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DESIGN PRACTICE FOR PACKED LIQUID LIQUID EXTRACTION COLUMNS

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Introduction

The use of countercurrent operating columns for liquid liquid extraction (LLE) moved in the focus of the design engineers with the upcoming use of extraction in the petrochemical industry involving the typical high volumetric flow rates. Today, towers with random and structured packing internals as well as separation trays operating in countercurrent LLE mode are widely spread all over the petrochemical and chemical industry.

K. Sattler divides the available technology for liquid liquid contacting into four groups [1]. In this view the decisive criteria for the selection of the contactor device is on one hand the physical properties of the system feed/solvent as it is characterized by the density difference and interfacial tension, and on the other hand the difficulty of the thermal separation in terms of required number of theoretical stages (NTS) to reach the desired raffinate and extract concentrations.
The four groups are:

- centrifugal extractors for difficult phase separation and relatively low NTS
- agitated columns with reciprocating, rotating or pulsating equipments for moderate phase separation requirements and higher NTS
- static columns for easy phase separation with low NTS
- mixer-settler batteries for a high requirement of NTS at easy phase separating conditions

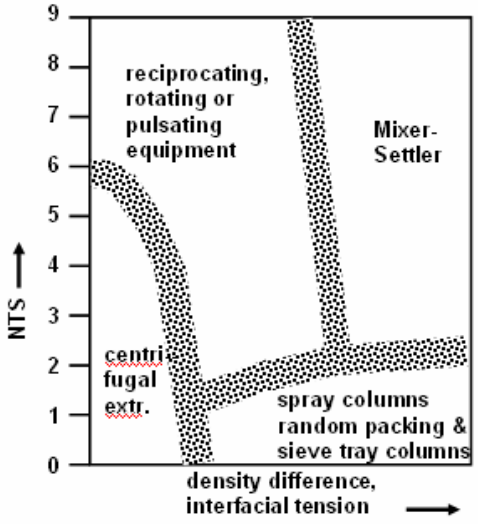

Figure 1: Application of different LLE contactors
(K. Sattler, 1995 translated by the author)

In literature other pre-selection criteria have also been published. However today in industry the use of packed columns (random or structured) for LLE applications will be in most cases found limited to operations where:

- the density differences between the carriers is higher than 30 – 50 kg/m^3
- the volumetric phase ratio Φ between dispersed drop phase and continuous phase is in the magnitude of $0.5 < \Phi < 5$
- the number of theoretical stages NTS ≤ 10

The essential advantages of packed columns compared to tray columns or other agitated contact devices are

- the high specific throughput capacity usually expressed in total flow of both phases per available column cross-sectional area [m^3/m^2h]
- easy operation and maintenance because no moving parts are involved
- for corrosive media are almost unlimited options for the material selection available, from stainless steel to high-alloyed metal, from polypropylene to PTFE, technical ceramics or pure carbon.
- a simple operation also at high pressure or temperatures

There is different function of the column internals in vapor/liquid services like distillation or absorption, where the specific surface of the packing provides the required area to perform mass transfer. In contrast, LLE columns the mass transfer area is almost independent of the packing surface, but is directly linked to the drop phase holdup in the tower. The main function of the packing is to provide an increased flow path length respectively more residence time for the drop phase. Coalesced drops are re-dispersed at the sharp edges of the packing and the residence time distribution of both phases should be kept as narrow as possible (plug flow) by minimizing any axial back mixing effect.

Comparing structured packed columns with random packing columns, it should be mentioned that the use of structured packing for LLE was not widely used before the 1980's. In many refinery applications, random packing is still the standard choice, partly for "historical reasons", but also often explained by the necessary possibility to follow frequently cleaning procedures after a certain period of operation. In the chemical industry the technical advantages of structured packing with higher operational flexibility (turn down), higher allowable bed heights and maximized throughput are taken more into consideration.

Design consideration

Solvent selection, solvent/feed ratio, NTS estimate

In general it should be stated at this point that the commercial available process simulation software today provides for many distillation services an excellent data base to predict the required NTS and the resulting internal hydraulic tower traffic quite precisely. However, for LLE separations this is more the exception. Some common applications like LPG/amine contactors are successfully simulated with commercial available simulation software like PRO II or AMSIM. In this case an advantageous solvent/feed ratio and the required corresponding NTS can be predicted for a desired

raffinate purity. But in the most cases, especially for the wide variety of chemical applications, proprietary methods and software is used, assuming that in a first stage an appropriate solvent has been selected by relying on process experience or theoretical considerations with subsequent successful lab testing. Experimental equilibrium shake tests under realistic conditions are providing still in many cases a first basis for an estimate about a useful feed/solvent ratio with the required NTS.

Selection of the dispersed phase

For a straight forward column design it is recommended in a early project phase to decide about the phase regime and determine the drop phase. Different criteria need to be considered, which are usually not promoting the same phase to be drop phase:

- the phase with the higher volumetric flow should be dispersed
- mass transfer direction should be preferred from continuous into drop phase
- the phase with the higher viscosity should be dispersed
- the phase with better wetting behavior on the packing material should be continuous
- inflammable liquids should be drop phase.

Packing material

Aside from corrosion aspects - the packing material in general is selected in order to optimize the wetting of the phases on the packing surface. The surface should be such that the dispersed drop phase wet the surface as little as possible, which is influenced by the physical fluid properties as well as the material type, texture and coating of the packing. In most of the cases metal packing is used preferable with aqueous continuous phase. Stainless steel will be wetted by either organic or aqueous phase, depending on the initial exposure of the surface, whereas plastic packing should be preferred when operating with organic as continuous phase. Ceramics are usually avoided due to the risk of their brittleness, blocking pumps and valves due to chipping and decomposition during operation. However they tend to be preferable wetted by an aqueous phase and might still be chosen for corrosion aspects. In LLE service it is recommended to degrease stainless steel packing from manufacturing oil recess in order to avoid serious start up problems caused by unexpected wetting behavior.

Fluid dynamics

There is a great number of hydraulic models published, empirical as well as theoretical, to predict the flooding capacity and dispersed phase holdup of packed LLE towers. For a first hydraulic design in order to provide diameter information for a feasibility investigation the following data are usually required:

- future feed capacity
- expected throughput of solvent
- liquid densities of both phases
- liquid viscosities of both phases
- interfacial tension of the system

The process engineer is using any one of those models or, if available, his plant experience for the explicit application to estimate the specific flooding capacity with the packing type in mind. Whereas for random packing the practice might be more oriented towards application experience the prediction of flooding capacity of Sulzer SMV(P) extraction packing based on developed design models can be worked out today with acceptable accuracy. However the most critical subject for a good estimate of the

flooding capacity is usually accurate information about the interfacial tension, which is the main factor to determine the expected drop size correctly, and in the most cases this information is missing in the starting phase of a column design.

Usually there is no dramatic scale up effect expected for the specific maximum throughput capacity of packed columns, but it should be mentioned that this kind of calculation procedures are not able to predict limitations by phase entrainment in the top or bottom of the column.

Appraisal of column height

Based on experimental phase equilibrium data out of shake tests and the process related information about feed, solvent and raffinate concentrations as well as flow rates the required NTS for the separation might often be determined in industrial practice by a simplifying continuum model like the HETS model with the McCabe-Thiele procedure. With an appropriate approach for the calculation of the mass transfer coefficients and expected effective mass transfer area a first estimate for the required column height under ideal plug flow conditions might follow according to the well known HTU model [2, 4]:

$$H_{col} = n_{th} * HETS$$

respectively

$$H_{col} = HTU_{ox} * NTU_{x}$$

Pilot tests

With the results of above mentioned simulation, appraisals and/or lab testing the engineer has enough information to decide about the feasibility of the separation in a packed tower. If he comes to a positive result, the preparation of pilot tests is the next step. These tests shall confirm the estimations in regards to the maximum throughput capacity, average drop size and will give HETS close to plug flow conditions. It furthermore shall provide important information about

- coalescing behavior at the interface
- problems with rag formation
- entrainment limitations
- corrosion problems
- fouling
- mutual solubility of the carriers under mass transfer conditions

For these tests it is strongly recommended to use original plant operating liquids, not synthetic mixtures to replicate plant fluids. The tests should be prepared with the goal to determine the flooding capacity at intended volumetric phase ratio and to do efficiency tests at 80% and 50% of the determined flooding capacity. The diameter of the pilot unit is usually in a range between 50 - 150 mm, packed height between 2 - 5 m.

Random packing used for industrial sized LLE columns are in most cases today 3rd generation rings (e.g. Nutter ring, I-ring) of 1.5" – 2". Since a ratio of $D_{Col} / d_{Ring} < 10$ leads to unacceptable wall effects, the use of industrial applicable ring sizes in a pilot unit would require an unacceptable large test column diameter. Therefore it is recommended to use - instead of the industrial applicable ring size - smaller rings for the pilot tests.

In case of structured packing the test column is usually equipped with the industrial packing type. This will eliminate the scale up risk on throughput, but limits the minimum pilot column diameter to 50mm and requires special efforts to minimize wall bypassing.

It is obvious that these kind of tests require quite some effort of preparation, equipment and solvent logistics. With 50 m^3/m^2h, a pilot column of ID=100 mm requires to handle close to 400 l/h liquids (feed + solvent) for a test run. Recent research work [3] is consequentially focusing on the preconditions to overcome this costly step of design without unreasonable risk to fail in the scale up. Different approaches are under investigation as there are

- scale up from mini plant test results (ID < 50 mm)
- direct scale up from single drop experiments
- column simulation based on drop population models

However, up to now industrial practice is not yet so far to waive the pilot column tests with acceptable confidence.

Scale up

Based on the results in the pilot tests a scale up calculation is required to consider the strong influence of the column diameter on the effective HTU by the main effect of axial back mixing. Different publications [e.g. 4, 5, 6, 7, 8] are available about the principle method of adding height of dispersion units (HDU) to the transfer unit (dispersion model):

$$HTU_{ox} = HTU_x + HDU_c + HDU_d$$

With the simplification, but also limitation of assuming constant physical system properties and constant operating parameter along the column height as well as insolubility of the carrier phases this model is also established in Sulzer's design practice.

Pulsation

When systems of high interfacial tension respectively with large expected average drop size should be contacted in packed columns sometimes additional agitation of the column volume by a pulsating device at the column bottom can improve the efficiency remarkable. The mechanical energy destroys extremely large droplets and therefore limits the drop size distribution. Increased mass transfer surface and improved radial distribution, but also some minor reduction of the throughput capacity can be expected. The designer provides to the operator an additional parameter for operational optimization, but has to justify considerable investment cost. Usually for smaller columns (ID ≤ 600 mm) the use of piston pulators are common, for larger diameters pendulum pulsators might be used. Typical operating parameters are a frequency < 150 min^{-1}, with an amplitude of 6 - 8 mm.

Packing types

Figure 2 presents the most used packing types by Sulzer for industrial sized LLE columns.

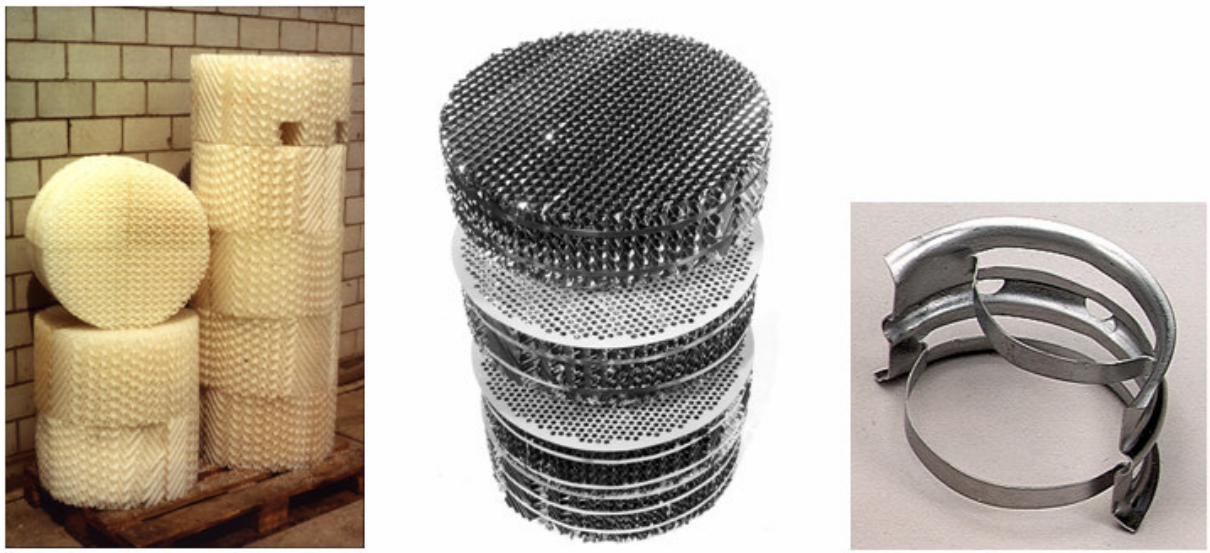

Figure 2: Sulzer LLE packing types,
SMV / SMVP / Nutter Ring

Nutter Rings

Typical applications for Nutter Rings are LPG/NGL amine contactors or caustic washers. For chemical applications the rings should be preferred when

- solids in the feed are expected
- medium hydraulic capacity is required
- volumetric phase ratio ≤ 3
- density differences < 200 kg/m3
- low NTS is required to fulfill the separation

For columns above 800 mm diameter a typical ring size is 1.5" or 2", a further reduction of the ring size should not bring notable efficiency improvements, but will limit the maximum throughput. Typical design characteristic:

- number of beds: up to five
- throughput: 30 – 40 m^3/m^2h (max. 60 m^3/m^2h)
- NTS ≤ 5
- material: metal or plastic

Sulzer SMV

Structured packing provides by far the highest specific throughput capacity compared to rings or trays. They are usually the first choice for revamp projects, especially when

- extremely high hydraulic capacity is required
- volumetric phase ratio ≤ 3
- density differences < 200 kg/m3
- medium NTS is required

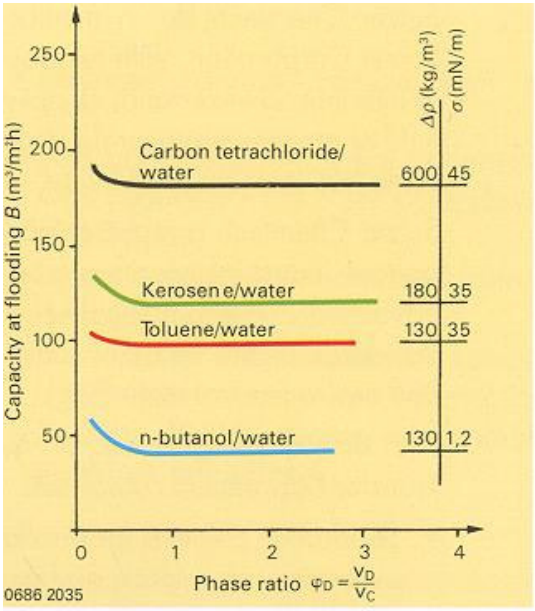

Figure 3: Sulzer SMV structured packing, max. capacity for different systems

With systems of high density difference, either with high interfacial tension like kerosene/water and carbon tetrachloride/water or lower interfacial tension like cracked naphtha/caustic soda [9] flooding capacities far above 100 m^3/m^2h have been found.
Typical design characteristic:

- specific surface 200 – 500 m^2/m^3
- number of beds: 1
- throughput: 50 – 90 m^3/m^2h
- NTS ≤ 6
- material: metal or plastic

Sulzer SMVP

The use of dualflow plates between the packing layers, which have usually a height of 210 mm, has not only a noteworthy positive effect in case of design constellations with strong axial back mixing. At the plates the drops are stopped and forced to coalesce and to be re-dispersed after passing the plate. These advantages "have to be paid" by a reduction of throughput capacity of the structured packing. Consequentially SMVP packing is typically used when

- medium hydraulic capacity is sufficient
- a high NTS is required
- volumetric phase ratio > 3
- density differences > 200 kg/m3

Typical design characteristic:

- specific surface 200 – 500 m^2/m^3
- number of beds: up to 3
- throughput: 35 – 60 m^3/m^2h
- NTS ≤ 10
- material: metal or plastic

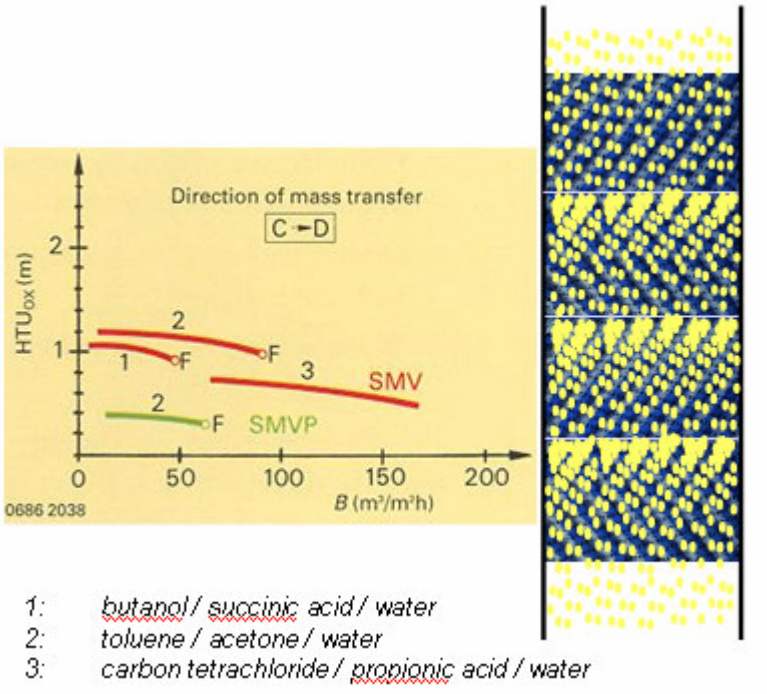

Figure 4: Sulzer SMVP structured packing
efficiency and max. capacity for different systems

Internals

Due to cost optimization separation columns are usually flanged, if the diameter does not exceed 800 mm, above this size the sections are welded together and the internals have to be inserted in pieces through manholes to be installed inside. Beside the nozzles for feeds and draw offs as well as interface and temperature control it is recommendable to install inspection glasses allow visual localization of the interface.

Distributors

Packing bed and coalescer unit are fixed between support and retaining grid. But the key to a well performing packed tower is the design of the liquid distribution devices and, if required, the design of the re-distribution tray. For the distributors in a bigger tower it is required to provide enough pressure drop to ensure at turndown conditions sufficient radial distribution quality, but avoid by all means spray effects caused by high exit velocities at the discharge holes with design rates. Finally sufficient open area needs to be provided.

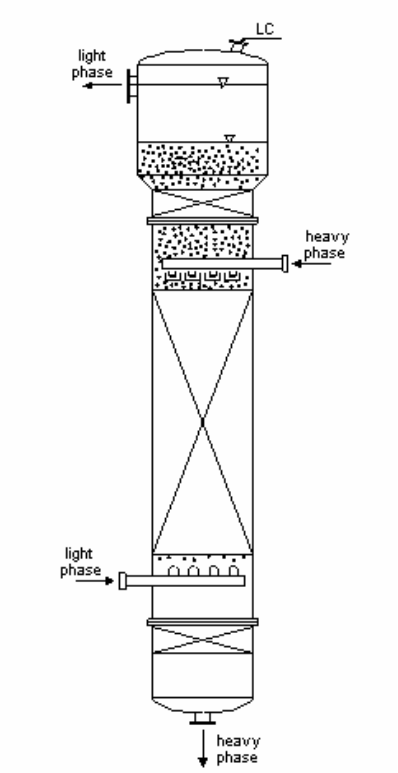

Figure 5: Column internals

Re-distribution trays

In most designs with random packing re-distributions are required after 2-3 m bed height to renew the drop size distribution quality. Also for structured packing beds it might be advisable under certain circumstances to avoid long bed heights (> 10-12 m). However, such a tray usually limits the turndown capability of towers with structured packing.

Figure 6: Re-distribution tray, ID 2700 mm

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Trouble shooting LLE columns

According to the experiences of Sulzer in the last decades trouble shooting efforts for non performing LLE towers should first concentrate on the following route causes:

- operation above capacity limit
- equilibrium limitations
- improper design or manufacture of internals, feed pipes or packing
- mistakes during installation
- underestimated back mixing (scale up failure)
- rag
- poor start up procedure or operation mode

Capacity limitations

Classical flooding in form of phase reversal as capacity limit is mainly constituted by the relative drop velocity calculated from density difference, viscosities and interfacial tension via average drop size and holdup. The most sensitive locations for a start of phase reversal in the tower are the entrance of the drop phase into the packing and a re-distribution trays.

Phase entrainment as capacity limit is usually caused by insufficient residence time in the coalescer section, too small draw off nozzles or valves or defective interface control.

Equilibrium limitations

Faulty designs failing due to equilibrium limitations have been seen, when the pilot tests were done with synthetic mixtures. Also a non performing regeneration of the solvent or of the temperature control could lead to such type of failures.

Fabrication and installation of the packing

Especially with smaller diameters the wall bypassing can create serious performance loss, not only in pilot column size. Without wall gaskets unrealistic high throughput capacities might be measured during pilot test. For bigger LLE columns different kind of wall viper devices are used. A correct orientation the collars during installation (open towards the drop phase) is important.

With increasing diameter the wall sealing issue becomes less important, but the segmentation concept for the portioned packing layer moves in the focus to avoid channeling through segmentation gaps of several layers without interruption.

A rag film on the packing as well as the wrong choice of material could create the same problem: a drop phase, that wets the packing material, moving through the column in cords on the packing surface. Last but not least, mechanical damage at the packing was found in some cases due to wrong handling during installation.

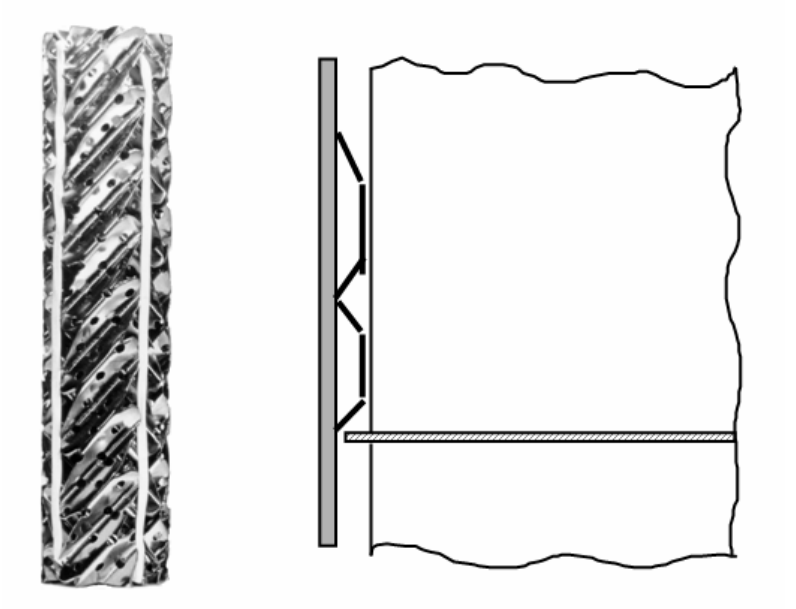

Figure 7: Wall bypassing: Teflon gaskets for pilot size / double mode wall vipers for industrial size

Large scale back mixing

Axial back mixing in the continuous phase of a static LLE column is mainly caused by the drag effect of the drops. Consequentially applications with slow continuous phase velocity and high drop phase holdup - the constellation at high volumetric phase ratio (drop phase/continuous phase) - are extremely sensitive to this appearance, especially in larger sized columns. Different or varying drop velocities caused by a wide drop size distribution as well as channeling, wall bypassing and large scale circulations at the phase inlet caused by high inlet velocities or extreme rate of local mass transfer are destroying all efforts to create plug flow conditions. The consequences are a reduced concentration gradient between the phases, resulting in smaller mass transfer rates and the requirement of additional packing height. In this matter a good choice of the packing type and a clever segmentation layout is important.

Rag problems

The accumulation of solid or quasi solid impurities at the interface can increase the coalescing time or promote the creation of a stable emulsion. Periodically it comes to problems with the interface control and the operator might be impelled to draw off this rag periodically from the interface via a separate nozzle. Filters in the feed lines as well as pH value control might help, where precipitation is expected. Some rag problems are caused by polymers that form due to reaction in the extractor. Unfortunately, packing can not solve fouling due to undesired side reactions, and either trays or spray columns might be a better choice.

Start up procedure

For the start up of a packed tower it is recommended to fill up the tower first with continuous phase. When the packing is completely flooded with continuous phase the continuous phase flow shall be stopped and the drop phase should be started up with approx. 20-30% of the expected flooding capacity. In a next step the design phase ratio should be adjusted at the same low level by starting up again the continuous phase

flow. Both flows, solvent and feed, should be increased in small steps at constant design phase ratio until design flow rates are reached.

Experience of Sulzer Chemtech

After 25 years of designing LLE columns with structured and random packing as well as with sieve trays Sulzer Chemtech can provide significant industrial experience for this special countercurrent column operation. More than 300 column have been successfully equipped, mostly with proprietary structured or random packing types. The maximum column diameter was 5.6 m, the maximum bed height 22 m. Up to 6 beds in one column have been realized.

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