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Application of side reactors on ETBE reactive distillation

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Abstract

Reactive distillation (RD) has demonstrated potential reduction in capital investment and operating costs. However, industrial RD is still limited for etherification, esterification and cumene systems. Expensive hardware requirement has reduced the benefits of the simpler RD flowsheet. Side reactors are introduced in this work to reduce the requirement of specific hardware design by shortening the reactive section of the RD column. Using the ethyl *tert*-butyl ether (ETBE) system as the case study, simulation results show that a shorter RD column with side reactors produced comparable performance to that of a longer RD column. This may lead to a further reduction of the cost of the column if smaller amount of the catalyst result in a decrease in the diameter or height of the column. Therefore, RD with side reactors is a promising configuration that should be investigated during the conceptual design phase.

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1. Introduction

Reactive distillation (RD), which integrates the functionality of distillation and reaction, is a favourable alternative to conventional series of reactor and distillation. This results from the reduction of the capital investment via the reduction of equipment such as pumps, piping, etc. It can also reduce the operational costs through overcoming distillation boundaries such as an azeotrope due to the presence of reaction and mitigate reaction limitations such as reaction equilibrium due to the continuous removal of the product [1]. As a result, RD is gradually becoming an important unit operation in industry for its productivity competitiveness and environmental benefits. Potential applications of the RD technology can be found elsewhere [2–4].

However, applications of RD in industry are still limited to a few reactive systems, mainly etherification (e.g. MTBE), esterification (e.g. methyl acetate), and alkylation (e.g. ethylbenzene or cumene) [5]. Detailed economic evaluation for a toluene disproportionation system shows that a significantly simpler flowsheet using RD technology is offset by the higher cost of the RD column when compared to a conventional technology [6]. Successful commercialisation of the RD technology requires specific hardware designs, which seldom correspond to those of conventional distillation. For example, high liquid hold up in reactive section for maximising conversion does not agree with the requirement of high interfacial area for good separation [7].

For heterogeneous catalyst RD, the design of the reactive section is considerably more challenging. The hardware design should be a compromise between the requirements of chemical reaction for small particle size and high catalyst loading, separation for large interfacial area between gas and liquid phases, and pressure drop for higher void fraction for gas–liquid flow [7]. The most important function of packed catalyst in RD is to provide adequate liquid-catalyst surface contact to promote reaction. This is especially crucial for slow reactions, which require a large catalyst hold up in the reactive section. At the design phase, adding an extra amount of catalyst hold up is also required to compensate for catalyst deactivation. However, this common practice can promote unwanted side reactions and added catalyst cost [8]. Therefore, structured catalytic packing with long life are often used [5]. In addition to the expensive costs of the catalyst, catalyst replacement is not convenient because it requires the shut down of the entire plant.

The concept of side reactors is introduced to overcome hardware design limitations [9]. It has been investigated for MTBE and TAME productions by employing a novel process technology [10]. Fig. 1 shows the schematic diagram of the RD column with series of side reactors. The conceptual design of RD column estimates the number of reactive and separation stages, the diameter and the height

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Nomenclature

EtOH	ethanol
ETBE	ethyl *tert*-butyl ether
FC	flow controller
iBut	isobutylene
LC	level controller
*n*But	*n*-butane
PC	pressure controller
Qr	reboiler duty (kW)
R	reflux ratio
RD	reactive distillation
RE	rectification section
RX	reactive section
SR	side reactor
ST	stripping section

of column, the location of the feed points, the selection of operating conditions, etc. [1,11,12]. It does not normally consider the application of side reactors. The side reactor has potential to reduce the requirement for catalyst loading in the reactive section. As a result, a shorter reactive section may be employed, leading to a potential reduction of the cost of the column provided the amount of the required catalyst results in a decrease in the diameter or height of the column. The side reactor can also be treated the same fashion as the pre-reactor, which has the advantages of the ease of shut down and catalyst replacement.

From a control point of view, the reactant conversion can be controlled at the reactor outlet and the final product purity can be controlled at the distillation column in conventional etherification processes. In the etherification RD, ideally both isobutylene conversion and ether purity can be controlled. The side reactor integrated into the RD column provides additional degrees of freedom to control the reactant conversion. The operating conditions of the side reactor are also not limited by distillation constraints.

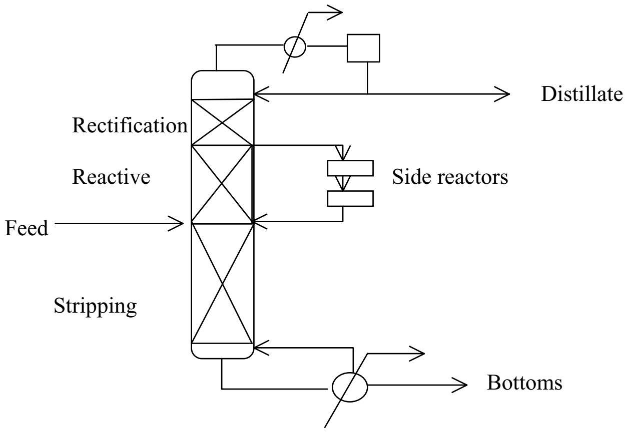

Fig. 1. Schematic flowsheet of RD column with side reactors.

In this work, the application of side reactors for ethyl *tert*-butyl ether (ETBE) RD is investigated. A continuous flow stirred tank reactor, isothermally or adiabatically, is used to represent the side reactor. A series of these reactors can be used to model a tubular reactor or a fixed-bed reactor. Performance of several designs of RD with side reactors is compared with respect to the overall isobutylene conversion and the ETBE purity of the bottom product. This simulation work is intended to provide alternative configurations for the RD before the final estimations of the column specifications and the operating conditions are completed. Therefore, it can support the conceptual design of RD and may be used as inputs to the detail equipment design.

2. ETBE reactive distillation

ETBE is synthesised from isobutylene and ethanol by using an acidic ion-exchange-resin such as Amberlyst-15. This exothermic reaction is equilibrium limited in the industrial temperature range (40–70 °C). The principal side reactions are dimerisation of isobutylene and hydration of isobutylene. The former can be minimised by using excess ethanol, and the latter is neglected in this process analysis because it occurs only in the presence of water. Although it is possible to perform all of the reactions inside the column, a pre-reactor is normally preferable in that it prevents catalyst deactivation, and thus loading/unloading of the internal column catalyst. In this work, the existence of the pre-reactor is simulated by adding some 30% of the ETBE in the feed stream, which is common in the commercial etherification processes. The effluent of the pre-reactor is fed into the RD column where a side stream is then taken to the side reactor. The product of the side reactor is returned to the RD column. The column contains catalyst on packed section above the feed point. Separation stages are required both above and below the reactive section to produce the necessary separation and to recycle the unreacted feed into the reactive section.

The column operating goal is high ETBE purity by eliminating high volatile components and high isobutylene conversion to maximise the value added by the process. Due to operational and control considerations, the reboiler duty is the main manipulated variable to optimise the ETBE purity while the reflux ratio or reflux rate is set constant (one-point control). The overhead pressure is maintained constant by adjusting the condenser duty. The condenser and reboiler sump levels are controlled by manipulating the distillate and bottom flow rates, respectively. These one-point control schemes (LV or (L/D)V) outperform other control schemes for set-point tracking and disturbance rejection of single feed ETBE RD columns [13]. The schematic flowsheet of the ETBE RD column with side reactor employing the LV scheme is shown in Fig. 2.

The steady state model of the ETBE RD is implemented using Aspen Plus and employing RadFrac based on an equilibrium-stage approach. This approach, which is

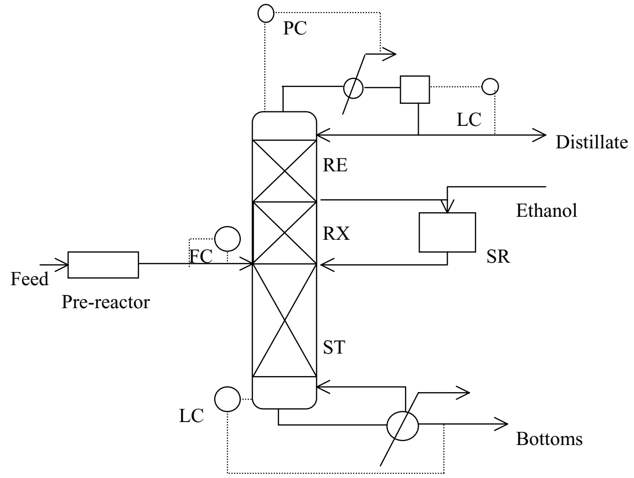

Fig. 2. Schematic flowsheet of the ETBE RD column with side reactor (CSR-1, CSR-2, CSR-3 designs).

satisfactory for MTBE reactive distillation columns [14], can be expected to provide reasonable results for the ETBE RD column. Both the ETBE synthesis and the dimerisation of the isobutylene are assumed to instantly reach equilibrium on each stage. Although the assumption may not represent the actual process, it can be used as the basis for evaluation and comparison of the overall performance. The details of the mathematical model for the ETBE RD in [15] is extended to include the side reactor model.

3. RD column designs

The specifications and operating conditions of the ETBE RD columns considered are shown in Table 1. All designs employ a total condenser and a partial reboiler. The basic design (B), a RD column without side reactor, consists of 28 theoretical stages including 7 rectifying, 7 reactive and 14 stripping stages, respectively. This basic design has been previously simulated [16,17] and is used as the basis for comparison of the RD performances in this work. The first design (CSR-1) simply adds a side reactor to the base case in order to gain an understanding of its effect on the overall column performance. The second design (CSR-2) considers less reactive stages with a side reactor. It is used to investigate the potential of the side reactor to reduce the number of reactive stages. Similar to the CSR-2 design, the third design (CSR-3) employs two side reactors in series while the number of reactive and separation stages are kept constant. This CSR-3 design considers the effect of adding catalyst to several side reactors, which does increase catalyst loading in each side reactor. The increased catalyst loading is expected to prolong the time between catalyst changeovers/regenerations. For the first three designs (CSR-1, CSR-2, CSR-3), the ethanol stream is fed to the side reactor to promote the ETBE synthesis because the side stream, which is taken from near the top column, is rich of isobutylene. This ethanol make-up also prevents the side reaction, dimerisation of the isobutylene, in the side reactor. The schematic configuration of the first three designs is presented in Fig. 2.

In contrast, the finally design case (CSR-4) considers a rather unique configuration. The effluent of the pre-reactor is fed to the side reactor instead of to the bottom of the reactive section. Apart from the reduced number of reactive stages, the benefit of the RD with side reactor is to provide an additional degree of freedom to control the isobutylene conversion while its operating conditions are reduced by the distillation column constraints. The CSR-4 case is intended to investigate possibilities of the side reactor to significantly replace the reaction, taking place inside the RD column. Most of the reaction is expected taking place in the side reactor. The RD schematic of the last design is shown in Fig. 3.

The side stream of the column is always withdrawn from the top of the reactive section and is then fed to the side reactor. The product of the side reactor is returned back to the same RD column at the bottom of the reactive section. This stream location is selected based on the idea that the side reactors are introduced to reduce the number of reactive stages, and therefore shorten the reactive section.

As in the pre-reactor, the liquid phase of the reacting system in the side stream should be such as to promote the ETBE reaction. Therefore, the side reactor operates at a high pressure of 1500 kPa. Although the temperature of

Table 1
RD column inputs and characteristics

Feed conditions		Column specifications	B	CSR-1	CSR-2	CSR-3	CSR-4
Temperature	30 °C	Number of RE stages	7	7	7	7	7
Rate	150 kmol/h	Number of RX stages	7	7	4	4	4
Composition (mol)	9.1% EtOH	Number of ST stages	14	14	14	14	14
	7.3% iBut	Side stream product/feed	–	9/15	9/12	9/12	9/12
	29.1% ETBE	Feed stage	16	16	13	13	–
	54.5% *n*But	Number of side reactor	–	1	1	2	1
Excess EtOH	5.0 mol%	Volume of side reactor (cum)	0.00442	0.00442	0.00442	0.00442	0.00442
Top pressure	709.1 kPa	Make-up EtOH (kmol/h)	1.73	1.73	1.73	1.73	NA
Reflux ratio	5.5	Side stream rate (kmol/h)	–	36	36	36	36
		Reflux ratio	5.5	5.5	5.5	5.5	5.5

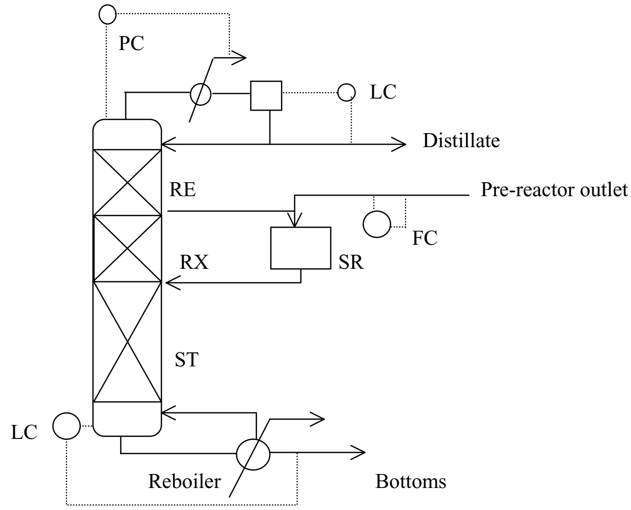

Fig. 3. Schematic flowsheet of the ETBE RD column with side reactor (CSR-4 design).

the pre-reactor normally operates at moderate temperatures (70–90 °C), a constant temperature of 70 °C is initially chosen for the side reactor. This nominal temperature is expected to increase the isobutylene conversion for this relatively fast exothermic reaction. Although this lower reactive temperature contributes to the slower reaction rates, adding more catalyst or extending the reactor residence time can be used to satisfy the equilibrium reaction assumptions. The composition of the side stream, which consists mainly of *n*-butane with a higher isobutylene content, is expected to significantly affect the side reactor performance. Based on the liquid composition in the top of the reactive stage resulting from the base case design, the lack of ethanol can be predicted from the side stream. Therefore, the side reactor requires ethanol make-up to promote the ETBE synthesis and minimise the polymerisation of the isobutylene.

Previous simulation results neglecting the dimerisation of isobutylene have shown that the reflux ratio and the reboiler duty should be optimised to obtain the maximum ETBE bottom product purity [17]. Considering the presence of output multiplicity phenomena, the outputs were always obtained at the optimum reboiler duty when approached from a larger value. The constant reflux ratio of 5.5, which was found to be satisfactory for the basic design, was again employed for the RD column designs of this work.

4. Simulation results

Due to the complex interactions between reaction and separation processes, the RD columns behave quite differently and often non-intuitively from that of conventional distillation columns. The introduction of side reactors adds additional complexity to the design. These design issues are described below and should be considered during the design and during the operation of the column to ensure optimal

Table 2
ETBE RD column with side reactors simulation results[a]

Property	B	CSR-1	CSR-2	CSR-3	CSR-4
RD column					
Condenser temperature (°C)	55.6	55.6	55.7	55.7	55.8
Reactive section temperature (°C)	56.6–90.4	56.8–89.2	57.1–70.7	57.2–73.6	57.2–76.5
Reboiler temperature (°C)	143.9	140.6	140.9	140.9	143.8
Bottom composition (mol%)	4.75 EtOH, 95.22 ETBE, 0.02 DIB	7.89 EtOH, 92.09 ETBE, 0.01 DIB	7.55 EtOH, 92.41 ETBE, 0.04 DIB	7.56 EtOH, 92.40 ETBE, 0.03 DIB	4.92 EtOH, 95.01 ETBE, 0.07 DIB
Distillate composition (mol%)	0.02 EtOH, 0.03 iBut, 99.94 *n*But	0.02 EtOH, 0.28 iBut, 99.69 *n*But	0.07 EtOH, 0.05 iBut, 99.87 *n*But	0.08 EtOH, 0.07 iBut, 99.85 *n*But	0.07 EtOH, 0.12 iBut, 99.80 *n*But
iBut conversion (mol%)	99.91	99.54	99.84	99.82	99.67
Condenser duty (kW)	2667	2674	2670	2670	2671
Reboiler duty (kW)	3082	3019	3057	3024	2798
Side reactor					
iBut conversion (mol%)	NA	−44.8	−28.9	−61.8	−47.2
Input composition (mol%)	NA	2.08 EtOH, 0.24 iBut, 97.18 *n*But, 0.51 ETBE	6.34 EtOH, 0.04 iBut, 93.30 *n*But, 0.31 ETBE	6.47 EtOH, 0.06 iBut, 93.05 *n*But, 0.42 ETBE	7.68 EtOH, 5.91 iBut, 62.81 *n*But, 23.60 ETBE
Input rate (kmol/h)		37.73	37.73	37.73	185.99
Output composition (mol%)	NA	2.29 EtOH, 0.36 iBut, 97.01 *n*But, 0.28 ETBE	6.43 EtOH, 0.12 iBut, 93.22 *n*But, 0.22 ETBE, 0.01 DIB	6.71 EtOH, 0.30 iBut, 92.81 *n*But, 0.16 ETBE, 0.01 DIB	17.98 EtOH, 4.10 iBut, 59.95 *n*But, 11.87 ETBE, 6.10 DIB
Output rate (kmol/h)		37.92	37.76	37.83	194.88

[a] EtOH: ethanol, iBut: isobutylene, *n*But: *n*-butane, ETBE: ethyl *tert*-butyl ether, DIB: di-isobutylene.

performance. Table 2 presents the key outputs of the simulations of the RD column with the side reactor performed as part of presented studies.

4.1. CSR-1 design

Table 2 shows that the CSR-1 design produced a lower ETBE purity and isobutylene conversion when compared to that of the base case design. The side reactor has the effect of decompose the ETBE, which was in the side stream taken from the top of the reactive section. The ETBE decomposition rate was about 0.0836 kmol/h, which ultimately contributed to the decrease in isobutylene conversion. The ethanol make-up used to minimise the dimerisation of isobutylene can have a favourable effect by reducing the ETBE decomposition rate. However, the ethanol make-up can also decrease the overall ETBE purity because the unreacted ethanol leaves as part of the column bottom product.

This analysis points to the detrimental effects of the side reactor when integrated into the RD column. This effect is similar to a large increase in the number reactive stages in the base case design [17]. For the longer reactive section, the detrimental interaction between the phase and chemical equilibrium can lead to decomposition of the ETBE product on the lower reactive stages. In other words, the CSR-1 design results imply that fewer number of the reactive stages is required if a side reactor is part of a RD column. This result is also confirmed by the CSR-2 design.

4.2. CSR-2 design

Table 2 shows that the CSR-2 design improved the ETBE purity and isobutylene conversion of the CSR-1 design results. The decrease in the number of the reactive stages results in less decomposition of the ETBE on the lower reactive stages. The temperatures of the lower reactive section, which produce higher chemical equilibrium constants, resulted in a higher ETBE purity. In the side reactor, the negative value of the isobutylene conversion corresponds to the ETBE decomposition rate. The side reactor of the CSR-2 design showed a lower ETBE decomposition rate of 0.0348 kmol/h. The ethanol make-up, which was added in the side reactor to minimise the side reaction, again caused a deterioration in the ETBE purity. However, the CSR-2 design results do confirm that the application of the side reactor can reduce the number of the reactive stages in the main RD column.

Compared to the basic design, the CSR-2 design showed a lower ETBE purity and a lower isobutylene conversion. However, the CSR-2 design reduced the number of the reactive stages at the same reflux ratio of 5.5 as that of the base case design. The optimum reboiler duty is lower than that of the base case column and may indicate non-optimum operating conditions.

For the CSR-2 design, Fig. 4 shows the effect of increasing reflux ratio and consequently reboiler duty. As for the base case design [17], the ETBE purity does not decrease with the increased internal rates. The reflux ratio of at least 5 was required to obtain the required ETBE purity of 92.4 mol%. However, this CSR-2 design could produce a higher ETBE purity than the base case design.

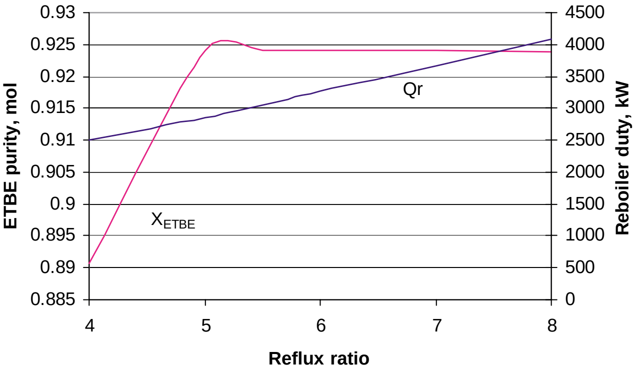

Fig. 4. Effects of the manipulated variables on the CSR-2 design (X_{ETBE} = ETBE purity, Qr: reboiler duty).

Fig. 5 shows the presence of multiplicity phenomena, which was obtained by varying the reboiler duty at the constant reflux ratio of 5 and 7, respectively. The figure shows that the same ETBE purity can be obtained at different combinations of the manipulated variables. For each reflux ratio, two reboiler duty values may result in the same ETBE purity. As for the base case design, the multiplicity phenomena are essentially always present, hence very tight control of the reboiler duty is required to maintain stable operation of the RD column with the side reactor.

Table 2 also shows that ETBE decomposes in the side reactor because its operating conditions shift the chemical equilibrium back to the reactants. However, changes in the temperature of the side reactor can only slightly affect the ETBE purity at the bottom product of the column, as the ETBE purity is mainly influenced by the column operating conditions. However, increasing the temperature of the side reactor reduces the required reboiler duty. At a constant reflux ratio of 5, the stable reboiler duties were 2868, 2852 and 2835 kW, for the constant side reactor temperatures of 60, 70 and 80 °C, respectively. Although increasing the temperature of the side reactor requires additional heat input, the

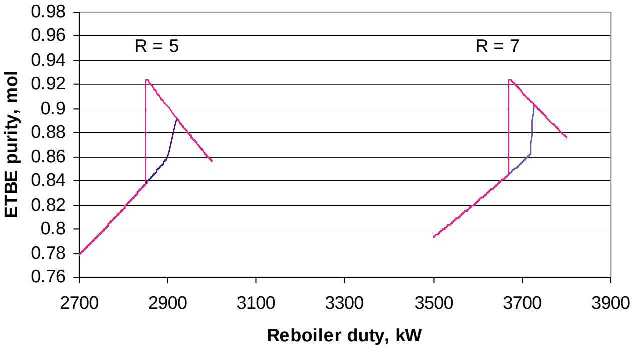

Fig. 5. Multiplicity phenomena of the CSR-2 design (R: reflux ratio).

lower reboiler duty of the main RD column does improve the economics. The exothermic nature of ETBE reaction in the side reactor can decrease the heat input required to maintain the temperature of the side reactor. Changing the side stream taken from the top to a lower part in the reactive section of the RD column decreased the ETBE purity. The side stream taken from the lower part contained more ETBE, which is then decomposed back to the reactants.

In fact, the side reactor of the CSR-2 design always decomposes the ETBE contained in the side stream. Changes in the operating condition of the side reactor can only minimise the ETBE decomposition rate.

4.3. CSR-3 design

For the CSR-3 design, two fixed-bed side reactors were used to investigate the effects of increasing the number of the side reactors. The first side reactor operated at a constant temperature of 70 °C and the second reactor temperature was 90 °C. The selection of the temperatures is based on the range of the reactive section temperature used in the base case design, namely between 56 and 90 °C.

Table 2 shows that the ETBE purity and the isobutylene conversion are similar to that of the CSR-2 design. Increasing the number of the side reactor, which corresponds to a larger catalyst hold up, does not improve effect on the ETBE purity or the isobutylene conversion. Therefore, one equilibrium side reactor is theoretically required to produce the targeted product specification. However, the actual size of this reactor could be quite large in order to meet the requirements of catalyst hold up. At the same reflux ratio of 5.5, Table 2 shows that the stable reboiler duty of the CSR-3 design is slightly lower than that of the CSR-2 design. This result implies that the extra amount of catalyst in the side reactor, which can prolong the time between the catalyst changeovers, may be compensated for by the reduced energy consumption.

The decomposition of the ETBE in the side reactors is clearly a problem with the CSR-3 design. The isobutylene conversions to ETBE were decreased by 61.8 and 28.9 mol% for the CSR-3 and CSR-2 designs, respectively. The second side reactor actually resulted in further decomposition of the ETBE, hence the ETBE decomposition was higher for the CSR-3 design. Changes in the temperature of the side reactors have little effect on the column performance or the overall ETBE purity and isobutylene conversion. However, higher side reactor temperatures resulted in a lower reboiler duty, similar to that of the CSR-2 design.

4.4. CSR-4 design

In the CSR-4 design, the pre-reactor output is fed directly to the side reactor and Table 2 shows that this configuration results in a higher ETBE purity and a higher isobutylene conversion for all CSR-1, CSR-2 and CSR-3 design cases. The same reflux ratio of 5.5 and the stable reboiler duty of 2798 kW, which are lower than that of the other designs, resulted in both higher ETBE purity and isobutylene conversion. Fig. 6 shows the effect of changes in the reflux ratio, and resultant reboiler duty on the ETBE purity. If the consumption of energy does not limit the economic feasibility, the column performance with respect to the ETBE purity (e.g. 95.2 mol%) and isobutylene conversion is comparable to that of the base case RD column. Therefore, the CSR-4 design, which employs a shorter reactive section with side reactor, is a reasonable alternative to the base case design.

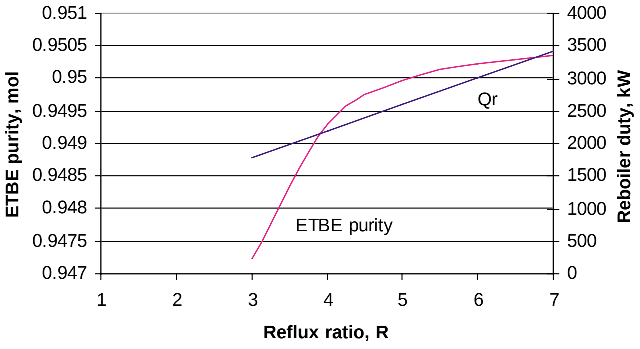

Fig. 6. Effects of the manipulated variables on the CSR-4 design (Qr: reboiler duty).

The shorter reactive section of the RD column configuration typically results in reduced capital costs. A further reduction in the capital cost of the column can be obtained if the reduced amount of the catalyst hold up results in decreased column diameter or height of the column. If the catalyst loading of the column is maintained at a similar amount to that in the base case design, the time for catalyst regeneration or changeover can be extended. However, the main reaction sites can relocate within the column during the life of the catalyst. This consequently change the theoretical number of the reactive stages and the column operating conditions may then need to be re-adjusted for stable performance. Compared to the base case design, the side reactor of the CSR-4 design, which can generally be treated the same as the pre-reactor, makes the shut down procedures and catalyst changeover much more convenient than that of the reactive section. The shut down of the base case design is required for the internal catalyst replacement while the catalyst changeover of the side reactor does not require the shut down of the entire plant. Therefore, the application of the side reactor in the CSR-4 design can lead to a reduction in both investment and operating costs.

The multiplicity phenomena observed for the CSR-4 design at a constant reflux ratio of 5.5 are shown in Fig. 7. At a certain range of the reboiler duty, both input and output phenomena exist and tight control of the reboiler duty is therefore required for the stable operation. The reboiler duty of 2800 kW produced two different ETBE purities, which were 89.9 and 94.9 mol%, respectively. The reboiler duty, which produced the best ETBE purity, should be approached from the larger value due to the output multiplicity. The

Fig. 7. Multiplicity phenomena of the CSR-4 design ($R = 7$).

multiplicity phenomena can be demonstrated by varying the reboiler duty at another reflux ratio. Like in the RD columns [18], the window of the multiplicity is wider for higher internal rates, e.g. both higher reflux ratio and reboiler duty.

For the CSR-4 design, the formation of the di-isobutylene (DIB) is an obvious problem. Table 2 shows that the isobutylene output rate is smaller than that of the total isobutylene input rate. On the other hand, the isobutylene conversion to ETBE has a negative value, which indicates that the ETBE in the input stream is converted back to the reactants. Therefore, the isobutylene mostly converted to the DIB in the side reactor. This analysis for the CSR-4 design implies two main problems with the side reactor, i.e. the formation of DIB and the decomposition of the ETBE.

The basic and CSR-4 designs, which produced similar ETBE purity and isobutylene conversion, can be compared based on their temperature profiles and reaction rates throughout the column. The comparison may be used for operational considerations and improving the CSR-4 performance.

The temperature profiles throughout the column for the two designs are shown in Fig. 8. The presence of the side reactor does not affect the rectifying temperature profiles as shown by their similar temperatures. However, the temperature of the CSR-4 design is higher in the reactive section. The temperature above stages 13–16 of the stripping section is also higher than that of the reactive section of the base case design. This higher reactive temperature resulted in a higher rate of the ETBE synthesis. In addition to the side reactor, the higher reactive temperatures result in the comparable ETBE purity even though the reactive section is shorter.

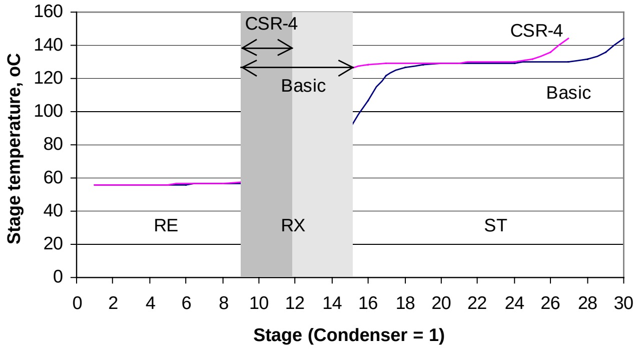

Fig. 8. Comparisons of temperature profiles for the base case and CSR-4 designs.

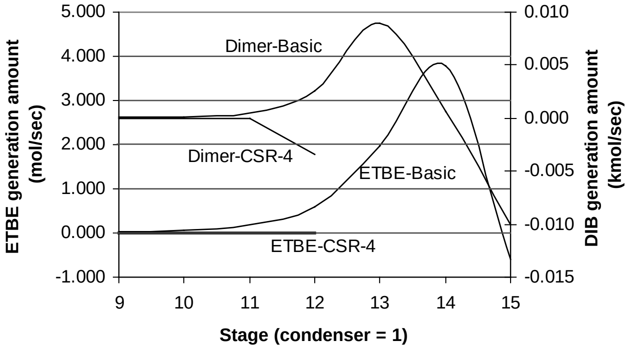

Fig. 9. Comparisons of generation amount for the base case and CSR-4 designs.

Fig. 8 shows the similarity between the temperature profiles for both the base case and CSR-4 designs. The profiles are same in the rectifying sections and then start increasing steeply in the middle of the reactive sections, both continue increasing to the top of the stripping section, flat for the rest of the stripping section before sharply increasing at the bottom of the column. It is clear that the reduced number of the reactive stages and the presence of the side reactor shift the temperature profile. The profiles indicate that an existing RD (for example, the basic) column can be fitted with side reactors by slightly modifying the operating conditions and the available control system structure. The selectivity and responsiveness of the measured temperature are both generally larger at the top of the stripping section. The available measured temperature sensors, which are used for an inferential control system to estimate the distillate and bottom compositions, need to be relocated depending on the catalyst activity.

Fig. 9 shows the corresponding ETBE and DIB generation amounts at the reactive stages of the columns. For the CSR-4 design, the ETBE and DIB generated were very small due to the lack of reactants in the reactive section. The higher temperature of the reactive stages also points to the lower reaction equilibrium constant for the ETBE synthesis. Due to the higher ratio between the ethanol and isobutylene, the DIB decomposed at the bottom of the reactive stages as shown by the negative value of the DIB generation amount. The excess ethanol, which results from fractionation effect in the reactive stages and the input stream from the effluent of the side reactor, can prevent the dimerisation reaction. However, the DIB is mainly formed in the side reactor as shown by the DIB composition of 6.17 mol% in the side reactor effluent and is withdrawn at the bottom product.

For the base case design, the ETBE and DIB formations gradually increased to their maximum rates at stages 13 and 14 before decreasing at the bottom of the reactive stages. The higher ratio between the ethanol and the isobutylene results in the decomposition of the DIB at the bottom of the reactive section. The ethanol excess is due to the fractionation effect of the longer reactive section. The higher temperature results in the lower ETBE rates at the bottom of the reactive stages and does decrease the equilibrium reaction constant.

4.5. Effects of key variables on the CSR-4 design

In spite of the ETBE decomposition and DIB formation in the side reactor, the CSR-4 design is a reasonable alternative to exiting RD configurations in that similar ETBE purity and isobutylene conversion can be achieved when compared to the base case design. Additional simulations were made to delineate the effect of key variables on the performance of the CSR-4 design.

Apart from changes in the column operating conditions (e.g. reflux ratio and reboiler duty) as discussed in the previous analysis, the selection of the side reactor operating conditions is crucial to minimise the side product formation as well as to prevent the ETBE decomposition. At a reflux ratio of 5.5, the stable ETBE purities were 95.03, 95.01, and 94.98 mol%, the reboiler duties of 2916, 2798, and 2668 kW, and side reactor temperatures of 60, 70 and 80 °C, respectively. As for the CSR-2 design, decreasing the side reactor temperature can slightly decrease the DIB formation and thus improve the ETBE purity at the bottom product. The higher side reactor temperature corresponds to a lower optimum reboiler duty, which does require lower energy consumption. Due to the little effect of pressure changes on the ETBE reaction rate, it can be also shown that the operating pressure of the side reactor does not significantly change the resulting ETBE purity.

Fig. 9 shows that the DIB decomposition occurs near the bottom of the reactive stages. Changing the feeding point of the effluent of the side reactor from the bottom to a slightly higher position in the reactive section could decrease the DIB formation and promote the ETBE synthesis due to more reactants entering the column. However, changing the feed point from stages 12 to 11 decreased the ETBE purity from 95.01 to 94.65 mol%, at the same reflux ratio and stable reboiler duty. The concentration of DIB in the bottom product decreased from 0.07 to 0.05 mol%. However, at the constant reflux ratio, the best reboiler duty was higher (2823 kW), which result in higher reactive temperature and consequently reduced the equilibrium constant, resulting in a lower ETBE purity in the bottom product.

Similar to the side stream of a distillation column, the side stream conditions are crucial variables, which are key to determining the product specifications. At a reflux ratio of 5.5 and a stable reboiler duty, the ETBE purities were 94.96, 95.02, and 95.04 mol% for the side stream rates of 108, 36, and 3.6 kmol/h, respectively. The result is contradictory to the previous assumption that the presence of the side reactor is used to shorten the reactive section of the column. Higher side stream rate, which was expected to be beneficial as the reactant was converted in the side reactor, decreased the ETBE purity.

The analysis shows that improved ETBE purity can result from the high internal rates (e.g. higher reflux ratio and reboiler duty), low side stream rate and low side reactor temperature. At a reflux ratio of 7, a side stream rate of 3.6 kmol/h and a side reactor temperature of 60 °C, the stable ETBE purity was 95.2 mol%, at a reboiler duty of 3540 kW. This ETBE purity is the same as that of the base case design obtained at a reflux ratio of 5.5 and a reboiler duty of 3082 kW, respectively. Hence, shorter RD column with side reactor can produce a similar ETBE purity and isobutylene conversion by using higher internal rates to that of the longer RD column without side reactor.

5. Conclusions

Extensive simulation work has been carried out to determine the effect of side reactors on the RD column for ETBE production. The RD column with side reactor acts to reduce the number of reactive stages. However, modification of the base case design RD configuration can also be done to produce same ETBE purity and isobutylene conversion as that of the base case RD design. The effluent of the pre-reactor is fed to the side reactor instead of at the bottom of the reactive section. The reduced number of the reactive stages results in a reduction of column cost provided that the amount of catalyst required results in a decrease in the diameter or height of the column. In addition, the side reactor can also be treated the same as the pre-reactor, which is more convenient for shut down operation and catalyst replacement.

The application of side reactor should be considered in more detail compared to other RD configurations during the conceptual design phase. The application of side reactor has economical and technical benefits, which can lead to wider applications of the RD technology. Although extensive simulations have been conducted, a more systematic approach is now being done to compare the possible RD designs.

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