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DISTILLATION WITH CHEMICAL REACTION AND APPARATUS SELECTION

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ABSTRACT

Reactive distillation was studied practically and theoretically for the esterification of succinic anhydride with methanol to produce in a first step monomethyl succinate and in a second one dimethyl succinate and water. It was shown that simulations using the ASPEN PLUS rigorous distillation model RADFRAC corresponds with experimental data quite well. With this fundament further calculations were performed simulating several kinds of reactive and distillation equipment. On basis of this, an apparatus selection is made related on energy consumption and relative conversion. Key parameters, as reaction velocity for the reaction term and the relative volatility (α from 1.2 to 14), affect markedly the selection of the apparatus of choice. The reaction column is the apparatus of choice for fast reactions and high volatilities considering the energy input. For low relative volatilities the choice is between the reaction column or the reactor with evaporation, depending on whether operating costs or investment costs are taken into account.

INTRODUCTION

Separation processes, which most frequently accompany chemical reactions, are distillation and extraction. The present contribution only deals with the study of reaction in distillation columns. The employment of multistage distillation in which chemical reactions take place is becoming more and more common in chemical industries. In recent years, increasing attention has been directed toward reactive distillation processes as an alternative to conventional processes by Mommessin and Holland (1), Terrill et al. (2) and Grosser et al. (3). The advantage is that two processes occur simultaneously in a single unit as a result of which capital and operating costs are considerably lowered. Such an operation is particularly suitable when one of the reaction products has a lower boiling point than the others present. In fact, the higher volatility of one of the reaction products decreases its concentration in the liquid phase, and therefore the reaction rate increases. Distillation conditions also produce higher temperatures which speed up most chemical reactions.

This has led to the development of a variety of techniques for simulating reactive distillation columns, which were carried out by Suzuki et al. (4), Nelson (5), Komatsu (6), Komatsu and Holland (7), Sawistowski and Pilavakis (8), Tierney and Riquelme (9), Murthy (10) and Agreda et al. (11). However, the problem of design of reactive distillation processes has not yet been addressed.

Modeling of reactive distillation columns requires the prediction of chemical and phase equilibria in addition to the solution of mass and energy balance equations. Because of the nature of the reactive system, it is usually difficult to predict chemical and phase equilibria for different systems with a single model simultaneously. Many previous workers have therefore relied on empirical models for predictions of chemical and phase equilibria when simulating reactive distillation columns (12).

Most publications about reactive distillation assume chemical equilibrium at each stage. The following work was performed taking the rate of reaction as rate- determining step in this reactive distillation process into account. In this study a possible process from the determination of the kinetic parameter to the simulation of a laboratory-scale model, is presented. The recent development of advanced thermodynamic models for high-precision predictions of selected properties has led to the development of simulation models for reactive distillation columns. The thermodynamic basis for these simulation models is the calculation of simultaneous chemical and phase equilibria (CPE). For the solution of the CPE problem, the simulation model only requires pure component data (critical properties, heat of formation, free energy, specific heat, viscosity, thermal conductivity, etc.) and some model parameters pertaining to the thermodynamic model being used. The proposed method for solving simulation problems is related to the design of multicomponent reactive distillation column operations.

For reasonable design of these separation processes quantitative information on kinetic parameter, phase equilibria and the thermodynamics in multicomponent mixtures needed. Suitable experimental equilibrium data are usually not available for given temperature, pressure, and composition of mixture. It is therefore necessary to estimate the desired equilibria from some appropriate correlation. A very useful correlation for this purpose seems to be the UNIFAC group-contribution method.

It will be demonstrated how a process with combined reaction and distillation is designed, especially for industrial requirements, and the limits of such process will be shown. A procedure for the evaluation of concentrations and temperature profiles in a distillation column with chemical reaction is presented.

EXPERIMENTAL METHOD

Apparatus and Procedure

Experiments were conducted at atmospheric pressure with various molar ratios of monomethyl succinate and methanol in the range of

0.048 to 0.091 using catalyst concentrations of 0.05 to 0.2 mol% relating to monomethyl succinate with different reflux ratios (0.5-3). In addition, the relation between liquid hold-up in the total column and the feed was varied between 420 and 1380 s (hydrodynamical residence time). The esterification of monomethyl succinate and methanol has been investigated in a laboratory-scale model, which is shown in Figure 1. The glass column (internal diameter, 5 cm; liquid volume per stage, 10 cm^3; liquid volume in the bottom, 100 cm^3) consists of 10 bubble-cap plates with one bubble cap at each stage. Monomethyl succinate and methanol are esterified to dimethyl succinate and water in a homogeneously catalyzed reaction using sulfuric acid as a catalyst. Removing the water by distillation improves the fractional conversion. The reaction velocity for an esterification reaction is intermediate fast, and the relative volatilities are low. The acid, together with the catalyst, is fed to the reaction column at stage 2 and is run countercurrent to the boiling alcohol, which is fed at stage 9. The vapor at the top of the column contains methanol, water, and a trace of dimethyl succinate. The catalyst is drawn off at the bottom of the reaction column, together with a certain amount of product and residue.

MODELING EQUATIONS

Phase equilibrium between the liquid and the vapor phase is assumed. The relevant equations are the material and enthalpy balance, the stoichiometric equations for each component, and the phase equilibrium equations. If a chemical reaction is taken into account within the frame of this model, an additional assumption is necessary. The liquid phase at each theoretical stage has to be perfectly mixed. This is only valid if the mass transfer velocity is much higher than the reaction velocity, and therefore this additional assumption is a restriction to the generality of the model. The relevant equations, with allowance for chemical reactions, are as follows:

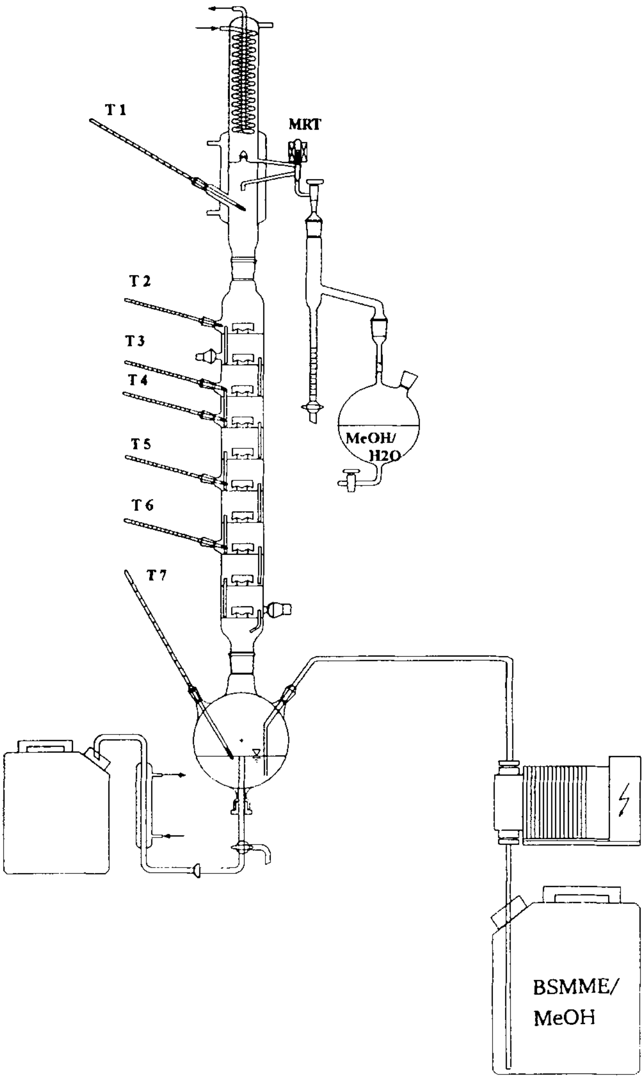


FIGURE 1. Laboratory-scale model

Material balance equation:

$$G_{n-1}y_{i,n-1} + L_{n+1}x_{i,n+1} + F_n z_{i,n} - (G_n + S_n^G)\, y_{i,n} - (L_n + S_n^L)x_{i,n} + \Delta R_{i,n} = 0$$

Enthalpy balance equation:

$$G_{n-1}h_{n-1}^G + L_{n-1}h_{n-1}^L + F_n h_n^F + Q_n - (G_n + S_n^G)\, h_n^G + (L_n + S_n^L)h_n^L + \Delta H_n^R = 0$$

Stoichiometric equations:

$$\sum_{i=1}^{M} y_{i,n} = 1 \qquad \sum_{i=1}^{M} x_{i,n} = 1 \qquad 1 \le n \le N$$

Phase equilibrium equation:

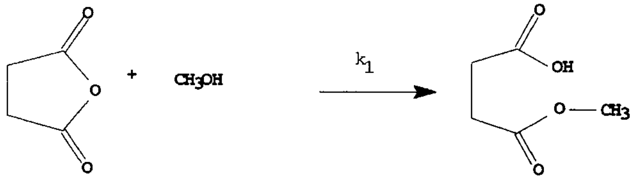
$$y_i = K_i x_i$$

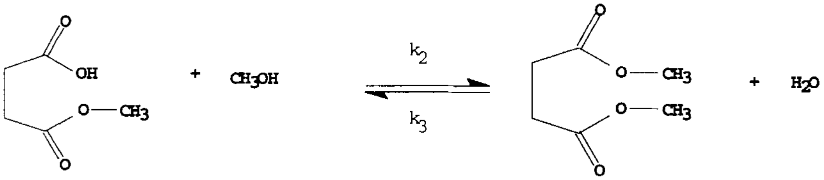
The usual approach to tray-to-tray calculations is to write the equations for the material balance of each component entering and leaving each stage and then to express the system of such equations for all stages in matrix notation. Normally, there would be a computation of equilibrium stages, but in this simulation, the kinetic model is included as ΔR_n in the material balance equation.

On the basis of this set of specifications, it is desireable to find the resulting compositions of the distillate and bottom products. The equations required to describe this column are developed in the order in which they are used in the proposed calculational procedure. These equations are solved sequentially in the following order. On the basis of assumed temperature and L/V profiles, the material balances, the physical equilibrium relationships, and the chemical rate expressions are solved for the moles of each component which reacts per stage and unit time and for the component flow rates. The formulation of UNIFAC-Redlich-Kwong is used with the commercial simulation software RADEFRAC from ASPEN PLUS ®

RESULTS AND DISCUSSION

Application to esterification reactions. As an example of application of the described method, the esterification has been considered as:





The generalized rate expression, which was evaluated with the integrated multifunctional simulation software package "SIMUSOLV" (Trademark of The Dow Chemical Company) in former studies (14), is used. All the necessary physical parameters of the different components are taken from literature (15). Since for dimethyl succinate no data were available, physical properties were determined by experiments and the UNIFAC group contribution method was applied.

By using the technology of reactive distillation, it is possible to get high reaction conversion and separation simultaneously in a reaction of the type which was described by Schönmakers (16). Liquid rich in A is fed to a stage between the top and the middle portion of the column. Vapor rich in B is fed to a stage near the bottom of the column. Reactant B is absorbed into the liquid phase where the reaction takes place, and product D is stripped from the liquid phase and drawn off at the top of the column. In the case of esterification, the order of volatility is dimethyl succinate, water, and methanol. The relative volatilities of several alcohol-water mixtures were determined as: $\alpha_{BuOH/H2O}$, $\alpha_{n\text{-heptanol}/H2O}$ and $\alpha_{n\text{-nonanol}/H2O}$ = 1.52; 6.5 and 14.95.

Simulation

For these studies, the simulation program is "ASPEN PLUS" (Trademark of Aspen Technology, Inc., Cambridge, MA), because the required physico-chemical parameters are stored in various data banks for a large number of components, and it can be used in a manifold range of applications.

The laboratory-scale model was optimized with this computer simulation program and compared with experimental data. The dependence of stage number and mass fraction is pointed out in Figure 2, where the curves represent the calculated values, while the symbols represent the experimental data, and it is shown that the calculated values fit the experimental data quite accurately. In this simulation, the tray efficiency has to be taken into account, which was found to be 57%. As only one bubble-cap per stage is used, the resulting value corresponds with the theoretically approved tray efficiency of 55-70%.

Set up for a combination of reaction and distillation process. Equipment in question are stirred vessels, cascades of stirred vessels, both with or without superimposed column, and reaction column, which are summarized in Figure 3. To increase the conversion the reaction parameters, like residence time, concentration of catalyst, temperature, and stoichiometric excess of one component, and the separation parameters, such as reflux, boilup, efficiency, and energy consumption, were optimized by varying the relative volatility and reaction velocity. The differentiation of the application related to energy consumption and conversion for these different types of equipment were determined. To support the selection of the most

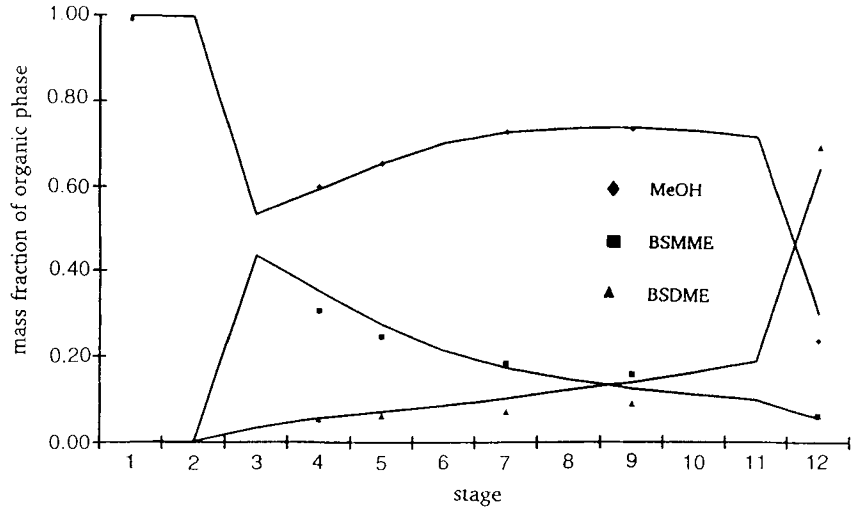
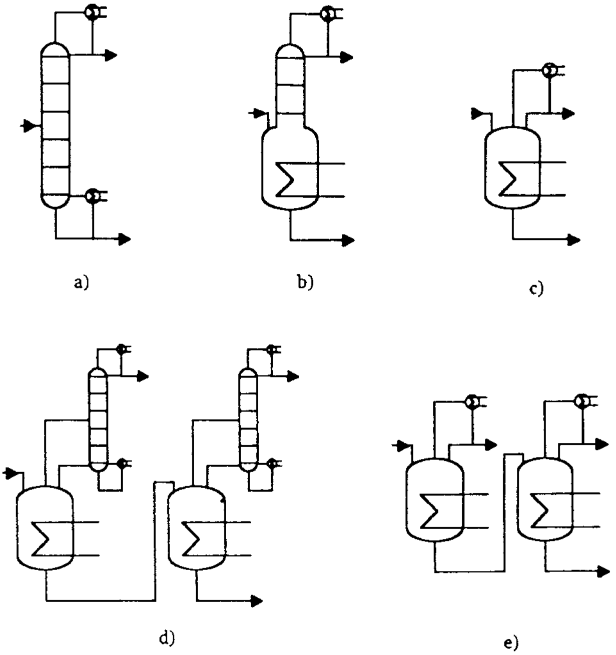


FIGURE 2. Comparison of experimental data and calculated values

suitable apparatus for a reaction with separation of one component, especially two parameters, the reaction velocity for the reaction term and the relative volatility, have to be considered. For the right choice of equipment, low and high relative volatility of the components have to be distinguished. The following simulations (Figure 4-6) were carried out by varying reaction velocity for components of low relative volatility (1.52) on the one hand and for high relative volatility (14.95) on the other hand, while all the other parameters remained constant.

Low volatility. Figure 4 shows the conversion for several kinds of equipment at a low reaction rate. It can be mentioned that independent of the choice of apparatus, about the same conversion can be obtained. In contrast to this is Figure 5, which takes a higher reaction rate into account, shows that the reaction column, the reactor with superimposed column, and the reactor with evaporation lead to the same conversion. For the reactor cascade with superimposed



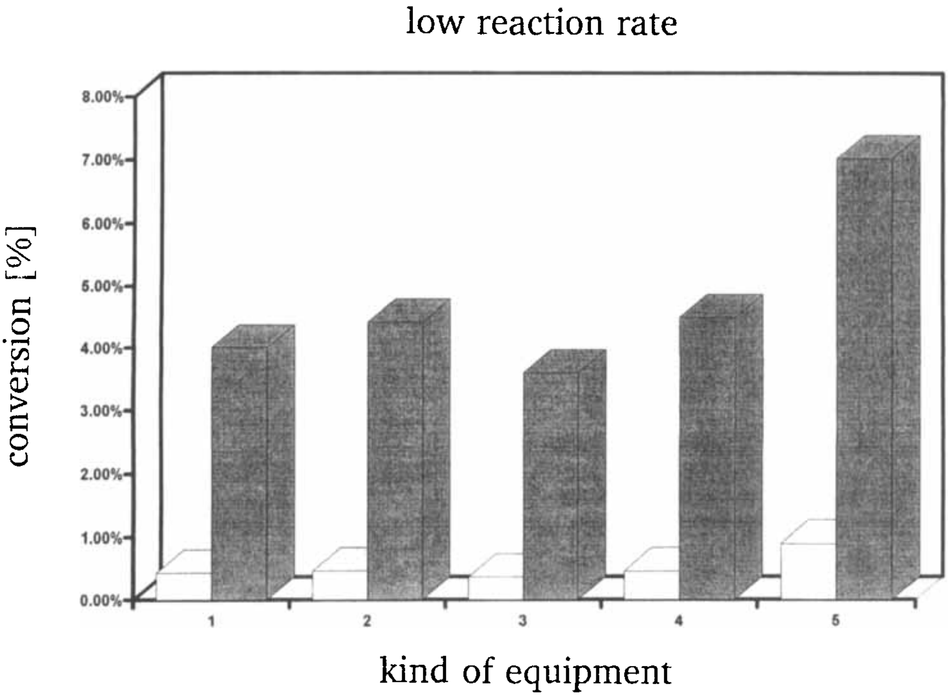
a) reaction column
b) reactor with superimposed column
c) reactor with evaporation
d) reactor cascade with superimposed column
e) reactor cascade with evaporation

FIGURE 3. Different kinds of equipment

column and reactor cascade with evaporation, there can be noticed a clear decrease in conversion.

Figure 6 points out the energy input for the considered apparatus at low reaction rates. It is obvious that the energy input of both reactor cascades is much higher than all of the other reactors. The energy inputs of reaction column, reactor with superimposed column, and reactor with evaporation are approximately equal.

High volatility. Considering Figure 4, an equal conversion can be obtained for reaction column, reactor with superimposed column,



1 reaction column
2 reactor with superimposed column
3 reactor with evaporation
4 reactor cascade with superimposed column
5 reactor cascade with evaporation

FIGURE 4. Choice of equipment as a function of conversion and low reaction rate (light plots: low volatility; dark plots: high volatility)

reactor with evaporation, and reactor cascade with superimposed column at low reaction rates, which is in contrast to the reactor cascade with evaporation, indicating an increase of conversion. In the case of high reaction rates (Figure 5), the reaction column is the equipment with the highest conversion and therefore, the apparatus of choice.

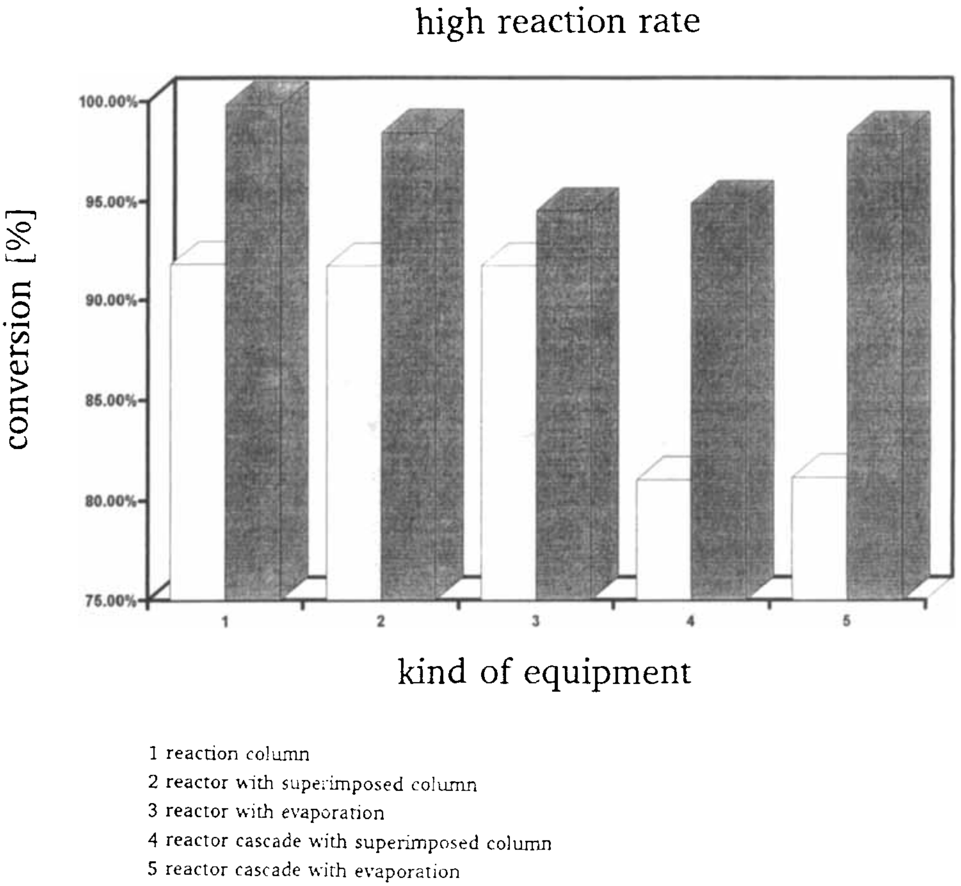


FIGURE 5. Choice of equipment as a function of conversion and high reaction rate (light plots: low volatility; dark plots: high volatility)

As is well known, the reaction column is the equipment set that consumes less energy, which can be seen in Figure 6. The reactor with superimposed column consumes the most energy, while the energy input of the remaining apparatus types are approximately equal.

The influence of volatility on conversion, which is shown in Figure 4, points out that the relation between high and low volatility remained constant. Therefore, the influence of relative volatility on the

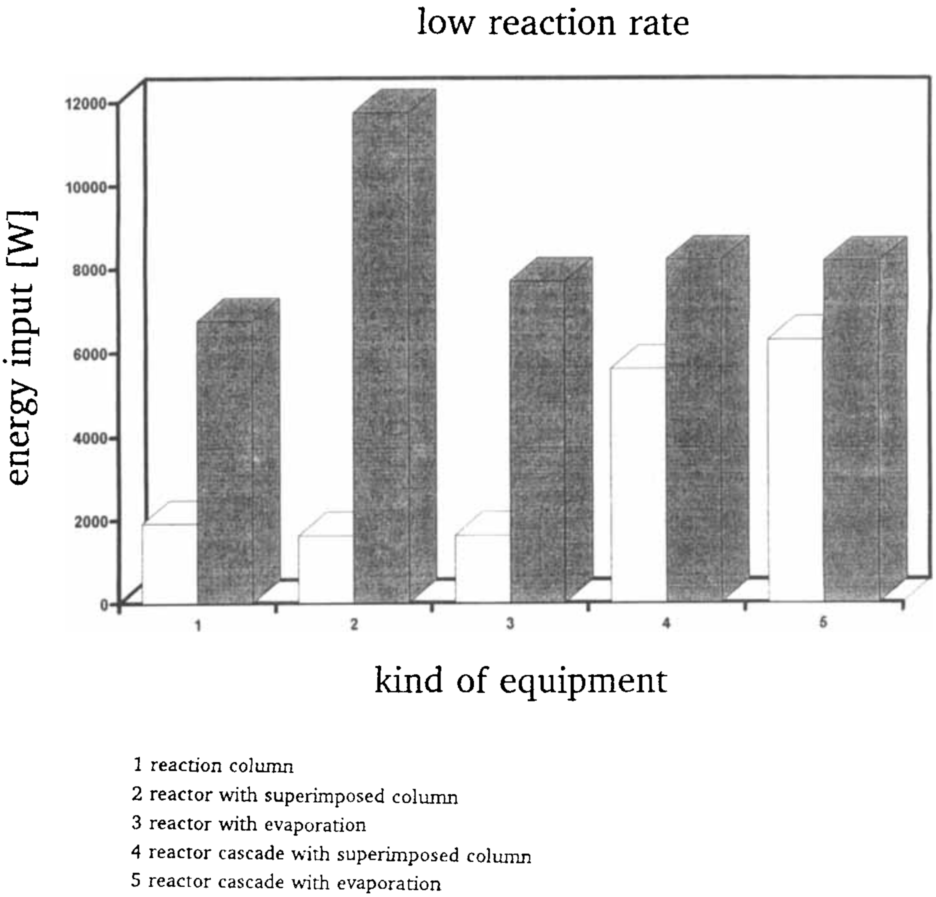


FIGURE 6. Choice of equipment as a function of energy input and low reaction rate (light plots: low volatility; dark plots: high volatility)

apparatus selection can be neglected. It also can be mentioned that for high volatilities, a higher conversion can be achieved than for low volatilities.

A similar trend can be recognized for high reaction rates, as shown in Figure 5. The relation of low to high volatility, expressed in percentage, is comparatively low to that at low reaction rates.

As a result of this reflection, it can be pointed out that the reaction column is the apparatus of choice for fast reactions and high volatilities considering the energy input. For low relative volatilities the choice is between the reaction column or the reactor with evaporation, depending on whether operating costs or investment costs are taken into account. Although the reactor with superimposed column is commonly used in industry, an evident disadvantage is its high demand for energy. Because of the high investment costs and the difficulties in automatic control, the reactor cascade with a superimposed column is scarce in industrial applications. Despite these disadvantages the reactor cascade with a superimposed column and the reactor cascade with evaporation, a simple and robust system, are similar to other apparatus with regard to energy input and conversion, except for high reaction rate and low relative volatility.

CONCLUSIONS

The reactive distillation of monomethyl succinate and methanol using sulfuric acid as a catalyst was studied in detail. Hence the residence time and not the chemical equilibrium at each stage was taken in consideration.

Several experiments, which were carried out in a laboratory scale column, were calculated with the help of a simulation software package and compared with the experimental values. The resultant simulation fits the data quite well. The information provided by these simulations and the exact knowledge resulting from the kinetic data give a profound simulation basis considering different apparatus set-ups.

As a result of this reflection, it can be pointed out that the reaction column is the apparatus of choice for fast reactions and high volatilities considering the energy input. For low relative volatilities the choice is between the reaction column or the reactor with evaporation, depending on whether operating costs or investment costs are taken into account. The future is in developing a short-cut equation, Reidetschläger (17) for quantitative prediction of the apparatus performance. Parameters are residence time, relative volatility, conversion, and kinetics of the system. Efforts will aim at minimizing the experimental expenditure on the one hand and increasing the application of computer simulation on the other, using appropriate kinetic information of the system considered.

NOMENCLATURE

G	steam flow [kmol h^{-1}]
x_i	molar fraction of component i in liquid phase [kmol $kmol^{-1}$]
y_i	molar fraction of component i in vapor phase [kmol $kmol^{-1}$]
L	liquid flow [kmol h^{-1}]
F	feed [kmol h^{-1}]
z	composition of feed
S	sidestream [kmol h^{-1}]
R_i	volume dependent rate of reaction of component i [kmol/m^3 h]
h	specific enthalpy [kJ/kmol]
Q	energy
ΔH^R	reaction enthalpy [kJ/h]
K	equilibrium constant
k_1, k_2, k_3	reaction rate constants [m^3 $kmol^{-1}$ h^{-1}]
c_{BSA}	concentration of succinic anhydride [kmol m^{-3}]
c_{H2SO4}	concentration of sulfuric acid [kmol m^{-3}]
c_{BSMME}	concentration of monomethyl succinate [kmol m^{-3}]
c_{BSDME}	concentration of dimethyl succinate [kmol m^{-3}]
c_{MeOH}	concentration of methanol [kmol m^{-3}]
c_{H2O}	concentration of water [kmol m^{-3}]
R	gas constant [J K^{-1} mol^{-1}]
T	temperature [K]
α	relative volatility
P_A	pressure of component A [bar]
P_B	pressure of component B [bar]
x_A	molar fraction of component A [kmol $kmol^{-1}$]
y_B	molar fraction of component B [kmol $kmol^{-1}$]

Subscripts

n	number of stages
A	component A
B	component B
C	component C
D	component D
i	component i

Superscripts

G	vapor phase
L	liquid phase
F	feed

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