*Distillation Absorption 2010*
*A.B. de Haan, H. Kooijman and A. Górak (Editors)*

# THE D+R TRAY: NOVEL LABORATORY EQUIPMENT FOR STUDYING HETEROGENEOUSLY CATALYZED REACTIVE DISTILLATION – DESIGN AND SIMULATION-BASED VALIDATION

Erik von Harbou[1], Markus Schmitt[2], Sandra Parada[1], Christoph Grossmann[2], Hans Hasse[1]
[1] Laboratory of Engineering Thermodynamics, University of Kaiserslautern, 67663 Kaiserslautern, Germany, hans.hasse@mv.uni-kl.de
[2] Global Process Technology, BASF SE, 67056 Ludwigshafen, Germany, markus.schmitt@basf.com

**Abstract**
In this paper, novel equipment for laboratory studies of heterogeneously catalyzed reactive distillation is described. The so called D+R tray equipment consists of a combination of conventional bubble cap trays with sections that are filled with catalyst and through which the liquid flows when it passes from one distillation tray down to the next. It is designed so that the catalyst can be easily changed, and its amount can be flexibly chosen. These are important advantages compared to catalytic packings. In the present study, D+R tray equipment built in glass in the 50 mm diameter scale was investigated. In order to proof the general functionality of the D+R tray, the fluid dynamic capacity and the tray efficiency of the distillation section as well as the residence time distribution (RTD) of the reactive section were systematically investigated in a series of preliminary tests. Afterwards, the D+R trays were tested in a comprehensive series of reactive distillation experiments. For these experiments, two test systems were chosen that had been studied thoroughly in previous work in different scales with catalytic packings[1-2]. The most important process parameters such as feed rate and amount of catalyst were systematically varied. High conversions of the reactants and high purities of the products were achieved. The reproducibility of the results is excellent. That proves the general performance and operability of the D+R tray equipment. Process simulations were carried out using a stage-based model. The process model is based on carefully validated models of the physico-chemical properties of the test systems from previous works. The tray efficiency was not adjusted but taken from the independent measurements so that the simulations are predictive. The comparison with the experimental data shows good agreement. With the same model, HCRD experiments carried out in previous work on the same test systems with catalytic packings are well described. This shows that experiments carried out with D+R tray equipment can be used for studying designs of HCRD processes with either catalytic packings or trays.

**Keywords**: Reactive distillation, Trays, Fluid dynamics, Residence time distribution, Esterification

## 1. Introduction

During the conceptual design phase of a new chemical process, the possibility of using reactive distillation (RD) is often studied, as RD has many potential advantages compared to a conventional process consisting of a reactor followed by distillation[3,4]. Especially for reactions where the conversion is limited by chemical equilibrium, the application of RD can be beneficial. The in situ separation of the products forces the reaction into the direction of the products, which enhances the conversion compared to conventional reactors. Heterogeneously catalyzed RD (HCRD) has obvious advantages over the homogenously catalyzed process, such as the possibility to choose the position and size of the reactive zone in the column freely and the fact that the separation and recycling of the catalyst can be avoided.

State-of-the-art internals for HCRD are reactive packings like Sulzer's Katapak-SP® or bales, whereas reactive trays are rarely used, neither in the laboratory nor in the production. HCRD packings have the disadvantage that any change concerning the catalyst requires disassembling of the column and typically purchasing a new set of packings, which is not only costly but also time consuming. This is an important disadvantage, especially in laboratory studies in which process variants have to be tested. Using laboratory HCRD packings, typically neither the type of catalyst nor its amount are varied. Furthermore, it is well known that undesired flow characteristics, such as stagnant zones and bypassing, can occur in HCRD packings[5]. To overcome these problems, new equipment for laboratory studies of HCRD based on trays was developed by BASF SE[6]. It consists of a combination of conventional bubble cap trays with sections that are filled with catalyst and through which the liquid flows when it passes from one distillation tray down to the next. It is designed so that the catalyst can be easily changed, and its amount can be flexibly chosen. In the present work, it was slightly modified and characterized in terms of its fluid dynamic capacity as well as regarding its properties as a reactor. Furthermore, D+R trays were used in HCRD experiments for the production of *n*-hexyl acetate and for the production of *n*-butyl acetate. The presented set-up allows fast and flexible studies of HCRD processes in the laboratory scale.

## 2. Description

The basic unit of the new equipment is a conventional bubble cap tray combined with a reactive section below. It will be called D+R tray in the following. Typically, several of these D+R trays are arranged together in one module. The column is then normally assembled from several modules, eventually combined with non-reactive separation modules, which can be either of tray or of packed type.

The D+R tray for laboratory scale HCRD studies is depicted schematically in Fig. 1. It consists of two parts, namely a standard bubble cap distillation tray (I), and a catalyst bed reactor (reactive section) mounted below (II). In the column, the liquid coming from above flows through the downcomer (1) onto the distillation tray (I) (see solid arrows in Fig. 1). The downcomer (2) connects the distillation tray (I) and the inlet zone of the catalyst bed. From there, the liquid flows upwards through the catalyst. Two sieves (3) immobilize the catalyst in the bed. The catalyst bed (grey area) can be filled through the upper catalyst port (4) and it can be emptied through the lower catalyst port (5). The liquid leaves the reactive section in the upper part through the downcomer (6) to the next column section. The gas bypasses the reactive section and flows directly upwards through the gas chimney (7) from distillation tray to distillation tray (see dashed arrows in Fig. 1). Gas that possibly emerges from the reactive section is purged through the venting pipe (8) into the distillation tray above. The two ports (9) can be used for taking samples before and after the catalyst bed. Furthermore, the set-up is equipped with a temperature measurement (10). The D+R modules employed in the present work contain two D+R trays. They are built in glass in the 50 mm diameter scale.

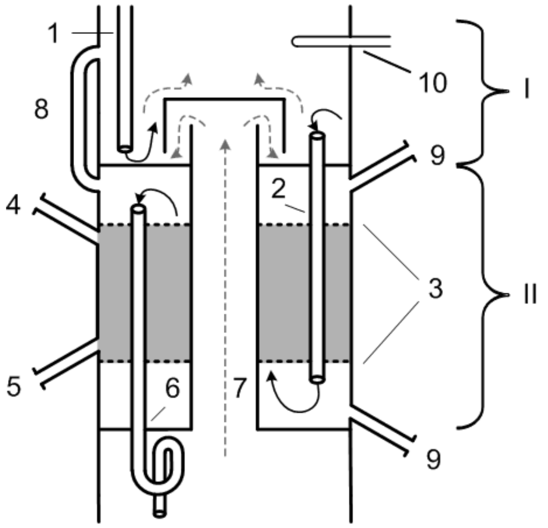

**Figure 1.** Schematic drawing of a D+R tray. (I) distillation section, (II) reactive section, (1), (2) downcomers, (3) sieves, (4) upper catalyst port, (5) lower catalyst port, (6) downcomer, (7) gas chimney, (8) venting pipe, (9) sampling ports, (10) temperature measurement. The grey area indicates the catalyst bed.

## 3. Preliminary test

Before the novel D+R tray was employed in HCRD experiments, it had been thoroughly tested. In order to characterize the distillation section of the D+R tray, the fluid dynamic capacity and the tray efficiency were determined experimentally.

The pressure drop of the D+R tray is only slightly greater at the same *F*-factor than that of a standard distillation tray alone. The D+R tray, however, allows a significantly higher fluid dynamic capacity. The operation of the D+R tray is stable up to an *F*-factor of 1.4 Pa$^{0.5}$ at 950 mbar. Using a standard distillation tray, flooding starts under these conditions earlier – at an *F*-factor of 1.0 Pa$^{0.5}$. This difference in the fluid dynamic capacity can be explained by the modified flow path. The downcomer (6) in Fig. 1 allows a significantly higher hydraulic height than a downcomer in a standard bubble cup tray. The tray efficiency, which was measured with a mixture of ethylbenzene and chlorobenzene under infinitive reflux at two different pressure levels (400 mbar and 950 mbar), lies in the range of 0.6. Fig. 2 shows the results of the measurements as well as a comparison with tray efficiency measurements of standard bubble cup trays. It can be seen that the D+R tray has a slightly higher tray efficiency than the standard distillation tray. This result concurs with the expectation as the significantly higher gas chimney in the D+R tray (see Fig. 1) reduces the liquid entrainment from the lower distillation tray to the upper distillation tray. Measurements of the tray efficiency at higher values of the *F*-factor are on the way.

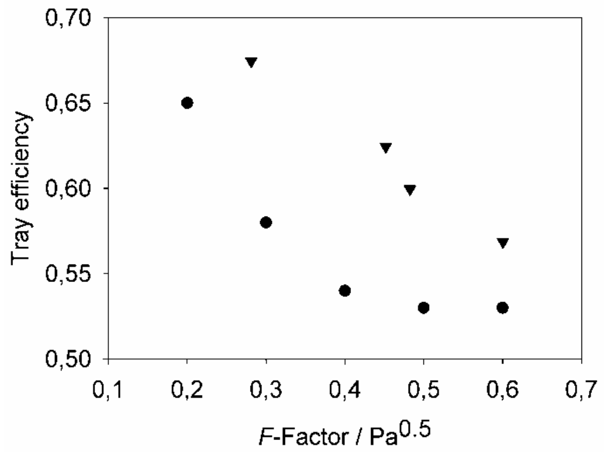

**Figure 2.** Tray efficiency as a function of the *F*-factor at 950 mbar:
▼ for D+R trays, ● for standard bubble cap trays.

An important goal in the development of the D+R tray was to obtain a uniform and well-defined flow through the catalyst. In order to confirm this, residence time distributions (RTD) of the reactive section were studied both experimentally and with CFD simulations showing that the flow through the catalyst bed in the D+R tray has basically plug flow characteristics. The primary experimental data and details on the CFD simulations are given by Schmitt et al[7].

## 3. HCRD experiments

HCRD experiments were carried out using the esterifications yielding *n*-butyl and *n*-hexyl acetate as test systems. The design of the experimental setup was chosen according to Schmitt et al.[1] for the production of *n*-hexyl acetate and Parada[2] for the production of *n*-butyl acetate. Fig. 3 depicts the setup of laboratory scale HCRD experiments for the production of *n*-hexyl acetate (left side of the figure) and for the production of *n*-butyl acetate (right side of the figure). The column comprises eight D+R trays in the reactive zone. The stripping zone contains non-reactive CY-packings (product of Sulzer Chemtech Ltd, Winterthur, Switzerland) as does the rectifying zone. The rectifying zone, however, is only employed for the production of *n*-butyl acetate. Furthermore, a decanter is used of which the aqueous phase is withdrawn as product while the organic phase is used as reflux. *n*-Hexyl acetate resp. *n*-butyl acetate is obtained as bottom product. In the present work, the strongly acidic ion-exchange resin Amberlyst CSP2 (Rohm and Haas) was used for catalysis of *n*-hexyl acetate whereas the acidic ion-exchange resin Amberlyst 46 (Rohm and Haas) was used for catalysis of *n*-butyl acetate.

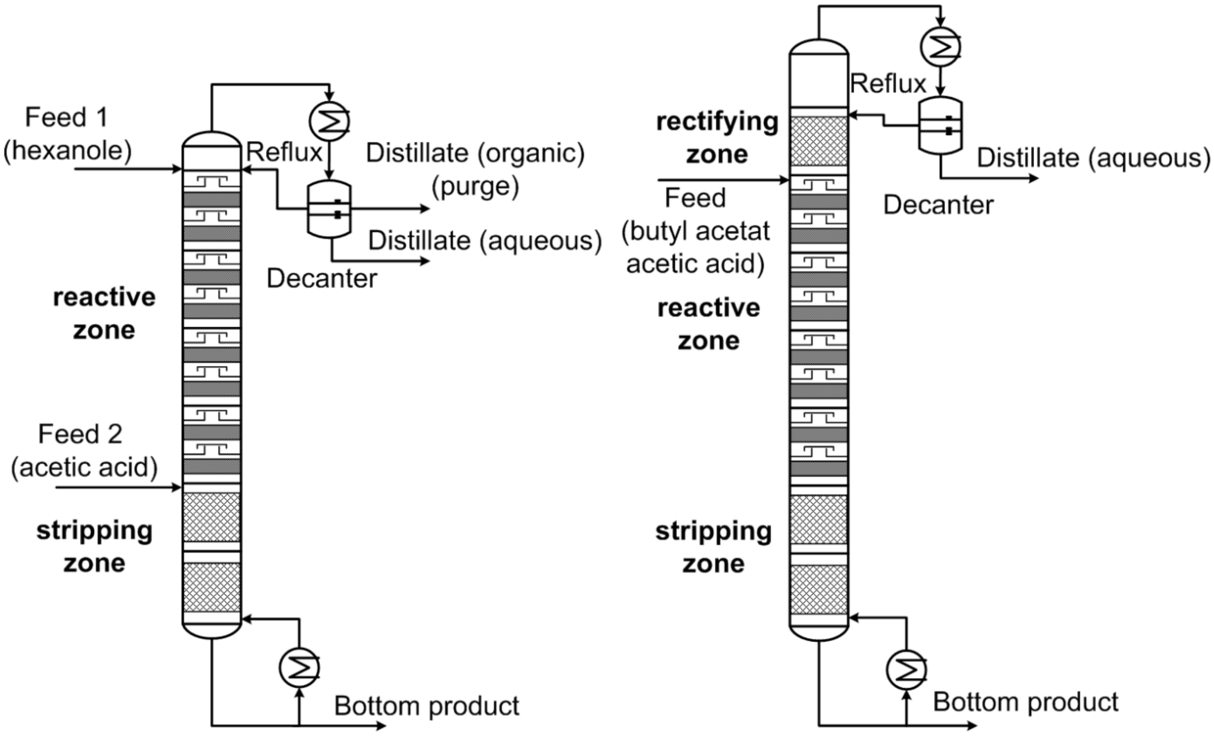

**Figure 3.** Setup of laboratory scale HCRD experiments for the production of *n*-hexyl acetate (left side) and for the production of *n*-butyl acetate (right side)

In total twelve experiments (six for the production of *n*-hexyl acetate and six for the production of *n*-butyl acetate) were carried out. The most important process parameters such as feed rate, feed composition, heat duty and amount of catalyst were varied systematically.

The reproducibility of the results is excellent. High conversions of the reactants and high purities of the products were achieved, which proves the general performance and operability of the D+R tray equipment. HCRD experiments for the production of *n*-butyl acetate carried out earlier with catalytic packings at the same feed to catalyst ratio yield conversions and purities of the products in the same range[2] (see Tab. 1).

**Table 1.** Comparison of HCRD experiments for the production of *n*-butyl acetate

| | Catalytic packings | D+R trays |
|---|---|---|
| Feed to catalyst (dry) ratio / g/(g h) | 11,5 | 11,0 |
| Acetic acid conversion rate / % | 93 | 94 |
| Product purity / Mass-% | 92,7 | 95,6 |

## 4. Simulation of the HCRD experiments

Process simulations were carried out with Chemasim (an in-house simulation tool of BASF SE, Germany) using a stage-based model for the distillation sections and a plug-flow reactor model for the reactive section. The process model is based on carefully validated models of the physico-chemical properties of the test systems from previous works[1,2]. The tray efficiency was not adjusted but taken from the independent measurements presented above. Hence, the simulations are predictive. Fig. 4

depicts a comparison of measured and simulated liquid phase concentration and temperature profiles of a HCRD experiments for the production of n-butyl acetate. Note that there are two values for the liquid phase concentration on each stage in the reactive zone. The first value (counted from the top of the column resp. from the direction of the liquid flow) is the concentration after the distillation tray and the second value is the concentration after the catalytic bed. Fig. 4 shows that the HCRD experiment using the D+R trays are well described by the employed models. With the same models, HCRD experiments carried out in previous work on the same test systems but with catalytic packings are well reproduced. This shows that experiments carried out with D+R tray equipment can be used for studying designs of HCRD processes with either catalytic packings or trays.

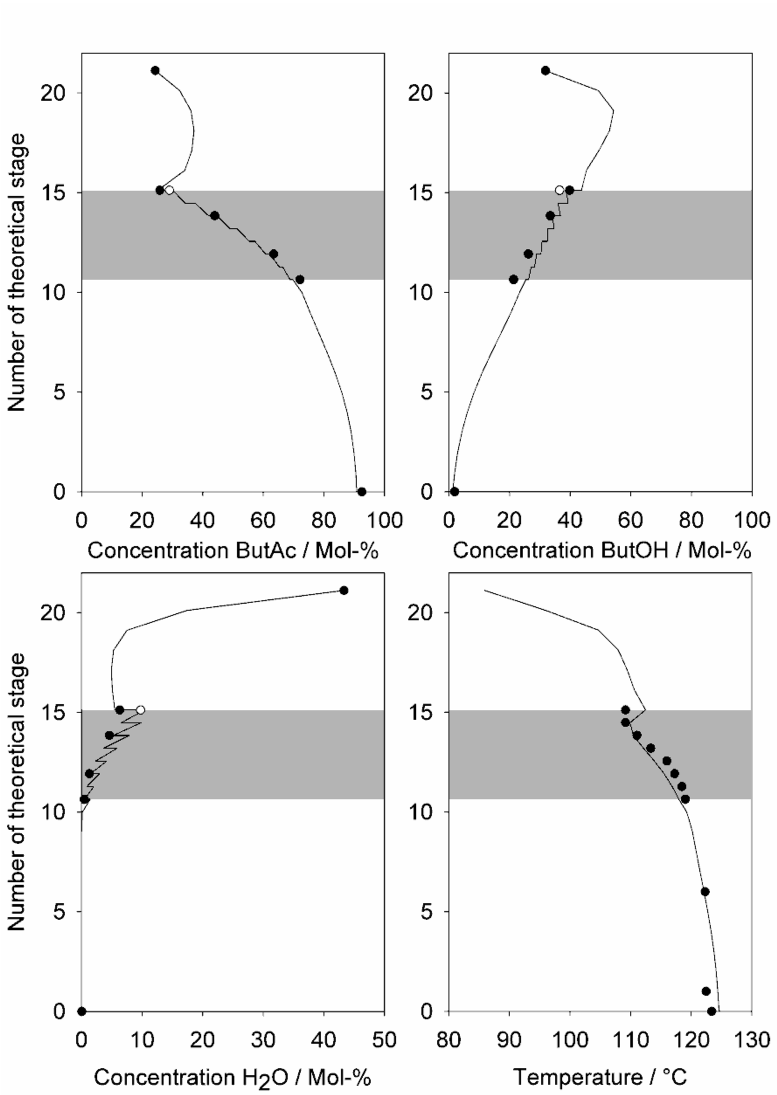

**Figure 4.** Liquid phase concentration and temperature profiles of a HCRD column equipped with D+R trays for the production of *n*-butyl acetate: comparison between experiments (● after the distillation section, ○ after the catalytic bed) and simulations (solid lines).

## 4. Conclusions

A new type of laboratory equipment for studying HCRD, the D+R tray, is presented. The D+R tray allows easy access to the catalyst, and, hence, facilitates variations of its type and mass. The pressure drop of the D+R tray at the same *F*-factor is only slightly greater than that of a standard distillation tray alone. The D+R tray, however, allows a significant higher fluid dynamic capacity. The tray efficiency lies in the range of 0.6. RTD experiments were carried out in order to test the fluid dynamic properties of the reactive section. From a comparison with CFD simulations it was found that the catalyst bed of the D+R tray can for practical purposes be regarded as a plug flow reactor. HCRD experiments were carried out using the esterifications yielding butyl and hexyl acetate as test systems. The reproducibility of the results is excellent. High conversions of the reactants and high purities of the products were achieved, which proves the general performance and operability of the D+R tray equipment. Predictive simulations of the HCRD experiments are in good agreement with the measured results. D+R trays allow fast and flexible studies of HCRD processes in the laboratory scale. They can be used for testing process models that allow designing not only HCRD processes with tray columns but also with catalytic packings. D+R trays, hence, provide a new, flexible and reliable way for obtaining the information needed for the design and scale-up of reactive distillation processes from laboratory experiments.

## References

1. M. Schmitt et al., *Chem. Eng. Process.*, 43 (2004) 397-409
2. S. Parada, *PhD thesis*, Universität Stuttgart (2009)
3. M.F. Doherty and G. Buzad, *Trans IchemE*, 70 (1992) 448–458
4. M.M. Sharma and S.M. Mahajani, in *Reactive Distillation* (eds. K. Sundmacher, A. Kienle), Wiley-VCH (2003)
5. P. Moritz and H. Hasse, *Chem. Eng. Sci.,* 54 (1999) 1367-1374
6. T. Adrian et al., *German Pat.* 19860598A1 (2000)
7. M. Schmitt et al., *Chem. Eng. Technol.,* 32 No. 9 (2009) 1313–1317