Plant Performance of a 13-ft.-diameter Extractive-distillation Column

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Plant performance data are presented for a 13-ft.-diam., 100-tray furfural extractive-distillation column separating iso- and *n*-butane from 1- and 2-butene. In addition to composition, temperature, pressure, and flow rate of the external streams, values are presented for vapor and liquid compositions and flow rates at a number of different locations within the tower. With the exception of the vapor compositions, which were determined experimentally, the internal conditions were determined by heat and material balances. These data permitted calculation of plate efficiency over various small sections of the column. In the 50-tray rectifying section, plate efficiency for the isobutane—1-butene separation was constant at 20%, and in the stripping section the plate efficiency varied from 25 to 45%. The average for the entire column was 25%.

The furfural-column plate efficiencies compare favorably with those predicted from laboratory tests made before the construction of the column to evaluate the performance of the tray design to be employed. The laboratory plate efficiencies were obtained for the desorption of oxygen from oxygen-rich water with air at the same conditions of volumetric gas and liquid rates to be encountered in the furfural column. When these values were suitably corrected for physical property differences between the two systems, the point efficiencies predicted from the laboratory data for the furfural column ranged from 35% near the top of the column to 25% near the bottom of the column, the average value being 29%.

Operating data have recently been obtained for a newly completed furfural extractive-distillation column at the Neches Company's butadiene plant (*15*). The tray design for this column was essentially the same as that recommended by the University of Delaware for the conditions of high loading and low gas throughput encountered in such columns. The Delaware recommendations were based on laboratory efficiency measurements for the desorption of oxygen from oxygen-rich water with air on a tray of this design (*4*). The purpose of this report is to compute the plate efficiency of the plant column from the operating data and to compare the result with the plate efficiency anticipated from the laboratory measurements.

NECHES TRAY DESIGN

The new Neches column trays were designed to give as good a vapor distribution as possible in spite of the conditions of high liquid loading and low vapor throughput found in furfural extractive columns. Tunnel caps placed parallel to the direction of liquid flow were shown to be superior to any other type of bubble cap for minimizing hydraulic gradient, and these caps were employed in the final design. Hydraulic gradients were further minimized by utilizing comparatively short lengths of liquid travel. In the 13-ft.-diam. tower required by Neches, a double split-flow system was used; that is, the liquid was split into four separate streams flowing across each tray. With this scheme the distance between inlet and outlet weirs for any one liquid stream was 20¼ in.

The caps themselves were 4 in. high 2½ in. wide, and 20 in. long, with 1-in.-high slots on ½-in. spacing. The slots were 5/16 in. wide at the bottom and 5/32 in. at the top. The outlet-weir height employed with these caps was 2½ in. To ensure as high an efficiency as possible with the extractive system where the mass transfer rate within the liquid phase is controlling, the liquid residence time on the tray was increased by use of a wide spacing between adjacent tunnel caps. The distance between adjacent cap faces was 4 in. The laboratory tests showed that even with this rather wide spacing, all the liquid was well contacted by the gas and the efficiency did not suffer. Complete results of the laboratory tests for this tray design have already been reported (*4*).

NECHES-COLUMN OPERATING DATA

The operating data taken in the plant are summarized in Tables 1 and 2. The column consists of two 50-tray units operated in series. The feed, mainly butanes and butenes, enters as a vapor below the fiftieth tray. The furfural-water extractive solvent enters onto the fifth tray from the top of the column and, being essentially nonvolatile, is removed from the bottom of the column along with the butenes. The solvent is recovered from the bottoms in a separate stripper column.

Table 1 shows the flow rate, temperature, and pressure of the various streams entering and leaving the tower. The large quantity of solvent required for this column is evident from this table.

Table 2 shows the composition of the various streams entering and leaving the tower. The main separation is between isobutane and 1-butene. The water content of the furfural is seen to be appreciable on a molar basis. Table 2 also summarizes the component and over-all material balances for the tower. Except for the components present in small amounts, the agreement between input and output is good and indicates that the plant data are accurate. For the purpose of making over-all enthalpy balances, the flow rates were slightly adjusted to give perfect material balance.

In the over-all enthalpy balance made for the column the enthalpies of the various streams were computed from the plant data given in Tables 1 and 2 and from enthalpy data for the C_4 hydrocarbon-furfural-water system (*11*). These enthalpies include the rather appreciable-heat-of-solution values for C_4 hydrocarbons in furfural-water (*16*). When enthalpies were based upon the pure liquids at 32°F. and 1-atm. total pressure and expressed in the units of British thermal units $\times 10^{-6}$/ 24-hr. day, it was found that the heat added by the reboiler was 2,583; the enthalpy of the solvent feed stream was 1,282; the enthalpy of the hydrocarbon feed stream was 287; and the enthalpy of the hydrocarbon reflux stream to the tower was 44. The sum of the input enthalpy quantities was 4,196. The output enthalpy quantities consisted of 3,783, which was the enthalpy of the bottoms product to the stripper, and 364, which was the enthalpy of the overhead vapor stream to the condenser, giving a total of 4,147. These figures show good agreement between input and output enthalpy quantities, again confirming the validity of the plant operating data. The computed enthalpies were adjusted slightly to obtain perfect balance, and these self-consistent values

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TABLE 1.—OPERATING CONDITIONS FOR FURFURAL EXTRACTIVE TOWER AND SOLVENT STRIPPER

Process stream	Total flow rate as metered, lb. moles/24-hr. day	Pressure, lb./sq. in. gauge	Temperature, °F.
C_4 Hydrocarbon feed (Fed as vapor below tray 50)	24,300	. . .	166
C_4 Hydrocarbon overhead product	13,950	86	112*
C_5 hydrocarbon reflux to tower	20,820	86	98
Solvent feed (fifth tray down from top)	411,500	. . .	130.5
Liquid transfer from bottom of upper 50-tray column to top of lower 50-tray column	465,000	91	144
Bottoms product to solvent stripper	429,860	98.5	292
Stripper overhead product	10,810	52	105*
Stripper reflux	33,960	52	84
Stripper bottoms product	418,300	58	315

*Condensation temperature.

are used in later calculations of vapor and liquid flow rates within the column.

VARIATION OF CONDITIONS WITHIN THE TOWER

A constant molar flow rate for vapor and liquid within the tower cannot be assumed in the present case and so for the purpose of computing the plate efficiency it is necessary to know the local operating conditions within the extractive column. Local values of vapor composition, temperature, and pressure were obtained in the plant test, and from these data and the known conditions external to the column, it was possible by heat and material-balance calculations to compute the liquid and vapor flow rates and liquid compositions within the tower. A sample calculation for this procedure is given in the Appendix. Results are given in Tables 3, 4, and 5. A check on the accuracy of the calculation may be made by comparing the computed total liquid flow rate at tray 51 with the metered flow rate of the liquid stream pumped from the bottom of the first 50-tray column section to the top of the second 50-tray column section. The two values are seen to agree within 3% in Table 3.

Table 3 also shows that although the liquid flow rates range from about 65 to 85 gal./(min.) (ft. of weir length), the corresponding vapor rates are only from 0.6 to 1.0 ft./sec. The high liquid rates result from the presence of the large quantities of solvent added to the column; the liquid on the trays contains 91 mole % furfural-water near the top of the column and 81 mole % furfural-water at the bottom. The furfural is essentially nonvolatile and the water only slightly so, which gives a vapor consisting mainly of C_4 hydrocarbons. The vapor flow rate is thus quite small compared with the liquid flow rate, which makes it more difficult to obtain good hydraulic characteristics and high plate efficiency for columns of this type. These factors are considered in more detail in a later section.

Table 3 shows that the vapor and liquid flow rates not only are unusual in magnitude but both increase considerably in proceeding from the top to the bottom trays of the tower. The change in liquid flow rate is wholly due to the change in flow of the C_4 hydrocarbons, rather than to any change in flow of solvent, which is essentially nonvolatile and constant in rate. The changes in C_4 hydrocarbons flow rate within the column are due to the highly nonideal nature of the multicomponent solution present. Isobutane and *n*-butane, which concentrate near the top of the column, are more nonideal with respect to furfural-water than the butenes, which concentrate near the bottom of the column; being more nonideal, the butanes have considerably less

TABLE 2.—COMPONENT MATERIAL BALANCES ON INPUT AND OUTPUT STREAMS TO FURFURAL EXTRACTIVE TOWER. ALL QUANTITIES ARE LB. MOLES/24-HR. DAY

	Input as metered			Output as metered				
Component	Hydrocarbon feed (51st tray from top)	Solvent feed (5th tray from top)	Total input to Tower	Overhead product	Stripper overhead product	Stripper bottoms product	Total output of tower	Percentage of deviation of material balance
Isobutane	8,650	0	8,650	9,030	54	0	9,084	−5.0
1-Butene	7,200	0	7,200	209	6,900	0	7,109	+1.3
n-Butane	3,659	0	3,659	2,985	585	0	3,570	+2.4
trans-2-Butene (low-boiling isomer)	2,020	0	2,020	0	1,840	0	1,840	+8.9
cis-2-Butene (high-boiling isomer)	292	0	292	0	562	0	562	−92.4
Isobutylene	656		656	0	541	0	541	+17.5
Butadiene	292	0	292	42	346	0	388	−32.9
Propanes	1,506	0	1,506	1,690	0	0	1,690	−12.2
Total hydrocarbons	24,300	0	24,300	13,950	10,810	0	24,760	−1.9
Furfural	0	283,500	283,500	0	0	284,500	284,500	−0.35
Water	0	128,000	128,000	470*	750*	133,800	135,020	—5.5
Total of all components	24,300	411,500	435,800	14,420	11,560	418,300	444,280	−1.9

*Computed values.

TABLE 3.—LOCAL OPERATING CONDITIONS WITHIN FURFURAL EXTRACTIVE TOWER

	Tray number, from top of tower								
	1	17	33	51*	67	83	95	97	99
Temp., °F.	112	133	136	145	149	153	157	158	163
Pressure, lb./sq. in. guage	86	87.4	89	91	93	95.5	97.5	97.8	98.2
Vapor rate from tray, lb. moles/24-hr. Day†									
Hydrocarbons	34,400	52,370	57,620	52,100	59,310	66,270	73,780	74,690	88,440
Water	470	1,230	1,480	1,600	2,090	2,480	3,070	3,110	4,160
Total	34,870	53,600	59,100	53,700	61,400	68,750	76,850	77,800	92,600
Total vapor rate from tray, ft./sec., based on bubbling area	0.378	0.620	0.678	0.615	0.691	0.764	0.842	0.852	1.020
Liquid rate to tray, lb. moles/24-hr. day†									
Hydrocarbons	20,600	38,570	43,820	62,830	70,040	77,000	84,510	85,420	99,170
Furfural	0	284,000	284,000	284,000	284,000	284,000	284,000	284,000	284,000
Water	0	132,260	132,510	132,630	132,120	133,510	134,100	134,140	135,190
Total	20,600	454,830	460,330	479,460‡	486,160	494,510	502,610	503,560	518,360
Total liq. rate to tray, gal./(min.) (ft. of weir), equal split of liquid flow within tower assumed	10.0	69.4	70.8	75.4	76.8	78.4	80.2	80.5	83.6

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*Tray below vapor feed.

†Flow quantities of vapor and liquid were computed by enthalpy balances as described in sample calculations.

‡The metered liquid transfer from the bottom of the upper 50-tray column to the top of the lower 50-tray column was 465,000 lb. moles/24-hr. day (*see* Table 1).

solubility for the solvent than the butenes. Under the conditions of nearly constant temperature and pressure existing in the column, the solubilities are in fact about inversely proportional to the activity coefficients of the C_4 hydrocarbon components. Thus for extractive columns where the added solvent improves the relative volatility of the feed components by affecting a large difference in their activity coefficients, liquid flow rates will always vary considerably within the column. And for the usual case of constant flow rate of streams external to the column, vapor flow rates within either the rectifying or stripping section increase by the same amount as the liquid rates.

CALCULATION OF NECHES-COLUMN PLATE EFFICIENCY

Plate efficiencies were computed over most trays of the column for the key components, isobutane and 1-butene, and in some regions of the column for the *n*-butane–1-butene separation. The calculations were made on a modified McCabe-Thiele diagram. Relative volatility

TABLE 4.—LOCAL COMPOSITION VALUES FOR KEY COMPONENTS WITHIN FURFURAL EXTRACTIVE TOWER

	Liquid composition to tray, mole % Solvent and water-free basis			Vapor composition from tray, mole % Solvent and water-free basis		
Location within tower*	Isobutane	*n*-Butane	1-Butene	Isobutane	*n*-Butane	1-Butene
Distillate†	....	....	....	64.7	21.4	1.5
Tray 10	52.7	31.2	5.8	56.0	28.5	4.6
Tray 17†	46.6	34.7	10.2	51.4	31.2	7.9
Tray 22	44.9	34.9	13.9	50.0	31.4	10.7
Tray 28	41.8	34.2	18.5	47.5	31.0	14.3
Tray 33†	38.5	32.7	22.4	44.7	30.0	17.4
Tray 38	35.1	31.4	26.3	42.0	29.1	20.6
Tray 43	31.6	29.9	30.5	39.0	28.0	24.0
Feed (introduced as vapor between trays 50 and 51)	....	....	....	35.6	15.2	29.6
Tray 51†	27.8	22.5	35.8	33.4	26.0	30.0
Tray 56	23.5	27.4	39.3	28.0	31.7	34.5
Tray 59	18.2	29.4	41.6	21.6	34.0	37.4
Tray 62	12.3	30.9	44.5	14.5	35.7	40.8
Tray 64	9.4	31.4	46.3	11.0	36.3	43.0
Tray 67†	6.1	32.0	49.1	7.1	36.8	46.5
Tray 72	3.1	29.9	53.8	3.5	34.2	52.0
Tray 78	1.6	25.8	59.7	1.8	29.3	59.0
Tray 83†	1.0	21.9	63.7	1.1	24.6	63.7
Tray 95†	0.6	10.6	71.3	0.6	11.3	72.4
Tray 97†	0.5	9.4	73.0	0.5	10.0	74.3
Tray 99†	0.5	8.6	69.5	0.5	9.0	70.2
Bottoms product†	0.5	5.4	63.7			

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*Trays are numbered from top of the tower.

†Composition of vapor streams from these trays obtained by sampling; other values obtained from plate number–vapor composition diagram; all liquid compositions computed by material balance, by use of flow rates from Table 3.

TABLE 5.—RELATIVE VOLATILITY VALUES WITHIN FURFURAL EXTRACTIVE TOWER

		Liquid composition on tray, water-free basis, mole %			Water concentration in solvent‡	Relative volatility values	
Tray No. from top of tower	Temperature, °F.	Sum of isobutane, *n*-Butane and 1-butene*	Other hydrocarbon components†	Total hydrocarbon concentration	Hydrocarbon-free basis, mole %	Isobutane to 1-butene	*n*-Butane to 1-butene
9	136	10.2	1.2	11.4	20.7	2.05	1.53
16	133	10.9	1.0	11.9	19.6	2.07	1.54
32	136	12.5	0.9	13.4	12.8	1.99	1.48
50	145	15.6	2.5	18.1	9.6	1.87	1.40
66	149	17.3	2.5	19.8	12.4	1.84	1.38
82	153	18.4	2.9	21.3	15.2	1.81	1.36
94	157	14.2	8.7	22.9	17.4	1.78	1.34

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*For relative distribution of these components, *see* Table 4.

†Consists of mostly propanes above the feed, and 2-butenes, isobutylene, and butadiene below feed.

‡Computed from known solubility relationships for water in hydrocarbon-furfural mixtures.

values for C_4 hydrocarbon-furfural-water mixtures are available from references *8, 14,* and *17* as a function of temperature and liquid composition. Special procedures were followed in employing these relative volatility data owing to the presence of many nonkey hydrocarbon components within the liquid and because of the existence of a separate water-rich liquid phase on all the trays of the column.

With regard to the latter problem, it is the composition of the solvent-rich liquid phase which determines the relative volatility; whereas the liquid compositions obtained by material and enthalpy balance calculations are those for the total liquid. Fortunately, data of Griswold and associates (*10*) are available for the conjugate liquid-phase compositions of the *n*-butane–furfural–water and 1-butene–furfural–water systems at temperatures and pressures of interest. These data show that when an excess of water is present, the water-rich liquid phase contains some furfural but essentially no C_4 hydrocarbons. Knowledge of the total liquid-phase composition along with the Griswold phase data permitted calculations to be made for the composition of the solvent-rich liquid phase for each tray considered. These values are shown in Table 5.

To obtain the proper values of relative volatility from the solvent-rich phase liquid composition and temperature, use was made of the fact that the total hydrocarbon composition and the water composition are the most important factors affecting relative volatility. The relative amounts of the various hydrocarbons present fortunately does not greatly affect the vapor-liquid equilibrium data. Thus to obtain the relative volatility of isobutane to 1-butene, data for the system isobutane – 1-butene – furfural–water were employed (*14*), with the isobutane concentration being taken as the sum of the actual isobutane concentration plus the concentrations of all other paraffin hydrocarbons (such as *n*-butane) present in the liquid. Similarly the 1-butene concentration was taken as the sum of the actual 1-butene concentration plus the concentrations of all other olefin hydrocarbons. Relative volatility data for the system *n*-butane–1-butene–furfural–water were computed from the data of references *8, 14,* and *17,* on the same assumption as before as to the effect of other hydrocarbon components. The resulting relative volatility values are given in Table 5.

TABLE 6.—EXPERIMENTAL LOCAL PLATE EFFICIENCIES WITHIN FURFURAL EXTRACTIVE TOWER

Location within tower	Experimental Murphree vapor efficiencies, %	
Between trays	Isobutane–1-butene separation	*n*-Butane–1-butene separation
10–17	25	24
17–22	21	22
22–28	20	20
28–33	19	20
33–38	19	20
38–43	21	20
43–51	21	†
51–56	21	†
56–59	33	†
59–62	44	†
62–64	40	†
64–67	40	†
67–72	35	†
72–78	25	27
78–83	*	27
83–95	*	33
95–97	*	30
Average for all trays considered	25	25
Average predicted efficiency (from Table 7)	29	32

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*Values inaccurate owing to very low isobutane concentrations.

†Local composition values in doubt in this region.

The modified McCabe-Thiele diagram was drawn up for the isobutane–1-butene separation by expressing values of vapor and liquid composition on a key basis, that is, as (moles of isobutane) / (moles of isobutane + moles of 1-butene). Operating-line compositions were computed from the data of Table 4, and equilibrium compositions from the relative volatility data of Table 5. The graphical stepwise procedure of Baker and Stockhardt (*1*) was used over small tray intervals to obtain the Murphree vapor-plate efficiencies shown tabulated in Table 6. Plate-efficiency values are not reported below tray 78 for the isobutane–1-butene separation owing to the inaccuracies caused by the very small isobutane compositions in this region of the column. Similar McCabe-Thiele procedures were followed for the *n*-butane–1-butene separation. Results were not reported for this pair between trays 43 and 72, as composition values were not too consistent in this region of the column.

The experimental plate-efficiency results shown in Table 6 are consistent in spite of the widely varying conditions of relative volatility and total flow rate within the column. Further, the efficiencies for the two different separations considered are also very nearly the same in spite of large differences in relative volatility between the two. However, to determine whether the magnitude and variation of the experimental efficiencies are reasonable, plate-efficiency prediction calculations have been made by the method of Gerster, Colburn, and associates (*7*) and are presented in the next section. Discussion of both sets of efficiency results then follows.

PREDICTION OF EFFICIENCY RESULTS FROM OXYGEN-DESORPTION DATA

As mentioned earlier, laboratory plate-efficiency measurements were made for the tray design recommended for use in the Neches extractive column. These measurements were made for a system in which the rate of mass transfer within the liquid phase is controlling: the desorption of oxygen from oxygen-rich water with air at atmospheric pressure and temperature. Plate-efficiency data were obtained under widely varying conditions of gas rate, liquid rate, outlet weir height, and slot spacing. Presentation and correlation of these results have been given elsewhere(*4*).

The Neches column trays considered in the predication calculations operated with a gas rate which varied from 0.61 to 0.80 ft./sec., with a liquid rate of from 70 to 80 gal./(min.) (ft. of weir), and with a depth of clear liquid on the tray computed by the Francis weir formula to be from 4.0 to 4.2 in. Under these same conditions the Murphree liquid efficiencies for the oxygen system were about 36%. The same variation in gas rate as that encountered in the Neches column caused the oxygen desorption efficiency to change as much as 1.5 efficiency %, increasing with increasing gas rate; the liquid-rate variation caused the efficiency to change as much as 5 efficiency %, increasing with decreasing liquid rate; and the effect of the small change in clear liquid depth upon efficiency was negligible.

As shown in reference *7*, it is more fundamental to work with transfer units instead of efficiency values. The number of liquid film transfer units, N_L, is related to fractional efficiency expressed in liquid concentration units, E_L, for the case of no liquid mixing on the tray, as follows:

$$N_L = -2.3 \log (1 - E_L) \qquad (1)$$

The value of number of transfer units for the C_4 hydrocarbon–furfural-water system, $N_{L_{\text{extractive}}}$ may be computed from the number of transfer units for the oxygen-water system $N_{L_{O_2\text{-water}}}$ by the following relationship(*6*):

$$N_{L_{extractive}} = N_{L_{O_2-water}} \left[\frac{(\mu/\rho D)_{O_2-water}}{(\mu/\rho D)_{extractive}} \right]^{\frac{1}{2}} \qquad (2)$$

In Equation (2), μ is the viscosity of the liquid, ρ is the density of the liquid, and D is the liquid molecular-diffusion coefficient for the diffusing component. The value of $\mu/\rho D$ for the oxygen-water system is 376 dimensionless units(*7*). For the extractive system, the liquid viscosity is 0.68 centipoise at the top of the column, where the solvent concentration is the greatest, and the corresponding value at the bottom of the column, where the solvent concentration is the least, is 0.47 centipoise(*9*). The liquid density for the extractive system varies only slightly, from 65.5 lb./ cu.ft. at the top of the column to 59.2 lb./cu.ft. at the bottom of the column(*9*). The diffusivity of C_4 hydrocarbons through the furfural solvent is estimated to vary from 1.75×10^{-5} sq. cm./sec. at the top of the column to 2.59×10^{-5} sq.cm./sec. at the bottom of the column(*18*). These data permit calculation of the dimensionless Schmidt group ($\mu/\rho D$) for the extractive system as 372 at the top of the column to 191 at the bottom. Variation of the liquid physical properties and the Schmidt group with tray number is shown in detail in Table 7*. Values of N_L for the oxygen-water system may now be converted by Equation (2) to the corresponding values for the extractive system. Results show that the $N_{L_{\text{extractive}}}$ values vary from 0.48 at the top of the column to 0.59 at the bottom.

As will be seen later, mass transfer resistance within the gas phase of the extractive system is quite small but not negligible. Prediction of the fractional vapor efficiency E_{OG}, including the mass transfer resistance of both the gas and liquid phases, can be made by use of the following equation(*7*):

$$\frac{1}{-2.3 \log (1 - E_{OG})} = \frac{1}{N_G} + \frac{mG/L}{N_L} \qquad (3)$$

In this expression N_G is the number of gas-phase transfer units for the extractive system, and mG/L is the ratio of the slope of the equilibrium curve to the slope of the operating line in dimensionless units.

A value of $N_G = 2.4$ for the extractive system was used in the prediction calculations. This same value was used by Gerster and coworkers in predicting efficiencies for their C_4 hydrocarbon–furfural pilot plant column and is based upon their experimental air-humidification data(*7*). The value of N_G obtained for the mass transfer of water vapor through air was converted to a value of N_G for the extractive system by an equation similar to Equation (2) with the $\mu/\rho D$ groups evaluated for the gas phase. The N_G value obtained in this manner agrees closely with that which would be obtained for the extractive system if predicted from some recent University of Delaware data for the absorption of ammonia from air into water on a 2-ft. bubble plate(*5*). Values of mG/L were taken from the modified McCabe-Thiele diagrams. Results for each term of Equation (3), as well as for the predicted value of E_{OG}, are shown in Table 7 as a function of tray number for both the isobutane–1-butene separation and for the *n*-butane–1-butene separation.

Inspection of Table 7 shows that values of mG/L and N_L both increase with increasing tray number, and so the term $(mG/L)/N_L$ and thus E_{OG} do not vary widely as a function of position within the column. It is also of interest to note the relative values of $1/N_G$ and $(mG/L)/N_L$ as they represent the relative resistances to mass transfer within the gas and liquid phases respectively. For all cases considered, 80 to 85% of the mass transfer resistance lies within the liquid phase. The reasons for this will be discussed later.

The calculation of predicted efficiency is important because it shows that there should be little change in efficiency with tray number and that the liquid-phase mass transfer resistance is controlling. It is perhaps of greater interest to discuss the probable accuracy of the predicted efficiency values. This accuracy depends upon whether all the factors of operation affecting mass transfer in the extractive column are the same as those on the oxygen-desorption test tray. The same conditions of volumetric gas rate, liquid rate, weir height, and cap design were employed; it is not possible, however, to be certain that other factors such as degree of mixing on the tray, gas and liquid holdup on the operating tray, and degree of disengagement of vapor from the liquid were identical for both the furfural column and the oxygen-desorption tray. Differences in vapor density and liquid viscosity in these two systems, which may be

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*Table 7 has been deposited as document 4756 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., and may be secured for $1.25 for photoprints or 35-mm. microfilm.

noted in Table 7, may affect the factors just mentioned to some degree. However, the greatest difference between the two units was in the length of the calming zone before the outlet weir. In both cases the tunnel caps were placed parallel to the direction of liquid flow and had a slotted length of 20 in.; but in the furfural column the distance from the last slot to the outlet weir was 2 in., and on the oxygen-desorption tray this distance was 12 in. Because of the high liquid rates employed, it was experimentally observed that in the latter case much of the gas was carried along into the calming zone of the oxygen-desorption tray, where additional mass transfer probably occurred. Thus the liquid on this tray could have been contacted by the gas for as much as 32 in., compared with 22 in. for the furfural-column tray. If the N_L values for the oxygen tray are reduced by a factor of 22/32 before being used in the prediction calculations, the maximum effect of this difference in tray layout can be determined. This has been done, and the resulting predicted efficiencies given in Table 7 are seen to be 7 to 9 efficiency % lower than when this difference in tray layout is ignored. If it is assumed that the actual correction for the oxygen-desorption tray calming zone is about one half the maximum correction just computed, then the average predicted efficiency for the isobutane–1-butene separation is 29%, and the average predicted efficiency for the *n*-butane–1-butene separation is 32%. These values compare well with the experimental efficiencies shown in Table 6. The predicted efficiencies assume the tray liquid to be well-mixed, but even if the tray liquid were assumed to be completely nonmixed, the predicted efficiency values would be increased by only 3 or 4 efficiency %.

DISCUSSION OF RESULTS

Both the experimental plant-performance data and efficiency values based upon laboratory measurements confirm that plate efficiencies for the furfural extractive column under examination are about 25 to 30%. It is now pertinent to examine the reasons for the low efficiency and then to determine whether anything can be done to improve it.

The prediction calculations are better suited to show the reasons for the low efficiency. They indicate that the rate of mass transfer within the liquid phase is quite low, which in turn limits and controls the efficiency of the entire mass transfer operation. The liquid-phase efficiency is low because of the adverse effect of the following variables:

1. *Low Gas Rate.* Liquid-phase efficiencies increase with increasing gas rate, because higher gas rates provide a greater interfacial area and one which is being renewed at a faster rate.

2. *Low Time of Contact of the Liquid with the Gas.* The greater the liquid contact time on the tray, the greater is the amount of mass transfer which can occur in the liquid phase. High liquid rates and a fairly small length of liquid travel are responsible for the low liquid contact time.

3. *Unfavorable Liquid Physical Properties.* Liquid phase efficiencies increase with decreasing liquid viscosity, with increasing liquid diffusivity, and with increasing liquid density. The present extractive system has a liquid viscosity about three times greater than a gasoline fraction at its boiling point.

Possibilities for overcoming these unfavorable factors which promote low plate efficiency are examined below:

1. *Increase in Gas Rate.* Very little can be done in the present column to increase the gas rate without increasing the already high liquid rate. If an extractive solvent somewhat more volatile than furfural were used, this would increase the gas rate and would be desirable from a plate-efficiency viewpoint.

2. *Increase in Liquid Contact Time.* The liquid contact time could be increased by use of a column of larger diameter; it is not likely, however, that the cost of such an increase would be less than the saving resulting from the fewer trays required. If the liquid stream were divided into only two parts instead of into four parts as in the present column, the length of liquid travel would be doubled, but because the quantity of liquid per pass would also be doubled, the liquid contact time on the tray would not be changed. The present arrangement has the advantage of a more uniform gas distribution owing to a lower hydraulic gradient of liquid. As mentioned earlier, the tunnel caps employed have a distance of 4 in. between adjacent cap faces which provides more liquid-contact time than any other type of bubble cap which could have been used. The comparatively wide cap spacing was shown in the laboratory tests not to have an adverse effect upon efficiency.

3. *Lower Solvent Viscosity.* Choice of a different solvent or use of an additive to the solvent would lower the viscosity. The additive should not affect selectivity. This latter possibility has been examined in detail in a recent publication by Baumgarten and Gerster(*2*).

The conclusion to be reached from the foregoing discussion is that with the high liquid rates and low gas rates which result from the extractive-distillation operation and with the furfural-water solvent employed, it is difficult to obtain a high plate efficiency with even the most carefully considered tray design. The present tray design appears to be highly satisfactory and represents a considerable improvement over the older Neches design in which large, closely spaced, round caps were employed on a single split-flow tray. Happel and associates(*13*) computed the tray efficiency to be 25% for this column, which has the same diameter (13 ft. I.D.) and handles the same feed components as the newer column. The hydrocarbon feed rate to the older column was only 4,300 bbl./day, however, compared with the 6,720 bbl./day fed to the tunnel-tray column. Thus the improved tray design permits considerably greater throughput without any change in plate efficiency. Neches engineers have also made performance comparisons for these two columns when operating at identical feed rates(*15*). At a feed rate below 8,500 bbl./day, purity of *n*-butylenes in the bottoms product is approximately 4.5 percentage points higher for the new column, and loss of *n*-butylenes in the overhead is 0.3 percentage point lower. At feed rates of about 9,200 bbl./day, loss of *n*-butylenes in the overhead is about 8% for the older column, but only 6% for the new. This would indicate that plate efficiencies for the new column are much more favorable than those for the old column at the higher throughput rates.

CONCLUSION

Sound procedures have been demonstrated for evaluating the performance of a commercial fractionator where vapor- and liquid-flow rates vary considerably within the column. The computed efficiencies compare favorably with those predicted by the method of Gerster, Colburn, and associates(*7*), indicating the usefulness of this procedure in showing when low efficiencies can be expected. In this case the nature of the extractive-distillation operation and the properties of the furfural-water solvent employed were shown to be responsible for the low order of magnitude for the plate efficiency obtained. Examination of possibilities for increasing the plate efficiency has indicated that the present column could not be improved upon in design or operation and is in fact superior to the furfural extractive columns designed for Neches during World War II.

ACKNOWLEDGMENT

These calculations were carried out under the sponsorship of the Federal Facilities Corporation, Office of Synthetic Rubber, in connection with the Government's synthetic rubber program.

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APPENDIX

Calculation of Flow Rates Within the Tower by Material and Enthalpy Balance Equations

To calculate the liquid and vapor rates at any location within an extractive distillation coumn, it is convenient to use equations requiring knowledge of the composition of only one stream and the temperatures of both streams. Grohse and associates (*12*) used such equations to analyze the performance of their extractive-distillation stripping column. Colburn (*3*) has presented the same type of extractive-distillation equations for the general case. His equations are summarized below:

ENRICHING COLUMN

Total Material Balance:

$$V_n = L_{n-1} + D - S \qquad (4)$$

where

V_n = moles of vapor leaving tray n per unit time
L_{n-1} = moles of liquid leaving tray n-1 per unit time
D = moles of overhead distillate withdrawn per unit time
S = moles of solvent added per unit time

Component Balance:

$$y_n V_n = x_{n-1} L_{n-1} + z_D D - x_s S \qquad (5)$$

where

y_n = mole fraction of component in vapor
x_{n-1} = mole fraction of component in liquid
z_D = mole fraction of component in distillate
x_s = mole fraction of component in entering solvent

Total Enthalpy Balance:

$$(\Sigma y_n H_n) V_n = (\Sigma x_{n-1} h_{n-1}) L_{n-1} + (\Sigma z_D i_D) D + Q_c - (\Sigma x_s h_s) S \qquad (6)$$

where

H_n = partial molal enthalpy of component in vapor
h_{n-1} = partial molal enthalpy of component in liquid
i_D = partial molal enthalpy of component in distillate
Q_c = enthalpy removed in condenser per unit time
h_s = partial molal enthalpy of component in entering solvent

Values of $x_{n-1} L_{n-1}$ are eliminated by substituting Equation (5) into Equation (6). The resulting equation is

$$V_n = \frac{Q_c + [\Sigma x_s(h_{n-1} - h_s)]\, S - [\Sigma z_D(h_{n-1} - i_D)]\, D}{\Sigma y_n\, (H_n - h_{n-1})} \qquad (7)$$

The foregoing equation is particularly useful in the present situation because it does not contain the liquid composition or flow rate for the tray considered. In the present case, where values are known for the composition, temperature, and enthalpy of the external streams and of the vapor within the column the only unknown values in the equation are the vapor rate V_n and the enthalpy of the liquid components on the tray h_{n-1}. The equation is used by assuming the liquid enthalpy values for the tray considered and then computing the resulting value of V_n. The liquid rate and composition values for tray n-1 are now readily computed by Equations (4) and (5), respectively, from which the validity of the assumed liquid enthalpy values is quickly determined.

As a sample calculation the determination of the flow rates within the tower at the seventeenth tray from the top may be considered. At this point the temperature is 133°F., the pressure is 87.4 lb./sq.in. gauge, the water content of the vapor is 2.3 mole %, the furfural composition of the vapor is negligible, and the hydrocarbon composition of the vapor is as given in Table 4. The properties of the streams external to the column are given in Tables 2 and 3.

Enthalpy charts are available for C_4 hydrocarbon–furfural mixtures (*11*), which greatly assist in the use of Equation (7). These charts include the large heat-of-solution values for C_4 hydrocarbons in furfural (*16*) and charts show that the relative amounts of the various C_4 hydrocarbons present in the solution do not greatly affect the enthalpy of the mixture. The partial enthalpy of the water present was computed separately and did not include any allowance for heats of solution of water in the mixture. This omission is justifiable, as most of the water existed on the trays as a second water-rich phase. The enthalpy and external flow-rate values used in Equation (7) are tabulated below. All enthalpy values are relative to the pure components at 32° F. in 1 atm. total pressure.

Enthalpy of Distillate $(\Sigma z_D i_D) D$:

Enthalpy of C_4 hydrocarbons	2,140 B.t.u./lb.mole
Enthalpy of water	1,190 B.t.u./lb.mole

Amount of C_4 hydrocarbons in distillate
13,800 lb. moles/day
Amount of water in distillate
470 lb. moles/day
Total enthalpy of distillate,
$(\Sigma z_D i_D)D = (2{,}140)\ (13{,}800) + (1{,}190)\ (470) = 30{,}100{,}000$ B.t.u./day

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Enthalpy Removed in Condenser Q_c:
Enthalpy of vapor to condenser (Table 3)
361,000,000 B.t.u./day
Enthalpy of reflux stream (Table 3)
44,000,000 B.t.u./day
Enthalpy of distillate
30,100,000 B.t.u./day

Enthalpy removed in condenser = 361,000,000 — 44,000,000 — 30,100,000 = 287,000,000 B.t.u./day

$(\Sigma z_D h_{16})D$:

Enthalpy of liquid on plate 16, h_{16}, is assumed to be 4,110 B.t.u./lb. mole for the C_4 hydrocarbon–furfural mixture, corresponding to an assumed 12 mole % C_4 hydrocarbon concentration in the water-free liquid; and 1,818 B.t.u./lb. mole is the enthalpy of the liquid water.
$(\Sigma z_D h_{16})D = (4{,}110)\ (13{,}800) + (1{,}818)\ (470) = 57{,}600{,}000$ B.t.u./day

Enthalpy of Entering Solvent, $(\Sigma x_s h_s)S$:
Enthalpy of furfural
3,725 B.t.u./lb. mole
Enthalpy of water
1,780 B.t.u./lb. mole
Furfural flow rate
284,000 lb. moles/day
Water flow rate
131,500 lb. moles/day
Enthalpy of entering solvent,
$(\Sigma x_s h_s)S = (3{,}725)\ (284{,}000) + (1{,}780)\ (131{,}500) = 1{,}292{,}000{,}000$ B.t.u./day

$(\Sigma x_s h_{16})S$:
Using the same values as taken above,
$(\Sigma x_s h_{16})S = (4{,}110)\ (284{,}000) + (1{,}818)\ (131{,}500) = 1{,}407{,}000{,}000$ B.t.u./day

$\Sigma y_{17}(H_{17} - h_{16})$:
Vapor enthalpy for C_4 hydrocarbons
10,840 B.t.u./lb. mole
Vapor enthalpy for water
20,100 B.t.u./lb. mole
Vapor contains 2.3 mole % water, the remainder C_4 hydrocarbons
$\Sigma y_{17}(H_{17} - h_{16}) = 0.977\ (10{,}840 - 4{,}110) + 0.023\ (20{,}100 - 1{,}818) = 7{,}000$ B.t.u./lb. mole

Substituting the above values into Equation (7) gives

$$V_{17} = \frac{(287+1{,}407-1{,}292-57.6+30.1)\ (10^6)}{7{,}000} = \frac{(374)\ (10^6)}{7{,}000}$$

$$= 53{,}600 \text{ lb. moles/day}$$

The total vapor quantity may be broken down as follows:

C_4 hydrocarbons in vapor at tray 17
$(0.977)\ (53{,}600 = 52{,}370$ lb. moles/day
Water in vapor at tray 17
$(0.023)\ (53{,}600) = 1{,}230$ lb. moles/day
The liquid quantities may be obtained by material balance:
C_4 hydrocarbons in liquid at tray 16
$L_{16} = V_{17} - D = 52{,}370 - 13{,}800 = 38{,}570$ lb. moles/day
Water in liquid at tray 16
$L_{16} = V_{17} - D + S = 1{,}230 - 470 + 131{,}500 = 132{,}260$ lb. moles/day
Furfural in liquid at tray 16
$L_{16} = S$ 284,000lb. moles/day
Total liquid at tray 16
454,830 lb. moles/day
C_4 hydrocarbon composition on tray 16 on a water-free basis 38,570/(38,570 + 284,000) = 0.119 mole fraction, which checks the originally assumed value used in evaluating the liquid enthalpy.

STRIPPING COLUMN

The corresponding equations used in the stripping column are given below.

Total Material Balance:

$$V_m = L_{m-1} - W \qquad (8)$$

where m and m—1 refer to adjacent trays in the stripping section
W = moles of bottoms withdrawn per unit time

Component Balance:

$$y_m V_m = x_{m-1} L_{m-1} - x_w W \quad (9)$$

where
x_w = mole fraction of component in the bottoms

Total Enthalpy Balance:

$$(\Sigma\, y_m H_m)\, V_m = (\Sigma\, x_{m-1} h_{m-1})\, L_{m-1} - (\Sigma\, x_w h_w)\, W + Q_s \qquad (10)$$

where
h_w = partial molal enthalpy of component in bottoms
Q_s = enthalpy added to system in reboiler per unit time

To eliminate values of $x_{m-1}L_{m-1}$, Equation (9) is substituted into Equation (10) to give

$$V_m = \frac{Q_s - [\Sigma x_w\ (h_w - h_{m-1})]\ W}{\Sigma\ y_m\ (H_m - h_{m-1})} \quad (11)$$

which is the working equation for computing local flow rates in the stripping section.

Consider as a sample calculation the determination of local flow rates and liquid compositions between trays 50 and 51 from the top of the column. The vapor feed is introduced below tray 50, but by use of the stripping equations, the vapor rate obtained will be that leaving tray 51 before joining the feed stream. At this point in the column the temperature is 145° F., the pressure is 91.0 lb./sq.in. gauge, the water content of the vapor is 3.0 mole %, the furfural composition of the vapor is negligible, and other required quantities are given in Tables 2 and 4. The calculations are made in the same manner as before, with the quantities required for Equation (11) taken as follows:

C_4 hydrocarbons and furfural — Water
$(\Sigma x_w h_w)W = (10{,}670)\ (294{,}730) + (4{,}680)\ (131{,}030) = 3{,}757{,}500{,}000$ B.t.u./day
$(\Sigma x_w h_{50})W = (4{,}650)\ (294{,}730) + (2{,}030)\ (131{,}030) = 1{,}636{,}500{,}000$ B.t.u./day
$\Sigma y_{51}(H_{51} - h_{50}) = 0.97\ (11{,}250 - 4{,}650) + 0.03\ (20{,}240 - 2{,}030) = 6{,}946$ B.t.u./ lb. mole
$Q_s = 2{,}494{,}000{,}000$ B.t.u./day
Substituting into Equation (11) gives

$$V_{51} = \frac{(2{,}494-3{,}758+1{,}637)\ (10^6)}{6{,}946} = \frac{(373)\ (10^6)}{6{,}946}$$

$$= 53{,}700 \text{ lb. moles/day}$$

By calculations similar to those above for the rectifying section, the C_4 hydrocarbon composition on tray 50 on a water-free basis is found to be 0.181 mole fraction.

Calculations of the same type were made for seven other tray locations within the tower. Complete results are given in Table 3.

(Presented at A.I.Ch.E. Houston meeting)