experimental ones. It can be seen that there are appreciable deviations between both distributions.

Acknowledgement

The financial assistance of the Science Research Foundation of the Ministry of Education, Japan (Grant No. 965147) is gratefully acknowledged. The authors also thank Mr. Tatsunori Ohta for carrying out part of the experimental work.

Nomenclature

K	=equilibrium ratio	[—]
K'	=ratio defined by Eq. (6)	[—]
MW	=average molecular weight	[—]
N	=number of plate	[—]
P	=vapor pressure	[atm]
t	=temperature	[°C]
t_0	=boiling point of kerosene fraction	[°C]
x	=mole fraction in liquid	[—]
y	=mole fraction in vapor	[—]
y^*	=vapor concentration in equilibrium with x , mole fraction	[—]
π	=total pressure	[atm]
<Subscripts>		
j	=stage number	
w	=still	

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(Presented at the 9th Autumn Meeting of The Soc. of Chem. Engrs (Fukuoka) on Oct. 17, 1975)