The Separation of Iso- and Normal Butyl Alcohols from Hydrocarbons by Azeotropic Distillation.

By **Ryoji NEGISHI** and **Chiharu ISOBE.**

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Two of the promising methods of the synthesis of iso- and normal butyl alcohols are first, the reaction of a mixture of hydrogen and carbon monoxide(1–5) under pressure in the presence of a suitable catalyst and, second, dehydration and polymerization of the lower alcohols(6–8) under ordinary or elevated pressures in the presence of a catalyst. By either method, the products are not pure iso- and normal alcohols, but contain

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(1) G. T. Morgan, R. Taylor, and T. J. Hedley, *J. Soc. Chem. Ind.*, **47** (1928), 117_{T}; R. Taylor, *J. Chem. Soc.*, **1934**, 1429; G. T. Morgan, Hardy, and Proctor, *J. Soc. Chem. Ind.*, **51** (1932), 1_{T}; G. T. Morgan and R. Taylor, *Proc. Roy. Soc.*, A **131** (1931), 533.

(2) G. Natta, *Osterr. chem. Zeitg.*, **40** (1937), 162.

(3) E. M. Bocharova, B. N. Dolgov, and Z. M. Prokhorova, *Khim. Tverdogo Topliva*, **6** (1935), 665; *Chem. Abst.*, **30** (1936), 2171.

(4) I. G. Farbenind., A. G., G. P. 625757 (1936).

(5) H. Tahara, Y. Tatuki, and J. Simizu, *J. Soc. Chem. Ind., Japan* (Supp. Binding), **43** (1940), 82.

(6) Neuman, Brit. P. 326812 (1923).

(7) O. Fuchs and W. Querfurth, G. P. 594672; U. S. 205078.

(8) Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, G. P. 674751 (1939); Brit. P. 478141 (1938).

a large number of hydrocarbons. Ordinarily, the alcohols are separated by distillation because of convenience and simplicity. However, owing to the circumstance that the alcohols are susceptible to the formation of azeotropic mixtures with a large number of hydrocarbons, straight forward distillation cannot be expected to give accurate results. Because of the fact that the alcohols form also azeotropic mixtures with water, distillation method can be so modified, taking advantage of the fact, to give a convenient and accurate separation of the alcohols from the hydrocarbons.

The purpose of this paper is to describe this method in some detail and to give the experimental results obtained from the measurements of alcohol-toluene and alcohol-gasoline mixtures. We have assumed in our case that the only water soluble substances are the alcohols. The separation of the alcohols from the mixtures containing such oxygenated compounds as the lower alcohols, aldehydes, and ketones, besides hydrocarbons will be the subject of a subsequent report, which will appear later in this bulletin.

In the present method, the following properties of the alcohols have been taken advantage of:

(1) The alcohols dissolve appreciably(9) (at 20°C. the normal dissolves 7.8% and the iso- 8.5% by weight) in water, while hydrocarbons do not(10).

(2) The alcohols dissolve completely in ether, while water does not but slightly.

(3) The alcohols form azeotropic mixtures with water, but not with ether.

Experimental Details.

A) **Purification.** *Normal Butyl Alcohol.* It was purified by a method similar to that given by Weissberger and Proskauer(11). It was washed with dilute sulphuric acid and then with sodium bisulphite. Then it was boiled with an aqueous KOH solution. A boiling fraction, 116.5–118°C., was first collected, and the final distillation was made over CaO. A fraction boiling at 117–118°C. was used.

Iso-Butyl Alcohol. A commercial product was first treated with quick lime and then distilled. A fraction boiling between 106.9–108.5 was collected.(12)

Toluene. It was purified(13) by washing with concentrated H_2SO_4 and with water. It was then dried over $CaCl_2$, and the final distillation was made over metallic sodium. A fraction boiling at 110–112°C. was collected.

Gasoline. Commercial gasoline(*) was purified by treating it with con-

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(9) A. Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., Vol. II, 1121 (1928).

(10) Int. Crit. Tables, III, 387 (1928). Dissolves but slightly.

(11) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, 126 (1935).

(12) Kuwada, "Solvents," Maruzen, 219 (1940). In Japanese.

(13) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7** (1939), 1087.

* "Rising Sun," brand, straight-run.

centrated H_2SO_4, KOH, H_2O, dried with $CaCl_2$, and finally distilled over metallic sodium. Fractions boiling from 50 to 130°C. were used.
Ether. It was first treated⁽¹⁴⁾ with concentrated sulphuric acid and then washed with KOH and water. It was then distilled over metallic sodium. A fraction, 36.0–37.0°C. was used.

B) **Method.** No special apparatus was used. 500 c.c. and 100 c.c. (for ether extractions) separatory flasks; calibrated 30 c.c. graduated cylinders, which were graduated to 0.1 c.c., with well-fitting ground glass stoppers; and a distillation set-up made of Terex glass with interchangeable ground glass joints were used. The distillation column was insulated by an annular space of air formed by fitting a glass tube over its whole length. The column was about 60 cm. in length and contained a Terex glass spiral. Heating was made either electrically or by gas. The temperature was measured by means of an alumel-chromel thermocouple connected to a potentiometer whose scale readings could be estimated to about 0.2°C.

The alcohols were first separated from the hydrocarbons by adding water 20 times⁽¹⁵⁾ the volume of the sample and shaken and left alone until all the alcohols had separated out from the hydrocarbon phase. It was shown by the results of Table 1 that 1.5 hours were sufficient to separate toluene completely (and also the alcohols; compare the results of Table 2) from the mixture. In order to break up the last traces of the emulsion formed by the system, the mixture was heated at 60°C. As it was indicated by the Table, 50°C. seemed not sufficient, and at this temperature the time of heating had to be longer. One shaking was adequate to remove practically all of the alcohols. The non-dissolving fraction was considered hydrocarbons. The validity of this assumption is justified, as shown by the results of Tables 1, 2, and 3.

To extract and concentrate the alcohols from such dilute aqueous solutions by means of some selective solvent appears unnecessarily tedious and wasteful in view of the fact that iso- and normal butyl alcohols form azeotropic mixtures with water in the respective proportions⁽¹⁶⁾ (by weight of alcohol), 67% and 57.6%, at the constant boiling points⁽¹⁶⁾, 90.0 and 92.6°C., respectively.

Distillations were carried out in the apparatus, which has been mentioned above. Until the last traces of the alcohol had disappeared, the boiling point was constant; moreover, the distillation could be made quite rapidly and roughly without fear of introducing serious errors. It was continued until 100°C.⁽¹⁷⁾. When it was completed, the distillates, which had separated out into two layers, were shaken to bring about an equilibrium between alcohol and water, and the respective amounts of the alcohol in the water and the water in the alcoholic phase were corrected for at the experimental temperature. The above method was sufficient to determine accurately the amounts of the alcohols in their binary systems

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(14) C. W. Porter, T. D. Stewart, and G. E. K. Branch, "Methods of Organic Chemistry," Ginn and Co., 70 (1927).

(15) V. G. Shaposhnikov and S. E. Pinchuk, *Chem. Abst.*, **30** (1936), 4787. They have suggested 35 fold addition in a similar separation.

(16) T. H. Durrans, "Solvents," Chapman and Hall, 102, 103 (1938).

(17) By 95°C practically all of the alcohols had been distilled out.

Table 1. Effects on Separation of Toluene of Time and Temperature.

Toluene-Iso alcohol Systems.*

Time left alone after shaking (hr.)	Conditions of aqueous layer	Temp. °C. of destroying emulsion	Time of heating (min.)	Toluene (c.c.)	Recovery %
1.0	Not quite clear	70	6	9.66	3.4
1.5	Clear	60	8	9.76	2.4
2.0	Clear	60	7	9.73	2.7
3.0	Clear	50	16*	9.71	2.9
4.0	Clear	60	6	9.75	2.5

* Break-up appeared not quite complete.

Toluene-Normal alcohol Systems.**

Time left alone after shaking (hr.)	Conditions of aqueous layer	Temp. °C. of destroying emulsion	Time of heating (min.)	Toluene (c.c.)	Recovery %
1.0	Not quite clear	60	9	9.64	3.6
1.5	Clear	60	7	9.72	2.8
2.0	Clear	60	6	9.80	2.0
3.0	Clear	60	5	9.79	2.1

** Conditions: toluene 10 c.c.; alcohol 10 c.c.; water 400 c.c.; time of shaking 5 minutes.

with hydrocarbons. If, however, a system contains both alcohols and hydrocarbons simultaneously, several additional steps must be made in order to separate the respective alcohols from each other. These additional operations involve, first, the extraction with ether(5) of the alcohols from the aqueous phase and, second, the separation of the alcohols by distillation.

Results. The simpler method has been used for the separation of iso- and normal alcohols from their respective binary systems with toluene, and the results obtained at 15°C. (unless otherwise stated) are shown in Table 2. The actual amounts of toluene and the alcohols lost are independent of the amounts of the respective components in the system. What this means is, among others, that the loss is mainly operational. The results of our measurements indicate that the method is quite simple and fairly accurate. At present, we do not have a suitable explanation of the fact that the loss of toluene in the normal system is consistently smaller than that in the iso- system.

For the mixtures consisting of iso-, normal butyl alcohols, and commercial gasoline, the more involved method was used. The alcohols were separated from the gasoline and concentrated as in the simpler method.

Then to the distillates a sufficient amount of $CaCl_2$ was added to saturate the aqueous phase. Then by four separate additions of the same volume as that of the distillates of ether, the alcohols were completely extracted from water. Ether and the alcohols were, then, separated from each other by distillation which presented no difficulty.

Table 2.

Normal Butyl Alcohol-Toluene Systems at 15°C.

Vol. c.c.		Toluene c.c.		Alcohol recovered c.c.				% Alcohol Loss
Alcohol	Toluene	Recov.	Loss	Alc. phase	Aqueous phase	Total	Loss	
5*	15	14.83	0.17	4.04	0.67	4.71	0.29	5.8
5*	15	14.83	0.17	3.54	1.21	4.76	0.24	4.8
10	10	9.72	0.28	8.73	1.13	9.86	0.14	1.4
10	10	9.77	0.23	9.04	0.79	9.83	0.17	1.7
15*	5	4.76	0.24	12.64	2.03	14.71	0.29	1.9
15*	5	4.83	0.17	12.37	2.35	14.72	0.28	1.9

* At 10°C.

Iso-butyl Alcohol-Toluene Systems.

Component c.c.		Toluene c.c.		Alcohol Recovered c.c.				% Alcohol Loss
Alcohol	Toluene	Recov.	Loss	Alc. phase	Aqueous phase	Total	Loss	
5	15	14.75	0.25	4.66	0.33	4.99	0.01	0.2
5	15	14.77	0.23	4.49	0.45	4.94	0.06	1.2
10	10	9.72	0.28	8.65	1.08	9.82	0.28	2.8
10	10	9.73	0.27	8.85	0.84	9.68	0.32	3.2
15	5	4.78	0.22	14.29	0.68	14.97	0.03	0.2
15	5	4.73	0.27	13.95	0.89	14.84	0.16	1.1

The iso-butyl alcohol range was taken from 100 to 111°C., and what had been left over undistilled was considered all normal alcohol. As indicated by Fig. 1 and Table 3, the separation of iso-butyl alcohol is complete, and although a range from 100 to 111°C. has been taken, in reality, practically all has come out at a constant temperature, 108.4°C. The range of temperature, 100 to 108°C., is due to the time lag in bringing the thermocouple to the proper temperature.

As can be seen from Table 3, the actual loss in c.c. of the gasoline is about the same in each run, but it is larger than that of toluene. This is probably due to a higher volatility of the gasoline. Regardless of the amounts of the individual alcohols, the loss in each run is about the same; moreover, it is of the same order of magnitude as that in the toluene-alcohol systems. This indicates that the loss is, as it has been already

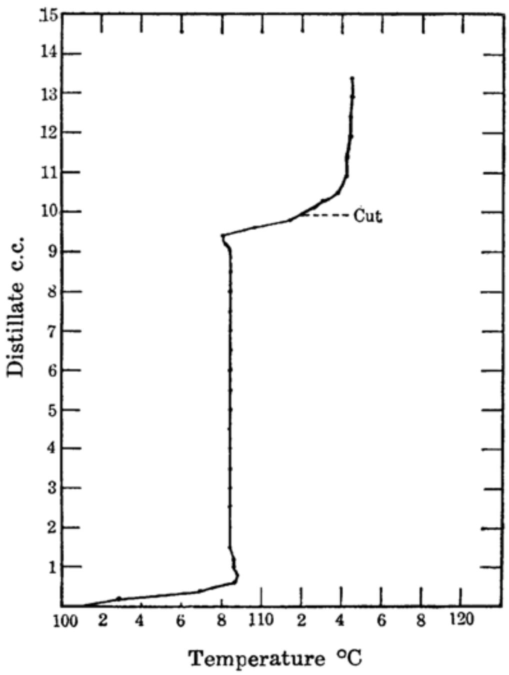

Fig. 1.

mentioned, chiefly mechanical. When the results of the two tables are compared, some information as to the sources of error involved in the present method may be gained. In Table 3 the amounts of iso- and of normal alcohols finally separated are always less than the original amounts and they are about the same as those in Table 2. What it means is that during the ether extractions and the final distillation the loss is negligible, and the main source of error seems either in the extraction by water of the alcohols or in the distillation of the azeotropic mixtures. By a number of preliminary runs the latter has been shown to give negligible error; therefore the chief source must be the former. The same inference can be drawn from the fact that some difficulties, which have been already referred to, are encountered with in connection with the extraction.

Table 3.

Iso- and Normal Butyl Alcohols-Gasoline Systems at 15°C.

Components c.c.			Gasoline c.c.			Iso-Alcohol c.c.			Normal Alcohol c.c.		
Gasoline	Iso-	Normal	Recov.	Loss	% loss	Recov.	Loss	% loss	Recov.	Loss	% loss
10	10	10	9.64	0.36	3.6	9.70	0.3	3.0	9.67	0.33	3.3
10	10	10	9.67	0.33	3.3	9.75	0.25	2.5	9.73	0.27	2.7
10	10	10	9.64	0.36	3.6	9.80	0.20	2.0	9.68	0.32	3.2
10	5	15	9.60	0.40	4.0	4.83	0.17	3.4	14.91	0.09	0.6
10	15	5	9.52	0.48	4.8	14.78	0.22	1.4	4.75	0.25	5.0

Finally, a word may be mentioned of the accuracy of the method. Since the actual loss is independent of the total amount of each component in the system, the larger the amount of the component, the smaller will be its percentage error. If the alcohol to be separated is about 5 c.c., the percentage error is about 5; for 10 c.c., it is about 3% ; and for over 15 c.c., it can be reduced to about 1%.

Summary.

A new method has been devised, employing the principle of azeotropic distillation, to separate iso- and normal butyl alcohols from hydrocarbons.

This method has been applied to the binary systems of iso- and normal alcohols with toluene. It has also been tried with the mixtures of the alcohols and gasoline. The individual components have been separated, and it has been shown that this method is accurate within 5% when the amount of the component to be separated is about 5 c.c.; 3% when it is 10 c.c.; and about 1% or less for the amount larger than 15 c.c.

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