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DEVELOPMENT AND MODELING OF MICRO DISTILLATION COLUMN

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Abstract
The design, manufacture, testing and modeling of a novel flat micro-distillation column is presented. Porous metal foam was used as distillation packing. The unit was operated in a horizontal orientation both with total reflux and with continuous feed. The separation efficiency in terms of height to a theoretical plate of 16 mm was determined with a mixture of n-Hexane and Cyclohexane. Operation of the device was stable and results were reproducible. The unit was operated unmanned over extented periods of time. Results were analyzed with McCabe-Thiele – method.

Keywords: Micro-scale distillation; Metal foam; Packing material

1. Introduction

The potential of microplants for speeding up process development is similar to what miniplants offered 20 years ago. The manufacturing cost of a microplant can be modest and the process configuration can be modified rapidly. The hold-up in a microplant is small, which makes the process inherently safer. Thanks to the improved safety, the process needs less monitoring, which may reduce labour costs. The small hold-up directly reduces chemical costs, which may be high for traditional process units, especially if industrial-scale production has not yet started.

The miniaturization of reactors and the unmanned operation is existing technology. Distillation columns, on the other hand, have so far been too complicated devices to be operated unattended. Although miniplant scale has been used to verify VLE models, longer test runs have been too labor intensive for universities[1]. A miniplant is often the first stage to detect problems caused by impurities build up with a recycle[2]. According to Wörz, the maximum cumulative residence time for the recycles should be lower than 24 hours[3]. To make good use of the potential in the microplant concept, micro distillation columns are of immense value. The hold-up of these types of units should be substantially smaller than the hold-up of the units used in miniplants. Despite the potential uses, literature recognises only few attempts to develop these units. Recent contributions in the field worth mentioning are Fink and Hampe[4], Seok and Hwang[5] and Silva et al.[6]

In this work we tackled the aspects mentioned above by constructing a distillation column consisting of flat plates. A sheet of metal foam was used as a distillation packing. The column was operated in a horizontal orientation with indirect heating via column walls.

2. Methods and materials

The shape used in the design of the distillation column was a flat plate. It was easy to manufacture and the heating could take place with a simple heating block with good thermal contact. A diagram of the equipment is presented in Figure 1. Wall material was stainless steel. Length of the column was 300 mm, widht 50 mm and height 20 mm. The chamber inside the column was 290 mm long, 30 mm wide and 5 mm high. The chamber was open towards the vacuum flange. KF40 vacuum flange was welded to the cold end of the column for maintenance access and for connecting the column to water cooled vertical condenser. A 3-mm-thick metal foam was placed on the bottom of the chamber and a 2-mm-thick metal plate was placed above the metal foam to reduce the chamber height to 3 mm and to eliminate open space from above the foam. The purpose of eliminating the open space was to force the vapour to flow through the liquid filled metal foam instead of open space thus increasing the

vapour-liquid contact. Dead volume in the vacuum connections was minimized by filling the parts halfway with Chemical Metal®. The equipment was heated indirectly via a 30-mm-thick aluminum plate attached below the column. A second aluminum plate was placed on top of the column, 20-mm-thick, to secure the heated plate on the column. A cartridge heater was embedded at the end of the aluminum plate. The temperature was controlled with time-delay and integration controller. Temperature of the packing was measured at five points from inside the metal foam. Temperature of the aluminum plate was measured at two points. The feed line was unheated. Feed was introduced with a syringe pump, ISCO 500D. Bottom product was drawn by gravitation from the rightmost sampling connection. Flow rate was controlled by a manual needle valve, which was coarse for the flow rates applied. Distillate was drawn via overflow at the vacuum elbow. The overflow was constructed outside of the column with a T-connection. Liquid level in the condenser was controlled by changing the elevation of the T-connection. Liquid level was observed visually through the condenser.

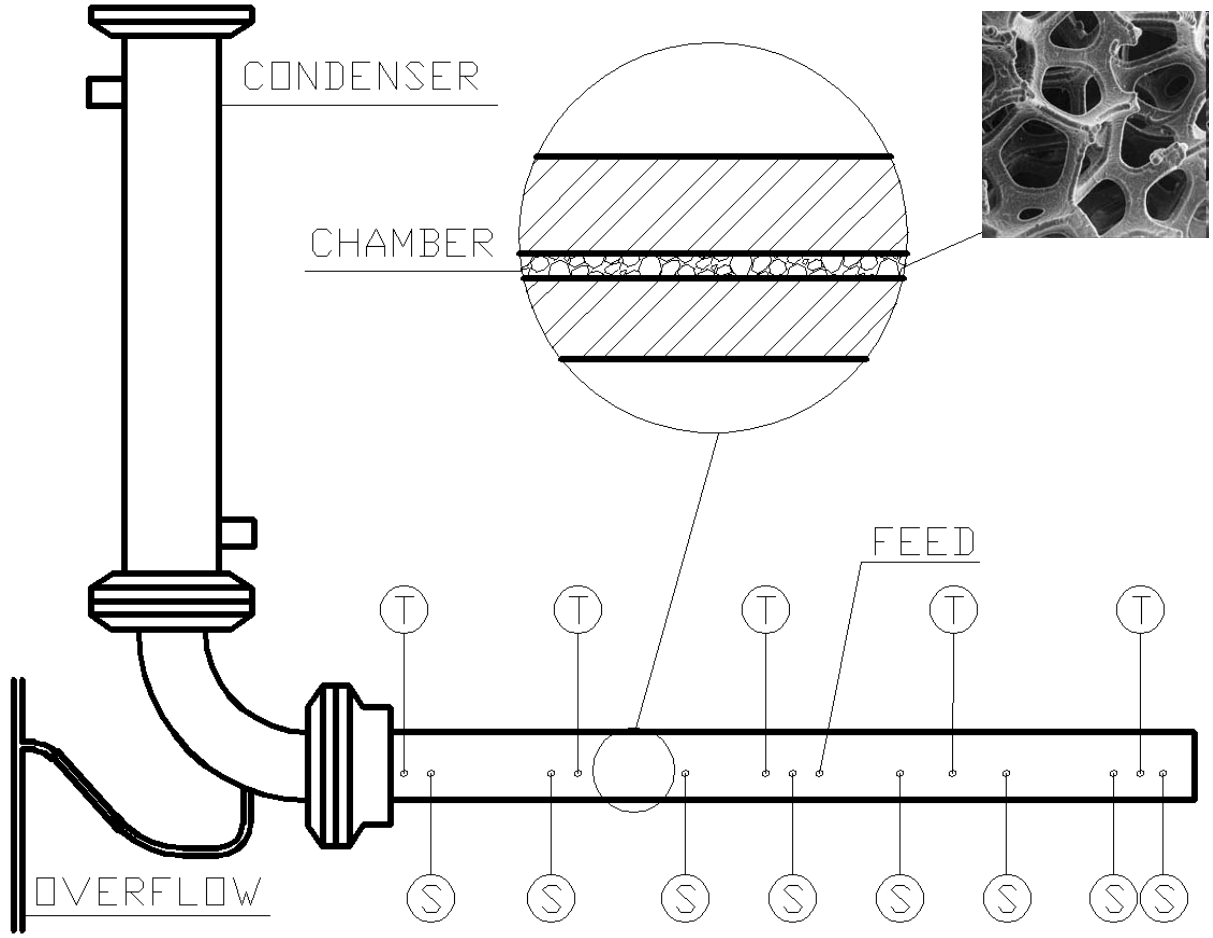

Figure 1. Diagram of the distillation column. S marks sampling connections and T marks temperature measurements. The right end of the column was the heated reboiler section. Aluminum plates above and below the column are not shown. Picture of the metal foam is by Recemat International[7].

Metal foam used as distillation packing was manufactured by Recemat International. The foam was 3-mm-thick and it was of an open-cell type with a porosity of over 95%. Specific surface area was 2800 m^2/m^3 and the average pore size was 0.6 mm[7]. In an open-cell foam the pores form an interconnected network. Thanks to this the foam was highly permeable, as reported by Khayargoli et al[8]. Metal foam was also easily workable. The column was characterized with an equimolar mixture of n-Hexane and Cyclohexane. Concentrations were determined with refractive index detector. Concentration error was estimated to be ±0.001.

3. Results and discussion

3.1 Total reflux experiments

Separation efficiency of the distillation column expressed in terms of height to a theoretical plate (HETP) was determined by total reflux experiments using an equimolar mixture of n-Hexane + Cyclohexane. The volume fed into the column at the beginning of experiment was 60 ml. The volume injected was large compared to void volume of the column (25 ml), but as reported earlier[10] the separation efficiency was higher when the liquid level in the condenser was above the top of the metal foam. Due to this the holdup in the vacuum elbow was high. In the best experiment the n-Hexane mole fraction obtained at the ends of the column was 0.001 and 0.54. Number of theoretical stages (NTS) equal to the concentrations was 18 ± 2, giving a HETP equal to 16 mm. Separation efficiency had improved significantly from the HETP of 25 mm reported in our previous work[9]. Measured concentrations and the NTS calculated from adjacent measurements is shown in Figure 2. It can be seen from the figure that the three measured concentration points at the condenser end of the column are at relatively same concentration. This indicates that no mass transfer is occurring at that part of the column. The solid line in the figure is a simulation of distillation with total reflux and thus represents indirectly the equilibrium line of the system. Thus in that concentration area you should expect rapid changes in the column per column length.

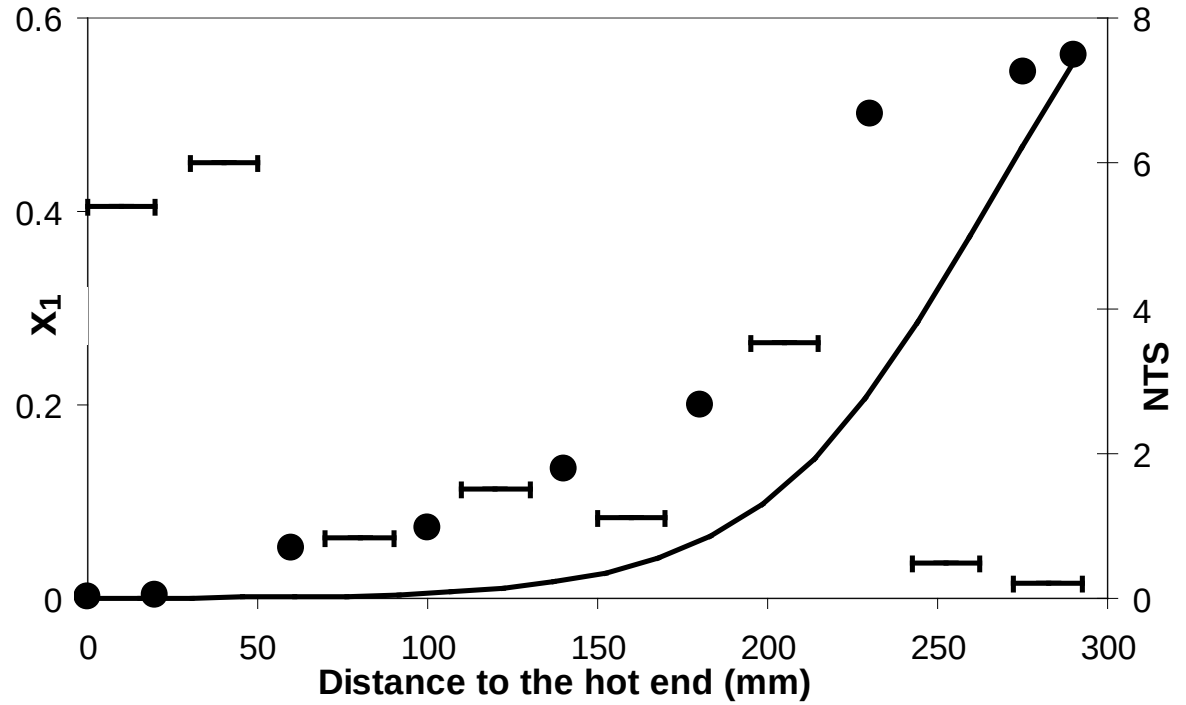

Figure 2. n-Hexane (1) + Cyclohexane distillation with total reflux; reboiler section is at the left; ● represents measured concentration, solid line represents simulation with total reflux, ⊢⊣ represents the number of theoretical stages between adjacent measurements.

The poor separation efficiency close to condencer was propably caused by decreasing vapour flow along the column and backmixing from the vacuum elbow. Heat losses of the column were relatively high, especially compared to energy consumption of vaporization; heating duty with an empty column was 54 W and with total reflux 77 W. In both cases the condenser was water cooled and the temperature of the aluminum plate was set to 88°C. The fluctuation in the heating power was up to ±5 W, depending on the air flow rate over the column and humidity of air. The temperature profile of the column, as shown in Figure 3, shows sharp decrease after the middle part of the column indicating inadequate heat transfer and vapour flow towards the condenser as well as the cooling effect of the condenser.

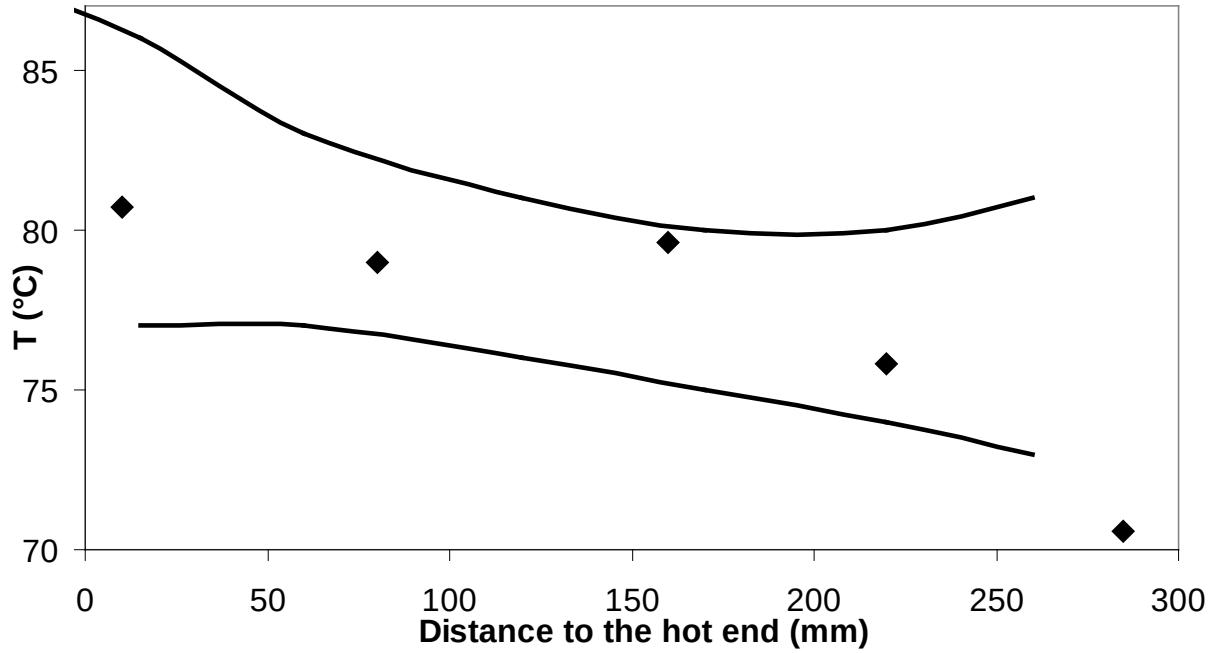

Figure 3. n-Hexane + Cyclohexane distillation with total reflux; reboiler section is at the left; ◆ represents the temperature inside distillation packing, solid line represents temperature profile of the aluminum plates.

3.2 Continuous flow experiments

A set of experiments was performed with varying feed flows as can be seen in Table 1. In the beginning of each experiment the heating duty was varied to find the highest separation efficiency. This was due to our earlier experience that the operation of the column was sensitive to the heating due to the difficulties in controlling the heat losses.

An example of the procedure to obtain the results shown in Table 1 is given for feed flow rate of 2 ml/min. The temperature of the reboiler section was changed incrementally from 80 to 94 °C. To compare the results obtained, NTS was calculated from the product compositions as if the distillation was with total reflux. This NTS was divided by the NTS obtained from distillation with total reflux (18) to obtain a relative separation efficiency. The relative separation efficiency as a function of the reboiler temperature is shown in Figure 4. The holdup in the experiments was set to 40±5 ml. It seemed to vary slightly as a function of the temperature of the reboiler, which means that the fraction of vapour in the reboiler also changed. The best separation efficiency was found at reboiler temperatures from 82 to 83 °C. Distillate n-Hexane mole fraction was 0.64 and bottom product mole fraction was 0.31. Deviation was ±0.007. Flow rate of the bottom product varied from 0.88 to 1.0 ml/min. Reason for this was the coarseness of the manual needle valve. However, the temperature and the flow rates were kept unchanged for the length of each experiment, usually for up to one working day.

At temperatures below the optimal temperature range the separation efficiency was lower due to insufficient vapour flow in the column. At temperatures above the optimal temperature range the separation efficiency was lower probably due to too high flow rate of vapour. These results are more than likely specific to this type of device and give only qualitative information of the phenomena. The flow rate of heavy product was unaffected at temperatures up to +115 °C. This would indicate that capillary forces were sufficient to keep the foam wet. In this type of metal foam packing we expect the capillary forces to provide the movement of the liquid.

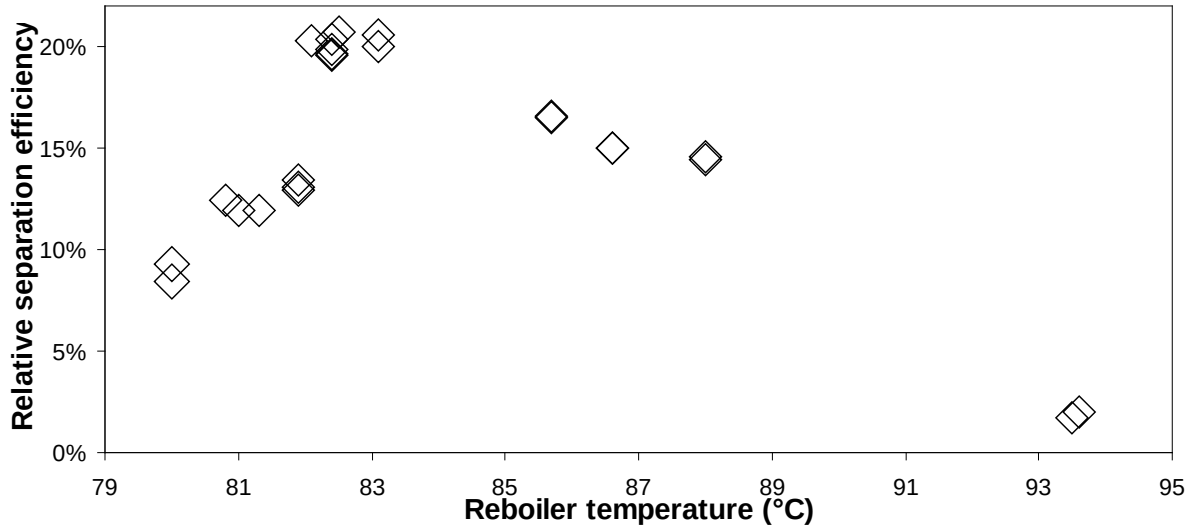

Figure 4. Separation efficiency with a feed flow rate of 2 ml/min of n-Hexane + Cyclohexane expressed as a fraction relative to separation with total reflux at various reboiler temperatures.

Continuous flow experiments with lower feed flow rates were conducted in a similar way. A simple analysis of the results was done by the McCabe-Thiele –method. We are fully aware that the assumptions of the method about the straight operating lines are not fulfilled in reality, but we feel however, that this analysis gives at least a qualitative view of the operation of the column. The slope of enrichment line and stripping line were calculated using the NTS value of the column with total reflux as the basis. This is shown in Figure 5a. The number of steps above the feed point varied between one and four, depending on feed flow rate. This result is in line with the results obtained from the concentration profile of the total reflux experiment shown in Figure 2. Conclusion is that the heat losses prevent satisfactory operation of the column above the feed line, aka in the enriching section. However, the results are promising as the trend in L/V ratio shown in Figure 5b depicts in a reasonable way the behaviour of the column. It indicates countercurrent liquid-vapour traffic inside the device as required for distillation, as the separation improves when liquid-to-vapour ratio decreases. The stripping section of the column seems to be able to strip the light component yielding virtually pure heavy component.

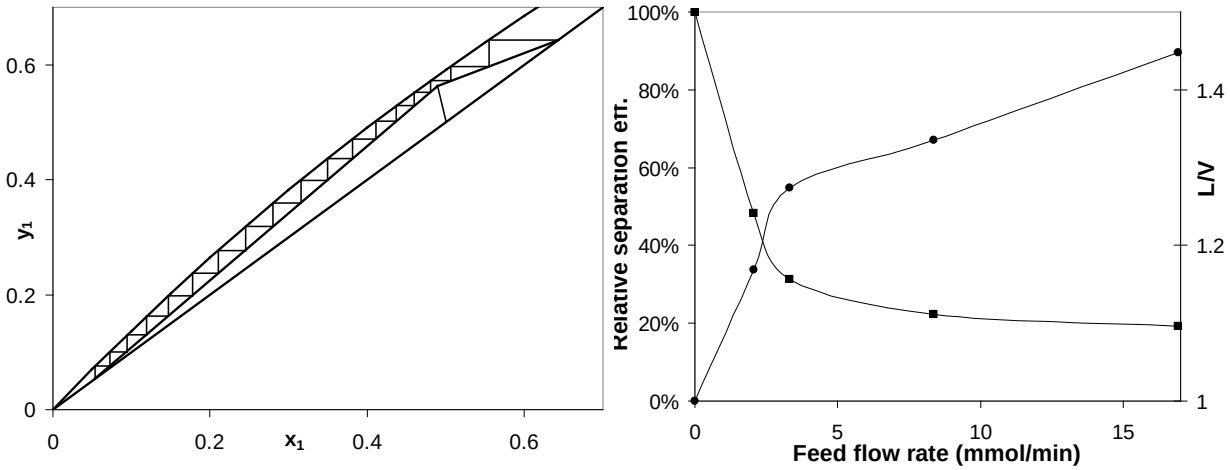

Figure 5 (a) McCabe-Thiele diagram for the experiment with feed flow rate of 0.25 ml/min of n-Hexane(1) + Cyclohexane **(b)** Results of the continuous flow experiments as a function of feed flow rate in mmol/min; ■ presents the relative separation efficiency compared to distillation with total reflux; ● marks the slope of the stripping line (L/V ratio)

Table 1. Distillation experiments with equimolar feed of n-Hexane (1) + Cyclohexane

Feed flow rate	Feed flow rate	x_1, bottoms	x_1, distillate	Slope of q	R/(R+1)	L/V
(ml/min)	(mol/min)	mole fraction	mole fraction	-	-	-
0	0	0.001	0.56	NA	1	1
0.25	2.1	0.054	0.64	0.86	0.52	1.17
0.4	3.3	0.22	0.70	1.0	0.56	1.31
1	8.4	0.24	0.61	1.1	0.10	1.34
2	16.9	0.32	0.64	1.2	0.28	1.44

4. Conclusions

A small scale distillation column was developed, suitable for operation in micro-plants. Simple, safe, unattended and stable operation was achieved for extended periods of time, even up to 3 weeks. Separation could be obtained both in a total reflux run and in continuous operation with varying feed flows. This device provided in its best NTS of 18 and a HETP of 16 mm.

In a small scale distillation column the heat transfered by the boiling of liquid is insufficient to compensate for heat losses. This can be seen particularly in the temperature measurements conducted for the experiments with total reflux. Also the analysis of the results by simple McCabe-Thiele –method showed consistent behaviour as the separation was almost only happening in the stripping section. This was due to decreasing vapour flow closer to the condenser and backmixing from the hold-up in the vacuum elbow.

A common solution for the heat losses is to use electrical tracing along the column, which is often too unstable for micro-scale distillation. In the design presented here the problem was solved by using thick metal walls to conduct the heat. This made the design also safer for unmanned operation, as in case of reboiler dry-out there was no risk of overheating. The modifications made to our earlier work[9], drawing of the distillate via an overflow pipe and the elimination of the vapour space from above the metal foam[10], significantly improved the ease-of-use of the column. Apparently as the vapour was forced to flow through the liquid filled metal foam packing the vapour-liquid contact increased thus improving the separation efficiency.

This device will make it possible to further miniaturize mini-plant technology to a micro-plant. It may enable the running of longer test runs for the studying of accumulation of impurities in recycles. It may also enable faster and cheaper process development and may allow research in universities to go further in testing ideas in process development.

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