Effects of Marangoni Surface Tension Forces on Modern Distillation Packings

Sebastian J. Proctor
BEL Engineering, Harbour City, Salford Quays, Manchester M5 2SP, U.K.

Michael W. Biddulph
Dept. of Chemical Engineering, University of Nottingham, Nottingham NG7 2RD, U.K.

Krish R. Krishnamurthy
BOC Gases R&D, Murray Hill, NJ 07974

New experimental data presented concern effects of Marangoni surface-tension forces on the mass-transfer efficiency of packed distillation columns. Various random packings of sizes 6 and 25 mm, as well as structured packings of sizes 30 mm diameter and 150 mm, were used with the system n-propanol/water. This system can behave either as a Marangoni positive system at low concentrations of n-propanol or as a negative system at high concentrations of n-propanol. It was confirmed that small packings show lower efficiencies for Marangoni negative systems, due to the breakup of the film of liquid on the packing surface. In the larger column, however, the situation is reversed with the negative mixtures often showing better efficiencies, especially at heavier loadings. This is attributed to the observation that spray and droplet formation are much more pronounced for the negative mixtures, providing extra surface for mass transfer and, hence, better mass-transfer efficiency. There are also some indications that the pressure drop is unexpectedly high for these conditions and that premature flooding can occur. This may have design implications for any mass-transfer device in which vapor and liquid phases are contacted in narrow passageways.

Introduction

Marangoni surface tension forces arise in distillation when the reflux liquid changes its surface tension resulting from mass transfer as it flows down the column. If the reflux liquid surface tension increases, the system is referred to as a positive system, which is the most common type. However, there are some systems in which the reflux-liquid surface tension decreases and these are called negative systems.

It has long been known that Marangoni surface tension effects can influence the behavior of distillation columns, and many articles have considered these effects, for example, Zuiderweg and Harmens (1958), Ellis and Biddulph (1967), Levich and Krylov (1969), Dijkstra and Drinkenburg (1990), and Pertler et al. (1995). It is well established that tray behavior is affected by the sign of the surface tension gradient, especially for small columns, producing froth for positive systems and spray and droplets for negative systems (Kalbassi, 1987). The effects are not as pronounced on commercial scale trays, which operate at higher loadings. It is also known that the effects are noticeable in small, random-packed columns, in which the positive mixtures create a stable film of liquid on the packing surface, while the negative mixtures cause film breakup, dry areas, and rivulet flow. Naturally, this makes the separation of positive mixtures more efficient than that of negative mixtures. Again, the effects are less noticeable in commercial scale columns, operating at heavier loadings and reducing the effect, for example, Van der Klooster and Drinkenburg (1979).

The development of the new generation of structured packings, and their use, instead of traditional column internals, raises the need to understand the mass-transfer and hydraulic behavior as affected by surface tension forces, since these can occur in commercial columns. Furthermore, a better understanding of the way these packings behave may have a beneficial effect on the future development of the next generation of packing. Some articles have considered the effects, for example, Semkov and Kolev (1991), Martin and Perez (1994), Zuiderweg and Yanagi (1992). Bravo et al. (1985) took account of Marangoni effects while deriving their extensive model for the efficiency of gauze-type structured packings under various distillation conditions.

This article describes an extensive experimental investigation of distillation using various random and structured packings, in small and pilot-scale columns. It is found that there are very noticeable differences between the effects of the sign of the surface tension gradient on the operation of small- and pilot-scale packings, not only concerning mass-transfer efficiency, but also concerning hydraulic behavior.

Experimental Studies

Small-scale packed column

The apparatus consisted of a 10-L capacity, electrically-heated reboiler with a standard glass column, 30 mm in diameter, and with sufficient height to allow bed depths of up to 210 mm. The sample points top and bottom and a water-cooled condenser completed the equipment, which was enclosed within a heated, temperature-controlled cabinet to minimize heat-transfer effects. The column was operated at total reflux. The packings studied were 6 mm Ceramic Berl Saddles, 6 mm Copper Gauze Berl Saddles, 6 mm Glass Raschig Rings, and Sulzer "DX" Gauze Structured Packing. Additional results were in a 25-mm diameter Glass Vigreux column. Experiments were also carried out on "Single Strip" pieces of plain steel sheet and dimpled steel sheet. The liquid flowed down both sides of the strip, but not down the glass walls. All this equipment is described in detail elsewhere (Proctor, 1996).

Pilot-scale column

The glass column was of diameter 150 mm, and height 1,000 mm. A chimney distributor provided good liquid distribution at the top of the packed bed. Samples of reflux liquid and liquid leaving the bottom of the packed bed were used to calculate the efficiency. The "packing bottom sample" was used to eliminate "end effects" of mass transfer in the Collector Plate, and samples were analyzed by using chromatography. The column was insulated, operated at total reflux, and liquid and vapor loading was obtained from the reflux liquid flow rate. A 300-L, steam-heated reboiler and a shell-and-tube, water cooled condenser completed the equipment. Pressure tappings at the top and bottom enabled the pressure drop through the bed to be measured. A small window in the insulation enabled the operation of the column to be observed through the glass wall. The packings studied were 25-mm Glass Raschig Rings (190 m^2/m^3), 25-mm Polypropylene Pall Rings (225 m^2/m^3), 25-mm Stainless Steel Pall Rings (341 m^2/m^3), 15-mm Stainless Steel Pall Rings and Norton 1T Structured Packing (220 m^2/m^3). Again, all this equipment is described elsewhere (Proctor, 1996).

Experimental systems

The main experimental system used was n-propanol/water. This system is especially useful for a study of Marangoni effects, since it has a minimum-boiling azeotrope at about 44% n-propanol, resulting in it being Marangoni positive at low n-propanol concentrations, while behaving as a Marangoni negative system at higher concentrations. Also, over the range of concentrations investigated (15%–90% n-propanol), the absolute value of the boiling mixture surface tension does not vary greatly (Figure 1). This means that the mixture properties are all very similar except for the sign of the surface tension gradient, which changes from +ve to −ve at the azeotrope. Some additional experiments were carried out using the system methanol/water. This is a Marangoni positive system, and these results facilitate comparison with earlier studies in various types of column.

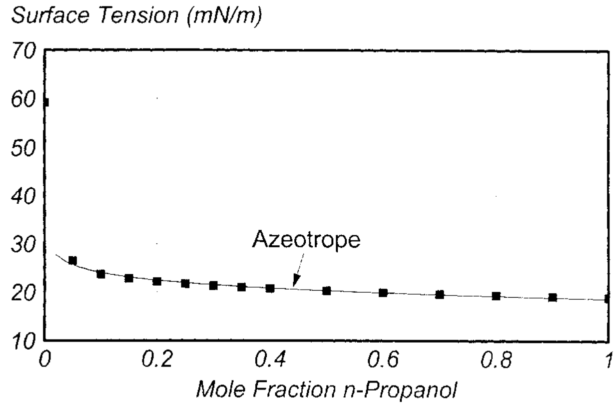

Figure 1. Surface tension of n-propanol/water at the boiling point.

Results

The height of an overall gas-phase transfer unit (H_{og}) was determined, using the usual equations, for each run, carried out at various loadings and total reflux

$$H_{og} = Z/N_{og} \tag{1}$$

where N_{og} is the number of transfer units $= \int_{Yb}^{Yt} dY/(Y^* - Y)$.

This was done for mixtures on either side of the azeotrope in the n-propanol/water system, and the values compared at equal *specific liquid loading* values. The specific liquid loading is calculated by dividing the liquid loading (m^3/m^2 s) on the column by the packing specific area (m^2/m^3), so it represents the liquid flowing across unit packing surface area.

Results for the small packings

The results for the small random packings indicated typical H_{og} values of 20–40 mm for the positive mixtures, and values of around 60–100 mm for the negative mixtures. Some typical values, those for the 6-mm Copper-Gauze Berl Saddles, are shown in Figure 2. The H_{og}^{+ve} values for the different small random packings were approximately inversely proportional to the specific surface area. The range of specific packing areas was 582–1,200 m^2/m^3. The Sulzer DX Gauze Structured Packing performed better in overcoming the detrimental effects of the negative surface tension forces, as illustrated in Figure 3. Here the positive H_{og} values were again

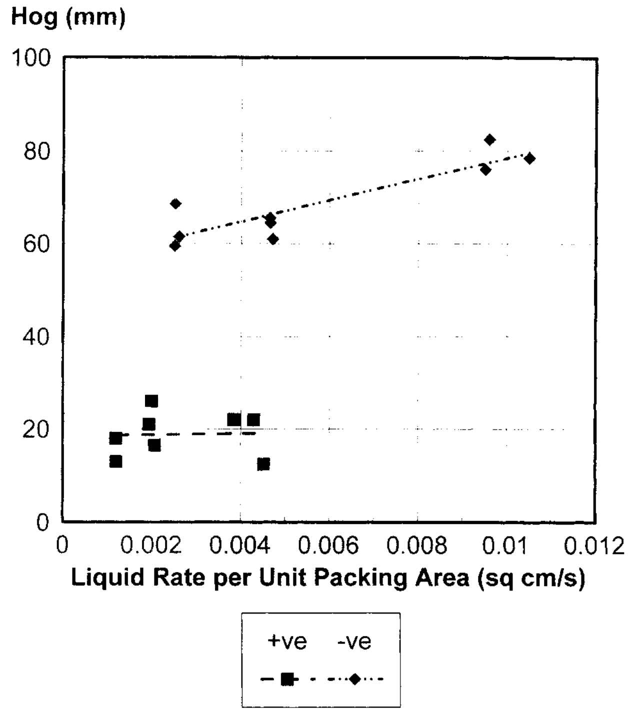

Figure 2. HTU values for 6-mm copper gauze saddles.

about 20–30 mm, but the negative H_{og} values were around 45–55 mm. This raises the possibility of defining an "Effectiveness" factor (E), indicating the ability of a particular packing to overcome the poor performance resulting from the negative Marangoni forces, in terms of the H_{og} values at similar conditions. It is suggested that the ratio $[H_{og}^{+ve}/H_{og}^{-ve}]$ be measured for the packing of interest, and that this is compared with the value of the ratio for a plain-surface packing with no contact points, *at the same area/volume*.

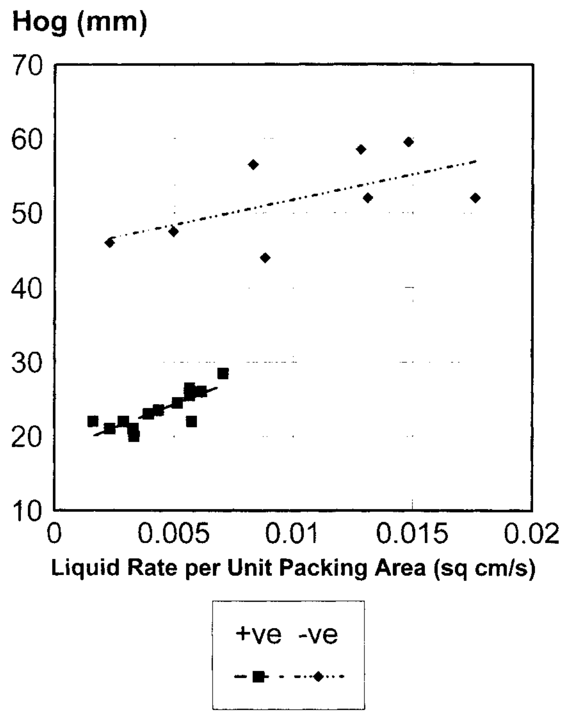

Figure 3. HTU values for Sulzer "DX" structured gauze packing.

The "Effectiveness" (E) would be defined

$$E = (R_S^* - R_P^*)/(1 - R_P^*) \quad (2)$$

where

$R_S^* = H_{og}^{+ve}/H_{og}^{-ve}$ for the packing of interest

$R_P^* = H_{og}^{+ve}/H_{og}^{-ve}$ for a plain surface with no contact points.

Both are at the same surface area/vol.

So, E represents the actual improvement achieved by the packing of interest compared with the maximum possible improvement, that is, if the negative system gave the same H_{og} value as the positive system. The value of R_P^* as a function of packing specific area is found from the extra experiments mentioned above, carried out in a glass Vigreux column, a glass wetted wall column and a plain steel strip installed into the small glass column. The value of E is determined from Figure 4. From this, it can be seen that the three small random packing studied all gave similar values of E, around 0.3, in spite of these packings having noticeably different surfaces. However, the Sulzer "DX" Stainless Steel Gauze Packing, with a similar surface and a specific area of 1,000 m^2/m^3, gave a value of E of around 0.5. The main difference between this packing and the small random packings was the number of contact points for re-distribution of liquid within the packing. This may confirm the suggestions of others that it is the number of contact points within a packing which is more important than the surface character in producing an effective packing. It is worth noting that an experiment on a dimpled steel strip with no contact points provided only a very modest improvement over a plain steel strip, an E value of about 0.1, confirming the above conclusion. This conclusion seems to make it clear that the provision of contact points will be an important consideration in the design of the next generation of structured packings.

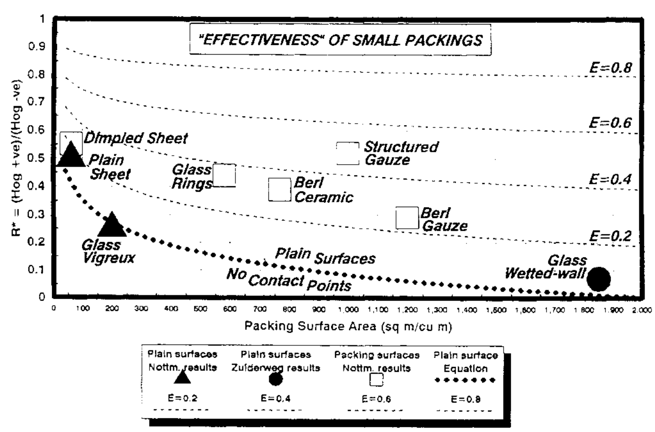

Figure 4. Effectiveness of some small packings.

Results for the larger packings

The results obtained for the larger random packings show different behavior. Here the specific liquid loadings are approximately ten times greater than those studied in the small column, and this clearly overwhelms the tendency for film breakup for the negative mixtures. One might expect that this would result in the H_{og}^{+ve} and H_{og}^{-ve} values being similar, since both should be operating in a similar way, with the packing surface completely covered by a liquid film. This is indeed the case at moderate loadings. However, at heavier loadings the negative side efficiencies become much better than the positive side values. A typical set of results is shown in Figure 5. Similar results were obtained for the other random packings studied. The Billet and Schultes 1993 model did not predict this trend. The results for the Norton 1T Structured Packing showed a similar outcome with the negative side H_{og} showing better values at the heavier loadings, as shown in Figure 6.

Pressure-drop observations

In the region where the H_{og}^{-ve} values were noticeably better than the H_{og}^{+ve} values, the pressure drop through the bed was observed to be surprisingly high. For the Norton 1T structured packing, the positive side pressure drop values were in good agreement with the vendor's data, but the negative side values were significantly higher, as shown in Figure 7, where the pressure drops are plotted against the F factor ($F = V\sqrt{\rho_v}$). (Note: The F factor is used as a way of including the effect of vapor density, as well as velocity in the vapor loading.) It was also observed that premature flooding occurred on the negative side compared with the expected flood point. This phenomenon, of higher pressure drop, coincided with the observation, through the glass column wall, of much more spray and droplet formation into the vapor phase than was evident for the positive mixtures. It therefore seems likely that the Marangoni instabilities for the negative mixtures were facilitating droplets being "torn" from the liquid film surface, creating more surface for efficient mass transfer, but generating a higher pressure drop through the packed bed. (It is known that Marangoni negative mixtures on small sieve trays can generate spray and show high efficiencies.) This is a potentially important observation, since many industrial columns have regions of Marangoni negative characteristics, and may be susceptible to unexpectedly poor hydraulic behavior if packing is used instead of trays. This aspect is the subject of continuing further study.

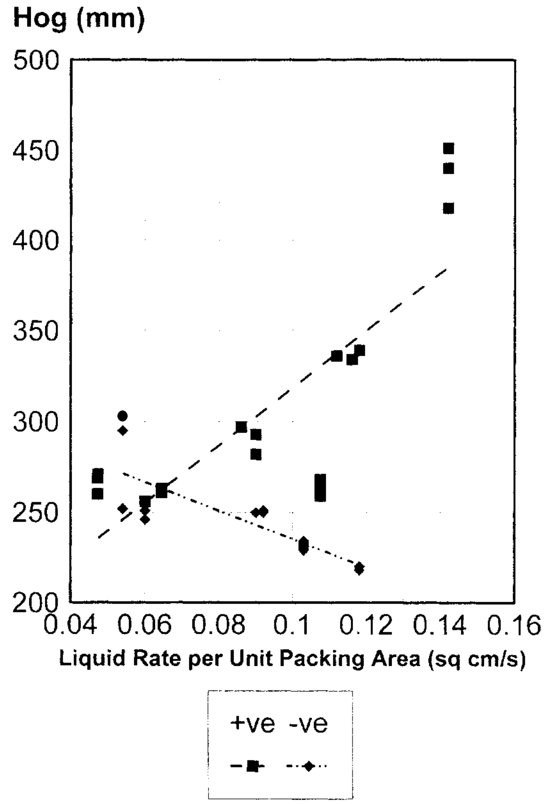

Figure 6. HTU values for NORTON 1T structured packing.

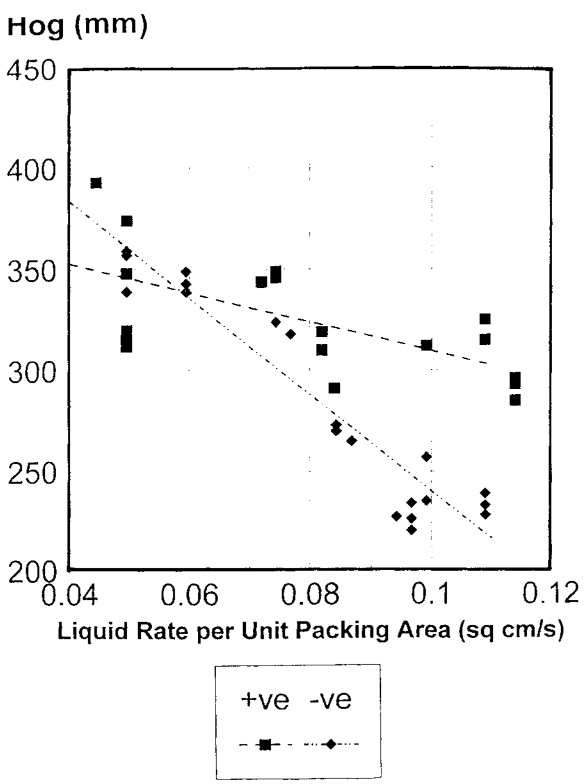

Figure 5. HTU values for 1-in. (25-mm) glass Raschig rings.

Conclusions

This study of the effects of Marangoni surface tension forces on the performance characteristics of various types of random and structured packing has provided new experimental data. The system used, n-propanol/water, enables the sign of the Marangoni surface tension gradient to be changed by simply changing the mixture composition.

It has been observed that in small-scale packings the previously observed tendency for the negative mixtures to experience film breakup, and hence lower mass-transfer efficiencies, has been confirmed. The number of contact and

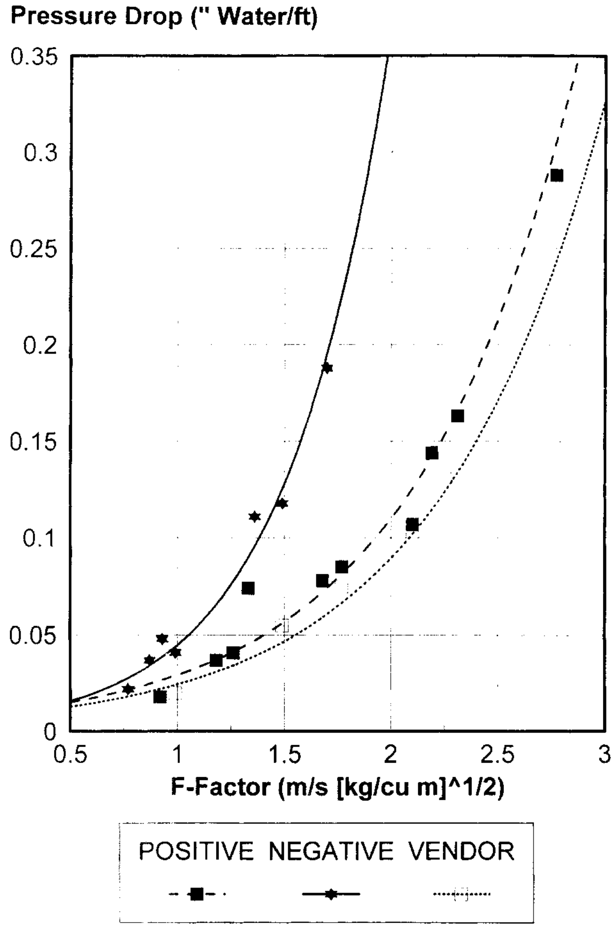

Figure 7. Pressure drop in NORTON 1T structured packing.

re-distribution points within a packing appears to be more important in reducing these adverse effects than different surface character. These results emphasize this aspect of packings, which will be important in the development of the next generation of packings.

It has also been observed that in larger-scale packings, both random and structured, the opposite behavior is found. At the heavier liquid loadings, the negative mixtures actually operate with higher mass-transfer efficiencies than do the positive mixtures. This is an observation which appears to be caused by the tendency of the negative mixtures to facilitate liquid droplets being "torn" from the film surface, generating spray and small drops in the vapor phase, and providing extra surface area for mass transfer. This situation coincides with the observation of unexpectedly high pressure drops for the negative mixtures. The positive-side pressure drop values for Norton 1T packing coincided with the vendor's data, but the negative-side values were significantly higher. In addition, premature flooding occurred on the negative side. As far as is known, this is the first report of this type of behavior, and it could be very significant in columns where Marangoni negative regions occur.

These observations concerning packed column behavior in distillation may be important in situations where packing replaces trays in columns, and may be significant in the continuing development of new generation packings.

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Notation

F = vapor-phase F factor, m/s $\sqrt{[\text{kg/m}^3]}$
R^* = ratio of H_{og} values, positive to negative
V = superficial vapor velocity, m/s
Y = vapor phase mole fraction more volatile component
Z = height of packing in the column, m
ρ_v = vapor density, kg/m^3

Subscripts

b = at the bottom of the column
P = for a plain surface with no contact points, at the same area/volume ratio
S = for the packing of interest
t = at the top of the column

Literature Cited

Billet, R., and M. Schultes, "Predicting Mass Transfer in Packed Columns," *Chem. Eng. Technol.*, **16**, 1 (1993).

Bravo, J. L., J. A. Rocha, and J. R. Fair, "Mass Transfer in Gauze Packings," *Hydroc. Proc.*, **64**(1), 91 (1985)

Dijkstra, H. A., and A. A. H. Drinkenburg, "Enlargement of Wetted Area and Mass Transfer due to Surface Tension Gradients: The Creeping Film Phenomena," *Chem. Eng. Sci.*, **45**(4), 1079 (1990).

Ellis, S. R. M., and M. W. Biddulph, "The Effect of Surface Tension Characteristics on Plate Efficiencies," *Trans. I. Chem. E.*, London, **45**, T223 (1967).

Kalbassi, M. A., "Distillation Sieve Tray Efficiencies," PhD Thesis, Univ. of Nottingham, U.K. (1987).

Levich, V. G., and V. S. Krylov, "Surface Tension Driven Phenomena," *J. of Fluid Mech. Ann. Rev.*, **1**, 293 (1969).

Martin, A. M., and A. C. Perez, "The Influence of Surface Tension on the Volumetric Mass Transfer Coefficient in Rectification," *Int. Chem. Eng.*, **34**(1), 76 (1994).

Pertler, M., M. Haberl, W. Rommel, and E. Blass, "Mass Transfer Across Liquid Phase Boundaries," *Chem. Eng. & Proc.*, **34**, 269 (1995).

Proctor, S. J., "Modern Distillation Devices," PhD Thesis, Univ. of Nottingham, U.K. (1996).

Semkov, K. R., and N. Kolev, "On the Evaluation of the Interfacial Turbulence in Gas-Liquid Mass Transfer: 1 & 2," *Chem. Eng. & Proc.*, **29**, 77, 83 (1991).

Van der Klooster, H. W., and A. A. H. Drinkenburg, "The Influence of Gradients in Surface Tension on the Mass Transfer in a Packed Column," *I. Ch. E. Symp. Ser.*, **56**, 2 (1979).

Zuiderweg, F. J., and A. Harmens, "The Influence of Surface Phenomena on the Performance of Distillation Columns," *Chem. Eng. Sci.*, **9**(2/3), 89 (1958).

Zuiderweg, F. J., and T. Yanagi, "Marangoni Effect, Liquid Phase Resistance or Maldistribution," *I. Chem. E. Symp. Ser.*, **128**, A181 (1992).

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