

# Simulation of the Butyl Acetate Synthesis *via* Catalytic Distillation\*

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This paper deals with the synthesis of butyl acetate by catalytic distillation. Main attention is paid to the computer simulations of the catalytic distillation of acetic acid and butanol as well as a comparison of the numerical results and the pilot plant experimental data. A mathematical model of this process is also discussed.

During the last two decades a rapid upturn in interest of carrying out chemical reactions simultaneously with distillation could be observed [1]. This process is usually called reactive or catalytic distillation. The reaction components can be transformed in the presence of a structured catalyst packing inside the distillation column and the reaction products can be continuously separated by fractionation [2] at the same time. Catalytic distillation has been applied mainly in the processes, where continual removal of the products makes it possible to overpass chemical equilibrium in the system in which reversible reactions take place.

Other advantage of reactive distillation consists in utilization of reaction heat for the product separation by recuperation in the case of an exothermic reaction [3]. Etherification [4] (*tert*-butyl methyl ether, *tert*-amyl methyl ether, *tert*-butyl ethyl ether), esterification [5] (methyl acetate) or alkylation [6] (isopropylbenzene) are typical examples of such industrial processes.

In the catalytic distillation process, a reaction zone, consisting of bundles of structured catalytic packing, is usually sandwiched in between stripping and rectifying sections of a rectification column which is conventionally equipped with an overhead condenser, reboiler and, in special cases, with a decanter (phase separator). Depending on their boiling points, the reaction components are fed either above or below the catalyst bed (see Fig. 1).

The catalytic distillation of acetic acid (AA) and butanol (NBA) has been chosen for the case study. Butyl acetate (BAC), the product of esterification cat-

alyzed by acid, is one of the most common solvents, used in the paints and coatings manufacture as well as a good industrial solvent. In spite of the modern trends towards lower aromatics content in coating solvents, consumption of butyl acetate is expected to grow in near future because of its lower impact on the environment, comparing to some other types of solvents (*e.g.* aromatics solvents).

## Mathematical Model of Catalytic Distillation

A simulation software was used for the modelling of the butyl acetate synthesis *via* catalytic distillation. Calculation of the axial composition and temperature profiles along the column was the aim of the computer simulation. The computer program allows solving the system of nonlinear algebraic equations, which, together with the correction for nonideal liquids and azeotrope mixture behaviour, describes mass and enthalpy balances of the designed catalytic distillation system. The scheme of the equilibrium column stage *j* is illustrated in Fig. 2, following eqns (1–4) describe the mass and enthalpy balances and the chemical equilibrium in each theoretical stage of the column [7]. Phase equilibria have been calculated using the NRTL equation.

The mathematical model was based on the assumption of simultaneous chemical as well as vapour–liquid equilibrium in all theoretical stages of the reaction zone of the column. To simplify the calculation, pressure drop along the column was neglected so the whole equipment was supposed to operate under at-

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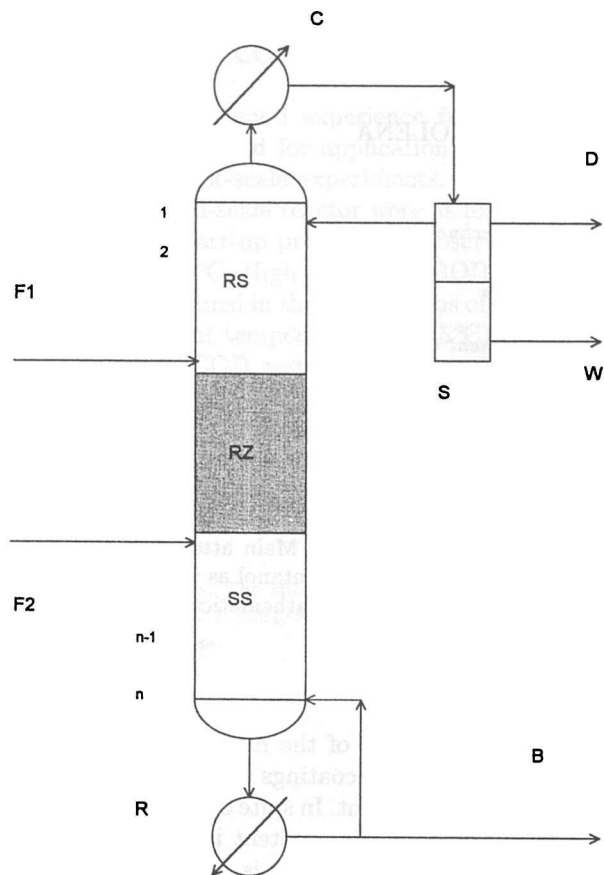


Fig. 1. Typical catalytic distillation column. Scheme for a heterogeneous distillate, 1, 2, ...,  $n$  are the stage numbers. B – bottom product, C – condenser, D – distillate, organic phase, F1, F2 – feeds to the column, R – reboiler, RS – rectifying section, RZ – reaction zone, S – phase separator (decanter), SS – stripping section, W – water phase.

atmospheric pressure. The liquid and vapour phases on every stage were ideally mixed.

Mass and enthalpy balances of section  $j$  are described by eqns (1) and (2), respectively

$$V_{j+1} + L_{j-1} + F = V_j + L_j \quad (1)$$

$$V_{j+1}H_{j+1} + L_{j-1}h_{j-1} + Fh_f + Q_j = V_jH_j + L_jh_j \quad (2)$$

where  $V$  and  $L$  are the vapour and liquid flow-rates ( $\text{kg h}^{-1}$ ) through the  $j$ -section,  $H$  and  $h$  are the enthalpies of the vapour and liquid mixtures ( $\text{kJ kg}^{-1}$ ),  $F$  is the feed rate ( $\text{kg h}^{-1}$ ), and  $Q$  is the heat input into the stage  $j$  (W).

The component material balance follows eqn (3)

$$V_{j+1}y_{j+1,i} + L_{j-1}x_{j-1,i} + Fx_{f,i} = V_jy_{j,i} + L_jx_{j,i} \quad (3)$$

where  $x$  and  $y$  are the mass fractions of each component in the liquid and vapour phases. The chemical equilibrium of the reaction in the reaction zone is described by eqn (4), in which  $K$  is the equilibrium constant and  $a$  is the activity of component  $i$ ,  $k$  is the number of components in the system,  $n$  are reactants,  $m$  products.

$$K = \prod_{i=1}^k a_i^{n_i} \dots a_k^m \quad n = +1, m = -1 \quad (4)$$

The mathematical model makes it possible to determine the influence of technological parameters (*i.e.* number of theoretical stages, feed position, reaction components mole ratio, *etc.*) on the efficiency of the catalytic distillation process. The mathematical model can only be applied in almost equilibrium state of the chemical reaction in the reaction zone of the column. If the reaction is far away from chemical equilibrium, the reaction zone behaviour should be described by an alternative, kinetics-based model.

Three variants of technological setup of the catalytic distillation are discussed in the paper. The individual variants differ by the feed positions (see Fig. 3). These variants of catalytic distillation model simulation were characterized by:

- separate feeds of the reactive components above the reaction zone of the column (variant A) or below it;

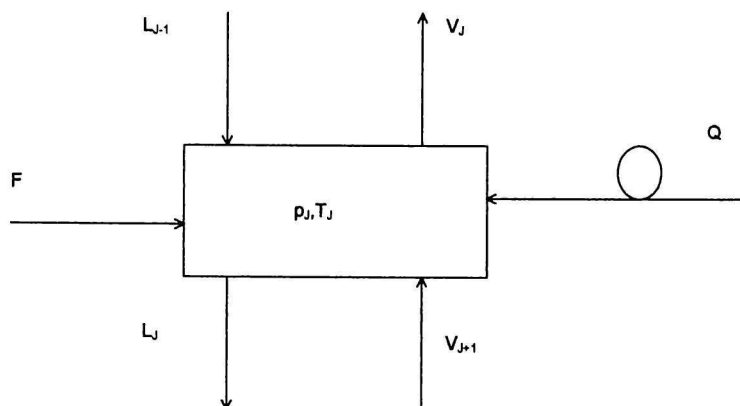


Fig. 2. Scheme of an equilibrium column stage under constant pressure and temperature.

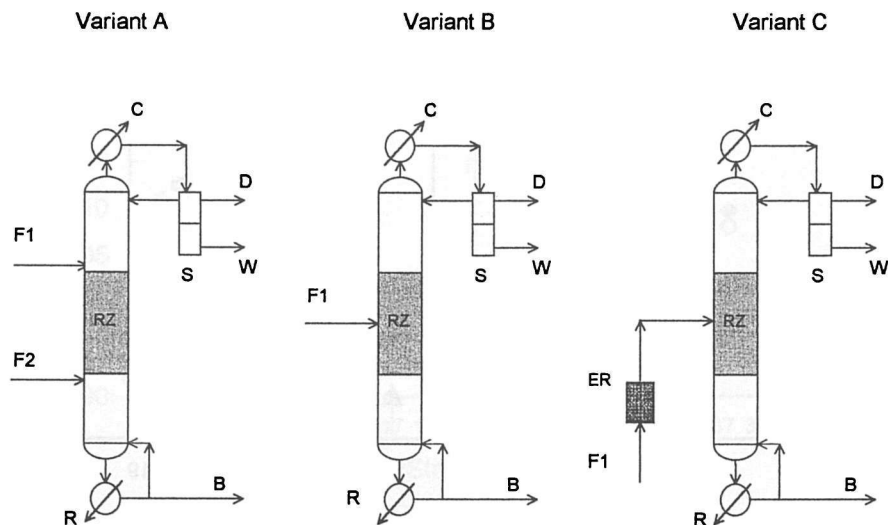


Fig. 3. Variants of the catalytic distillation column setup. ER – esterification reactor; for the symbols used see Fig. 1.

Table 1. Bottom Product Composition Calculated for Different Feed Setup and Reaction Zone Efficiencies (an Esterification Reactor is Added behind the Column in Variant C)

Number of stages in RZ	Product mass fraction (mass %)								
	Variant A			Variant B			Variant C		
	BAC	AA	NBA	BAC	AA	NBA	BAC	AA	NBA
1	87.32	5.41	7.26	97.43	2.12	0.45	98.03	1.79	0.17
3	–	–	–	98.36	1.55	0.097	98.62	1.35	0.027
5	–	–	–	98.54	1.44	0.021	98.72	1.27	0.005

$F (F1 + F2) = 1.94 \text{ kg h}^{-1}$ ,  $B = 1.63 \text{ kg h}^{-1}$ , reflux =  $6.23 \text{ kg h}^{-1}$ ,  $x_{\text{NBA}}/x_{\text{AA}} = 1.08$ . SS = 10 TS, RS = 10 TS, condenser = total, calculation precision:  $\pm 10^{-6}$ ; AA – acetic acid, NBA – butanol, BAC – butyl acetate.

– mixed feed of both components in the middle of the reaction zone (variant B) – this variant is possible only in the case of close boiling points of both reaction components;

– combination of an esterification reactor and a catalytic distillation column (variant C) – reaction mixture of nearly equilibrium composition containing AA, NBA, water; BAC is fed to the reaction zone.

In all of the simulation calculations, three different efficiencies of the reaction zone (1, 3, and 5 theoretical stages) were considered.

The product, butyl acetate, was withdrawn from the column in all cases as a bottom stream. Two-phase liquid mixture, containing water and organic phases, was distilled overhead. This heterogeneous mixture was split into the two phases in a separator. This continuous removal of the water phase shifted chemical equilibrium towards the products. The main part of organic phase of the distillate was refluxed back to the column.

### Model Solution

The results of the catalytic distillation model sim-

ulation are summarized in Table 1, where the product compositions in cases of different feed configurations and reaction zone efficiencies are compared. The other parameters of the system like the reaction components ratio, feed flow-rate, reflux ratio, and the bottom product flow-rate were constant.

The results indicated high concentration of butyl acetate in the bottom product in case of the variant C representing a combination of an esterification reactor and a reactive distillation column. The feed to the middle of the reaction zone of the column was of almost equilibrium composition, *i.e.* approximately 55 mass % butyl acetate, 20 mass % butanol, 13 mass % acetic acid, 12 mass % water. In case of variant A, separation of the reactive components feed streams resulted in the lowest butyl acetate concentration in the product. Variants B and C represent a successful arrangement of the catalytic distillation of butyl acetate. The comparison of butyl acetate axial concentration profiles in the column in cases B and C is presented in Fig. 4. It was found that there is only a small difference between variants B and C in terms of butyl acetate concentration in rectifying section of the column.

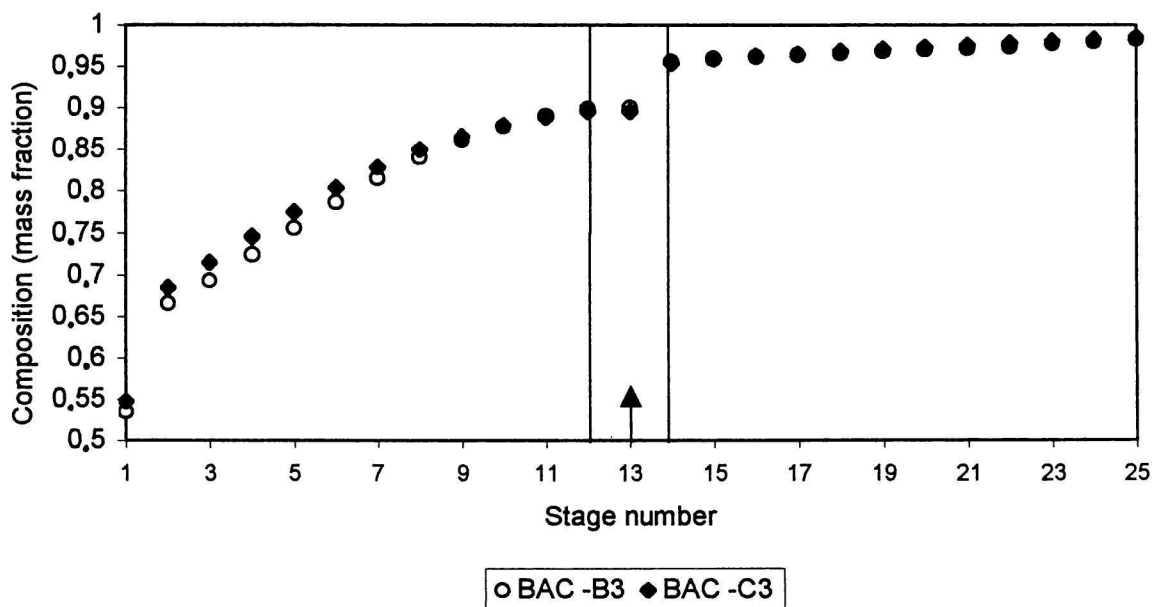


Fig. 4. Butyl acetate concentration profiles along the column in variants B, C. 3 theoretical stages of the reaction zone, for simulation conditions see Table 2.

There is a positive effect of number of reaction stages on the butyl acetate concentration in the bottom product in case of variants B, C (see Table 1). As the difference in butyl acetate purity in cases of the reaction zone consisting of 3 and 5 stages, respectively, is relatively low, the reaction system setup with 3 theoretical stages in reaction zone was chosen for experimental verification.

The reactor combined with the catalytic distillation column increases the performance of the system because of the greater amount of catalyst used. In this case, the column only finishes up the reaction, converting the remainders of the starting components in an equilibrium mixture produced by the reactor.

## EXPERIMENTAL

Using the simulation software, the pilot plant parameters were designed (see Table 2). Due to proximity of both reaction components boiling points (AA 118.5°C and NBA 117.5°C), their mixture was introduced to the middle of the reaction zone. Suggested apparatus parameters were optimized on the basis of sensibility analysis. Both the stripping and rectifying sections of the column had a little bit higher efficiency (20 theoretical stages) comparing to that used in the simulation (10 stages). The data measured, *i.e.* all streams flow-rates, compositions, temperature, *etc.* were used as the input parameters estimation for the catalytic distillation process simulation.

The continuously operating esterification reactor contained a fixed bed of catalyst (acidic ion ex-

Table 2. The Parameters of the Pilot Plant Equipment

Parameter	Value
Number of stages – stripping section	20
Number of stages – rectifying section	20
Number of stages in reaction zone	3
Position of the feed (together NBA + AA)	in the middle
Temperature of the feed/°C	boiling point
Excess of butanol in feed/mole %	5
Temperature in separator/°C	40

changer). The reaction zone was located between 22–24 theoretical stages of the column, the equilibrium feed (55 mass % butyl acetate, 20 mass % butanol, 13 mass % acetic acid, and 12 mass % water) being introduced into the middle of the reaction zone, *i.e.* to the 23rd theoretical stage.

## RESULTS AND DISCUSSION

A comparison of the simulation output and the experimental results is given in Table 3. There is apparently good agreement between the simulated and measured bottom product and reflux streams compositions. The analytically determined water content in the reflux stream is higher than the calculated value, the most probable reason being the axial flow of both phases in the decanter. Water dispersion, being not perfectly separated from the organic phase in the decanter, was also partially refluxed. The simulated tem-

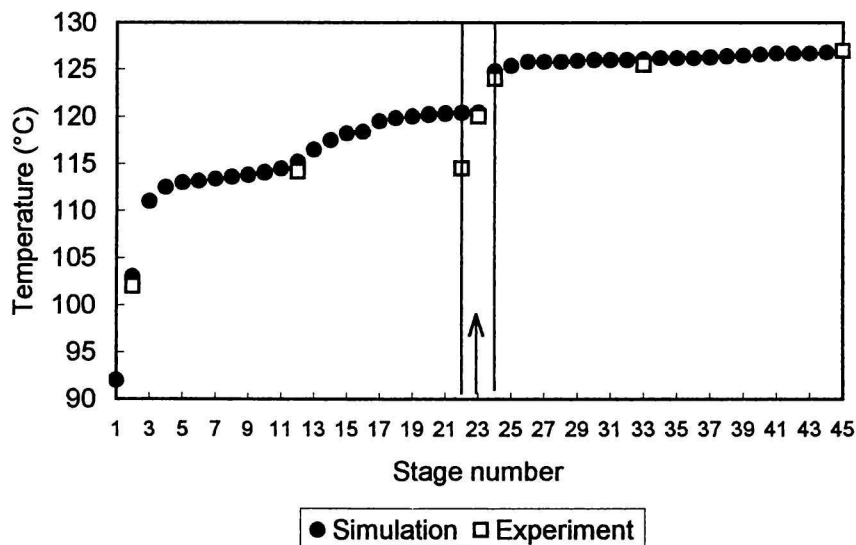


Fig. 5. Temperature profile along the column during catalytic distillation of acetic acid and butanol: Variant C, vertical lines indicated the reaction zone.

Table 3. Comparison of Simulated and Measured Results of Butyl Acetate Catalytic Distillation – Variant C

Parameter	Simulation	Experiment
Feed flow/(kg h <sup>-1</sup> )	2.75	2.75
Feed composition/mass %		
acetic acid	13.2	13.2
butanol	21.6	21.6
butyl acetate	56.5	56.5
Product/(kg h <sup>-1</sup> )	2.14	2.38
Product composition/mass%		
acetic acid	0.04	0.06
butanol	–	0.24
butyl acetate	99.94	99.21
Reaction water/(kg h <sup>-1</sup> )	0.35	0.39
Organic phase/(kg h <sup>-1</sup> )	0.265	0.210
Reflux/(kg h <sup>-1</sup> )	11.5	10.88
Reflux composition/mass%		
water	10.26	30.52
acetic acid	0.74	0.4
butanol	50.48	42.42
butyl acetate	38.52	26.65
F-factor/(m s <sup>-1</sup> (kg m <sup>-3</sup> ) <sup>0.5</sup> )	0.426	0.418

perature profile also fits the measured data very well (Fig. 5) proving suitability of the mathematical model used [8, 9].

Comparing the experimental and theoretical temperature profiles (Fig. 5) a good agreement can be observed. Water content in the stripping section of the column is sufficient to form the mixture close to the azeotropic one with minimum boiling point.

This situation is demonstrated also in Fig. 6 where the simulated reaction component concentration pro-

files along the column are shown. It is apparent that the bottom part of the stripping zone of the column is filled with nearly pure butyl acetate, thus the temperature profile in this section of the column is flat. Both acetic acid and butanol are distilled out from the stripping section to the reaction zone.

## CONCLUSION

Presented simulation results confirm the possibility of butyl acetate synthesis *via* catalytic distillation of acetic acid and butanol. If the esterification reaction proceeds fast enough to reach almost chemical equilibrium in the reaction section of the column, the simulation software utilized provides results, which fit very well the pilot plant data. High purity butyl acetate can be prepared *via* catalytic distillation, the concentration of both unreacted components acetic acid and butanol in it being very low. If the column setup described above is used, the produced butyl acetate is dry, being thus suitable for demanding industrial applications. This is a great advantage of the proposed process [10].

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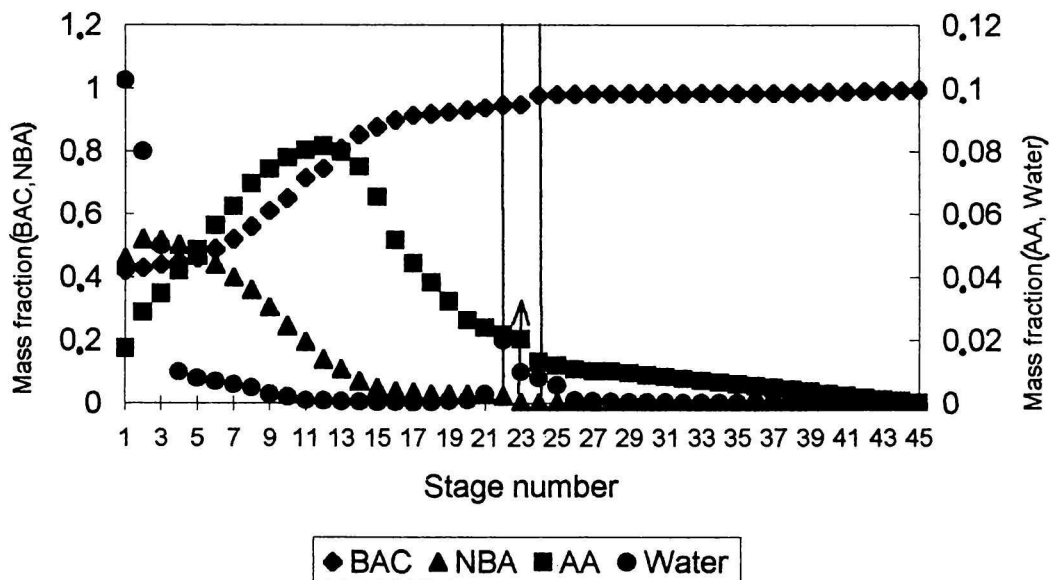


Fig. 6. Simulated reaction components concentration profiles along the column, for details see Table 3. AA – acetic acid, NBA – butanol, BAC – butyl acetate.

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