Ethyl acetate synthesis by coupling of fixed-bed reactor and reactive distillation column—Process integration aspects

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ABSTRACT

Coupling of a fixed-bed reactor and a reactive distillation column was used for acetic acid and ethanol esterification utilizing strong acidic ion-exchange resin as catalyst. Laboratory experiments were focussed on the investigation of catalyst loading effect on reaction conversion in a fixed-bed reactor at the temperature interval between 60 and 120 °C with partial separation of products in the form of their azeotropic mixture by the flash distillation. This procedure increased the reaction conversion above chemical equilibrium. The experimental results achieved with a reactive distillation column of the overall efficiency of 14 theoretical stages (1 reaction stage) were successfully compared with numerical simulation by means of AspenPlus software.

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1. Introduction

The esterification of acetic acid (AA) and ethanol (EtOH) is in principle well known and industrially verified process. Ethyl acetate is mainly used as solvent in paints and coatings industry, inks production and as industrial solvent in many other branches of industry. Worldwide supply of ethyl acetate represented 1.3 mil tonne in 2005. During last decade this demand kept slightly increasing in a rate of 4% per year.

The most common strategy of producing ethyl acetate consists in a simple esterification of ethanol with acetic acid in the presence of acidic catalyst. The reaction conversion is limited by chemical equilibrium. The mixture of products and unreacted starting components should be separated and raw ethyl acetate (EtAc) should be purified. The separation is complicated because of the formation of heterogeneous azeotrope, which contains less water in comparison to the water produced by chemical reaction. Therefore part of the reaction water is to be separated together with non-reacted acetic acid as bottom product. In general, the purification of raw EtAc/EtOH/water mixture is very expensive and environmental unfriendly. In a process, where only equilibrium conversion of reactants can be achieved, an energy demanding separation process has to be incorporated. It is also necessary to recycle big quantities of unreacted starting components. Thus, an integrated esterification process with selective separation of ethyl acetate is desirable.

Reactive distillation, which combines chemical reaction and efficient purification, can be a process of this kind. Besides all, it represents an environmental friendly way of the alkylacetates production and can be a solution of the problems specified above [1]. Chemical reaction is carried out in a reaction zone of a rectification column. So the products are distilled out from the reaction zone, and the chemical equilibrium of the reaction is thus shifted towards products.

The main advantages of reactive distillation consist in:

- Simpler technology with minimum separation units.
- Integration of chemical reaction with product separation in a multifunctional unit.
- Direct utilization of reaction heat for reaction mixture distillation just inside reaction zone resulting in energy saving.

The reaction zone of the column is most frequently packed with a structured, oriented wire mash packing, which is filled inside by heterogeneous catalyst. The oriented structure combines the role of catalyst with the role of distillation internal. The only disadvantage of these structures is high price and strict requirement for long thermal stability of the catalyst activity. Although it is possible to feed starting components directly to the reactive distillation column, it is often advantageous to use a primary reactor in combination with a reactive distillation column. Starting components are converted to chemical equilibrium, the reaction is then finished in the reactive

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distillation column. The increase of productivity is a usual effect of the primary reactor [2]. This reactor can also take part as "guard reactor", preventing expensive catalytic packing in the reactive distillation column from being poisoned by basic impurities possibly present in the feed. Most frequently, a fixed-bed or a trickle-bed reactor is used for this purpose [3]. In case of esterification, the equilibrium mixture from the primary one pass reactor is introduced into the reaction zone of the reactive distillation column. Reaction water is simultaneously distilled out from the catalytic packing in the reaction zone, the forward esterification reaction being thus speeded up. If higher esters (e.g. butyl acetate or 2-methyl-propyl acetate) are prepared, the separation of the whole amount of the reaction water in distillate is possible, so high-purity ester can be withdrawn as a bottom product. This is a big advantage of the process [4]. On the contrary, in case of ethyl acetate, due to its very low boiling point, which is moreover very close to that of ethanol, the final product should be withdrawn in the distillate [5].

It is significant for the esterification process, that the head product of the reactive distillation column splits into two liquid-phases, the compositions of which are influenced by existence of heterogeneous and homogeneous azeotropes, see Table 1. If the reaction and separation conditions are favorable for the formation of heterogeneous distillate, ethyl acetate is concentrated in its organic phase. Continuous removal of the organic and water phases from the system shifts the chemical equilibrium even more to the product site, i.e. to very high or total conversion of chemical equilibrium limited reaction.

From separation reasons, maximum ethanol conversion needs to be achieved in the ethyl acetate process, so the process control has to respect this urgent need. In addition, an equilibrium mixture was fed into the reaction distillation column in our experimental setup. Being also supported by our previous experience with similar processes (butyl acetate, 2-methyl-propyl acetate) [2,9,10], these were the reasons to assume that the equilibrium based model (TEQ, see below) can provide reliable results when used in simulation of the ethyl acetate process, namely when the process setup consists in a combination of a reactive distillation column and a primary fixed-bed reactor. This combination represents more important significance for industrial application (higher throughput, robust control, safeguard reactor for possible catalytic poisons elimination, etc.).

Mathematical simulation of the reactive distillation process is a complex problem.

The models for RD simulation described in literature can be divided into several groups:

1. Total equilibrium model (TEQ) is the simplest approach supposing both phase and chemical equilibria on every stage of reactive section of distillation column. The only parameter describing the reaction system is its chemical equilibrium constant (temperature dependent). This model can be applied mainly for slow chemical reactions (e.g. in case ion-exchange resins instead of mineral acids as catalysts).
2. Common approach in the literature is EQ model with kinetically expressed rate of chemical reaction. This more sophisticated model (EQ) means vapour stream leaving the tray is in equilibrium with liquid leaving the tray; chemical reaction is described

by kinetic equations as functions of temperature and concentrations or activities. In this case, a long list of reaction parameters is needed for the simulation: kinetic constants, reaction orders, activity coefficients, activation energies of forward and backward reactions.
3. The most complicated approach is represented by rate based (non-equilibrium, NEQ) models which take into account heat and mass transfer through V–L interface, again accompanied by chemical reaction, described by kinetic equations as functions of temperature and concentrations or activities. This type of model needs also an adequate and accurate description of hydrodynamic conditions in the reactive distillation column. The non-equilibrium model (NEQ) takes into account heat and mass transfer through V–L interface using two film models which require proper mass and heat transfer coefficients estimation.

The quality of simulation results using both EQ and NEQ models is strongly dependent on accuracy of the kinetics data. On the other hand, based on the literature, the kinetic model seems to be applicable in wider range of reaction conditions. Many scientific papers [11,15–17] describe simulation of reactive distillation by means of the kinetic model, bringing evidence that this model provides relevant results even at low conversions or in strongly diluted solutions when the equilibrium based model is most probably bound to fail. It has also been disclosed that the equilibrium model cannot describe the role of the catalyst volume in the column properly. What's more, the kinetic based model is the only choice if unstable column regime needs to be simulated. But this is not the case of ethyl acetate synthesis investigated in this study.

The prediction of the phase equilibrium in the reaction zone, in the upper separation zone as well as in the condenser is very complicated. Because of the presence of water phase and organic phase, there are altogether three phases to be described. Generally, a proper equation of state is needed for modelling of this phase system. For the phase systems, which can be described by Fick's law, the NRTL equation of state can be advantageously used. Two films model of liquid/vapour interaction, utilizing Maxwell–Stefan theory is another, quite complicated, option [12–14].

In this paper, ASPEN Plus software (RADFRAC module) was chosen for the simulation of RD column, using equilibrium model (TEQ). The thermodynamic V–L equilibrium was assumed as being established at the V–L interface, NRTL equation of state was used also for the prediction of three phase separation system on the top of the column, where the reaction water was separated. This assumption of the phase equilibrium has been proven as acceptable for adequate pilot-plant results verification [4,9,10].

The separation of reaction water from the reaction zone of the reaction distillation column in the form of azeotrope represents another serious problem. In case of ethyl acetate synthesis the stoichiometric products ratio (water/ethyl acetate = 0.204) is two times higher then the ratio of these components in ternary azeotrope (water/ethyl acetate = 0.109). Thus, only one half of water formed by esterification can be separated as water phase of the heterogeneous distillate and the rest of it has to be separated by the re-boiler outlet stream. To solve this problem, additional acetic acid feed has to be installed to the column (see Fig. 1). This surplus of acetic acid, diluted by excess of reaction water, is withdrawn as a re-boiler out-

Table 1
Boiling points of reaction components and composition of azeotropic mixtures.

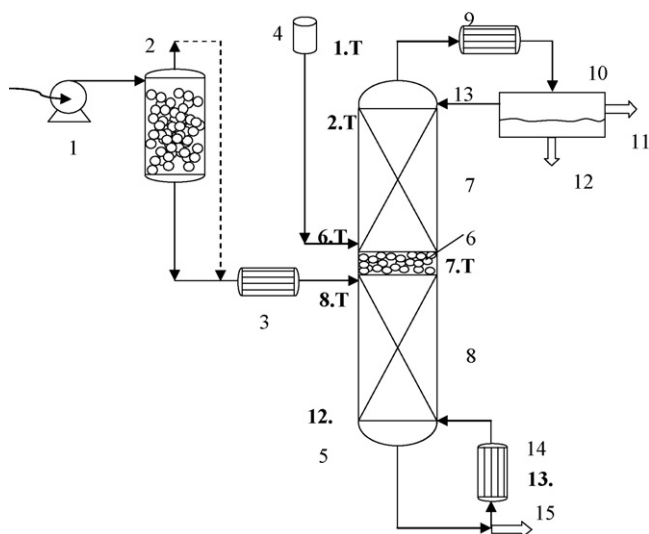| System	Boiling point (°C)	Ethanol wt.%	Ethyl acetate wt.%	Water wt.%	Azeotrope
Ethanol–water	78.2	95.6	–	4.4	Homogeneous
Ethyl acetate–water	70.4	–	91.9	8.1	Heterogeneous
Ethanol–ethyl acetate	71.8	31.0	69.0	–	Homogeneous
Ethanol–ethyl acetate–water	70.2	8.4	82.6	9.0	Heterogeneous

Fig. 1. Schematic description of experimental reactive distillation system with integrated fixed-bed reactor (theoretical stages in the column sections, re-boiler and condenser are bold-marked). 1—Pump injecting equimolar acetic acid/ethanol mixture, 2—fixed-bed primary reactor, 3—pre-heater, 4—additional feed of acetic acid surplus, 5—reactive distillation column, 6—reaction zone, 7—rectification section, 8—stripping section, 9—condenser, 10—decanter, 11—organic phase, 12—water phase, 13—reflux stream, 14—re-boiler, 15—bottom product.

let stream. This diluted acetic acid stream has to be re-concentrated to be used in the process again, which is not necessary if acetic anhydride is used, instead of acetic acid.

It was the main objective of this paper, to characterize the reaction system, consisting of a primary reactor and a reactive distillation column, in which ethyl acetate is synthesized, both on experimental and simulation basis. The lab scale experimental data were fitted by simulation with the use of an equilibrium based model. It is another objective of this study, to verify whether relatively simple and easy to use equilibrium based model can be utilized successfully to scale up the process the similar way as it was done in case of 2-methyl-propyl acetate synthesis [6].

2. Experimental

A fixed-bed reactor (i.d. 30 mm, length 0.5 m) with thermo stating jacket was used for the catalyst activity tests. Equimolar mixture of acetic acid (glacial, 100%) and ethanol (p.a. grade, 96%) was fed to the reactor containing acidic catalyst (ion-exchange resin, $C_{H+} = 5$ equiv./kg) by means of a piston pump, from a tank placed on a digital balance. Reaction conversion was calculated from the concentration of unconverted acetic acid, evaluated by titration. All experiments were made at atmospheric pressure. The tests at lower temperatures (60 and 70 °C) were made in a trickle-bed reactor. At temperatures above boiling point of the reaction mixture (90–120 °C) the reaction took part on a partly wetted catalyst bed, being accompanied by flash distillation of the azeotropic mixture. Co-current flow of the liquid reaction mixture and inert gas (nitrogen, flow rate 1.7 ml/s) through the bed of catalyst was maintained in all experiments.

Another set of experiments was performed in a lab scale unit, consisting of a common, one pass, packed bed reactor (in which partial evaporation of liquid reaction mixture took place), filled with strong acidic ion-exchanger catalyst, coupled with a reactive distillation column. The reactive distillation column (glass tube i.d. 30 mm, total length 2 m) consisted of three sections of overall efficiency 11 theoretical stages (TS). The distillation column efficiency had been tested by acetic acid–water binary mixture. The reaction zone of the efficiency of 1 TS (realized as a bag, containing spherical

acidic catalyst) was sandwiched between symmetric stripping and rectification sections (packed beds of stainless steel wire triangle spirals o.d. 3 mm) of the same length and the efficiency of 5 TS; re-boiler and condenser representing one theoretical stage each. The distillate was cooled down in a condenser and both organic phase (OP) and water phase (WP) were separated in a decanter, which was additionally tempered. Part of the organic phase was refluxed back to the head of the column, the rest of it, and also the water phase, being withdrawn as overhead streams.

The fixed-bed reactor outlet stream was introduced to the lower edge of the reaction zone, i.e. the equilibrium reaction mixture was fed below the reaction zone of the column. The upper edge of the reaction section was equipped with another side tube flange for feeding of additional surplus of acetic acid. Both in the fixed-bed reactor and the catalytic section of the reactive distillation column, *Purolite CT151* (Purolite Internat., Ltd.) strong acidic ion-exchanger (5H+ equiv./kg) was applied as catalyst. The scheme of the integrated reactive distillation system is shown in Fig. 1.

3. Results and discussion

Following experimental results were obtained:

- catalyst activity tests from fixed-bed reactor
- axial temperature profiles and the distillate as well as the bottom products analyses from laboratory reactive distillation experiments.

The data were used as input for the design of reactive distillation column and finally, the complex system, including a primary reactor and a reactive distillation column, was scaled up by means of the simulation model discussed above [7].

3.1. Fixed-bed reactor

The reaction mixture was fed at atmospheric pressure to the fixed-bed reactor, filled by ion-exchanger. The outlet stream was analyzed by GC method. All technological streams were sampled and analyzed by GC method using HP 5890 II device. A 60 m/0.2 mm capillary column coated with SPB™ (Supelco) was employed. An IS method using 2-methylbutanol as internal standard was applied. Acetic acid was also determined by titration using 0.05 N NaOH. Plot of ethanol conversion values, evaluated from primary experimental data at different reaction temperatures, in dependence on time coordinate W/F is shown in Fig. 2.

At lower temperature (60 °C), ethanol conversion approached chemical equilibrium value. In case of acetic acid and ethanol equimolar mixture feed, the equilibrium ethyl acetate concentration in the product represents 64 mass%. At temperatures above
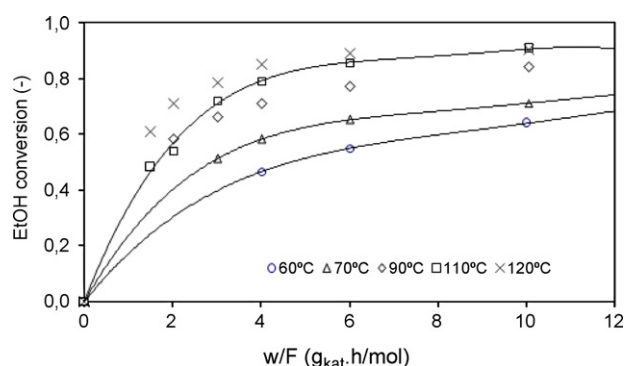

Fig. 2. Ethanol conversion at different reaction temperatures as a function of catalyst loading. Pressure 0.1 MPa, equimolar feed of ethanol and acetic acid.

Table 2
Average conversion of ethanol in fixed-bed reactor at different reaction temperatures for equimolar reaction mixture (experimental conditions see Fig. 2).

Temperature (°C)	Ethanol conversion (mass%)	
	Experiment	Process simulation
60	79	70
70	78	74
90	89	90
110	90	91
120	90	91

70 °C, the reaction products were partially vaporized in the form of azeotropic mixture, part of the reaction mixture being thus separated from the catalyst. Therefore, much higher conversion of esterification could be achieved, compared to chemical equilibrium conversion. At temperatures between 110 and 120 °C, the ethanol conversion of more then 90% was reached, see Fig. 2. Similar reactor performance had already been reported for carrying out the esterification of acetic acid with n-butanol in a trickle-bed reactor [3]. However, in case of feed temperature below boiling point of the reaction mixture and the catalyst temperature 120 °C all reaction components are fully evaporated and the system works in a flash distillation regime. The values of ethanol conversions, achieved at different reaction temperatures in the fixed-bed reactor, are summarized in Table 2.

However, the ion-exchanger is thermally stable up to 110 °C only. In addition, as can be seen from Table 2, only small increase of ethanol conversion was observed at temperature above 90 °C. Thus, from enthalpy balance and technology point of view it can be concluded that the optimal temperature in primary reactor should be maintained at 90 °C. At this temperature, assuming equimolar feed of starting compounds, the ethanol conversion of 89.6 mass% can be reached, the composition of equilibrium stream achieving following values: 74.7 mass% ethyl acetate, 5.6% acetic acid, 5.4% ethanol and 14.3% water. When the molar ratio of acetic acid towards ethanol in the feed slightly increases, reaching the value of 0.52/0.48, the conversion of ethanol increases to 92.2 mass%. Due to higher concentration of non-reacted acetic acid, the concentration of ethyl acetate is decreased to 74.0%, but the ethanol concentration remains only 3.05% in this case. This outlet reaction mixture was used for the reactive distillation experiments.

3.2. Reactive distillation

The reaction mixture from previous experiments was fed below the reaction zone of the column, namely on 8th TS, numbered from the top of the column, see Fig. 1. In case of ethyl acetate synthesis, very high conversion of ethanol needs to be achieved. The separation strategy is therefore based on decantation the water phase from cooled distillate, which is possible only at low ethanol concentration in the upper part of the reactive distillation column. To avoid the accumulation of water and ethanol in the system, additional surplus of acetic acid was introduced above the reaction zone of the column, see tank and stream 4 in Fig. 1. The reaction zone itself was represented by only one theoretical reactive distillation stage.

The lab scale experiments were performed till the simultaneous steady state of the reaction and separation was reached. Continuous removal of water phase from the distillate and refluxing only the organic phase can be considered as basic and most important condition, making the production of high-purity ethyl acetate possible. Effective water removal is possible only in a steady state regime of the reactive distillation column. Stabilization of the column is apparent from time dependence of the temperature profile—see Fig. 3.
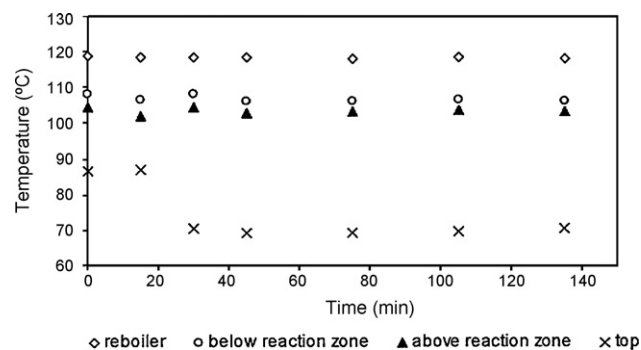

Fig. 3. Temperature profile along the column in time. Reflux ratio 1:10, pressure 0.1 MPa; feed composition see Section 3.1; (◇) re-boiler; (○) below reactive section; (▲) above reactive section; (×) top of column.

The distillate composition and axial temperature profile were considered as main indicators of steady-state regime of the reactive distillation column. The steady-state was reached when both distillate composition and temperature profile along the column remained constant with time on stream. The axial temperature profile is illustrated in Fig. 4, together with temperatures above and below the reaction zone and the re-boiler temperature. It is apparent from the head temperature curve that in this experiment, at least 150 min period of stabilization was necessary to reach the steady-state regime.

Establishing of phase equilibrium in quite a complex liquid–liquid–gas system on the top of the column is documented by the head temperature profile in Fig. 3. After 20 min, the expected separation temperature of 70 °C on the head of the column was adjusted. On the other hand, at short reaction–separation time (shorter than 60 min), the temperatures above and below the reaction zone oscillated remarkably. Thus, from the processing point of view, it is advantageous to temper the column for at least 60 min before the reactive distillation experiment begins [8].

3.3. Experiment and process simulation

The process simulation was made using ASPEN Plus simulation software (RADFRAC module). The phase equilibrium of both water and organic phases, as well as phase equilibrium in the column and primary reactor were described by NRTL-equation of state. The integration accuracy was set to $\pm 1 \times 10^{-5}$. Build-in database of the software was utilized for all calculations.

An optimized ethyl acetate reactive distillation experiment, selected from larger set of experiments made, is illustrated in
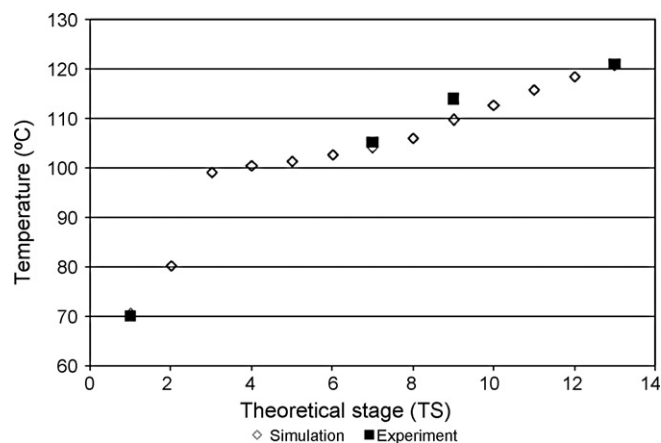

Fig. 4. Temperature profile along the column—experiment versus simulation (experimental conditions—see Table 3).

Table 3

Process experiment of ethyl acetate reactive distillation, coupled with fixed-bed primary reactor. The experimental results are compared with the process simulation results, achieved at the same reaction and separation conditions. The feed temperature to the column was 90 °C.

Parameter	Experiment	Process simulation (AspenPlus Radfrac Module)
Feed equilibrium mixture flow rate (g/h)		26.7
Feed surplus of AA flow rate (g/h)		7.0
Reflux ratio		1:10
Re-boiler product flow rate (g/h)		9.5
Organic phase flow rate (g/h)	19.4	21.8
Water phase distillate (g/h)	3.88	3.71
Organic phase composition (mass%)		
EtOH	2.1	2.99
AA	0.3	0.4
Ethyl acetate	92.8	92.8
Water	4.8	3.7
Water phase composition (mass%)		
EtOH	n.a.	7.3
AA	0.8	1.2
EtAc	n.a.	8.8
Water	n.a.	82.5
Re-boiler product composition (mass%)		
EtOH	0	Traces
AA	96.6	96.4
EtAc	0	Traces
Water	3.4	3.6

Table 3. The process parameters of the experiment, as well as those used for the process simulation, are listed there. Thus, for proposed hardware and the efficiency of the column sections, only feed streams mass flow values, re-boiler product mass flow and reflux ratio were fixed for the simulation. The rest of the parameters resulted from the experiment.

The organic phase composition indicates excellent separation of acetic acid from the organic phase of the distillate, the acetic acid concentration remaining low, only ca. 1% wt., also in water phase of the distillate. Ethanol concentration in the organic product was however ca. 2–3 mass%, so it is clear that final purification of ethyl acetate is inevitable, though only small amount of ethanol is to be separated and recycled. As ethanol is quite easy to separate by distillation, the presence of ethanol in the organic phase of the distillate is much less harmful then presence of acetic acid. The re-boiler product consists of acetic acid partly diluted by reaction water. This stream can be recycled back to the primary reactor after water separation, which can be made by distillation, membrane separation or by adding a defined amount of acetic anhydride.

The process simulation data fit very well to the lab scale experimental results so the simulation method can be without any doubt used for the design of a pilot-plant and planning experiments in larger scale as well as for the process scale up. The small difference between the measured and calculated mass flow rates of the distillate phases can be explained by non-ideal separation of water and organic phases in decanter during the experiment. The temperature profile along the column can also be predicted with high accuracy by the process simulation. A comparison of measured and calculated temperature profiles along the reactive distillation column is given in Fig. 4.

Temperature profile in the rectification section as well as the temperature value in decanter represent key parameters of the ethyl acetate process. The adjustment and control of these parameters influence very decisively the process performance. These facts were taken into consideration in subsequent pilot-plant research which resulted in patenting the process [7].

4. Conclusions

A reactive distillation unit, suitable for the synthesis of ethyl acetate by esterification of acetic acid and ethanol, was presented. This unit consists of an equilibrium fixed-bed primary reactor and a reactive distillation column. Main accent was put on lab scale experiments and their description by a process simulation model. Crude, acetic acid free, ethyl acetate can be advantageously produced as distillate of the reactive distillation column in the form of its organic phase, containing only small amount of ethanol in concentration below 3 mass%. The process simulation fitted the experiments very well. The simulation using simple total equilibrium model (TEQ) is therefore utilizable for the process scale up and intensification.

There is a lot of papers in the literature, dealing with the simulation of reactive distillation, using the rate based models with MS equations, for which it is sometimes very difficult to find appropriate parameters (all binary mass transfer coefficients).

This study shows a particular reactive distillation case, where also very simple mathematical model could predict the behavior of a reactive distillation column with appropriate accuracy. Thus, presented model can be used for the design of ethyl acetate synthesis process and optimization of its performance condition.

References

[1] K. Sundmacher, A. Kienle, Reactive Distillation: Status and Future Directions, Wiley-VCH, Auflage: 1, 2002.
[2] J. Hanika, Q. Smejkal, J. Kolena, 2-Methylpropylacetate synthesis via catalytic distillation, Catal. Today 66 (2001) 219–223.
[3] J. Hanika, M. Kucharova, J. Kolena, Q. Smejkal, Multi-functional trickle bed reactor for butylacetate synthesis, Catal. Today 79–80 (2003) 83–87.
[4] Q. Smejkal, M. Soos, Comparison of computer simulation of reactive distillation using AspenPlus and HYSYS software, Chem. Eng. Process. 41 (2002) 413–418.
[5] H.-Y. Lee, H.-P. Huang, I.-L. Chien, Design and control of homogeneous and heterogeneous reactive distillation for ethylacetate process, Comp. Aided Chem. Eng. 21 (2006) 1045–1050.
[6] Q. Smejkal, J. Kolena, J. Hanika, 2-Methylpropyl acetate synthesis in a system of equilibrium reactor and reactive distillation column, Chem. Eng. Sci. 56 (2001) 365–370.
[7] J. Kolena, J. Lederer, P. Morávek, J. Hanika, Q. Smejkal, D. Skála, A process and apparatus for production of ethyl acetate, Czech. Pat. 292620 (2003), TW Pat. 284635 (2001), Jap. Pat. 2003535814 (2003), US Pat. 6,693. 213 (2004), EP 1220829 (2005).
[8] D. Skála, Diploma Thesis, Institute of Chemical Technology Prague, 2000.
[9] J. Hanika, J. Kolena, Q. Smejkal, Butylacetate via reactive distillation—modelling and experiment, Chem. Eng. Sci. 54 (1999) 5205–5209.
[10] Q. Smejkal, J. Hanika, J. Kolena, Simulation of the butyl acetate synthesis via catalytic distillation (Eng), Chem. Pap. 54 (2000) 165–170.
[11] C. Noeres, K. Dadhe, R. Gesthuisen, S. Engell, A. Gorak, Model-based design, control and optimization of catalytic distillation processes, Chem. Eng. Process. 43 (2004) 421–434.
[12] J.C. Maxwell, On the dynamical theory of gases, The Scientific Papers of J.C. Maxwell, 2, 1965, pp. 26–78.
[13] J. Stefan, Über das Gleichgewicht und Bewegung, insbesondere die Diffusion von Gemischen, Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Wien 63 (1871) 63–124.
[14] E.L. Cussler, Diffusion—Mass Transfer in Fluid Systems, 2nd ed., Cambridge University Press, 1997, ISBN 0-521-56477-8.
[15] C. Buchaly, P. Kreis, A. Gorak, Hybrid separation processes—combination of reactive distillation with membrane separation, Chem. Eng. Process. 46 (2007) 790–799.
[16] N. Calvar, B. Gonzalez, A. Domingues, Esterification of acetic acid with ethanol: reaction kinetics and operation in a packed bed reactive distillation column, Chem. Eng. Process. 46 (2007) 1317–1323.
[17] R. Krishna, R. Taylor, Modelling reactive distillation, Chem. Eng. Sci. 55 (2000) 5183–5229.