

METHYL ACETATE HYDROLYSIS IN A REACTIVE DIVIDED WALL COLUMN

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INTRODUCTION

One important target of the development of new processes is the reduction of energy and a reduced number of equipment compared to established processes. Developing such improved processes by process integration can successfully be carried out by combining unit operations in one apparatus. Well known integrated processes are Reactive Distillation (RD) that can be beneficial for both reaction and separation and the Divided Wall Column (DWC) which is used to carry out several distillation steps in one column. The combination of both Reactive Distillation and Divided Wall Column in one apparatus leads to the Reactive Divided Wall Column (RDWC). That novel concept is investigated in the European Project INSERT using the hydrolysis of Methyl Acetate as a test system. The examination consists of three parts. The first part is the simulation of the process using a model which was developed in the framework of INSERT. Mini plant experiments at BASF using a configuration which consists of four glass columns are the second part while the third part are pilot plant tests at Sulzer Chemtech, using an industrial scale Reactive Divided Wall Column in one column shell with a diameter of 220 mm.

INSERT

In the project INSERT 14 European companies and universities from 8 countries have been working together. The aim of the succession project of the project INTINT is to develop further steps for the Integration of SEparation and Reaction Technology. It is funded by the European Community, the Swiss Federal Office for Education and Science and the involved companies. The project is subdivided in a theoretical and an experimental part. The present paper reports on results from one out of six test systems studied in the experimental part.

METHYL ACETATE HYDROLYSIS

The synthesis of Methyl Acetate and the reverse reaction, the hydrolysis of Methyl Acetate are popular test systems for studies of Reactive Distillation [1, 2]. Compared to the conventional processes the number of columns is extremely reduced. In this presentation the hydrolysis of Methyl Acetate is studied which is important in the production of Polyvinyl Alcohol. The equilibrium of the reaction of Methyl Acetate with Water to Acetic Acid and Methanol lies on the side of the educts.



Using Reactive Distillation it is possible to increase conversion by continuously removing the products from the reaction zone. The products Methanol and Acetic Acid and remaining water are withdrawn from the Reactive Distillation Column as a bottom product and are separated in at least one further column.

A disadvantage of this Reactive Distillation Process is that the products and remaining water are not separated in this column and have long residence time in the sump of the column and the downstream piping. So the formation of Methyl Acetate as a back reaction will happen and it is not possible to produce Methanol free of Methyl Acetate.

By combining the Reactive Distillation Column and the following separation column in a Reactive Divided Wall Column with Methanol as a side product stream, the residence time of Methanol together with Acetic Acid and water in the sump is reduced to a minimum. Furthermore no piping is needed before the Methanol is separated from the water and the Acetic Acid and the number of needed columns is reduced also.

PROCESS SIMULATION

A proper simulation is the basis for the design of a Reactive Divided Wall Column. Standard simulation tools like Aspen or PRO/II can be used to simulate such columns. A typical flowsheet of such a simulation is presented in Figure 2. The Divided Wall

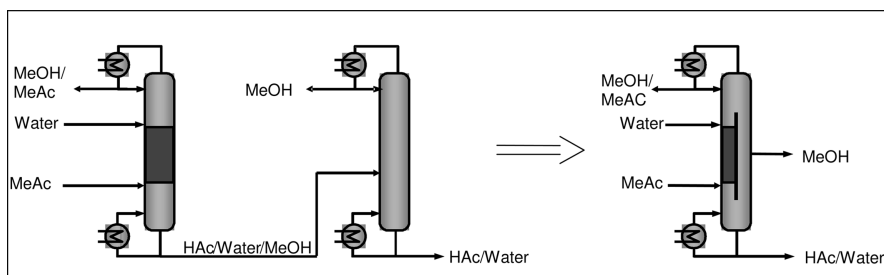


Figure 1. Principle of combining the reactive distillation column with the following separation column to form the reactive divided wall column (RDWC)

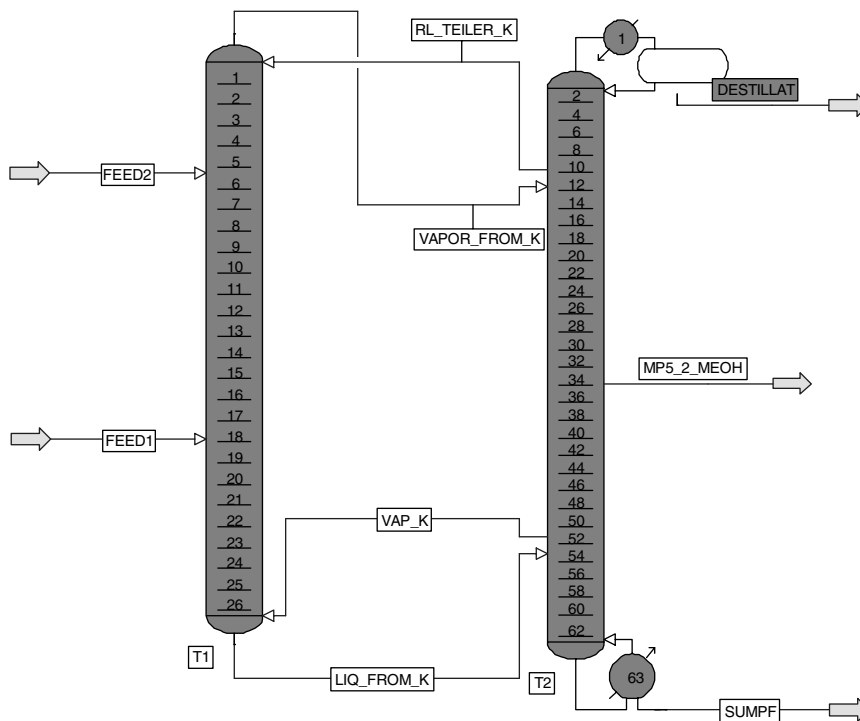


Figure 2. Flowsheet for the simulation of the reactive divided wall column

Section is simulated using two combined columns. The stages 6 to 17 of the left column are simulated as reactive stages in which the reactions, that means the hydrolysis of the Methyl Acetate and in some cases as back reaction the formation of Methyl Acetate from Methanol and Acetic Acid, takes place.

REACTION KINETICS

For the simulation of the process reaction kinetic data is needed. In the present work, Amberlyst 48 was used to catalyze the hydrolysis of Methyl Acetate. As data on kinetics of that reaction was not available in literature, it was measured at University of Stuttgart in a tubular fixed bed reactor. This reactor type is especially suited for such studies as discussed in [3]. Figure 3 shows the reactor. It consists of nine tubes with varying length (RR_01–RR_09) filled with the catalyst. The entire set-up is immersed in a thermostating bath. After each tube sampling points (X1 to X10) are installed. Experimental series at different temperatures and initial concentrations were carried out which cover the entire

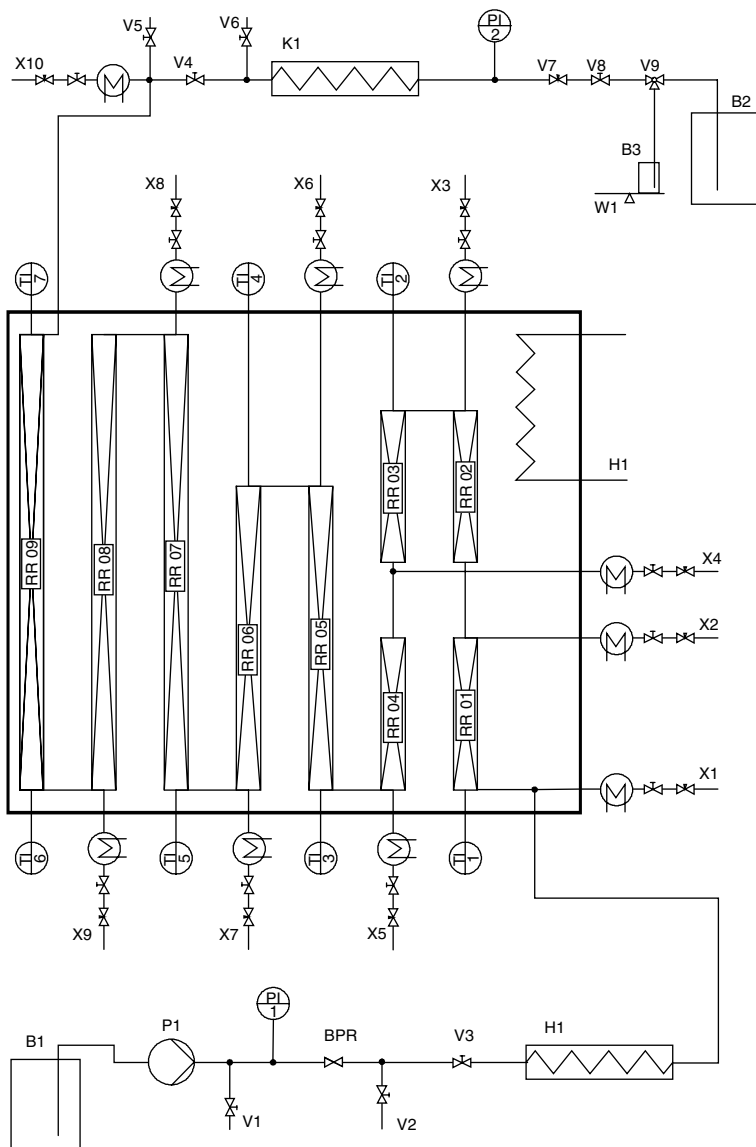


Figure 3. Tubular fixed bed reactor for measuring heterogeneously catalyzed reaction kinetics

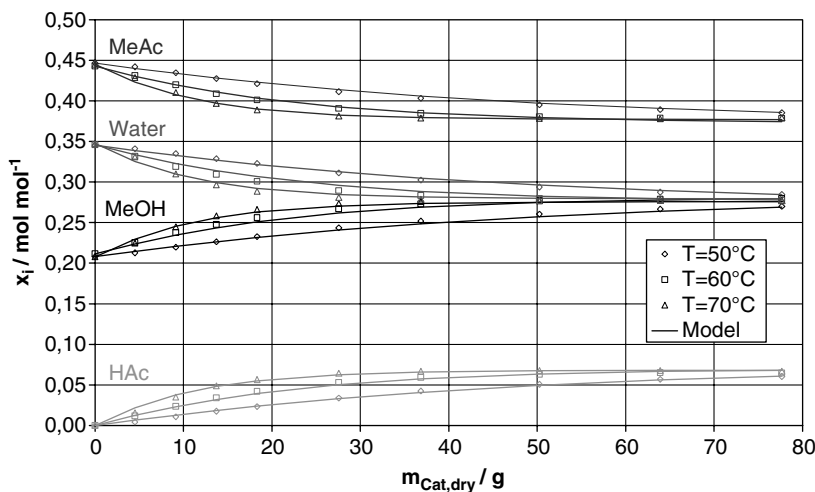


Figure 4. Comparison between reaction kinetic model and experimental data

range of conditions encountered in the reactive zone of the column. The experimental data was modelled with a pseudo-homogeneous second order reaction kinetic model based on activities and is thermodynamically consistent to the vapourliquid equilibrium model.

The latter is based on UNIQUAC with parameters found from literature data [4]. Correlations for the reaction kinetic constants were determined from a simultaneous fit to all available data sets.

In Figure 4 a comparison between model prediction and experimental data is shown for experiments with the same initial composition (45 mol% Methyl Acetate, 35 mol% Water and 20 mol% Methanol) but different temperatures. The pseudo-homogeneous model describes the kinetics experiments qualitatively good with relative errors below 3.5%.

MINI PLANT EXPERIMENTS

Based on the data obtained by simulation, a laboratory scale Reactive Dividing Wall Column was designed and installed in a miniplant laboratory at BASF. The schematic diagram of the bench-scale unit is shown in Figure 5. A four column system is used, representing the four sections of the dividing wall column: pre- and main column, rectifying and stripping section. The column segment representing the dividing wall part is realized by two independent columns in parallel. By mounting the plant in this way, different advantages for experimental studies can be achieved: better access to internal flows and measurement of liquid and vapour split ratio above and below the dividing wall.

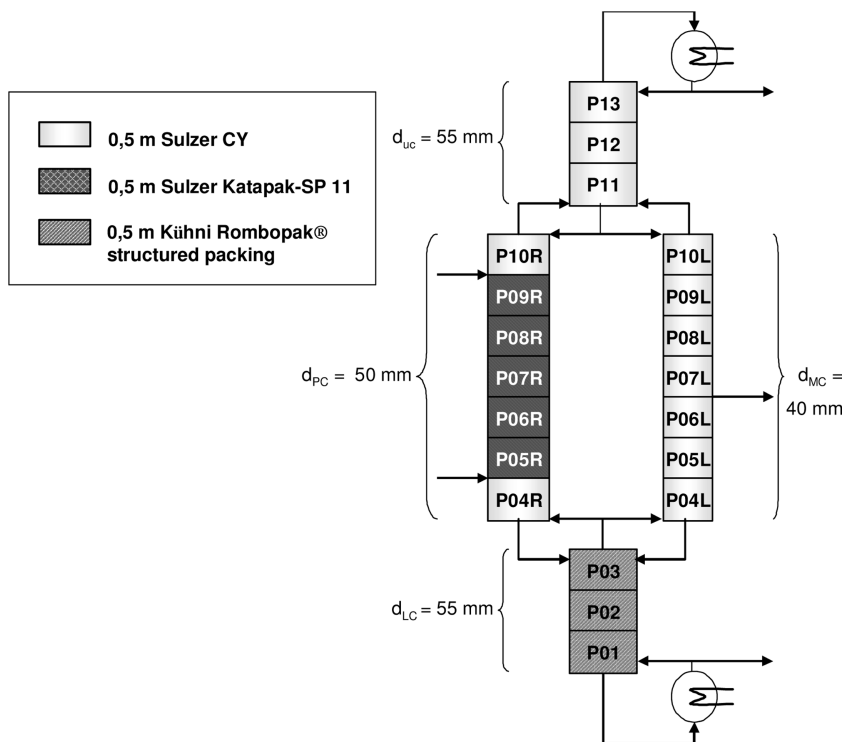


Figure 5. Schematic sketch of the lab-scale reactive divided wall column

The total packing height of the dividing wall column is about 6.5 m. The upper and lower columns are 1.5 m high each with a column diameter of 55 mm. Both parallel columns are 3.5 m high with internal diameters of 50 mm for the pre-column and 40 mm for the main column. This represents an asymmetric dividing wall column with transversal area relation of 61% to 39% (pre- to main column).

The non-reactive sections of the four column system are equipped with structured packing elements of type Sulzer CY or Kühni Rombopak, respectively. The reactive section contains Sulzer Katapak-SP 11 filled with Amberlyst 48 as catalyst.

RESULTS

A total of 23 successful experiments have been performed. For the experimental procedure, an azeotropic mixture of 81 wt.% Methyl Acetate (MeAc) and 19 wt.% Methanol (MeOH) was used as feed. Table 1 shows the results of the experiment which has been

Table 1. Main characteristics of the basis experiment

Stream		Flow rates	Composition
Feed	H ₂ O	590 g/hr	100% H ₂ O
	MeAc/MeOH mole ratio H ₂ O/MeAc = 3.0	1000 g/hr	81,0% MeAc 19,0% MeOH
Products	Distillate	485 g/hr	81,7% MeAc 18,3% MeOH
	Side Draw Product	262 g/hr	98,6% MeOH 1,3% MeAc 0,1% H ₂ O
	Bottom Product	804 g/hr	62,9% H ₂ O 37,1% HAc
Reflux		8000 g/hr	
Conversion	MeAc: 49,5%		

taken as the basis for several parameter studies (feed rate, reflux, molar ratio H₂O: MeAc and liquid split ratio).

INDUSTRIAL SCALE REACTIVE DIVIDED WALL COLUMN

Based on simulations with the previously described model and the results of the tests at BASF an industrial scale Reactive Divided Wall Column was set up and operated at Sulzer Chemtech in Winterthur. Figure 6 shows a sketch of the column. The used packing types are MellapakPlus 752.Y and Katapak-SP 11 filled with Amberlyst 48 as catalyst. The inner diameter of the column is 220 mm and the total height of the packing section including the collectors and distributors is approx. 14.3 m. The wall is placed in the middle of the column section. One of the main points in running such a Divided Wall Column is to ensure a proper distribution of the liquid and vapor to both sides of the divided column sections.

The liquid from the top bed is completely taken out of the column divided into two defined flows and fed back onto the divided sections of the column.

The gas will distributed across the two column sections, so the same pressure drop on both sides is resulting. During the column operation this distribution can only be influenced with a change of the liquid distribution to the column sections.

RESULTS

Several different tests were performed during two weeks of column operation in November 2005 and one week in March 2006. The main parameters which were examined in these tests were the distribution of the liquid between the two column sections, the feed rates and with this the loading in the column, the distillate rate and the feed composition.

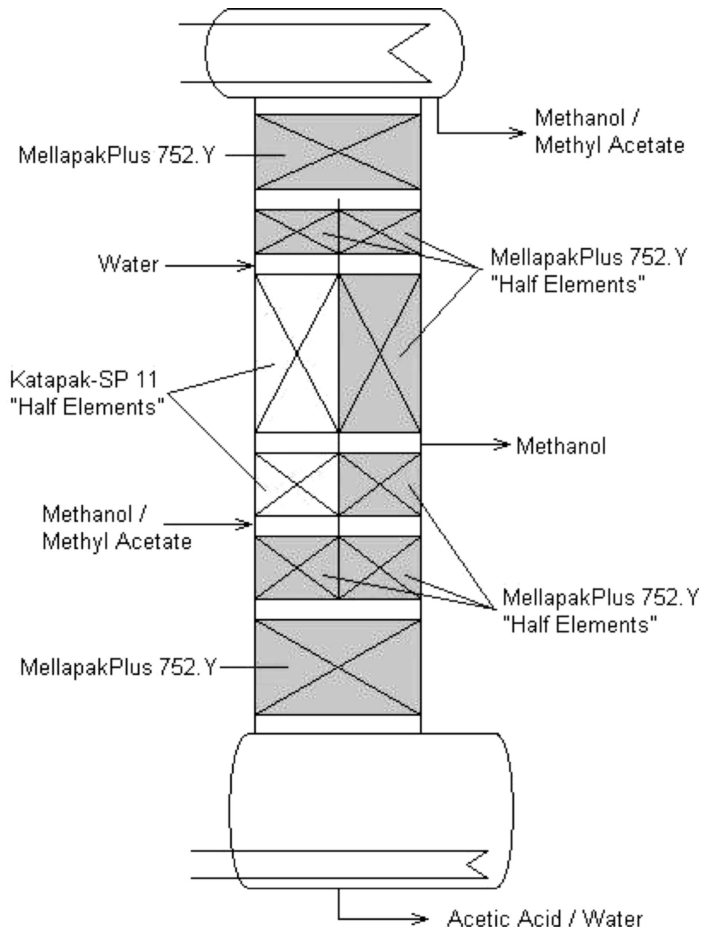


Figure 6. Sketch of the reactive divided wall column diameter: 220 mm; Total packing height: 11.74 m

The maximum Methanol purity in the side draw which was achieved during the tests was 92.1% while the maximum Methyl Acetate conversion was 82.2%.

A typical result of these tests is presented in Table 2 and Figure 7. In that experiment 79.1% of the Methyl Acetate in the feed was converted to Methanol. The main part of the unconverted Methyl Acetate was found in the side draw and led to a decreased Methanol purity. If a higher Methanol purity is desired this could be achieved by either reducing the Methyl Acetate feed or by increasing the distillate stream.

Table 2. Typical result from a pilot plant experiment

Stream		Flow Rate/kg/h	Composition/mass-%
Feed	Water	6.96	100 Water
	Methyl Acetate	6.59	99.3 MeAc
Products	Distillate	0.48	81.6 MeAc 18.2 MeOH
	Methanol	3.39	70.3 MeOH
	Side Draw Product		28.6 MeAc 1.0 Water
	Bottom Product	9.67	55.0 Water 45.0 HAC
Reflux		258.2	

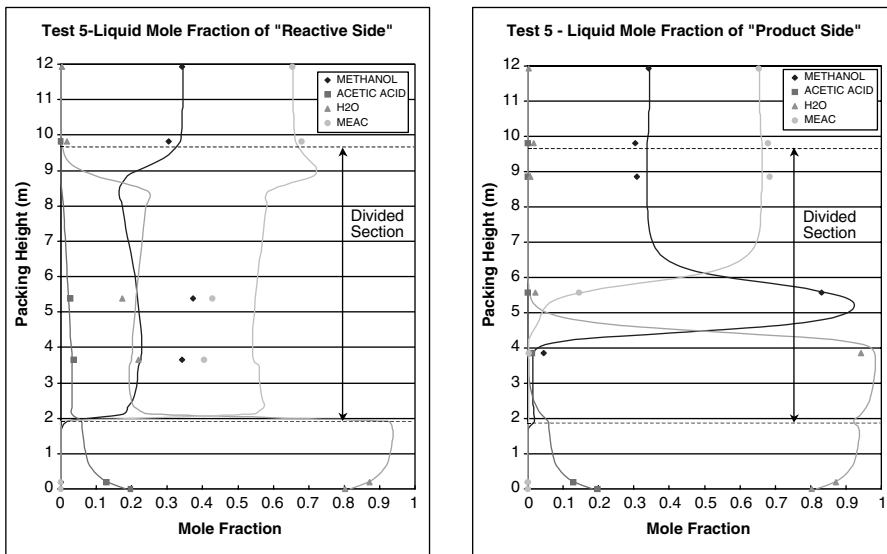


Figure 7. Comparison of experimental pilot plant data of a reactive divided wall column with model calculations. In both pictures concentration profiles from the bottom to the top of the column are shown. The sections in the middle differ: left: reactive section, right: non reactive section

The measured mole fractions of the components in comparison with the simulation are presented in Figure 7. The description of the behaviour for all non reactive parts, i.e. the not divided bottom and top section as well as the product section of the divided part is in good agreement with the measured values. The description of the behaviour in the reactive section shows bigger differences, the simulated Methyl Acetate concentration is too high while the Methanol concentration is too low.

Two reasons for this difference can be discussed. Firstly it is possible that conversion of the Methyl Acetate happens mainly in the upper part of the Katapak-SP 11 bed near the water feed or secondly the separation in the Katapak-SP 11 section is not described correctly by this simulation. A vapor sample was also taken but not shown in this figure. The sample nozzle for this vapor sample is in the upper third part of the Katapak-SP 11 bed. The measured mole fraction of Methyl Acetate was 0.709 while the calculated value is 0.712, so these values correspond very well to each other.

The simulated temperature profiles of each column section, which are presented in Figure 8, correspond very well to the measured values, even in the Katapak-SP 11 section where the bigger differences in the mole fractions arose. One bigger deviation is on the

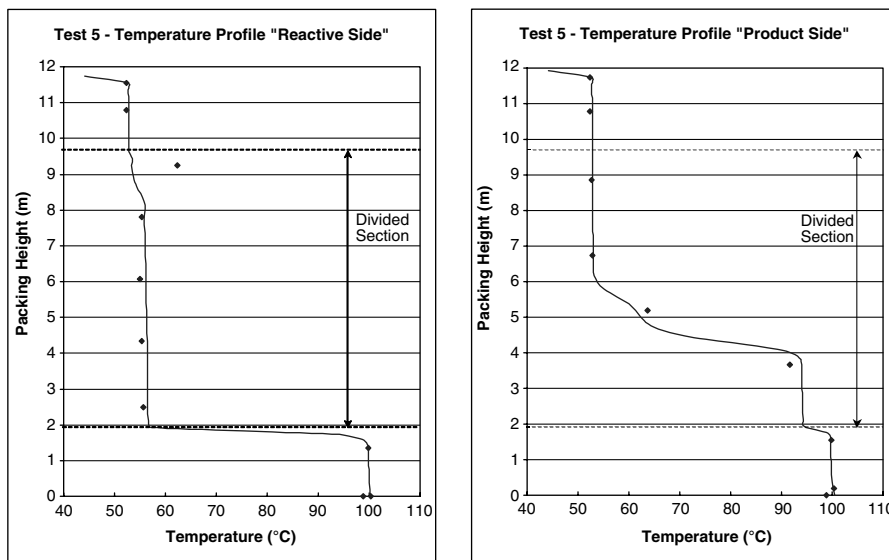


Figure 8. Comparison of experimental pilot plant data of a reactive divided wall column with model calculations. In both pictures temperature profiles from the bottom to the top of the column are shown. The sections in the middle differ: left: reactive section, right: non reactive section

Reactive Side, where the temperature measurement at 9.2 m packing height showed higher values than calculated.

SUMMARY AND CONCLUSION

The presented experimental results show that the operation of a Reactive Divided Wall Column is possible. Different possibilities to evaluate such a process were presented here: The use of a four column system in a laboratory scale allows determining a great number of different parameters. The operation of a Reactive Divided Wall Column in one column shell allows on the other hand to evaluate the behavior of the reaction and separation process as it would occur in an industrial scale column. Different process conditions like column loadings, feed conditions and liquid distribution over the two column sections were examined in both systems.

The results received so far, did not show the required Methanol purity and the wanted Methyl Acetate conversion but they are a good basis for further investigations in this field. The experimental results are in good correspondance to the simulated processes. So it can be expected that improvements achieved in a simulation will also be found in an industrial scale column.

With this Reactive Divided Wall Column a process alternative for the hydrolysis of Methyl Acetate is available, which leads to a further reduction of devices compared to the Reactive Distillation process and minimizes the back reactions of Methanol and Acetic Acid to Methyl Acetate.

The use of the Reactive Divided Wall Column is not limited to the hydrolysis of Methyl Acetate. It should be suitable for all processes in which the product of a Reactive Distillation is the intermediate boiling component.

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