

# Trays inhibit foaming

## Mechanical design avoids fouling in extractive distillation process

M. R. Resetarits, J. L. Navarre and D. R. Monkelbaan, UOP, Tonawanda, New York,  
G. W. A. Hangx and R. M. A. van den Akker, DSM, Geleen, the Netherlands

**P**olymerization plugging associated with foaming is avoided in a high-thruput unit at the DSM petrochemical plant in the Netherlands (Geleen) by revamping the 1,3-butadiene column with Multiple Downcomer (MD) trays. The trays were designed to function near, or in, the spray regime of tray hydraulics. In this case of the butadiene extractive distillation column where dimethylformamide (DMF) is used as the solvent, severe foam-induced problems were eliminated, and a capacity increase was effected.

Trayed distillation, absorption and stripping columns sometimes foam. This can lead to capacity problems, separation problems or both. Chemical engineers are often confronted with design problems associated with vapor-liquid contacting columns that foam. Common examples are amine towers, hot carbonate towers, glycol towers, demethanizers and some depropanizers. In November 1986, DSM investigated the possibility of improving the performance of the Nippon Zeon process to extract 1,3-butadiene from a mixed C<sub>4</sub> stream that was vaporized after originating from an ethylene plant. The DSM C<sub>4</sub> extractive distillation column presented an unusual case of a processing problem where the fouling problem resulted from foaming at high thruputs.

**Extractive distillation.** Dimethylformamide (HCON(CH<sub>3</sub>)<sub>2</sub>), is a polar, organic molecule whose liquid has a high boiling point (153°C) along with an affinity for forming complexes. Because of these characteristics, DMF is an excellent solvent. Gases such as acetylene, butadiene, isoprene, sulfur dioxide and hydrogen chloride are so soluble in DMF that they can be selectively extracted from other inorganic gases and hydrocarbons.<sup>1</sup>

1,3-Butadiene is difficult to separate from other C<sub>4</sub> hydrocarbons, especially isobutene and 1-butene by normal distillation. However, DMF acts in essence as a solvent for 1,3-butadiene. The DMF in contact with the mixed C<sub>4</sub> stream decreases the volatility of 1,3-butadiene versus the other C<sub>4</sub> compounds. In fact, the separation of 1,3-butadiene from 1-butene (both to 98% purity) requires approximately 180 theoretical trays by conventional distillation but only 15 theoretical trays using a solvent and extractive distillation.<sup>2</sup>

DMF appears to be the perfect solvent for 1,3-butadiene purification. However, in isolated cases, foaming, polymerization and polymerization fouling can occur. Those problems are sometimes associated with carbonyl compounds in the mixed C<sub>4</sub> feed streams. Pure DMF aerated by air and nitrogen in a cell designed to test a liquid's foaming tendency does not foam. However, field cases in which DMF-C<sub>4</sub> processes have shown foaming tendencies have been reported.<sup>3</sup>

**Foams.** Foams can result from the presence of mixtures, impurities, surface active agents, solid particles or heat or mass transfer that conveys on bubbles the ability to resist coalescence with one another.<sup>4</sup> Also, the consensus is that on distillation trays, low vapor rates, high froth heights and small deck perforation diameters favor foam formation in systems capable of producing stable foams. Foam theory often refers to two different foam types, depending on the nature of the mechanism of the foam formation and stabilization. These types are known as Ross foams and Marangoni foams.

**Ross foams.** Ross foams, or phase-separation foams, typically occur in systems with a single liquid phase that is at or near the point at which it would separate into two liquid phases. For a two-component system, this point is referred to as the critical point; and for a three-or-more-component system, the point is called the plait point.<sup>4</sup> Many articles have been written on Ross foams, and one article even linked Ross foams to a DMF-C<sub>4</sub> process.<sup>3</sup>

For Ross foams, the maximum foam production occurred under conditions of temperature and concentration when a transition to two separate liquid phases was imminent.<sup>5</sup> However, once the second liquid phase develops, one of these phases acts to destroy the foam, especially if that phase is present in small amounts and has a lower surface tension.<sup>4,6</sup>

**Marangoni foams.** Mass-transfer-induced foams are the result of a phenomenon known as the Marangoni effect. It is the most common mechanism for conferring stability upon a film. In fact, most dynamic foams are stabilized only by Marangoni effects.<sup>5</sup>

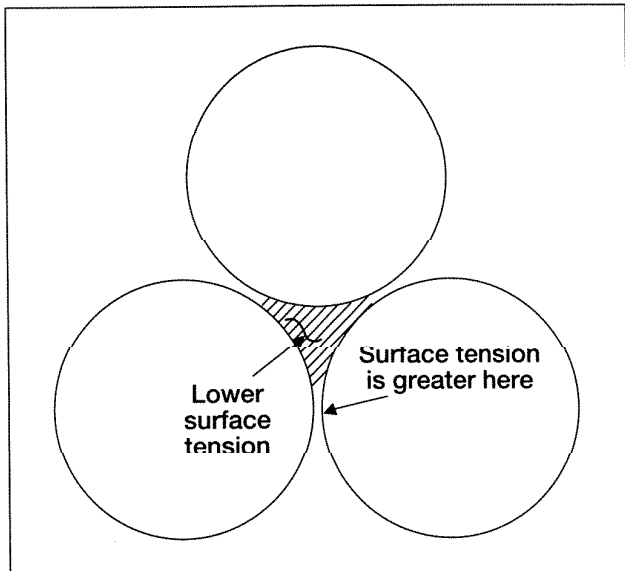


Fig. 1. Foaming by Marangoni effect.

Normal froths on distillation trays undergo film thinning as a result of the drainage of fluid from the froth bubbles through gravity and capillary actions. This drainage leads to film thinning and finally to film rupture (i.e., bubble coalescence). In the presence of Marangoni forces, the rate of film thinning and bubble coalescence is drastically reduced. In essence, this reduction comes about through mass-transfer-induced Marangoni effects. These effects are achieved through positive surface tension gradients, which occur during the mass-transfer process. A positive surface tension system is one in which the surface tension at the bubble surface is greater than the surface tension elsewhere in the fluid (Fig. 1). The stability of the foam is conferred via the flow of liquid from an area of low surface tension (the froth) to an area of high surface tension (the foam). This stability yields thicker, more stable films and bubbles and a stable foam results.

For a Marangoni foam to develop, the surface tension of the liquid must increase during mass transfer on the trays.<sup>7</sup> In fact, an increase in surface tension in the down-flowing liquid of one dyne/cm per theoretical tray typically indicates a potential for Marangoni foaming. Therefore, Marangoni foams are dependent on mass-transfer-induced surface tension increases, which can occur when the more volatile constituent has a lower surface tension.

**Tray hydraulics.** Froth depth, perforation diameter and vapor velocity affect foam formation and stability on distillation trays. The spray regime, or fluidization region, can be visualized as liquid droplets entrained in a matrix of vapor. The vapor phase is the continuous phase. The froth regime is essentially the opposite. Vapor bubbles are dispersed in a continuous liquid. Because foams, like froths, are also a continuous liquid, the operation of a column within the froth regime should promote foam formation just as operation in or near the spray regime should, and does, promote foam disruption.<sup>4</sup>

Alter froth depth, perforation diameter and/or vapor velocity affects the regime or region in which a column

operates, and, thereby, the degree of foaming the column experiences. Experiments have shown that deep froths (small, closely spaced perforations) and low vapor velocities favor foam formation and foam stability.<sup>5</sup> Therefore, reducing froth heights, increasing diameters of deck perforations and increasing vapor velocities are all mechanisms for decreasing foaming in distillation columns.<sup>7</sup>

Froth-height reduction can be achieved by increasing weir length, decreasing weir height or both. In either case, the froth height is reduced, and the system shifts toward the spray regime and away from the froth regime, thereby mitigating or inhibiting foaming.

**Foam inhibition.** The tray shown in Fig. 3 is often ascribed with foam inhibition and antifouling capabilities. Foam inhibition can be attributed to such things as the long outlet weirs, evenly spaced downcomer spouts and short liquid flow paths. The antifouling capabilities can be attributed to a minimization of stagnant areas and a reduction of liquid residence times in the column.

Trays designed with long outlet weirs are the main reason they have inherently low froth heights. Because reducing froth heights is one of the major foam-reduction mechanisms, MD trays impart antifoaming capabilities to systems in which they are used.

Large foam beds are further impeded by the short liquid flow paths of the trays. Because they have many long outlet weirs over which froth and foam flow, the formation of large stable foam beds, as may be seen above the froth of single-pass trays, is less probable.

The accumulation of fouling debris is far less likely if the tray design has less stagnant area, especially for trays that do not require receiving pans and inlet weirs. This absence of stagnant areas is also an advantage concerning the DMF process because areas of stagnation tend to produce more polymer and, as a result, increase polymer fouling.

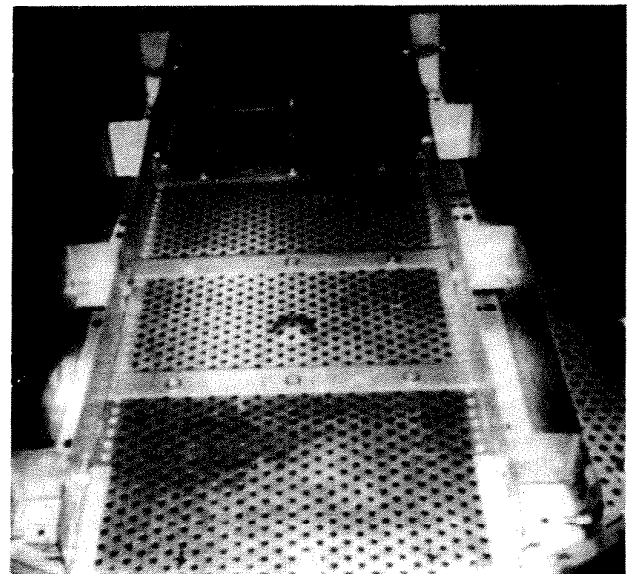


Fig. 2. Typical MD tray.

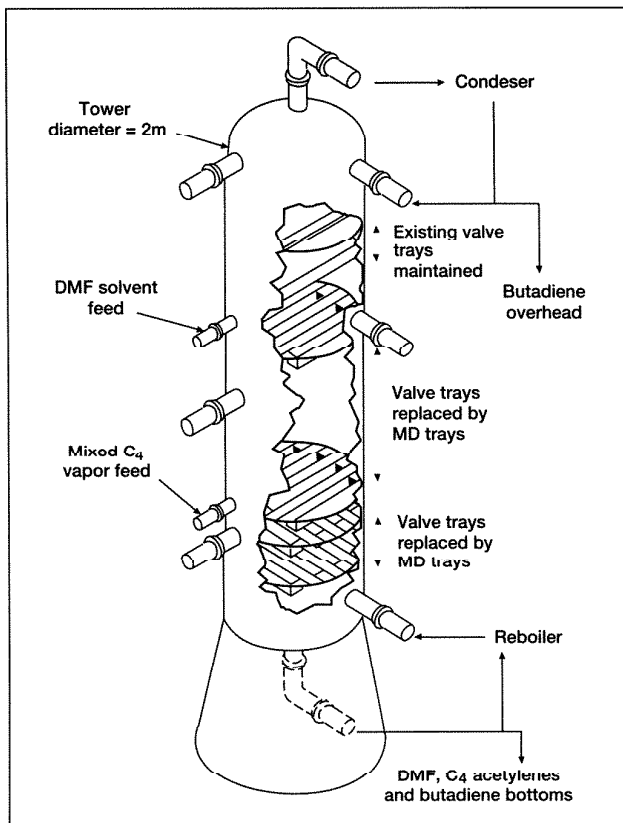


Fig. 3. Column revamp.

Reduced liquid residence time is advantageous from the standpoint of fouling matter, such as polymeric material, which appears and grows in columns. By reducing the time a given liquid resides on a tray, the amount of polymer and the relative length of the polymer chains are reduced. This chain shortening further reduces the likelihood of polymer buildup and eventual polymer blockage of a set of trays.

**Original column.** DSM considered the possibility of employing trays to defoam and defoul the second extractive distillation column in their butadiene purification train. The original (as-built) column employed single-pass valve trays approximately 2 m in diameter. From its commissioning, the column was plagued by foaming and fouling. The top section would become plugged by a dark tarlike polymer, which steadily reduced the tower's capacity and required extensive work at annual planned shutdowns (and in one case in 1985, caused an unplanned shutdown) to return the column to service. Workers once found the entire tray space above the DMF feed tray filled with polymer.

To reduce the severity of the problem, silicone oil was used in the DMF solvent feed as an antifoam (and antifoul) agent. They also removed two of the trays immediately below the DMF solvent feed and lowered the position of the DMF solvent feed nozzle to lessen the foaming and polymerization in the top tray section and provide a smooth entry for the solvent onto the new lowered feed tray. This action was taken prior to UOP's involvement. DSM succeeded in reducing, but not eliminating, the severity of the column's problems.

Immediately after the aforementioned feed point revamp, DSM observed a reasonably low pressure drop across the cleaned and recommissioned column. With time, however, the column's pressure drop increased to the point that liquid could no longer get down the column and a shutdown and recleaning was required. These troublesome shutdowns were scheduled on an annual basis.

DSM made some important observations about the fouling. The fouling tended to be most severe above the DMF feed point. The polymer tended to form between the tray decks, not on them. Investigators theorized that these stable foams were initiated below the DMF feed but were carried to the trays above. Once there, these stable foams stagnated, and the rampant, in-foam polymerization that occurred caused sheets of polymer to form above the normal froths of the tray decks.

Some literature sources state that this dark tarlike polymer is a polybutadiene that forms from 1,3-butadiene in the liquid phase with peroxides acting as catalysts.<sup>2</sup> The literature mentions that acetylenes lead to problems with foams, polymer deposition and equipment blockages. These catalysts appear to be necessary for the initiation of polymerization, but unfortunately, acetylenes that are quite soluble in DMF and peroxides form easily in the presence of oxygen or air. The literature also indicates that the foam stability promotes in-foam polymerization and that the key to the mitigation of fouling is foam inhibition.

**Tray design.** The MD trays were designed to replace the existing, original single-pass valve trays. The primary objectives of the tray design were to reduce foaming and fouling. A capacity increase of 10% was also sought in the design of the trays.

Foam reduction was achieved through the use of large perforations (19 mm) and, of course, through froth height reduction via the long outlet weir of the trays (5.2 m) versus that of the conventional trays that were previously employed (1.3 m). With the large diameter perforations and the reduced froth height, the spray regime of hydraulic operation was lessened. The larger holes would plug far less easily, if at all, compared to smaller perforations. The large holes may have also facilitated the downward passage of sediments that may have otherwise accumulated on the trays.

Engineers suspected that a smooth bubbling area may reduce the adherence and accumulation of polymeric sediments on the tray decks. As a result, 14-gauge type 304 stainless steel was chosen for the tray material. Manways were specified in the bubbling areas to allow internal column inspections and, if need be, tray cleanings.

**Revamp.** The new trays were fabricated by a qualified distillation tray manufacturer under UOP's supervision. Each tray employed two downcomers. Each downcomer employed six groups of spouts in its bottom. Tray deck perforations were 19 mm in diameter.

The trays were employed at the same tray spacings that DSM had employed with the conventional single-pass

valve trays. Specifically, spacings of 380, 570 and 610 mm were used. Typical MD trays are spaced at only 330 mm and have been used at spacings as close as 203 mm. The design was expected to yield smooth operation at an increased C<sub>4</sub> hydrocarbon feed rate. This feed rate was roughly 110% of the old feed rate.

**Results.** At first, the original column before the revamp operated smoothly after recleaning, but the pressure drop gradually increased. This rise in pressure drop continued until the feed rate to the column had to be reduced to maintain the necessary separation. Usually, production could be continued until the next scheduled shutdown of the plant even though the column capacity gradually decreased. A shutdown usually took place every year. Sometimes an unplanned shutdown of the column was necessary to literally shovel each tray free of the fouling polymer. This task was a substantial, but necessary, one that had to be performed before the column could be returned to service.

The C<sub>4</sub> extractive distillation column at DSM was recommissioned following the tray revamp. A break-in period was required to allow DSM's operations staff to become acquainted with the revamped column. Lag times, pressure drops and flexibilities were different than they were with the conventionally trayed tower. Once the staff became comfortable with the tower, the pressure drop and flooding characteristics were monitored.

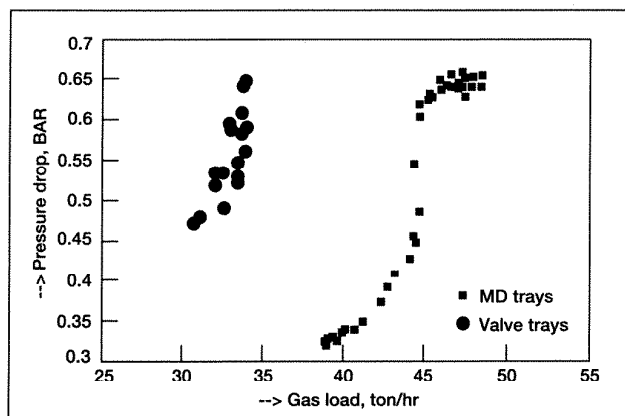


Fig. 4. Pressure drop as a function of the gas load for valve and MD trays.

Fig. 4 shows the results of the revamp with regard to the pressure drop of the column. It shows that a significant decrease of the pressure drop was achieved with the trays and that a much higher capacity is possible in the new situation. The revamped column has, in fact, been in service for two years between the shutdowns of 1987 and 1989 without a significant increase in pressure drop. During the shutdown of 1989, the column was inspected and found to be totally clean, an experience the staff had never had before. Apparently, the new trays have inhibited foaming in the tower as predicted. With the cessation of foaming, renegade polymerization has also been prevented.

Unplanned shutdowns and cleanings, as well as gradual decreases in feed rate, are no longer necessary. In fact, the trays inhibited foaming so well that the silicone antifoam is no longer required.

With some tray revamps, the separation capability of the column is reduced slightly. In the case of the revamp at DSM, the column's separation performance was maintained with the higher hydraulic capacity of the column, these increases caused no complications. In the subject column, an increase of 20% over the old feed rate was realized, and an even higher capacity appears to be possible.

#### ACKNOWLEDGMENT

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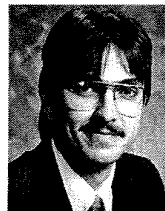
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#### The authors

**Michael R. Resetarits** is Group Leader of UOP's Separations Development Group in Tonawanda, New York. His primary fields of expertise are distillation and extraction, with 17 years of experience. Mr. Resetarits holds a BS degree in chemical engineering from The State University of New York at Buffalo, an MS degree in chemical engineering from Northwestern University and an MBA degree from Canisius College.

**J. L. Navarre** is Area Sales Manager Europe/Middle East for UOP's Advanced Distillation and Heat Transfer Technologies. Prior to joining UOP, he was in European Marketing Technical Services with Monsanto Europe S.A. He received a PhD in nuclear science from The University of Louvain.



**D. R. Monkelbaan** is a Staff Engineer with UOP's Separations Development Group in Tonawanda, New York. He performs process engineering and develops and designs contact equipment for refineries and chemical plants. Mr. Monkelbaan acquired a BS in chemical engineering in 1985 from The State University of New York at Buffalo.

**G. W. A. Hangx** is currently Leader of Workgroup Distillation in the process department of DSM Research. He is mainly involved in improving, revamping and development of distillation separations within DSM.