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COMBINING DISTILLATION AND HETEROGENEOUS CATALYTIC REACTORS

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The hardware design of reactive distillation (RD) columns pose severe challenges with respect to the choice and design of the hardware; the requirements of reaction (i.e. high liquid or catalyst holdup) are not in consonance with the requirement of separation (high interfacial area). In this paper we examine an alternative to the RD concept, namely a distillation column networked with a single side (external) reactor, which we call the SR concept. For the case study of tertiary-amyl ether (TAME) production by reaction of isoamylene (IA) with methanol, we show that employing the SR concept it is possible to meet the design targets of IA conversion, TAME purity in bottom product and TAME impurity in top product using just one side reactor. From detailed hardware designs, we see that the RD column is significantly taller than the distillation column in the SR configuration; this is due to the placement of the catalyst load *within* the RD column. We conclude that the SR concept will be competitive with the RD column configuration provided the IA conversion targets are not too stringent.

Keywords: reactive distillation; side-reactor; TAME synthesis; column hardware; column design.

INTRODUCTION

There is considerable industrial and academic interest in reactive distillation (RD) as a means of improving the conversion of equilibrium-limited reactions such as etherifications and esterifications (Doherty and Malone, 2001; Taylor and Krishna, 2000). In a heterogeneously catalysed RD column we need to maximize the catalyst holdup to achieve high conversions. The requirement of high catalyst holdup in a RD column is not consonant with the requirement of good *in-situ* separation, for which we need to maximize the interfacial area between vapour and liquid. All available hardware configurations (tray or packed RD columns) represent a compromise between the conflicting requirements of reaction and separation (Krishna, 2002; Taylor and Krishna, 2000).

One way to overcome the above-mentioned hardware problems with RD columns, while maintaining the benefits of *in-situ* separation with reaction, is to employ the side-reactor (SR) concept (Baur and Krishna, 2003; Jakobsson *et al.*, 2002; Schoenmakers and Buehler, 1982; see Figure 1). In the SR concept the reactor feed is withdrawn from the distillation column and the reactor effluent is returned back to the same column. The SR could be a conventional catalytic packed bed reactor operating in liquid phase and therefore there are no hardware design problems or conflicting requirements with regard to *in-situ* separation. Furthermore, the reaction conditions within the SR (e.g. temperature) can be adjusted independently of those prevailing in the distillation column by appropriate heat exchange.

In principle we can distinguish four configurations for linking the SRs to the distillation column; these are shown in Figure 1(a)–(d). The pump around can be located in such a way that liquid bypasses intermediate stages; see Figure 1(a). The liquid is withdrawn from stage j and possibly mixed with an additional feed stream before it is pumped to an SR. The stream leaving the SR is fed back to the column at stage k. The amount of liquid pumped around, L_{RPA}, can either be specified by an absolute molar flow rate or by a pump-around ratio, *RPA*, with regard to the molar flow entering the stage below, L_j. In this case the reactor throughput is limited to a maximum fraction of the internal flows in the distillation column. Increasing the pump around flow rate above that limit would dry out the intermediate stages in the column, and significantly decrease the separation performance. We call this configuration *co-current reactive pump-around.* Figure 1(b) shows an alternative configuration where the SR flows are *counter-current* to the internal liquid stream in the distillation column. The throughput in the reactor can exceed the original internal flows in the distillation column, but also might cause flooding on intermediate stages and demands additional

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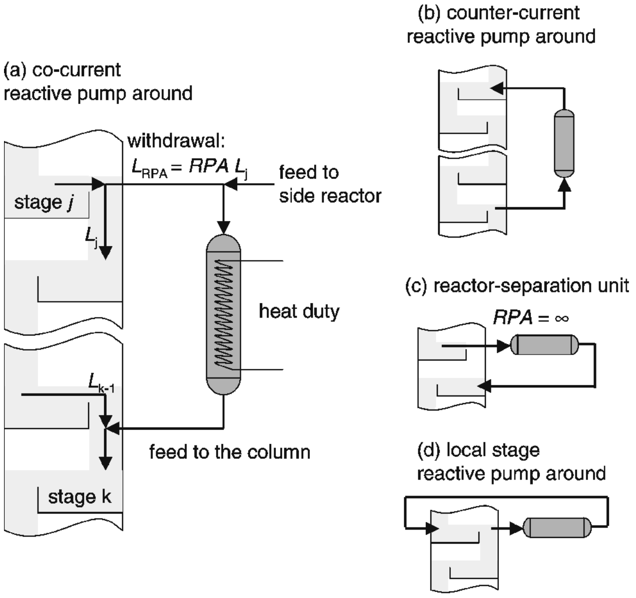

Figure 1. Schematic diagram of different side reactor configurations, adapted from Baur and Krishna (2003).

energy input. Both configurations (a) and (b) cause a change of internal flow rate.

Co- and counter-current reactive pump-around configurations have two limiting cases, shown in Figure 1(c) and (d), respectively. Of practical importance is the case where the stream leaving a stage is completely re-routed through an SR before it is fed back to the stage below; see Figure 1(c). We call this configuration a reactor-separation unit. Since no stages are bypassed, the entire liquid stream leaving the stage will be pumped through the reactor. The product stream of SR might be fed to the downcomer at the same stage; see Figure 1(d). This configuration is called the 'local stage reactive pump-around'.

The determination of the required number of SRs, along with the liquid draw-off and feedback stages needs careful attention and consideration. For manufacture of methyl acetate (MeOAc), Baur and Krishna (2003) developed an algorithm to determine the optimum location of the SRs and showed that at least six SRs, with a high pump-around ratio *RPA* of about 6, are required to obtain the 99% conversion levels obtainable in an RD column. The conversion obtained with one SR is limited to below 80%. Since the number of SRs to meet the high 99% conversion level targets for MeOAc production is exceedingly large, the SR concept cannot compete with the RD concept that is currently in commercial use. In another study, Jakobsson *et al.* (2002) have used just one SR for the isobutene dimerization process. However, no comparison was presented with a conventional RD column, nor are details of the achieved conversion levels given.

The MeOAc process study of Baur and Krishna (2003) shows the SR concept in a pessimistic light, and the major objective of our paper is to demonstrate that for *etherification* processes the SR concept could be much more attractive. We undertake a case study for production of tertiary amyl-ethyl (TAME) in order to underline the benefits of the SR concept over RD.

BASE CASE DESIGN FOR RD COLUMN

TAME is formed by reversible, acid-catalysed, exothermic reaction of iso-amylenes (IA), consisting of the isomers 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B), with methanol

$$\begin{aligned} &\text{methanol} + \text{2M1B} \leftrightarrow \text{TAME} \\ &\text{methanol} + \text{2M2B} \leftrightarrow \text{TAME} \end{aligned} \tag{1}$$

The two iso-amylenes undergo isomerization according to:

$$\text{2M1B} \leftrightarrow \text{2M2B} \tag{2}$$

The reaction kinetics for equations (1) and (2) are given by Sundmacher, Hoffmann and co-workers (Sundmacher *et al.*, 1999; Thiel *et al.*, 1997). The reaction equilibrium constant was calculated following Rihko and Krause (Rihko *et al.*, 1997; Rihko and Krause, 1995). The catalyst activity has been specified as $900\,\text{eq}[\text{H}^+]\,\text{m}^{-3}$; the overall catalyst volume depends on the type of packing and voidage in the reaction zone.

The process scheme used in our design study essentially follows that of Subawalla and Fair (1999), as adapted by Baur and Krishna (2002) and shown in Figure 2(a). The flow scheme consists of a pre-reactor followed by an RD column. The use of an isothermal pre-reactor is advantageous because high overall TAME production rates can be obtained. In our study we assume a pre-reactor with an IA conversion of 62.7%. Essentially we aim for a minimum IA conversion of 92%, maximum TAME impurity in top product of 50 ppm and a minimum TAME purity of 99.6% in the bottoms product from the RD column. Using short-cut methods, the conceptual design of the RD column consists of a total condenser (stage 1) and a partial reboiler (stage 35), and a total of 35 theoretical stages; see Figure 2(a). The column is divided into three sections, consists of: (1) a rectifying section (four stages); (2) a reactive section in the middle (19 stages) loaded with $36\,\text{m}^3$ of supported acid catalyst; and (3) a stripping section (10 stages). The effluent from the pre-reactor, which contains $157\,\text{kmol}\,\text{h}^{-1}$ of TAME, is fed in the middle of the stripping section in order to ensure that TAME in the pre-reacted feed is stripped off before it reaches the reactive zone, otherwise it will revert back to IA and methanol at the bottom of the reactive section.

The equilibrium stage (EQ) model was used to determine the performance of the chosen RD column configuration. Vapour pressures were calculated with the extended Antoine equation. The liquid phase activity coefficients were estimated using the UNIQUAC model, and vapour phase fugacity coefficients were determined using the Soave–Redlich–Kwong equation of state. The parameters used are reported in our previous study (Baur and Krishna, 2002). As shown in Table 1, the RD column is able to achieve the specified design targets with a reflux ratio of 1.5 and a reboiler load of 17.66 MW. The performance of RD configuration is specified in Table 1 and the liquid phase mole fractions profiles in the column are shown in Figure 3(a).

THE SR CONCEPT FOR TAME

Let us now consider the performance of a distillation column, networked with a single SR. In order to get an idea of the influence of the placement of the SR on the IA conversion, we fix the value of *RPA* at 1, and consider all

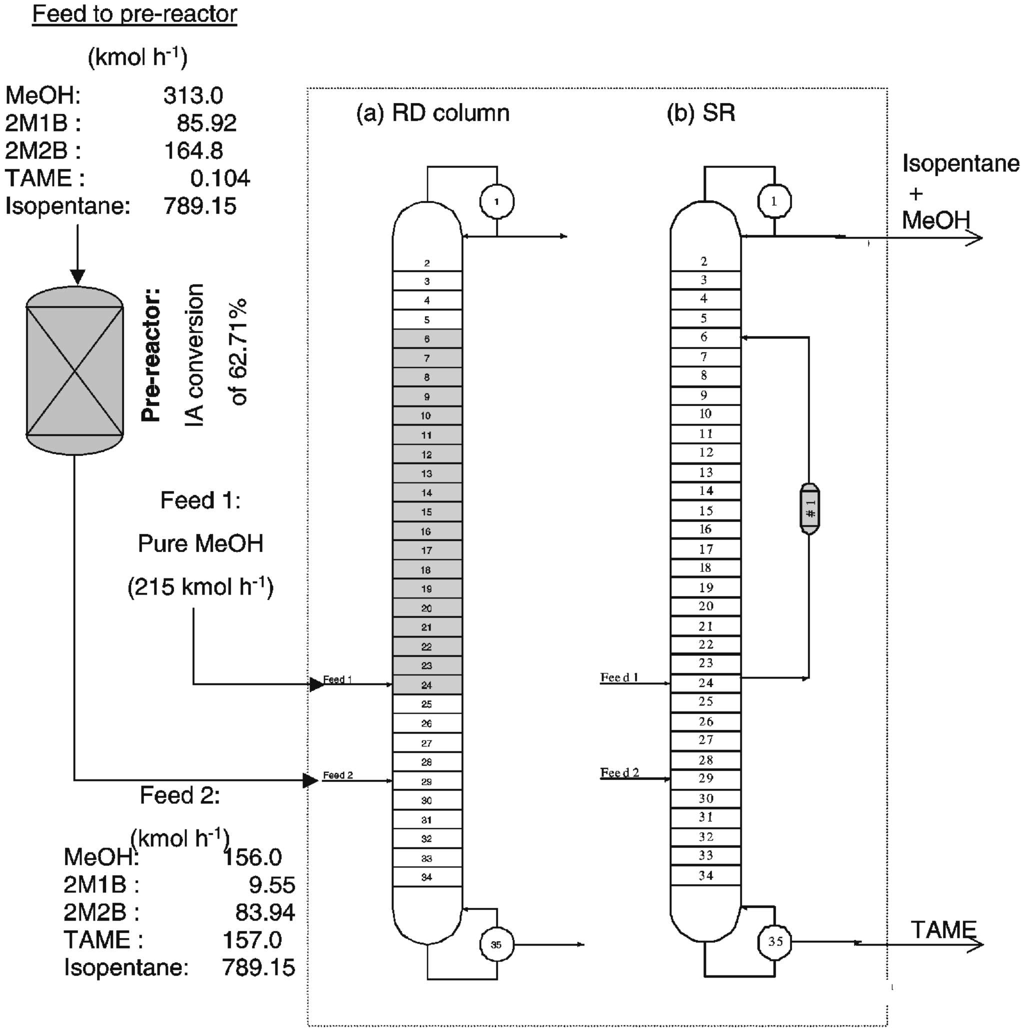

Figure 2. Two different configurations for TAME synthesis: (a) RD concept, and (b) distillation column networked with one SR. The process details are given in Baur and Krishna (2002) and Subawalla and Fair (1999). The reaction zones are marked in grey.

possible combinations of the liquid withdrawal and liquid feedback stages; the calculations are shown in the conversion map in Figure 4. The reflux ratio of the distillation is kept at 1.5, equal to the RD column. In determining the overall conversion level, the side reactor is assumed to have a catalyst activity corresponding to 900 eq[H^+] m^{-3} and the amount of catalyst is varied such that chemical reaction equilibrium is achieved in every case. This will ensure that the conversion in the side reactor is the maximum achievable. The co-current reactive pump around concepts (see Figure 1a) all lie in the left upper triangular region of Figure 4 and have IA conversion levels in the 79–79.5% range. The performance of the local stage reactive pump-around (see Figure 1d) are described by the conversion levels along the diagonal line and conversions are practically independent of the stage number and have values of 79.5% range. The reaction–separation units (see Figure 1c) lie parallel to the local stage pump-around and have a slightly higher conversion of 84.5%. This higher conversion is due to the fact that the entire liquid is routed through the side reactor ($RPA = \infty$). The counter-current reactive pump around concept (see Figure 1b) have conversion levels as in the bottom right triangular region of Figure 4. The best configuration corresponds to the SR whose feed is withdrawn from stage 24 and whose effluent is routed back to stage 6; this yields an IA conversion of 87.5%. This ‘best’ configuration is pictured in Figure 2(b).

From the results of Figure 4 we can conclude that the counter-current pump-around (stage 24 back to stage 6) has the potential of meeting with the design targets, after adjustment of the reflux ratio R and the pump-around ratio RPA. The influence of these two parameters on (a) IA conversion, (b) TAME impurity in top product, (c) TAME purity in bottom product, and (d) the bottom product flow rate are shown in Figure 5. The desired targets are also indicated in Figure 5 by means of dotted lines. Increasing both R and RPA has the general effect of improving the IA conversion and reducing the TAME impurity in the top product. All target specifications are met with a choice $R = 2$ and $RPA = 1.4$. We proceed further with detailed designs of the column hardware considering two configurations of the SR concept: case A, $R = 2$, $RPA = 1.0$ (IA conversion = 91%), and case B, $R = 2$, $RPA = 1.4$ (IA conversion = 92%). The performances of these two SR configurations are specified in Table 1 and the liquid phase composition profiles are shown in Figure 3(b) and (c).

Table 1. Design specifications and performance of RD and SR configurations.

Description	RD concept	SR concept: case A	SR concept: case B
Number of theoretical stages			
Rectifying section	4	4	4
Reactive zone	19	19	19
Stripping section	10	10	10
Feed location			
pure MeOH feed located on stage	24	24	24
pre-reacted feed located on stage	29	29	29
Operation			
Reflux ratio	1.5	2.0	2.0
Reboiler load, MW	17.66	21.83	21.69
Operating pressure, bar	4.5	4.5	4.5
IA overall conversion, %	97	91	92
TAME impurity in the distillate, ppm	8.92	29.15	30.14
TAME purity in the bottom product, %	99.92	99.74	99.17
Catalyst specifications			
catalyst activity, eq[H^+] m^{-3}	900	900	900
catalyst volume, m^3	36	36	55
Side-reactor specifications			
Pump-around ratio, *RPA*	n.a.	1.0	1.4
Liquid is withdrawn from stage	n.a.	24	24
Side-reactor effluent is routed back to stage	n.a.	6	6
IA conversion within side-reactor, %	n.a.	51.51	48.13

HARDWARE DESIGN COMPARISONS FOR RD AND SR CONCEPTS

The equilibrium (EQ) stage model for distillation column, detailed earlier (Baur and Krishna, 2002) was used to determine the vapour and liquid loads inside the distillation column and these are plotted in Figure 6. We note that, for the SR configurations A and B, the liquid loads are much higher in the reaction section than for the RD configuration. This is due to the pumping around of the liquid. For SR case B, the RPA = 1.4 and the liquid loads are significantly higher than for case A. For hardware design purposes it was convenient to divide the distillation column into four sections as specified in Table 2 and shown schematically in Figure 6. Owing to the strong variation of the liquid flows in the stripping section we carried out the hydrodynamics and mass transfer calculations in two separate stripping sections III and IV. Note that the 'Reaction' section for the SR concept is non-reactive. We choose Sulzer BX packing for all four sections of the SR concept. For the RD configurations, we use catalytic bales in the reactive section II (Baur and Krishna, 2002). The pressure drop and mass transfer (HETP) calculation procedures are as outlined in earlier work (Baur and Krishna, 2002; Rocha *et al.*, 1993, 1996; Subawalla *et al.*, 1997).

The column diameter was chosen so as to remain below an 80% flooding limit in all sections. For all three configurations, a choice of 3.5 m column diameter ensured that this constraint was met; the percentage flood values are shown in Table 2. For all three configurations the sections II and IV are limiting factors for flooding. Furthermore, we notice that the increased liquid flow in case studies A and B does not alter the column diameter. Generally speaking, a counter-current SR will predominantly increase the liquid flow rate, but not significantly the vapour flow rate. This is

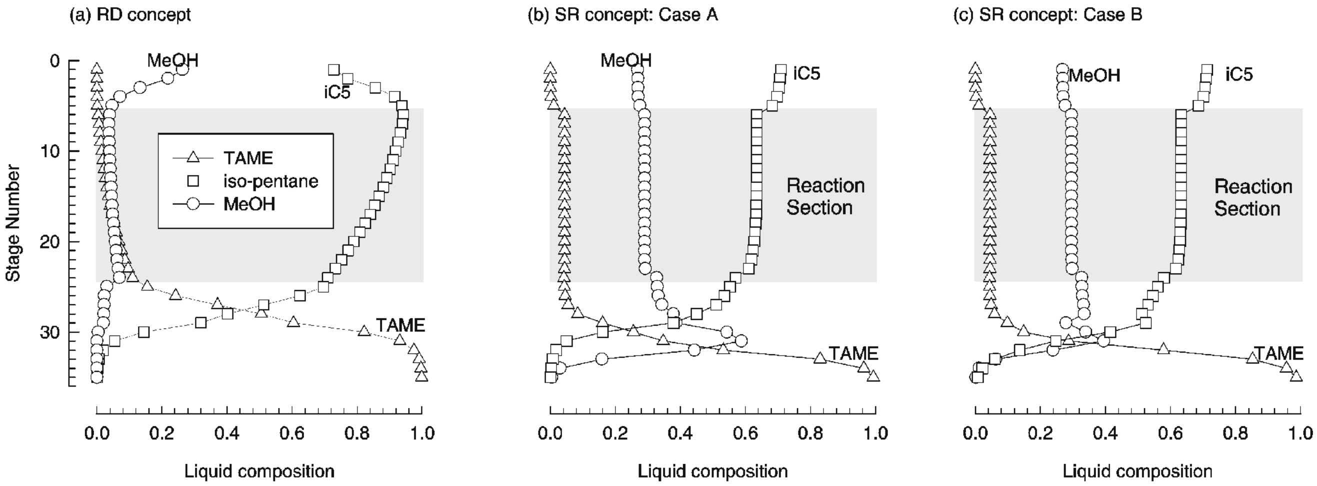

Figure 3. Liquid phase mole fraction profiles for TAME, iso-pentane and MeOH for RD and SR configurations.

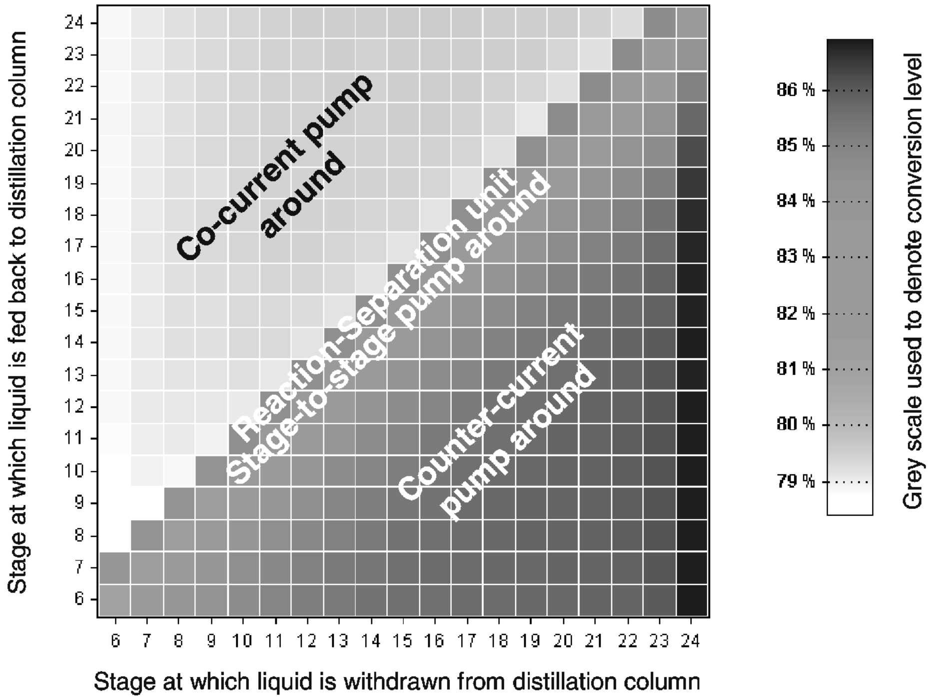

Figure 4. Overall IA conversion map for all the possible configurations that a separation column and a single SR can be networked each another. The pump around flow ratio *RPA* was fixed to 1.0 in all cases, except for the reaction-separation unit (Figure 1d). The reflux ratio *R* of the distillation column is 1.5.

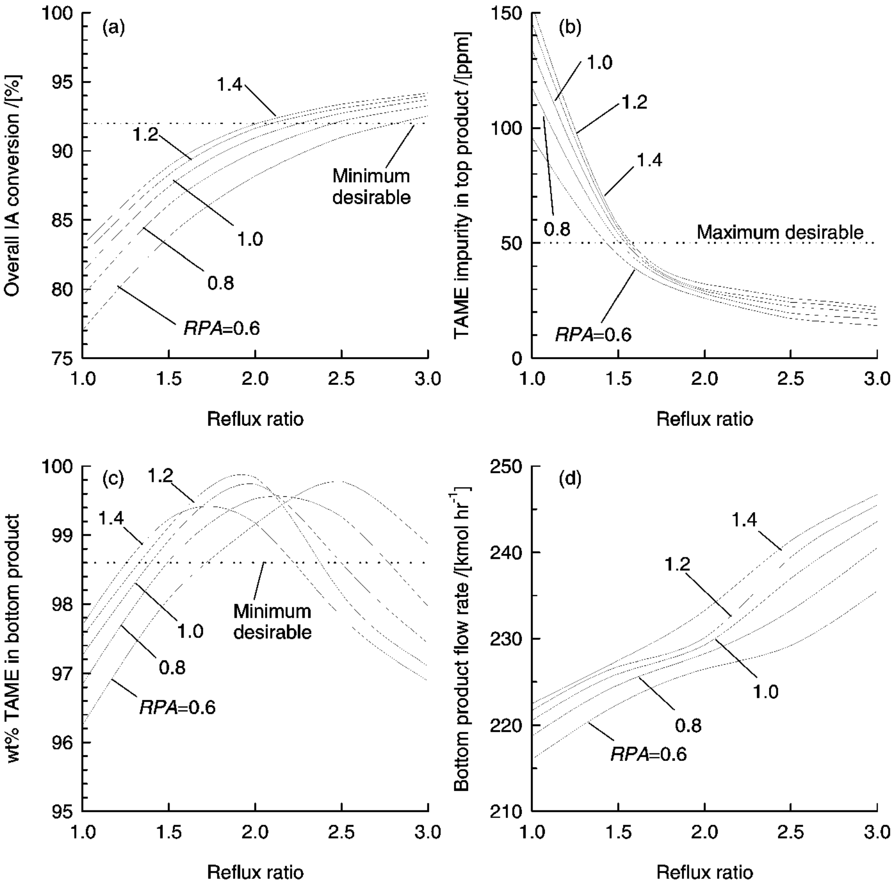

Figure 5. Performance of the SR concept as a function of the reflux ratio in the distillation column, *R*, and the pump-around ratio *RPA* through the side reactor. The side-reactor configuration corresponds to that shown in Figure 2(d).

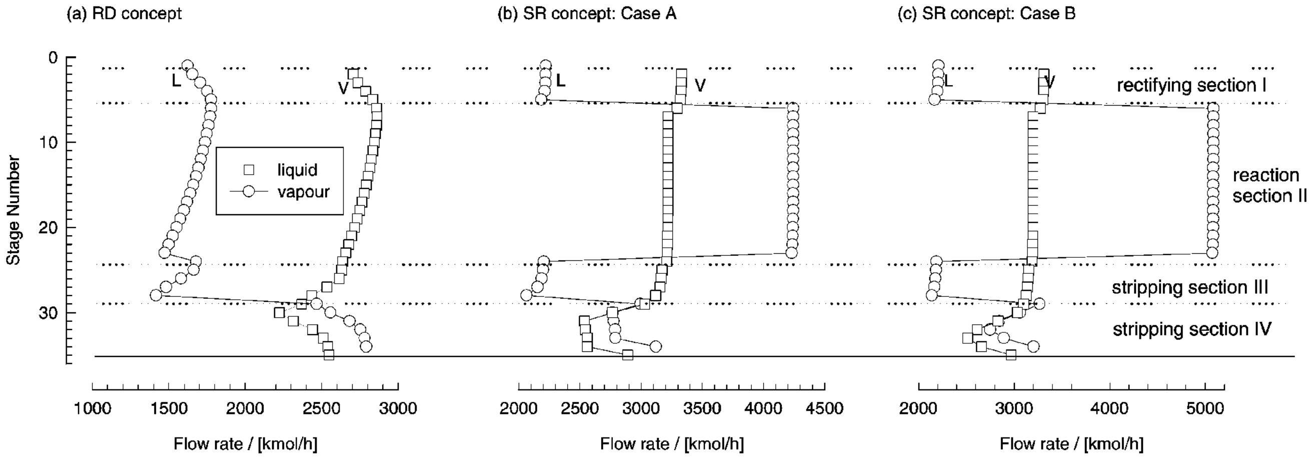

Figure 6. Molar flow rates of vapour and liquid phases in the distillation column for (a) RD configuration, (b) SR case A, and (c) SR case B.

advantageous for the actual hardware design of the column and might allow variation of the pump-around ratio over a large range.

From the estimated HETP values, the heights of the individual sections can be determined and these are given in Table 3. The total column height required for the RD column is 21.6 m. The SR case A requires a total column height of 14.5 m and for the SR case B the total column height required is 16.2 m. In SR case B, the higher pump-around ratio (1.4) leads to a significantly higher liquid load in section II and a poorer mass transfer performance (higher HETP).

For the design of the side reactor for the SR concept, we estimated the required catalyst volume in order to reach chemical equilibrium in an adiabatic operation. For case A (*RPA* = 1), the catalyst volume required is 36 m^3, identical to the catalyst holdup within the RD column. For case B (*RPA* = 1.4), the catalyst volume required is 55 m^3; this is caused by decreasing driving force in the reactor (Baur and Krishna, 2003). We note that the overall gain in conversion from increasing *RPA* from 1 to 1.4 is only 1%, but this extra conversion demands 19 m^3 extra catalyst load in the side reactor and extra distillation column height of 1.7 m. This underlines the fact that improving conversion in the SR concept can only be achieved with significant extra costs. In the RD configuration, the achievement of high IA conversion is not a problem and 97% conversion is achieved with 36 m^3 catalyst load within the column. However, the reactive section requires special hardware such as catalyst bales or KATAPAK (Baur and Krishna, 2002); these packings have a significantly poorer mass transfer performance than Sulzer BX. The height of the reactive section II is significantly higher for RD than for both SR configurations, because of the need to accommodate 36 m^3 of catalyst *within* the column.

Let us compare the total vessel volumes required for RD and SR configurations. For the RD column the total packing

Table 2. Vapour and liquid loads for the three configurations.

	Rectifying	'Reaction'	Stripping	
Section	I	II	III	IV
Initial stage	2	6	25	30
Final stage	5	24	29	34
Number of stages	4	19	5	5
RD configuration				
Internal liquid flow rate, kmol h^{-1}	1700.211	1625.293	1546.906	2629.368
Maximum liquid load, $m^3 s^{-1}$	0.061	0.061	0.059	0.125
Internal vapour flow rate, kmol h^{-1}	2769.645	2760.811	2536.492	2386.692
Maximum vapour load, $m^3 s^{-1}$	4.456	4.515	4.278	4.752
Percentage flood	51	80	49	78
SR concept (case A)				
Internal liquid flow rate, kmol h^{-1}	2202.251	4238.071	2134.416	2943.148
Maximum liquid load, $m^3 s^{-1}$	0.062	0.117	0.059	0.134
Internal vapour flow rate, kmol h^{-1}	3326.63	3253.599	3164.069	2783.337
Maximum vapour load, $m^3 s^{-1}$	5.205	5.177	5.046	4.867
Percentage flood	58	73	55	75
SR concept (case B)				
Internal liquid flow rate, kmol h^{-1}	2188.652	5079.059	2163.949	3007.17
Maximum liquid load, $m^3 s^{-1}$	0.062	0.14	0.059	0.14
Internal vapour flow rate, kmol h^{-1}	3307.219	3232.957	3157.998	2808.524
Maximum vapour load, $m^3 s^{-1}$	5.175	5.145	5.014	4.945
Percentage flood	58	78	55	80

Table 3. Column configurations.

		SR concept	
Description	RD concept	Case A	Case B
Column diameter, m	3.5	3.5	3.5
Estimated heights in sections, m			
Rectifying: section I	0.792	1.80	1.79
'Reaction': section II	17.86	8.93	10.57
Stripping: section III	1.106	2.22	2.22
Stripping: section IV	1.879	1.57	1.63
Total height of packing, m	21.637	14.52	16.21
Total volume of packing, m^3	208	140	156
Packing type			
Non-reactive sections	Sulzer-BX	Sulzer-BX	Sulzer-BX
Reactive sections	Bales	n.a.	n.a.

volume is 208 m^3 (see Table 3). For the SR case A, the total vessel volume is 140 m^3 (for distillation column; see Table 3) plus the volume of the side reactor of 60 m^3 (containing 36 m^3 of catalyst with voidage of 40%). Therefore the total vessel volumes are almost the same for RD and SR (case A).

The energy demand of SR depends on the reboiler load and on the additional energy to overcome the pressure drop when rerouting the liquid through the side reactor. Figure 5(a) shows that smaller RPA ratios will require larger reflux ratios in order to obtain the same conversion. The larger reflux ratio invoke larger internal streams which in turn increases the reactor throughput for a fixed RPA. The actual energy demand for pumping the liquid from stage 24 to stage 6 (approx 10 kW) is only a small fraction of the energy required for vaporizing the liquid in the reboiler (approximately 21 MW). Therefore, we can conclude it is less energy-consuming to increase the reactor throughput by means of a higher *RPA* ratio than by higher reboiler loads. However, we should keep in mind that high *RPA* ratios will reduce the chemical driving forces in the reactor which in turn increases the catalyst demand and limit conversion. Therefore, we fix the reflux ratio in the SR configuration at 2 in the present case study. This in turn results in significantly higher energy consumption compared with RD; see Table 1.

While a detailed economic study will be required to compare RD and SR configurations, we can generally conclude that RD will be preferred for achieving high conversion targets. For modest conversion targets the SR concept will be competitive as regards capital costs, but the energy costs may be higher than for RD.

CONCLUSIONS

In this paper we have carried out a comparative design study for production of TAME using either *in-situ* reaction in a distillation column (the RD concept), or networking a side reactor to a distillation column (SR concept). The desired IA conversion target of 92% can be achieved with only one side reactor, using the configuration shown in Figure 2(b) and a pump around ratio $RPA = 1.4$. Choosing $RPA = 1.0$ leads to a slightly lower conversion of 91%. A detailed hardware design of the RD and two SR configurations shows that the RD configuration requires a significantly taller reactive section II, due to the need to accommodate the catalyst load within the column in the RD case *and* due to significantly higher HETP required for Catalyst Bales.

The side reactor concept has a higher energy demand than the RD concept due to the higher reflux ratio used in the distillation column.

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