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ENHANCING PRODUCTIVITY OF SIDE REACTOR CONFIGURATION THROUGH OPTIMIZING THE REACTION CONDITIONS

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A comparison between reactive distillation (RD) and side-reactor concept (SRC) has been done using industrial examples. The industrial examples were chosen to present different types of reactions; equilibrium-limited [tert-amyl methyl ether (TAME) production] and selectivity-limited (2-methylbutene dimerization). In both cases, reactive distillation has been proved to be a good process alternative. At low internal and recycle flow rates, traditional SRC with adiabatic reactor train fails to reach similar conversions and selectivities to RD. However, optimizing the conditions in the reactor train of the side reactor concept improves the performance of the process remarkably, making it a prominent process alternative to reactive distillation.

Keywords: reactive distillation; side reactor; TAME; diisobutylene.

INTRODUCTION

Environmental issues are increasingly important for the chemical industry. At the same time the pressure from the global market on price and quality of the products increases. This leads to a demand for better productivity and better utilization of raw materials and utilities, i.e. a need for new processes and a continuous need to improve the existing ones. Investors, on the other hand, are looking for a return on their investment which sets tightening demands for the time and cost of the new process development.

Process intensification is one way to meet some of these challenges. Here we concentrate on combining reaction and distillation. It is obvious that distillation is the most important separation method in the chemical industry. In terms of installed capacity and energy usage, the commitment of the process industry to this unit operation is enormous. Reactive distillation (RD) is a process where the reactor is placed inside a distillation column. This process has shown great economical and environmental benefits in some existing applications [production of MTBE (Smith and Huddleston, 1982), methyl acetate (Agreda et al., 1991), etc].

The benefits of RD are usually listed as savings in capital and operation cost of the process either by simplifying considerably the separation part of the process or by making the recycle streams smaller, thus ending up with

less equipment and reduced usage of raw materials and utilities compared with conventional processes. The physical and technical background for this can be seen in the review article of RD by Taylor and Krishna (2000). It must be kept in mind that the applicability of RD is highly dependent on the chemical system at hand. There are elegant ways of defining the suitability of a chemical system for it by analyzing the reactive distillation areas (Taylor and Krishna, 2000; Bessling et al., 1997a, b; Barbosa and Doherty, 1988a, b; Ung and Dogerty, 1995). Optimum or at least feasible process conditions must be found both for the separation and reaction. In addition the properties of the reaction must be such that the requirement of the residence time is not limited by practical hardware aspects such as the placement of an adequate amount of catalyst in the column. If a reaction is otherwise suitable for reactive distillation but it is slow, a large volume of catalyst needs to be placed inside the column. There is a contradiction between the requirements of having as much catalyst as possible in the RD column for the reaction and at the same time having a large void fraction to benefit the separation and enabling the counter-current two-phase flow conditions. Taylor and Krishna (2000) and Pyhälahti (1996) have reviewed hardware structures of catalytic distillation. It is concluded that a large catalyst holdup is reached, most probably by having the catalyst arranged in beds with vapour bypass and arranging the separation on every other stage by a normal distillation tray. The reactive stage is then actually a kind of catalytic tubular reactor without separation. If we add to this reasoning the catalyst deactivation, which is usually handled by adding an excess of catalyst to

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the reactor, we might conclude that the placement of the desired catalyst amount inside the RD column is in practice impossible for low reaction rates. Another typical way to compensate for catalyst deactivation is to raise the reactor temperature. This is at least difficult in a RD column. We agree with the reasoning of Althaus and Schoenmakers (2002) that, considering RD in a broader sense, disintegrating the reactor from the column is most useful.

In order to overcome the problems of RD and to maintain the benefits of the combined process, applying the side reactor concept (SRC; Jakobsson et al., 2002) or reactive pump around concept (RPA; Althaus and Shoenmakers, 2002; Baur and Krishna, 2002) can be considered. In SRC and RPA the flow is taken from the distillation column and introduced into a reactor or a series of reactors. In SRC the reactor or the reactor series is often temperature-controlled, or otherwise manipulated to reach optimal yield. Most often tubular reactors are applied. Reactor effluent is returned to the distillation column. The final product is then obtained from the distillation just as in RD processes. Compared with RD, adequate catalyst amounts are more easily arranged in SRC and RPA where traditional reactor types and catalyst structures can often be used. Also, the reaction conditions in SRC and RPA are less limited by the distillation requirements.

One of the early works on applying side reactors is the pioneering work of Schoenmakers and Buehler (1982). They investigated the use of SRC as an option for homogeneously catalysed RPA processes. According to them the disadvantages that arise from the use of mineral acids, i.e. the loss of products in the separation step in which the catalyst is separated from the products, can be avoided by the use of a heterogeneously catalysed side reactor. Schoenmakers and Buehler concluded that heterogeneous catalysis in external reactors using ion exchange resins as catalysts is equivalent to homogeneous catalysis in an RD column with respect to conversion and energy consumption. The test reaction they used was the esterification of carboxylic acids.

Sundmacher and Qi (2003) investigated combinations of reaction and distillation using an ideal binary mixture with a reversible reaction. Using mathematical analysis they concluded that theoretically a system with reactive total reboiler is the best configuration considering both productivity and reliability of design. Their conclusion was based on the result, that best performance could be obtained with an infinitely high recycle flux φ ($\varphi = B/F$, i.e. the ratio between the reflux flow rate B and the feed flow rate F). This solution can be seen as a single-stage reactive distillation column, which therefore faces most of the same limitations as traditional RD columns.

The main benefits of the side reactor concept compared with RD can be derived from problems in the use of RD in the case of a slow reaction. The adequate catalyst holdup is easily arranged in well-known standard reactors with standard catalyst. The reactor block in SRC is often treated as a series of consecutive reactors, in which the product of one reactor is led to the next one without controlling the intermediate conditions. Also the reactor selection is often limited to ordinary adiabatic packed bed reactors. However, optimizing the inlet temperatures and reaction conditions in the reactor series can, and generally does, improve the efficiency of the side reactor configuration remarkably. Since once-through conversion in the reactor train increases, the

flow rates can be reduced. Also the amount of catalyst in the system diminishes in most cases.

METHODS

Process Selection

A reversible chemical reaction with unfavourable reaction equilibrium and with a significant heat of reaction may be a good candidate for a combined process. In addition, if the chemical system is such that the distillation temperature range and the practical reaction temperature overlap, the catalyst is thermally stable and the rate of reaction and the selectivity to the desired product is high enough in this temperature range, then RD is a good candidate. A technical solution to place the catalyst inside the column must be found. The most important application of reactive distillation today is production of ethers used as gasoline enchanters. These fuel ethers are, for example, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and tert-amyl ethyl ether (TAEE). Ethers have been produced using reactive distillation for decades (Foerst, 1955).

Baur and Krishna (2002) studied the use of side reactors in MeOAc production. They were able to match the conversion of RD column with three reactive pump-arounds, but the process alternatives they ended up with included very high internal flow rates and rather complicated process configurations. The production of methyl acetate is a commonly seen example in demonstrating the applicability of RD. One might argue, however, that this particular process is not the best example for general comparison between RD and other process alternatives, since it contains specific features that make it exceptionally suitable for RD. The azeotropes of the MeOAc production mixture make reactive distillation the most suitable combined process for MeOAc production (Agreda et al., 1991; Siirola, 1995). Furthermore, fairly easily separated products and the dependence of the reaction extent on the reaction temperature rather than the amount of catalyst favour reactive distillation as a process alternative for MeOAc production. Baur and Krishna made an important observation, however, showing that, if each reactive stage in and RD column is replaced with a reactive pump-around, the performance of an optimized RD column can be matched. This suggests that there is room for development in the field of optimizing SRC or RPA configurations, and that performance of SRCs and RPAs should, at least theoretically, be superior to that of RDs.

Generally it seems that, applying the side reactor concept, the requirement of overlapping distillation and reaction temperatures and many of the hardware aspects of the reactor can be relieved compared with RD solutions. The amount of catalyst that can be placed inside the reactor is not limited to such an extent; standard mature reactor technology can be used, the temperature can be controlled to favour the reaction independently from the column and adequate free space for separation is available in the distillation column.

Modelling

According to experience of the authors to speed up the design the intensive use of the modern modelling tools is

necessary. The approach the authors have used in development of new processes is the use of holistic models where the sub models like reaction kinetics and VLE models are developed independently from each other. We point out that to compare these two combined processes we need true kinetic data of the reaction to get a feel of the true catalyst holdup needed in the process. Reaction models based on equilibrium consideration are normally not of great value; on the contrary they might even be misleading.

In the holistic model these sub models are combined with hydrodynamic and mass and energy transfer models to describe the behaviour of the equipment. We point out that we are in doubt about using or developing generic design rules for these combined processes since we are afraid that they might hide the economical optimum of the process choice. This is due to different local conditions like cost of utilities, etc.

As the framework of the modelling we have used the sequential modular flowsheet program FLOWBAT. The program has features by which the user can define the calculation order of modules selected for the simulation. These have an effect on the convergence of the overall process material balances. There are also several methods to be used for convergence acceleration.

FLOWBAT has several optimization algorithms and in-house cost estimation capabilities for major equipments.

Reactor Models

The core of almost all the chemical processes is the part where the chemical reaction takes place. Here we consider heterogeneously catalysed reactions, so an obvious alternative for the reaction to occur in is a packed-bed reactor. Reactor models used in the examples are pseudohomogeneous plug-flow models for packed-bed reactors. The catalyst and fluid phases are considered as one pseudo-phase, and mass transfer between the two real phases is not considered to be a significant factor in calculations. Radial flow, temperature, pressure and concentration profiles are regarded as flat.

One of the advantages of SRC over reactive distillation is the possibility to use various types of reactors (or separators, for that matter) instead of just limiting oneself to the counter current catalytic gas–liquid–solid reactor that is basically the case in the reactive part of catalytic distillation. Trickle-bed and CSTR reactor models among others are available for use in process design.

Distillation

When combining distillation and reaction, one of the key models is obviously the distillation model. The model library contains a typical ideal stage distillation model. This model is adequate for many cases. However, the distillation problem in SRC is usually multicomponent in nature and involves one or more side draws of the column. Location of the correct position of the side draw might be critical in a real column when the intermediate boilers form bell-shaped composition profiles in the column. The composition of trace components in the side-draw might also be significant for the reactor performance. Thus we regard models calculating real plates useful in SRC calculations. Our distillation simulator contains also the possibility of

calculating the rigorous multicomponent Murphree efficiencies during column calculations. This enables the calculation with real column plates and not only with ideal stages. This is done in such a way that first binary NTUs (number of transfer units) are estimated for all components. Then Murphree point efficiencies are calculated from these NTUs using the two-film theory and the Maxwell–Stefan mass transfer equations. For large plates, mixing models for liquid and vapour flows on the plate are used to obtain the plate efficiencies. See Ilme (1997) for details of the implementation and other aspects of the model.

Another approach is the rate-based approach, in which the heat and mass transfer including multicomponent interactions between the components is directly calculated using heat and mass transfer coefficients on the plate. In this approach, the film theory and the Maxwell–Stefan equations for diffusion are applied too. The rate-based modelling concept was first introduced in a series of papers by Krishnamurthy and Taylor (1985a–d, 1986) then the model was further developed to a second-generation model (Taylor et al., 1994). The equations and variables presented in this paper are the basis of our implementation. The model includes the following hydrodynamic models— completely mixed vapour, completely mixed liquid—vapour plug flow, mixed pool model, eddy diffusion model based on analytical or numerical solution of the equations. Some further aspects of the implementation are presented by Kenig et al. (1999).

Reactive Distillation

Two types of reactive distillation models are available in our modelling tool. The first one is based on the equilibrium model (Kettunen, 1998) that was later expanded into real plate model by including the calculation of plate efficiencies (Hyvärinen, 1998). In this model the reaction rate is taken into account as a source term in the mass balances. This is the standard way of taking the reaction into account in many commercial simulators. This is the case also in the second type of RD model in our rate-based model, but in that we have also included a model for fast reactions that take place in the liquid film by Kenig and Górak (1995) and a model for reaction and mass transfer in macroporous catalyst by Sundmacher and Hoffman (1996).

Side Reactor Model

The available process simulation software tends to have problems in modelling all the relevant physical and chemical phenomena of the processes, but often the problem lies in the convergence properties. Non-linearities caused by, for example, thermodynamic functions, reaction kinetics and heat and mass transfer combined are a tricky combination to solve even without recycle structure, not to mention with it. In case of reactive distillation solving the flowsheet is not an issue, since recycle streams are usually not present. Here, as well as often with SRC, the problem lies in the convergence of the distillation column. Multicomponent mixtures with azeotropes demand accurate models, and are rarely even close to linear.

One of the recent developments is a combined distillation side reactor model (Jakobsson et al., 2002). This combination is particularly interesting when new processes are

developed since the interaction between the reactor and the distillation column is strong and tends to lead to convergence problems with traditional techniques. The unit block contains both the distillation column model and the models for the coupled reactors. To linearize the equations, tubular reactors are solved as series of CSTRs. This enables the model equations to be solved simultaneously in one block and not sequentially as is done when the reactor/distillation systems are solved by traditional flowsheet programs. Fast convergence allows this unit model to be efficiently used in optimization calculations.

INDUSTRIAL EXAMPLES

TAME Production

One commercially successful example of the application of SRC is the process for TAME production. In the process C5-tertiary olefins are converted to *tert*-amyl-methyl-ether (TAME). Details of the process have been described by Jakkula *et al.* (1994), Koskinen *et al.* (1996), and Järvelin *et al.* (1996). TAME is formed as a product of either 2-methyl-2-butene or 2-methyl-1-butene and methanol. The main reactions of producing TAME are as presented in Scheme 1.

TAME reaction is an equilibrium-limited (Rihko *et al.*, 1994, 1996) reaction where high conversion can be achieved only by combining multiple stage reactors with a separation system. The reaction rate increases with temperature, whereas at lower temperatures the reaction equilibrium is shifted towards the products. Figure 1 shows the temperature dependence of both reaction rate and reaction equilibrium constants for both 2-methyl-2-butene and 2-methyl-1-butene. Combined reaction and separation allows sufficiently high reaction temperatures, since the product is being constantly removed and adjusting the temperature for more favourable equilibrium becomes less significant.

When applying reactive distillation to TAME production these benefits can be exploited to a certain extent. There are, however, a number of relatively heavy components at the reaction mixture, that force the distillation temperature to be fairly high. This leads to either a need for large catalyst
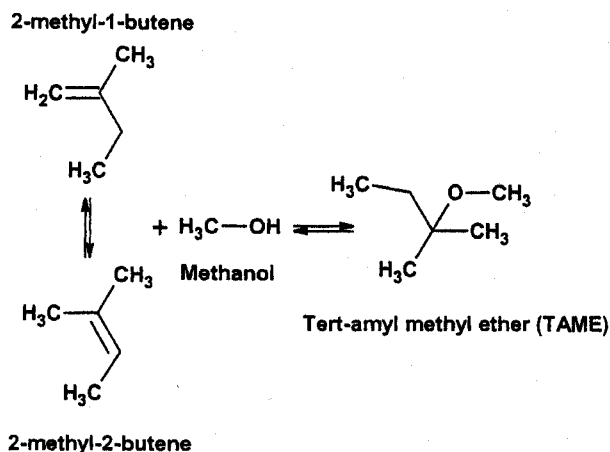
amounts or alternatively to long residence times in the reactive stages of the column. The contradiction between the requirements of reaction and separation is well shown here. If either high catalyst amounts or large inner flows due to the demand for high residence times are applied to achieve feasible conversion, the reactive distillation column becomes very large. Applying the side reactor concept to production of TAME does not necessarily remove the need for large catalyst amounts, but the catalyst can be better exploited when the single-phase operating conditions are more freely adjustable.

Klemola (1996) studied the economics to produce TAME and higher ethers by several process alternatives including RD and SRC. The conventional process alternatives based on sequence of fixed bed reactors and distillation turned out to be non-profitable. However the combined processes (RD and SRC) were found to be profitable. According to Klemola, the profitability of the processes were very sensitive to the bulk chemical prices. Klemola's study was based on 2.25×10^6 tons of reformulated gasoline. One can claim that the order of profitability might change between these process alternatives along with the capacity of the plant. An educated guess would be that the smaller the production the more profitable compared with others is the conventional plant. On the other hand the economics of RD might be better exploited in large plant. In some cases the RD-column seems to be a remarkably expensive reactor, as Stitt (2001) states in his study of the feasibility of RD. The expensiveness of the RD reactor might be the reason why only large capacity MTBE plants are built with RD technology.

TAME process was simulated with both RD and SRC. Process configurations are depicted in Figure 2(a) and (b). In RD (Figure 2a), the column had a total of 30 ideal stages, of which 13 were reactive (stages 11–23). The amount of catalyst at one stage was set to be 800 kg, adding up to a total of 10,400 kg dry catalyst in the entire column. Feed was introduced below the reactive zone, in order to prevent the light precursors from leaving the column with top product without meeting the catalyst first. The column operated at a pressure of 5 bar, which set the reaction temperature to a feasible level (to around 343 K).

When SRC (Figure 2b) was applied, an amount of catalyst identical to RD-case (10,400 kg) was divided between three reactors in series. The first reactor contained 1160 kg, the second 3490 kg and the third 5750 kg of catalyst. The diameter of the column was 3.3 m for each of the reactors and lengths for the first, second and third reactors were 1, 2 and 6 m, respectively. The reactors operated at pressure of 15 bar, and without any external heating or cooling. The inlet temperatures were regulated in the case of optimized SRC. A distillation column with 30 ideal stages was used here as well. The feed from the third reactor was introduced at stage 10, and the recycle stream back to the reactors was taken from stage 20. The column operated at pressure of 5 bar.

In Figure 3 the conversions of a reactive distillation system and two different side reactor configurations are plotted against the reflux ratio of the system. In each configuration the catalyst amount is the same in the system. The feed composition is also the same for each configuration. The feed consisted of equimolar amounts of methanol and 2-methyl butene. It can be seen that the

2-methyl-1-butene

Scheme 1. Simultaneous etherification and isomerization reactions involved in TAME synthesis.
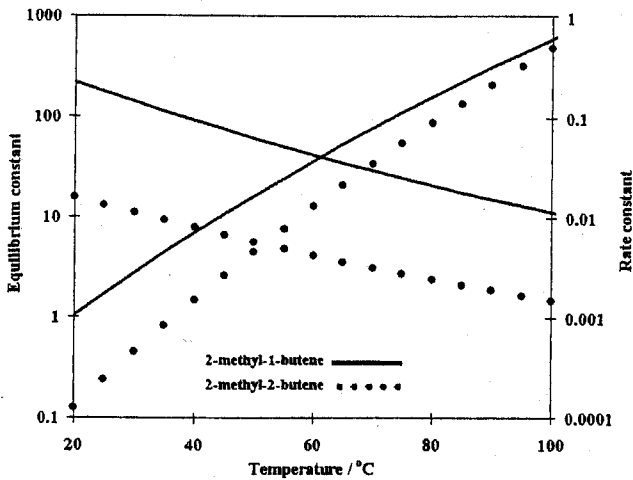
Rate and equilibrium constants for TAME

Figure 1. Rate and equilibrium constants of TAME as a function of temperature at temperature interval 20–100°C. The reaction rate constant, increasing with temperature, can be read from the right. The equilibrium constant, decreasing with increasing temperature, can be read from the left.

conversion in the reactive distillation column reaches its maximum value at relatively low reflux flow rates. Conversion in the adiabatic SRC (no heating or cooling between the reactors) rises steadily with the reflux ratio, reaching and surpassing the conversion of RD at high reflux ratios. The conversion of an adiabatic SRC stays below the one of RDs
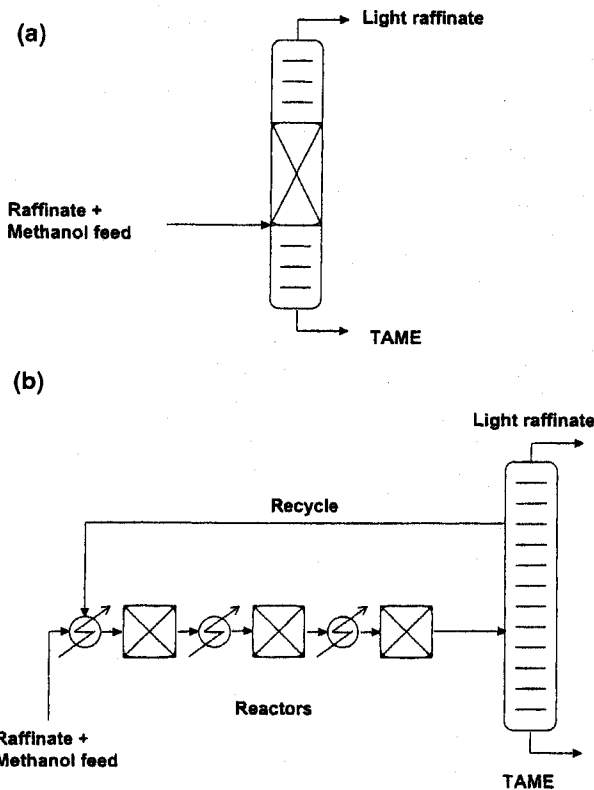

Figure 2. Process configurations for producing TAME. (a) Reactive distillation column; (b) side reactor concept. In case of optimized side reactor concept, reactor feed temperatures are controlled by heat exchangers before the reactors.

at lower reflux ratios, because part of the reflux flow is not going to the reactors, but is needed for the mass transfer purposes. Also the gas phase never meets the catalyst.

When the inlet temperatures of the reactors are optimized, the results show a remarkable improvement in the conversion. Even with very low reflux ratios the conversion in the SRC exceeds the maximum obtainable conversion for RD. In the case of TAME reaction, the reason for increased conversion is clear. Since high temperatures favour high reaction rates, high conversion can be achieved in the first reactor with high inlet temperature and low catalyst amounts. Low temperatures and high residence times can then be applied to the latter reactors, yielding a conversion higher than can be achieved with adiabatic reactor train.

The feed is introduced into the reactor series when SRC is applied. Owing to this, the conversion in SRC is at least the once-through conversion of the reactor series. In optimized case, the conversion of SRC at its minimum corresponds to the optimized once-through conversion of three tubular reactors in series. In adiabatic SRC, the once-through conversion is not so high, since all the potential of the reactor series has not been used.

Commercial TAME processes applying RD use a pre-reactor with a conversion of 65–70% (Klemola, 1996). The RD column feed then has a precursor/product ratio of around 1/3 in weight fractions. At these high conversion levels the superiority of SRC cannot be demonstrated as clearly as for lower conversion levels. A number of simulations with a pre-reactor were performed in order to find optimal process conversions for SRC and RD. Both process alternatives could be optimized to give a conversion above 90%.

At higher conversions, when a pre-reactor is applied, SRC loses part of it advantage. Since the output of the pre-reactor, which is the feed to the SRC, already has high conversion, it is not useful to introduce it to the reactor train. Hence the feed is introduced in the distillation column, and only the recycle stream from the column is led through the reactor train. However, more flexible reactor and catalyst options together with less restricted hardware design give SRC the upper hand. Therefore, as Klemola's study revealed, SRC is a better alternative in TAME production when the objective is purely economical.
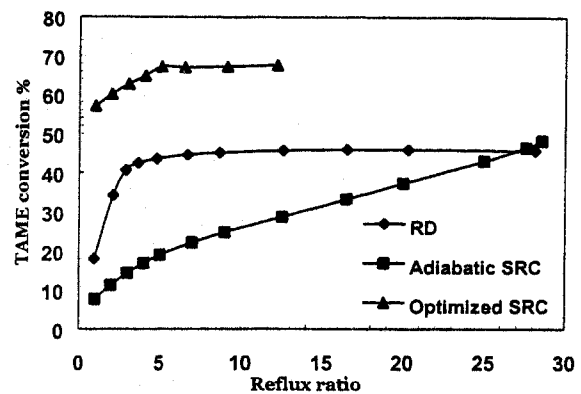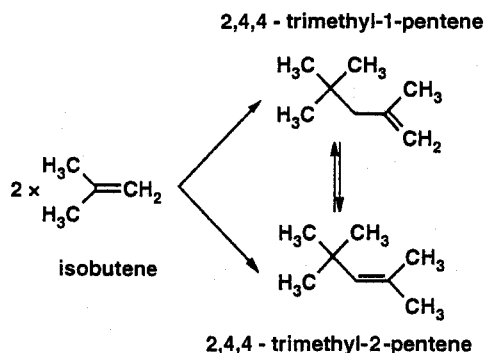

Figure 3. Comparison between conversions of reactive distillation, adiabatic side reactor concept and reactor train-optimized side reactor concept. TAME conversion is plotted against reflux ratio. For SRC the reflux flow rate is combined recycle and reflux flow rate.

Isobutylene Dimerization

In this process 2-methylbutene (isobutylene) is dimerized into 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (isooctene) according to Scheme 2. This process is particularly interesting since it can replace traditional MTBE process units if the forth coming MTBE ban in California expands. This reaction is not limited by reaction equilibrium, but prevention of oligomerization is desirable to maintain the quality of the product. Oligomerization takes place if the temperature of the reaction mixture is too high, whereas at lower temperatures the conversion of isobutylene remains unfeasibly low. The reaction is a catalytic liquid-phase reaction, which sets requirements for the reactor pressure. Therefore the operating window for the reaction is fairly limited, which is known to be problematic from the reactive distillation point of view. When SRC is applied, the possibility of manipulating both the reaction and separation conditions is again significantly better.

The reaction is highly exothermic so it could still be an interesting candidate for reactive distillation. Hyvärinen (1998) investigated the possibilities of a RD process to produce diisobutylene at an industrially relevant scale. In the study the ideal stage reactive distillation model was used. The kinetic model is an in-house model. UNIFAC was used as the activity coefficient model. By trial and error some interesting designs was found, of which some key figures are represented in Table 1. These designs have 78 ideal stages. The feed is introduced on stage 7 (stage 1 is the reboiler). The combined dimer and the isooctane composition was kept under 0.7 mol% in the simulations. Some of the designs included an external reactor.

The authors are fully aware that these designs are based on trial and error and are found through simulation with a preliminary model. Despite of this we believe that these results give useful ideas to consider. Designs A, B and D seem to be reasonable in respect that 300 kg of dry catalyst per ideal stage might be possible to implement in a RD column. However, the conversion of the isobutylene is not high enough in designs A and D. Design B demonstrates how the conversion can be increased by a higher reflux ratio, in this case 30.0. This value is obviously unrealistic, which can be seen from the reboiler duty of 97.3 MW. Comparison of designs A and C shows how increasing the total amount of catalyst in the column affects the conversion. The conversion is significantly higher but the amount of catalyst reaches

a value 1600 kg dry catalyst per ideal stage, this being unfortunately an unrealistic amount of catalyst per ideal stage.

A recent application to produce diisobutylene with a side reactor process is proposed by Sloan *et al.* (2000). The isooctene product is taken from the bottom of the distillation column and the unreacted C4-stream is recycled into the reactor section. A schematic block diagram of the process is presented in Figure 4. The side reactor concept does not place as strict restrictions on the amount of catalyst in the system as reactive distillation. Optimizing the inlet temperatures in the reactor train, and using one external reactor to push the overall conversion towards 100% gives promising results even without any external heating or cooling. As Table 2 shows, optimizing the feed temperatures of the reactors allows the overall conversion to reach as high a figure as over 99%, keeping the selectivity at the same time over 95%. The advantage of optimized SRC shows again in the fact that the selectivity can be increased at the cost of conversion, if desired, still keeping the overall yield at a higher level than is possible with RD.

Design A from Table 1 was picked as a reference process in comparing the performance of SRC in isobutylene dimerization. The results of the comparison are presented in Figure 5, where the overall yield of diisobutylene is plotted against the reflux ratio of the distillation column. The catalyst amount was 18,000 kg dry catalyst in total in all simulations for RD and SRC. In the case of adiabatic SRC the inlet stream to reactor train was at the same temperature as the column side-draw plate. In case of optimized SRC, the inlet temperatures of the reactors in the reactor train were optimized.

The results are not as spectacular as in TAME production (Figure 3), but it must be kept in mind that, even though heuristic, the optimization of reactive distillation column was holistic, including feed compositions, number of ideal plates, pressure, etc. The performance of the optimized SRC still exceeds that of RD at every reflux ratio. The performance curves of RD and optimized SRC overlap only at the vicinity of the optimal reflux ratio of RD, 4.8.

Adiabatic SRC does not in this case reach the performance of RD at high reflux ratio, but the quality of the product actually starts to decline at high reflux ratios. This is

2,4,4 - trimethyl-1-pentene

2,4,4 - trimethyl-2-pentene

Scheme 2. Simultaneous dimerization and isomerization reactions involved in isooctene synthesis.

Table 1. Column details, conversions and selectivities for four optimized reactive distillation columns for isobutylene dimerization.

Design	A	B	C	D
Pressure in column (MPa)	1.58	1.51	1.4	1.58
Reflux ratio	4.8	30.0	4.8	4.8
Reboiler duty (MW)	14.8	97.3	14.8	9.4
Catalytic stages in column	12–71	12–56	12–71	12–71
Dry catalyst on stage (kg)	300	300	1600	300
Dry catalyst in the column (kg)	18,000	13,500	96,000	18,000
Dry catalyst in the whole system (kg)	21,475	16,975	99,475	18,000
Conversion of isobutene in the column	91.2	95.3	95.3	93.0
Conversion of isobutene in the whole process	93.4	96.5	96.4	93.0
Dimer selectivity in column	88.2	94.2	86.0	89.3
Dimer selectivity in the whole process	90.9	95.3	89.2	89.3
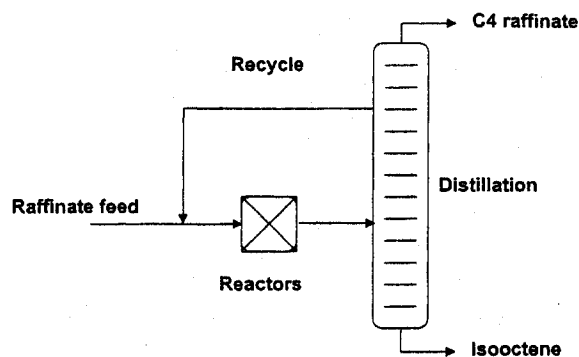
Figure 4. Schematic block diagram of the SRC process for dimerising isobutylene.
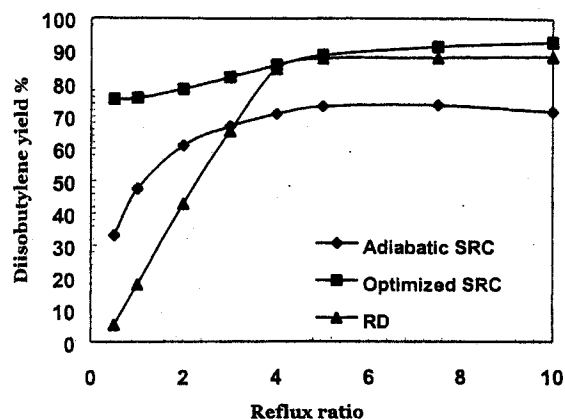

Figure 5. Comparison between conversions of reactive distillation, adiabatic side reactor concept and reactor train-optimized side reactor concept. Diisobutylene yield is plotted against reflux ratio. For SRC the reflux flow rate is combined recycle and reflux flow rate.

most probably due to the high flow rate through the reactors, which causes the temperature in the reactors to increase less. This leads further to lower reaction rates.

DISCUSSION AND CONCLUSIONS

In this paper, aspects of industrial applications of a side reactor configuration combining reaction and distillation are discussed. A comparison between reactive distillation and both adiabatic and temperature controlled side reactor configuration is done in terms of industrial examples. The examples used present two different types of reactions, equilibrium-limited reaction of TAME production and selectivity-limited reaction of isobutylene dimerization.

The main reactions of both processes, TAME and dimerization, show characteristics that makes the process configuration combining closely distillation and reaction attractive. In both cases the side reactor configuration shows good techno-economical properties. The main advantage, according to the authors, of SRC over RD is the capability of having the full potential of both reactor and distillation units in use. This feature is highlighted at low conversion levels, as was shown in the TAME example.

The contradiction between the large catalyst holdup and high residence times required by the reaction and the large vapour space required by the distillation diminishes the applicability of RD. There are additionally the well-known limitations of RD, like the narrow operating window and difficulties with the catalyst inside the column.

The results gained from both examples show that the side-reactor concept gives not only more freedom of choice

in process design but is often a superior choice in terms of efficiency and economics. The full advantage of SRC is capitalized when the operating conditions in the reactor train are optimized.

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Table 2. Process details, conversions and selectivities for four optimized side reactor configurations for isobutylene dimerization.

Design	A	B	C	D
Pressure in column (MPa)	1.0	1.0	1.0	1.0
Reflux ratio	2.3	2.7	3.6	3.5
Reboiler duty (MW)	22.2	22.1	21.8	22.7
Dry catalyst in the system (kg)	57,148	57,148	57,148	57,148
Conversion of isobutene in the whole process	98.1	97.8	97.5	99.3
Dimer selectivity in the whole process	95.8	96.5	97.3	95.5

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