Vapor-Liquid Equilibrium Data for Propylene-Propane System

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Vapor-liquid equilibria were determined for propylene-propane at 320 p.s.i.a., using a modified Othmer still and a packed column. Experimentally determined isobaric relative volatilities confirm values calculated by thermodynamic correlation of previously published isothermal data and establish the validity of extrapolation of the published data above 90% propylene.

THE MANUFACTURE of polypropylene requires a propylene feedstock having a purity of 99% or higher. Since the relative volatility of propylene with respect to propane is low, a high degree of fractionation is needed to obtain good recovery of high-purity propylene from a fluid catalytic cracking stream containing about 60% propylene. Accurate relative volatility data are essential to the determination of fractionation requirements.

Isothermal vapor-liquid equilibria have been reported by Reamer and Sage (*4*) for 10°, 40°, 100°, 160° and 190° F., and by Hanson, *et al.* (*2*), for 25.5°, 82.7° and 134.9° F. The range of liquid compositions was about 10 to 90% propylene. Design of the fractionator requires data at constant pressure rather than constant temperature. In addition, although relative volatilities probably can be extrapolated above 90 mole per cent propylene with reasonable accuracy, obtaining actual data in the region of 90 to 99% propylene would insure that no abnormalities exist. Therefore, the equilibrium relationship was studied in the laboratory, covering the range 40 to 99 mole per cent propylene. A constant pressure of 320 p.s.i.a. was used to simulate an installation where ambient cooling water would be used to condense the overhead product. Lower pressures favor the separation but require refrigeration.

EXPERIMENTAL WORK

Vapor-liquid equilibrium determinations were made in a series of eight equilibrium still runs and nine packed column runs, all operated at total reflux. The equilibrium still runs covered the range 41.7 to 92.5 mole per cent propylene. Because of the extremely small enrichment obtained in one theoretical stage above about 90% propylene, relative volatility data above this concentration become less reliable. The packed column runs, covering the range 42.5 to 99.0 mole per cent propylene, were designed to permit extension of the equilibrium curve to constant fractionation efficiency, which appears justified for this system in view of the similarity in physical properties between propylene and propane. On this basis, a relatively constant number of theoretical plates for the entire series of runs would indicate the validity of the extrapolation of a given relative volatility curve above 90% propylene.

The single-stage runs were made in a modified Othmer type still, shown in Figure 1. The body of the still is a 13-inch length of 2-inch I.P.S. stainless steel pipe fitted with a sidearm condenser. The still is heated at the bottom and enclosed over the remainder of its length in a constant-temperature bath filled with oil, which was held at the same temperature as the boiling liquid within the still. The overhead vapors are condensed and returned directly to the bottom by gravity flow. Sample connections are provided in the stillpot and in the overhead return line.

The still was charged with various mixtures of Phillips Petroleum Company research grade propylene and propane. Operation was at constant overhead pressure of 320 p.s.i.a. After equilibration, three pairs of overhead and bottoms samples were removed at two-hour intervals, using evacuated 10-ml. gas sampling tubes. In order to avoid absorption of the gas in stopcock grease, sample tube closures were made with Tygon tubing fitted with screw clamps.

The packed column runs were made in a 1-inch I.P.S. stainless steel, well-insulated column packed with 15 inches of Helipak No. 3008 stainless steel packing. The apparatus

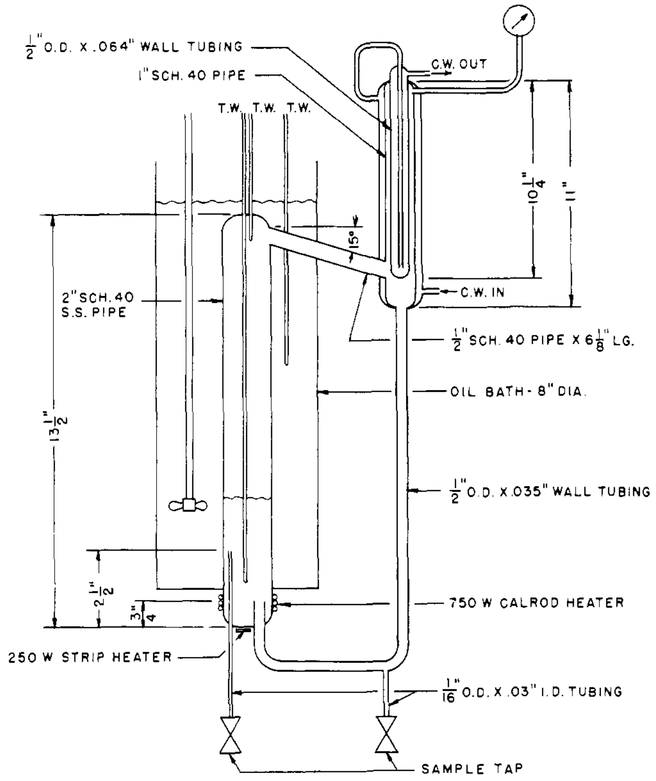

Figure 1. Vapor-liquid equilibrium still

is shown in Figure 2. The overhead pressure was 320 p.s.i.a., and the boil-up rate was constant for all runs. Sampling procedure was the same as for the single-stage runs.

All samples were analyzed on a modified Consolidated Electrodynamics Corporation Model 21-102 mass spectrometer. The difference in propane content between a given pair of overhead and bottoms samples was determined with a precision of ±0.02 to ±0.10%.

RESULTS

The results of the equilibrium still runs are given in Table I. Figure 3 shows experimentally determined isobaric relative volatility plotted as a function of propylene concentration with an extrapolation to 100% propylene. The results of the packed column runs are given in Table II. For each run the relative volatilities corresponding to the measured overhead and bottoms liquid composition were read from the plot of experimental isobaric data of Figure 3. The number of theoretical plates for each packed column run was then calculated from the Fenske equation:

$$N = \frac{\log_{10} (x_1/x_2)_{\text{top}} (x_2/x_1)_{\text{btm.}}}{\log_{10} \alpha_{\text{avg.}}} \qquad (1)$$

where

N = Total number of theoretical plates (including reboiler)
x = Mole fraction in liquid
α = Relative volatility of propylene with respect to propane
$\alpha_{\text{avg.}}$ = $1 + [(\alpha_{\text{top}} - 1)(\alpha_{\text{btm.}} - 1)]^{1/2}$

Subscripts top and btm. refer to top and bottom of column, respectively.

Subscripts 1 and 2 refer to propylene and propane, respectively.

The values calculated from Equation 1 are included in Table II. The relative constancy in the number of theoretical plates indicates that the assumed extrapolation of the experimental relative volatility curve above 90% propylene is justified and that no abnormalities exist.

DISCUSSION

The experimental isobaric relative volatility data plotted in Figure 3 cannot be compared directly with the isothermal data previously reported. However, using basic thermodynamic relationships, the published data were converted to an isobaric basis at 320 p.s.i.a., corresponding to the pressure used in the present study. The procedure was outlined by Hill (*3*).

Liquid phase activity coefficients for each component, γ_i, were computed from the published relative volatility data, using the van Laar equation. The temperature dependence of the van Laar constants was developed by Hill.

The deviation coefficients for each component, θ_i, were computed from the following equation, derived by Hill, which accounts for deviations of the pure component vapors from the ideal gas laws and for the effect of pressure of liquid fugacity:

$$\log_{10} \theta_i = (P_i^\circ - P)(\underline{\beta}_i - V_i^l)/2.3\,RT \qquad (2)$$

where

P_i° = Vapor pressure of pure component i, p.s.i.a.
P = Total pressure, p.s.i.a. = 320 for this study
$\underline{\beta}_i$ = Integrated average residual vapor volume for component i over the pressure range from P_i to P, cu. ft./lb. mole.
V_i^l = Molecular volume of component i in the liquid phase, cu. ft./lb. mole.
R = Gas constant = 10.73 (p.s.i.a.) (cu. ft.)/(lb. mole) (° R.).
T = Absolute temperature, ° R.

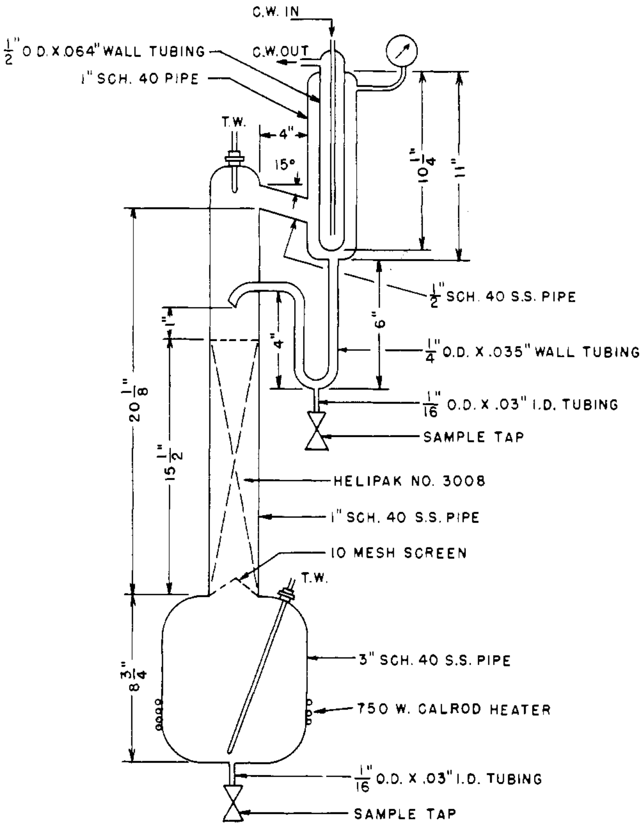

Figure 2. Packed reflux column

Table I. Experimental Vapor-Liquid Equilibria for Propylene-Propane System at 320 P.S.I.A.

	Composition: Mole %				
	Vapor		Liquid		Relative Volatility,[a]
Run No.	Propylene	Propane	Propylene	Propane	α
A-1	44.51	55.49	41.68	58.32	1.1224
A-7	51.87	48.13	48.99	51.01	1.1221
A-8	55.48	44.52	52.82	47.18	1.1131
A-6	63.73	36.27	61.37	38.63	1.1060
A-3	69.09	30.91	66.95	33.05	1.1034
A-2	79.33	20.67	77.81	22.19	1.0945
A-5	83.36	16.64	82.11	17.89	1.0915
A-4	92.99	7.01	92.45	7.55	1.0833

[a] $\alpha = \dfrac{(\text{Propylene/Propane})_{\text{vapor}}}{(\text{Propylene/Propane})_{\text{liquid}}}$

Table II. Distillation of Propylene-Propane Mixtures in a Packed Column at Total Reflux and 320 P.S.I.A.

	Composition: Mole %					Total Theoretical Plates.
	Overhead		Bottoms			
Run No.	Propylene	Propane	Propylene	Propane	$\alpha_{\text{avg.}}$[a]	N[b]
B-1	70.70	29.30	42.52	57.48	1.1106	11.3
B-2	85.86	14.14	67.62	32.38	1.0951	11.8
B-3	91.51	8.49	79.36	20.64	1.0886	12.2
B-5	94.78	5.22	87.37	12.63	1.0843	11.9
B-8	96.54	3.46	91.73	8.27	1.0819	11.7
B-4	97.53	2.47	93.94	6.06	1.0808	12.0
B-7	97.55	2.45	94.17	5.83	1.0806	11.7
B-6	98.65	1.35	96.76	3.24	1.0792	11.7
B-9	99.01	0.99	97.80	2.20	1.0788	10.7

[a] $\alpha_{\text{avg.}} = 1 + [(\alpha_{\text{top}} - 1)(\alpha_{\text{btm.}} - 1)]^{1/2}$; data obtained from Figure 3. [b] Calculated from Equation 1.

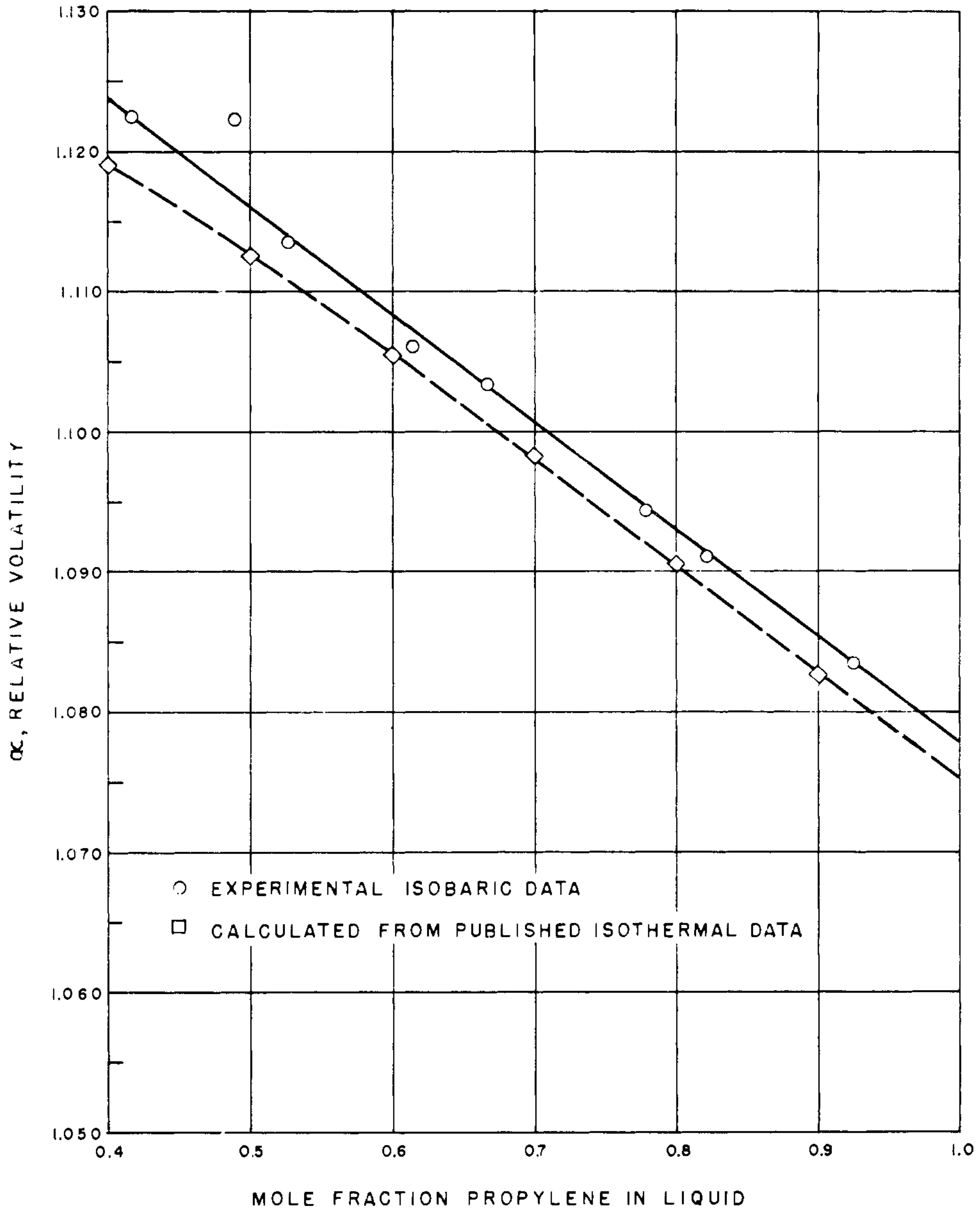

Figure 3. Relative volatility of propylene with respect to propane at 320 p.s.i.a.

Values of P_i° were obtained from the data of Reamer and Sage (*4*). Values of $\underline{\beta}_i$ and V_i' were obtained from the data of Farrington and Sage (*1*) and Reamer, Sage and Lacey (*5*). These data were correlated with temperature and pressure to obtain equations for use in machine computation of the relative volatility. The correlations for P_i° were developed by Hill, and the equations for $\underline{\beta}_i$ and V_i' were obtained by regression analysis on an IBM 704 Computer.

Isobaric relative volatilities then were calculated from the following relationships:

$$\alpha = \gamma_1 P_1^\circ \theta_1 / \gamma_2 P_2^\circ \theta_2 \qquad (3)$$

$$P = x_1 \gamma_1 P_1^\circ \theta_1 + x_2 \gamma_2 P_2^\circ \theta_2 = 320 \text{ p.s.i.a.} \qquad (4)$$

For each given liquid phase composition, the bubble point temperature was obtained by trial and error computation satisfying Equation 4. Then the corresponding values of γ, P° and θ were substituted in Equation 3 to obtain α. An IBM 7090 Computer was used in these calculations.

The calculated isobaric relative volatilities are given in Table III and are included in Figure 3 for comparison with the experimental data. The calculated values based on the published data are about 0.003 units lower than the experimental results of the present study.

Table III. Calculated Vapor-Liquid Equilibria for Propylene-Propane System at 320 P.S.I.A. Based on Published Data

Liquid Composition: Mole %		Bubble Point Temperature: ° F.	Relative Volatility, α
Propylene	Propane		
40	60	135.9	1.1190
50	50	134.3	1.1123
60	40	132.8	1.1053
70	30	131.5	1.0981
80	20	130.2	1.0905
90	10	129.1	1.0827

Two basic differences in experimental method between the previous and present studies are noted. First, an Othmer-type still was used in the present work compared to equilibrium cells in the other investigations. Both techniques have inherent shortcomings, and it is difficult to establish which is more accurate. The other difference is in analytical methods. The present work used mass spectrometric techniques whereas previous investigators used chemical methods. Reamer and Sage measured propylene content by volumetric determination of hydrogen consumption upon catalytic hydrogeneation. Hanson, *et al.*, determined the reduction in gas volume upon absorption of the propylene in sulfuric acid. It would seem that the more recently developed mass spectrometric technique is basically superior to the chemical methods, although evaluation of the quantitative effect on relative volatility would require additional study.

The good agreement between the present and published data tends to confirm the validity of the method used for correlating the isothermal data and provides confidence in the extrapolation of the previous relative volatility data above the 90% propylene level. These results thus increase the reliability of fractionator calculations in the region of high-purity propylene, where the requirements are most severe.

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Vapor-Liquid Equilibria at Atmospheric Pressure

II. 1-Butanol-Benzene System

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Vapor-liquid equilibrium values have been determined at atmospheric pressure for 1-butanol-benzene system, using a modified Gillespie still. Experimental data meet the thermodynamic requirements of Gibbs-Duhem equation. The constants *A* and *B* for van Laar equation have been determined.

LIQUID VAPOR equilibria for the system 1-butanol-benzene have been determined at 20° C. by Tryhorn and Wyatt (*8*), at 25° C. by Allen Lingo and Felsing (*1*) and at 45° C. by Brown and Smith (*3*). No published vapor-liquid equilibrium data at 760 mm. of Hg pressure is available, except that of Bonauguri, Bicelli and Spiller (*2*), who made the measurements at 743 to 758 mm. of Hg pressure. However, no information is given about the temperatures at which x-y data were taken, and whether any corrections were made for pressure deviations. In view of this, present measurements were made to determine the vapor-liquid equilibrium compositions at 760 mm. for 1-butanol-benzene system. The experimental results are given in Table I, and the temperature-composition, and x-y curves are shown in Figure 1 and 2, respectively. The activity coefficients were calculated from the equation

Table I. Experimental Data for 1-Butanol-Benzene at 760 mm. of Hg

Temp., ° C.	x_1	y_1	$y_{1\,\text{calcd.}}$	γ_1	γ_2
80.09	1.000	1.000	1.000	1.0000	...
80.16	0.954	0.966	0.961	1.0104	3.4293
80.21	0.948	0.963	0.957	1.0122	3.2943
80.28	0.942	0.960	0.954	1.0132	3.1813
80.39	0.928	0.952	0.947	1.0165	3.0597
80.67	0.897	0.947	0.934	1.0371	2.7719
80.87	0.848	0.920	0.910	1.0591	2.3641
81.36	0.790	0.904	0.892	1.1005	2.0065
81.98	0.714	0.885	0.870	1.1698	1.7159
83.19	0.631	0.867	0.855	1.2501	1.4567
84.54	0.560	0.847	0.844	1.3215	1.3213
86.39	0.475	0.819	0.822	1.4259	1.2074
88.28	0.397	0.787	0.785	1.5509	1.1370
89.69	0.369	0.779	0.782	1.5820	1.0596
92.25	0.308	0.724	0.735	1.6560	1.0575
95.60	0.234	0.660	0.672	1.7905	1.0443
98.70	0.180	0.590	0.595	1.9103	1.0345
100.22	0.161	0.560	0.565	1.9450	1.0201
102.22	0.134	0.510	0.510	2.0091	1.0193
107.10	0.085	0.380	0.386	2.0830	1.0026
112.00	0.040	0.217	0.215	2.2304	1.0005
116.90	0.004	0.025	0.024	2.2754	1.0005
117.70	0	0	0	...	1.0000

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