Countercurrent Heat Exchange with Vaporizing Immiscible Transfer Agent

PETER HARRIOTT and HERBERT WIEGANDT

Cornell University, Ithaca, New York

This paper investigates a countercurrent heat exchanger which seems particularly suited to large-scale heat transfer operations between aqueous streams for which extremely close temperature approaches are desired.

In the Cornell exchanger a volatile, immiscible liquid is added to the stream to be cooled. This stream passes through a series of flash-vaporization chambers each at a progressively lower pressure. The stream to be heated flows through a series of condensing chambers each at a progressively higher pressure. The vapor transfers from each vaporizer to its related condenser. By selection of a suitable transfer agent the pressure gradient can be great enough to permit stable operation with simple hydraulics and at the same time the pressure gradient can be small enough to make practical the use of a gravity cascade as an alternate to interstage pumping for the condenser sequence.

For purposes of evaluating the behavior of the heat exchanger the laboratory studies were divided into three parts. 1. A two-stage exchanger with packed-bed condensers was constructed and tested with methylene chloride as a transfer agent to verify the self-balancing and gravity-flow features that will be important in a multistage, commercial unit. Tests were run also with just one condenser in use. In some of the single-condenser runs part of the condenser was made inactive to simulate a smaller condenser. These tests served to extend the performance data beyond that achievable at the maximum pumping rates for the two-stage operation. 2. A sieve-plate contacting unit was evaluated for its performance as a condenser. 3. Smaller scale tests were conducted for the flashing of a pentane-water system to establish the validity of generalizations from the methylene chloride-water system. Methylene chloride was selected for reasons of convenience and safety, but it is denser and far more water soluble than are the paraffin hydrocarbons.

TWO-STAGE ASSEMBLY

Figure 1 is a diagram of the experimental two-stage unit. The evaporators and condensers were constructed from sections of Pyrex pipe. Temperatures were measured with thermometers reading to 0.1°C. and calibrated. Manometers were used for reading static pressures and in conjunction with calibrated orifices for measuring flow rates.

The condensers had a 9-in. depth of ½-in. Intalox saddles. The liquid distributor was an assembly of ¼-in. diameter pipe nipples set into a pipe coupling and drilled with staggered 3/16-in. diameter holes to provide adequate distribution with a total of sixty holes. A shielded gas bleed withdrew a small, regulated flow of vapor from the space beneath the packing. The vapor-purge line terminated with an atmospheric condenser. The condensed methylene chloride which settled out in the first-stage condenser could be transferred to the evaporator system through a connection line. The first-stage evaporator had two distribution plated in the riser section. The first or lower one, with ¼-in. diameter holes on ½-in. centers, served essentially to disperse the transfer agent into the water and was positioned 1 ft. in advance of the second or upper distributor. The second distributor, with ½-in. holes on 1-in. centers, provided contacting after the boiling was already well underway. The flashed liquids flowed out through the side arm and entered the second-stage evaporator through the interconnecting seal leg. For comparison purposes the second-stage contacting was carried out in downflow with the entering liquid pouring on the high side of a distributor plate canted at 15 deg. and having fifty 5/16-in. diameter holes in the plate area below the feed zone. The liquid flowed in a thin layer across the plate and formed a wedge-shaped pool at the low end of the plate. The amount of the holdup varied somewhat with the throughput. The liquid primarily came through the last holes and fell to the reservoir section below the plate. Vapor generated by boiling in the reservoir passed through the thin layer of liquid flowing across the plate. The liquid depth in the reservoir section could vary 6 in. for operating convenience.

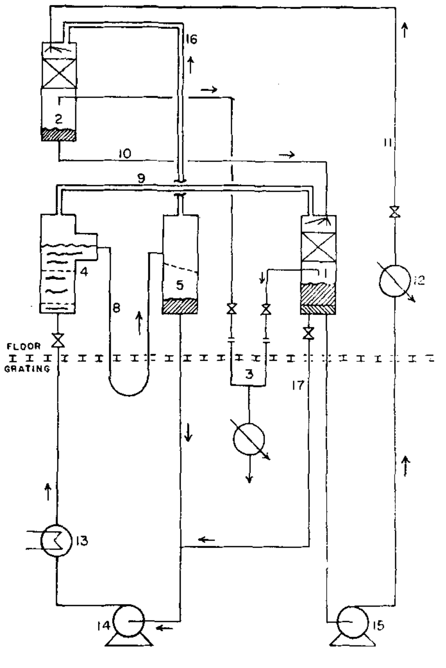

Fig. 1. Two-stage assembly. 1. First-stage condenser. 2. Second-stage condenser. 3. Noncondensible bleed. 4. First-stage evaporator. 5. Second-stage evaporator. 6. Manometers for flow and pressure. 7. Manometers for flow and pressure. 8. Liquid transfer line between evaporators. 9. Vapor transfer line, first stage. 10. Liquid transfer line between condensers. 11. Liquid feed line to second-stage absorber. 12. Cooler for circulating condenser flow. 13. Heater for circulating evaporating flow. 14. Evaporator flow pump. 15. Condenser flow pump. 16. Vapor transfer line, second stage. 17. Return line for condensed transfer agent.

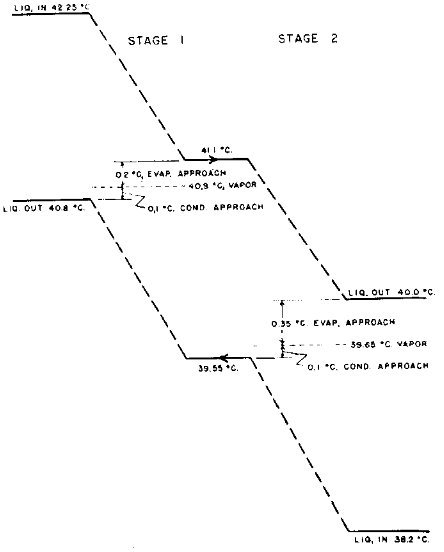

Fig. 2. Performance of two-stage assembly.

The liquid from the second-stage evaporator flowed through a recirculation pump and a steam-heated double-pipe heat exchanger located on the floor below and back to the first-stage evaporator. Methylene chloride could be added to the recirculation line from a reservoir on the floor above.

Operation

A mixture of water and 5 to 15% by volume of methylene chloride was controlled at a selected feed temperature and flow rate and circulated through the two evaporators. Water at a selected feed temperature and flow rate was circulated through the two condensers. A small purge rate was set for each condenser. The unit then established its own steady state balance. The liquid flow between evaporators was aided by the decrease in evaporator pressure in the direction of flow. The difference in elevation permitted liquid flow by gravity between condensers in the direction of increased condenser pressure.

Performance is represented in Figure 2 which shows the results for one run. There was little variation in performance among the many other runs. If the operating temperature was higher, the system pressure was higher accordingly. Also if the condenser flow was increased relative to the evaporator flow, the higher temperature stage would assume a greater portion of the total heat exchanged.

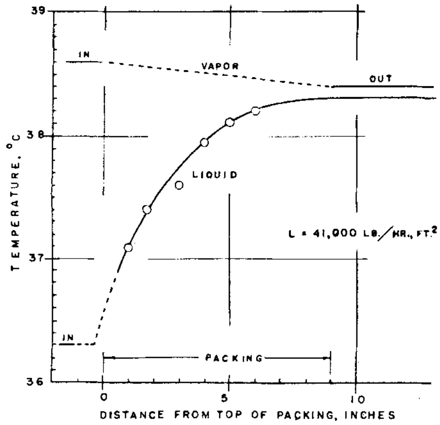

Fig. 3. Temperature profile in packed condenser.

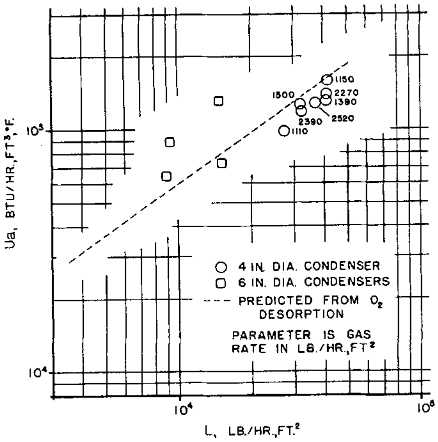

Fig. 4. Performance of packed condensers.

The approach temperatures of the condensers were slightly less than 0.1°C. The approach temperatures of the evaporators fell between 0.2° and 0.4°C. with no consistent pattern insofar as the smaller value was sometimes achieved by the first-stage evaporator, sometimes by the second, by neither, or by both. For the run represented in Figure 2 the liquid flow in the condenser circuit was 37.5 lb./min. (C_p = 1.0) and the flow of water-methylene chloride mixture in the evaporator circuit was 57 lb./min. (C_p of mixture = 0.94). The calculated heat from the evaporator is 13,000 B.t.u./hr. and that gained by the condenser is 10,500 B.t.u./hr. Thus, not allowing for errors in measurement, a total of 2,500 B.t.u./hr. was lost to the surroundings and to the bleed.

Close approaches were readily achieved in each evaporator-condenser stage. The size of the temperature step between the two stages depended on the difference between the entering temperature of the warm stream and the entering temperature of the cold stream. In the example given, terminal temperature differences are about three times as great as the approach temperature between the evaporator and condenser. For practical applications it means that the terminal temperature differences will be established essentially by the number of stages. If the heat balance is such that the terminal approach will be closer at one end of the exchanger than at the other, fewer stages will be required for a specified approach at the pinch end. For example in the Cornell process for saline water conversion, in which it is appropriate to load the sea-water stream with excess butane as part of the overall process considerations, the terminal approach temperatures at the warm end of the cascade should be less than 2°C. in ten stages.

PACKED CONDENSERS

Water leaving the condensers of the two-stage unit was so close to equilibrium that accurate heat transfer coefficients could not be obtained from the terminal temperatures. For some runs temperature profiles were used to calculate coefficients for the section 2 to 4 in. from the top of the bed. To get data at high liquid velocities a smaller condenser was made from one of the 6-in. diameter glass sections by dividing it with a vertical baffle to have a cross-sectional area equivalent to a 4-in. diameter condenser. The half-round section was packed with 9 in. of ½-in. Intalox saddles, and a perforated-plate distributor was placed above the bed. With this unit the exit liquid was 0.1° to 0.3°C. cooler than the vapor temperature, and coefficients were calculated either from the total heat transferred and the log-mean driving force, or from temperature profiles such as that of Figure 3. The drop in vapor temperature is caused by the slight pressure drop across the packing.

Figure 4 shows that the volumetric heat transfer coefficients increase with the 0.4 to 0.6 power of the liquid rate and reach 150,000 B.t.u./(hr.) (cu.ft./°F.) at a liquid rate of 40,000 lb./(hr.) (sq.ft.). The packing appeared almost completely wetted at this liquid rate, and higher liquid rates might not lead to appreciably higher coefficients. The flooding rate for this packing is about 136,000 lb./(hr.) (sq.ft.) at zero gas flow. The gas rates were varied from 1,100 to 2,500 lb./(hr.) (sq.ft.), with no noticeable effect on the heat transfer coefficient. A slight increase in coefficient with gas rate might be expected because the gas would accelerate the liquid flowing over the packing.

The performance of the packed condenser can be predicted fairly well by applying the penetration theory (*4*) to published mass transfer data. The resistance to heat transfer in the organic phase is assumed negligible because of condensation by drops, and the resistance in the water layer is calculated from oxygen desorption data as shown below:

For ½-in. Berl saddles, oxygen-water system, 77°F. $H_L = 1.8$ ft. or $k_La = 267$ hr.$^{-1}$ at $L = 30{,}000$ lb./(hr.) (sq.ft.)

$$D_{O_2-H_2O} = 9.7 \times 10^{-5} \text{ sq. ft./hr. at } 25°\text{C.}$$

$$\frac{h}{k_L} = \frac{2\sqrt{c_p\,\rho k/\pi t}}{2\sqrt{D/\pi t}} = \sqrt{\frac{c_p\,\rho k}{D}} = 475$$

$$Ua \cong ha = 475\,k_La = 127{,}000 \text{ B.t.u./(hr.) (cu.ft./°F.)}$$

Data for counterflow condensation of water vapor on Aroclor in a column packed with 1-in. rings were recently published by Wilkie, Cheng, Ledesma, and Porter (*7*). Their values of the height of a transfer unit correspond to overall coefficients of about 6,000 B.t.u./(hr.) (cu.ft./°F.) for liquid rates of 20,000 to 30,000 lb./(hr.)(sq.ft.). Based on oxygen-water data and the penetration theory a coefficient of 25,000 is predicted for Aroclor. The fourfold difference may be caused by the high viscosity of Aroclor, which increases the contact time, or by channelling. In an earlier study Coons (*1*) reported high coefficients for direct condensation of water and organics in spray contactors.

SIEVE-PLATE CONDENSERS

The direct condensation of methylene chloride with water was also studied with a sieve-plate contactor. A ¼-in. plate with sixty ⅛-in. holes on ½-in. triangular spacing was mounted between 1-ft. sections of 6-in. glass pipe. The downcomer was a 1 in. pipe with a lip that directed most of the flow to the sides rather than directly towards the weir. The overflow weir and downcomer were 1½-in. pipe.

In most runs water was heated 1 to 2°C. in passing through the condenser, and the exit temperature was 0.5° to 1.5°C. below the condensation temperature of the entering vapor. Vapor above the liquid surface had a condensation temperature 0.2° to 0.3°C. below that of the entering vapor because of pressure drop through the plate. The heat transfer coefficients in Figure 5 are based on the temperature rise of the water, the bubbling area (0.09 sq. ft.), and, arbitrarily, on the average condensation temperature minus the exit liquid temperature. The coefficients based on the log-mean driving force would be about half as great.

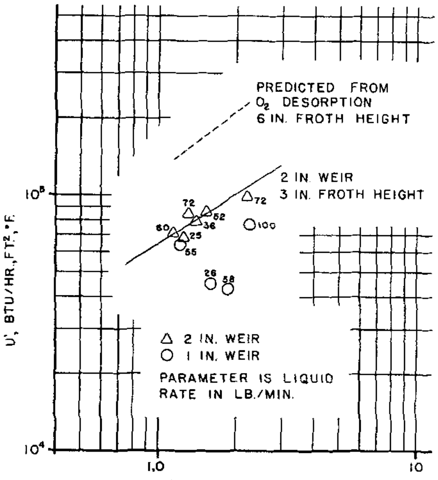

Fig. 5. Performance of sieve-plate condenser.

With a 2-in. weir the overall coefficients ranged from 70,000 to 100,000 B.t.u./(hr.) (sq.ft./°F.), increasing with superficial gas velocity. From 1 to 7% of the inlet gas was vented, and the liquid temperature was adjusted to condense the remainder at a pressure slightly above 1 atm. Once the inerts were purged, the performance was independent of the venting rate. The slight increase in coefficient with liquid rate could result from the greater depth of liquid or from less backmixing of the liquid. The data for a 1-in. weir show considerable scatter, probably because these tests were made before a standard procedure for purging inerts was developed. Data for the sieve plate condenser were compared with the data of Gerster and Foss (*2*) for oxygen desorption on a plate with 3/16-in. holes. The oxygen data were corrected for backmixing and reported by Gerster (*3*) as $k_L\bar{a}$ values.

For a 2-in. weir at $F = 0.5$

$$k_L\bar{a} = 0.4 \text{ sec.}^{-1} = 1440 \text{ hr.}^{-1}$$

$$k_L' = 1440 \times 0.2 \frac{\text{cu. ft. liquid}}{\text{sq. ft. tray area}} = 288 \text{ ft./hr.}$$

Applying the penetration theory and the same factor used in the packed column comparison one obtains

$$U'_{\text{predicted}} = 288 \times 475 = 137{,}000 \frac{\text{B.t.u.}}{\text{(hr.) (sq.ft./°F.)}}$$

Though the vapor density may not affect the condenser performance, the velocity is corrected with the F factor. For methylene chloride $v_o = 1.13$ ft./sec. at $F = 0.5$. The predicted coefficients are twice the calculated values, and the difference may be even greater because the exit temperature was used to calculate the coefficients. The main reason for the lower values is that the froth height in the direct-contact condenser was only half that in the desorption study and there was almost no spray above the liquid surface.

The sieve-plate coefficients correspond to volumetric coefficients up to 400,000 B.t.u./(hr.) (cu.ft. of froth/°F.). Although these are higher than the coefficients for the packed columns, packed columns were used in the two-stage exchanger because the liquid could be heated almost to the temperature of the entering vapor. With the sieve plate the pressure drop through the liquid and backmixing on the plate made such a close approach impossible. When a very close approach is not needed, and when high liquid and vapor velocities are considered, a sieve plate might be preferable.

UPFLOW EVAPORATOR

A separate, smaller scale evaporator study permitted the safe use of a hydrocarbon (pentane) transfer agent and comparison of its behavior with that of methylene chloride. The flashing tests were carried out at 1 atm. in a single-

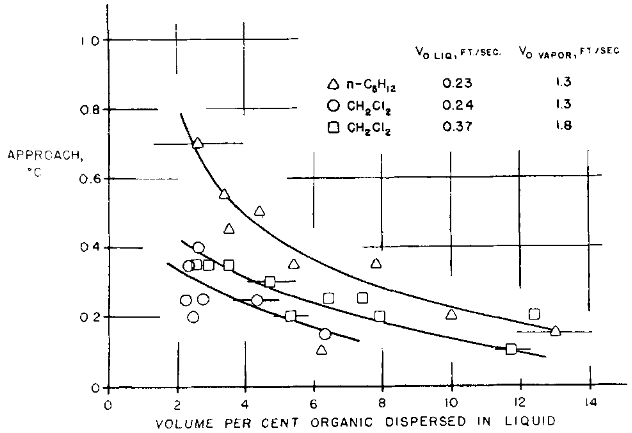

Fig. 6. Performance of 2-in. diameter vertical evaporator comparison between *n*-pentane and methylene chloride.

pass vertical evaporator made of 2-in. glass pipe topped by a 4-in. diameter disengaging chamber. Warm tap water and either methylene chloride or *n*-pentane were metered separately, mixed in a tee, and fed to the bottom of the 2-in. pipe. A sieve plate with forty-four ⅛-in. holes was placed 1 ft. from the top of the pipe to promote dispersion, and for some tests a second plate with twenty 3/16-in. holes was placed 2 in. from the top. The temperature of the entering and leaving liquid and the condensation temperature of the vapor were measured with 0.1°C. thermometers.

The performance of the small evaporator was similar to that of the first unit in the two-stage exchanger. When the liquid mixture was only slightly superheated, boiling started a few inches below the surface, and the top layer of fluid was only mildly agitated. With a superheat of 1.5° to 3°C. boiling started 1 to 2 ft. below the surface, and the area for heat transfer was much greater. The approach to equilibrium was not significantly affected by the feed temperature because the greater area permitted more heat to be transferred at about the same driving force.

The approach to equilibrium depended primarily on the amount of organic liquid dispersed in the water, as shown by Figure 6. An inverse dependence was expected, since the vapor was 90 to 95% organic and the liquid mostly water, and most of the heat for vaporization had to be transferred from the water to the vaporizing organic drops. The points plotted represent the average volumetric concentration of organic in the liquid. The change in concentration is shown for a few points by a horizontal line.

The approach to equilibrium was not as close with pentane as with methylene chloride, partly because of the low density of pentane which decreases its holdup in upflow. Also the solubility of methylene chloride in water is about 2% compared with 0.02% for pentane, and some of the methylene chloride vapor may come from bubbles initiated in the water phase which grow by transfer of dissolved methylene chloride. Increasing the liquid flow rate at a constant inlet temperature slightly increased the difference between liquid and vapor temperature. Two sieve plates in series gave essentially no better performance than did a single plate, but other modifications might have merit. Particularly of value would be greater opportunity for final vapor release from thin layers such that there is negligible submergence pressure. This suggests passing the liquid over packing, at least for the final part of the flashing.

The data were not corrected for the effect of air dissolved in the incoming water. The measured vapor temperature was slightly lower at low vapor rates than at high vapor rates, and calculations indicated about 0.3% air in the vapor for the runs shown. If the liquids had been deaerated, the measured approach might have been as much as 0.1°C. closer.

Because the driving force was not measured along the length of the evaporator, true heat transfer coefficients are not reported. However as an estimate the exit driving force can be used and evaporation assumed to occur in the last foot of pipe. For the top curve of Figure 6 at 6 vol. % organic these assumptions give an overall coefficient of 170,000 B.t.u./(hr).(cu.ft./°F.).

CONCLUSIONS

Countercurrent heat transfer between aqueous streams with multistage units which transfer heat by means of a vaporizing-condensing immiscible transfer agent results in an overall stage temperature approach of less than 0.5°C. at liquid rates of 40,000 lb./(hr.)(sq.ft.) in the condensers and 84,000 lb./(hr.)(sq.ft.) in the evaporators. The actual temperature approach in a specific case will depend on the number of stages. The hydraulics are inherently stable, and no basic problems are in evidence which limit the magnitude of scale up.

ACKNOWLEDGMENT

The authors are grateful to Peter Klugherz and Newton Landis, who participated in all phases of this investigation.

NOTATION

a = transfer area, sq. ft./cu. ft. of column
$\bar{a}$ = transfer area, sq. ft./cu. ft. of liquid
c_p = heat capacity, B.t.u./(lb.)(°F.)
D = diffusivity, sq. ft./hr.
F = $v_o\sqrt{\rho}$, ft./sec. (lb./cu. ft.)$^{1/2}$
h = heat transfer coefficient, B.t.u./(hr.)(sq.ft./°F.)
H_L = height of a transfer unit based on liquid resistance, ft.
k = thermal conductivity, B.t.u./(hr.)(sq. ft./°F.)/ft.
k_La = volumetric mass transfer coefficient, liquid phase, hr.$^{-1}$
$k_L\bar{a}$ = mass transfer coefficient based on liquid holdup, hr.$^{-1}$
k'_L = mass transfer coefficient based on bubbling area, ft./hr.
L = liquid rate, lb./(hr.)/(sq. ft.)
t = contact time or age of surface elements, hr.
v_o = superficial velocity, ft./hr.
Ua = overall volumetric heat transfer coefficient, B.t.u./(hr.)(cu.ft./°F.)
U^1 = heat transfer coefficient based on bubbling area, B.t.u./(hr.)(sq.ft./°F.)
ρ = density, lb./cu. ft.

LITERATURE CITED

1. Coons, K. W., *Direct Condensers*, Bul. 3, Eng. Exp. Sta., Univ. of Alabama, University, Alabama (June, 1953).
2. Foss, A. S., and J. A. Gerster, *Chem. Eng. Progr.*, **52**, 28 (1956).
3. Gerster, J. A., et al., "Final Report, University of Delaware," p. 46, Am. Inst. Chem. Engrs., New York (1958).
4. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
5. Houghton, G., P. D. Ritchie, and J. A. Thomson, *Chem. Eng. Sci.*, **17**, 221 (1962).
6. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., p. 288, McGraw-Hill, New York (1952).
7. Wilke, C. R., C. T. Cheng, V. L. Ledesma, and J. W. Porter, *Chem. Eng. Progr.*, **59**, No. 12, p. 69 (1963).

Manuscript received November 11, 1963; revision received March 16, 1964; paper accepted March 30, 1964. Paper presented at A.I.Ch.E. Pittsburgh meeting.