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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.

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