DISTILLATION COLUMN WITH REACTIVE PUMP AROUNDS: AN ALTERNATIVE TO REACTIVE DISTILLATION

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Abstract

The hardware design of reactive distillation (RD) columns poses severe challenges with respect to the choice and design of the hardware; the requirements of reaction (i.e. high liquid or catalyst holdup) is not in consonance with the requirement of separation (high interfacial area). In this paper we examine an alternative to the RD concept, viz. a distillation column networked with a number of side (external) reactors. If each distillation stage is linked to a side reactor, the performance of the RD column is matched exactly. From a practical point of view it is desirable to reduce the number of side reactors to say 3 – 6. The precise location of the chosen number of side reactors and the manner in which the liquid draw-offs and reactor effluent re-entry to the distillation column needs to be chosen carefully. We have developed an algorithm to determine the optimum configuration of the side reactor concept in order to maximize conversion. For the case study of methyl acetate production, we see that it is possible to match the conversion level of an RD column by appropriate choice of the number of side reactors and the pump around ratio. The higher the conversion target the larger the number of side reactors and pump around ratios. For modest conversion levels, say < 90%, even a 3-side reactor configuration will be able to match the performance of the RD column. The study presented here reveals the potential, and limitations, of the side reactor concept for use as an alternative to RD technology.

Keywords: reactive distillation; equilibrium stage model; nonequilibrium stage model; methyl acetate; column hardware; hydrodynamics; mass transfer; flooding; side-reactors; pump-arounds;

INTRODUCTION

Reactive distillation (RD) is enjoying a lot of attention from industry and academia because of the many advantages over the conventional reaction-followed-by-separation concept [1,2]. The successful commercialisation of RD technology requires special attention to hardware design that does not correspond to those for conventional (non-reactive) distillation. In most RD applications the Hatta number is less than unity [3] and therefore there is no enhancement of mass transfer due to chemical reaction. In order to maximize productivity in a homogeneously catalysed RD column we need to maximize the liquid holdup. In a heterogeneously catalysed RD column we similarly need to maximize the catalyst holdup. The requirements of high liquid or catalyst holdup in an RD column are not in consonance 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 [2].

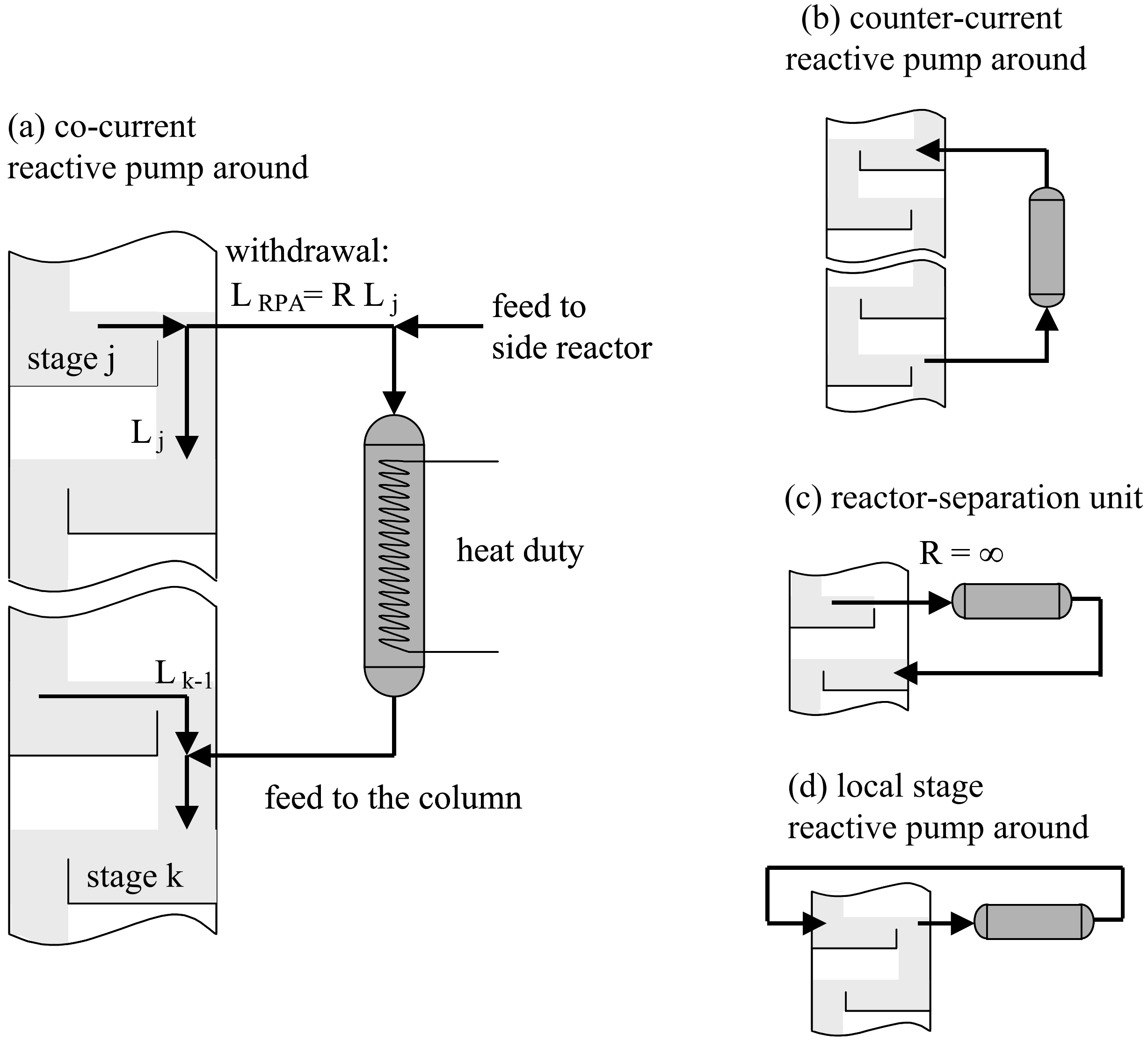


Figure 1. Schematic diagram of side reactor configurations

There is another issue that mitigates against the idea of carrying out the reaction within a distillation column; this relates to catalyst deactivation. The traditional way to compensate for the catalyst deactivation, i.e. adding excess catalyst or increasing the reaction temperature, is seldom feasible in RD applications.

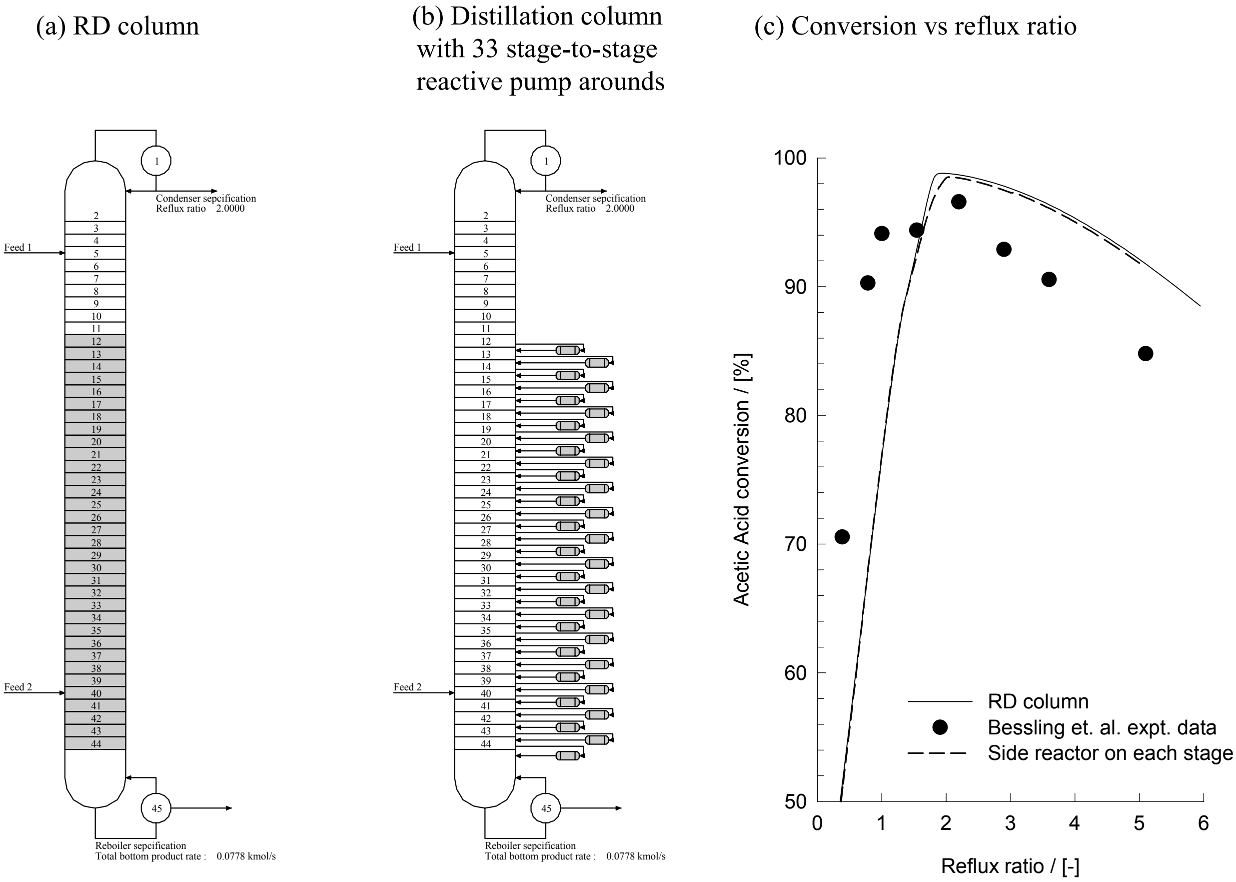
One way to overcome the above mentioned hardware problems with RD columns, while maintaining the benefits of in-situ separation with reaction, is to employ the side-reactor or external reactor concept [4,5]; see Fig. 1. In the side reactor concept the reactor feed is withdrawn from the distillation column and the reactor effluent is returned back to the same column. The side reactor could be a conventional catalytic packed bed reactor operating in liquid phase and therefore there are no hardware design problems or conflicts. Furthermore, the reaction conditions within the side reactor (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 side reactors to the distillation column; these are shown in Figure 1(a) –(d). The pump around can be located in such a way that liquid is bypassing intermediate stages; see Fig. 1 (a). The liquid is withdrawn from stage j and possibly mixed with an additional feed stream before it is pumped to a side reactor. The stream leaving the side reactor 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 ratio, R, 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 side reactor 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 raise the danger of flooding on intermediate stages and demands additional energy input. Both configurations (a) and (b) cause a change of internal flow rate, which affects the operation line. This can cause the driving force for mass transfer to decrease or exergy losses to increase.

Co- and counter- current reactive pump around configurations have two limiting cases shown in Figure 1 (c) and (d), respectively. The product stream of side reactor might be fed to the downcomer at the same stage; see Fig. 1 (d). In this case same limitations apply as already mentioned for a counter-current configuration. Of practical importance is the case where the stream leaving a stage is completely re-routed through a reactor before it is fed back to the stage below; see Fig. 1 (c). We call this configuration reactor separation unit. Since no stages are bypassed, the entire liquid stream leaving the stage will be pumped through the reactor. If the catalyst load is small enough to be placed in the downcomer an *external* reactor is not required [2].

In order to meet the process requirements of conversion, more than one side reactor may be required. Clearly, the determination of the optimum number of side reactors, along with the liquid draw-off and feed-back points to the distillation column need careful attention and consideration. The first major objective is to compare the performance of the side reactor concept with a conventional RD column, with regard to the liquid, or catalyst, holdup. The second major objective of the present communication is to develop an algorithm to determine the optimum way to connect a given number of side reactors to a distillation column in order to maximize the conversion. We demonstrate our algorithm by considering the case study for production of methyl acetate (MeOAc).

In the modelling to be presented below, the reactor itself is modeled by a series of single phase CSTR reactors, where the catalyst load and heat duty is evenly distributed. By choosing a sufficient number of CSTR reactors in series, say $N_{CSTR} = 10$, the reactor represent an ideal plug flow reactor. The model also allows operating the reactor adiabatically, isothermally, or with external heat supply.


(a) RD column

(b) Distillation column with 33 stage-to-stage reactive pump arounds

(c) Conversion vs reflux ratio

Figure 2. Comparison of HOAc conversion between a reactive distillation column and a column designed by means of a reactor-separation concept when the reflux ratio is varied. The overall catalyst load is 99 m^3 in both cases.

CASE STUDY OF METHYL ACETATE SYNTHESIS

Consider the production of methyl acetate by the acid-catalysed esterification reaction of acetic acid with methanol. This reaction is made difficult by a variety of factors: (a) reaction equilibrium limitations, (b) difficulty of separating AcOH and H2O, and (c) presence of MeOAc – H2O and MeOAc – MeOH azeotropes. Conventional processes use one or more liquid-phase reactors with large excess of one reactant in order to achieve high conversions of the other. In the conventional process the reaction section is followed by eight distillation columns, one liquid-liquid extractor and a decanter. This process requires a large capital investment, high energy costs and a large inventory of solvents. In the reactive distillation (RD) process for methyl acetate, invented by Eastman Chemical Company [6,7] the process is carried out in a single column. In this single column high-purity methyl acetate is made with no additional purification steps and with no unconverted reactant streams to be recovered. By flashing off the methyl acetate from the reaction mixture, conversion is increased without using excess of one of the reactants. The reactive column has stoichiometrically balanced feeds and is designed so that the lighter reactant MeOH is fed at the bottom section and the heavier acetic acid is fed at the top. The column consists of three sections. The reaction takes place predominantly in the middle section, shaded grey. The bottom section, serves to strip off the MeOH from water and return it to the reaction zone. The vapours leaving the reactive section consists of the MeOAc – MeOH azeotrope which is "broken" in the rectifying section by addition of AcOH which acts as entrainer.

The starting point for our studies is the conceptual design of the RD column discussed in detail by Doherty and Malone [1]. The column operates at a pressure of 1 atm. We employed a partial reboiler and a total condenser. The non-reactive section contains 10 theoretical stages and 33 catalytically active theoretical stages in the reactive section. The reactants methanol and acetic acid are fed stoichiometrically with a feed flow rate of 280 kmol/h on the stages 5 and 40; see Figure 2 (a). A pseudo-homogenous rate model adopted from Doherty and Malone [1] describes the reaction. The rate expression is given by

$$r = c_l\, k_f \left(\alpha_{HOAc}\alpha_{MeOH} - \frac{1}{K_{eq}} \alpha_{H_2O}\alpha_{MeOAc} \right) \tag{2}$$

with the forward reaction rate constant:

$$k_f = 2.7033 \times 10^5 \left(-6287.7 / T \right) \quad \mathrm{s}^{-1} \tag{3}$$

and the equilibrium constant:

$$K_{eq} = 2.32\, \exp\left(782.98 / T \right) \tag{4}$$

Furthermore, Doherty and Malone [1] reports that the liquid phase activity coefficients are very well represented with the parameters listed in Table 1. We did not consider the formation of the side product dimethyl ether and water from methanol. Doherty and Malone report that the side reaction has a minor impact on the column performance at atmospheric pressure. A macroreticular ion-exchange resin such as Amberlyst 15W is used as a catalyst. The catalyst is introduced at the top of the reactive section. Further we assumed that the volumetric liquid holdup on a theoretical stage is 3 m^3. We first consider a distillation column with 33 stage-to-stage reactive pump-arounds; see Fig. 2 (b). The bottom product flow rate is fixed at 280 kmol/h, whereas the reflux ratio is varied. The catalyst load in each of the 33 reactors corresponds to 3 m^3 catalyst load on each reactive stage in the reactive distillation column. Calculations of the conversion in the RD column (Fig. 2 (a)) and the 33-side reactor configuration (Fig. 2 (b)) using the EQ stage model [2,9] are shown in Fig. 2 (c) for varying reflux ratios. The results are in reasonably good agreement with the experimental results of Bessling et al. [8]. As can be seen from the Figure 2, the separation-reaction unit concept is equivalent to an RD column. In cases where the catalyst load is small, the catalyst can be placed in the downcomer and so functions as a reactor [2]. If the space in the downcomer were not sufficient, one would have to connect 33 reactors to the column. This is practically not a desirable design and would result in high investment costs. Therefore, our objective is to reduce the number of reactors and find configurations with high selectivity and conversion.

Table 1. Wilson binary interaction parameters and Antoine equation adopted from Doherty and Malone [1].

Wilson binary interaction parameters

Component I	Component j	b_{ij} [K^{-1}]	b_{ji} [K^{-1}]
Acetic acid	Methanol	2535.202	-547.5248
Acetic acid	Methylacetate	1123.144	-696.5031
Acetic acid	Water	237.5248	658.0266
Methanol	Methylacetate	813.1843	-31.1932
Methanol	Water	107.3832	469.5509
Methylacetate	Water	645.7225	1918.232

Parameters for the Antoine Equation. $\ln(P_{sat}) = a + \frac{b}{T + c}$

Component	a	b	c
Acetic acid	22.1001	-3654.62	-45.392
Methanol	23.4999	-3643.31	-33.434
Methylacetate	21.152	-2662.78	-53.46
Water	23.2256	-3835.18	-45.343

*Remark: P_{sat} is given in Pa and T in K

SEARCH ALGORITHM FOR LOCATING REACTIVE PUMP AROUNDS

In order to locate and determine the side reactors we developed an algorithm based on a simple one-dimensional search. Considering the fact that catalyst load, heat duty, flow rate and locations of the pump arounds are unknown parameters, it is advisable to reduce the complexity of the problem in the first step. Therefore, we assume that the side reactor operates adiabatically and at chemical equilibrium. We also fix the operating conditions for the distillation column. Once the algorithm has placed the side reactors, we will check whether changing reflux ratio and bottom flow rates results in a better performance. If this is the case, we restart the configuration search. With these assumptions, only location and throughput of N_{RPA} side reactors remain unknown. Hence, we have to determine N_{RPA} continuous parameters for the pump around throughputs and $2 \cdot N_{RPA}$ discrete parameters for the in- and outlet locations of the side reactors. The pump around ratios with regard to the liquid flow leaving the stage above determines the throughput of a side reactor. Simulations showed that evaluating a configuration with slightly different pump around locations might already be hard to converge due to significant changes of internal composition and flow profiles. In particular, this is true if the pump around ratio exceed unity. Therefore, we decided to employ a line, i.e. one-dimensional, search algorithm with a limiting step size of moving an in- or outlet of a side reactor by only a single stage up or down. The search direction for the discrete line search algorithm is determined by the steepest conversion increase when the locations of single side reactors are varied. This implies that the N_{RPA} reactive pump arounds are decoupled. Hence, not all-possible search directions are considered in order to limit computational costs. We follow the search direction until a continuing decrease of conversion is detected for a consecutive number of iterations. This is done in order to pass small local maxima caused by small local variation in conversion when following the search direction. The local maxima along the search path are recursively evaluated. Finally, the algorithm terminates if no search direction is found in which conversion increases by locally re-locating a single reactive pump around. It should also be clear that with the line search algorithm for location of the side reactors, the optimum solution could be one of the four types shown in Fig. 1.

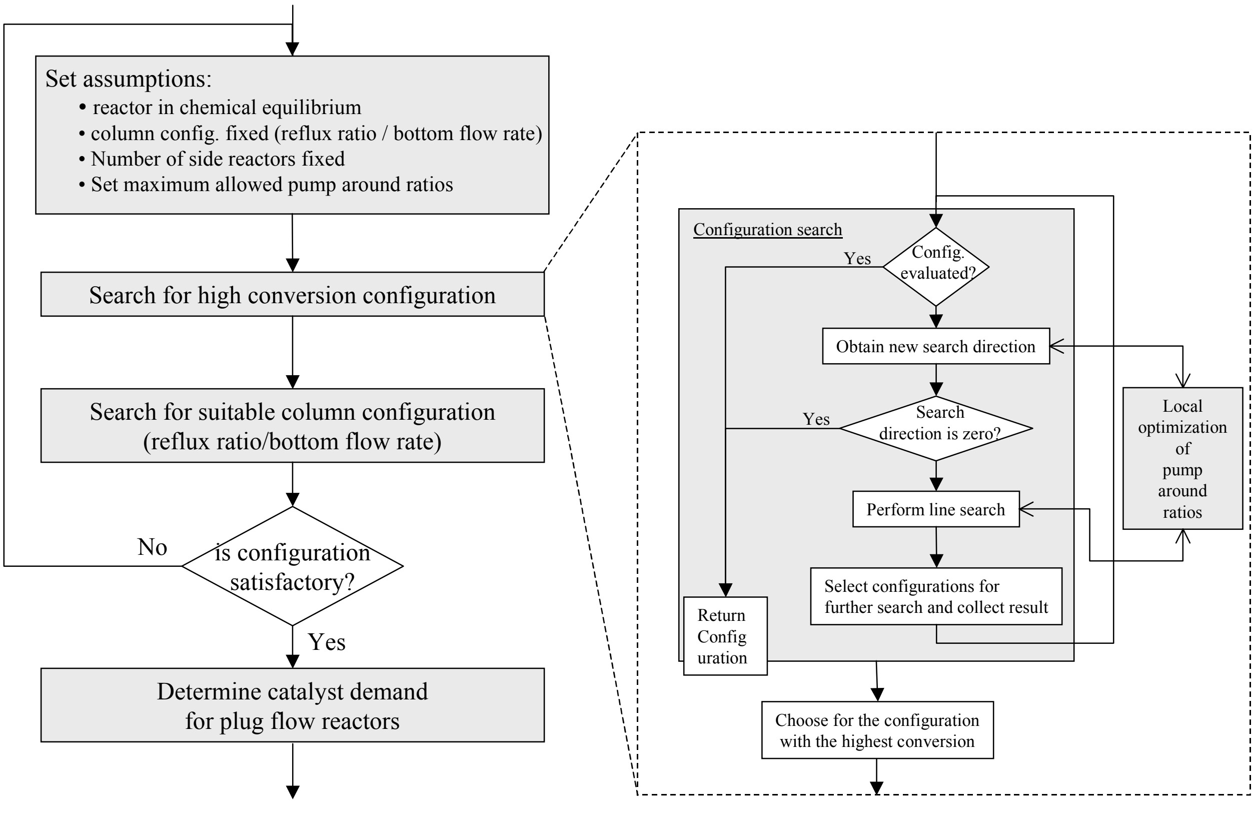


Figure 3. Simplified diagram of the search algorithm used to determine side reactor configurations.

Each time a new configuration is evaluated, an inner optimization using a conjugate gradient approach calculates the optimal throughput. In most cases, increasing throughput, i.e. increasing pump around ratios, results in an increase of conversion. Since our objective function is restricted to the overall conversion, it is useful to introduce a limiting value, R_{max}, for the pump around ratio. In case of a reactor-separation unit (Fig. 1 (b)), the limiting value is always set to R_{max} = 15, which corresponds to a throughput of over 90 % of the flow leaving the stage under consideration.

The algorithm described above is straightforward and pragmatic. Several simulations under equal conditions but with different initial configurations resulted in similar and comparable final configurations. Although the algorithm does not necessarily detect local optima, it provides useful information about promising configurations, that serve for further investigation. The resulting configurations also give a good starting point for detailed configuration refinements.

SIDE REACTOR CONFIGURATIONS FOR MEOAC SYNTHESIS

On the basis of the information in Fig. 2 (c) we choose a reflux ratio of 2 in the optimisation studies for side reactors. In order to study the influence of the throughput through each side reactor we varied the limits of R_{max}, for co- and counter current reactive pump arounds, whereas for a reactor separation unit R_{max} is always 15. Figures 4,5,6 and 7 show the optimum configurations obtained with 3,4,5 and 6 side reactors. For every choice of the number of side reactors, we consider the choice of the pump around ratio R_{max} = 1,2,3,4 and 5. Configuration 4/3 refers, for example to the case for which N_p = 4 and R_{max} =3. For each column configuration, we have depicted the locations of the side reactors, their production rates and the MeOAc composition profile along the column height.

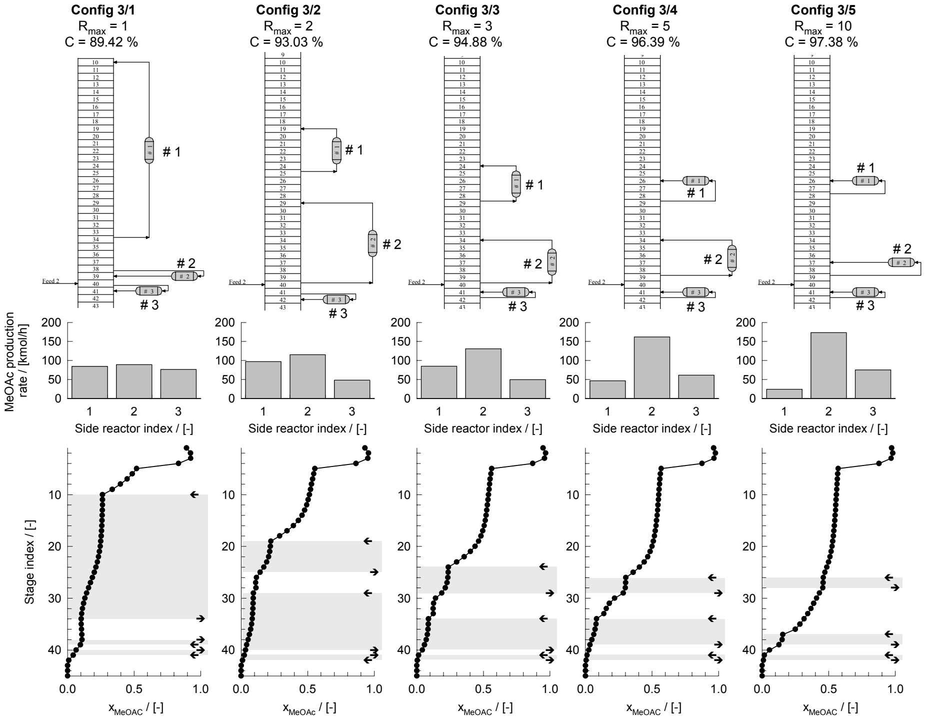


Figure 4. Column configurations with 3 side reactors. C denotes the overall HOAc conversion and R_{max} the maximum limit of the reactive pump around ratio. The production rates and the MeOAc composition profile along the column height are shown for each configuration. The grey shaded area in the MeOAc composition profile denotes a region with changed internal flow rates due to reactive pump arounds. The arrows pointing towards the y-axis denote the outlet location of a side reactor and the arrows pointing away from y-axis denote the inlet location of a side reactor.

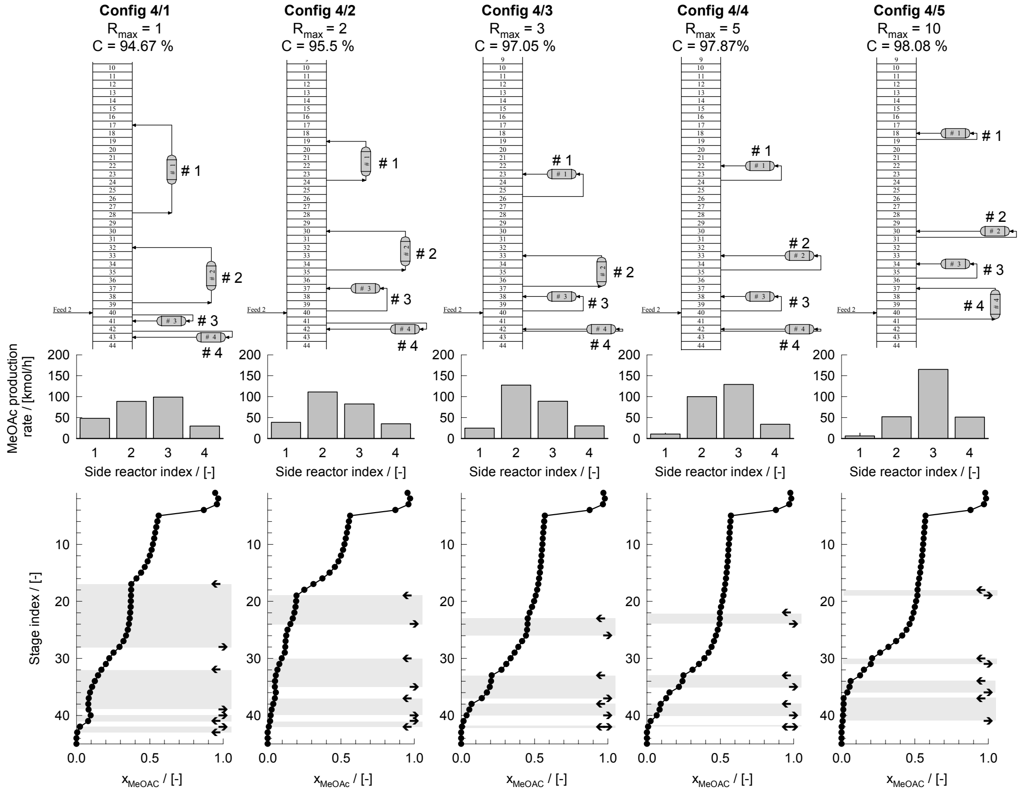


Figure 5. Column configurations with 4 side reactors; see explanations in Fig 4.

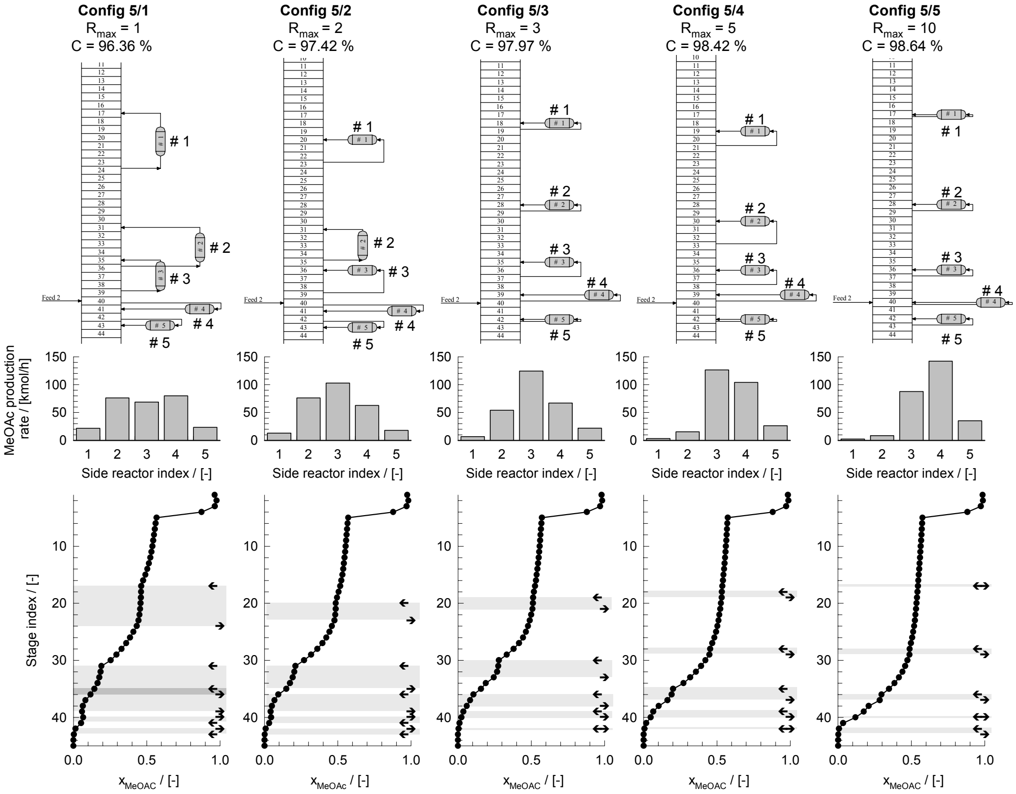


Figure 6. Column configurations with 5 side reactors; see explanations in Fig 4.

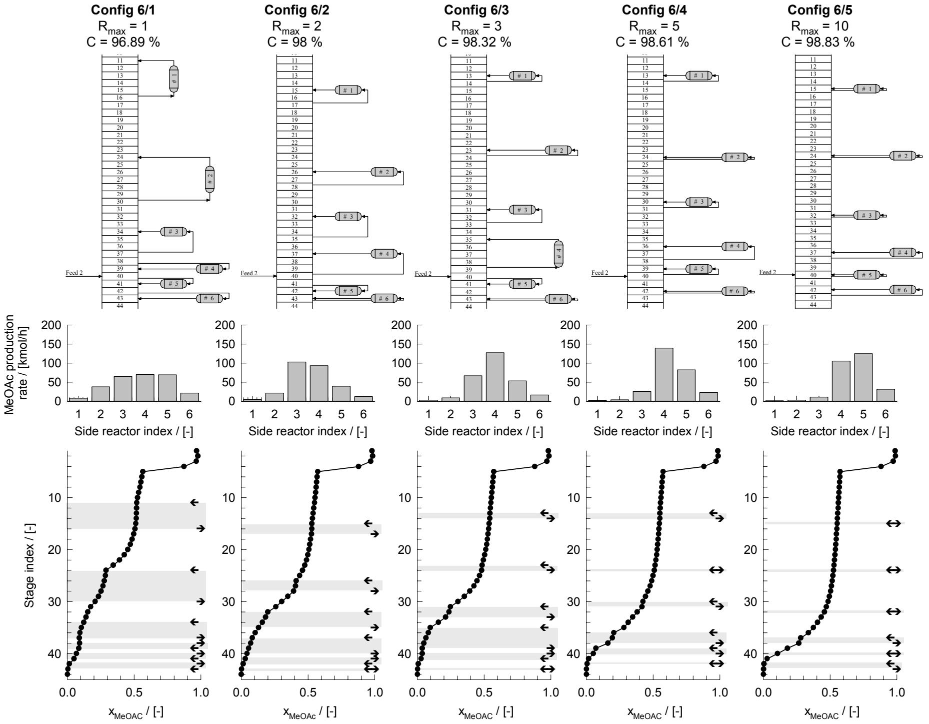


Figure 7. Column configurations with 6 side reactors; see explanations in Fig 4.

The analysis of all simulations reveals some common observations with regard to the proposed side reactor configurations:

High reactor throughput due to high pump around ratios and counter-current configurations are beneficial for conversion.

Counter-current operating reactive pump around causes an increase of the internal flows and therefore results in larger reactor throughput. Further, the inner optimization loop for the pump around ratio almost always hits its maximum limit R_{max} in order to provide a large throughput. Major drawback of high pump around ratios and counter-current operation is the high energy demand.

When pump around ratios are restricted to comparable low pump around ratios a reactor-separation unit gets attractive. However, bypassing stages, i.e. co-current reactive pump around configurations, were not found to be beneficial in the present case study.

Co-current reactive pump around were not found to be beneficial since (1) the reactor throughput of a co-current reactive pump around is limited to a fraction of the internal flows, and (2) low internal flow rates on the intermediate stages cause a decrease in separation. In case of a reactor separation unit the throughput is nearly equal to the liquid flow leaving the column and no stages are bypassed. It turned out that for low pump around ratio such a configuration could be superior to a counter-current configuration.

Recycle flows caused by counter-current side reactor configurations influence significantly the thermodynamic driving forces on intermediate stages. As a consequence it is preferable to reduce the number of intermediate stages when the recycle flow rates are large.

Mixing effects of the reactor flow and the internal column flow have a significant impact on the separation capabilities of intermediate stage in a counter-current side reactor configuration. Therefore, the thermodynamic driving forces for mass transfer and the reactor inlet composition of the side reactor, i.e. the chemical driving force in the side reactor, are affected. For the limiting case of very high pump around ratios the concentration gradient between the inlet and outlet of the side reactor nearly vanishes. Hence, assuming the side reactor to operate at chemical equilibrium, all liquid compositions on the intermediate stages are forced close to chemical equilibrium. This is not advantageous for separation and so the number of intermediate stages is obviously minimized – for very high pump around ratios the recycle could even involve only a single stage. Figure 4-7 also indicates that with increasing recycle, i.e. increasing pump around ratios R_{max}, fewer intermediate stages are preferred.

Large recycle flows cause small chemical driving forces in the side reactors. This will result in high catalyst demand.

The chemical driving force of the side reactor also vanishes with fading composition gradient between the reactors in and outlet. This effect, however, is compensated by a large throughput that maintains high conversion. In practice such configurations with small chemical driving forces will, however, require large catalyst loads.

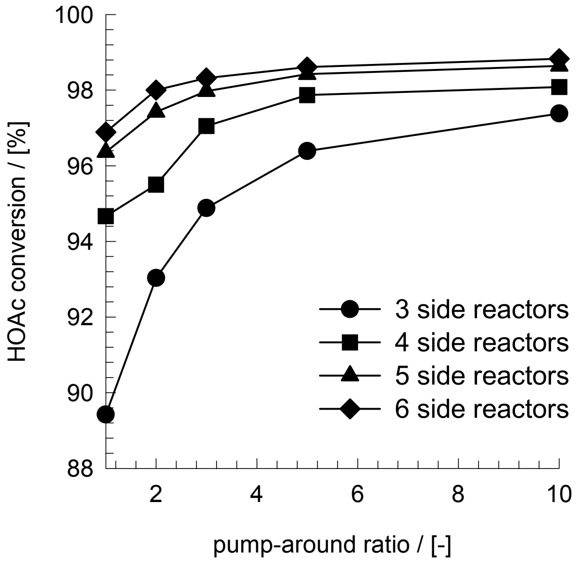
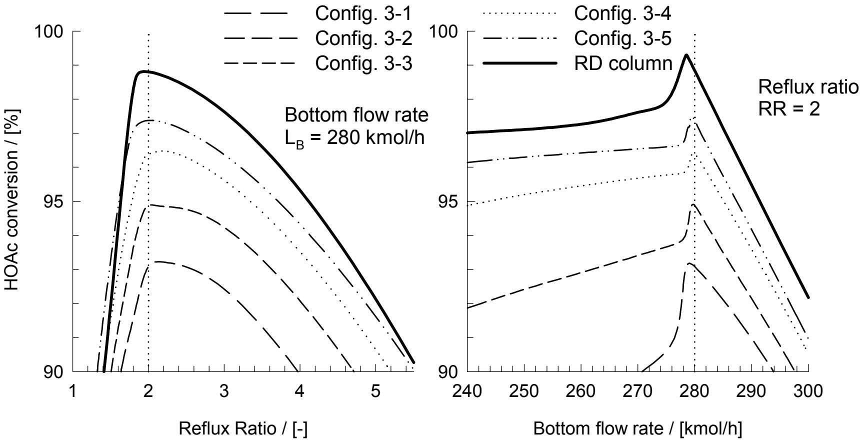


Figure 8. Diagram summarizing HOAc conversion for the configurations presented in Fig. 4-7.

Figure 8 summarizes the performance of all configurations with regard to conversion versus pump around ratio. As expected, additional side reactors and high reactor throughput lead to improved performance. It is an economical trade off between configurations with larger recycle flows and, in return, with fewer side reactors or with lower throughput but more side reactors. The first choice calls for high catalyst loads and energy costs, whereas latter one results in higher investment costs.

a) Distillation column with 3 side reactors



b) Distillation column with 5 side reactors

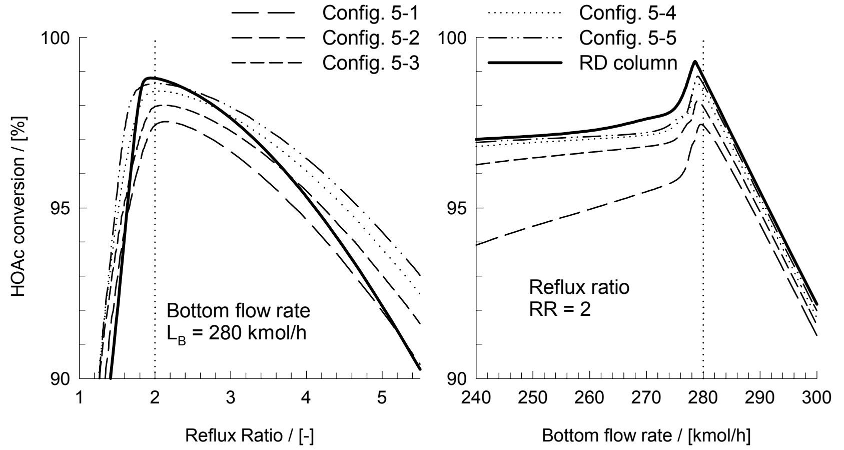


Figure 9. Homotopy diagrams of HOAc conversion with regard to reflux ratio and bottom flow rate for configurations with (a) 3 and (b) 5 side reactors.

Figure 9 shows the homotopy diagram of MeOAc conversion with respect to reflux ratio and bottom flow rate for a column with 3 and 5 side reactors. Also shown in the Figures is the performance of the RD column (shown in Fig. 2 (a)). The operation points for columns with side reactors are satisfactory. As can be seen both cases show a qualitative match with the behaviour of a comparable RD column This indicates that in case of the present study the design guidelines for reactive distillation appear to be valuable tools when designing a column with side reactors.

Furthermore, we tried to increase conversion by moving the feed from the column to the side reactors. Since the HOAc feed is also used for extractive distillation in the rectifying section, we have not been able to detect a relevant increase in conversion when feeding part of HOAc directly to a side reactor. In contrast most of our attempts result in less conversion. Distributing the MeOH feed to side reactors result in equivalent overall conversion. Latter configuration change might be attractive with regard to hardware design, since a feed to the column could be replaced.

CATALYST DEMAND

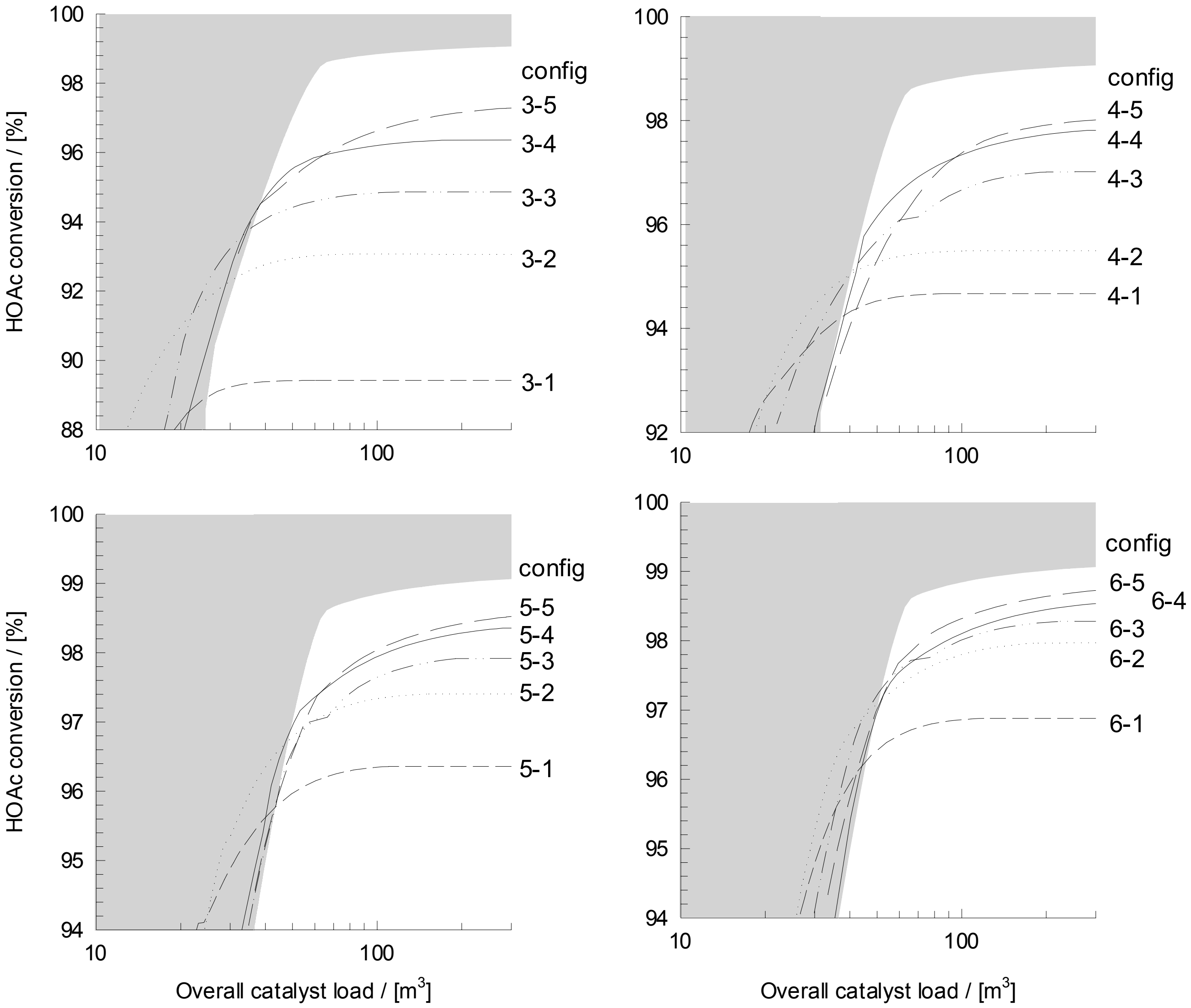


Figure 10. Diagram of HOAc conversion with respect to the overall catalyst demand. The grey shaded area denote cases for which a side reactor configuration would result in higher conversion with equal amount of catalyst. The configuration labels corresponds to the ones in Fig 4-7.

Figure 10 shows the dependence of catalyst load on conversion. The grey shaded area denotes case for which a side reactor configuration would yield higher conversion than a reactive distillation column with a catalyst load evenly distributed on each stage. The lines denote the side reactor configurations as presented and denoted in Figs 4-7. When previously designing the configurations, we assumed chemical equilibrium for the side reactors in order to determine the catalyst load. We modeled the side reactor as a plug flow reactor. For better comparison we also expressed the catalyst load of a side reactor in terms of liquid volume and used the same kinetics as in case of reactive distillation design. The initial catalyst load and distribution was estimated by minimizing the catalyst load required in order to match at least 99.9% of reactor conversion at chemical equilibrium.

For the MeOAc process, if the target conversion is say 90%, even a 3-side reactor configuration demands a lower catalyst load than an RD column. From the results presented in Fig. 10 we see that increasing the number of side reactors and the pump around ratio, we can match the catalyst demand of the RD column for any specified conversion level.

Figure 10 shows the drop in conversion when the catalyst load in each reactor is proportionately reduced. For small catalyst loads the side reactor concept appears to be superior to a reactive distillation column. This is caused by the advantage of using a plug flow side reactor. On the other hand the side reactor concept is not attractive if high purity and conversion specification have to be met. Note, in the present case study purity and conversion is linked since the two products are recovered at the top and bottom of the column, what makes it particularly attractive for reactive distillation. Furthermore, when comparing the catalyst demand of the side reactor configurations with high and low pump around ratios, we notice that high recycle flows are not economical. As mentioned before high recycle flow rates require high energy demand as well as low driving forces; consequently one requires significantly more catalyst load in order to reach close to chemical equilibrium; see Fig. 10.

CONCLUDING REMARKS

In this paper we have developed an algorithm to determine the optimum configuration of the side reactor concept in order to maximize conversion. For the case study of MeOAc production, we see that it is possible to match the conversion level of an RD column by appropriate choice of the number of side reactors and the pump around ratio. The higher the conversion target the larger the number of side reactors and pump around ratios. For modest conversion levels, say < 90%, even a 3-side reactor configuration will be able to match the performance of an RD column.

The study presented here reveals the potential, and limitations, of the side reactor concept for use as an alternative to RD technology.

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NOTATION

L	Liquid molar flow rate	mol s^{-1}
N_{RPA}	Number of reactive side reactors	
R_{max}	Limit for the pump around ratio	
V_{cat}	Volumetric liquid holdup	m^3

Abbreviations

HOAc	Acetic acid
MeOAc	Methylacetate
MeOH	Methanol

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