

INVESTIGATION OF DIFFERENT COLUMN CONFIGURATIONS FOR THE ETHYL ACETATE SYNTHESIS VIA REACTIVE DISTILLATION

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ABSTRACT

The ethyl acetate synthesis via reactive distillation is studied theoretically and experimentally using different catalytic packings. Experiments are carried out in laboratory scale in a 50 mm diameter column, packing height of 3 m, and in semi-industrial scale in a 162 mm diameter column, packing height of 12 m. The experimental set-up is similar for both cases. The commercially available packings studied are Sulzer KATAPAK[®]-S and Montz MULTIPAK[®]-1.

Modelling is performed with a rate-based stage model. The simulation environment ASPEN Custom Modeler[™] is used for the implementation of the model equations. The results of rate-based simulations agree well with the corresponding experimental results. In addition, suitable operating conditions and the influence of the height of the catalytic section on conversion and product purity are investigated.

INTRODUCTION

Reactive distillation has been successfully used in several important industrial processes and its field of application is expanding. The design of reactive distillation processes still remains a challenge since it is difficult to obtain process models able to reliably describe the effects of simultaneous reaction and separation and to ensure a safe scale-up from laboratory experiments to industrial plants.

The use of solid catalysts in reactive separation processes has led to a new design of column internals on the basis of trays, random and structured packings. The internals for reactive separations have to enhance both separation and reaction and maintain a sound balance between them.

Therefore the choice of catalytic column internals as well as the placement of catalytic and non-catalytic zones in the column are crucial for the overall performance of the column.

This study deals with the heterogeneously catalysed esterification of ethanol and acetic acid to ethyl acetate and water by reactive distillation. Experiments are performed in two different scales, in a 50 mm and in a 162 mm diameter column. Rate-based modelling is applied for this system. The simulations are compared with experimental results. The influence of the height of the catalytic zone and of the catalytic column internals on the overall performance is investigated.

CATALYTIC COLUMN INTERNALS

The basic concept of reactive distillation has already been applied in the 1920's [1]. Nevertheless, the recent progress in modelling and simulation, as well as impressive examples realised in industrial practice, such as methyl acetate production via reactive distillation [2], have led to increasing interest in such processes.

The integration of both reaction and distillation in one apparatus can result in significant capital and operational cost savings, especially in the case of equilibrium limited reactions, such as esterifications and etherifications. Due to the continuous removal of products from the reaction zone both conversion and selectivity are increased. Another benefit is that for exothermal reactions the heat of reaction is directly used for the evaporation of liquid components and thus contributing to energy savings. Furthermore, in some cases reactive distillation can be applied for the separation of azeotropic or close boiling mixtures, like e.g. the separation of meta- and para-xylene [3]. However, reactive distillation is not suitable for extreme reaction conditions, such as reaction pressure far above 10 bar or temperature far above 400°C. Design and control of such processes remain - due to their complexity - challenging tasks.

In the past decade much of the research in this field has focused on the use of solid catalysts for reactive distillation. This process is known as catalytic distillation. No separation of the catalyst is necessary, if the solids are immobilised in packings, on trays or in form of a catalytic coatings, what is advantageous as compared to homogeneously catalysed reactive distillation. Some investigations have also been made on solid catalysts distributed as slurry on trays [4]. The use of immobilised catalyst facilitates the exact definition of reaction and separation zones. However, one of the major disadvantages of catalytic distillation is the catalyst renewal in case its deactivation is high, since the catalyst support has to be replaced or refilled with new catalyst. The positioning of catalyst containers in the downcomers and on trays has also been investigated [5, 6].

On the basis of structured and random packings two different techniques have been established. The first technique is the catalytic coating of packings [7, 8] or even the manufacturing from catalytically active material. The second method is the immobilisation of granular catalyst in bags as part of these internals. The advantages of granular catalyst is a better accessibility due to the larger surface compared to coatings of catalytically active material. Among these packings are catalytic bales [9],

tea bags, and structured packings such as Sulzer KATAPAK[®] and Montz MULTIPAK[®].

In this work two different types of packings have been selected for investigation, Sulzer KATAPAK[®]-S and Montz MULTIPAK[®]. Both packing types combine the benefits of modern structured packings, such as low pressure drop and high throughput and offer the advantages of heterogeneous catalysis.

Whereas for KATAPAK[®]-S the granular catalyst is embedded between two wire gauze sheets (Figure 1), MULTIPAK[®] consists of corrugated wire gauze sheets and catalyst bags made of the same material assembled in alternate (Figure 2).

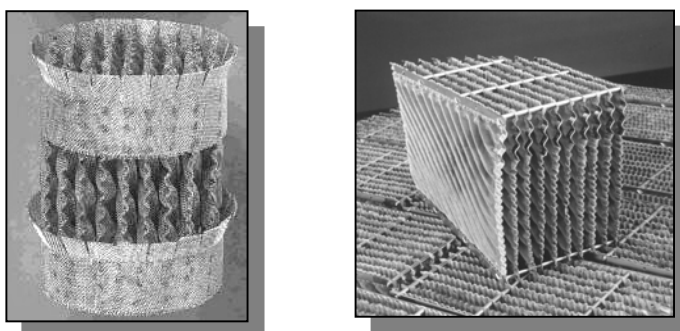


Figure 1: KATAPAK[®]-S laboratory packing (left), KATAPAK[®]-S 250.Y (right)

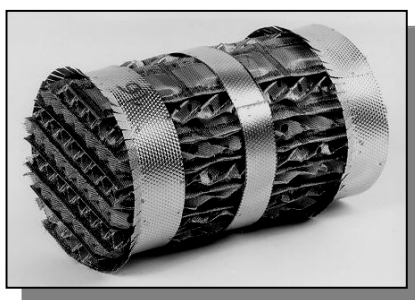


Figure 2: Catalytic packing MULTIPAK[®]

Compared to conventional non-reactive structured packings the specific surface area is moderate. Pressure drop is low for all three types of packings. Flooding occurs at F-factors of about 2 for moderate liquid loads. Details on the applied commercially available packings are shown in Table 1.

The construction of Montz MULTIPAK[®] enables high column loads via open channels for the vapour flow and sufficient mass transfer efficiency by a segmentation of the catalyst bags and numerous contact spots with the wire gauze sheets. The construction of laboratory-scale and technical-scale packings is very close in order to ensure a similar hydrodynamic behaviour. Experimental investigation of the synthesis of methyl acetate has proven its applicability for catalytic distillation [10].

Table 1: Geometric data of the applied catalytic packings

	Sulzer KATAPAK [®] -S Laboratory	Montz MULTIPAK [®] -1	Sulzer KATAPAK [®] -S 250.Y
Diameter [mm]	50	50	162
Height [mm]	100	166	210
Hydraulic diameter [mm]	6.4	9.5	22.5
Specific surface area [m ² /m ³]	270	317	125
Material	Wire gauze		
Wet catalyst content [kg/m]	0.25	0.29	3.20

The KATAPAK[®]-S construction benefits from large catalyst contents and, similar to MULTIPAK[®], high column loads due to the open channels for the vapour flow. The separation efficiency for the laboratory packing is considerably high, with NTSM (number of theoretical stages per meter) values of about 3, further increasing near the loading region [11]. However, separation efficiency is lower for the industrial type KATAPAK[®]-S 250.Y, because of the smaller specific surface area. Several authors have studied reactive distillation processes with KATAPAK[®]-S, with good results, among them the synthesis and hydrolysis of methyl acetate [12] and the formation of 2-methyl-propyl acetate [13].

MODELLING BASIS

Because of the complex interactions of both separation and reaction phenomena, the prediction of the overall performance of internals in reactive distillation columns is difficult. Therefore, in this work mathematical models have been developed and validated.

For the investigation of complex integrated separation processes like the synthesis of ethyl acetate via reactive distillation, reliable models are essential in order to reduce the development time and expensive experimental investigations.

Traditional equilibrium stage models and efficiency approaches are often inadequate for reactive separation processes. In multicomponent mixtures diffusion interactions can lead to unusual phenomena and it is even possible to observe mass transport of a component in the direction opposite to its own driving force - the so-called reverse diffusion [14]. For multicomponent systems, the stage efficiencies are different for different components and may range from $-\infty$ to $+\infty$. To avoid possible significant errors in the parameter estimation, it is necessary to take into account the actual mass and heat transfer rates and hydrodynamics [14, 15].

Therefore, in this work a more physically consistent way is used by which a direct account of process kinetics is realised. This approach for the description of a column segment or so-called stage is known as the rate-based approach [16]. The essence of this approach is that actual rates of multicomponent mass transport, heat transport

and chemical reactions are considered immediately in the equations governing the stage phenomena. Mass transfer at the vapour-liquid interface is described via the well known two-film model.

Multicomponent diffusion in the films is covered by the Maxwell-Stefan equations which can be derived from the kinetic theory of gases [17]. The influence of the process hydrodynamics is taken into account by applying correlations for mass transfer coefficients, specific contact area, liquid hold-up, residence time distribution and pressure drop. The two-film model concept has been extended by considering chemical reactions in the bulk phases and, if relevant, in the film regions. A sketch of the applied non-equilibrium stage model is shown in Figure 3. The necessary hydrodynamic correlations for the catalytic packings have been obtained experimentally in the context of the European research project INTINT (INTElligent Column INTernals for Reactive Separations).

The models described above are implemented into the simulation environment ASPEN Custom Modeler™ (ACM).

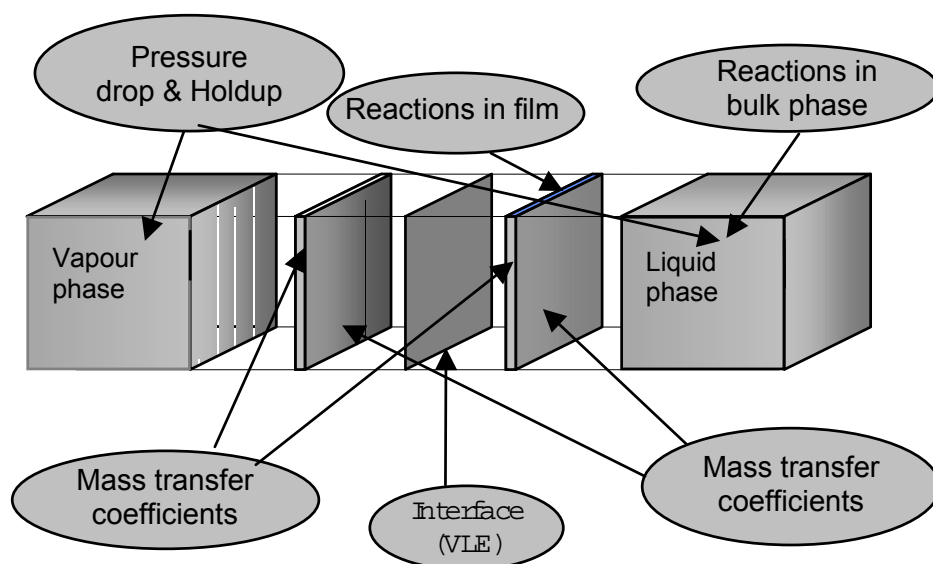


Figure 3: Sketch of an extended two-film model

Supplementary models have been developed for peripherals, such as reboiler, decanter, pre-reactor, heater and condenser. These models are linked in the simulation flowsheet of ACM. ASPEN physical properties database Properties Plus™ is connected with the models and allows comfortable changes of chemical systems as well as the implementation of measured properties data. Three different modelling depths have been implemented in ACM an extended equilibrium stage model, a rate-based model with effective diffusivities and and a rate-based model with the Maxwell-Stefan equations. The results presented in this paper have been obtained with the last model.

CHEMICAL SYSTEM

Ethyl acetate is a commodity chemical substance produced and used worldwide. It is primarily used as a solvent for paints and coatings (80 kt/yr, all numbers for Western Europe 1997), printing inks (65 kt/yr) and adhesives (36 kt/yr), as a process solvent (38 kt/yr), a chemical feedstock (15 kt/yr), and for cosmetics and food (12 kt/yr) [18]. Mainly two production processes for ethyl acetate are currently used [18, 19]:

- Esterification of ethanol and acetic acid in the presence of an acid catalyst, usually sulfuric acid (the main production method in Western Europe).
- Tishchenko reaction of acetaldehyde in the presence of an aluminum ethoxide catalyst (the main production method in Japan).

Recently, for synthesis of ethyl acetate heterogeneously catalyzed reactive distillation has been commercially applied. Kolena et al. [20] and Wu and Lin [21] both suggest the combination of a pre-reactor and a reactive distillation column to carry out the reaction. The only difference between the processes is the location of the pre-reacted feed to the reactive distillation column. The process of Kolena et al. [20] is nowadays commercialized by Sulzer Chemtech Ltd [22].

The boiling points of the pure components at atmospheric pressure are ranged as follows: ethyl acetate (EtAc) 77.2 °C; ethanol (EtOH) 78.3 °C; water (H₂O) 100.0 °C; acetic acid (HAc) 118.0 °C. There are three binary azeotropes and one ternary azeotrope shown in Table 2 with respective boiling points at atmospheric pressure. The normal boiling points for the pure components as well as the compositions of the azeotropes have been obtained from ASPEN Properties Plus™ and show satisfactory agreement with the data available elsewhere.

For a feasibility study, reactive distillation lines have been analysed by Kenig et al. [23]. Due to the presence of minimum boiling azeotropes, it is not possible to obtain high purity ethyl acetate at the top of the column, but a ternary mixture with non-converted ethanol and water as a by-product. A liquid-liquid phase separation at the top of the column allows a further enrichment of ethyl acetate.

Table 2: Calculated azeotropic data of the system

Azeotrope	wt%	wt%	wt%	T [°C]
EtOH-H ₂ O	95.7	4.3		78.2
EtOH-EtAc	29.7	70.3		71.8
EtAc-H ₂ O	91.0	9.0		71.5
EtOH-EtAc-H ₂ O	13.1	78.4	8.5	70.4

However after the decanter further separation steps are necessary in order to obtain pure ethyl acetate. The solubility of water in ethyl acetate at 25°C is about 3.0wt%; the solubility of ethyl acetate in water at 25°C is 9.9wt% [24].

REACTIVE DISTILLATION EXPERIMENTS

Experiments were carried out in two different columns. The first one is a laboratory scale column with 50 mm diameter and a total packing height of 3 meters whereas the second one is a semi-industrial scale column with 162 mm diameter and a packing height of about 12 meters. Both columns are operated at atmospheric pressure and are equipped with a liquid-liquid separator for the distillate stream.

Both column set-ups have a separation section below and above the catalytic section. The bottom section is used to separate acetic acid from the other components and the top section is mainly used to keep acetic acid in the reaction zone.

The laboratory scale experiments were performed in a 50 mm inner diameter glass column, with a silver lined vacuum jacket. The rectifying section consists of 1.0 m Sulzer DX packing. The catalytic section is equipped with 1.0 m either Sulzer KATAPAK[®]-S or Montz MULTIPAK[®]-1, filled with a commercial cation exchange resin. The stripping section consists of 1.0 m Sulzer BX packing. The basic set-up is shown in Figure 4.

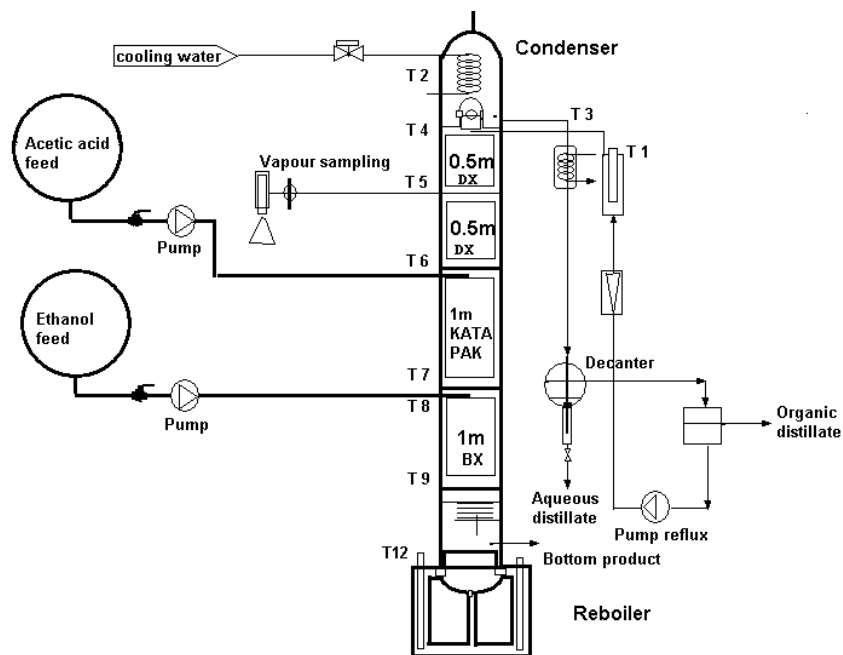


Figure 4: Column set-up of the laboratory column (50 mm diameter)

The temperatures in the column were measured using 6 glass jacketed Pt100 thermocouples. Besides, temperatures are measured in the condenser, reboiler, flow path from the condenser, and reflux flow path. The product from the condenser is introduced into a decanter (a separation funnel). In case of liquid-liquid phase separation, the aqueous phase is withdrawn completely. A part of the organic phase is fed back to the column as reflux. The acetic acid feed (in some experiments enriched with reaction products) is located between the rectification and catalytic sections. The ethanol feed is located between the catalytic and stripping sections.

The reactants are fed to the column at room temperature. Investigated operating conditions performed with KATAPAK[®]-S are represented in Table 3.

Table 3: Operating conditions of 50 mm diameter column with KATAPAK[®]-S

Experiment nr.	HAc flow [g/h]	EtOH flow [g/h]	Molar ratio HAc/EtOH [-]	reflux ratio [kg/kg]	D/F-ratio [kg/kg]	Qh [W]
1	516	197	2.01	6.65	0.50	560
2	396	306	1.00	5.57	0.65	640
3	395	298	1.02	6.24	0.57	566
4	396	303	1.02	5.57	0.65	505
5	396	303	1.00	5.63	0.64	470
6	397	306	1.00	3.98	0.64	375
7	477	355	1.03	4.16	0.76	690

For the column operation it is desirable to withdraw non-converted excess acid at the bottom in order to avoid an additional purification step. The stream can be recycled to the acetic acid feed. Therefore, in most experiments, an excess of acetic acid was fed to the column.

The compositions were determined using a HP 6890 gas chromatograph. The GC column was CP wax 52CB, ID 0.25 mm, length 25 m. Methyl-iso-butylketone was used as internal standard, and acetone was added to prevent phase separation. The temperature program of the GC was: 4 min. at 60 °C, then a constant increase of 20°/min until 150°C was reached. The water content of the samples was determined by Karl Fischer titration.

The 162 mm diameter semi-industrial column shown in Figure 5 has a set-up similar to the laboratory column. The rectifying section consists of 4.3 m and the stripping section of 3.1 m MELLAPAK[®] 500.Y. The catalytic section is equipped with 5.3 m KATAPAK[®]-S 250.Y, filled with the same commercial cation exchange resin. As in the case of the laboratory column acetic acid is fed above and ethanol below the reaction zone. Both liquid feeds are preheated to temperatures slightly below their boiling points. The semi-industrial column has about 7 sample locations along the column height where either liquid or vapour samples can be withdrawn.

Table 4: Pilot plant characteristics

	Set-up 1 (DSM Research)	Set-up 2 (Sulzer Chemtech)
Column diameter	50 mm	162 mm
Rectifying section	1.0 m (Sulzer DX)	4.3 m (MELLAPAK [®] 500.Y)
Reactive section	1.0 m (Sulzer KATAPAK [®] -S Laboratory) or 1.0 m (Montz MULTIPAK [®] -1)	5.3 m (KATAPAK [®] -S 250.Y)
Stripping section	1.0 m (Sulzer BX)	3.1 m (MELLAPAK [®] 500.Y)
Operating pressure	Atmospheric	Atmospheric
Insulation	Silver lined vacuum jacket	Heated jacket
Condenser type	Total condenser	Total condenser
Feed rate (total)	1-1.5 kg/h	40-50 kg/h
Sample points	1 (vapour)	4 (vapour), 3 (liquid)
Decanter operated at	20°C	40°C

The characteristics of the two column configurations are summarised in Table 4.

Though only for the laboratory column experimental results with KATAPAK[®]-S are available at the moment, theoretical studies on both column scales and on the influence of the different column internals for the laboratory scale set-up have been accomplished.

In addition to the pilot plant experiments and the determination of the hydrodynamic and mass transfer correlations for the applied catalytic packings, the reaction kinetics is determined. The kinetics is adjusted to a pseudo-homogeneous approach showing an exponent 1,5 dependence on the acetic acid concentration:

$$r_i = v_i \cdot (k_{fwd} \cdot x_{EtOH} \cdot x_{HAc}^{1,5} - k_{bwd} \cdot x_{H_2O} \cdot x_{EtAc}).$$

The equilibrium conversion and thus the maximum conversion in conventional reactors is about 63.8% at 30°C and decreases to 54.4% at 100°C, if the reactants are fed in equimolar composition.

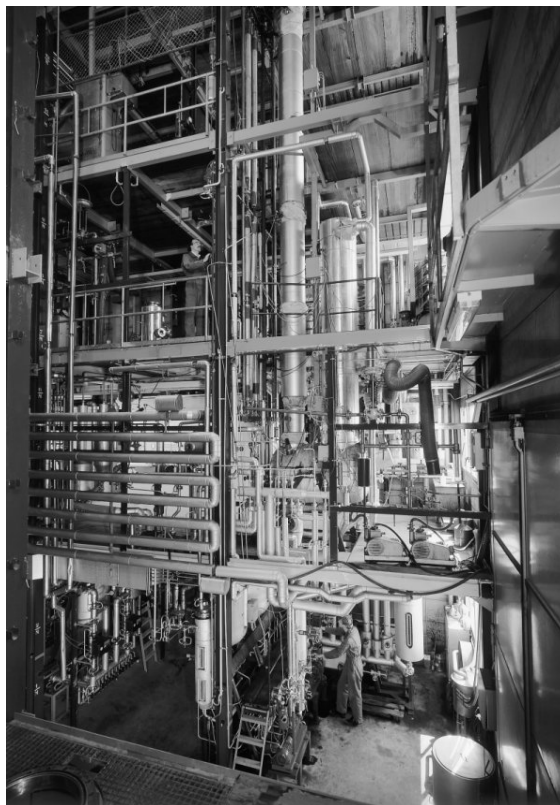


Figure 5: pilot plant set-up at Sulzer Chemtech (162 mm diameter)

EXPERIMENTAL AND THEORETICAL RESULTS

For the description of the vapour phase the Hayden O'Connell equation of state was used accounting for the non-idealities of this phase due to the dimerisation of acetic acid. The UNIQUAC method was used for the calculation of the activity coefficients.

The conversion in the column is limited by the catalyst amount installed, and thus by the height of the catalytic section. Experimental investigations show conversions of up to 64% for ethanol, summarised in Table 5. The concentrations of ethyl acetate in the distillate and acetic acid in the bottom stream are listed in Table 6. Except for experiment 6, the simulated and experimental results agree very well.

Table 5: Experimental and calculated conversion

Experiment nr.	X(HAc) [-]		deviation [%]	X(EtOH) [-]		deviation [%]
	experiment	simulation		experiment	simulation	
1	0.338	0.327	3.09	0.674	0.659	2.21
2	0.417	0.432	-3.51	0.411	0.429	-4.48
3	0.350	0.355	-1.38	0.361	0.361	0.05
4	0.548	0.526	4.01	0.544	0.528	2.93
5	0.537	0.528	1.50	0.551	0.530	3.67
6	0.546	0.564	-3.22	0.566	0.562	0.69
7	0.621	0.618	0.50	0.638	0.637	0.16

The thermodynamic description of the investigated system predicts the occurrence of miscibility gaps at low ethanol concentrations [24]. Since the ethanol conversion in the experiments 1-7 is not high enough, the occurrence of two liquid phases is not observed.

Although the water content in the ethanol feed will negatively influence the reaction rate, in order to achieve liquid-liquid separation, it is better to use 96wt% ethanol.

Table 6: Experimental and calculated composition of distillate and bottoms

Experiment nr.	distillate			bottoms		
	w(EtAc) [-]		deviation [%]	w(HAc) [-]		deviation [%]
	experiment	simulation		experiment	simulation	
1	0.683	0.687	0.08	0.999	0.983	1.61
2	0.505	0.535	6.85	0.999	0.965	3.40
3	0.491	0.500	4.34	0.901	0.903	-0.22
4	0.665	0.662	1.60	0.795	0.792	0.42
5	0.669	0.672	3.92	0.781	0.771	1.31
6	0.679	0.702	11.69	0.783	0.736	6.03
7	0.659	0.667	3.63	1.000	0.986	1.36

The lowest conversion was achieved in experiment 3 (Table 5). The simulations are able to mirror this behaviour, whereas the analysis of the concentration profiles reveals that water significantly accumulates in the reactive section and thus promotes the reverse reaction. By further increasing the distillate-to-feed ratio (Table 3) water is forced to the top of the column and acetic acid accumulates in the reactive section and significantly increases the reaction rate, because of the exponent 1.5 dependence shown in reaction equation. The conversion increases accordingly.

In Figure 6 the measured and calculated temperature profiles are compared for the conditions of experiment 7 (Table 3).

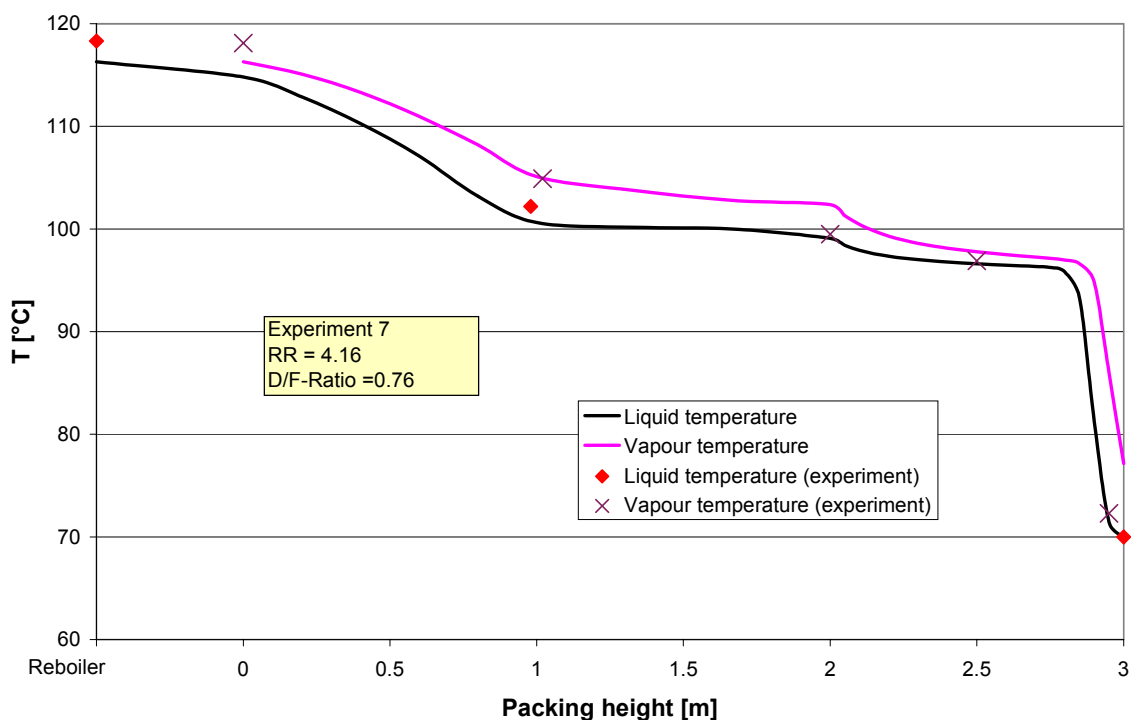


Figure 6: Temperature profiles in laboratory column: lines – calculations, points – experiment

The agreement between experimental and theoretical results is very good. Small differences in the vapour phase temperature probably result from the arrangement of the thermocouples and occasional contact with the liquid phase.

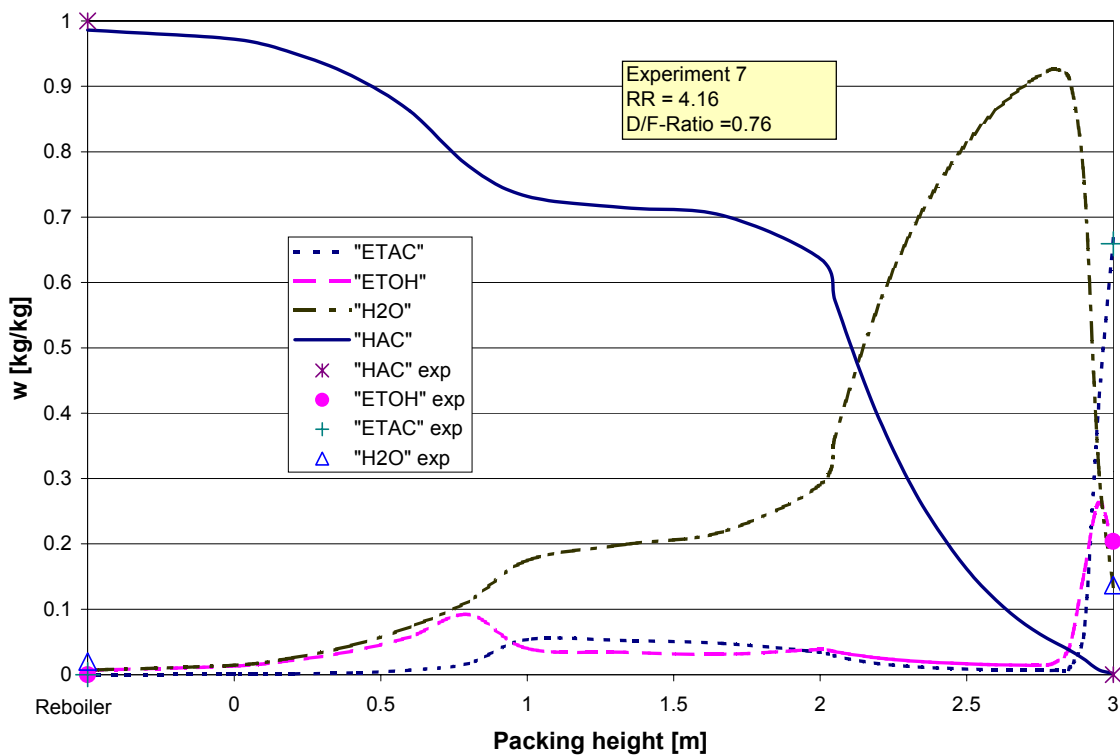


Figure 7: Liquid phase concentrations in laboratory column: lines – calculations, points – experiment

The liquid phase concentration profiles in Figure 7 correspond to the temperature profiles in Figure 6. The concentration profiles show a rather high concentration of acetic acid in the reaction zone and thus improved conversion compared to other experiments.

Simulations have also been carried out for 1 m Montz MULTIPAK[®]-1 instead of Sulzer KATAPAK[®]-S. For the new column configuration the total catalyst mass is about 16% higher. Since the separation efficiency of both packings is similar the differences in performance are low. For the conditions of experiment 7 (Table 3), the conversion increases only by 0.25%. The increase in product purity is about the same.

The influence of the height of the catalytic zone on conversion and product purity is investigated. If the height of the catalytic zone is doubled and 2 m of KATAPAK[®]-S are used, for operating conditions similar to experiment 7, the conversion increases only about 2.5%. The moderate increase in conversion for this case can be explained by an analysis of the corresponding concentration profiles, since not in every part of the enhanced catalytic section the reactant concentration is as high as in case of 1 m KATAPAK[®]-S shown in Figure 7. For a total feed rate of 0.83 kg/h, a molar ratio acetic acid to ethanol of 1.03 and reflux ratio of 4.16 the highest conversion is obtained at very high D/F-ratios. These simulations are performed without liquid-liquid phase separation.

Table 7: Maximum conversion and product purity for different heights of the catalytic zone

Catalytic zone	D/F-ratio [kg/kg] / Qh [W]	Conversion EtOH/HAc [-]	Distillate w(EtAc) [-]	Bottoms w(HAc) [-]
1 m KATAPAK [®] -S	0.913 / 790	0.848 / 0.822	0.757	0.996
2 m KATAPAK [®] -S	0.971 / 830	0.947 / 0.917	0.795	0.997
2 m KATAPAK [®] -S	0.993 / 850	0.954 / 0.925	0.783	0.997

For one meter catalytic packing the maximum in conversion and the maximum product purity are obtained at the same operating conditions, while for two meters catalytic packing the product purity decreases though conversion is still increasing with higher distillate-to-feed ratio until the maximum conversion of 95.4% for ethanol is reached. The reason of this phenomenon is that non-converted acetic acid is forced to the top of the column in small amounts. By a slight further increase of the catalytic zone total conversion of ethanol can be achieved for the selected operating conditions. Once the ethanol conversion is sufficiently high and thus the ethanol concentration in the distillate is small, liquid-liquid phase separation of the distillate stream is possible.

The influence of the liquid-liquid separation on the product purity is shown for the semi-industrial column. For the simulation results presented in Figure 8, the following operating conditions were used: the total feed rate is 51.4 kg/h and the molar feed ratio of acetic acid/ethanol 1.12. The water content in the ethanol feed is 4wt%. The distillate-to-feed ratio is 0.95 and the reflux ratio is 2.4.

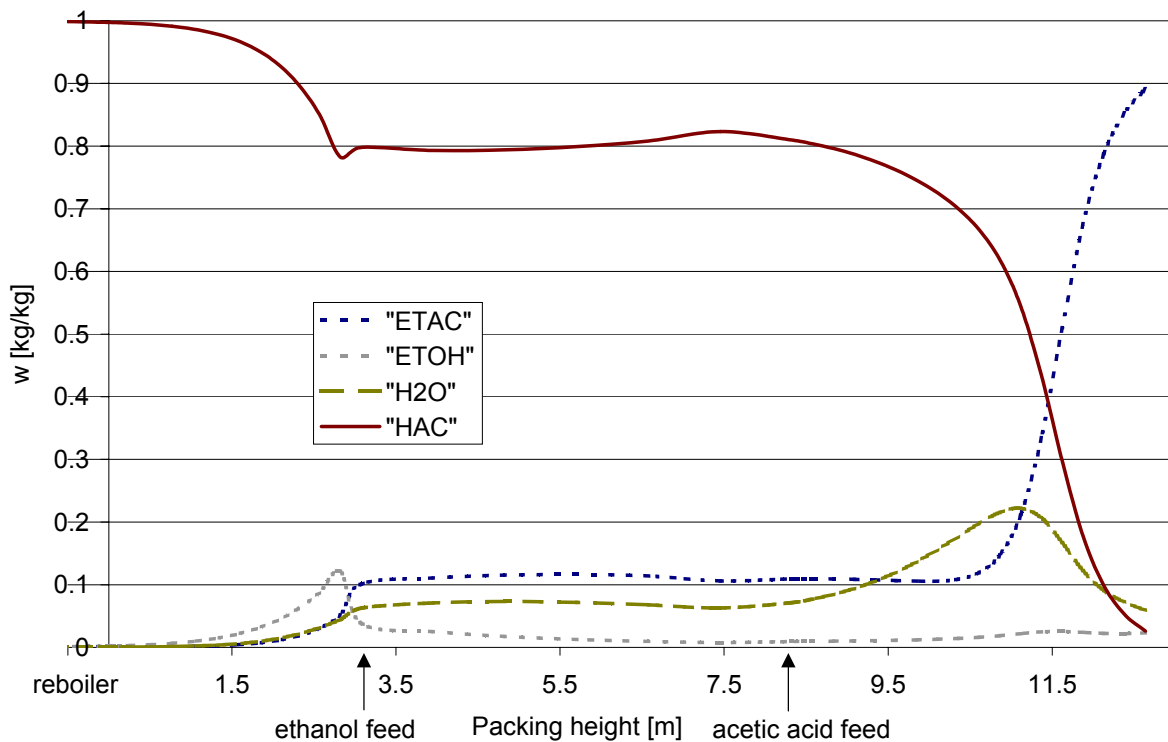


Figure 8: Liquid phase concentration profiles (semi-industrial column) with decanter

As shown in Figure 8 highly pure acetic acid is withdrawn at the bottom of the column. The acetic acid concentration in the catalytic zone between the two feeds is very high thus enhancing the reaction rate. The concentration at the top of the column is the concentration of the organic phase reflux.

The condensate fed to the decanter has a composition of about 85wt% ethyl acetate. The product is enriched in the organic phase to more than 89wt%, however there is still about 10wt% of ethyl acetate in the aqueous distillate.

The flow rate of the aqueous distillate is low with about 7.5 kg/h, whereas 41 kg/h organic distillate is withdrawn. In the discussed case the conversion of ethanol exceeds 99.9% while the conversion of acetic acid is about 90.6%.

CONCLUSIONS

In this work, the synthesis of ethyl acetate by heterogeneously catalysed reactive distillation is investigated. Since the choice of column internals and arrangement of catalytic and non-catalytic zones have significant influence on the overall performance, different configurations are experimentally and theoretically investigated. Modelling of this process is accomplished with a rate-based stage model.

Experiments are performed in two different scales, in a 50 mm and in a 162 mm diameter column with two different catalytic internals. The simulations are in a very good agreement with the results obtained in several laboratory scale experiments with KATAPAK[®]-S. The models are able to describe the process behaviour in an entire range of operating conditions and result in a better understanding of the process.

Theoretical investigations show that the performance of KATAPAK[®]-S and MULTIPAK[®]-1 is very similar in laboratory scale. The simulations are further applied for investigations of the scale-up from the laboratory to the semi-industrial set-up.

The production of ethyl acetate via reactive distillation can significantly increase conversion as compared to conventional reactors. Total conversion of ethanol can be obtained with moderate column heights and without using a pre-reactor. An excess of acetic acid is necessary to achieve complete conversion of ethanol and therefore almost ethanol-free top product. Furthermore, a high acetic acid concentration in the catalytic section of the column increases the reaction rate.

ACKNOWLEDGMENTS

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NOMENCLATURE

<i>D/F-ratio</i>	distillate to feed ratio	kg/kg
<i>k</i>	reaction rate constant	mol/kg s
<i>NTSM</i>	number of theoretical stages per meter	1/m
<i>Q_h</i>	reboiler heat duty (neglect of heat losses)	W
<i>T</i>	Temperature	°C
<i>r_i</i>	reaction rate of component <i>i</i>	mol/kg s
<i>w</i>	mass fraction	kg/kg
<i>x</i>	mole fraction	mol/mol
<i>X</i>	conversion	
<i>v_i</i>	stoichiometric coefficient of component <i>i</i>	

Subscripts

EtOH	Ethanol
EtAc	Ethyl acetate
HAc	Acetic acid
H ₂ O	Water
bwd	backward reaction

eff	effective
fwd	forward reaction
sim	Simulation

REFERENCES

1. Backhaus, A.A. (1921), Continuous processes for the manufacture of esters, US Pat., No. 1400849
2. Agreda, V.H., P.H. Partin, and W.H. Heise (1990), High Purity Methyl Acetate Via Reactive Distillation, Chem. Eng. Prog., 86(2), 40-46.
3. Saito, S., T. Michishita, and S. Maeda (1971), Separation of Meta- and Para-Xylene Mixture by Distillation Accompanied by Chemical Reactions, Journal of Chemical Engineering of Japan, 4(1), 37-43.
4. Linang, W., Z. Wang, Y. Jin, Z. Yu, and S. Yang (1996), Performance of a Three-Phase Fluidized Bed as a Reactive Distillation Device, Chem. Eng. Technol., 19, 456-461.
5. Carland, R.J. (1994), Fractionation Tray for Catalytic Distillation, US Pat., No. 5308451
6. van Baten, J.M., J. Ellenberger, and R. Krishna (2001), Hydrodynamics of Reactive Distillation Tray Column With Catalyst Containing Envelopes: Experiments vs. CFD Simulations, Catalysis Today, 66, 233-240.
7. Kunz, U. and U. Hoffmann (1995), Preparation of Catalytic Polymer/Ceramic Ionexchange Packings for Reactive Distillation Columns, in Preparation of Catalysts VI, G. Poncet, Editor. Elsevier Science B.V., 299-308.
8. Lebens, P.J.M., F. Kapteijn, S.T. Sie, and J.A. Moulijn (1999), Potentials of Internally Finned Monoliths as a Packing for Multifunctional Reactors, Chemical Engineering Science, 54, 1359-1365.
9. Johnson, K.H. and A.B. Dallas (1994), Catalytic Distillation Structure, US Pat., No. 5348710
10. Górak, A. and A. Hoffmann (2001), Catalytic Distillation in Structured Packings: Methyl Acetate Synthesis, AIChE Journal, 47(5), 1067-1076.
11. Moritz, P. and H. Hasse (1999), Fluid Dynamics in Reative Distillation Packing Katapak-S, Chemical Engineering Science, 54, 1367-1374.
12. Moritz, P., S. Blagov, and H. Hasse (2001), Reactive Distillation Process Design and Scale-Up. Proceedings Separations Technology Topical Conference, AIChE Annual Meeting 2001, 2, 906-913.

13. Hanika, J., Q. Smejka, and J. Kolena (2001), 2-Methylpropylacetate Synthesis via Catalytic Distillation, *Catalysis Today*, 66, 219-223.
14. Taylor, R. and R. Krishna (1993), *Multicomponent Mass Transfer*, New York: John Wiley and Sons, Inc.
15. Kenig, E. and A. Górak (1995), A Film Model-Based Approach for Simulation of Multicomponent Reactive Separation, *Chem. Eng. Process.*, 34(2), 97-103.
16. Seader, J.D. (1989), The rate-based approach for modeling staged separations, *Chemical Engineering Progress*, 85, 41-49.
17. Hirschfelder, J.O., C.F. Curtiss, and R.B. Bird (1964), *Molecular Theory of Gases and Liquids*, New York: Wiley.
18. SRI (1999), *Chemical Economics Handbook*: SRI International.
19. Ullmann, F. (2001), *Encyclopedia of Industrial Chemistry*. sixth edition ed. Electronic Release.
20. Kolena, J., J. Lederer, P. Moravek, J. Hanika, Q. Smejkal, and D. Skala (1999), Zpusob vyroby etylacetatu a zarizeni k provadeni tohoto zpusobu (Process for the production of ethyl acetate and apparatus for performing the process), *Czech Pat.*, No. Cz PV 3635-99
21. Wu, K.-C. and C.-T. Lin (1999), Catalytic processes for the preparation of acetic esters, *U.S. Pat.*, No. 5,998,658
22. Moritz, P. (2002), Product Information "Ethyl Acetate Production by Reactive Distillation", in *Brochure of Sulzer Chemtech Ltd.*
23. Kenig, E.Y., H. Bäder, A. Górak, B. Beßling, T. Adrian , and H. Schoenmakers (2001), Investigation of ethyl acetate reactive distillation process, *Chemical Engineering Science*, 56, 6185-6193.
24. Arce, A., L. Alonso, and I. Vidal (1999), Liquid-Liquid Equilibria of the Systems Ethyl Acetate + Ethanol + Water, Butyl Acetate + Ethanol + Water, and Ethyl Acetate + Butyl Acetate + Water, *Journal of Chemical Engineering of Japan*, 32(4), 440-444.