Analysis of processing systems involving reaction and distillation: the synthesis of ethyl acetate

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Abstract

The integration of reaction and separation into a single process unit, i.e., reactive distillation, may offer several advantages over conventional systems that use a reactor followed by a distillation column. In this paper we explore the operational characteristics of reactive distillation and highlight some of its potential benefits, using the production of ethyl acetate as an illustrative example. With this aim, the two types of systems are compared employing different reactor types and a number of performance indicators, such as yield, conversion, purity, specific energy consumption and residence time. A sensitivity analysis is carried out on some variables and parameters, in order to explore and define the distillation columns operating conditions. As expected, results point to a clear advantage of reactive distillation, allowing for the azeotrope to be surpassed and for the overcoming of chemical equilibrium, favouring an increase in conversion and product purity, along with reduced operating costs.

1 Introduction

Reactive distillation (RD) systems, where reaction and separation take place in the same unit, present several potential advantages over conventional systems based on a reactor and distillation column (R+DC) combination. Although major limitations exist on the industrial applicability of this complex and difficult to operate process, when practicable, it allows for the reduction of both capital and operating costs due not only to process integration but also to the specific characteristics of the process itself.

A stronger case for RD is made for those reacting systems which exhibit reversible reactions and/or azeotropes, since in such cases conventional separations are more difficult and expensive. The conversion of reactants in a reaction zone inside the column allows for the separation of the products as they are formed, increasing the reaction extent and preventing the formation of azeotropes and secondary reactions and hence improving yield. Heat integration and the recycling of unused reactants are other benefits that contribute to the economic advantage of this operation. In addition, if the reaction is exothermic, the heat of reaction is used in situ for vaporisation, resulting in a reduced reboiler duty.

Several suitable RD processes have been described, such as etherifications, nitrations, esterifications, transesterifications, polycondensations, alcylations and halogenations (Kenig et al., 2001). Doherty & Buzad (1992) and Taylor & Krishna (2000), among others, describe the advantages of RD in industrial applications. The reduction of the number of equipments used is a major feature of RD, which is exemplified in the case of the production of methyl acetate at Eastman Kodak, where a remarkable saving in investment was achieved, since the use of RD allowed for a reduction to one single RD

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column instead of nine columns plus a reactor Schoenmakers & Bessling (2003). Despite the advantages presented, several factors may limit the successful application of RD. Since the application of this technology is highly dependent on the characteristics of the reacting system, it may not always be feasible. Thus, the relative volatility of reactants and products must allow for the separation of the desired product; for some systems the pressure and temperature conditions for the separation may not be the most adequate for the chemical reaction; reactive azeotropes may be formed.

The complex interactions inside the column due to the simultaneous occurrence of reaction, vapour-liquid equilibrium and mass transfer, and the possibility of several steady-states make, the operation difficult and place high requirements on design and control. Although the first patents date back to the 1920s Taylor & Krishna (2000), and a growing interest in the area is noticeable for the last 35 years (Sundmacher & Kienle, 2003), there is still a considerable lack of practical knowledge and experience in the area.

There are a number of feasibility methods which can be used to prospect the adequacy of RD for a particular reacting system (Giessler et al., 1998, Chadda et al., 2000, Gadewar et al., 2002). The aim of this work is, however, to investigate those relevant aspects that need to be taken into account by the engineer, when considering the use of RD. For this, an illustrative example, which is a successful case, i.e. the synthesis of ethyl acetate by the esterification of the acetic acid with ethanol, is used and a comparison between two alternative processing systems carried out: (a) conventional reactor followed by distillation column and (b) RD system. The analysis of steady state simulation results for the systems (a) and (b) is used to highlight the advantages of the RD over the conventional approach, on the basis of different criteria, such as product specification, yield, conversion, equipment size and energy demand.

2 System description

Ethyl acetate is an organic solvent used in industrial lacquers and enamels and for the production of photographic films, adhesives and nail varnishes. It is also used as an extraction solvent in the production of pharmaceuticals and food, and as a carrier solvent for herbicides. Ethyl acetate (EtAc) is produced, among other processes, in an esterification reaction between acetic acid (AA) and ethanol (Et), giving ethyl acetate and water (W).

$$\underset{\text{AA}}{CH_3COOH} + \underset{\text{Et}}{CH_3CH_2OH} \rightleftharpoons \underset{\text{EtAc}}{CH_3CH_2COOCH_3} + \underset{\text{W}}{H_2O}$$

The rate of reaction as described by (Lee & Dudukovic, 1998) is given by:

$$r = e^{\left(\frac{-7150}{T}\right)}\left(48500\, C_{AA} C_{Et} - 12300\, C_W C_{EtAc}\right) \tag{1}$$

where C_{AA}, C_{Et}, C_W and C_{EtAc} are concentrations (mol l^{-1}) of acetic acid, ethanol, water and ethyl acetate, respectively, r is the reaction rate (mol l^{-1} s^{-1}) and T is temperature (K). As suggested by this equation, reaction kinetics are low and the equilibrium constant (3.94) is temperature independent and limits the attainable equilibrium conversion to 66.5%. The reaction normally takes place in the presence of sulphuric acid as a catalyst (homogeneous catalysis). The azeotropes for this system are shown in Table 1 and it may be seen that the low boiling ternary azeotrope (EtAc/EtOH/W) limits the purity of ethyl acetate obtainable by conventional distillation to 58.7%.

Table 1 – Normal boiling points and azeotropes for the ethyl acetate system

AA mol%	Et mol%	EtAc mol%	W mol%	BP ºC
	15.9	58.7	25.4	70.1
		69.0	31.0	70.6
	44.6	55.4		71.8
	90.8		9.2	77.1
		100.0		78.2
	100.0			78.4
			100.0	100.0
100.0				117.9

Adapted from (Kenig et al. 2001)

The characteristics of this highly non-ideal quaternary system, with three binary and one ternary azeotropes, made it a successful case in RD: the reaction is reversible and the kinetics are low, which would require a long residence time to reach near equilibrium conditions; the presence of azeotropes makes it unsuitable for conventional distillation; the volatilities of the components are favourable to the separation of the ethyl acetate in the distillate.

3 Modelling

Two processing scenarios were defined and the steady state simulation results for both systems analysed. In case of system (a) we used three different reactor types (CSTR, battery of CSTR in series and plug flow) followed by a distillation column, while in system (b) a single RD column was used. For both systems the reaction is considered to occur only in the liquid phase. The catalyst, sulphuric acid, is not explicitly used in the simulation, but its effect is accounted for by using adequate reaction kinetics (see equation (1)). Considering that the uncatalysed reaction is about 100 times slower than the catalysed one (Lee & Dudukovic, 1998) and that the sulphuric acid is fed with the acetic acid, the limited extent of reaction, which may occur in the trays of the RD column above the feed tray, can be neglected, which justifies the approach used.

The simulation work was conducted on the Aspen Plus package, with the NTRL-HOC model being employed for the column, since this has proved successful with this system (Tang et al., 2003). NRTL is used to calculate liquid activity coefficients, while the Hayden-O'Connell equation of state, which predicts dimerization in the vapour phase, is used to calculate thermodynamic properties for the vapour phase.

3.1 Reactor followed by separation

For the three reacting systems the pressure was set to 1 atm and the temperature of the feed stream and reactor to 60 ºC. Different residence times (RT) were tested to determine the operational conditions for the reactors. Table 2 and Table 3 sum up these results. Increasing residence time leads to an increased conversion, with the higher values indicating near equilibrium conditions, at the expense of long residence times.

The molar fraction of ethyl acetate reaches a maximum of 0.3256 in the stream leaving the PFR, for a residence time of 5 hours. This is taken as the inlet stream for the distillation column.

Table 2 – Conversion (%) at 60 ºC

Reactor \ RT (h)	1	2.5	5
CSTR	31.10	44.59	52.88
5 CSTR	37.57	54.81	65.10
PFR	39.88	58.28	65.29

Table 3 – EtAc mole fraction at 60 ºC

Reactor \ RT (h)	1	2.5	5
CSTR	0.1551	0.2224	0.2637
5 CSTR	0.1874	0.2734	0.3136
PFR	0.1989	0.2907	0.3256

In order to purify the ethyl acetate, a distillation column with 13 trays was set. Sensitivity analysis were conducted on some parameters and variables - feed tray (FT), reflux ratio (RR) and distillate rate (DR) - in order to adjust the operational conditions. The procedure applied, and the results obtained are summarized in Table 4. Starting from the initial conditions shown, the variable or parameter along the sequence was varied in turn over the indicated range in order to maximize yield, under the condition that the composition of the distillate remains within an acceptable narrow range. When the gain in yield is negligible, the prior value of the variable is kept. The same variable/parameter may occur more than once in the sequence if further gains are envisaged. The mole fraction obtained for the ethyl acetate in the distillate stream is 0.5336, which corresponds to a global yield of 64.51% and a reactor conversion of 65.29%. The column operates at 1 atm, feed point on tray 3 and the temperature varies between 95.25 and 70.25 ºC, at the reboiler and condenser, respectively. Figure 1 shows the liquid composition in the column and Figure 2 (a) summarizes the final operating conditions.

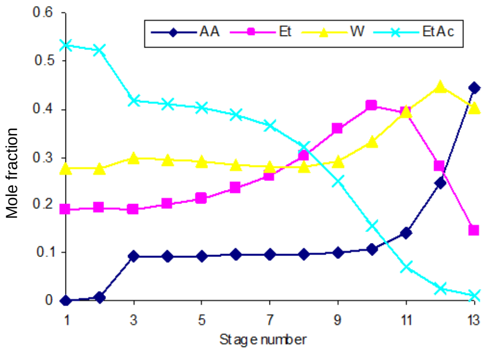


Figure 1 - Liquid composition profile (case (a))

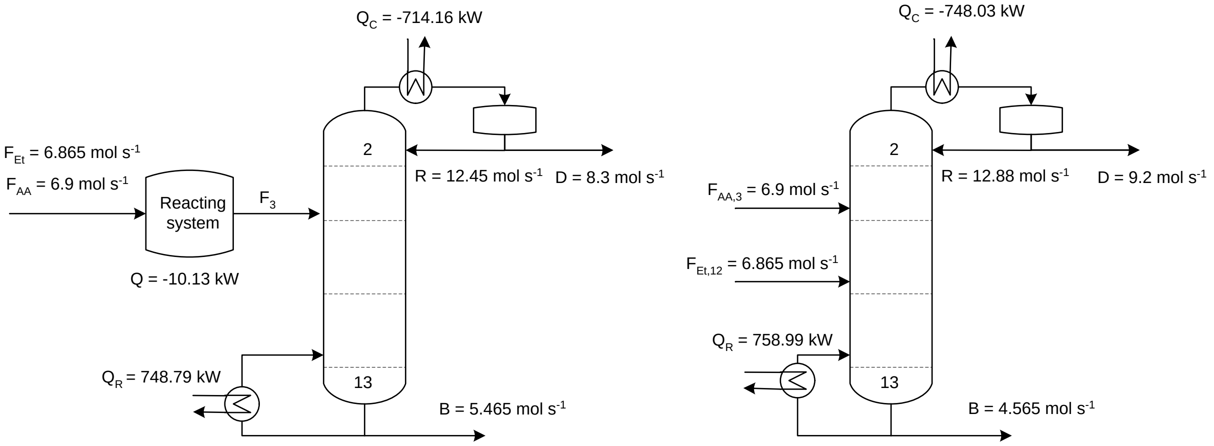
Table 4 – Sensitivity tests procedure applied to the distillation column operating conditions (case (a))

Test variable/parameter (range)	Operational conditions			Performance indices	
	RR	FT	DR (mol s^{-1})	Y (%)	EtAc (mole fraction)
Initial conditions	1.5	6	6.68	52.10	0.5354
RR (0.1-10)	1.5			52.12	0.5356
FT (1-13)		3		52.27	0.5372
RR (0.1-6)	1.5			52.27	0.5372
DR (1-13)			8.3	64.51	0.5336
RR (0.1-6)	1.5			64.51	0.5336
FT (2-6)		3		64.51	0.5336

3.2 Reactive distillation

Preliminary tests were conducted under conditions typical of a configuration commonly reported for this system, that is, 13 trays, a single feed point (tray 6) and a reflux ratio of 10. The ethyl acetate composition (51.8%) is found to be below the azeotrope composition (55.4%) for the binary ethanol-ethyl acetate azeotrope, the conversion (64.9%) below the equilibrium (66.0%) and a very low yield (22.65%) achieved.

An analysis of the operating conditions was then undertaken. The values of RR, FT, DR and, now, also the RT, were varied in an attempt to improve column performance. The procedure used was similar to the one presented in Table 4. The values obtained were RR = 4, DR = 9 mol s^{-1}, FT = 6, Y = 68.23% and EtAc = 0.5205. Only minor changes were achieved in purity and conversion (< 0.5%), although an improvement of about 46% was registered for the yield.



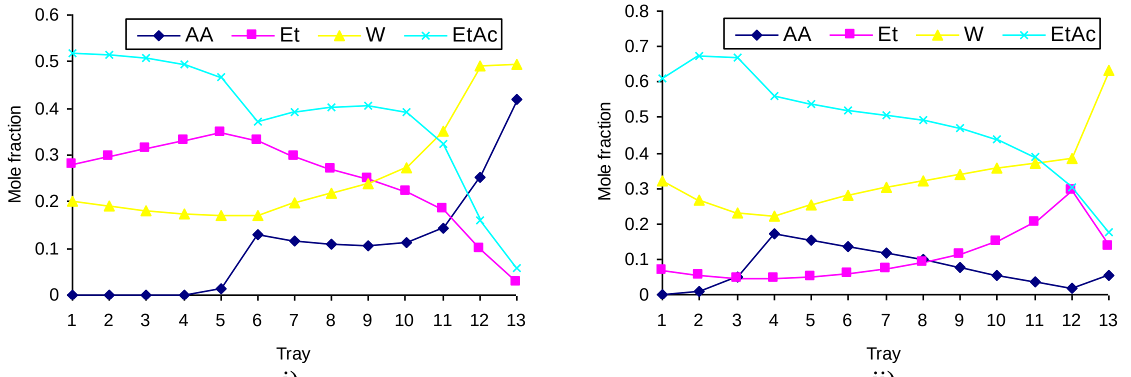
(a) **(b)**

Figure 2 – Schematic representation of the simulated systems showing final operating conditions

The composition profile obtained with this first configuration is shown in Figure 3 i) and it is noticeable that the acetic acid is displaced towards the lower section of the column, resulting in very low concentrations on the upper section and, thus, very low reaction rates being achieved in this zone irrespective of the presence of the catalyst. Also, much of the ethanol feed leaves the column top, and its concentration on the lower section is quite low. These results suggest that a two feed point configuration, whereby the acetic acid is fed near the top and the ethanol near the bottom, would be more appropriate, as it would allow a better distribution of the reactants along the column.

Hence, a new configuration with the specifications presented in the first column of Table 5 was implemented and new sensitivity tests applied according to the previous procedure. In the case of the feed trays, a complete experimental design was employed for the simulation, whereby 13x13 column configurations were explored. The best yield (68.70%) was found for FT = 4 for the acetic acid and FT = 12 for the ethanol. Figure 4 and Figure 5 show the influence of each feed location. The residence time was analysed next. For trays 1 to 12 the residence time was adjusted to 90 seconds, while for the reboiler (tray 13) a higher value of 900 seconds was selected to account for the larger residence times required in real systems.

When RR was tested, a value of 1.8 leading to a yield of 68.96% was obtained. The DR was subsequently tested and its value changed to 9.2 mol s^{-1} leading to a better yield of 90.00%. As it can be seen in Figure 6, the maximum yield is in fact above this value, but it corresponds to a very unfavourable value of ethyl acetate purity, in a region with a negative slope. As a compromise the indicated value of DR was selected, which corresponds to EtAc = 0.6716. A final improvement was achieved for RR = 1.4 which resulted in Y = 90.08% and EtAc = 0.6716.



i) ii)

Figure 3 – Profile composition in liquid over the RD column: i) one feed point (tray 6), ii) two feed points (trays 4, 12)

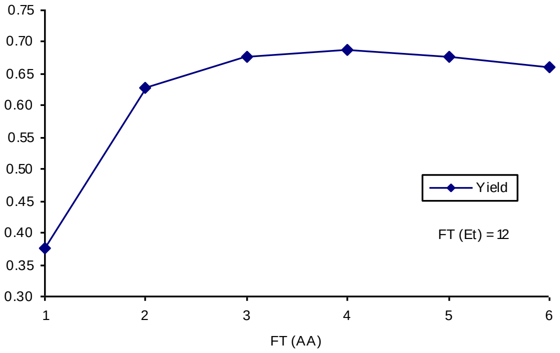


Figure 4 - Influence of AA feed location

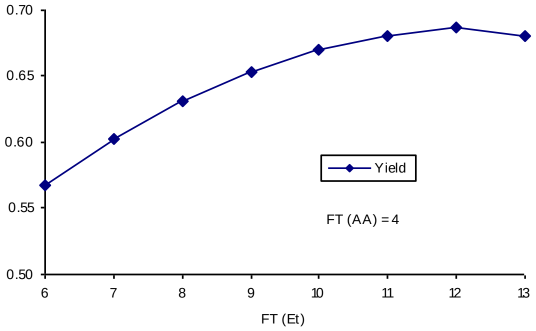


Figure 5 – Influence of Et feed location

4 Analysis and final remarks

In this work, steady-state simulation was applied to the comparison of the performance between a conventional R+DC and a RD column. Both cases dealt with the same reacting system, namely the synthesis of ethyl acetate.

Indices familiar to the plant engineer were employed in association with a sensitivity evaluation procedure in order to adjust the operating conditions of the two systems and to assess their relative performance.

For the same feed conditions, the RD system is found to lead to a substantially higher yield together with higher product rate, purity and lower residence time (see Table 6). The heat demand is similar for both systems, with an apparent slight advantage of case (a), when the reboiler and condenser heat-loads are directly compared. However, a

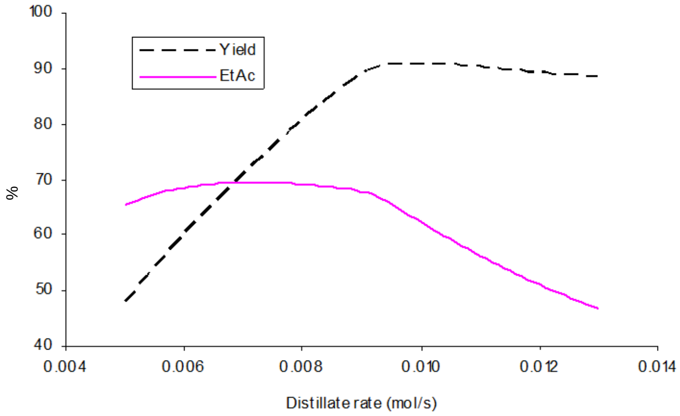


Figure 6 – Influence of distillate rate in yield and EtAc purity

clearer advantage of the RD system is found, when both the distillation rate and mole fraction, which are significantly more favourable in case (b), are taken into account in an integrated index such as the specific energy consumption (SEC = Qr / (DR * C_{EtAc})), which measures the energy requirements per mole produced.

Table 5 - RD column specifications

	Initial conditions	Final conditions
Number of trays	13	13
Feed trays	2 (AA), 12 (Et)	4 (AA), 12 (Et)
Reflux ratio	2.0	1.4
Residence time (s)	1580	1980
Distillate rate (mol s^{-1})	6.68	9.20

If this index is extended to include the total energy demand, with the inclusion of the energy removed at the condenser and at the reactor, the values 243.72 and 332.61 kJ mol^{-1} are found, respectively for systems (b) and (a), which again point to a clear advantage of RD over R+DC and to lower operating costs for the former.

A simple economic evaluation exercise would also demonstrate, in the case of RD, the need for lower capital investment and a higher return, given the lesser requirements on equipment and the more satisfactory product specifications, which are achieved with unit integration, which, in the present case, proves instrumental in overcoming both equilibrium restrictions and at least one ternary azeotrope.

Table 6 – Comparison of final results achieved with the systems tested

	System (a)	System (b)
DR (mol s^{-1})	8.3	9.2
Y (%)	64.52	90.08
C_{EtAc} (mole fraction)	0.5336	0.6721
RT (s)	> 18000	1980
Q_r (kW)	748.79	758.99
Q_c (kW)	-714.16	-748.03
Q_{rs} (kW)	-10.13	-
SEC (kJ mol^{-1})	169.07	122.75

Although the application of this technology is system dependent, for adequate reacting systems the process integration can lead to remarkable results. Reduced number of equipments, higher conversion and greater product purity, together with a shorter processing time, clearly demonstrate the advantages of process integration

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